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Original Research

Estimation of partition coefficients (K_d) of polycyclic aromatic hydrocarbons in fractured aquifer

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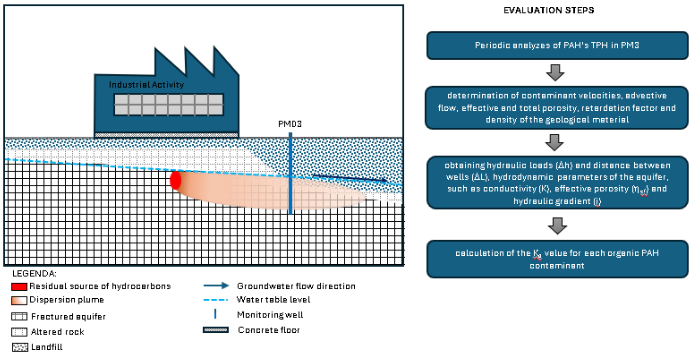

Abstract: In the period between 2016 and 2021, after remediation and risk assessment in an industrial area contaminated by polycyclic aromatic hydrocarbons (PAH), groundwater quality control was promoted, using a network consisting of 8 monitoring wells. Monitoring of the environmental recovery stage was certified by the substances: TPH, o-Xylene, 1,2,4-Trimethylbenzene, Naphthalene, Xylenes, Phenanthrene, Anthracene, Chrysene, Benzo(a)pyrene and Total PAHs. The focus of the evaluation was on well PM03, given its greater representativeness and proximity to a residual source of contamination. Water circulation at this interface occurs mainly in a fractured environment belonging to the Serra Geral aquifer system. At this point, the substances of interest showed different migration speeds (V_{cont}) and attenuation (V_r). Based on the determination of total (n), effective porosity (η_{ef}), hydraulic conductivity (K) and the relationship between the advective flow velocity of water (V_r) and contaminants (V_{cont}), the retardation factors (R) and the partition coefficients (K_d).

Keywords: Contaminant behavior, environmental monitoring, retardation, partition coefficient, TPH.

Introduction

The mechanisms that act in the formation and development of contamination plumes in groundwater can be portrayed through physical and chemical processes. The main processes involved in determining transport parameters in saturated porous media are advection and hydrodynamic dispersion. The main factors involved in bio-physical-chemical processes are sorption, decay, hydrolysis, volatilization and biotransformation. In a post-remediation site during the closure monitoring process, residual levels of polycyclic aromatic compounds were identified. Based on the conceptual contamination model, the primary mechanisms governing the transport or migration of the most active compounds are mechanical dispersion, retardation, and biodegradation. Biodegradation plays an important role in the decay of petroleum hydrocarbons. In these components, microorganisms promote oxidation reactions that involve the reduction of other substances available in the subsurface environment, such as oxygen, nitrate, iron and manganese oxides, sulphate and carbon dioxide, ranging from an oxidizing environment to a strongly reducing one [1].

Retardation interferes with the speed at which dissolved contaminants advance. With retardation, the dissolved contaminants move at a lower speed than the advective flow, because of sorption phenomena. Sorption refers to the partitioning of contaminants between the pore water and the solid phase [1].

In the sorption process, one of the most relevant terms is the partition coefficient (K_d), which reflects the partitioning of chemical species between the solid matrix and the dissolved phase. It depends on the properties of the medium, the characteristics of the chemical substance, and its interaction with other components involved in the reaction. Its determination is specific to each species. Generally, it can be established for soil through laboratory tests (batch equilibrium and column tests) [2].

The adsorption of the organic contaminant in soil depends on the organic matter content present. In this case, the higher the amount of solid organic matter in the soil, the greater the retention of the contaminant by the organic matter [3].

The study conducted in an area undergoing post-remediation monitoring enabled the determination of partition coefficients and retardation factors (R) for components of residual contamination of Polycyclic Aromatic Hydrocarbons in a fractured aquifer medium dominated by volcanic rocks from the Serra Geral Formation [4].

The study area, affected by industrial activities, underwent remediation after being contaminated by petroleum hydrocarbon spills, using Multi-Phase Extraction (MPE) techniques and ex situ soil treatment (removal of contaminated material for external treatment) via soil bioremediation. Following the completion of remediation measures, environmental control of the site was maintained through periodic water quality analyses conducted via a network comprising eight monitoring wells (Figure 1).

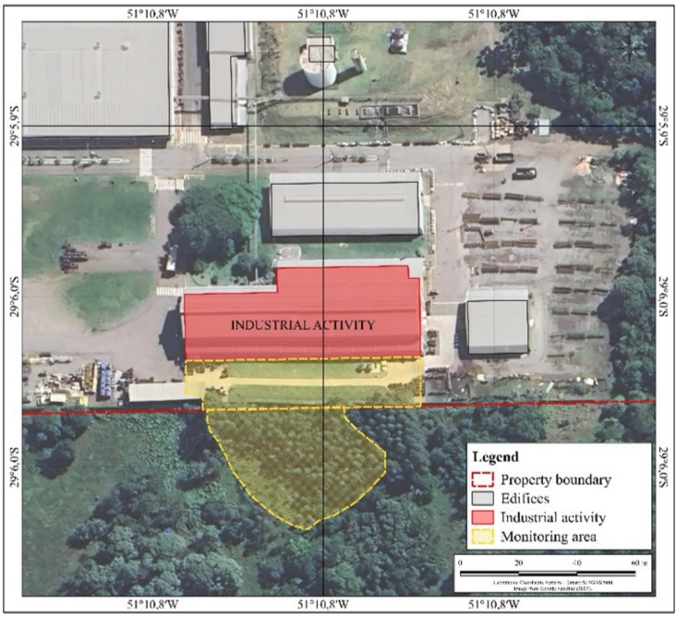

Figure 1. Situation of the site under analysis and contours of the monitoring area.

Sampling campaigns were conducted from October 2016 to January 2021. The analyzed components included individual compounds from the Polycyclic Aromatic Hydrocarbons (PAH) class, as well as total petroleum hydrocarbons (TPH) and TPH fractions.

During the monitored period, anomalous concentrations of SQIs, notably TPH, were observed in well PM03, indicating the possibility of residual contamination originating from an upstream source.

From the analysis of TPH fractions at this point, it was found that the predominant carbon ranges were diesel (C14 – C20), lubricating oil (C20 – C40), and secondarily kerosene (C11 – C14).

Diesel and oil ranges contain heavier organic substances, with carbon structures ranging from 14 to 40. In heavier mixtures, the priority substances are polycyclic aromatic hydrocarbons (PAHs).

The Total Petroleum Hydrocarbons (TPH) served as an indicator of the stage of hydrocarbon contamination remediation through natural attenuation of groundwater. For comparative reference of TPH concentrations, the Dutch Reference Framework STI – Values (Government of the Netherlands) was used [5].

The individual components of PAH, represented by parameters such as o-Xylene; 1-Methylnaphthalene; 2-Methylnaphthalene; Acenaphthene; Acenaphthylene; Anthracene; Phenanthrene; Fluorene; and Naphthalene, showed greater relevance for water quality control and determination of retardation factors (R) and partition coefficients (K_d). As a reference for water quality, the guideline values of CONAMA Resolution 420/09 [6] and Board Decision No. 125/2021/E from CETESB [7] are applied.

Throughout the monitored period, the concentrations of individual PAH components did not exceed the minimum intervention guideline values. However, according to the Dutch Reference Framework, TPH results remained above the investigation threshold value between 4/04/17 and 3/07/20.

The study aimed to determine retardation factors (R) and distribution coefficients (K_d) based on field and on-site laboratory parameters.

Experimental Section

The water quality monitoring campaigns post-remediation of an industrial area contaminated with hydrocarbons were conducted at 8 monitoring wells, with one located upstream and 7 downstream (Figure 2).

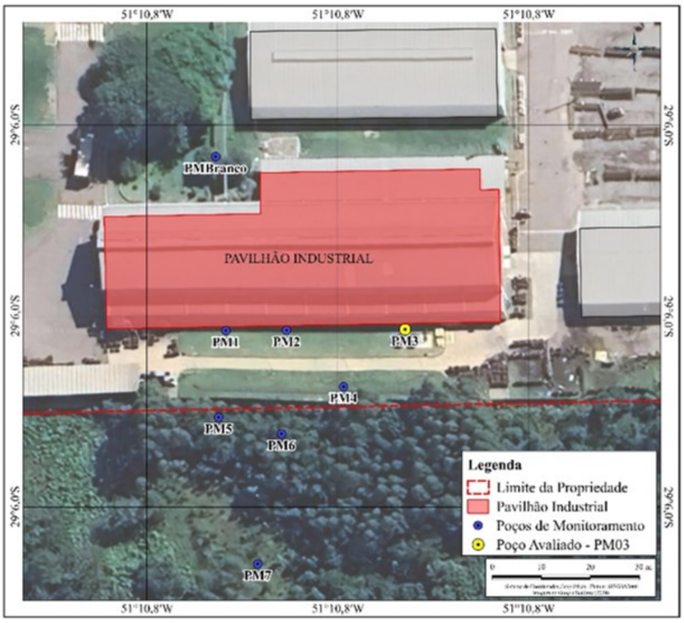

Figure 2. Distribution and identification of the monitoring wells network.

In accordance with the conditions established by the environmental agency, sampling and analysis campaigns conducted between April 2018 and December 2019 occurred on a quarterly basis. Two additional campaigns followed on 3/07/21 and 6/01/21. Based on historical results from previous campaigns and risk analysis, the selection of chemicals for monitoring was limited to specific individual components of the Polycyclic Aromatic Hydrocarbons (PAH) class, including total petroleum hydrocarbons (TPH) and TPH fractions.

The low flow sampling methodology was employed for sampling, in accordance with the procedures established in standard NBR 15847:2010 [8]. The laboratory analytical methods applied were as follows (Table 1):

Table 1. Applied laboratory analytical methods.

Components	Methodology
PAH	EPA 3510C:1996 / EPA 8270E:2018
TPH - Total Petroleum Hydrocarbons	EPA 8015C:2007
TPH Fingerprint Range - Total Petroleum Hydrocarbons	

Due to the anomalous concentrations observed in total TPH and PAH parameters during the monitored period in well PM03, a study focused on the transport and attenuation behavior at this sampling point. To facilitate chronological analysis, the results were represented using concentration versus sampling period graphs. Based on the observed anomaly, the study was extended to locate the residual contamination source upstream of well PM03.

The control of medium properties and contaminant migration facilitated the determination of transport parameters (R and K_d) of the involved components. The determination relied on the following expressions and procedures.

According to [1], the retardation factor can be estimated considering the velocity of advective flow (V_r) divided by the velocity of the contaminant (V_{cont}):

$$V_{cont} = V_r / R \tag{1}$$

The contaminant transport velocity (V_{cont}) was calculated based on the ratio between the distance from the residual contamination source to the sampling point (6.735 m) and the time elapsed from the installation of the monitoring well to the peak concentration reach of each component.

Darcy's law provides an estimate for the advection flow velocity (V_r) from the following equation:

$$V_r = K.i / \eta_{ef} \tag{2}$$

being:

K is the average hydraulic conductivity of the aquifer formation (L/T);

i is the hydraulic gradient determined by the difference in hydraulic head over distance (Dh/DL);

hef is the average effective porosity of the aquifer formation (L^3/L^3).

The hydraulic conductivity of the saturated medium (K) was estimated from pumping tests conducted at monitoring well PM03. In this well, effective porosity was estimated using hydrodynamic data from the aquifer. The hydraulic gradient (i) of the water table was determined from the piezometric and local flow map.

A retardation is influenced by factors such as the density of the geological material, its porosity, and the partition coefficient between soil and water (K_d), and can be represented by the following equation:

$$R = 1 + (\rho_b / n).K_d \tag{3}$$

being:

R the retardation factor (dimensionless);

ρ_b the bulk density of the undisturbed geological material (M/L^3);

η total porosity (L^3/L^3);

K_d the partition coefficient (or distribution coefficient) between soil and water (L^3/M).

The total porosity (n) of the aquifer was established by correlation with effective porosity. The rock density (rb) was obtained from laboratory tests on core samples extracted from near the site under analysis.

To calculate K_d the following expression was used:

$$K_d = S / C \tag{4}$$

being:

S the concentration of the contaminant in the soil (M_{cont}/M);

C the concentration of the contaminant in the water (M_{cont}/L^3).

The higher the K_d, the greater the tendency for the contaminant to become adsorbed to the soil or sediment.

When the contaminant is organic, K_d is assessed by:

$$K_d = K_{oc}.f_{oc} \tag{5}$$

being:

K_{oc} is the partition coefficient between solid organic matter and water (L^3/M);

f_{oc} is the volumetric content of organic carbon in soil (%).

Another term used to determine the mobility of organic components is the octanol-water partition coefficient (Kow). Kow is defined as the ratio of the equilibrium concentration of an organic contaminant in the octanol phase to the concentration of the contaminant in the aqueous phase.

In most cases, the immiscible solvents used are n-octanol and water. As such, it is a measure of the compound's hydrophobicity. This property is moderately temperature-dependent and is generally measured at 25 °C [9].

$$Kow = \frac{[X]n-octanol}{[X]agua} \qquad (6)$$

being:

X is the concentration (mass/volume) in the specific solvent. Kow values are unitless and are usually expressed as logKow, a relative indicator of the tendency of an organic compound to adsorb to soil. Log Kow values are generally inversely related to water solubility and directly proportional to the molecular weight of a substance.

Table 2 presents reference values for Log Koc, Log Kow, and K_d coefficients for the evaluated organic contaminants.

Results and Discussion

The concentration progression graphs of total TPH and individual PAH parameters for well PM03 from October 2016 to January 2021 are shown in Figure 3. For comparative assessment of arrival times, an integrated graph of periods (days) versus relative concentrations of each component was developed (Figure 4).

The determination of the K_d value relied on Equations 1, 2, 3, which required determining parameters such as contaminant velocity and advective flow, effective and total porosity, retardation factor, and geological material density. Based on arrival times (Table 3) and distance from the source, the contaminant velocity (V_{cont}). was obtained. It is worth noting that the accuracy of arrival times is linked to the interval between samplings, which occurred quarterly and biannually.

Table 2. Physical and chemical properties of hydrocarbons.

Hydrocarbon	CAS Registry Number	Chemical formula	Density (g/cm^3)	Organic carbon-water partition coefficient (Log K_{oc})	Octanol-water partition coefficient (Log K_{ow})	Soil-water partition coefficient (K_d)
O-Xylene	95-47-6	C_8H_{10}	0.88	2.11	3.12	0.72
Naphthalene	91-20-3	$C_{10}H_8$	1.14	2.97	3.29	3.57
2-Methylnaphthalene	91-57-6	$C_{11}H_{10}$	1	3.39	3.86	7.43
1-Methylnaphthalene	90-12-0	$C_{11}H_{10}$	1	3.4	3.87	7.58
Acenaphthylene	208-96-8	$C_{12}H_8$	1.02	1.4	4.07	-
Acenaphthene	83-29-9	$C_{12}H_{10}$	1.2	3.69	3.98	14.7
Fluorene	86-73-7	$C_{13}H_{10}$	1.2	3.88	4.18	23.13
Anthracene	120-12-7	$C_{14}H_{10}$	1.25	4.15	4.45	70.5
Phenanthrene	85-01-8	$C_{14}H_{10}$	1.18	4.15	4.46	-

Source: [10–12].

Table 3. Parameters and results obtained for determining retardation factors (R) and partition coefficients (K_d) between soil and water for individual PAH components in the residual contamination plume.

Parameter	t_{cont}	t_{cont}	L	V_{cont}	V_r	R	ρ	η	K_d (calculated)
Unit Component	**month**	**year**	**m**	**m/yr**	**m/yr**	**dimensionless**	**(kg/L)**	**-**	**-**
o-Xylene	21.47	1.79	6.74	3.76	157.65	41.88	2.3	0.0533	0.95
Naphthalene	24.23	2.02	6.74	3.34	157.65	47.27	2.3	0.0533	1.07
2-Methylnaphthalene	24.23	2.02	6.74	3.34	157.65	47.27	2.3	0.0533	1.07
1-Methylnaphthalene	24.23	2.02	6.74	3.34	157.65	47.27	2.3	0.0533	1.07
Acenaphthylene	24.23	2.02	6.74	3.34	157.65	47.27	2.3	0.0533	1.07
Acenaphthene	26.96	2.25	6.74	3.00	157.65	52.59	2.3	0.0533	1.20
Fluorene	26.96	2.25	6.74	3.00	157.65	52.59	2.3	0.0533	1.20
Anthracene	26.96	2.25	6.74	3.00	157.65	52.59	2.3	0.0533	1.20
Phenanthrene	26.96	2.25	6.74	3.00	157.65	52.59	2.3	0.0533	1.20

Legend: t_{cont} – time of arrival of the contaminant at the concentration peak; L – distance from the residual source to the sampling point (PM03); V_{cont}- contaminant velocity; V_r – actual velocity of advective flow of the center of mass; R – retardation factor; r - density of geological material; n – total porosity; K_d – partition coefficient.

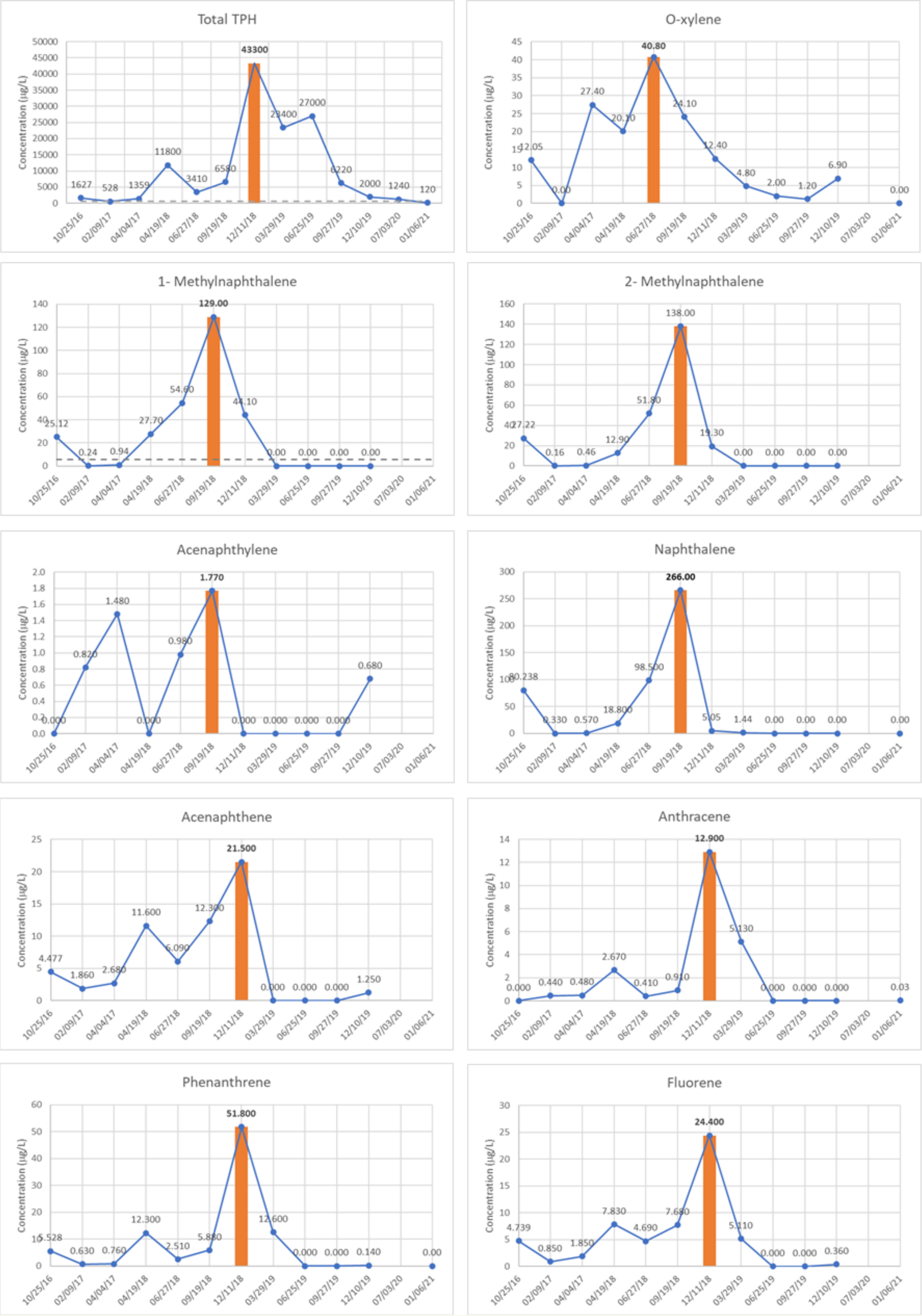

Figure 3. Line graph showing the evolution of TPH and individual PAH concentrations from the analysis campaigns conducted at well PM03 between October 25, 2016 and January 6, 2021.

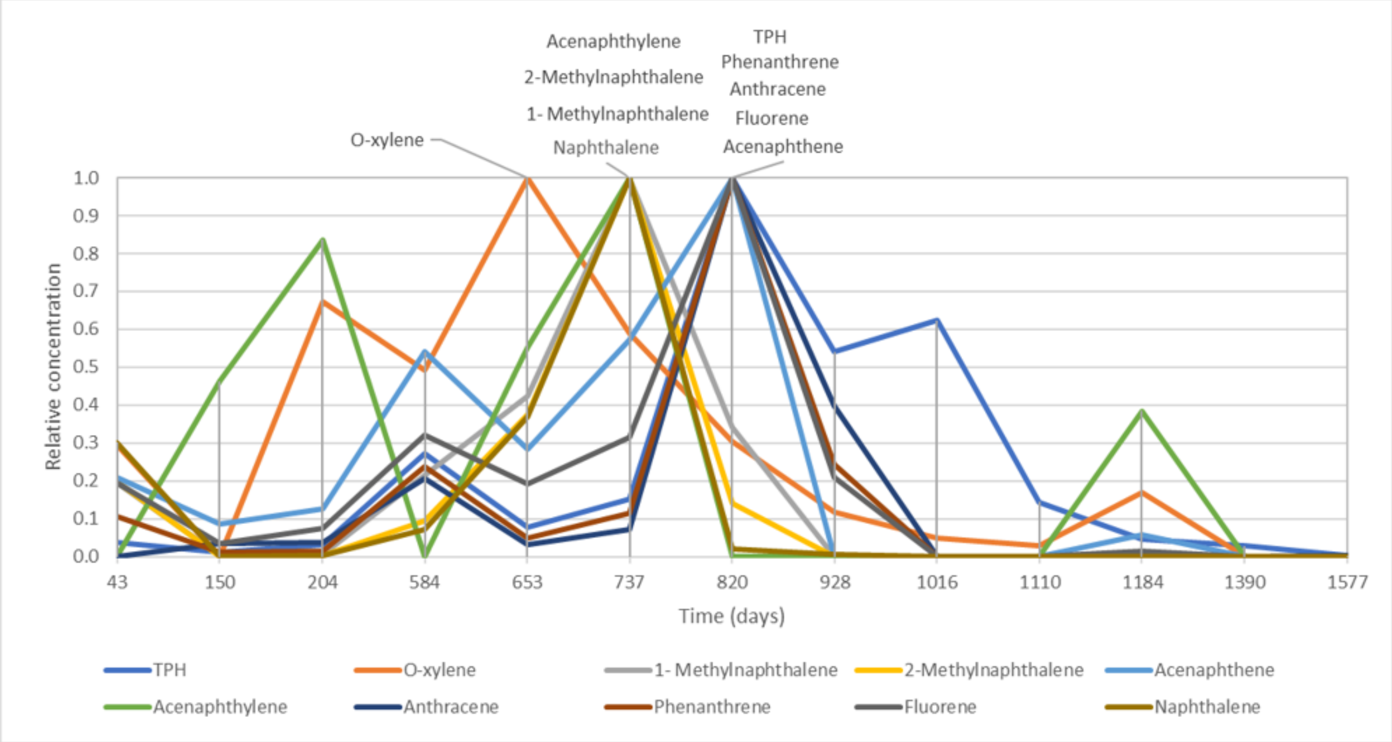

Figure 4. Line Curves of arrival times versus relative concentrations of individual PAH components and TPH.

Using Equation 2, the advective flow velocity (V_r) was determined.

The pumping tests conducted at well PM03 and upstream wells enabled the determination of hydraulic heads (Dh) and distances between wells (DL), as well as the determination of hydrodynamic parameters of the aquifer, such as conductivity (K), effective porosity (η_{ef}) and hydraulic gradient (i). The values of these parameters corresponded to an effective porosity η_{ef} equivalent to 2.42% (or 0.0242) and K equal to 157.65 m/day. The characterization of the local aquifer medium (moderately altered and fractured volcanic rock) and correlation with the effective porosity value resulted in a total porosity of 2.45% (0.0245). Finally, with the help of Equation 3, the K_d value was calculated for each organic PAH contaminant. The relationship of all calculated factors is shown in Table 3.

Conclusions

The order of arrival times for the analyzed components can be subdivided into 3 distinct intervals corresponding to 653, 737, and 820 days (Figure 3). The first arrival time corresponds to the component o-xylene, the second interval to the components acenaphthylene, 2-methylnaphthalene, 1-methylnaphthalene, and naphthalene, and the third interval to the components acenaphthene, anthracene, phenanthrene, and fluorene. It is noteworthy that TPH is consistent with the latest arrival stage, considering that its composition encompasses the set of hydrocarbons evaluated.

The determination of retardation factors (R) and partition coefficients (K_d), although not resulting in distinct values due to the sampling frequency, proved satisfactory and better adjusted to the conditions of the environment under analysis.

The calculated K_d values generally appear close to 1, indicating a balance of preference between the solid phase and the aqueous phase. Referenced values show a more significant disparity among individual PAH components. The reason for the observed balance may be related to the low concentration of organic matter or organic carbon in the fractured aquifer medium, which is the primary component responsible for retaining organic contaminants in the solid matrix of the medium.

Given the low K_d values, the distinction in arrival times may be strictly associated with the interaction between water and dissolved organic contaminants (solubility) and differences in the densities of PAHs. In comparative terms, among the referenced indices (Table 2), the one that showed the greatest agreement with the arrival order (or arrival times) of contaminants in the scenario under analysis was density (g/cm³). The scatter plot illustrates the correlation between density values and calculated K_d values for the evaluated components, fitted with a logarithmic trend line with an R^2 value of 0.8757 (Figure 5).

It's worth noting that more sensitive adjustments to K_d values could be achieved with increased sampling frequency, consequently allowing for distinct arrival times to be defined for all evaluated components.

The results obtained facilitated the identification of migration parameters (K_d and R) characteristic of the evaluated organic contaminants in situ, thereby providing more closely aligned insights into the environmental conditions and the assessed components. This expanded the understanding of attenuation and transport mechanisms of organic contaminants in fractured aquifers.

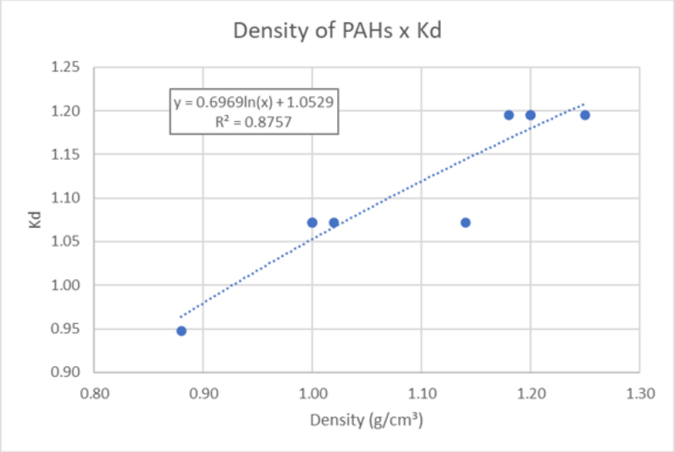

Figure 5. Scatter plot of PAHs densities x calculated K_d with fitted logarithmic trend line.

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Authors Contribution

F. Boff: Methodology, Validation, Formal Analysis, Writing-Original Draft; A. Clemes: Writing-Review & Editing; J. K. Cocconi: Conceptualization & Writing-Review; B. M. Maffessoni: Writing-Review & Editing; L. Oliboni: Writing-Review & Editing. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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