

Modeling the Transport of Petroleum Products by Soil Filter Method

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Abstract

Our paper deals with the diffusive model of hydrocarbon migration in the soil. To assess the risk of groundwater contamination by hydrocarbons migrating in the soil, a mathematical model had been applied. Incorporation of diffusion into the equation of mass transport enables the description of hydrocarbon transport deep into the soil profile. The biodegradation equation makes it possible to consider the effect of microorganisms upon reduction of hydrocarbon concentrations, especially oil fractions. To verify a theoretical model, a series of experiments on a so-called soil filter were carried out. Finally, a theoretical model was used to determine the parameters that shows the behavior of different contaminants through soil.

Keywords: petroleum-derived product transport, transport in porous media, infiltration into soil, organic compound leakage, hydrocarbon transport in soil

Introduction

Petroleum products are extremely harmful for the natural environment. Although the development of industry has increased the demand for energy based on petroleum products, both their distribution and exploitation pose a considerable threat to the natural environment and biosphere. It is a well-known fact that contamination of water and soil by toxic organic compounds is one of the major problems of the contemporary world.

The identification of processes of migration and degradation of petroleum products in soil is of great importance for environmental engineering, and especially for the technology of waste disposal on landfills (deep-into-ground infiltration of effluents containing petroleum products). It also deals with the migration of petroleum products from typical contaminated areas (petrol stations, petroleum product storehouses, firing grounds) as well as with their release into the soil due to car and rail accidents [1-2].

Migration of petrochemical pollutants can take place in gaseous, liquid or solid phases, but also as a combination of the phases [3-11].

Water in the soil environment forms a mixture with petroleum products. The hydrocarbon components are very difficult to separate. The flow of hydrocarbon products through the soil causes physical, chemical and biochemical changes.

The direction and rate at which contaminants spread are dependent not only on their own properties, but also on soil properties.

Petrochemicals when entering the soil due to gravitational force and diffusion initially move vertically through the aeration layer. In the aeration layer (unsaturated) some of them get adsorbed on rock material while others infiltrate deep into soil frequently and reach the underground water-table [12].

Transport of petroleum products (non aqueous) is mostly influenced by their density, viscosity, and surface wetting [8]. Some petroleum constituents show a certain degree of water-solubility, and is considerably high for aromatic hydrocarbons, including benzene, toluene, and xylene, which has an extremely harmful carcinogenic character.

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One of the major problems in environment protection is determining the contamination concentration and the volume of soil to be extracted and treated. It seems that the assessment of the migration rate of petroleum products in porous soil by means of ground filter may help solve the problem.

Theoretical Model Description

The problem of environmental migration of organic compounds in soil has been discussed by many authors [13-16]. The mathematical description of petroleum product migration needs more study and analysis.

The purpose of the present experiments is to confirm the hypothesis of petroleum hydrocarbons penetrating the ground following the diffusive model of petroleum contaminant migration, with biodegradation the next equation:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial z^2} - \mu_i C_i \quad (1)$$

The following initial boundary condition in the sand-hydrocarbon system is proposed:

$$C_i(z, 0) = 0 \quad \text{for } 0 < z < S \quad (2)$$

$$C_i(0, t) = C_{oi} \cdot \exp(-\mu_i t) \quad \text{for } t \geq 0 \quad (3)$$

$$\frac{\partial C_i}{\partial z} = 0 \quad \text{for } t > 0 \text{ and } z = S \quad (4)$$

The solution (1) describing the transport of hydrocarbons in the ground is the equation:

$$C_i(z, t) = \frac{C_{oi} \cdot S}{\sqrt{4 \cdot \pi \cdot D_i \cdot t}} \exp\left\{-\left[\frac{z^2}{4 \cdot D_i \cdot t} + \mu_i \cdot t\right]\right\} \quad (5)$$

To verify the theoretical model, experiments were conducted on a model of the soil filter filled with dry matrix. The concentration of petroleum hydrocarbons in individual segments of the column was determined after the set migration time.

Three soil matrices with high water permeability and low sorption were used (since such a system is unfavourable in terms of contamination of ground waters).

The suggested theoretical model can be practically implemented to assess the degree of ground contamination after some definite time of leakage of petroleum product to the soil.

For the simplified theoretical model (1), the second term of the right-hand side of the equation allows us to consider the effect of microorganisms upon changes of hydrocarbon concentration in the soil. As hydrocarbon concentration in the system where their migration takes place is usually higher from that of biogenic elements (N, P), it has been assumed that the decomposition reaction of the migrating hydrocarbons is of the first order. The result is the

linear relation of the natural logarithm of hydrocarbon concentration in the function of time.

$$\Delta \ln C_i = -\mu_i \cdot \Delta t \quad (6)$$

Experimental Test Rig Description and Methodology

The test stand experimental model of the soil filter was designed as shown in Fig. 1. A column-shaped model of the soil filter with diameter $\phi=135$ mm and height $H=2,000$ mm was made of polypropylene.

The column is a segmented structure consisting of cylindrical elements 100 mm high with 18 identical test cells of the following parameters: height of the element $H=100$ mm, inside diameter $\phi=135$ mm, outside diameter $\phi_z=137$ mm.

The sand deposit was used as a model to simulate the penetration of petroleum contaminants from the soil surface toward underground waters.

The presented model was verified for three different sand soils to check whether it worked regardless of the assumed effective diameter of deposit graining and porosity indicator.

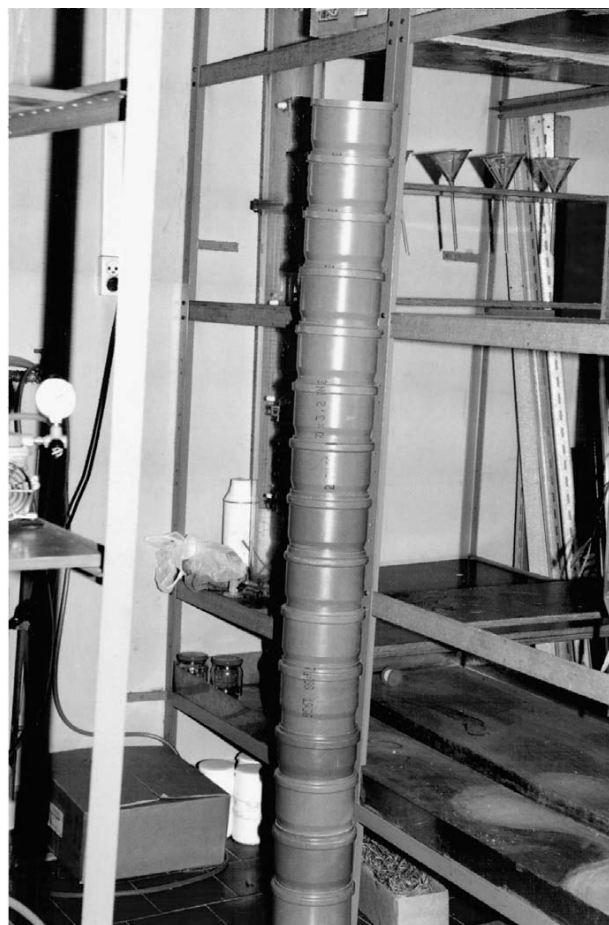


Fig. 1. The experimental model of soil filter for testing hydrocarbon migration.

Table 1. Specification of some more important physical parameters of the sand used in experiments.

Parameter	Value	Unit of measurement
d_{\min}	0.033	[mm]
d_{10}	0.22	[mm]
d_{60}	0.35	[mm]
d_{80}	0.45	[mm]
d_{\max}	4.0	[mm]
K_r	1.6	-
K_{80}	2.0	-
ρ_o	1,690	[kg·m ⁻³]
s	0.110	[%]

Table 2. The physical properties of tested soil.

Sorted sand fraction	Minimum diameter of sand grains, d_{\min} [mm]	Maximum diameter of sand grains, d_{\max} [mm]	Porosity index, ϵ [%]
Soil No. 1	0.5	2.0	34
Soil No. 2	0.25	0.5	33
Soil No. 3	0.033	0.25	31

In order to test migration of petroleum contaminants, the three aromatic hydrocarbons benzene, toluene, and xylene (isomers mix) and the two aliphatic hydrocarbons (octane rating) n-heptane, and 2,2,4-trimethylpentane were used.

The function of hydrocarbon concentrations in the model of soil filter $C_i(z, t)$ – the value considered in equation (1) – can be determined by measuring the hydrocarbon concentration in each of the 18 segments of the column in relation to the assumed migration time.

The distribution of the selected hydrocarbon concentrations on the soil filter was experimentally examined after 24 hours. The subsequent experiments consisted of increasing the migration time of petroleum products in the soil of the concentration determined in individual segments of the column. The tests were conducted for the following exposure time of hydrocarbons: 48 , 96, 192, and 384 hours.

The biodegradation process of petroleum hydrocarbons was tested in cell 19 (Fig. 2) of the parameters as follows: element height $H=200$ mm, inside diameter $\phi=135$ mm, outside diameter $\phi_z=137$ mm.

Sand fractions of soil Nos. 1, 2, and 3 were obtained by sieve separation (according to PN-ISO98/B-04481). The physical parameters are presented in Table 1.

The value of the effective diameter is $d_e=0.31$ mm

The sand from two mines, in Borowa Góra and Opole, was mixed in proportion 1:1 and dried at 105°C to eliminate temporary humidity.

To obtain model soil of varied granulometric composition the sand was divided into three fractions of fine, medium and coarse grain sizes. 200 g of sand was passed through a set of three sieves of decreasing mesh diameters: $d_3=2.0$ mm, $d_2=0.5$ mm and $d_1=0.25$ mm. The granulometric concentration of the sand filling the column was presented in Table 2.

The biodegradation rate of petroleum hydrocarbons was tested in a single solid filter, cell No. 19, where 290 kg/m³ of the tested hydrocarbon was inserted into the sand matrix, which corresponded to filling the pores at 100% volume. The cell 19 was sealed from the top and the petroleum hydrocarbon concentrations were determined by means of gas chromatography after 24, 48 , 96, 192, and 384 hours, respectively.

The soil filters were filled with filtering material (soil 1, 2 or 3) directly on the supporting layer of the height of 0.2 m, which consisted of fine gravel of grain size from 4 to 8 mm. Individual segments of the soil filter were filled with sand by funnel moving spirally from the soil filter centre to its edges in order to keep the deposit uniform. By putting successive segments, the whole column was filled with deposit. A single cylinder was filled to 90% of its volume and then after the next segment of the column had been added the cylinder was completely filled with sand. Test cell No. 1 on the top of the soil filter was filled with granular material containing petroleum hydrocarbons. The whole system was sealed by a cylinder locked from the top in order to eliminate the loss of mass caused by evaporation.

The migration of petroleum hydrocarbons with regard to biodegradation was tested in laboratory conditions at a temperature of (293±0.5) K, and relative humidity of atmospheric air in the room (70±2.5)%. Each test conducted for a set time of hydrocarbon migration (24, 48 , 96, 192 and 384 hours) requires dismantling the column from the top and separately determining the concentrations of petroleum products in the sand deposit for the cells from No. 1 to 18.

The amount of analyte necessary for extraction was obtained from the sample reduced to a mass of 30 g by quartering method. The sample was divided into three



Fig. 2. The sand matrix treated by hydrocarbons in the soil filter.

Table 3. The values of biodegradation rate constant μ_i in the model soil filter for probability $(1-\alpha = 0.95)$.

Hydrocarbon	Biodegradation rate constant $\mu_i \cdot 10^3$, [d ⁻¹]		
	Sample of soil No. 1	Sample of soil No. 2	Sample of soil No. 3
Benzene	(4.8±1.0)	(4.8±1.0)	(4.9±0.9)
Toluene	(4.0±0.4)	(3.9±1.1)	(3.8±1.0)
Xylene	(2.5±0.7)	(2.5±0.8)	(2.5±0.7)
Isooctane	(6.0±2.0)	(5.8±1.6)	(5.9±1.5)
n-Heptane	(5.9±1.5)	(5.9±1.9)	(5.8±2.0)
C-H Mixture	(4.4±1.0)	(4.3±1.0)	(4.5±1.2)

equal parts, three testes were made for one measuring point on the curve) and subjected to extraction by carbon disulfide [17].

To prepare the samples for analysis, 10 g of the averaged sand matrix containing petroleum hydrocarbons and 10 cm³ carbon disulfide CS₂ was taken and placed into a conical flask. The conical flask was shaken for 1 minute and refrigerated for 24 hours. The measured quantity of hydrocarbons in the sample was made after cold extraction (conducted at 4°C) by chromatographic method.

Chromatographic tests were carried out by Computer Integrator Chroma 2.2. To measure the concentration of petroleum hydrocarbons (±5%), a gas chromatograph of type N-503 INCO was used.

In order to establish the correction resulting from extractant's loss of mass, the mass of the conical flask with its concentration before cold extraction and just before analysis were weighed on the electronic scales of accuracy up to ±0.01 g. The concentration of hydrocarbons in the matrix was corrected by the formula:

$$C_i = C_{i.ch} \cdot \frac{M_{k2} - M_{k.mx}}{M_{k1} - M_{k.mx}} \quad (7)$$

Migration of petroleum hydrocarbons was tested for the following different parameters:

- hydrocarbon exposure time: 24, 48, 96, 192 and 384 hours
- the initial concentration of petroleum hydrocarbons in cell No. 1 was C_{0i} : 290 kg/m³_{d.m.}, 145 kg/m³_{d.m.}, and 72 kg/m³_{d.m.}
- the tests were conducted for three soil matrices separately, as shown in Table 2
- the tests of equivalent diffusion coefficients and constant biodegradation rate were repeated three times

Theoretical Result Verifications

Experiments were conducted for sand-benzene, sand-toluene, sand-xylene (isomers mix), sand-heptane, and sand-isooctane assuming dry conditions, soil and hydrocarbons of kinematic viscosity $\nu < 2 \cdot 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ [10].

Measured values of the loss of benzene concentration in time in soil No. 1 is shown in Fig. 3:

The value $-\mu_i$ is calculated from the equation of the regression line:

$$\begin{aligned} \hat{y} &= a_i \cdot x + b_i \\ \hat{y} &= -0.0048 \cdot x + 5.6679 \end{aligned} \quad (8)$$

The constant of benzene loss measured experimentally at 20°C and relative humidity of 70% equals $4.8 \cdot 10^{-3} \text{ d}^{-1}$. The same value was obtained for soil No. 2 while for soil No. 3 it was $4.9 \cdot 10^{-3} \text{ d}^{-1}$.

The overall results of μ_i and the values of equivalent diffusion coefficient D_i for the selected hydrocarbons are presented in Tables 3 and 4.

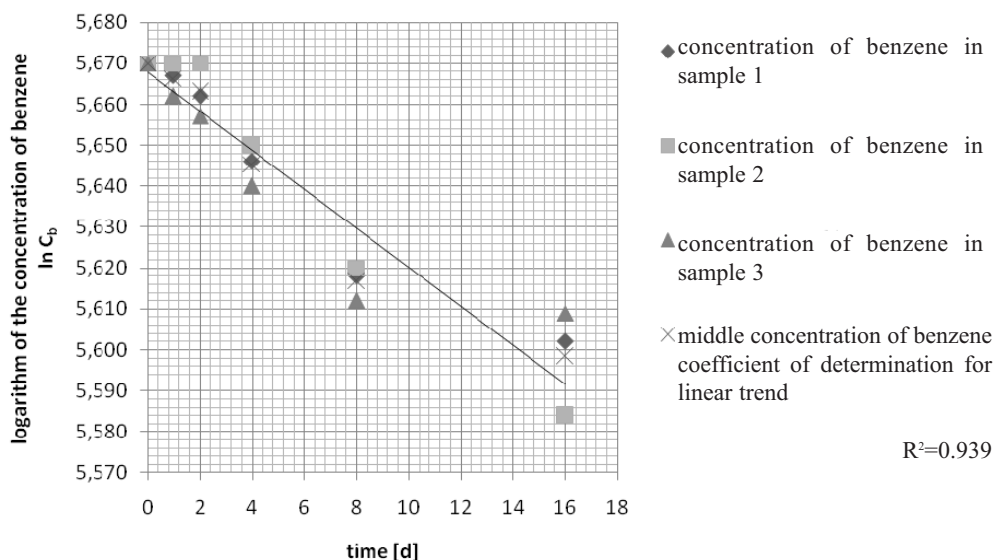


Fig. 3. The loss of benzene concentration in time in soil deposit, soil No. 1.

Table 4. The values of equivalent diffusion coefficient D_i in the model soil filter for probability $(1-\alpha = 0.95)$.

Hydrocarbon	Equivalent diffusion coefficient $D_i \cdot 10^7$, [m ² ·s ⁻¹]		
	Sample of soil No. 1	Sample of soil No. 2	Sample of soil No. 3
Benzene	(3.5±0.5)	(3.5±0.5)	(3.3±0.6)
Toluene	(3.6±0.4)	(3.5±0.5)	(3.3±0.6)
Xylene	(8.1±0.3)	(8.1±0.5)	(8.0±0.5)
Isooctane	(24±2)	(24±3)	(21±3)
n-Heptane	(10±3)	(10±3)	(9.9±0.3)
C-H mixture	(3.6±0.7)	(3.7±0.5)	(3.5±0.5)

According to the plan of the experiments a full set of tests on benzene migration in a porous media was carried out. The only restriction was providing the example of hydrocarbons' concentration distribution that enabled assessment of equivalent diffusion coefficient. Equation 6 shows the correlation between experimental data and function $u(z^2, t)$, which was determined by the least squares method:

$$\hat{y} = a_i(t) \cdot \exp[-b_i(t) \cdot z^2] \tag{9}$$

Function $u(z^2, t)$ is one of many probable solutions of the equation (1). The substitution $x=z^2$ was applied. The value of diffusion coefficient was determined from equation (7):

$$D_i = -\frac{1}{4 \cdot b_i \cdot t} \tag{10}$$

The C_i concentration, where $i = b, t, x, h, o$ (the first letters are the abbreviations of the names of the tested hydrocarbon) was calculated from formula 11:

$$C_i = C_{oi} \cdot \exp(-\mu_i \cdot t) \tag{11}$$

Equation 11 enables taking into account the effect of hydrocarbons biodegradation upon the real concentration of hydrocarbon "i" at the time when it is determined in the matrix.

The concentration of hydrocarbons at 16 days will be greater at the bottom of the column due to migration. This is due to the absence of a continuous flow of hydrocarbons to the top of the column. On the contrary, hydrocarbons were brought once on $d = 0$ day.

Statistical Assessment of Experimental Results

The effectiveness of correlation was verified by means of test F, calculating the value of characteristics:

$$F = \frac{(n - 2) \cdot R^2}{(1 - R^2)} \tag{12}$$

The result obtained was compared with the values from distribution tables $F_{\alpha,1,n-2}$.

For the set confidence level $\alpha = 0.01$ for $n = 6$:

$$F = \frac{(6 - 2) \cdot R^2}{(1 - R^2)}$$

The value of coefficient of determination was obtained for biodegradation constant μ_i , when the loss of benzene concentration was tested in time for soil No. 1. The value obtained was: $R^2 = 0.9397$;

$$F = \frac{(6 - 2) \cdot (0.9397)}{(1 - 0.9397)}$$

$$F = 62.3$$

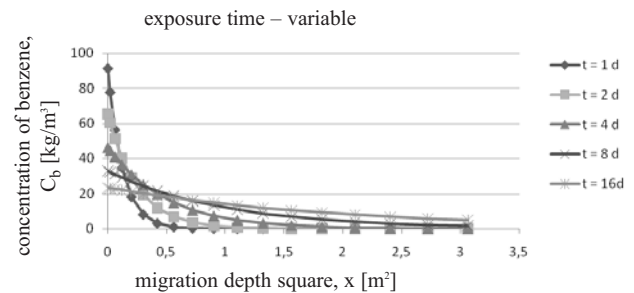


Fig. 4. Distribution of benzene concentration in the model soil filter in relation to migration time (soil No. 1).

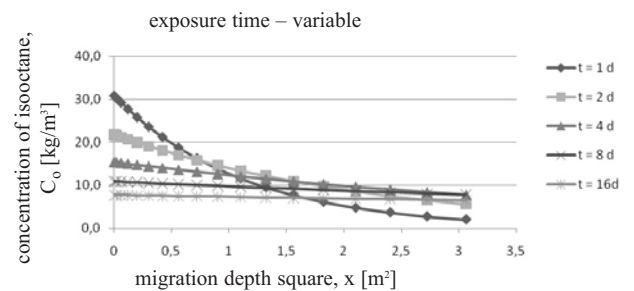


Fig. 5. Distribution of isooctane concentration in the model soil filter in relation to migration time (soil No. 1).

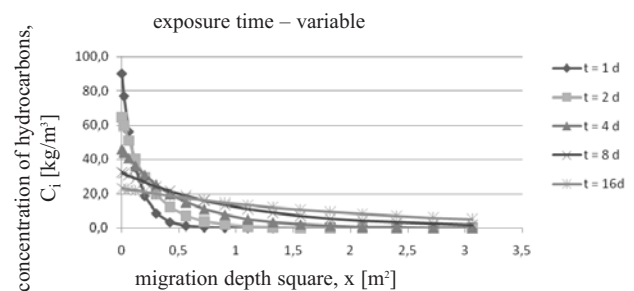


Fig. 6. Distribution of hydrocarbons mixture concentration in the model soil filter in relation to migration time (soil No. 1).

The value from the distribution tables $F_{\alpha,1,n-2} \cdot F_{kr} = 21.2$

$$F > F_{kr}$$

Correlation (8) is significant.

Results and Discussion

On the basis of the model tests on migration of petroleum hydrocarbons conducted by means of soil filter, the migration of petroleum hydrocarbons can be predicted.

One of the feasible solutions of the assumed model equation (1) is function (5). The correlation equation of experimental data expressed by the function $u(z^2, t)$ enabled us to determine the equivalent diffusion coefficient D_i .

The equivalent diffusion coefficient D_i for petroleum hydrocarbons is dependent upon the type of sand soil and assumes values in the range $(3.3 \div 24) \cdot 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ (Table 4).

The equivalent diffusion coefficient of petroleum hydrocarbon mixtures is close to the values of the equivalent diffusion coefficient of benzene and toluene for soil Nos. 1, 2, and 3 (Fig. 4, Table 4) and is $(3.5 \div 3.7) \cdot 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$.

Benzene has the lower value of the equivalent diffusion coefficient, which is $3.5 \cdot 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ (Table 4). It is, however, considered to be the key component of petroleum hydrocarbon mixture. Despite low diffusion coefficient, benzene has the highest water solubility and acutest toxicity.

It was proved that the value of D_i coefficient of the key component was practically constant for the three selected initial concentrations of hydrocarbons: $C_o = 290 \text{ kg} \cdot \text{m}^{-3}$, $C_o = 145 \text{ kg} \cdot \text{m}^{-3}$ and $C_o = 72 \text{ kg} \cdot \text{m}^{-3}$.

In the experiment the biodegradation constant in the sand matrix influenced the concentration loss of the key component (Table 3); the biodegradation constant μ_i changed in the range $(2.5 \div 6.0) \cdot 10^{-3} \text{ d}^{-1}$.

The value of biodegradation constant is practically not dependent upon the grain size of the soil matrix. For toluene it is $(3.8 \div 4.0) \cdot 10^{-3} \text{ d}^{-1}$, which is about 5% of μ_i , the smaller result.

Conclusions

The results of model experiments carried out on the model of soil filter in the experimental conditions: $T = (293 \pm 0.5) \text{ K}$, relative humidity: $(70 \pm 2.5)\%$, and dry sand enable drawing the following conclusions:

1. The value of the equivalent diffusion coefficient D_i of the key component is not dependent upon initial concentration of petroleum product but upon the type of the migrating petroleum product and it may have different values for different types of soil.
2. The value of biodegradation constant is practically not influenced by the grain size of the soil matrix.
3. The assumed migration model (1) enables assessing the concentration of the selected petroleum hydrocarbons in isotropic dry soil after t time of contamination onset on any depth z .
4. In practice, to make this assessment one should:

- a) determine the concentration of petroleum hydrocarbons in the surface layer of the soil matrix,
- b) determine the composition of petroleum hydrocarbons mixture,
- c) apply model coefficients from Tables 3 and 4 to determine the function (5).

Nomenclature

- α – confidence level, [1]
 a_i, b_i – parameters of the trend function, [1]
 C_i – concentration of key component “i” in the matrix, $[\text{kg} \cdot \text{m}^{-3}]$
 C_{oi} – initial concentration of key component “i” in the matrix, $[\text{kg} \cdot \text{m}^{-3}]$
 $C_{i.ch.}$ – key component concentration determined by chromatographic method after CS_2 extraction, $[\text{kg} \cdot \text{m}^{-3}]$
 d_e – effective diameter of sand grains, [mm]
 d_{min} – minimum diameter of sand grains, [mm]
 d_{max} – maximum diameter of sand grains, [mm]
 d_{10} – sieve size that permits passage of 10% by weight of the sand, [mm]
 d_{60} – sieve size that permits passage of 60% by weight of the sand, [mm]
 d_{80} – sieve size that permits passage of 80% by weight of the sand, [mm]
 D_i – equivalent diffusion coefficient of key component “i”, $[\text{m}^2 \cdot \text{s}^{-1}]$
 ε – porosity index, [%]
 ϕ – inside diameter of soil filter, [mm]
 ϕ_z – outside diameter of soil filter, [mm]
 F – Snedecor’s distribution function, [1]
 F_{kr} – value from the distribution tables, [1]
 H – height of soil filter, [mm]
 i – the symbol standing for the first letter of the tested hydrocarbon ($i = b, t, x, h, o$)
 K_r – coefficient of graining non-uniformity, d_{60}/d_{10} [1]
 K_{80} – coefficient of graining non-uniformity, d_{80}/d_{10} [1]
 M_{k1} – mass of conical flask with extraction mixture immediately before and immediately after CS_2 extraction, [g]
 M_{k2} – mass of conical flask with extraction mixture after 24-hour CS_2 extraction, [g]
 M_{kmax} – mass of conical flask with soil matrix contaminated by petroleum hydrocarbons before extraction (without CS_2), [g]
 μ_i – hydrocarbons’ biodegradation coefficient, $[\text{s}^{-1}]$
 n – number of measurements, [1]
 ρ_o – bulk density, $[\text{kg} \cdot \text{m}^{-3}]$
 R – coefficient of determination, [1]
 s – humidity of sand, [%]

- S – the maximum depth of hydrocarbon penetration through the ground, [m]
 t – migration time, [s]
 T – temperature, [K]
 v – kinematic viscosity, [m²·s⁻¹]
 x, y – two quantitative variables X and Y
 z – direction of hydrocarbons' migration, [m]

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