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Influence of particle size and organic carbon content on distribution and fate of aliphatic and aromatic hydrocarbon fractions in chalks

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Abstract

Although great efforts had been devoted to investigate the fate and transport of various hydrocarbon sources in major aquifers, there is still a need to better understand and predict their behavior for robust risk assessment. In this study, the fate and distribution of the aliphatic and polycyclic aromatic hydrocarbons (PAHs) of diesel fuel in chalk aquifer was investigated using a series of leaching column tests and then modelled using the Contaminant Transport module of the Goldsim software. Specifically the influence of chalk particle size on the behaviour and fate of the hydrocarbons was investigated. Distribution coefficient (K_d) between the water and chalk solid phase according to chalk particle sizes was determined for each hydrocarbon group. The larger sizes of chalk particles have higher K_d values. After 60 d of leaching using a water flow of 45 mm d^{-1}, most of the aliphatic and aromatic hydrocarbon compounds of the diesel were retained within the top 5 cm chalk layer and none of the targeted hydrocarbons were detected in the leachate from the four particles sizes chalk. Further to this, the results showed that the chalk is capable of holding more hydrocarbons than sand and chalk can limit their migration of hydrocarbons. The numerical results and the Monte Carlo analysis showed that the migration of the alkanes and PAHs is greatly retarded by the organic carbon in chalk. It is also observed that the initial mass of the alkanes and PAHs and their respective partition coefficients are important for the decaying of the source at the surface immediately after the spill and the rate-limited dissolution is responsible for entrapping the hydrocarbons in the top layer of the chalk. Overall these results can

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help to better inform risk assessment and help decision for the remediation strategy.

Keywords: aliphatic and PAHs, distribution coefficient, chalk, leaching, environmental fate and transport modeling, Monte Carlo analysis

1. Introduction

Chalk is found extensively in Northwest Europe and it is the most important aquifer in the UK, which accounts for 60% of the groundwater used for drinking water in England [1]. Chalk is a white limestone constituted of 99% of calcium carbonate ($CaCO_3$) with minor marl and flint layers and very low mineral oxide content (mainly MnO_2, $Fe(OH)_3$) with a high porosity (between 35-45%) and low effective permeability [2]. It consists of matrix blocks bounded by interconnected fractures and its hydraulic conductivity is approximately 10^{-8} m s^{-1}. The hydraulic conductivity of chalk is within the range of clays, which reflects chalk has a low ability to transmit water [3]. It is widely publicized in UK that the quality and quantity of available groundwater from the chalk aquifer is under increasing pressure due to various environmental and anthropogenic activities including among other pollution due to agriculture, diesel spill from retailing fuel station, increasing population and water consumption, increasing land development [4-7].

Between 2003 and 2009, it was reported that approximately 100,000 L diesel was spilled into chalk aquifer in Southern England. However limited information is available on the fate and transport of the hydrocarbon components of diesel in chalk [4]. A study carried out by Ashley (1994), showed that the hydrocarbon components of diesel 10 years after a spill occurred remained in the top layer of the chalk subsoil [5]. Indeed the low hydraulic conductivity of the chalk acts a barrier for the contaminants to migrate into the groundwater.

In the meantime, chemical and mechanical weathering contributes to the formation of

carbonic flows which react with the calcite of the chalk and the formation of fractures and fissures [8]. While the fractures represent only 1% of the blocks, they have a higher hydraulic conductivity and can contribute to solutes and chemicals to migrate and being transported more quickly – so there is a risk that pollutants such as hydrocarbons can reach the groundwater [8]. Therefore, the chalk is not 100% impermeable for all the contaminants. Additionally, whether the main components of diesel, comprising aliphatic and aromatic hydrocarbons can leach into the groundwater still needs to be studied.

Many authors have taken an interest in the transport of diffuse pollution (mainly pesticides from agriculture and MTBE for diesel or gasoline) and solute transport across the unsaturated zone of chalk [7, 9-11]. They often used lysimeter approach to recreate in the laboratory, with some simplification, phenomena likely to be encountered in the field and leaching tests to study the fate and transport of contaminants in solid matrices [12, 13]. The finding of several studies is in agreement with a slow transport velocity and therefore the unsaturated zone of the chalk will significantly delay the contaminants before reaching the groundwater. However, if there is presence of fractures in the unsaturated zone, the water and solutes from the surface can infiltrate through the chalk and reach the groundwater very quickly, and so there is a potential risk of rapid transport of contaminants [14].

The migration of hydrocarbons in subsoil is influenced by the physicochemical properties of soil and chemicals, including: (1) soil matrix characteristics such as field capacity, porosity, bulk density, texture composition and particle size distribution; (2)

chemicals properties such as solubility, vapour pressure, Henry's law constant, K_{oc} and K_{aw}. Dondelle derived partition coefficient (K_d values) for PAHs in sediment, sandy and silty soils using batch equilibrium experiment and showed that even small amounts of anthropogenic activated carbon-type organic matter in the contaminated soil samples can contribute to higher sample-specific K_d [15]. However, to the best of the author's knowledge, studies on the determination of K_d values for aliphatic and aromatic fractions in chalk are rarely conducted.

Several studies have shown that rainwater and solute transport mechanisms through the unsaturated zone are partly controlled by the soil as well as the type and thickness of the superficial layers, which act as a buffer that extends the drainage period and reduces the proportion of fracture flow [14, 16]. However, the role of superficial formations and clay-with-flints in particular, is not well known.

Although great efforts had been devoted to investigate the fate and transport of petroleum hydrocarbons in the subsurface, the experimental methods are time consuming and highly dependent on the soil and hydrocarbons properties. Some environmental uncertainties, such as the spatial distribution of contaminants, are difficult to be investigated using experimental approach [17]. Accordingly, environmental modelling provides a science-based structure to develop the fate and transport of hydrocarbons. It makes the hydrocarbons migration process more intuitively and helps to find out the main influencing factor(s) more easily. Over the last two decades, much more information on volatile organic compounds (VOCs), especially BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) and ether oygenates,

non-aqueous phase liquids (NAPL) and PAHs in the unsaturated zones has become available from laboratory and numerical simulations [17,18,19,20,21]. Specifically, Karapanagioti et al [17] critically reviewed models and codes dealing with the description of contaminant attenuation in the subsurface. Six models from nineteen public domain models were selected and only a limited number of these models considered vapor phase diffusion, despite its significance in practical applications [17, 18,19]. Three of the selected models treated contaminants as mixtures of more than one compound with variable properties. However, only two of them include degradation, which is also an important attenuation mechanism. New approaches trying to overcome model limitations, in terms of compound number they can handle, were also suggested while keeping the computational requirements reasonable. In another study, Panday et al [20] used a composite model to take into account the main environmental processes influencing the transport of hydrocarbons in the subsurface. The composite model was developed for assessing the multiphase migration of crude oil in subsurface at a spill site in Minnesota and the authors found the modeling results coinciding well with the field scale [20]. Soil leachability modelling for petroleum hydrocarbons fate and transport in vadose zone has also been proposed to determine site specific target levels (SSTLs) for benzene and naphthalene [22] at underground storage tank sites. The authors found that many of the simplifying assumptions made limit the accuracy of the model. Also they identified that the overestimation of organic carbon content or the underestimation of the hydraulic conductivity would results in the derivation of SSTLs of several orders of magnitude too large and therefore potentially inappropriate to

derive conservative screening and SSTLs at sites [22].

As highlighted above modelling contaminant transport in the subsurface can be complicated since a number of environmental parameters, transport phenomena and chemical reaction processes are taking place and must be integrated into numerical simulation. The objective of this study is therefore to provide further insights into the distribution and fate of alkanes and PAHs in chalk. To do so, a series of chalk column tests have been set up to: (1) measure the K_d values for aliphatic and aromatic fractions in chalk-water system; (2) investigate the effect of chalk particle size on leaching property of aliphatic and aromatic hydrocarbons in chalk; (3) describe the vertical distribution of aliphatic and aromatic hydrocarbons in chalk profile after the leaching test; and (4) simulate the fate and transport of petroleum hydrocarbons fractions in chalk using the Goldsim simulation platform and (5) identify the governing physicochemical properties using a sensitivity analysis. The Goldsim simulation platform was chosen as it is a flexible and graphical tool for the fate and transport of contaminants simulation. Most importantly, it can represent the uncertainties in processes and uncertain events (such as flooding) by specifying model inputs as probability distributions and disruptive events [23].

2. Materials and methods

2.1 Chalk sample preparation and characterization

The chalk was obtained from an excavated pile at Cranfield Ordnance Test and Evaluation Centre (UK). Stones and plant roots were removed and then the chalk

samples were air dried at room temperature of 25 °C for a week. The chalk samples were crushed using a ceramic hammer and then fractionated using a series of sieves as coarse (Ø 0.63-2 mm), medium (Ø 0.2-0.63 mm) and fine (Ø < 0.2 mm) particles. The unsieved chalk samples are defined "as received" sample.

2.2 Hydrocarbon characteristics and batch experiments settings

The diesel fuel used in this study was obtained from a commercial service station (density: 0.837 g mL^{-1}). The hydrocarbon composition of the diesel were divided by the equivalent carbon number (ECn), which is related to the boiling point of alkanes and retention time in gas chromatography columns [24]. 30 mL of diesel was poured into 0.5 kg of chalk and get the diesel concentration of 50 g kg^{-1} (wet matter, water content <1.84%). Then the samples were left more than 12 hours at room temperature to equilibrate before use.

2.3 Distribution coefficient determination

The distribution coefficients (K_d) of the aliphatic and aromatic fractions were determined using batch leaching test. Specifically, 30 mL rainwater (pH:8.77, dissolved organic carbon: 6.70 mg L^{-1}), collected at Cranfield University campus and stored in a high density polyethylene (HDPE) bucket, was added to 2, 3 and 6 g of chalk spiked with diesel at 50 g kg^{-1}. The equivalent liquid-solid ratios (L/S) were 15, 10 and 5, respectively. The tubes were then sealed and placed on a shaker table at room temperature at 150 rpm for 7 d. The tubes were then centrifuged (151 g for 20 min) and 5 mL of the liquid phase was collected for hydrocarbon content analysis (concentration

of the hydrocarbon fraction considered in the water phase: Cw). Then $1/C_w$ was plotted against L/S to determine the pore water concentration (Y axis intercept = $1/C_{p,w}$) [15]. The concentrations of contaminants remaining in chalk $C_{s,e}$ after equilibrium were calculated from the mass balance equation [15]:

$$C_s \cdot S = C_{s,e} \cdot S + C_w \cdot V \quad (1)$$

Where C_s is the initial contaminant concentration in chalk (mg kg^{-1}), $C_{s,e}$ is the concentration in chalk after equilibrium (mg kg^{-1}), C_w is the concentration in water phase after equilibrium (mg L^{-1}), S is the mass of chalk (kg) and V is volume of water (L) [15].

The distribution coefficient K_d (L kg^{-1}) for each hydrocarbon fractions was then determined using Equation 2 ($C_{s,e}$) [15]:

$$K_d = C_{s,e}/C_{p,w} \quad (2)$$

2.4 Leaching column test

The leaching system is illustrated in Fig. SM-1 in Supplemental Materials (SM). A 0.02 m layer of gravel was placed at the bottom of the PVC column (0.104 m internal diameter x 0.58 m length) and a 0.01 m layer of sand was laid on the gravel. Then a layer of the fine, medium, coarse and as received particle chalk of 0.41 m thick was introduced with an increment of approximately 0.05 m and was compacted with the aid of a rammer. Between the increments, the packed uppermost surface was disturbed with a shovel to ensure a better contact of the increments. To reproduce the environmental humid condition, the soil columns were then saturated with rainwater and a 0.02 m layer of diesel spiked chalk was placed on top of the clean chalk. To prevent any movement

of chalk in the top layer during the leaching process caused by any disturbance process, such as the water addition process, a 0.01 m layer of sand was placed on the diesel contaminated chalk. The porosity of the samples in the packed columns was calculated using $n = 1 - \rho_b/\rho_s$, where ρ_b is the bulk density of the chalk [M L^{-3}], and ρ_s is the chalk particle density [M L^{-3}]. The Loss on Ignition (LOI) of chalk was determined as described in BS EN 13039:2000 [19]. The hydraulic conductivity was calculated using Darcy's law. The properties of chalk are listed in Table SM-1. Rainwater (pH:8.77, dissolved organic carbon: 6.70 mg L^{-1}) was added manually from the top of each column every day and the average volume added to the fine, medium, coarse and as collected samples were 9, 33, 387 and 182 mL, respectively. 5 mL water leachates were collected every 3 d. After 60 d, the chalk in the column has been pushed out and 5 g chalk samples were collected at a depth of 0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35 m, respectively. All the conditions were carried out in triplicate.

2.5 Sample extraction and analysis

The concentration of aliphatic and aromatic hydrocarbons in water was determined by solvent extraction previously described by Guo et al [25]. Briefly, 5 mL water sample was placed in a 5 mL volumetric flask. Then a mixture of 50 μL of n-hexane and 500 μL acetone were added to the sample turning it into emulsion. Another 500 μL of acetone was added into the solution 2 minutes later to break down the emulsion. Once the mixture was cleared, 35 μL of the upper layer extract was collected for GC-MS analysis.

The solvent extraction in soil samples were described by Risdon et al [26]. Briefly, 5 g chalk samples were chemically dried with 5 g anhydrous sodium sulphate in 50 mL Teflon centrifuge tubes. Then added 4 mL acetone and sonicated for 2 min, another 6 mL acetone and 10 mL hexane were added to the samples and sonicated for 10 min. After that the samples were centrifuged for 5 min at 3000 rpm and the supernatants were passing through a filter column fitted with a glass receiver. The samples were then resuspended in 10 mL of acetone/hexane (1:1) and sonicated for 15 min, centrifuged for 5 min at 3000 rpm and filtrated. The sonication and filtration steps were repeated twice. The supernatants were then cleaned using Florisil columns. Finally, the solution volume was adjusted to 50 mL.

GC-MS analysis was performed with Agilent 6890N-5973. A fused silica capillary column HP-5MS (30 m×0.25 mm i.d. and 0.25 μm film thickness) was used. Operating conditions were as follows: injector port temperature 320 °C; helium as carrier gas at a flow rate 1.1 mL min^{-1}. The column temperature was increased from 60 °C to 220 °C at 20 °C min^{-1}, then to 310 °C at 6 °C min^{-1}, and held for 7 min. A 3 μL volume was injected splitless. A solvent delay of 2.5 min was employed. The MS system was operated in electron impact ionization mode with an ionizing energy of 70 eV, scanning from m/z 45 to 450. The ion source temperature was 250 °C and quadrupole temperature 150 °C. Blank samples were analyzed every 20 samples.

2.6 Statistical analysis

Regression and correlation analysis between log K_d values, average chalk particle sizes

and molecular weight of the aliphatic and aromatic hydrocarbons were carried out using SPSS version 20.

2.7 Modeling of petroleum hydrocarbons fate and transport in chalk

The fate and transport of hydrocarbons in chalk was simulated using GoldSim v11.0. The Contaminant Transport Module was selected and the modelling framework mainly contains Material, Pathway, Input and Result. The properties of chalk, water and contaminants were defined in the element of Material. A schematic of simulation of diesel transport in chalk is illustrated in Fig. SM-2.

A Source and Sink pathway was created before and after the chalk layers to contain the fluid flow into and out of the chalk layers. Next, the properties of the Pathway were defined according to the parameters used in the leaching test experiment and were listed in Table 1. To simulate the random distribution of diesel in the contaminated chalk, the top layer was divided into 10 sub layers. The contaminants mass in the top layers 1-9 were set as normal distribution with the mean mass of 10% of the total mass and a standard deviation of 0.5% of the total mass. The contaminants mass in layer 10 was the results of total mass subtract the mass in layers 1-9. The diesel impacted chalk layers and distribution relationship were put in the element of contaminants. The selected petroleum hydrocarbon fractions and their initial mass in the chalk were listed in Table SM-2. The alkanes and PAHs properties were listed in Table SM-3 and Table SM-4 [27]. In the Monte Carlo analysis, the water flux rate, chalk porosity and chalk organic carbon content were multiplied with a Normal Distribution parameter, whose mean value is 1

and the standard deviation is 0.1. The probabilistic simulations were set with 100 realizations with 1 random seed.

Partition coefficient, water solubility, initial mass, flux rate and porosity were selected to do the sensitivity analysis. The sensitivity analysis was done by changing one variable at a time and keeping all the other variables at their central value. To realize the variation of partition coefficient, water solubility and initial mass, an influence factor was multiplied to the values listed in the Table SM-2. The lower bound, upper bound and central value are listed in the Table SM-5. The sampling points for each variable is set to 99 and considering the contaminants concentration are also related to the leaching time, four simulation duration, 10 days, 100 days, 1000 days and 10000 days, was set to investigate the difference.

3. Experiment results and discussion

3.1 Identification of alkanes and PAHs in chalk

The concentrations of n-alkanes and PAHs in diesel spiked chalk are showed in Fig. SM-3. The main n-alkanes in chalk were ranging between C_{10} and C_{26} and they were divided into three groups according to their carbon numbers: EC_{10-12}, EC_{12-16}, EC_{16-26}. The respective average concentration was 964, 1913 and 2481 mg kg^{-1}. In regards to the PAHs in chalk, the main compounds were the 2-4 rings PAHs including Naphthalene (Naph), Acenapthylene (Acp), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Ant) and Pyrene (Pyr). The concentrations of PAH varied between 0.1 and 12 mg kg^{-1} with a higher abundance for Naph. The average

concentration of total n-alkanes was 5358 mg kg^{-1}, which was 218 times higher than the total PAHs one (24.6 mg kg^{-1}). Such concentration level of total alkanes in the chalk is 107 times higher than the recommended cleanup levels for residential land use and 10 times higher than the industrial levels [29].

The dominance of the alkanes was expected as the n-alkanes are the main diesel components [28]. However as the PAHs are recognized as carcinogenic compounds, it is necessary to characterize their concentrations in chalk. The main PAH of concern was Naph followed by Phen and Flu. Naph concentrations exceed the residential levels by 3 times, while the other PAHs were below the screening level for residential land use [30].

3.2 Distribution coefficient

The $C_{s,e}$ and $C_{p,w}$ values are reported in Table 2 and the K_d values are presented in Table 3. The results indicate that the hydrocarbons bind strongly to the chalk particles and the concentrations in the water phase were 2-4 orders lower than the solid phase which is in good agreement with other studies [20].

The K_d values for the alkanes were estimated using

$K_d=K_{oc}\times f_{oc}$,

where K_{oc} is the organic carbon partition coefficient and f_{oc} is the organic carbon fraction in the soil [31]. The estimated K_d values of the alkanes were 1-3 magnitudes higher than the experimental values. This is because the K_d values are site specific and they vary with the composition of soil, such as organic matter and surface area of the

minerals [32]. The K_d values of the PAHs determined in this study were in the same order of magnitude compared with those obtained in contaminated manufactured gas plant (MGP) soil in the Midwest of USA, which have an organic carbon content ranging between 3.1% and 3.9% [15]. In contrast, they were 1-2 magnitude lower than those obtained in MGP soils in California and New York respectively, which would be due to the high organic carbon content in the soil (7.1%-56.1%) [15]. Therefore these results highlight how organic carbon content in the soil matrix considered influenced the partitioning coefficient of the hydrocarbons. The K_d values for the different chalk particle sizes increased in the order of fine > medium > coarse > as collected (Table 3). This is attributed to the larger size particles which have more pore-throats and blind pores smaller than 1 μm [8]. When the alkanes and PAHs get into the pores inside of the chalk matrix, because of the water in blind pores is nearly stagnant, the main route for hydrocarbons to leach into water phase was diffusion. Compared to the movement within water stream, the diffusion into water phase is more slowly. Meanwhile, the specific surface area of chalk increased with the decreasing of particle diameter. In the same size particles, the K_d for the alkanes were similar, while they increased with molecular weight for PAHs.

The relationship of log K_d between chalk and the alkanes and PAHs properties was regressed into the Equation (3) with R^2=0.647 and $p<0.01$, where D is the average chalk particle size (mm), MW is the mole molecular weight (-).

$$\log K_d = 0.027D + 0.017MW + 0.033 \quad (3)$$

Equation (3) also reveals D and MW have positive relationship with log K_d.

3.3 Concentration in chalk and leachate

After 60 d infiltration of rainwater, the alkanes and PAHs were retained in the upper 5 cm of the chalk column (Fig. 1), which means chalk can restrain the mobility of alkanes and PAHs. It is due to the contaminants being strongly bound by the NOM and micropore of chalk and their migration are limited by the matrix diffusive release into water in chalk [11]. Similar finding has been reported by Ashley [5] who found little diesel penetrated beyond 1 cm in chalk aquifer in 10 y. Compared to the leaching tests carried out by Zhang et al [33], where PAHs in the silt and sand can migrate 6 cm downward in 40 d, the migration rates were slower in chalk. The fate and transport of hydrocarbons in sand, silt, and chalk were summarized in Table 4 [31, 33]. Although the total volume of water added to the coarse chalk was 42 times that of the fine chalk, the amount of contaminants residue in the chalk show little difference, which also demonstrates the strong absorption ability for the four particle sizes of chalk.

During the 60 d leaching test, the hydrocarbons can be dissolved into water and adsorbed to the soil particles. However, the alkanes and PAHs were not detected in the leachate in all of the leachate samples during the experiment. This is because the pore-throats in chalk have a strong capacity for absorbing the contaminants and can hamper the contaminants moving into the water phase. Similar results were obtained in sand and coarse silt having the same particle size and porosity range than the chalk used in this study [33]. None of PAHs were detected in the leachate during a period of 40 d [31]. In contrast, another experiment carried out by Yang et al, showed that concentration of total petroleum hydrocarbons reached 19 mg L^{-1} in the leachate from

the sand [31]. It may be due to the different water infiltration rate used as Yang chose a rate of 239 mm d^{-1} [31], which is significantly higher than 6 mm d^{-1} used in Zhang's experiments [33] and 1 to 45 mm d^{-1} used in our study. When the water infiltration rate is lower than 45 mm d^{-1}, the hydrocarbons have enough time to diffuse into the pore-throats or be absorbed by the soil particles surface, therefore the hydrocarbons were not detected in the leachate. When the water infiltration rate is as high as 239 mm d^{-1}, the hydrocarbons of those dissolved in water are absorbed by soil particles limitedly, which results in hydrocarbons leaching out with the leachate.

4. Modeling fate and transport of the alkanes and PAHs

4.1 Influence of organic carbon content

Chalk was set without organic carbon and thus the partition coefficient was 0. Simulation duration was 10 days and with 1000 steps. As shown in Fig. 2, the alkane fractions and PAHs in the effluent reached peak concentration at different time. For alkanes, peak concentration of the EC_{6-8} fraction occurred after 1 day while EC_{8-10} fraction peak occurred around 2.7 day. The EC_{8-10} and EC_{10-12} fractions have a wider peak than the EC_{6-8}, which is attributed to the higher initial mass of EC_{8-10} and EC_{10-12} in the top layer. The peak concentration differences are also related to the solubility of the fractions; when a fraction reaches its solubility limit, its concentration in leachate would not change. Fig. 2(a) also indicates Phen and Flt concentrations were higher than any other PAHs. This is again due to the initial mass differences; the initial mass of Phen and Flt present in diesel were 7-470 times higher than other PAHs. The release

order of the PAHs is Naph, Acp, Ace, Flu, Ant, Pyr and IND (around 1 day)> Phen (1.3 days)> Flt (2 days)> Chr, BbF, BaP, BkF, DaA and BgP (5.7 days).

It takes much less time for the alkanes and PAHs to migrate out of the chalk when no organic carbon content is taken into account, compared to the leaching experiment results described in Section 3.3. This is because the chalk used in Section 3.3 contains some organic carbon, which can strongly hamper the migration of hydrocarbons. In the next simulation scenario, the organic carbon in chalk will be taken into consideration.

Although chalk has low organic carbon content, the effect of organic carbon on the fate and transport of petroleum hydrocarbons in chalk still need to be investigated. It is because organic carbon has strong ability to absorb the organic chemicals, which influences the transport of the hydrocarbons in soil. The Loss on ignition (LOI) of the chalk used in Section 3 is less than 2% and LOI includes organic carbon loss and inorganic mineral loss. In this scenario chalk was set with an organic carbon content of 0.01, thus the partition coefficient is 0.01Kow. Organic carbon in chalk can delay the hydrocarbon migration, if the simulation duration still set to be 10 days, most of the hydrocarbons would not leach. Therefore the simulation duration is set to be 1000 days with 100000 steps.

Compared to the results of chalk without organic carbon described in Fig. 2(a), the retention time of alkanes and PAHs in the chalk with 0.01 organic carbon have been delayed (Fig. 2(b)). It needs approximately 140 days to reach the max concentration time of EC_{6-8}, while it takes more than 1000 days for EC_{8-10} and other alkanes. Higher MW PAHs have a longer retention time in chalk and are less prone to leach out in the

early phase. To reach the max concentration, it takes 36 days, 140 days, 172 days, 419 days and 460 days for Naph, Ace, Acp, Phen, and Ant, respectively and the relationship of release time between log K_d and MW was regressed into the Equation (4) with R^2=0.931 and p=0.069, where t is the release time (d), MW is the mole molecular weight (-).

$$t = 139.542 \log K_d + 5.331 MW - 885.267 \quad (4)$$

It takes more than 1000 days for other PAHs to reach the peak concentration. All the maximum concentrations in the leachate have been reduced by 5.5 to 4×10^{19} times (Table SM-6). For example, considering the 1% organic carbon in the system, the maximum EC_{6-8} concentration in the leachate reduced by 140 times. The organic carbon also prolonged the leaching time. Correspondingly, EC_{6-8} for example takes 400 days to leach out, while it takes only 2 days from the organic carbon free chalk. This difference can be explained by the fact that the hydrophobic chemicals would tend to partition to the organic carbon instead of water. The n-alkanes and PAHs concentrations were below 0.002 mg L^{-1}, this can explain why they were not detected in the leachate of the leaching experiment in Section 3.3 and the experiment carried out by Zhang et. al [31].

The distribution of EC_{8-10}, Naph, Phen, Pyr, total alkanes and total PAHs in the chalk is shown in Fig. SM-3. It took 325 days for EC_{8-10} to reach the maximum concentration of 1.85 mg kg^{-1} at depth of 10 cm (Fig. 3(a)). The maximum concentration of alkanes within the first 20 cm of the chalk column was after 537 days while it was 890 days and more than 1000 days for 30 cm and 40 cm, respectively. Meanwhile the peak concentration decreased with the increased depth and the peak width has been extended

accordingly. The distribution of EC_{12-16} and EC_{16-35} in chalk was not plotted because more than 99.9% of them were trapped in the top layer and little was migrated into water phase due to the low water solubility and high Kow.

The concentration of total alkanes and total PAHs in chalk profile is illustrated in Fig. 4. The alkanes were mainly retained in the top 10 cm layer and reach a maximum concentration of 40 mg kg^{-1} at 4 cm after 1000 days. Naph, Phen and Pyr have relatively higher water solubility than other PAHs and they migrated through the chalk layer more quickly, which resulted a waving of concentration in the chalk profile. The maximum concentration of PAHs in the chalk was less than 3 mg kg^{-1} after 1000 days. The modelling results of hydrocarbons distribution in chalk profile are in accordance with the experiments results in Fig. 1.

4.2 Monte Carlo analysis results

Uncertainties are present in many conditions, such as the changing soil porosity, organic carbon content, and water infiltration rate, which influence the hydrocarbons transportation in subsurface. The results of Monte Carlo analysis show that the environmental uncertainties influence the contaminant concentrations and their transportation time in the subsurface (Fig. 5). The total alkanes concentration varied from 6.27×10^{-4} mg L^{-1} to 2.43×10^{-3} mg L^{-1} at day 116 and the total PAHs concentration varied from 6.55×10^{-4} mg L^{-1} to 2.07×10^{-3} mg L^{-1} at day 342. The maximum concentration for the alkanes and PAH was reached between 116 and 183 days and 342 to 560 days, respectively (Fig. 5). There are more than 85% of probabilities for the total

alkanes to get the maximum concentration between day 116 and 128 while for the PAH the maximum concentration will be reached between day 342 and 388 (Fig. 5). These results provide some insights into the time ranges for the hydrocarbons to reach a certain concentration in the leachate, which could facilitate to evaluate the fate and transport of hydrocarbons in the environment with many uncertainties or when some environmental parameters are not available. To the best of the author's knowledge, this is the first time that Monte Carlo analysis data focus on alkanes and PAHs migration in soil are generated.

4.3 Sensitivity analysis

The sensitivity analysis results are showed in Fig. 6 and the x-axis represents the results for different values of independent variables. The gray bar shows that the value was produced by the Lower Bound (Low), while the black bar indicates that the value was produced by the Upper Bound (High). The solid vertical line represents the value when the Central Values are used for all independent variables. The variables are organized from top to bottom according to the total range of results produced. Figure 6 shows that the parameters have different sensitivities on the concentration in effluents when the duration is different. For example, the change of partition coefficient is at the top of the chart, which means organic carbon content produces the largest range of the hydrocarbons concentration in leachate within 100 days (Fig. 6(a) and (b)). When longer durations are considered, the flux rate is less sensitive. For the longer period, the initial mass is the most sensitive to the concentration in the effluent (Fig. 6(c) and (d)).

It is due to the contaminants has left the system in the effluent and the more contaminants, the longer time needed to leach out.

5. Conclusions and recommendations

The results of this study indicate that alkanes and PAHs are preferentially bounded by to the chalk particles than being dissolved in the water phase. The larger sizes of chalk particles have higher K_d values. Due to the porous structure of chalk and the hydrophobic properties of the alkanes and PAHs, the chemicals migration rate was slower than that in sand and silt system as summarized in Table 4 This means chalk can act as a barrier for the hydrophobic chemicals if the preferential flow in macropores and cracks are neglected. Based on this study, a few conclusions can be drawn which have some implications for the monitoring strategies and remediation processes in chalk aquifers. The K_d of the hydrocarbon fractions is related to the chalk particle size, and therefore predicting hydrocarbon migration in chalk based on a non-representative particle size would overestimate the hydrocarbons mobility.

Simulation results indicate the concentration of alkanes and PAHs in leachate and chalk profile depends on the water solubility, partition coefficient and organic carbon content in chalk. The hydrocarbons that have higher water solubility and low partition coefficient leached more easily from the chalk. 99% of the total alkanes and PAHs were retained within the 40 cm layer after 1000 days of leaching with water flux rate of 1.2 L day^{-1}. However the more soluble compounds, such as EC_{8-10} and Naph, totally migrated out of the 40 cm chalk layer in 1000 days. The migration of petroleum

hydrocarbon is greatly retarded by the organic carbon in chalk. Sensitivity analysis indicated that the partition coefficient and the initial petroleum hydrocarbon mass significantly influenced the transportation of the petroleum hydrocarbons in the subsurface.

Considering the hydrophobic contaminants in the chalk system show little chances to get into the aquifer, the contamination in the chalk could be treated by long period remediation approaches, such as monitored natural attenuation. These findings can decrease the extensive sampling, reduce the disturbance to the site as well as reduce the energy consumed in the site investigation.

Acknowledgement

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Table 1

System data used in the calculation

Parameter	Value	Parameter	Value
Water volume in Source	1000 m^3	Diesel spiked chalk layer	0.01 m
Water hold capacity in Sink	1000 m^3	Uncontaminated chalk layer	0.4 m
Dry density of chalk	1638 kg m^{-3}	Flux rate	1.2 L d^{-1}
Chalk porosity	0.46	Fluid saturation	1
Soil column diameter	0.102 m	Dispersivity of the chalk	0.001 m
Soil column height	0.41 m	Number of cells	10

Table 2

$C_{e,s}$ and $C_{p,w}$ of the alkanes and polycyclic aromatic hydrocarbons (PAHs)

	Fine		Medium		Coarse		As received	
	$C_{s,e}$, mg kg^{-1}	$C_{p,w}$, mg L^{-1}	$C_{s,e}$, mg kg^{-1}	$C_{p,w}$, mg L^{-1}	$C_{s,e}$, mg kg^{-1}	$C_{p,w}$, mg L^{-1}	$C_{s,e}$, mg kg^{-1}	$C_{p,w}$, mg L^{-1}
EC_{10-12}	897	3.03	863	2.15	799	1.02	1098	0.55
EC_{12-16}	1825	6.81	1720	4.79	1559	2.26	2128	1.31
EC_{16-26}	2437	8.72	2255	6.04	1967	2.84	2706	1.61
Naph	11.3	5.56E-02	12.83	3.82E-02	9.35	3.82E-02	12.53	1.08E-02
Acp	0.1956	8.44E-04	0.1335	6.99E-04	0.4849	2.2E-04	0.6251	3.89E04
Ace	0.0983	5.08E-04	0.19	3.15E-04	0.1372	1.8E-04	0.2917	1.33E-04
Flu	1.4	2.87E-03	1.172	9.68E-04	0.9128	6.47E-04	1.606	4.31E-04
Phen	9.18	4.39E-03	9.94	1.93E-02	7.65	1.83E-03	11.03	9.50E-04
Ant	0.51	1.63E-03	0.43	2E-03	0.44	5E-04	0.53	3.97E-04
Pyr	0.445	1.16E-04	0.36	5.45E-05	0.36	3.57E-05	0.49	1.73E-05

Table 3

Calculated log K_d of alkanes and polycyclic aromatic hydrocarbons (PAHs) in chalk

	Fine	Medium	Coarse	As received
EC_{10-12}	2.47	2.6	2.89	3.3
EC_{12-16}	2.43	2.56	2.84	3.21
EC_{16-26}	2.45	2.57	2.84	3.22
Naph	2.31	2.53	2.39	3.06
Acp	2.36	2.28	3.34	3.21
Ace	2.29	2.78	2.88	3.34
Flu	2.69	3.08	3.15	3.57
Phen	3.32	2.71	3.62	4.06
Ant	2.49	2.33	2.94	3.13
Pyr	3.58	3.82	4.00	4.45

Table 4

Summary of fate and transport of hydrocarbons in sand, silt, and chalk [29, 31]

	Sand	Silt and sand	Chalk
Particle size, mm	0.1-1	0-2	0-50
Porosity	0.3-0.52	0.4-0.52	0.47-0.5
Organic carbon content, %	0.15-0.36	3.71-4.52	<2
Type of hydrocarbons	TPH	PAHs	TPH and PAHs
Water infiltration rate, mm d^{-1}	239	6	1-45
Experimental duration, d	2.4	40	60
Concentration in leachate, mg L^{-1}	19	Not detected	Not detected
Hydrocarbons infiltration depth, cm	>30	6	<5

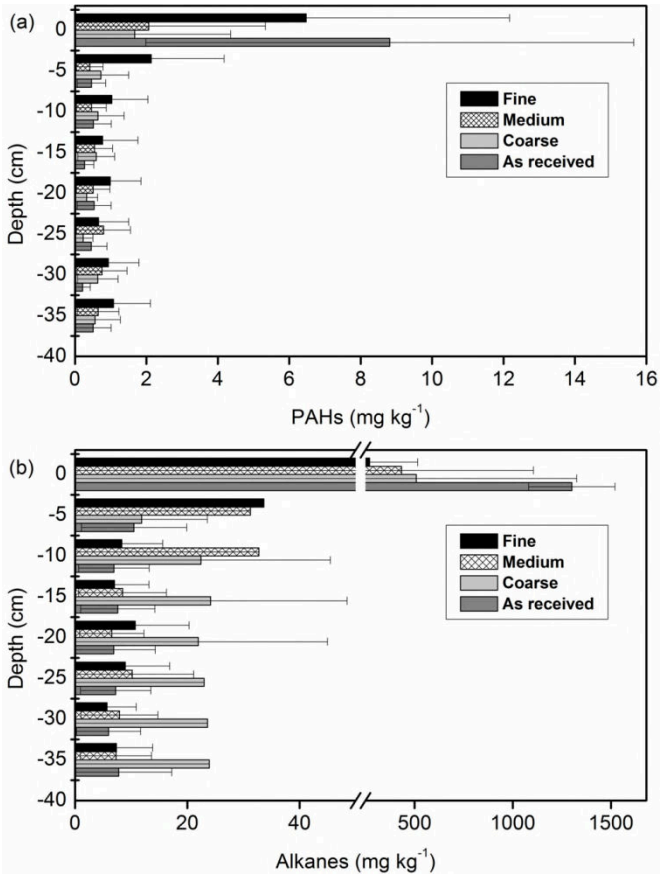

Fig. 1 Concentration of (a) PAHs, (b) alkanes in the chalk profile. Error bars correspond to the standard deviation (n=3).

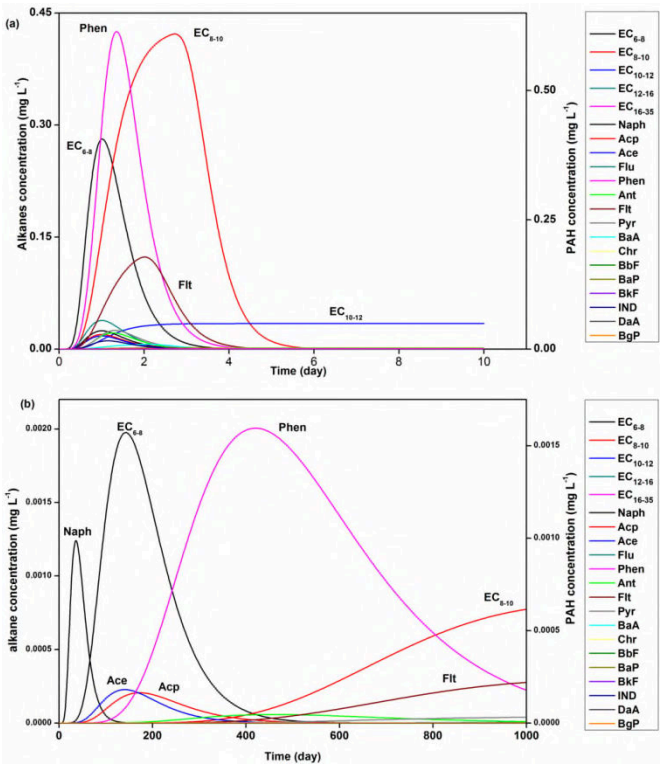

Fig. 2 Alkanes and PAHs concentration in the leachate from (a) chalk without organic carbon, (b) chalk with 0.01 organic carbon.

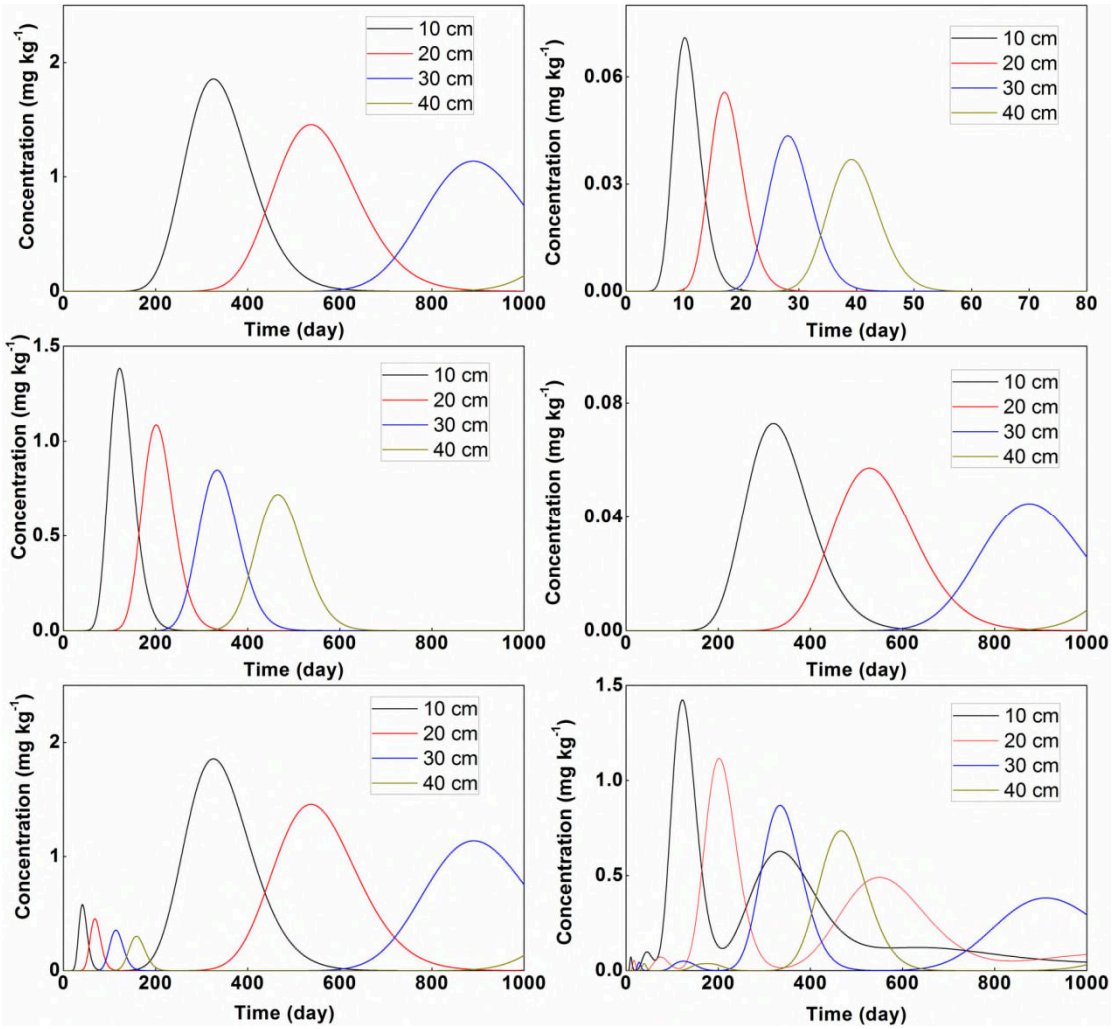

Fig. 3 Selected alkanes and PAHs concentrations in the chalk at depth of 10 cm, 20 cm, 30 cm and 40 cm.

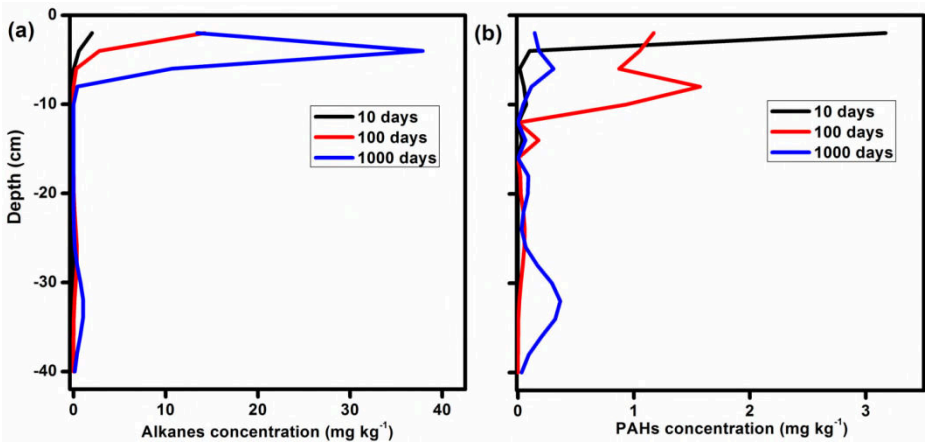

Fig. 4 Total alkanes and total PAHs concentration in chalk profile (a) Total alkanes; (b) Total PAHs.

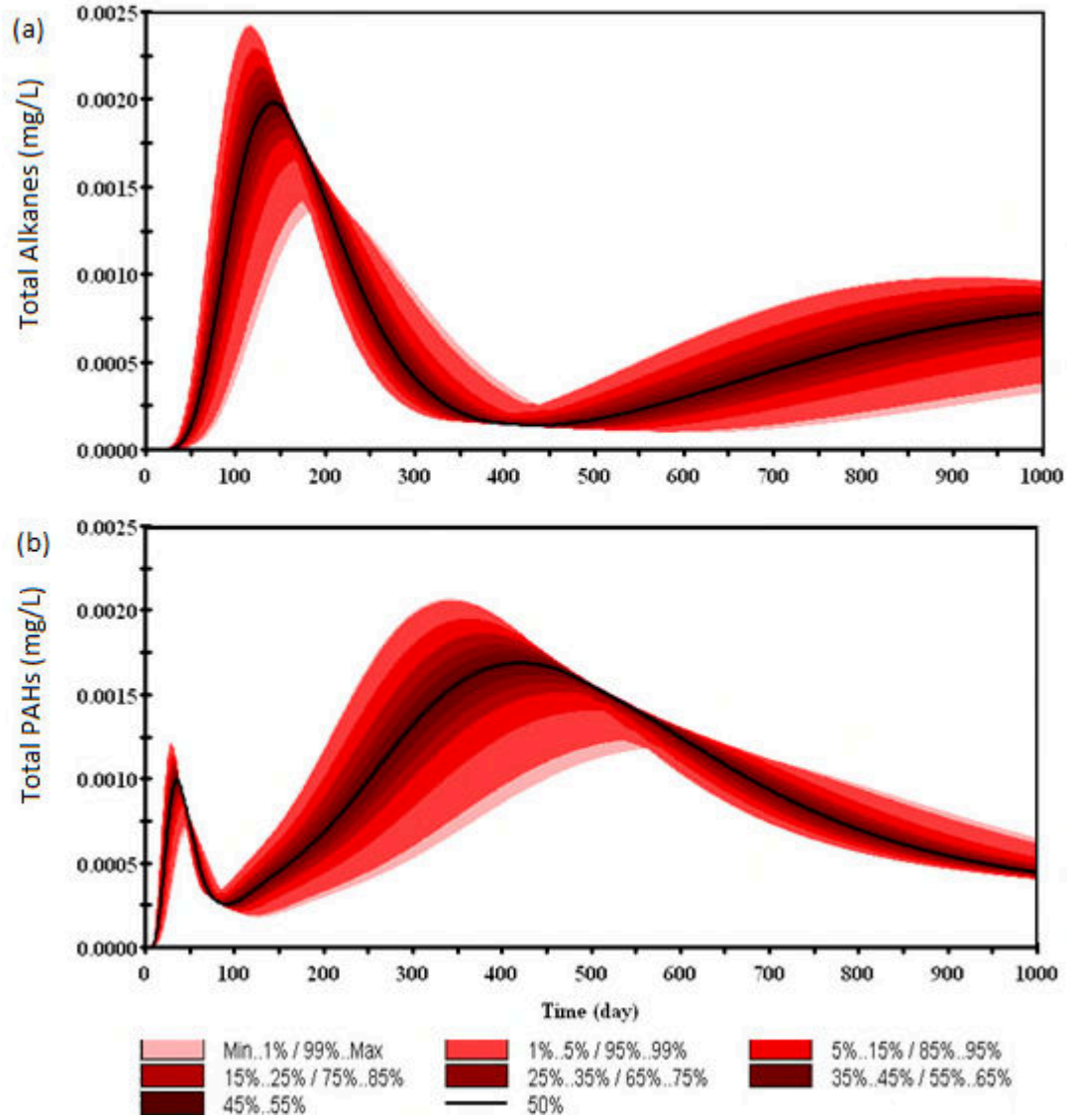

Fig. 5 Monte Carlo analysis results of total alkane and total PAHs concentration in leachate (a) Total alkanes; (b) Total PAHs.

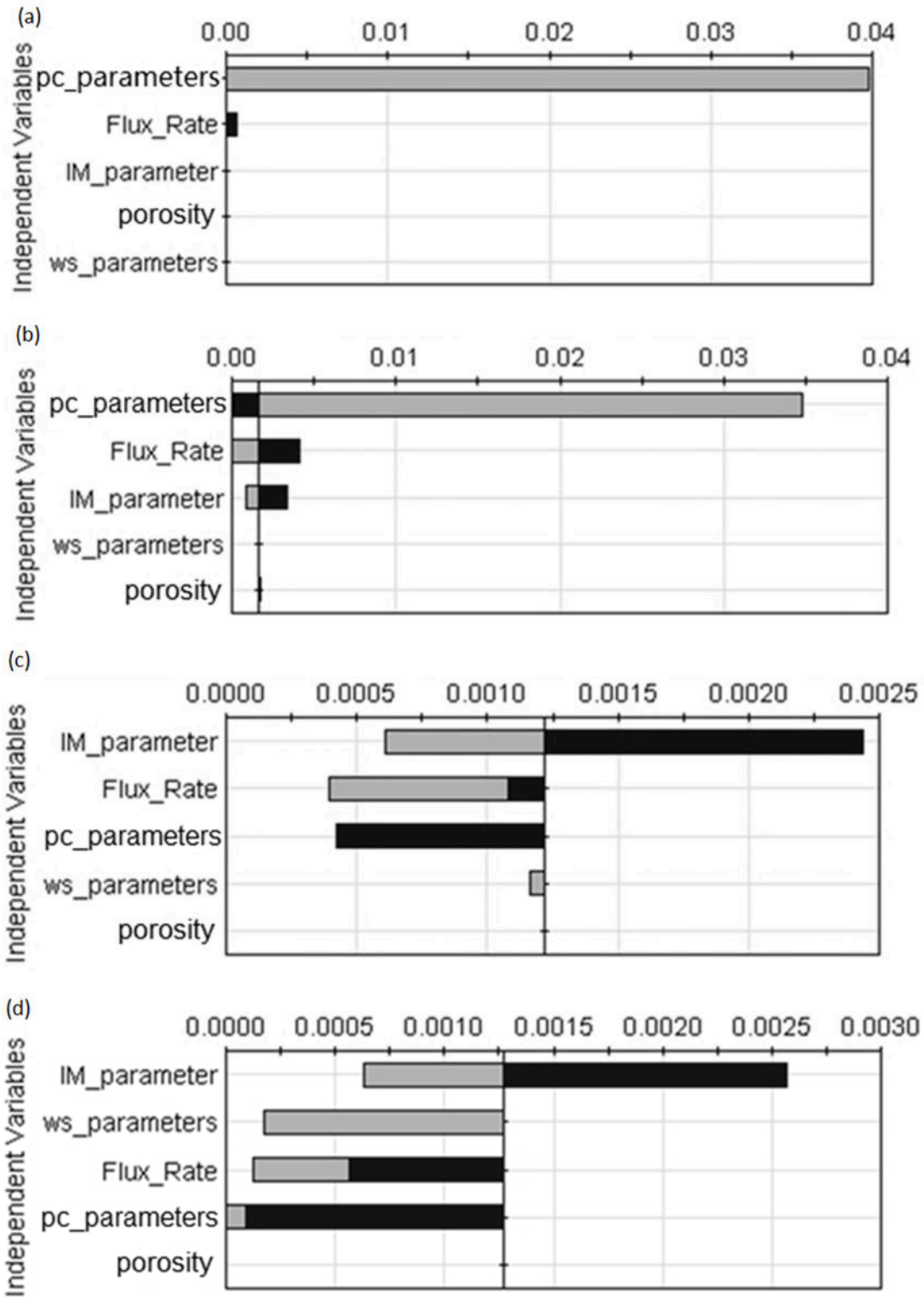

Fig. 6 Sensitivity analysis results Tornado sensitivity charts: (a) 10 days; (b) 100 days; (c) 1000 days; (d) 10000 days. The gray bars were corresponding to the lower bound results while the black bars were corresponding to the upper bound.

Supplementary Materials

Influence of particle size and organic carbon content on distribution and fate of aliphatic and aromatic hydrocarbon fractions in chalks

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Table SM-1

Properties of the chalk

	Fine	Medium	Coarse	As collected
Particle size, mm	< 0.2	0.2-0.6	0.6-2	<50
Bulk density, 10^3 kg m^{-3}	1.26	1.25	1.23	1.33
Porosity, %	49.62	49.98	50.45	46.60
Loss on ignition, %	1.58	1.84	1.83	1.11
Hydraulic conductivity, m s^{-1}	1.69E-8	1.04E-7	5.9E-7	3.75E-7

Table SM-2

Selected petroleum hydrocarbon fractions and the initial mass used for the simulation

Name	Initial Mass mg	Name	Initial Mass mg	Name	Initial Mass mg
EC_{6-8}	0.3892	Ace	0.0351	Chr	0.1365
EC_{8-10}	1.2404	Flu	0.0741	BbF	0.0195
EC_{10-12}	16.1	Phen	0.92625	BkF	0.0195
EC_{12-16}	1540	Ant	0.02925	BaP	0.0078
EC_{16-35}	555.1	Flt	0.3705	IND	0.0195
Naph	0.04875	Pyr	0.04875	DaA	0.00195
Acp	0.039	BaA	0.0195	BgP	0.0078

Table SM-3

Physicochemical properties of the petroleum hydrocarbon fractions [1]

Group	Equivalent Carbon (ECn)	Molecular Weight	Water solubility, $mg \cdot L^{-1}$	Log k_{oc}	Log k_{ow}
EC_{6-8}	7	100	5.40	3.60	4.10
EC_{8-10}	8.8	130	0.43	4.50	5.20
EC_{10-12}	11	160	3.40E-2	5.40	6.30
EC_{12-16}	15	200	7.60E-4	6.70	7.90
EC_{16-35}	20	240	2.50E-6	8.80	10.40

Table SM-4

Physicochemical properties of US EPA listed PAHs [1]

Name	Ring numbers	Molecular Weight	Water solubility, $mg \cdot L^{-1}$	Log k_{oc}	Log k_{ow}
Naph	2	128	30	3.26	3.30
Acp	3	152	3.93	3.79	3.94
Ace	3	154	1.93	3.79	3.94
Flu	3	166	1.68	4.05	4.18
Phen	3	178	1.2	4.32	4.46
Ant	3	178	0.076	4.31	4.45
Flt	4	202	0.2	4.8	4.93
Pyr	4	202	0.077	4.84	4.88
BaA	4	228	0.01	5.36	5.76
Chr	4	228	0.0028	5.81	5.37
BbF	5	252	0.0012	5.91	5.78
BkF	5	252	0.00076	5.90	6.11
BaP	5	252	0.0023	5.90	6.13
IND	6	276	0.062	6.43	6.7
DaA	6	278	0.0005	6.42	6.54
BgP	6	276	0.00026	6.43	6.5

Table SM-5

Lower, Upper and median input values for the sensitivity analysis

Parameter	Lower bound	Median	Upper bound
Partition coefficient [pc]	0	0.01	0.05
Water solubility [ws]	0.1	1	10
Initial mass [IM]	0.5	1	2
Flux rate, $L\ day^{-1}$	0.2	1.2	2.2
porosity	0.287	0.46	0.639

Table SM-6

Compare the maximum concentration of alkanes and PAHs in the leachate

	Organic carbon : 0% , mg L^{-1}	Organic carbon : 1%, mg L^{-1}	Concentration Ratio
EC_{6-8}	2.8E-01	2.0E-03	1.4E+02
EC_{8-10}	4.2E-03	7.7E-04	5.5E+00
EC_{10-12}	3.4E-02	2.3E-08	1.5E+06
EC_{12-16}	7.6E-04	2.4E-24	3.2E+20
EC_{16-35}	2.5E-06	0	∞
Naph	3.5E-02	9.9E-04	3.5E+01
Acp	2.8E-02	1.6E-04	1.8E+02
Ace	2.5E-02	1.8E-04	1.4E+02
Flu	5.5E-02	4.9E-06	1.1E+04
Phen	6.1E-01	1.6E-03	3.8E+02
Ant	3.1E-02	4.6E-05	6.7E+02
Flt	1.8E-01	2.2E-04	8.2E+02
Pyr	3.6E-02	3.1E-05	1.2E+03
BaA	9.1E-03	1.0E-04	9.1E+01
Chr	2.8E-03	7.3E-09	3.8E+05
BbF	1.2E-03	1.6E-07	7.5E+03
BkF	7.6E-04	2.5E-14	3.0E+10
BaP	2.3E-03	3.2E-14	7.2E+10
IND	1.6E-02	2.2E-19	7.3E+16
DaA	5.0E-04	1.3E-23	3.9E+19
BgP	2.6E-04	4.5E-22	5.8E+17

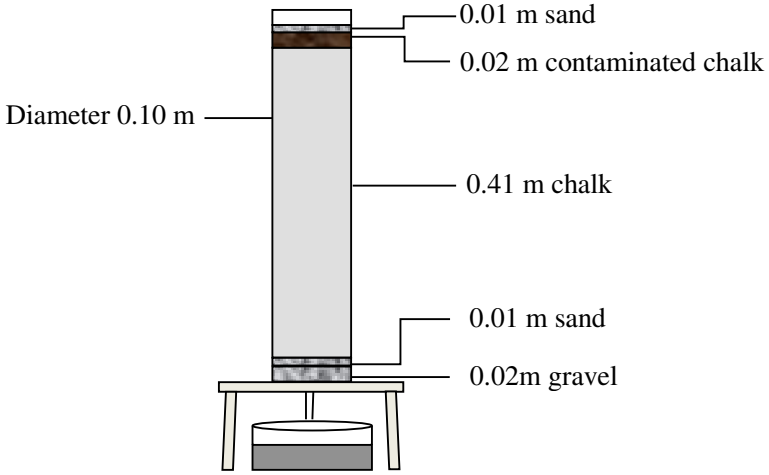

Fig. SM-1 Schematic of the diesel transport column in chalk

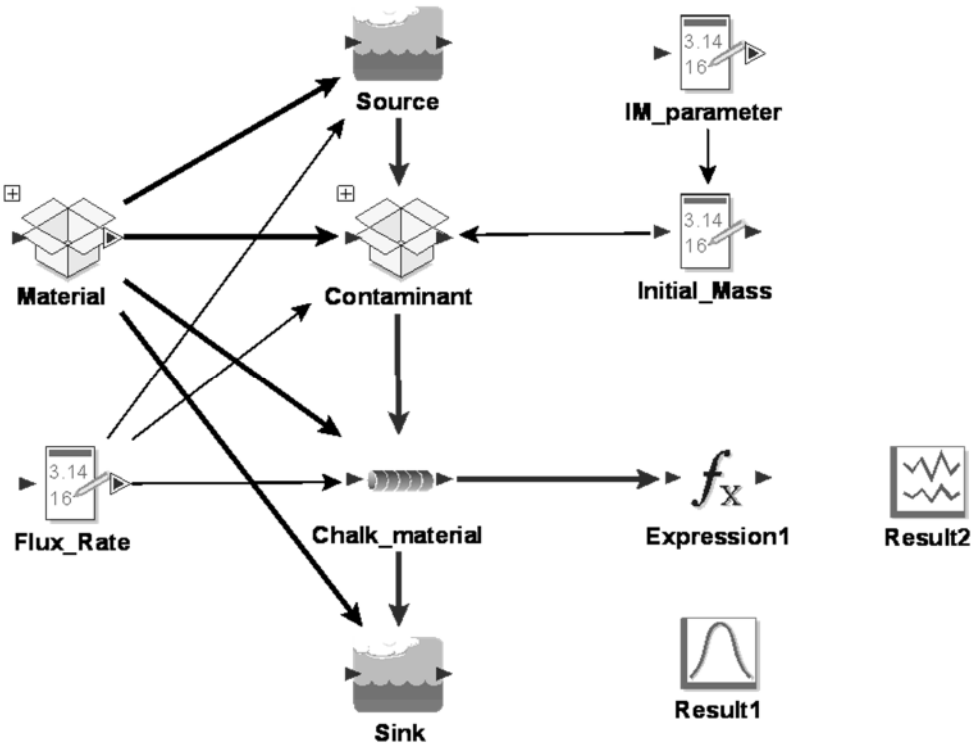

Fig. SM-2 Schematic of simulation of diesel transport in chalk

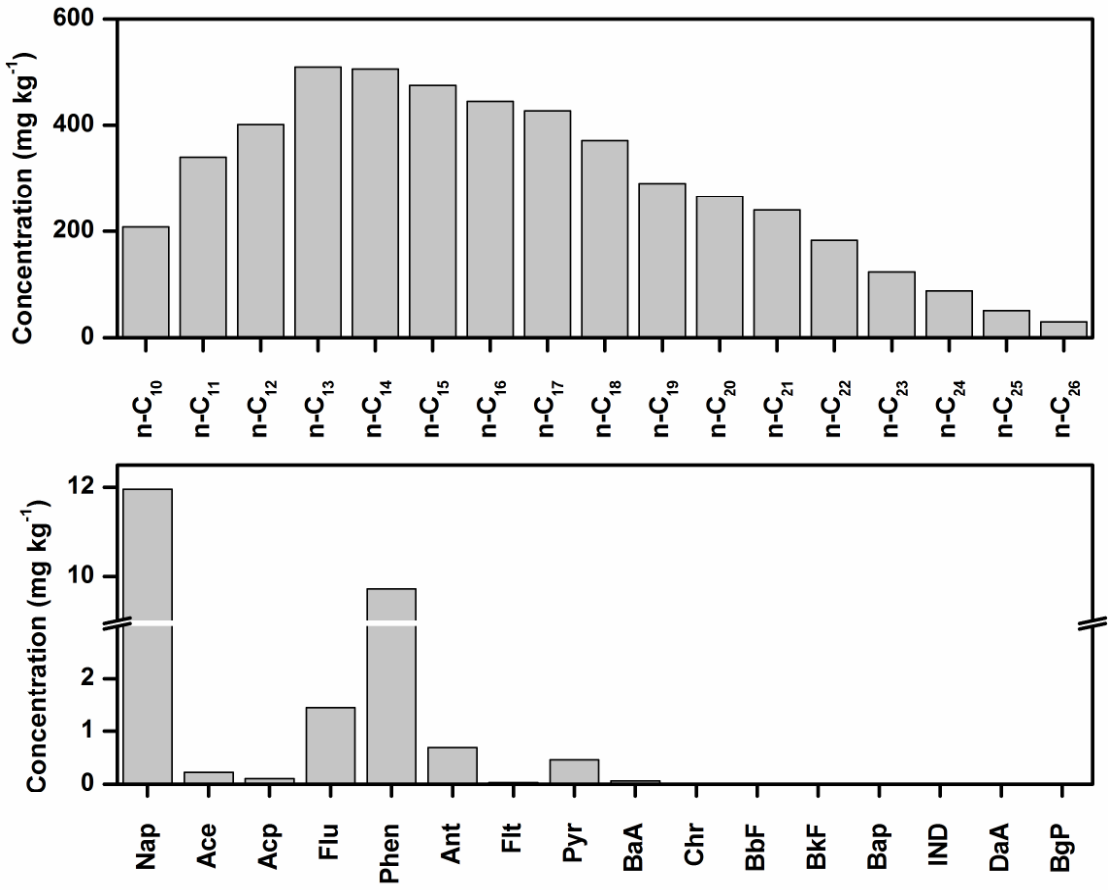

Fig. SM-3 Concentrations of alkanes and PAHs in diesel spiked chalk

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