Soils' Pollutions by Petroleum Products Accounting for Biodegradation and Concentration-Dependent Diffusivity

Elie SIMO[1*], Jimy Synclair KENHAGO WATIA[2], Steve Christopher SONGONG TSAKEU[1] and Pierre Kisito TALLA[2]

[1]Physics Department, Faculty of Science, University of Yaounde I, P.O. Box 812 Yaounde - Cameroon
[2]Physics Department, Faculty of Science, University of Dschang, P.O. Box 96 Dschang - Cameroon
* Corresponding author: esimotc@yahoo.com

Abstract— *We have developed a model of the migration of hydrocarbon compounds in soils using diffusive formalism. Biodegradation of pollutant by microbial organisms have been considered.*

We have adopted a configuration of concentration-dependent diffusivity. The nonlinear diffusion equation governing the system was solved numerically using the DOPRI5 fourth-and-fifth-order Runge-Kutta variable step integrator. The highest depth attainable in the ground depends on the type of contaminant considered and on its initial concentration at the ground surface. We obtained that, the maximum depth reached by the contaminant increases with the increasing value of the initial concentration. This maximum depth also declined with increasing coefficient of biodegradation. The distribution profiles of the pollutant shown that the degree of penetrating of the pollutant increases with the time period. We have found a good agreement between the results derived here and those of Zygadlo and Gawdzyk. at low concentrations. While important discrepancies appear at high concentrations.

Keywords—Hydrocarbon contaminated soils, Porous media, Diffusion, Biodegradation, DOPRI5 Runge-Kutta integrator.

I. INTRODUCTION

During the last 60 years, there has been a lot of oil pollution in terrestrial areas due to human activity. As a consequence, one observes an enormous effect on the quality of the soil in some parts of the world. This study focuses on the petroleum-contaminated soils (Kang et al. 1996, Labieniec et al. 1996, Bai et al. 1996). Let us recall that, contaminants or pollutants are referred to the increase in concentration of certain substance to higher level than that they occur naturally, arising from an external source. Such actions are generally connected to human activities. Petroleum products, generally released in different sites included gasoline, jet fuel, or diesel fuel.

Petroleum oil is a complex mixture of substances, the majority of which are hydrocarbons. In the present work, we address the problem of the release of hydrocarbons on the soil surface. Let us mention, firstly, that this maneuver can occur accidentally during production, transportation, tanker accidents ... It can also be caused voluntarily by the harmful actions of human beings. For instance, pipe lines can be destroyed during wars, some ill-intentioned people can dump waste oil tankers in the nature. Such actions have been reported as the main cause of soil pollution. Several researches related to this topic of soil contaminants have been carried out worldwide (Haapkylal 2007, Das and Chadron 2011, Verbruggen et al. 2011, Wolfson 2012, Aerospace 2005). So, hydrocarbon contaminants involved in this study can be located in various areas, namely, in pipelines and pumps, in intermediate and product storage facilities, waste storage and disposal areas, drainage systems, terminals and distribution centers ... Further indications can be obtained in the reference (Nancarrow et al., 2001).

As a consequence of various spills, dangerous petroleum compounds contaminate soils, leading to major detrimental effects on the environment. Anyway, a number of spills of petroleum compounds are recorded here and there all over the world. One of the more remarkable spills is the spill of about 200.000 barrels of crude oil from the oil tanker Exxon Valdez in Prince William Sound, Alaska in 1989 \cite{hagar89}. Other cases of petroleum spills onto agricultural lands through petroleum operations have been registered in many sites in Nigeria as reported by the following papers: (Awobajo 1981, Grevy 1995, Moffat and Linden 1995). This contribution relies essentially to those potential sites, scattered here and there to the four corners of the world being contaminated with petroleum products. It is very important to emphasize that: these petroleum contaminants shall not remain indefinitely on the ground surface. They must inevitably penetrate in the soil

following the well-known diffusive model of compounds in porous media. Soils can obviously be treated as porous materials.

Here, we shall carry our studies on four particular petroleum compounds; namely: benzene, toluene, xylene, Isooctane. It can be highlighted that, in soils contaminated with petroleum and derivatives, the aforementioned compounds stand out compared to others (Andrade and Augusto 2010, Souza et al. 2011). That is why, we are particularly interested in these hydrocarbons. In the present work, we take into consideration the biodegradation aspect of the contaminants, among other things. Biodegradation is the process by which organic substances are broken down into smaller compounds by enzymes produced by living microbial organisms. The paper is organized as follows: We present the model in the next section. Section three stands for the implementation of the DOPRI5 fourth-and-fifth-order Runge-Kutta variable step integrator for the numerical investigations. In this section, computational results are followed by discussions and commentaries. Section four is devoted to the conclusion of the paper.

II.   THE MODEL

It is reasonable to characterize soils as porous media material. Some unwanted substances released in the soil could, unfortunately, modified its structure. Among them, we can name petroleum derivatives, as we mentioned earlier. Theoretically speaking, a porous soil has the ability to absorb pollutants until its pores are saturated. At this stage, it is said that the soil has reached the so called capillary saturation state. Capillary suction is a fundamental transport mechanism to describe the petroleum hydrocarbons absorption in soil. Strictly speaking, this process is basically a convective phenomenon. Meanwhile, in the context of soils contaminated with petroleum it is sufficiently accurate to contemplate the liquid transport in soils as a diffusion phenomenon. The capillary petroleum compound movement is related to the capillary suction stress which emerges as the result of curved liquid surfaces in the pore system of most soils. The suction process is described by the Fick's law

$$g_c = -D(C)\nabla C$$
(1)

Here, $C(z, t)$ stands for the concentration of petroleum hydrocarbons at a point z at time t, D is the pollutant diffusion coefficient or the diffusivity for short; and g_c is the pollutant flux density. A certain quantity, Q of the pollutant disappears by biodegradation during the diffusion process. Biodegradation is one of mechanisms

of natural attenuation of the pollutant in the ground. Q is defined as

$$Q = -\mu C$$
(2)

where μ refers to the biodegradation coefficient of the considered pollutant. This decrease is usually taken into account in analytical or numerical models by solving a differential equation of the type:

$$\frac{\delta c}{\delta t} = -\mu C$$
(3)

This approach has a sense in steady state. By contrast, in non-steady state, i.e., when the flow in each point varies with time, the Fick's equation needs to be completed by the balance equation:

$$\frac{\partial c}{\partial t} = -\nabla g_c$$
(5)

If we consider biodegradation of pollutant, the Fick's law (5) is transformed into

$$\frac{\partial c}{\partial t} = -\nabla g_c - \mu C$$
(6)

This coefficient μ describes the attenuation of the process. The attenuation consisting in the reduction of the contaminants transported by a biodegradation of the later. Biodegradation of petroleum compounds by natural populations of microorganisms represents one of the primary mechanisms by which petroleum contaminants are eliminated from the environment. Petroleum compounds are, indeed, rich sources of carbon and the hydrocarbon within it are readily oxidized aerobically with the release of carbon-dioxide by a variety of microorganisms found in the ground. More details can be found in the reviews (National Academy Press 1985, Atlas and Bartha 1992). Let's mention that expressions (4) and (5) of the flux density are associated only to the steady states: this corresponds to the situation where the flux is not a function of time. In not steady regimes, i.e. at each position the flux varies with time. In this context, the petroleum hydrocarbon balance equation should be introduced. Putting together equations (5) and (6) yields

$$\frac{\partial c}{\partial t} = \nabla[D(C)\nabla C] - \mu C$$
(7)

So, the general equation of the petroleum contaminant diffusion is a second order partial derivatives equation. This equation (7) cannot be solve analytically so long as the diffusivity D depends on the concentration. If we consider one-dimensional transfer of the pollutant, this master equation (7) is transformed into

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(D \frac{\partial c}{\partial z}\right) - \mu C$$
(8)

z measures the penetrating depth of the pollutants in the soil.

Now, we consider the restrictive case where the diffusion coefficient is constant. The petroleum hydrocarbons penetrating the ground is described by the following equation in one dimension:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - \mu C$$
(9)

We introduce the following boundary conditions in the soil-hydrocarbon system under consideration:

$C(0,0)=0$ for $0 < z < S$,   (10)

$C(z,0)=0$ for $0 < z < L$,   (11)

$\frac{\partial C}{\partial z} = 0$ pour t 0 et z=S.   (12)

Here, C_0 is the initial concentration of the petroleum component at the surface; L is the maximum depth that the pollutant can reached when penetrating in the ground. Thus, Eq. (9) corresponds to the case where the diffusivity is not a function of the concentration. This equation was used by Zygadlo and Gawdzyk (2010) for the description of the migration of petroleum compounds in soil.

In a number of works related to this topic, authors have restricted their analysis on situations where the diffusivity coefficient is considered as a constant parameter. Really speaking, this is not generally the case and the effect of the concentration-dependence of the diffusivity could be large. In this chapter, we focus our attention on the specific case where the diffusivity coefficient is expressed as a function of the concentration of the contaminant in the soil.

To begin, let's mention that it is usually impossible to obtain a closed-form analytical solution for the equation of diffusion when the coefficient of diffusion depends on concentration. This observation shall constrain us to think about the digital approach in the continuation of this work. In addition, thanks to numerical methods, one can gain some understanding of the diffusion process and propose a functional form of the concentration-dependence of the diffusivity. In this vein,

Greer (Greer, 2016) made use of the finite difference technique to construct a linear composition dependence of the diffusivity. Their investigations lead them to the conclusion that the assumption of linear composition dependence for the diffusivity has a physical basis. Greer found it necessary to confirm the validity of its approach by combining its own method with the Boltzmann-Matano (Wierzba, 2013) method. They used the Boltzmann-Mateno method to build the diffusivity as a function of the composition from experimentally determined composition profiles. Meanwhile the numerical technique gave them the ability to predict the composition profile. As a result, necessary informations about the behavior of the diffusivity as a function of composition could be obtained. In this section, we treat the diffusivity as linearly dependent on the concentration under the aforementioned brilliant developments by Greer (Greer, 2016):

$$D = aC + b$$
(13)

The constants a and b are approximated by the values

$$a = 3,5 . 10^{-8} \text{ and}$$
$$b = 5.1 . 10^{-7}$$
(14)

This expression results from a great agreement between a numerical method (Greer, 2016) and an experimental method (Wang, 1951).

III.   THE IMPLEMENTATION OF THE DOPRI5 FOURTH-AND-FIFTH-ORDER RUNGE-KUTTA VARIABLE STEP INTEGRATOR FOR THE NUMERICAL RESOLUTION: DISCUSSIONS

As we mentioned earlier, the analytical resolvability of the processing of this model is questionable. Because the nonlinear equation of diffusion (6), governing the system, do not have an obvious analytical solution, we opted for a numerical computation. The master equation of this contribution is solved numerically using the DOPRI5 fourth-and-fifth-order Runge-Kutta variable step integrator. It should be recalled that only quite numerical analysis could lead to physically acceptable solutions. A numerical method is said to be stable if numerical errors, e.g., those errors generated by round off, are not amplified, and the approximate solution remains bounded. This requirement applies to time-stepping schemes and iterative solvers alike. It is worth notice that, the notion of stability highlights the relationship between the exact solution of the discrete problem and the actually computed solution that includes round off and iteration errors. Nowadays, all the mathematical tools necessary for the study of the stability

are available in the case of linear problems with constant coefficients. The most popular technique is unquestionably the well-known Von Neumann method. See, for instance, these references (Von, 1950). On the other hand, nonlinear problems are more difficult to analyze and may require a stronger form of stability. So, it is important to solve this problem using a quite appropriate technique. In this sense, a Runge-Kutta method using DOPRI5 as integrator is introduced for describing accurately the nonlinear diffusion of petroleum contaminants in porous materials like soils.

The basis of the method is to discretize the spatial part of the operator and keep the temporal part as such. This approach allows to increase the precision of the approximation in time and space independently and easily. We choose as space discretization the finite volume approximation where the operator is integrated over reference volumes. The finite volume method is well suited for the numerical simulation of various types of conservation laws, such as the nonlinear equation of diffusion describing the migration of hydrocarbon compounds in the present work. This method was also used for the description of the nonlinear diffusion of moisture in concrete (Simo et al., 2017). As solver for the differential equations, we use the Runge-Kutta method of order 4-5 introduced by Dormand and Prince (1986) implemented as the FORTRAN with DOPRI5 code by Hairer and Norsett (1987). This integrator has the merit of ensuring an excellent control of the step sizes with a dense output. Here, a sophisticated setting of the parameters allows for the adaptation of the code to the problem and the needs of the users. With the necessary input data, the model calculates the resulting pollutant content in the ground.

The simulation we perform here are based on normalized quantities. Dimensionless quantities are introduced via below anzats

$$C = C_0 \bar{C}, \quad t = t_0 \bar{t}, \quad z = l_0 \bar{z}, \tag{15}$$

$$\mu = \mu_0 \bar{\mu}, \quad a = a_0 \bar{a}, \quad b = b_0 \bar{b} \tag{16}$$

where $\bar{C}$ is the normalized concentration of the pollutant measured in units C_0; $\bar{\mu}$ is the normalized coefficient of degradation measured in units μ_0; $\bar{a}$ and $\bar{b}$ are the normalized coefficients of the function of diffusivity measured in units a_0 and b_0, respectively. l_0 is the characteristic distance. Here, $\bar{t}$ is the dimensionless time parameter measured in units t_0. So,

t_0 is the time constance. Plugging the transformations (15) and (16) into the diffusion equation (6) leads us to the following equation, in dimensionless units, after some algebra:

$$\frac{\partial \bar{C}}{\partial \bar{t}} = \frac{\partial}{\partial \bar{z}} \left[\left(CC_1 \bar{a} \bar{C} + \bar{b} \right) \frac{\partial \bar{C}}{\partial \bar{z}} \right] - \mu \mu_1 \bar{\mu} \bar{C} \tag{17}$$

With

$$t_0 = \frac{l_0^2}{b_0}; \quad CC_1 = \frac{a_0 C_0}{b_0} \quad \text{and} \quad \mu \mu_1 = \frac{l_0^2 \mu_0}{b_0} \tag{18}$$

Table. 1: Input data related to four different types of petroleum hydrocarbon

Petroleum Hydrocarbon	Benzene	Toluene	Xylene	Isooctane
Diffusion coefficient $D_0 . 10^7$ $[m^2/s]$	3.5	3.6	8.1	24
Biodegradation rate constant in the soil $\mu . 10^8 \ [s^{-1}]$	5.55	4.63	2.89	6.94

The Tab.1 represents the input data used for the computational process according to the contribution of Zygadlo and Gawdzyk (2010).

Our numerical investigations focus on four different types of petroleum components. Namely, Benzene, Toluene, Xylene and Isooctane. To really dig inside this crucial environmental problem, we firstly perform calculations based on benzene, a well-known hydrocarbon contaminant. At the beginning of the process, only the surface of the ground is polluted. All the pores of the soil are supposed to be empty; so far as this petroleum component is concerned. As soon as the hydrocarbon is spilled on the surface of the ground, the pollutant component does not cross the concerned portion of the soil instantaneously from the surface to the maximal depth. It takes some time to penetrate the soil. The rate of penetration can be observed in Fig. 1. This figure clearly indicates the positions reached by benzene inside the ground at given periods. The pollution of the entire portion of the ground necessitates some time. Benzene moves gradually and slowly through the porous media. So, in this case where the initial concentration of benzene at the surface is setting to the value $C_0 = 100 \ Kg/m^3$, one can notice, for instance that: after a period $t = 50 \ days$ only 340.36 m depth has been attacked by the pollutant product. The remaining of the ground is not yet affected by benzene as it can be seen

in Fig. 2. The covering of the maximum depth attainable 728.92 m is observed approximately $t = 250\ days$ after the spill of pollutants. Figs. (1, 2) also indicate that as the benzene moves through the soil, its amplitude decreases gradually from its maximal value at the surface to zero. The concentration of the pollutant does not decreases significantly at the beginning of the process, as soon as one pours the hydrocarbon compounds. It first declines slowly before falling abruptly to zero, after a certain time. In Fig. 2, we can obtain precise indications on the maximum distances reached by the pollutant in the ground at different periods.
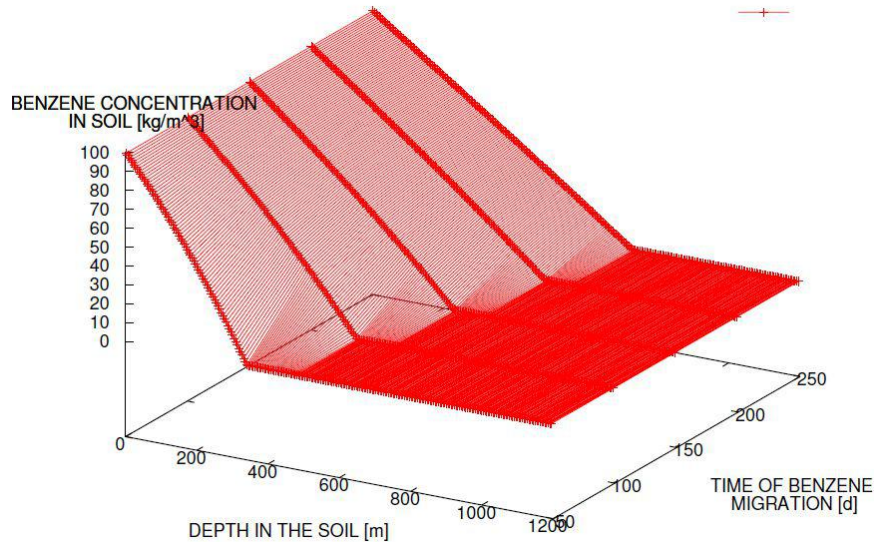
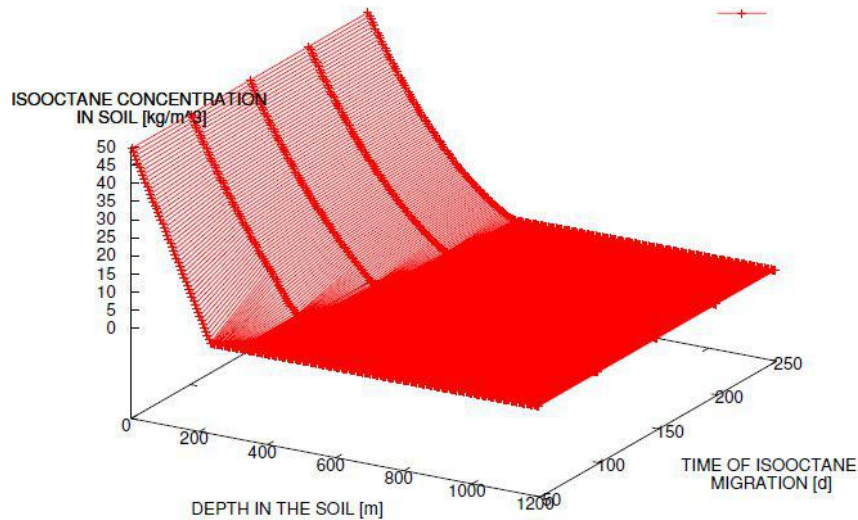

Fig. 1 Time evolution of Benzene content in the ground. The initial concentration of benzene at the surface is setting to the value $C_0 = 100\ Kg/m^3$.
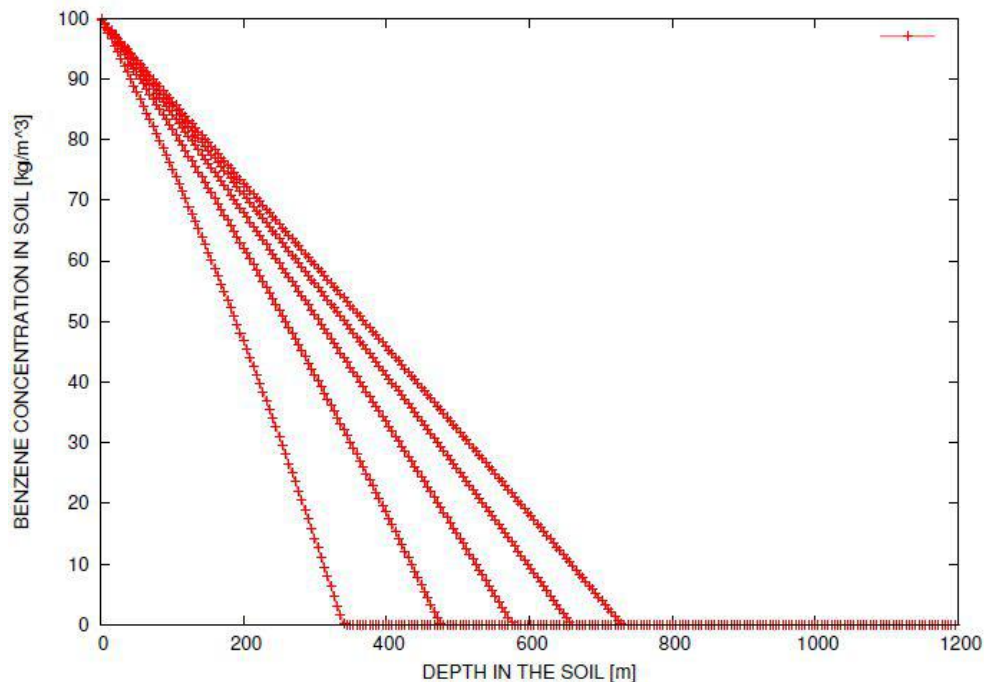
Fig. 2 Benzene content in the ground in terms of the distance from the ground surface. The initial concentration of benzene at the surface is setting to the value $C_0 = 100\ Kg/m^3$

During the migration's process described in this paper, a constant concentration is maintained at the surface.

Now, our numerical investigations focus on three other types of petroleum contaminants. Namely, Toluene,

Isooctane and Xylene. We analyze the contaminant distribution in the ground as a function of the time for each single hydrocarbon. As a result, we obtain that computational processes lead practically to the same profile as in the case of benzene. This allegation is clearly expressed on Figs. (3, 4, 5). These curves show that the maximal depth attainable by the contaminant in the ground is not always the same. It varies from one contaminant to another, depending on the value of its biodegradation coefficient in the soil. So, for an initial concentration on the surface of the ground fitted at

$C_0 = 50 \, Kg/m^3$ and for the same temporal period, i.e. d $t = 250 \, days$, the maximal depth attainable is obtained with Xylene $z_{max} = 534.61 \, days$ whereas the minimal one is obtained with Isooctane $z_{min} = 412.65 \, days$. As a bit of explanation, we can hypotesize that the most penetrating contaminant is the one associated to the lowest coefficient of degradation in soil.

Fig. 3 Time evolution of Isooctane content in the ground. The initial concentration of Isooctane at the surface is setting to the value $C_0 = 50 \, Kg/m^3$
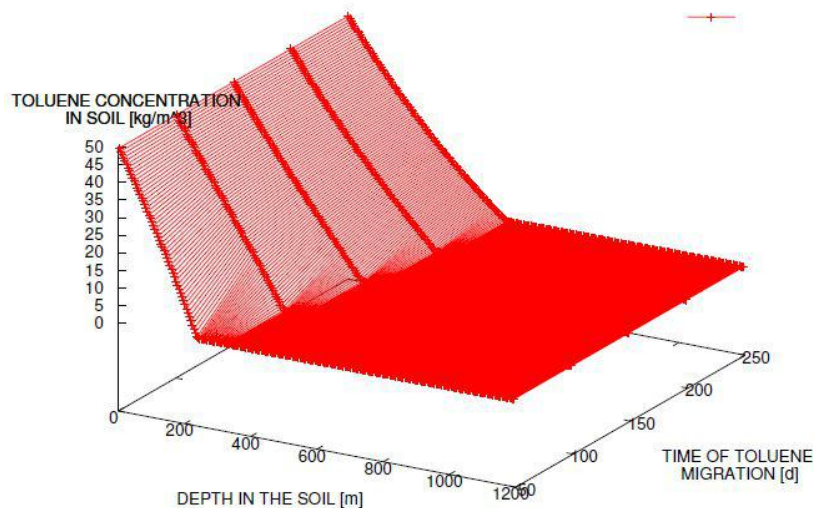

Fig. 4   Time evolution of Toluene content in the ground. The initial concentration of Toluene at the surface is setting to the value $C_0 = 50 \, Kg/m^3$
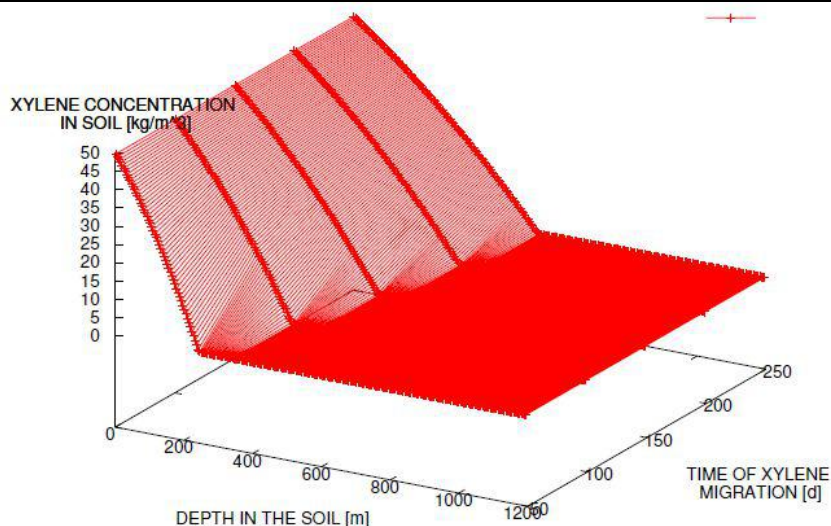
Fig. 5 Time evolution of Xylene content in the ground. The initial concentration of Xylene at the surface is setting to the value

$$C_0 = 50 \, Kg/m^3$$

From the Fig. 6, it is clear that the maximum depth attainable by the contaminant increases as the coefficient of biodegradation decreases, as it was expected. The general trend, in terms of the maximum depth of hydrocarbon penetration through the ground, is as follows:

Xylene > Toluene > Benzene > Isooctane

This trend is consistent with the data from the table Tab. 1 relating to the coefficient of biodagradation of the contaminants considered in this contribution.
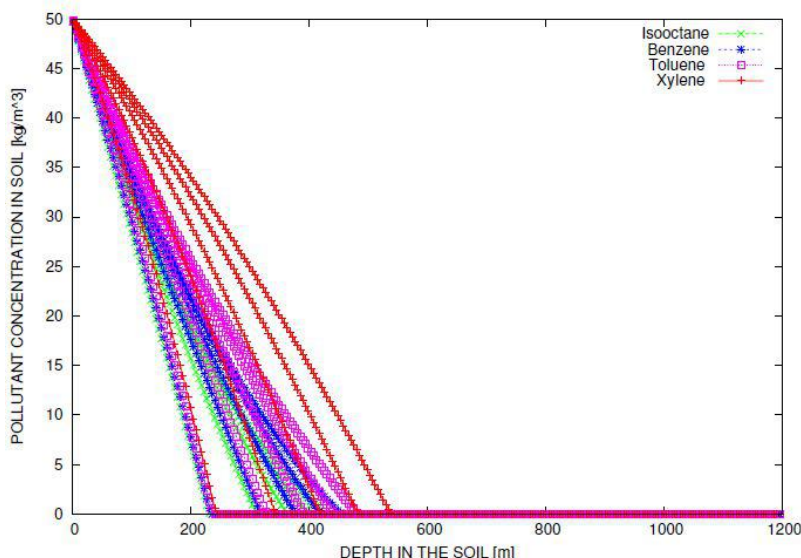
Fig. 6 Contaminants' content in the ground in terms of the distance from the ground surface. Curves are drawn for the four hydrocarbon components considered in his paper: the green curve corresponds to the Isooctane, the blue curve corresponds to the Benzene, the purple curve corresponds to the Toluene and the red curve corresponds to the Xylene. The initial concentration of each contaminant at the surface is setting to the value $C_0 = 50 \, Kg/m^3$

3.1 IMPACT OF THE INITIAL CONCENTRATION OF THE POLLUTANT ON ITS PENETRATION IN THE GROUND

Analyses are carried out using benzene as the pollutant. The profile of benzene distribution is shown if Figs. (7, 8) for three different values of the initial concentration of the benzene on the ground surface. These curves give clear indications on the maximum depth attainable by the contaminant according to its initial concentration. These plots reveal that: any decrease of the initial concentration would lower the maximum depth of penetration of the benzene through the ground.
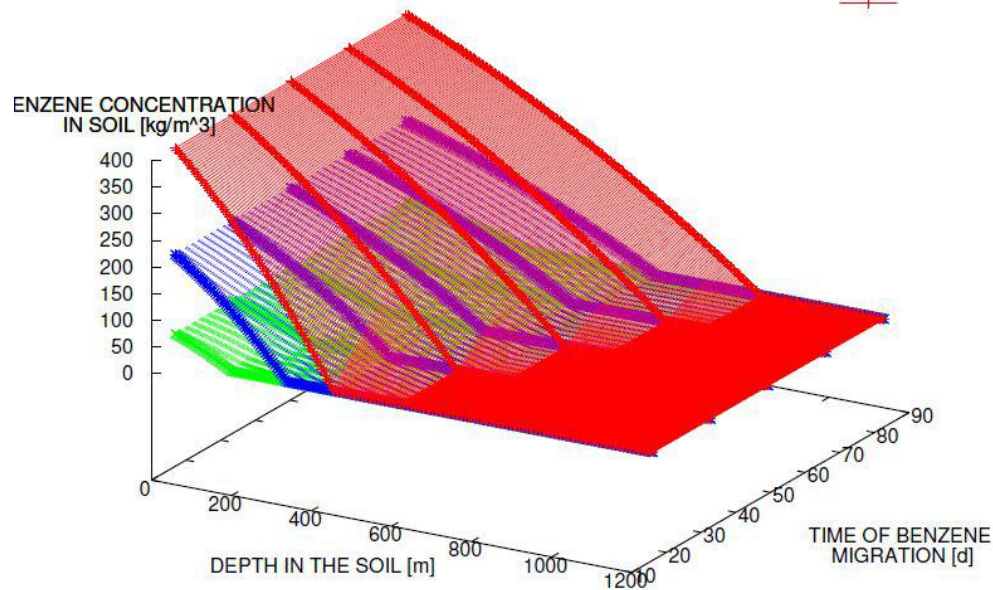
Fig. 7 Time evolution of Benzene content in the ground. In this figure, three initial concentrations are considered:
$C_0 = 50\ Kg/m^3$ *is shown by the green curve;* $C_0 = 200\ Kg/m^3$ *is shown by the blue curve and*
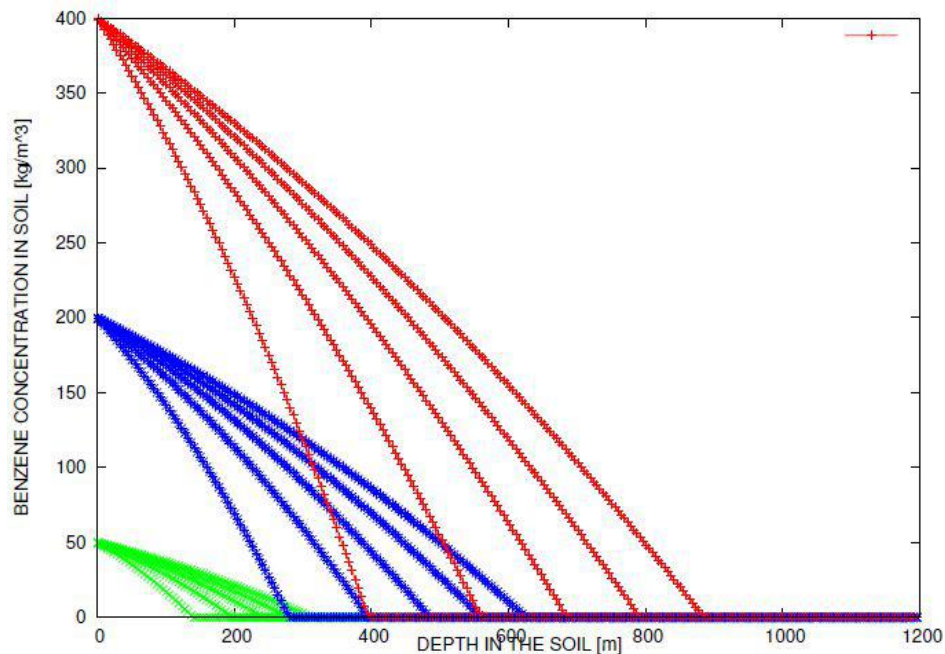$C_0 = 400\ Kg/m^3$ *is shown by the red curve. The temporal period is fitting to* $t_0 = 83.33\ days$

Fig. 8 Spatial profile of benzene distribution in the soil at different time intervals. In this figure, three initial concentrations
are considered: $C_0 = 50\ Kg/m^3$ *is shown by the green curve;* $C_0 = 200\ Kg/m^3$ *is shown by the blue curve and*
$C_0 = 400\ Kg/m^3$ *is shown by the red curve. The temporal period is fitting to* $t_0 = 83.33\ days$

We perform computations for different values of the initial concentration of the petroleum component on the surface of the ground. For each single value of the initial concentration, we determined the highest depth attainable by the pollutant in the ground. In this section of the work, were our analyses are based on benzene, some selected values describing this process are given in Tab.2.

Table.2 - Different values of the initial concentration of benzene at the surface (ICS) and associated maximum depth of benzene penetration through the ground (MDBP). It should be recalled that MDBP is expressed in meters and ICS in Kg/m^3.

ICS	50	75	100	125	150	175	200	225
MDBP	314.77	385.54	444.28	498.49	543.67	588.86	629.52	665.66

ICS	250	275	300	325	350	375	400
MDBP	701.81	737.95	769.58	801.20	823.83	859.84	887.05

To get an idea about the progress of the pollutant in the soil, based on its initial concentration at the ground surface. We have plotted the curve indicating the maximum depth reached by benzene versus the initial concentration of the hydrocarbon spilled at a given location. We obtain that, for initial concentration ranging from 50 to $400Kg/m^3$, the evolution of the maximum depth reached by the pollutant experiences a quasi-parabolic process. One can refer to the results plotted in Fig. 9. The maximum depth of benzene penetration through the ground (MDBP) as a function of the initial concentration of benzene at the surface of the ground.
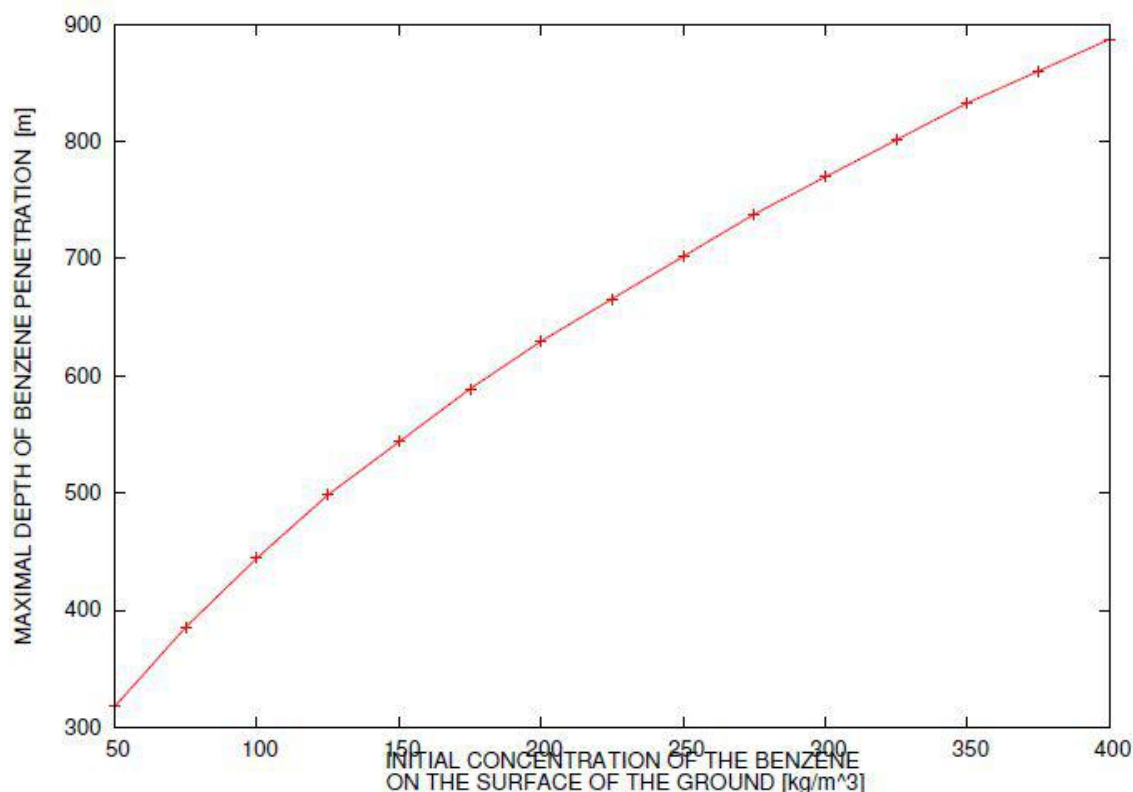

Fig. 9: *The maximum depth of Benzene penetration through the ground (MDBP) as a function of the initial concentration of benzene at the surface of the ground.*

3.2 IMPACT OF THE TEMPORAL PERIOD ON THE POLLUTANT MIGRATION IN THE GROUND

Now, we want to gather some informations about the impact of the temporal period on the depth of the pollutant migration. In order to compare the degree of benzene penetration in the ground, according to the duration, we present three different configurations in Figs. (10, 11, 12). Each of these figures results from the plotting of the computational results at two different temporal periods. The profiles of the contaminant distribution in the ground are exhibited. From these curves, one can infer that the maximum depth attainable by the pollutant grows with the temporal period. To confirm this aspect of the problem, we perform a series of computations for different values of the temporal periods ranging between 41 days and 416 days. Fig. 13 confirms the above profile of the maximum depth attainable as a function of the temporal period. We can notice that, when

we consider two fairly close temporal periods, the shift between the results is not very important. The reader can refer to Fig. 10, for instance. Here, the two periods involved are: $t_0 = 41.66\ days$ and $t_0 = 83.33\ days$. In contrast, the shift between the results becomes very significant when the difference between temporal periods is very large. Figs. (11, 12) illustrate very well such a situation. The couple of periods considered here are $(41.66\ days, 250\ days)$ and $(208.33\ days, 416.67\ days)$, respectively.
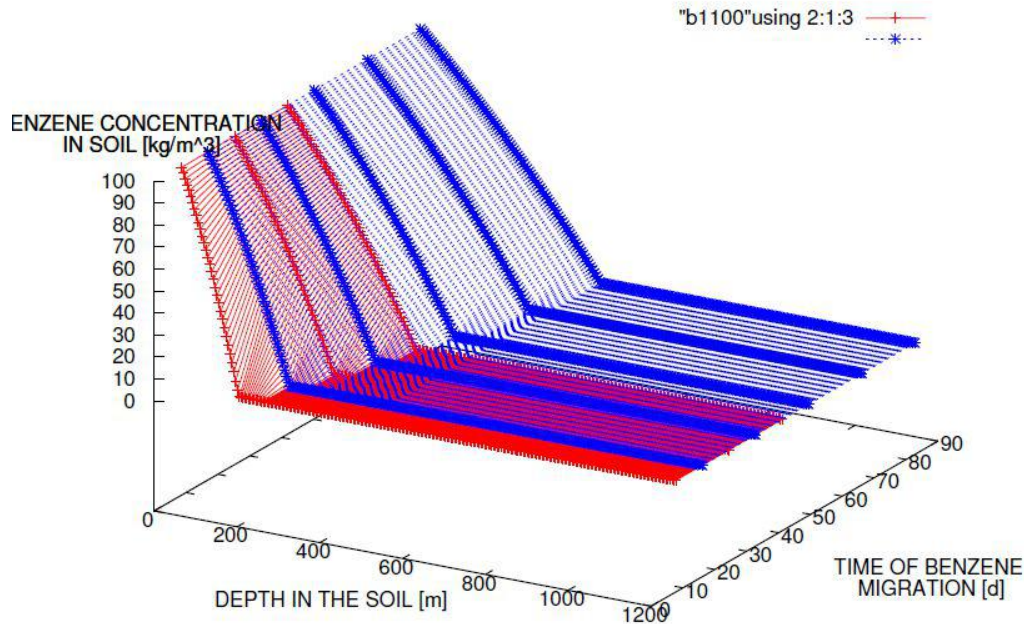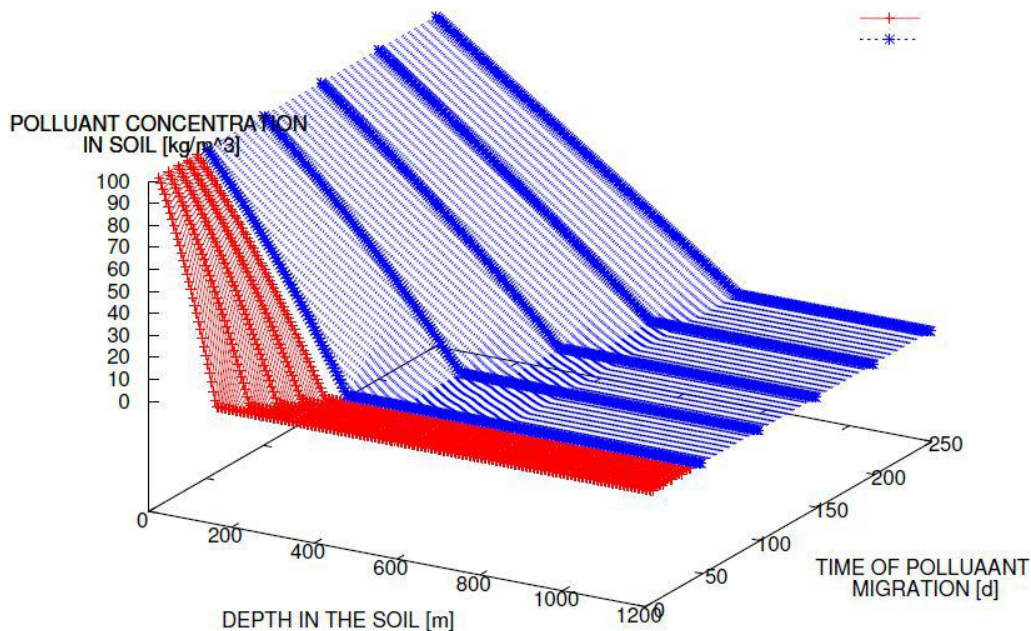

Fig. 10 Time evolution of Benzene content in the ground. Here, two different temporal periods are considered: The red curve shows the case corresponding to the period $t_0 = 41.66\ days$. The blue curve shows the case corresponding to the period $t_0 = 83.33\ days$. The initial concentration of benzene at the surface is setting to the value $C_0 = 100\ Kg/m^3$.
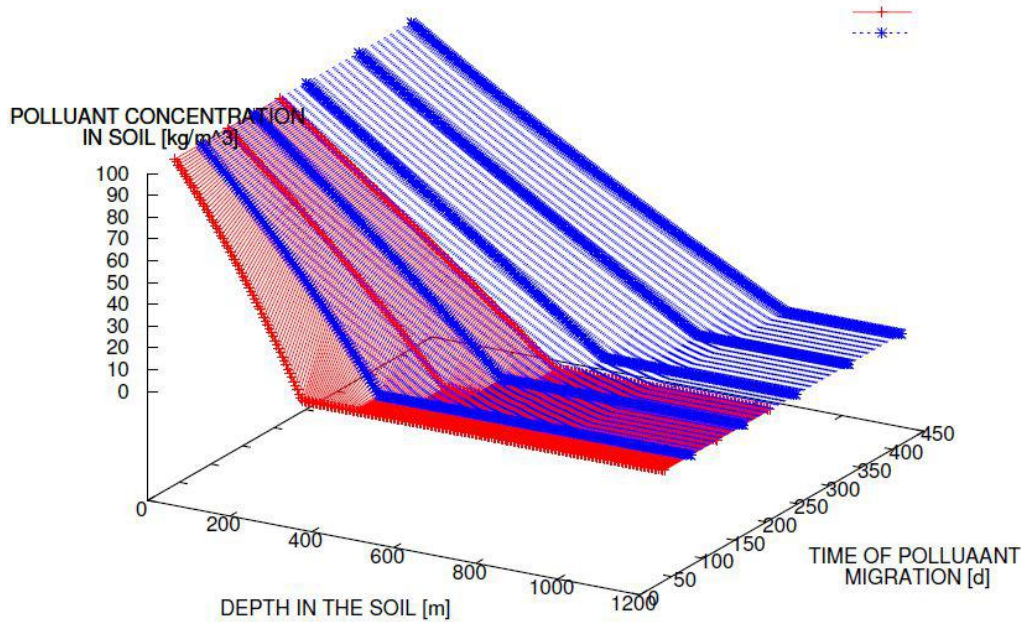

Fig. 11 Time evolution of Benzene content in the ground. Here, two different temporal periods are considered: The red curve shows the case corresponding to the period $t_0 = 41.66\ days$. The blue curve shows the case corresponding to the period $t_0 = 250\ days$. The initial concentration of benzene at the surface is setting to the value $C_0 = 100\ Kg/m^3$.

Fig. 12 Time evolution of Benzene content in the ground. Here, two different temporal periods are considered: The red curve shows the case corresponding to the period $t_0 = 208.33\ days$; *The blue curve shows the case corresponding to the period* $t_0 = 416.67\ days$. *The initial concentration of benzene at the surface is setting to the value* $C_0 = 100\ Kg/m^3$.
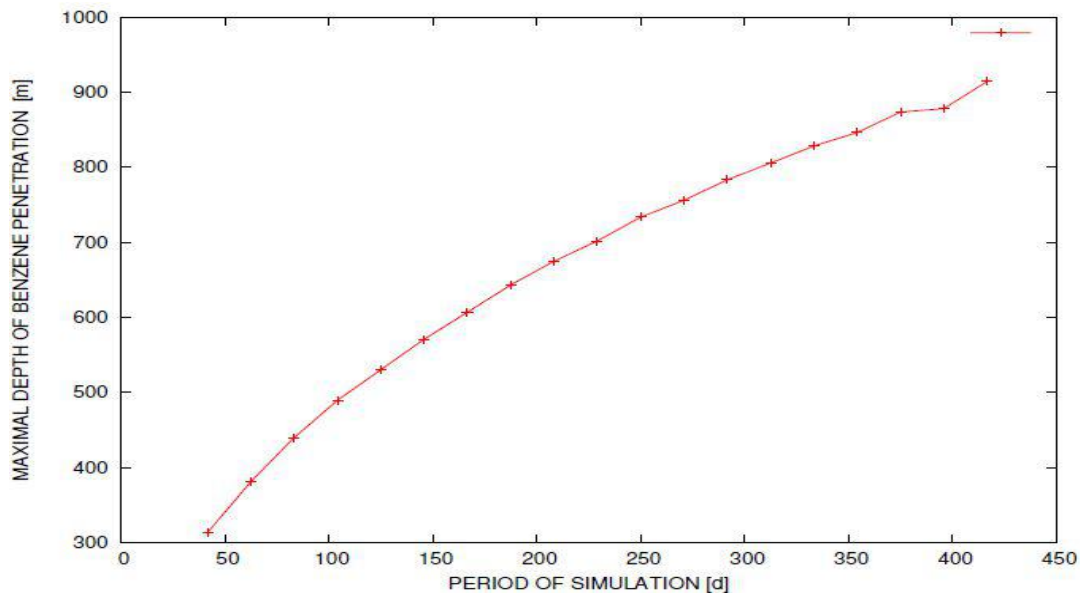

Fig. 13 The maximum depth of benzene penetration through the ground (MDBP) as a function of the temporal period for an initial concentration of benzene at the surface of the ground fitting at the value $C_0 = 100\ Kg/m^3$.

3.3 COMPARAISON BETWEEN THIS MODEL AND ZYGADLO MODEL

We compare the composition profiles generated by our numerical technique to those derived from the diffusion equation with constant diffusivity proposed by Zygadlo and Gawdzyk (2010). The computational results plotted in Fig. 14 for an initial concentration $C_0 = 25\ Kg/m^3$, shows very good agreement with the results by Zygadlo and Gawdzyk (2010). This agreement persists for $C_0 = 50\ Kg/m^3$ (see Fig. 15).

As the initial concentration C_0 increases, one notice a discrepancy between the two results. This is, in fact, visible in Fig.16. This offset grows and becomes quite significant for somewhat large values of C_0. The reader can refers to the Fig. 17.
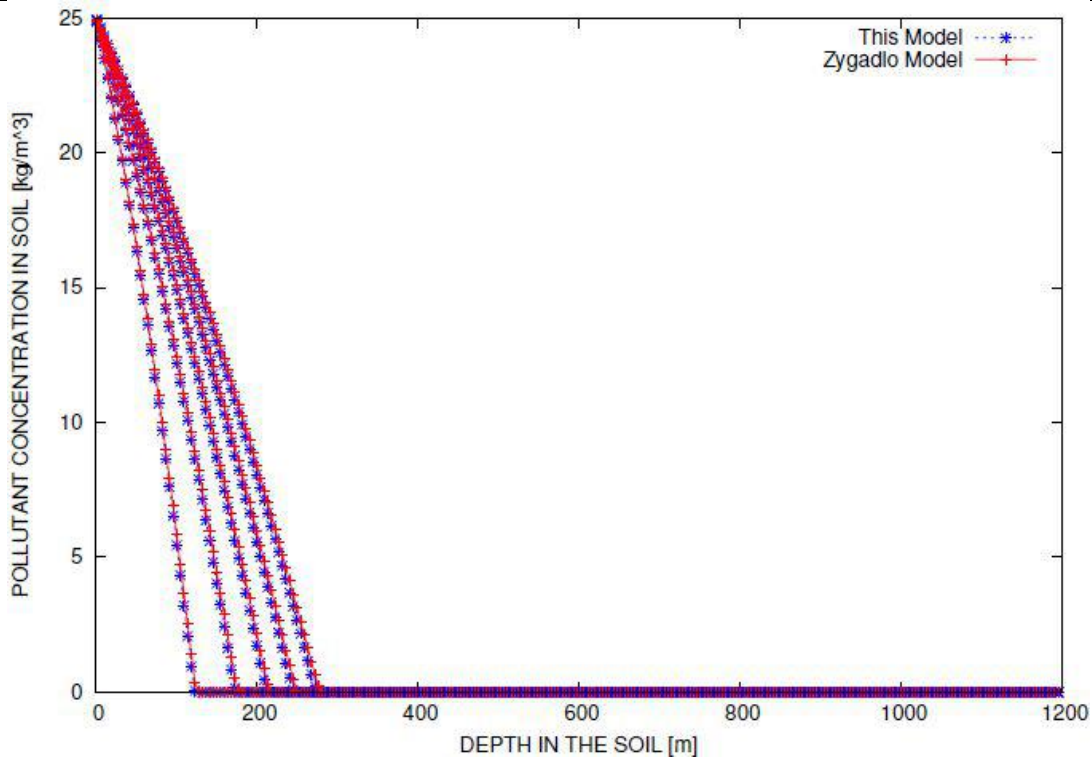
Fig. 14 Benzene content in the ground in terms of the distance from the ground surface for this model and Zygadlo model. The initial concentration of benzene at the surface is setting to the value $C_0 = 25 \; Kg/m^3$.
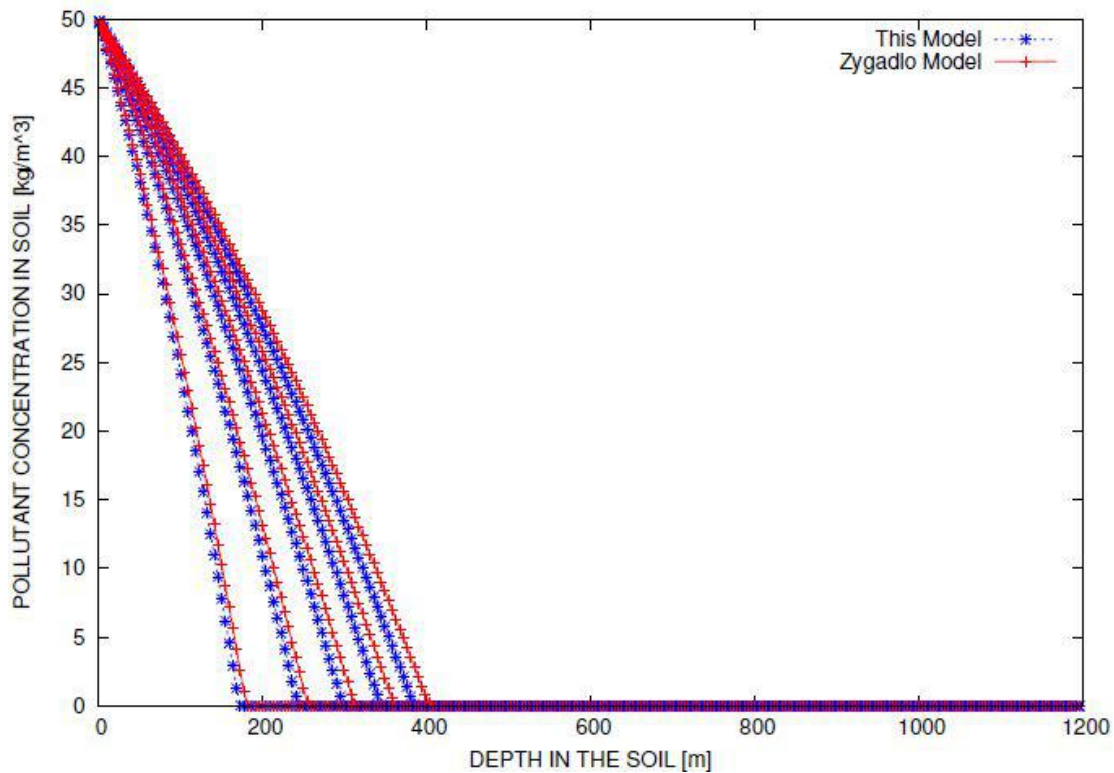

Fig. 15 Benzene content in the ground in terms of the distance from the ground surface for this model and Zygadlo model. The initial concentration of benzene at the surface is setting to the value $C_0 = 50 \; Kg/m^3$.

Fig. 16 Benzene content in the ground in terms of the distance from the ground surface for this model and Zygadlo model.

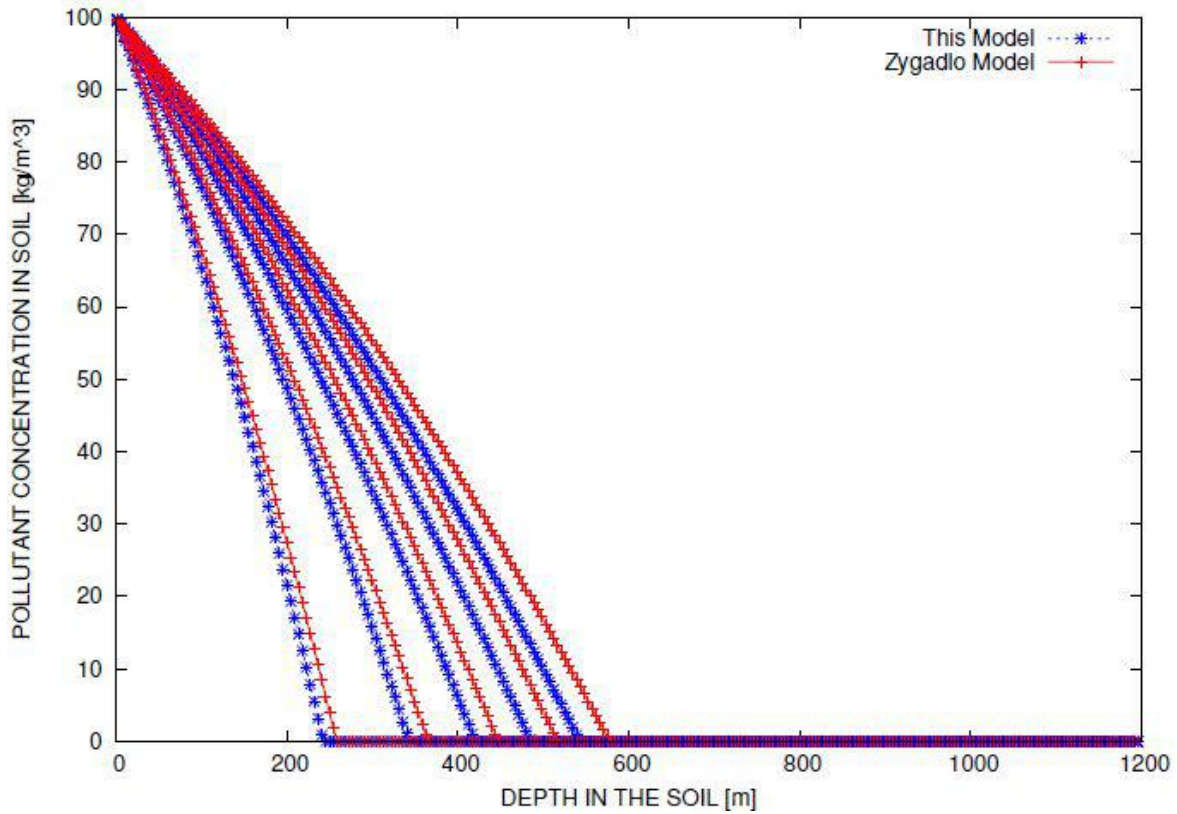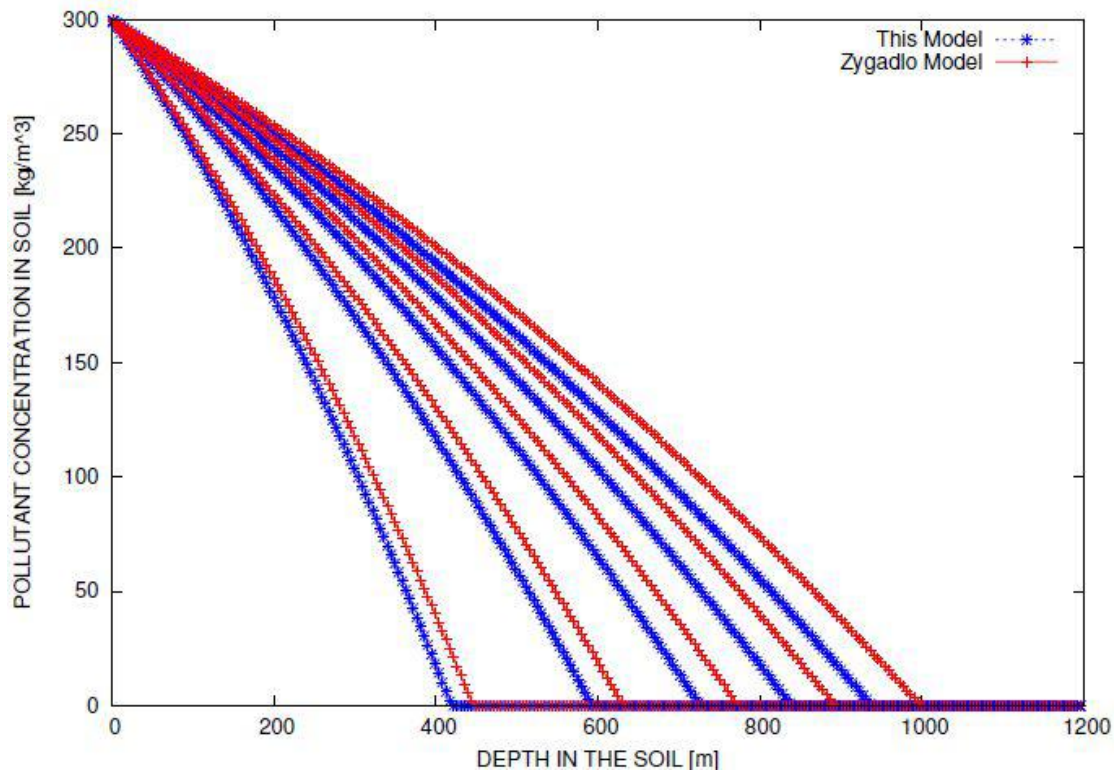The initial concentration of benzene at the surface is setting to the value $C_0 = 100\ Kg/m^3$.

Fig. 17 Benzene content in the ground in terms of the distance from the ground surface for this model and Zygadlo model.

The initial concentration of benzene at the surface is setting to the value $C_0 = 300\ Kg/m^3$.

Our computational technique reveals that, it is incorrect to ignore the concentration-dependence of the coefficient of diffusivity in the process of migration of petroleum contaminants in soils. This assertion is mostly justified in the case of somewhat higher concentrations. The conclusion could be different for small concentrations. In this case, the change between the results derived from the two models is could be neglected.

IV. CONCLUSION

We have considered petroleum hydrocarbon contaminated soils in this paper. The migration of these petroleum contaminants was investigated. Calculations were carried out with regard to the biodegradation process of the components. The reason being that the majority of toxic hydrocarbon components of petroleum are biodegradable. We assumed that the coefficient of the diffusion is not constant and we introduced a concentration-dependent function. Boltzmann-Matano analysis was used to approximate the linear composition dependence of the diffusivity.

The master equation of diffusion describing the system could not be solved analytically. To gain some understanding of the system behavior, we introduced the fourth-and-fifth-order Runge-Kutta method using DOPRI5 code as the integrator. The discretization of space followed the finite volume technique. The DOPRI5 code has been used as the integrator. Four hydrocarbon components are involved in this contribution, namely Xylene,Toluene, Benzene and Isooctane. For each pollutant, we are interested by the profile of its distribution in the ground. We have plotted a number of curves to show the distribution of contaminants in the ground and their degree of penetration.In various circumstances, the maximum depth of hydrocarbon penetration through the ground has been computed. Computational results have shown that, for the same period of time and for the same initial concentration of contaminant at the ground surface, Xylene was the most penetrating contaminant in our context. For a bit of explanations, we can remind that Xylene has the smallest Coefficient of biodegradation.

The efficiency of our formalism was checked by comparing the concentration profile obtained in our case with those exhibited by Zygadlo and Gawdzyk . Calculations were performed for different values of the initial concentration of the petroleum component. We have presented the profile of the distribution of contaminant in soil at different concentration ranges. Then, the predictions by Zygadlo and Gawdzyk (2010) are plotted in the same figures. By doing so, some discrepancies have emerged. Although, we have obtained very good agreement at low concentrations, important

shifts are confirmed for high concentrations. We arrived at the conclusion that Zygadlo and Gawdzyk formalism has underestimated the pollutant distribution in soil at somewhat high concentrations. In fact, the discrepancies between the two models are increased at high concentrations.

Nomenclature

C	hydrocarbon concentration in the ground $[Kg/m^3]$
$\overline{C}$	normalized hydrocarbon concentration $[-]$
C_0	initial concentration of the hydrocarbon at the surface $[Kg/m^3]$
D	coefficient of the diffusion of the hydrocarbon $[m^2/s]$
g_c	hydrocarbon transport flux density $[Kg/(m^2 s)]$
L	maximum depth attainable in the ground $[m]$
l_0	units of the measurement of a distance $[m]$
Q	quantity of pollutant disappearing by biodegradation
t	time $[d]$
$\bar{t}$	normalized time parameter $[-]$
t_0	units of the measurement of time
z	depth of penetration of the pollutant $[m]$

REFERENCES

[1] Aerospace, Mechanical Mechatronic Engg**. (2005)** University of Sydney.

[2] **Andrade, J.A., and Augusto, F. (2010). "**I.C.S.F Jardin, Biorremediacao de solos contaminadod por petroleo e seus derivados." Ecletica quimica 35(3), pp. 17-43.

[3] **Atlas, R.M., and Bartha, R. (1992). "**Hydrocarbon biodegradation and soil bioremediation." Adv.

[4] **Awobajo, A. O. (1981).** "An analysis of foil spill incidents in Nigeria." Proceedings of National seminar on petroleum industries and Nigerian environment, Warri, pp. 57-63. Microb. Ecol. 12, pp. 287-338.

[5] **Bai, M., Roegiers, J. C., and Inyang, H. I. (1996).** "Contaminant transport in nonisothermal fractured porous media." Journal of Environmental

Engineering 5, 175.

[6] **Charney, J., Fjortoft, R., and Von Neumann J. (1950).** "Numerical integration of barotropic vorticity equation." tellus, pp.237-254.

[7] **Das, N., and Chandron, P. (2011).** "Microbial degradation of petroleum contaminants: an overview." Biotechnology Research International, doi: 4061/2011/941810.

[8] **Dormand-Prince (1986).** journal of computational and applied mathematics 15, pp. 201-203

[9] **Edenhofer, O., Pichs Madruga, R., Sokona, Y., Seyboth, K., Matschoss, P., Kadner, S., Zwickel, T., Eickemeir, P., Hansen, G., Schlomer, S., and Von Stechow, C** (eds**) (2011).** Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[10] **Greer, J. R. (2016).** Class notes Ch. 1, Fick's Laws and Macroscopic Diffusion. Example of using Fick's laws: concentration-dependent diffusivity, pp. 1-35.

[11] **Grevy, P. (1995).** The Niger Delta Nigeria Pollution assessment study. Report to the World Bank. Carl Bro international Glostrup Denmark 125.

[12] **Haapkylal, P., Ramade, F., and Salvat, B. (2007).** "Oil pollution on coral reefs: a review of the state of knowledge and management needs." Life Environ t. 57(1-2), pp. 91-107.

[13] **Hagar, R. (1989).** "Huge cargo of North Slope oil spilled." Oil Gas J. 87, pp.26-27.

[14] **Hairer, E., Norset, S., and Warnner, G. (1987).** "solving ordinary differential equations." Springer-Verlag,Berlin.

[15] **Kang, S. H., and Oulman, S. (1996).** "Evaporation of petroleum products from contaminated soil." ournal of Environmental Engineering 5, 384.

[16] **Labieniec, P. A., Dzombak, D. A., and Siegrist, R. L. (1996).** "Soil risk assessment model for organic contaminants in soil." Journal of Environmental Engineering 5, 338.

[17] **Moffat, D., and Linden, O. (1995).** "Perception and reality: Assessing priorities for sustainable development in the Niger River Delta." Ambio. 24(7-8), pp. 527-532.

[18] **Nancarrow, D. J., Adams, A. L. , Slades, N. J., and Steeds, J. E.** (2001). Land contamination: Technical guidance on special sites: petroleum refineries, R and D Technical report P5-042/TR/05, Environnment Agency.

[19] National Academy of Sciences, Oil in the sea-inputs, fates, and effects. National Academy Press**(1985)** Washington. D. C.

[20] **Simo, E., Dzali Mbeumo, P. D., and Mbami Njeuten, J. C. (2017**). "Moisture transfer in concrete: numerical determination of the capillary conductivity coefficient." Slovak Journal of Civil Engineering vol. 25 (1), pp. 10-18.

[21] **Souza, T. S., Cfristofoletti, C. A., and Fontanetti, C. S. (2011).** "Ecotoxicological assays in soils contaminated by petroleum hydrocarbons,.."In: Visser J. (ed), Ecotoxicology around the globe, New York: Nova Science Publishers 247.

[22] **Verbruggen, A., Moomaw, W., and Nyboer, J. (2011)** "Annex I: Glossary, Acronyms, Chemical symbols and prefixes, Vol. 106." IPCC special report on renewable energy sources and climate change mitigation pp. 953-972

[23] **Wang, J. H. (1951).** J. Amer. Chem. Soc. 73 510.

[24] **Wierzba, B., and Shibinski, W.S. (2013).** "The generalization of the Boltzmann-Motano method." Physica A: Statistical Mechanics and its Applications 392, 4316.

[25] **Wolfson, R. (2012).** Energy from Earth and Moon in Energy, Environment, and Climate, 2nd ed., New York, NY: W.W. Norton and Company, ch. 8, pp. 204-224.

[26] **Zygadlo M., and Gawdzyk, J. (2010). "** Modeling the transport of petroleum products by soil filter method." Polish J. of Environ. Stud. 19 (4), pp. 841-847.