



Original Research Article

# Migration of petroleum hydrocarbons from ground surface to groundwater accounting for a liquid Arrhenius model

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The process of petroleum hydrocarbons migration from the ground surface to groundwater was analyzed. We assumed that the diffusivity is linearly dependent on the concentration in soils. A liquid Arrhenius model of diffusion was adopted in groundwater. The nonlinear diffusion equation of the system was solved numerically. In this sense, we introduced the method of fourth-and-fifth-order Runge-Kutta using the DOPRI5 code as integrator. We sought for conditions under which petroleum products spilled on the ground surface can reach water tables. Three hydrocarbon products were involved in the calculations: benzene, toluene and xylene. We assessed the concentration of pollutants, when they reach the groundwater, for different depths to water. We found that the reachability and the degree of contamination of the water table depend on four main parameters: 1) the value of the initial concentration on the soil surface, 2) the depth to water, 3) the time period and 4) the type of hydrocarbon. For instance, calculations have shown that 5.0kg/m<sup>3</sup> Xylene takes about one hour to reach a water table located at 120 m. This study presents separate curves describing the contaminant distribution in soil and groundwater. When Benzene reaches the water table, it takes about 250 days to cover 10 cm depth in the water. Here, the descending motion is significantly slowed.

**Key words:** Petroleum-contaminated soils and water, drinkable water, porous media, diffusion, liquid Arrhenius model, biodegradation, DOPRI5 Runge-Kutta integrator.

## INTRODUCTION

Here, we address the problem of the release of hydrocarbons on the ground surface. It is worth noting that, such maneuvers can occur accidentally during daily regular actions including: production, transportation, and tanker accidents. Let us mention that unfortunately, these actions could be caused voluntarily by the harmful actions of human beings. As examples, we can list some disturbing

situations recorded here and there across the world: destruction of pipelines during wars, dumping of waste oil tankers in nature by some ill-intentioned people. Such actions have been reported as the main cause of water and soil pollution (Awobajo, 1981; Hagar, 1989; Grevy, 1995; Kang et al., 1996; Labieniec et al., 1996; Haapkyal et al., 2007; Das et al., 2011; Souza et al., 2011). Therefore, there

## Nomenclature

$C$	hydrocarbon concentration [ $Kg/m^3$ ]
$C_{0s}$	initial concentration of the hydrocarbon at the surface of the soil [ $Kg/m^3$ ]
$C_{0w}$	initial concentration of the hydrocarbon at the surface of the groundwater [ $Kg/m^3$ ]
$D_s$	coefficient of the diffusion of the hydrocarbon in the ground [ $m^2/s$ ]
$D_w$	coefficient of the diffusion of the hydrocarbon in water [ $m^2/s$ ]
$H$	Depth to water [m]
$M_{hyd}$	molar mass of the hydrocarbon
$L$	maximum depth attainable by the pollutant [m]
$t$	Time [s]
$T$	absolute temperature [ $^{\circ}K$ ]
$z$	depth of penetration of the pollutant [m]
$\mu_{bs}$	Biodegradation rate constant in soil [ $s^{-1}$ ]
$\mu_{bw}$	Biodegradation rate constant in water [ $s^{-1}$ ]
$\mu_w$	dynamical viscosity of the water [ $Kg/(m.s)$ ]

has been a lot of oil pollution in terrestrial and aquatic areas, due to human activity, during the last decades. Subsequently, one observes an enormous effect on the quality of water in some parts of the world. Even drilling water collected in the groundwater, even hundreds of meters into the ground, no longer have a guarantee that it is suitable for drinking.

Nobody should be insensitive to the quality of water which is distributed to human beings for their daily consumption. It becomes a global concern. The problem of drinkable water has also attracted the attention of Fernández-Luqueño and its co-workers (2016). They analyzed the quality of drinking water in the northern Mexico region, using the techniques of physicochemical and microbiological characterization. They examined the presence of certain hazardous parameters and verified if their concentrations were above the World Health Organization (WHO, 1998) guideline values. As one can see, their main preoccupation was the quality of drinking water and its suitability for human consumption. In the same vein, Li and co-workers (2014) proposed a review of soil pollution and site remediation policies in China. The authors reviewed the appropriate environmental policies applied by the Chinese government in order to remedy the negative impacts of the pollution of soils, on the health of the population; since these pollutants, coming from emissions of industrial releases, could probably reach the groundwater. In such situations, the risks of contamination become unavoidable. Testoni and co-workers (2016) were rather interested by the scenarios of possible migration of radionuclide in basic environmental matrices such as soil and groundwater. Nowadays, it is well established that, groundwater is one of the main radionuclide transport pathways in the environment. Their investigations allowed them to give clear indications about the presence or not of radionuclide elements in groundwater.

Otherwise, it is noteworthy that, there is a great discrepancy between the quality of water intended for consumption in developing and developed countries. The situation is more critical in developing countries. Here, people suffer seriously from water-borne diseases. This aspect of the problem was addressed by Rizak and Hruddy (2007). In their contribution, they managed to associate the international community on the crucial need to take preventive and safety measures towards the quality of the drinking water. Such actions are taken in order to protect the population from the high risk of contracting water-borne diseases.

In this study, we focused our attention on the contamination of groundwater by petroleum compounds. Petroleum products spilled on a given site, on the surface of the earth, begin their migration in the soil. In this work, we want to underline that these products could pass through the soil and reach the groundwater. Therefore, any drilling done in this site, in view to collecting water for consumption, will constitute a danger for the population. Thus, this study addresses the delicate item of petroleum-contaminated soils and groundwater. As we emphasized earlier, we shall be mostly interested on the impact of pollutants in groundwater. Petroleum products, generally released in different sites include gasoline, jet fuel, or diesel fuel. In a particular case where spills lead to ground water contamination, certain hydrocarbon compounds such as benzene, toluene and xylene will partition into ground water. It can be highlighted that, in soils and water contaminated with petroleum and derivatives, the aforementioned compounds stand out compared to others (Williams et al., 2006; Andrade et al., 2010; Souza et al., 2011). That is why, we are particularly interested on these hydrocarbons. In the present work, we took into consideration the biodegradation aspect of the contaminants, among other things. As a bit of explanation, we can underline that, 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: The next section is devoted to the materials and methods. Section three stands for implementation of the DOPRI5 numerical code. Let us note in passing that DOPRI5 is an explicit Runge-Kutta method of order (4)5 with step-size control and continuous output due to Dormand and Prince (1986). In this section, the computational results are followed by discussions and commentaries.

## MATERIALS AND METHODS

### Presentation of the model

Capillary suction is a fundamental transport mechanism to describe petroleum hydrocarbon absorption in soil. The suction process is described by Fick's law. In this context, Fick's equation needs to be completed by the balance equation. By doing so, one obtains the general equation of

**Table 1.** Numerical values of biodegradation rate constant in soil and in groundwater

Petroleum Hydrocarbon	Benzene	Toluene	Xylene
Biodegradation rate constant in soil $\mu_{bs} \cdot 10^7 [s^{-1}]$	5.55	4.63	2.89
Biodegradation rate constant in groundwater $\mu_{bw} \cdot 10^7 [s^{-1}]$	4.40	3.59	0.92

the petroleum contaminant diffusion. The reader can refer to (Simo et al., 2019).

$$\frac{\partial C}{\partial t} = \nabla[D_s(C)\nabla C] - \mu_{bs}C \quad (1)$$

Here, C represents the concentration of petroleum hydrocarbons at a point P at time t.  $D_s$  is the pollutant diffusion coefficient or the diffusivity for short. So long as the diffusivity  $D_s$  depends on the concentration, the analytical solvability of this second order partial derivatives equation (1) is questionable. This equation (1) tells us that, a certain quantity of the pollutant disappears by biodegradation during the diffusion process. The parameter  $\mu$  refers to the biodegradation coefficient of the considered pollutant (Atlas, 1992). A considerable number of toxic hydrocarbon components of petroleum are biodegradable. Biodegradation is probably the most important reaction mechanism for the degradation of hydrocarbons in aquatic environments. This concept refers to the transformation of hydrocarbon products into simpler substances. Such process being controlled largely by bacteria, fungi, and yeast. It should be understood that, biodegradation is facilitated by temperature in the range of  $293^{\circ}K - 313^{\circ}K$ . In a number of hydrogeological systems, biodegradation is the most important process that removes btex from ground water. Btex being a group of contaminants consists of benzene, ethylbenzene, toluene and three isomers of xylene. For a better understanding, the reader can refer to (Cozzarelli et al., 1994; Edwards et al., 1992; Thierrin et al., 1993; Lovley et al., 1995). The biodegradation rate constant in ground water for Benzene, Toluene and Xylene are given in Table 1.

If we consider one-dimensional transfer of the pollutant, the master equation of the system (1) is transformed into

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left[ D_s(C) \frac{\partial C}{\partial z} \right] - \mu_{bs}C \quad (2)$$

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

We introduce the following boundary conditions in the system under consideration:

$$C(0,0) = 0 \quad (3)$$

$$C(z,0) = 0 \text{ for } 0 < z < L \quad (4)$$

$$\frac{\partial C}{\partial z} = 0 \text{ for } t > 0 \wedge z = L \quad (5)$$

Here,  $C_0$  is the initial concentration of the petroleum component at the surface; L is the maximum depth that the pollutant can reach when penetrating the ground.

In this model, we treat the diffusivity as linearly dependent on the concentration following brilliant developments by Greer and co-workers (2016). The reader can also refer to the papers by (Wierzba et al., 2013; Simo et al., 2019).

$$D_s = aC + b \quad (6)$$

The constants a and b are approximated by the values

$$a = 3,5 \cdot 10^{-8}; b = 5,1 \cdot 10^{-7} \quad (7)$$

Now, we are interested in the movement of the petroleum product as soon as it reaches the water table. A number of works have recorded the general problem of diffusion through water of hydrocarbons found in petroleum (Saraf et al., 1963; Witherspoon et al., 1965; Sahores et al., 1966). Wang (1951) perfected the capillary-cell method of measuring diffusion coefficients. In this contribution, we introduce temperature-dependent diffusivity of petroleum hydrocarbons in water following Worch's model (Worch, 1993; Worch, 2004). Thus, the evolution of the diffusivity is derived from the following equation:

$$D_w(T) = 3,595 \cdot 10^{-4} \frac{T}{M_{hyd}^{0.58} \mu_w} \quad (8)$$

Here,  $\mu_w$  is the dynamic viscosity of the water and  $M_{hyd}$  is the molar mass of the hydrocarbon:

$$\mu_w = \mu_0 \exp(G(T)) \quad (9)$$

and

$$G(T) = a_w + b_w \frac{T_0}{T_w} + c_w \left( \frac{T_0}{T} \right)^2 \quad (10)$$

We shall make use of the following empirical fit for this viscosity (Auld et al., 2005) in the remainder of this work

$$a_w = -1.94; b_w = -4.80; c_w = 6.74 \quad (11)$$

Therefore, we adopted a liquid Arrhenius model in water.

The temperature-independent pre-exponential factor,  $\mu_0$  being the value of the dynamic viscosity at a reference temperature which in this context takes the value

$T_0 = 273.16^\circ K$  corresponding to  $\mu_0 = 0.001792 \text{ Kg}/(m.s)$  and  $T$  is the absolute temperature.

For small depths,  $z \leq 20 \text{ m}$ , we assumed that the soil has a constant temperature which is approximately the temperature at the surface. The more one descends in the Earth's crust, the hotter the rock and groundwater become. The temperature of the soil increases as the depth increases. For depths  $z$  in the range  $20 \leq z \leq 100 \text{ m}$ , the temperature is located in the intervals  $9^\circ C - 15^\circ C$ . For all  $z$  above 100 m, there is a temperature gradient: Each 100 m additional depth corresponds to a temperature elevation of  $3^\circ C$ . In this sense, one can write

$$T = T_{ref} + 3 \frac{z-z_0}{100} \quad (12)$$

Here,  $T_{ref} = 15^\circ C$  and  $z_0 = 100 \text{ m}$ .

Table 1 gives biodegradation rate constants of BTX in groundwater (Buscheck et al., 1995). The reader can also refer to (Weidemeier et al., 1996). This table also represents biodegradation rate constants of BTX (Benzene, Toluene and Xylene) in the soil, according to the contribution of Zygadlo and Gawdzik (2010).

#### Techniques of computation: implementation of the Dopri5 fourth-and-fifth-order Runge-Kutta variable step integrator for the numerical resolution

It can be seen that the nonlinear equation of diffusion (2), governing the system, does not have an obvious analytical solution. Therefore, we opted for a numerical computation. Physically acceptable solutions could be obtained only if the numerical method involved in the computation is quite stable. In this sense, numerical errors, e.g., those errors generated by round off, are not amplified, and the approximate solution remains bounded. In the current context, all the mathematical tools necessary for studying 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, this reference (Smith, 1985). The stability option applies to time-stepping schemes and iterative solvers alike. The notion of stability refers to the relationship between the exact solution of the discrete problem and the actually computed solution that includes round off and iteration errors. It should be noted that nonlinear problems are more difficult to analyze and may require a stronger form of stability. Therefore, it is important to solve this problem using a suitable technique. It is fundamentally what motivated the choice of the Runge-Kutta method of orders 4(5), associated with the DOPRI5 integrator, for computation of our results. By doing so, we can accurately describe the nonlinear diffusion of

petroleum contaminants in porous materials like soils and also in groundwater. This method was introduced by Dormand and Prince (1986) and Charney et al. (1950) and implemented as the FORTRAN code. Details about the implementation can be found in the book (Hairer et al., 1987).

The basis of the method is to discretize the spatial part of the operator and keep the temporal part as such. This approach makes it possible 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) and in the paper (Simo et al., 2019). The DOPRI5 integrator used in this technique plays a crucial role. It 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 and in the groundwater at different time periods.

We performed our numerical computations having in mind a previous study by WHO (1998), providing guidance as to tolerable levels of petroleum hydrocarbon fractions in drinking-water, in the event of spills of petroleum oils.

## RESULTS AND DISCUSSION

As mentioned earlier, our numerical investigations focused on three different types of petroleum components namely Benzene, Toluene, and Xylene. We sought for conditions under which petroleum hydrocarbons spilled on a given site, on the surface of the earth, can reach the water table with a concentration higher than the threshold values indicated in Table 2. It is clear from this table that, a tiny amount of benzene in water can produce important damages in the body. It can be excessively harmful to humans even at very low concentrations. Concerning the two other hydrocarbons evaluated in this paper, namely toluene and xylene, the threshold value of their concentrations in water that could be dangerous to humans is significantly higher than the threshold value assigned to benzene.

As soon as hydrocarbon products are spilled somewhere on the ground surface, the depth attained by the groundwater shall be a function of the relief of the site. In different locations on the surface of the earth, it should rise or fall depending if the considered land is more or less mountainous (Fetter, 1994).

Tables 3, 4, and 5 indicate the various depths  $H$  to water, and the concentration of the pollutants under consideration

**Table 2.** Threshold of tolerable petroleum hydrocarbon concentration in drinking-water (WHO, 1998)

Petroleum Hydrocarbon	Toluene	Xylene	Benzene
Threshold value of concentrations ( $Kg/m^3$ )	0.7	0.5	0.01

**Table 3.** Different values of the initial concentration of benzene at the surface ( $C_{0s}$ ) and corresponding concentration of benzene ( $C_{0w}$ ) when it reaches the water table. The depth to water is setting to the value.  $H = 80 m$ 

$C_{0s} (Kg/m^3)$	0.05	0.1	0.5	1	5	10
$C_{0w} (Kg/m^3)$	0.008934	0.02347	0.47253	0.723476	1.6140	3.1370
$C_{0s} (Kg/m^3)$	15	25	50	150	250	
$C_{0w} (Kg/m^3)$	6.9447	9.9754	46.055	117.78	209.51	

**Table 4.** Different values of the initial concentration of benzene at the surface ( $C_{0s}$ ) and corresponding concentration of benzene ( $C_{0w}$ ) when it reaches the water table. The depth to water is setting to the value  $H = 100 m$ .

$C_{0s} (Kg/m^3)$	0.05	0.1	0.5	1	5	10
$C_{0w} (Kg/m^3)$	0.0044787	0.011655	0.46606	0.651655	0.79041	1.0825
$C_{0s} (Kg/m^3)$	15	25	50	150	250	
$C_{0w} (Kg/m^3)$	4.5213	5.1974	5.1974	108.37	197.89	

**Table 5.** Different values of the initial concentration of benzene at the surface ( $C_{0s}$ ) and corresponding concentration of benzene ( $C_{0w}$ ) when it reaches the water table. The depth to water is setting to the value  $H=150 m$ .

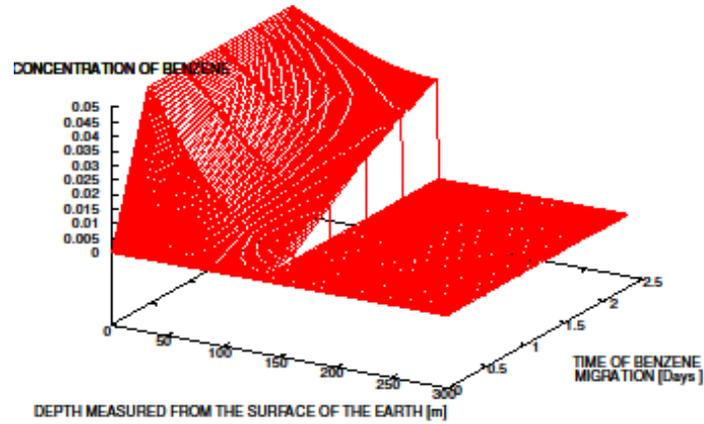
$C_{0s} (Kg/m^3)$	0.05	0.1	0.5	50	150	250
$C_{0w} (Kg/m^3)$	0.00035976	0.0020798	0.35308	42.250	84.292	167.92

as soon as they reach the groundwater. Interestingly, at each position on the ground surface, the depth to water can be determined thanks to the remarkable work performed by Fan and coworkers (Fan et al., 2013). The main principle is as follows: For fixed values of the depth to water,  $H$ , and the time period,  $t_0$ , we estimate the concentration of the hydrocarbon product at the soil-water border. Calculations are performed for different values of the initial concentration at the soil surface. Thanks to these tables, predictions should be made once petroleum products are spilled somewhere, as whether the aquifer could be affected or not. The main point being: for a given depth to water,  $H$ , what is the minimal value of the initial concentration of the hydrocarbon, at the surface of the soil that could contaminate the groundwater? These tables also indicate the degree of contamination of water. Discussions were made according to Table 2, indicating the threshold values of tolerable petroleum hydrocarbon concentration in drinking-water. For instance, from Table 3, we obtained that a water table situated at a depth  $H=80 m$  cannot be contaminated by an initial concentration  $C_{0s} = 0.05 Kg/m^3$  of Benzene. Subsequently, for all

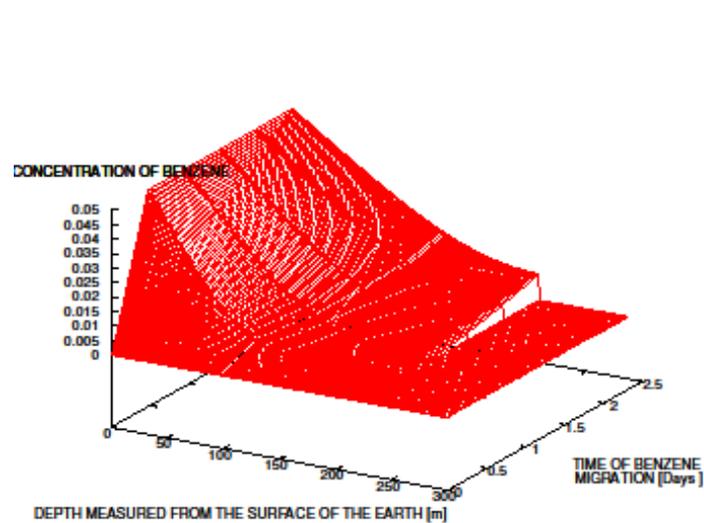
aquifers located at a depth greater than  $H=80 m$ , the quality of drinkable water should not be affected. On the other side, for all initial concentrations  $C_{0s} \geq 0.1 Kg/m^3$ , this same water table could be contaminated by this hydrocarbon. In the same conditions, all aquifers exhibiting a depth  $H < 80 m$ , shall also be affected by this pollutant.

As can be seen in Tables 4 and 5, no contamination is expected for depth  $H = 100 m$  and above when the initial concentration of benzene is equal to  $C_{0s} = 0.05 Kg/m^3$ . It is clear from these tables that high initial concentrations at the ground surface facilitate the process of migration of petroleum hydrocarbon into the ground and result, inevitably, in very important attainable depths.

We start by performing calculations based on benzene, a well-known hydrocarbon contaminant (Figs. 1 to 3). At the beginning of the process, only the surface of the ground was polluted. The concentration of the pollutant does not decrease significantly at the beginning of the process, as soon as one pours the hydrocarbon compounds. It first declines slowly before falling abruptly after a certain time.



**Figure 1:** time evolution of Benzene content from the surface of the earth to groundwater. The initial concentration of benzene at the surface is setting to the value  $C_{0s} = 0.05 \text{ Kg/m}^3$ . Depth to water being  $H=100 \text{ m}$



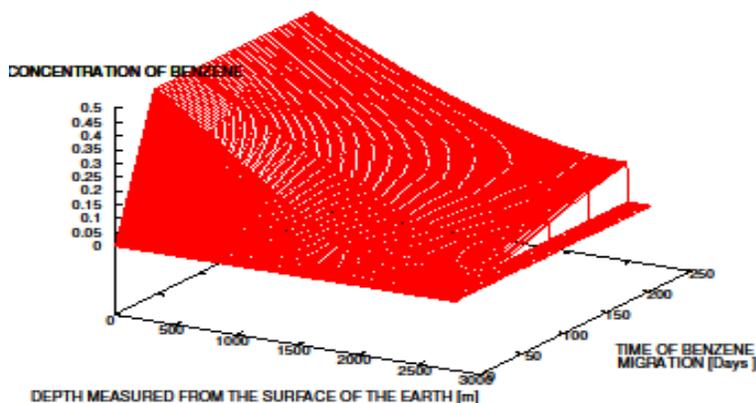
**Figure 2:** time evolution of Benzene content from the surface of the earth to groundwater. The initial concentration of benzene at the surface is setting to the value  $C_{0s} = 0.05 \text{ Kg/m}^3$ . Depth to water being  $H= 200 \text{ m}$

These figures clearly indicate the process of Benzene migration from the surface of the soil to the groundwater. The positions reached by benzene inside the ground at given periods are well-represented. From these figures, one can infer that as the petroleum hydrocarbon moves through the soil, its amplitude decreases gradually.

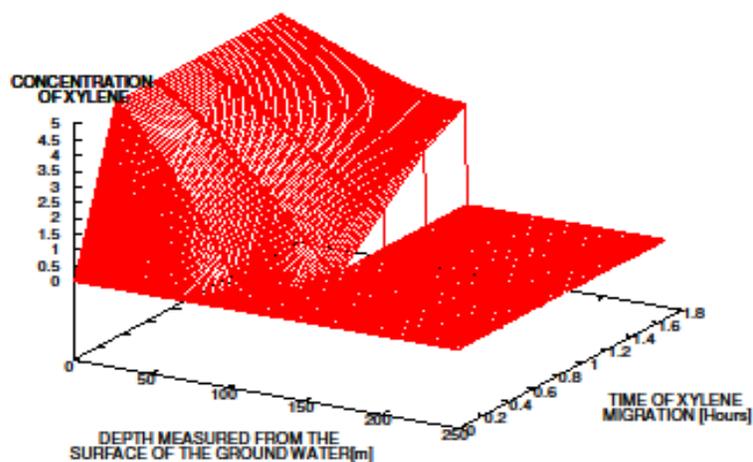
From Figure 1, we observed that, for a water table situated at a depth  $H=100 \text{ m}$  beneath the ground, contamination starts after approximately 0.3 day. In this case, the initial concentration at the ground surface was  $C_{0s} = 0.05 \text{ Kg/m}^3$ . Figure 2 corresponds to the same

situation with  $H = 200 \text{ m}$ . Here, the groundwater is affected after a period of about 1.5 days. So, it takes naturally more time when the depth to water becomes more important. In Figure 3, the initial concentration of benzene is  $C_{0s} = 0.5 \text{ Kg/m}^3$ . From this figure, it appears that groundwater situated at 1800 m can be polluted after approximately 150 days.

Let us conduct the same investigations with Xylene and Toluene. We found that with an initial concentration  $C_{0s} = 5 \text{ Kg/m}^3$  of Xylene, there was a rapid



**Figure 3:** Time evolution of Benzene content from the surface of the earth to groundwater. The initial concentration of benzene at the surface is setting to the value  $C_{0s} = 0.5 \text{ Kg/m}^3$ . Depth to water being  $H=2000 \text{ m}$



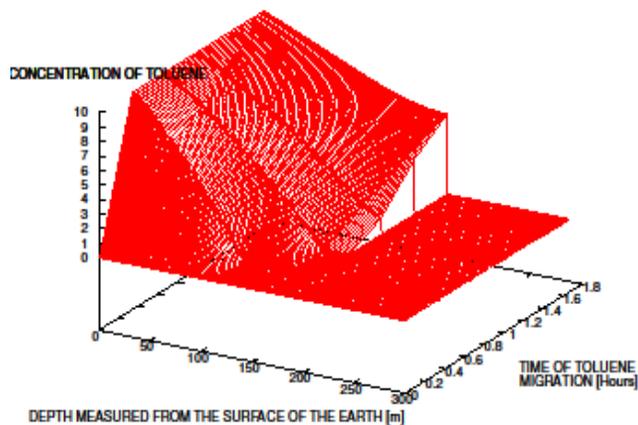
**Figure 4:** time evolution of Xylene content from the surface of the earth to groundwater. The initial concentration of Xylene at the surface is setting to the value  $C_{0s} = 5.0 \text{ Kg/m}^3$ . Depth to water being  $H= 120 \text{ m}$

contamination of groundwater situated at  $H = 120 \text{ m}$ . The process took place in less than 0.6 hour. These results are shown in Figure 4. In the same vein, we performed computations using Toluene as the hydrocarbon product. The corresponding initial concentration was set to the value  $C_{0s} = 10 \text{ Kg/m}^3$ . The associated results are presented in Figure 5. In this case, the petroleum hydrocarbon reached groundwater situated at  $H = 100 \text{ m}$  in only 0.4 hour.

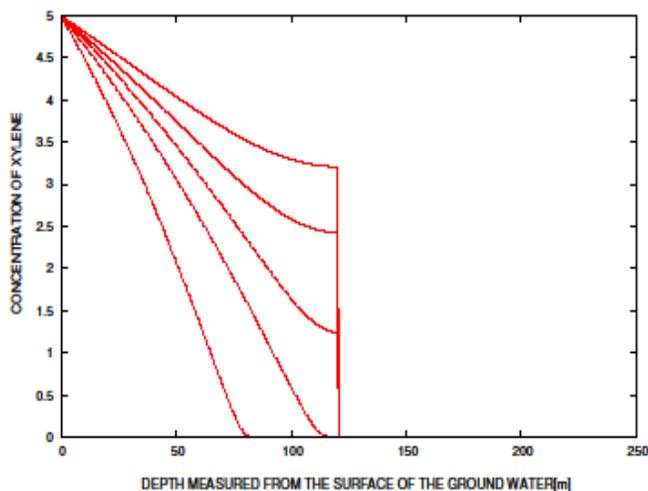
In Figure 6, we can obtain precise indications on the maximum distances covered by Xylene at different periods. The vertical line indicates the position of the water table in this specific region.

Positions reached by Xylene inside the ground at given periods are well-represented. This figure tells us that at periods  $t_{01} = 0.333 \text{ hour}$  and  $t_{02} = 0.666 \text{ hour}$ , Xylene had not yet reached the water table. All portions of the ground under consideration had not yet been attacked by the pollutant product. At this moment, the groundwater is not affected by Xylene. At subsequent periods  $t_{03} = 1.00 \text{ hour}$ ,  $t_{04} = 1.333 \text{ hour}$  and  $t_{05} = 1.666 \text{ hour}$ , the hydrocarbon product had already reached the groundwater. The process of contamination is progressive.

At the soil-water border, the concentration drastically

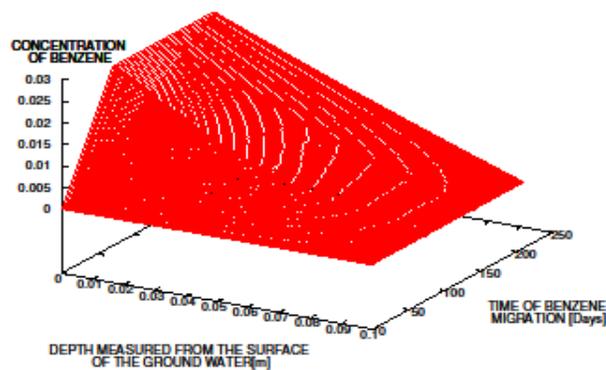


**Figure 5:** time evolution of Toluene content from the surface of the earth to groundwater. The initial concentration of Toluene at the surface is setting to the value  $C_{0s} = 10.0 \text{ Kg/m}^3$ . Depth to water being  $H= 100 \text{ m}$ .

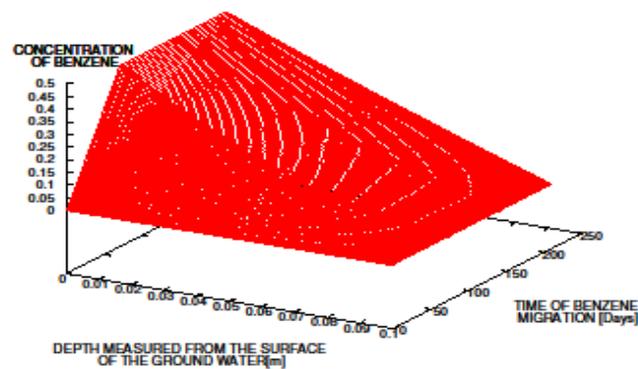


**Figure 6:** Spatial profile of Xylene distribution, from the surface of the soil to groundwater, at different time intervals. In this figure, the initial concentration is  $C_{0s} = 5.0 \text{ Kg/m}^3$ .

decreases. The pollutant does not easily continue its transversal motion. So, the descending motion is significantly slowed because the nature of the oil's motion is modified in the water region. On the contrary, it has a tendency to spread on the surface of the water. Indeed, it is a fact that, petroleum hydrocarbons are mostly less dense than water. Subsequently, they have the tendency to float around the surface of the ground water due to gravity. One can observe the spreading of the oil on water at the soil/water border from the point of impact on the water. Thus, downward motion into an aquifer is not significant enough. It is rather the process of spreading on the surface



**Figure 7:** time evolution of Benzene content in the groundwater. In this case, the initial concentration of benzene at the border soil-water is  $C_{0sw} = 0.0267 \text{ Kg/m}^3$ . Depth to water being  $H= 40 \text{ m}$ .

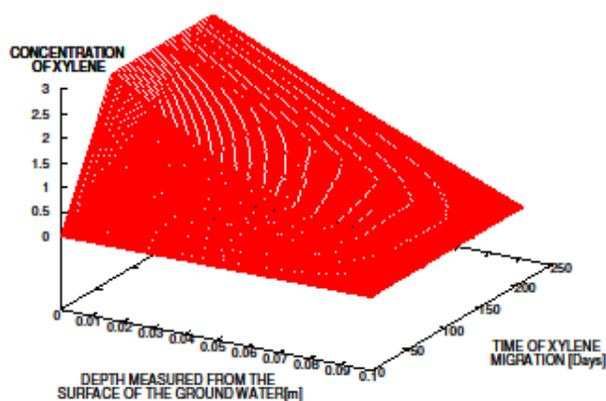


**Figure 8:** time evolution of Benzene content in the groundwater. In this case, the initial concentration of benzene at the border soil-water is  $C_{0sw} = 0.4660 \text{ Kg/m}^3$ . Depth to water being  $H= 100 \text{ m}$ .

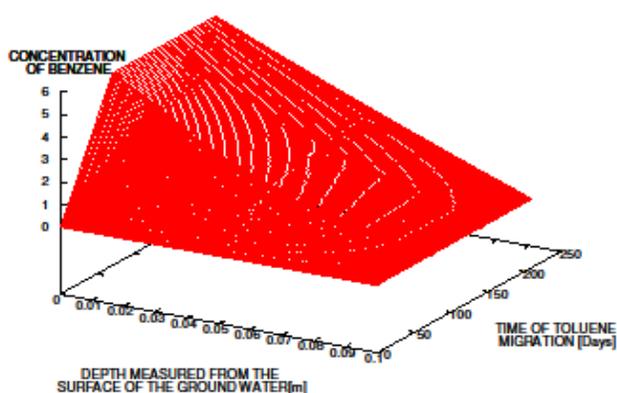
which predominates.

If we carefully examine the profile of the curves drawn in Figures (1-5), we will observe a sharp break of the concentration values at the soil-water border: values become exceedingly low. The gap is very sensitive at the border; hence, one might be tempted to suggest that concentrations approach zero-values in the water. This is not the reality. It is just a feeling, because these concentrations exist but they are very small compared to the ones recorded in soils. To have a clear idea on the profile of the concentration of petroleum products in water, we drew separate curves to show the diffusion process of these products in water.

The diffusion process in water is represented in Figures (7-10). The first thing that gained our attention is the



**Figure 9:** Time evolution of Xylene content in the groundwater. In this case, the initial concentration of Xylene at the border soil-water is  $C_{0sw} = 2.7071 \text{ Kg/m}^3$ . Depth to water being  $H = 40 \text{ m}$ .



**Figure 10:** Time evolution of Toluene content in the groundwater. In this case, the initial concentration of Toluene at the border soil-water is  $C_{0sw} = 5.5670 \text{ Kg/m}^3$ . Depth to water being  $H = 100 \text{ m}$ .

smallness of the depth attainable by the pollutant in the groundwater. This depth does not exceed 10 cm. The pollutant component does not cross the concerned portion of the groundwater instantaneously from the surface to the maximal depth. It takes some time to penetrate the water. The rate of penetration can be observed in the figures. Calculations have shown that, the covering of the maximum depth is observed approximately  $t = 250 \text{ days}$  after the moment that the hydrocarbon reaches the surface of the groundwater. Therefore, the penetration of the pollutant in this small portion of the water necessitates a somewhat high time period.

## CONCLUSION

In this study, we have addressed the problem of drinkable water. It is important that we draw attention to the quality of water distributed in households in every part of the world. Therefore, people should receive water that is safe and purified for human consumption.

We have considered the process of contamination of soils and groundwater by petroleum hydrocarbons. The migration of petroleum contaminants in groundwater, through soils, 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 diffusion in soils is not constant and we introduced a concentration-dependent function. Boltzmann-Matano analysis was used to approximate the linear composition dependence of diffusivity. Besides, we adopted the temperature-dependent diffusivity of petroleum hydrocarbons in water following Worch's model.

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 the DOPRI5 code as integrator. The discretization of space followed the finite volume technique.

Let us notice in passing that depth to water increases as land-surface elevation increases. Such remarks are well-consistent with the concept that water-levels are typically greater beneath hills than valleys. As soon as petroleum products are spilled on a site, the depth to water at that specific position plays a significant role in our analysis. Computational results naturally led to the conclusion that: the degree of pollution decreases as the depth to water increases. We conducted studies on three particular petroleum compounds; namely: benzene, toluene and xylene. For each petroleum compound under consideration with an initial concentration,  $C_{0s}$  at the surface of the soil, we assessed the value of its concentration at the soil/water border. The reachability of groundwater depends on  $C_{0s}$  and on the depth to water. It is obvious that, the type of hydrocarbon involved in this process should also be taken into consideration. By doing so, we were able to indicate in which cases spills can lead to the contamination of groundwater.

As soon as the petroleum product is spilled on the surface of the ground, it triggers its migratory movement in the soil. We have plotted a number of curves to show the distribution of contaminants in the ground and in the groundwater. A drastic collapse of the hydrocarbon content was quite visible at the border of the two media. This situation was expected for two specific reasons: (i) Calculations performed in the undergoing paper revealed that there is a great discrepancy between the numerical values of the diffusion coefficients in the two different

media. Diffusion coefficients in soils are very high compared to the same coefficients in water. (ii) Generally speaking, petroleum products are lighter than water; hence it is difficult for them to penetrate into water. Benzene, like the other products, moves gradually and very slowly through water. Conversely, they have a tendency to spread on the surface of water. The computational process has shown that, the covering of the maximum depth attainable in groundwater, i.e. around 10 cm, is observed approximately after a time period  $t_0 = 250 \text{ days}$ . The duration is assessed after triggering the process on the surface of the groundwater. We have conducted the same investigations with Xylene and Toluene. The same profile of solution have been obtained. Let's mention that, we have drawn separate curves to show the profile of the pollutant distribution in soils and in groundwater.

Throughout this work, we were mainly concerned with the quality of water that is held beneath the surface of the earth. This problem of petroleum pollution has gained our attention mostly because of the importance of groundwater for drinkable water supply. Computational results have shown that, the potability of groundwater could be questionable in sites suffering from petroleum products spills. Thus, care should be taken, as far as this matter of drinkable water is concerned.

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### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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