VOL. 04 NO. 2,
MAY, 2024
E-ISSN 3027-1533
P-ISSN 3026-8648

African Scholar Publications & Research International
www.africanscholarpub.com

Journal of African Innovation & Advanced Studies (JAIAS)

Numerical Prediction Of Non-Speciated Total Petroleum Hydrocarbon Concentration Groundwater In Gbene-Ue, Tai (Ogoniland), Rivers State, Nigeria

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Abstract

In modelling and risk assessment of total petroleum hydrocarbon and heavy metals in groundwater in parts of Ogoniland in Dor-um, Gbene-Ue, five (5) different boreholes (BH1-BH5) were analyzed for total petroleum hydrocarbons (TPH) and heavy metals concentration using Gas chromatography–mass spectrometry and atomic absorption spectrophotometer respectively based on field data collected for the study. Numerical simulation approached was used for this study with MATLAB ODE45 numerical scheme. The numerical result shows that on the base day of our experimental time here called the initial condition, the total petroleum hydrocarbon concentration for the various borehole were as 31.88 for BH1, 151.23 for BH2, 117.31 for BH3, 110.93 for BH4, 24.96 for BH5 which increases monotonically to a converging saturated value of 82.49 for BH1, 293.44 for BH2, 245.04 for BH3, 235.10 for BH4, 65.86 for BH5 on the 360th day of our experimental time. The full result of this investigation is well presented and discussed as well in this study.

Keywords: Vulnerability, Numerical Simulation, Modeling, Risk.

Introduction

Groundwater are particularly vulnerable to contamination from agricultural, industrial and municipal sources. Surface water bodies receive wastewater from industrial and municipal sources, agrochemicals may leach into them, air-borne pollutants may dissolve in surface water and they receive overland run-off which washes surface debris thereby polluting underground water quality. As a result, all surface waters

require treatment before they are supplied for drinking-water, whether the source is a river, lake or reservoir (Chukwu, 2011).

There are a number of interventions which will help to protect the quality of surface waters, principal amongst these are: land-use control within the catchment; and proper setting of intake structures away from potential sources of pollution and preferably upstream of them; treatment of effluent and discharges leaving industrial plants and municipal sewage treatment works, and; the establishment and enforcement of effluent quality standards. Conversely, where surface water is used as a source of drinking-water, it is appropriate to ensure that land use within the catchment is controlled and preferably limited to activities which are relatively non-polluting. This can be problematic as some activities may already be established which do cause pollution and in these cases, adequate standards of effluent quality should be established and enforced (Raikwar *et al*., 2012). Land-use control has tended to be more effective when applied to artificial reservoirs, principally because in many countries these have been located away from intensive human activity. However, land-use controls may be difficult to introduce as the creation of a large body of water may attract industry which will have effluent discharges. Reservoirs may promote intensive arable agriculture which utilizes inorganic fertilizers and pesticides which may pollute the reservoir.

In addition, in many countries, standards have been or are being developed and enforced governing the quality of effluent that may be discharged into a river or standing body of water and in many countries, national bodies concerned with water are trying to shift the onus onto producers to treat wastewater prior to discharge - the 'polluter pays' principle (USEPA, 2019). However, few countries have managed to enforce compliance with these standards and large-scale pollution continues. In many countries the penalties for exceeding quality standards are minimal and as the cost of installing treatment processes in the plant greatly exceed the accumulated cost of fines, there is little incentive for the producer to invest in treatment technology. This situation is often exacerbated by the time it takes for cases involving pollution to reach court, further reducing the real cost to the producer. The rigorous enforcement of compliance with effluent quality standards backed up with adequate legislation which has penalties which reflect the severity of the pollution event will make a significant contribution to the improvement in surface water quality (Sharma *et al*., 2014).

However, positive influence should also be exerted to assist industry to employ discharge treatment in their plants (in the case of oil multinationals operating in the study area). This may include awareness raised in the industry sector and technical advice concerning technology choice and may also involve other incentives to industry, such as tax breaks or subsidies, to promote the use of treatment of effluents. Sediments in surface waters also interact with pollutants in the aquatic environment and can become "reservoirs" of pollution. Where chemical contaminants, particularly metals, are in water there are commonly ion exchange reactions with minerals in the sediment and diffusion of chemicals into the sediment which leads to contaminant build-up. Furthermore, where there is significant organic material in sediments or the base of streams, metals form organic complexes. These processes may remove contaminants from the water in the short-term, but may be released back into the aquatic environment at a later date, usually in response to a specific flood event. Thus,

stopping a polluting activity will not lead automatically to a rapid reduction in contaminant concentration in surface waters (Ashraf *et al*., 2010).

Groundwater is a vital resource for sustainable social and economic development around the world (Papaioannou, 2010; Garcia-Diaz, 2011). Stored groundwater is generally purified and filtered during infiltration through natural soils and sediments (Khadri and Pande, 2016; Moharir *et al*., 2017). Therefore, the quality and quantity of groundwater storage tends to be more stable than surface water. Thus, majority of people in the world primarily depend on groundwater for their drinking water (Morris, 2003). It is reported that groundwater provides drinking water for over 1.5 billion people and supports approximately 40% of agriculture in the form of irrigation (Siebert, 2010). Therefore, protecting groundwater resources, including efficient use and conservation measures, are an important strategy of water resources plan in both developing and developed countries.

However, natural processes, anthropogenic activities, and climate change significantly influence the quality and quantity of groundwater. In many world watersheds, lakes, rivers, wetlands and the associated ecosystems have experienced impacts and thus, the vitality, availability, quality and quantity of these water resources face serious threats. Elevated concentrations of chemical elements and biological constituents exist in the environment, and depending on geo-environmental backgrounds, water pollutants may exhibit spatial and temporal variations (Srivastava *et al*., 2016). Anthropogenic processes, such as discharge of untreated sewage water to water bodies, fertilization, and over exploitation, and oil pollution, have changed groundwater quantity and quality (Jacinta *et al*., 2017; Singh *et al*., 2018), leading to soil-water and air pollution (Jacinta *et al*., 2017). For example, excessive application of chemical fertilizer could result in groundwater contamination (Lewandowski *et* al., 2015; Srivastava *et al*., 2016). Nitrogen leaching, namely the downward transport and percolation of nitrate from the root zone to the soil layers, is one of the aggravating causes for groundwater contamination, especially in irrigated areas (Di Curzio *et al*., 2016; Kumar *et al*., 2018). However, it is still unclear how the anthropogenic and natural factors drive the change in the fluxes and storages of water, and associated groundwater quality. Consequently, a linked understanding of surface water and groundwater quality over space and time is critical for the assessment and management of such vital resources and ecosystems services, particularly in arid and semi-arid regions (Bhanja *et al*., 2018; Moharir, 2019).

Conversely, underground oil depots are among the main polluting sites of soil and groundwater because of the leakage of oil storage tanks and oil transshipment spills (Kim *et al*., 2015; Sun *et al*., 2015; Sun *et al*., 2017). When an oil tank leaks, oil will pollute the surrounding groundwater and soil. As a non-aqueous liquid, oil will be first intercepted in the soil pore (Borgman *et al*., 2019), which will not only change the soil structure and lead to settlement, but also become a potential source of contamination for groundwater. Over time, even pollutants trapped in the vadose zone will migrate vertically into an aquifer under the effect of leaching (Brakorenko and Yemelianova, 2011; Hang *et* al., 2015; Hornero *et* al., 2016; Romanov, 2018). According to previous research, the composition of stored oil products at service stations or underground oil tanks is complex and controlled by production processes

and standard requirements (Kaczynska *et* al., 2015; Temerdashev *et al*., 2017; Jeon *et al*., 2017).

Similarly, the environmental risk of oil well tanks leakage increases as the wells or tanks age with time. According to the US Environmental Protection Agency's (USEPA) statistics for 2011, 71% of the buried oil tanks in the USA that have operated for more than 10 years have leaked (USEPA, 2011). For example, as of 2015, most service stations in China still used single-wall tanks (Wen *et al*., 2015). An investigation and monitoring of soil and groundwater at 242 service stations in six provinces of China showed that the proportion of pollutants detected at the stations in each province was 24-89% (Jia, 2016). In the red beds regions of southwestern China, many rural residents still extract drinking water directly from groundwater that has not been purified or treated. If such drinking water sources are close to a source of pollution, human health can be harmed through drinking contaminated water. Therefore, research on the prevention and control of groundwater pollution cannot be ignored (Xue *et al*., 2019).

Mathematical formulations

1 Flow and Transport in Groundwater

Darcy's law (*an equation that describes the flow of a fluid through a porous medium*) is the fundamental principle which governs how groundwater moves in the subsurface porous medium. In general terms, groundwater movements control the contaminant transport. So, groundwater modeling refers to the mathematical representation of the Darcy flow system with specific hydrogeological conditions. In general, the groundwater flow and contaminant transport in the porous medium are three-dimensional (Bear *et al.,*1992). However, groundwater flow in saturated thickness of an unconfined aquifer is practically horizontal. In this context, all the models are built on the assumption that the aquifer (a saturated geological formation that contains and transmits "significant" quantities of water under normal field conditions (gravel, sand, volcanic and igneous rocks, limestone)) flow is essentially horizontal, that is 2-dimensional approach is used to describe the groundwater flow through porous medium. Darcy's law along with the equation of conservation of mass (for any system closed to all transfers of matter and energy, the mass of the system must remain constant over time, as the system's mass cannot change, so the quantity can neither be added nor be removed. Therefore, the quantity of mass is conserved over time) is equivalent to the groundwater flow equation which is one of the basic relationships of hydrogeology.

Using the required model formulation (Sterner et al., 2011) and considering the fact that Total Petroleum Hydrocarbon pollutants are found in the channel flow of water from a clean source in groundwater with a flow volume V, most importantly that the inflowing water channel has a concentration C(t) from the quantity of the introduced Total Petroleum Pollutant P(t). Furthermore, we assume that the water channel has a flow rate f(t) and is well mixed and maintains a constant volume with outflow rate f(t).

Then the change in amount of pollutant = Amount of pollutant entering the clean water source –Amount of pollutant leaving the clean water source and satisfies the model equation:

$$\frac{dA(t)}{dt} = f(t).P(t) - f(t).C(t) \qquad (1)$$

$$A(0) = A_0 \geq O$$

In this scenario, the amount of pollutant entering the water channel is the product of the relative abundance of the pollutant entering the water channel with the flow rate of the water channel, $f(t).p(t)$. Furthermore, the amount of pollutant leaving the water channel has the same flow rate. On the assumption that the water channel is well-mixed, the concentration in the out flowing water channel will be equal to the concentration $c(t)$, of the pollutant in the water channel. Therefore, the amount of pollutant leaving the water channel (borehole source) is the product of the out-flow rate f(t) by the concentration of the pollutant $c(t)$ leaving the water channel (borehole source). Thus, the required model formulation is expressed as follows:

$$\frac{dA(t)}{dt} = f(t).P(t) - f(t).C(t)$$
$$A(o) = Ao \geq O$$

Moreso, Since the water source maintain a constant volume V, then the concentration of the pollutant can be expressed as, concentration $= \frac{Amount}{volume}$

$C(t) = \frac{a(t)}{v}$

$\frac{dC(t)}{dt} = \frac{1}{v}\frac{da(t)}{dt}$

On substitution into the given equation, we have

$$\frac{dC(t)}{dt} = \frac{1}{v}.[f(t).P(t) - C(t)]$$
$$C(0) = Co \geq 0$$
$$\frac{dC(t)}{dt} = \frac{-f}{v}[C(t) - P(t)]$$
$$C(0) = Co \geq 0$$

Rational for additive environmental perturbation

When a model formulation fails to account for many significances complication such as irregular variations of pollutants entering the groundwater source, issues of stratification and other complication like the uptake and re-entering of the pollutant through interaction with micro-organism (microbials) found in groundwater are major factors in modeling considerations. Furthermore, the water source flow rate varies mostly as well as the leaching of the pollutant into the water source which is highly dependent on groundwater movement and rate of pollutant introductions. In this context, the new model formulation due to environmental perturbation (Akpodee and Ekaka-a, 2019) can be defined as:

$$\frac{dC(t)}{dt} = -\frac{f}{v}[C(t) - P(t)] + rni * Rand(1) \quad (2)$$
$$C(0) = C_0 \geq 0$$

Analytical method of solution for the concentration of total petroleum hydrocarbon pollutant in groundwater.

$$\frac{dC}{dt} = \frac{-f}{v}(C - P)$$

$$\frac{dC}{dt} + \frac{f}{v}\,C = \frac{fp}{v}$$

This is a linear first order ordinary differential equation with integral factor

$I.F = e^{\int \frac{f}{v} dt} = e^{\frac{ft}{v}}$

Multiplying equation with the I.F, we have

$$e^{\frac{ft}{v}}\,\frac{dC}{dt} + e^{\frac{ft}{v}}\,\frac{fC}{v} = \frac{fPe^{\frac{ft}{v}}}{v}$$

$$\frac{d}{dt}\left(e^{\frac{ft}{v}} * C(t)\right) = \frac{fPe^{\frac{ft}{v}}}{v}$$

Integrating both sides, we have

$$\int d\left(e^{\frac{ft}{v}} * C(t)\right) = \int \frac{fPe^{\frac{ft}{v}}}{v}\,dt$$

$$C(t)e^{\frac{ft}{v}} = \frac{v}{f}\left(\frac{fP}{v}\right).e^{\frac{ft}{v}} + k_1$$

$$C(t)e^{\frac{ft}{v}} = Pe^{\frac{ft}{v}} + k_1$$

$$C(t) = \frac{Pe^{\frac{ft}{v}}}{e^{\frac{ft}{v}}} + \frac{k_1}{e^{\frac{ft}{v}}}$$

$$C(t) = P + k_1 e^{\frac{-ft}{v}}$$

$$C(o) = C_o$$

$$C_o - P = k_1$$

$$C(t) = P + (C_o - P)e^{\frac{ft}{v}} \qquad (3)$$

This is the predictive model for the concentration of the Total Petroleum Hydrocarbon pollutant in the ground water source over time.

To investigate the qualitative characteristics of the concentration of pollutant of groundwater source due to Total Petroleum Hydrocarbon over a longer duration of time, we consider $limC(t)\ as\ t \to \infty$, expressed mathematically:

$$\lim_{t \to \infty} C(t) = \lim_{t \to \infty} \left[P + (C_o - P)e^{\frac{-ft}{v}}\right] \qquad 3.23$$

$$limC(t) = limP(t) + \lim (C_o - P)e^{\frac{-ft}{v}} \quad as\ t \to \infty$$

$$\lim_{t \to \infty} C(t) = P \qquad (4)$$

Which is the maximum relative abundance of the total petroleum hydrocarbon pollutant in ground water source over a longer duration of time.

Method of solution

Numerical Iterations Mathematical Preliminaries

Following Akpodee (2019), when numerical solutions to initial value problems (IVPs) are required, that is it cannot be obtained by analytical means, it is necessary to use numerical methods. From the numerical methods that exist in solving initial value problems, we have

only considered the popular fourth order Runge-Kutta method in this study as part of the mathematical preliminaries. The mathematical structure and the theoretical definitions of this method are presented as follows:

The fourth-order Runge-Kutta (R-K) method is an accurate and flexible method based on a Taylor series approximation to the function $f(x, y)$ in the initial value problem

$$\frac{dy}{dx} = f(x, y) \tag{5}$$

Subject to the initial condition $y\ (x_o) = y_o$

The increment *h* in *x* may be changed at each step, but is usually kept constant so that after *n* steps, we have

$$x_n = x_o + nh \tag{6}$$

The Runge-Kutta algorithm for the determination of the approximation y_{n+1} to $y(x_{n+1})$ is

$$y_{n+1} = y_n + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \tag{7}$$

Where,

$$k_1 = hf(x_{n,}y_{n,})$$
$$k_2 = hf(x_n + \frac{1}{2}h,\ y_n + \frac{1}{2}k_1)$$
$$k_3 = hf(x_n + \frac{1}{2}h,\ y_n + \frac{1}{2}k_2)$$
$$k_4 = hf(x_{n+1,}\ y_n + k_3)$$

The local error involved in the determination of y_{n+1} from y_n is $0(h^5)$

For the purpose of this study, it is a good numerical analysis practice that in the event of a complex dynamical system that can not admit an analytical solution for the qualitative analysis of Total Petroleum Hydrocarbon pollutant concentration in ground water, we have to adopt an alternative method which is most efficient and robust to study the qualitative behavior of the impact of total Petroleum Hydrocarbon Pollutant on groundwater. This challenging environmental problem will be tackled computationally using MATLAB ODE45 numerical scheme.

In this study, the submission and rationale that underpin the choice of numerical simulation approach (Iterations) on the impact of Total Petroleum Hydrocarbon pollutant on groundwater mathematical model formulation are stated as follows:

i. The closed-form solution (Exact solution by direct integration) maybe very complicated and difficult to evaluate analytically because of its complex environmental complication.
ii. There is no other choice which is to say that in such situation or scenario, no closed-form solution can be found.
iii. Computational approach required a large number of steps (Iterations) with chosen small step size so that a great deal of round off error can be accumulated.
iv. This approach will enhance multiple precision computations on our predictions and projections.
v. The water quality can be estimated accurately because of its role in commercial consumption and its role in environmental decision and policy making by environmental protection agencies.

Results and Discussions.

Numerical Results of the Solution Trajectories of Total Petroleum Hydrocarbon Concentration over time in Groundwater forDor-um, Gbene-Ue.

Here, the numerical simulation of the total petroleum hydrocarbon concentration in groundwater for a specific period between 0(30)360 days alongside the graphical trend of the solution trajectories is well presented

Table 1: Non-Speciated Total TPH Concentration for Gbene-Ue, BH(G1-G6)

Parameters/ Boreholes	Unit	Limit of Detection	039D-BH01	039D-BH02	039D-BH03	039D-BH04	039D-BH05	039D-BH06	DPR Target Value	EGASPIN Intervention Limit
Non-Speciated Total TPH	µg/l	-	31.88	151.23	117.31	110.93	24.96	-	50	600

Table 2: Selected Groundwater Parameters for Gbene-Ue (Dor-um)

Parameter	Value	Unit	Justification
Average annual precipitation	269.9	cm/y	Nigerian Meteorological Agency (NiMet, 2018). Seasonal Rainfall Prediction Data for Ogoniland
Saturated aquifer thickness	10.45	m	Value based on assumed deltaic sequence thickness
Hydraulic conductivity of unconfined aquifer in which dilution occurs	233.27	cm/day	Calculated mean value based on site value for silty clay
Hydraulic gradient	0.0029	-	Site data
Groundwater plume width at source	5.47	m	Assumed value based on dimensions of affected soil area
Length of affected soil parallel to assumed groundwater flow direction	15.9	m	Assumed value based on dimensions of affected soil area
Effective Porosity	0.25	-	Literature value based on silty clay
Plume width at GW/SW discharge	-	m	Nominal value based on source data
Plume thickness at GW/SW discharge	-	m	Nominal value based on assumed saturated thickness

Table 3: Qualitative Behaviour of Non-Speciated Total TPH Concentration for Gbene-Ue, (Dor-um) BH(G1-G6) within time interval 0(30)360 days

Time(Days)	G1(BH1)	G2(BH2)	G3(BH3)	G4(BH4)	G5(BH5)	G6
0	31.8800	151.2300	117.3100	110.9300	24.9600	0
30.0000	34.6106	161.2813	125.7385	119.0131	27.1262	0
60.0000	37.5597	171.7449	134.6037	127.5316	29.4708	0
90.0000	40.7419	182.6049	143.9042	136.4869	32.0067	0

120.0000	44.1726	193.8407	153.6353	145.8768	34.7475	0
150.0000	47.8674	205.4276	163.7881	155.6957	37.7074	0
180.0000	51.8424	217.3366	174.3498	165.9340	40.9013	0
210.0000	56.1140	229.5343	185.3032	176.5780	44.3443	0
240.0000	60.6986	241.9836	196.6268	187.6097	48.0522	0
270.0000	65.6126	254.6441	208.2949	199.0067	52.0412	0
300.0000	70.8721	267.4721	220.2772	210.7422	56.3275	0
330.0000	76.4928	280.4216	232.5397	222.7853	60.9275	0
360.0000	82.4899	293.4447	245.0442	235.1009	65.8578	0

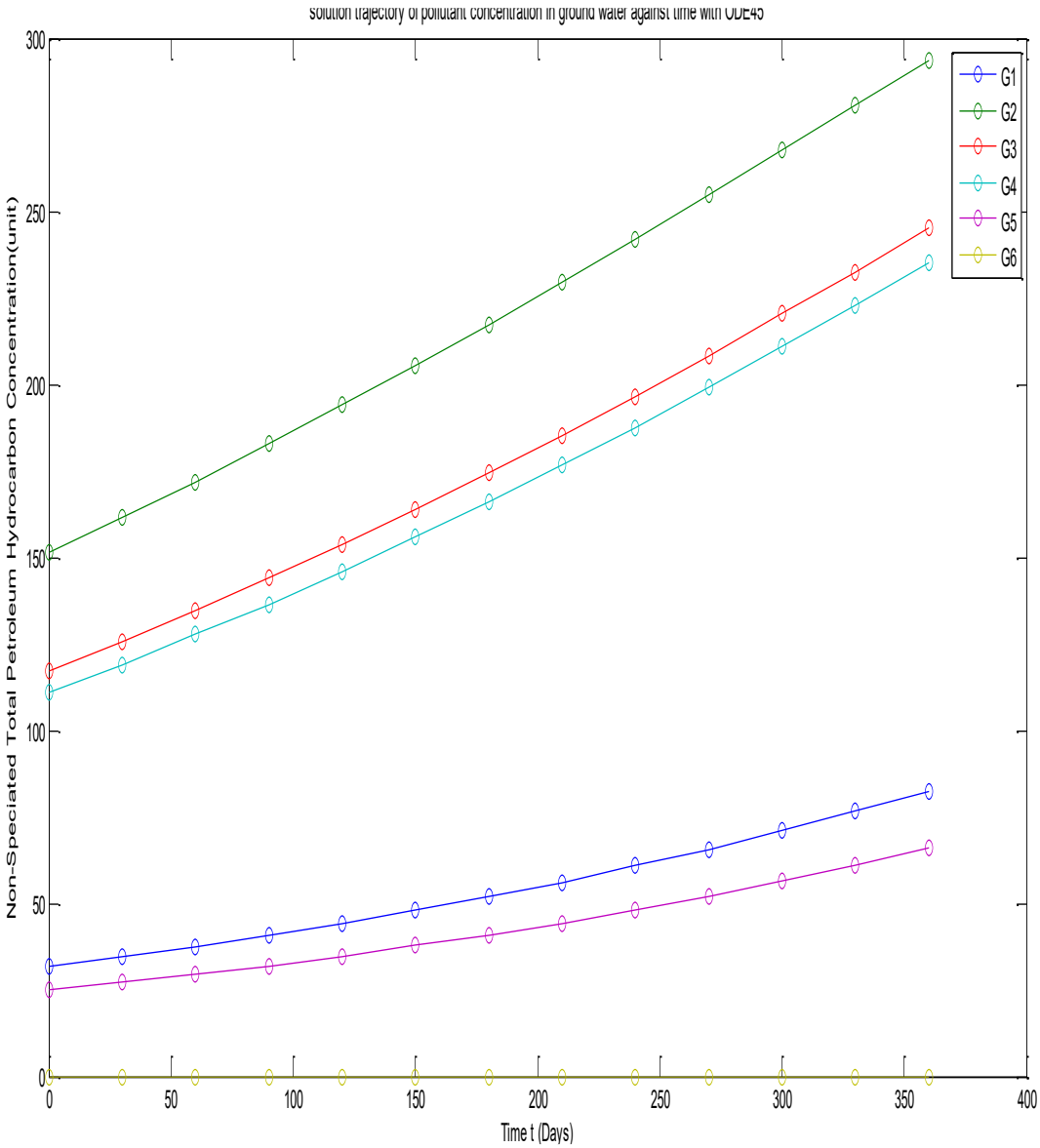


Fig. 1a Solution trajectory of Non-Speciated Total TPH Concentration for Gbene-Ue, Dor-um BH(G1-G6) within time interval 0(30)360 days

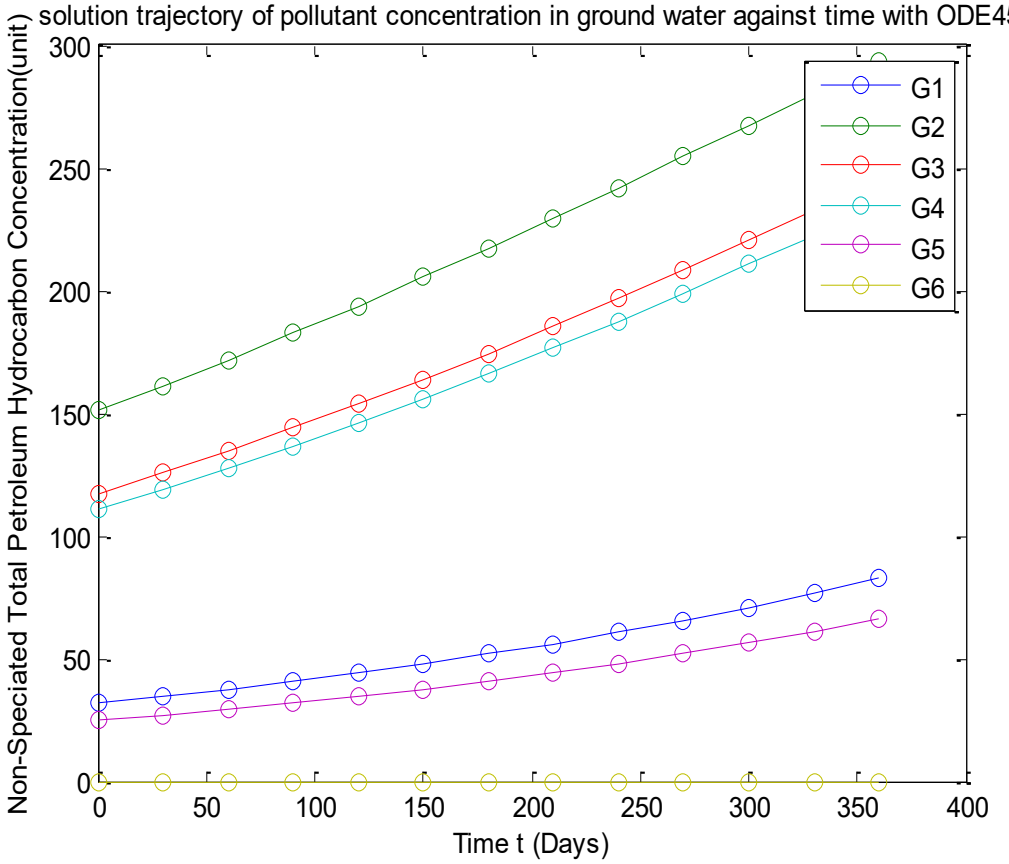


Fig. 1b Solution trajectory of Non-Speciated Total TPH Concentration for Gbene-Ue, Dor-um BH(G1-G6) within time interval 0(30)360 days

The results output indicates that on base day here called the initial condition, the numerical simulation using diffusion model equation shows that the result obtained were in line with the field data.

Furthermore, as the time range from the thirtieth 30th day up to the 360th day, the various coordinates show a monotonic increase in the non-speciated TPH concentration which saturates to various converging points on the 360th day. The numerical result shows that on the base day of our experimental time here called the initial condition the TPH concentration for the various borehole were as 31.88 for BH1, 151.23 for BH2, 117.31 for BH3, 110.93 for BH4, 24.96 for BH5 which increases monotonically to a converging saturated value of 82.49 for BH1, 293.44 for BH2, 245.04 for BH3, 235.10 for BH4, 65.86 for BH5 on the 360th day of our experimental time.

Each sampling point shows a gain in the non-speciated TPH concentration which some are closer to the environmental guideline and standards for the petroleum industry in Nigeria (EGASPIN) permissible limit. This observation will serve as a guide to the environmental protection agencies and will be useful as a check in terms of possible environmental impact mitigations and when there is constant and steady emission of the pollutant from its source.

Conclusion

Based on the detail experimental investigations, the conclusions derived are as follows:
i. The Concentration of TPH in the groundwater obtained from the study areas are reasonably high (however, slightly below EGASPIN intervention value of the initial condition). However, the TPH concentration may exceed the EGASPIN intervention value in the 410th day if all condition remains constant.
ii. Based on the WHO standard, water from the study area is mostly contaminated with TPH mostly from oil spillage source in the study areas.

Recommendations

The pollution level is generally adjudged to be high; nevertheless, there is need for frequent evaluation and strict enforcement of the environmental laws and adequate remediation of the polluted areas.

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