ANALYTICAL MODELLING OF ATTENUATION OF VOLATILE PETROLEUM HYDROCARBONS IN THE VADOSE ZONE

Elazhari Ali, Abdulmagid*, Russell Davenport** and David Werner***

Abstract: We applied the measured kapp and Kd parameter values in an analytical model to estimate the extent of the volatile petroleum hydrocarbons from a known source zone, and to compare the model analyses results based on batches experimental data with results based on parameters determined in a field lysimeter experiment. The analytical results of how far a constituent can migrate from a 50cm source zone before its attenuation, based on the field lysimeter date, the distance (r 95%) ranged from 75cm to 350 cm away from the source zone. 75 to 100cm distance from the source zone illustrates the 95% attenuation of toluene and n-octane respectively. While the attenuation distance of cyclohexane and methylcyclopentane was 200 and 250cm respectively, n-pentane, n-hexane and iso-octane have 95% attenuation distance of 350, 200 and 225cm respectively. These data suggest that the significant differences in the attenuation distance from the source zone between the laboratory data and the field data was related to the difference in the apparent biodegradation rates, which were faster for the soil investigated in the laboratory in this study. The data presented illustrate the phenomenon of biodegradation and sorption of VPHs in the unsaturated zone and the analytical model analyses data results demonstrate the VPHs extent of migration form source zone under different scenarios (source zone radius, biodegradation rate and sorption distribution coefficients). All data show that biodegradation by indigenous microorganisms is the key parameter controlling the fate and transport of contaminants in the subsurface.

Keywords: Biodegradation; petroleum volatile hydrocarbons; analytical model.

INTRODUCTION

An important topic in groundwater and soil quality management is natural attenuation. It has been reported that the efficiency of natural attenuation is impacted by three key processes, diffusion, sorption and biodegradation (Karapanagioti *et al*, 2001).

Material and Methods

This study simulated the migration and the fate of 12 VOCs vapours mixture in the unsaturated zone. In order to examine the efficiency of the indigenous microorganisms in degrading VOCs, the apparent biodegradation rates and the sorption coefficients were determined. The experiment was performed by setting-up two laboratory batch microcosm experiments. The first set contains live sand, and abiotic controls were prepared by autoclaving the sand for the second set. Then, 1ml of the headspace gas of a vial containing the fuel mixture at 25^{o}C was injected into the batches and VPHs concentrations were monitored for up to 7 days.

In order to establish a comprehensive understanding of the soil and groundwater risks for VPHs, it is useful to assess the degradation rate by including it in an analytical model that can calculate the attenuation of the vapour concentration C_a with radial distance r, from the source zone. For this purpose Equation (1) from (Hohener *et al*, 2006) is applied.

For a constant spherical source with radius r_0 in a homogenous infinite porous medium, the

*Petroleum Training and Qualifying Institute, P.O Box 6184, Tripoli, Libya, a.elazhari@ptqi.edu.ly
,*School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK.

attenuation of the vapour concentration C_a with radial distance r is:

$$C_a(r,\infty) = \frac{C_{a0} r_0}{r} e^{-\sqrt{\frac{k_{app}}{D'}}(r-r_0)} \quad (1)$$

Where:

$Ca(r,\infty)$: The steady-state vapour concentration as a function of distance from the source

C_{a0}: The concentration near the source

r_0 [cm]: The radius of the source

r r [cm]: The distance from the source

K_{app} [s^{-1}]: the apparent biodegradation rate in the batch experiments

D': The sorption-affected gas-phase diffusion coefficient can be calculated as:

$$D' = f_a \tau_a D_a \quad (2)$$

Where:

τ_a denotes the tortuosity factor τ described by the model of (Millington and Quirk, 1961).

$$\tau_a = \frac{\theta_a^{2.33}}{n_{tot}^2} \quad (3)$$

D_a $\left[\frac{cm^2}{s}\right]$ the molecular diffusion coefficient in air can be calculated according to the method of Fuller as outlined in (Schwarzenbach *et al*, 1993).

f_a: the mass fraction of the compound in the soil air can be calculated according to the method of (Werner and Hohener, 2003):

$$f_a = \frac{1}{1 + \frac{\rho_s (1-\theta_t)}{K_s \theta_a} + \frac{\theta_w}{H\theta_a}} \quad (4)$$

Where, θ_a θ_w and θ_t denote the air-filled, the water filled, and total porosity respectively, and ρ_s denotes the density of the solids.

K_s $\left[\frac{mol\, cm^{-3}\,(air)}{mol\, g^{-1}\,(solid)}\right]$ denotes the air-solid partitioning coefficient, which can be defined as the ratio between the Henry's law constant and the solid-water partitioning coefficient K_d.

RESULTS AND DISCUSSION

Solid-water distribution coefficient determination

The measured K_d values ranged from 0.90 ± 0.6 for m-xylene to 377 ± 103 for n-octane. The K_d results demonstrate that the monoaromatics have the lowest measured K_d values because they are more soluble than alkanes. On the basis of the water solubility and volatility it is expected that each compound will be sorbed or partition into either soil solids, soil air and/or soil water (Christophersen *et al*, 2005; Karapanagioti *et al*, 2005).

The maximum vapour-phase concentration of the most VPHs was recorded just 4 hrs after incubation, and then most of the PP constituents' mixture decreased continuously until day 3. The differences between sterile and live soil demonstrates that the vapour concentration of these compounds decreased because of biodegradation.

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Apparent biodegradation rate determination k_{app}

The measurement of biodegradation rates by indigenous microorganisms is the first step in microbiological characterization. These measurements can be complicated by low microbial population or by the absence of species capable of degrading contaminants. In addition, optimum conditions of temperature, oxygen nutrients supply, and contaminant availability due to low solubility or strong sorption can limit degradation rates, especially in early tests where these limiting factors are not well defined (Providenti *et al*, 1993).

The main objective of microbial degradation tests is to determine whether the indigenous microorganisms are capable of bioremediation when condition are optimized.

A variety of mathematical expressions have been suggested to describe the kinetics of biodegradation reactions. These models have been increasing in complexity as they attempt to accommodate the numerous variables that can affect the biodegradation rate in the natural

environment. However, the main limitation of some of the VOC transport models is that they have not included biodegradation at all. Additionally, other transport models limitations have been using simplified representations such as first-order reaction kinetics, or Michaelis-Menten kinetics. First-order reactions, which assume a constant biomass, are normally observed in short incubation studies conducted at low chemical concentrations.

The data measured in the live microcosms were significantly different to those in abiotic soil within the first 5 days. The compounds showed a faster decrease in live microcosms compared to abiotic microcosms.

Profiles of vapour-phase concentrations of the VOCs in live soil are shown in Fig. 2. It can be seen that the vapour-phase concentration of these compounds decreased sharply within 50 hours. The maximum vapour-phase concentration of the most VOCs was recorded just 4 hrs after incubation, and then most of the PP constituents' mixture decreased continuously until day 3. The differences between sterile and live soil demonstrates that the vapour concentration of these compounds decreased because of biodegradation. The measured vapour-phase concentration in Figure 2 was used to

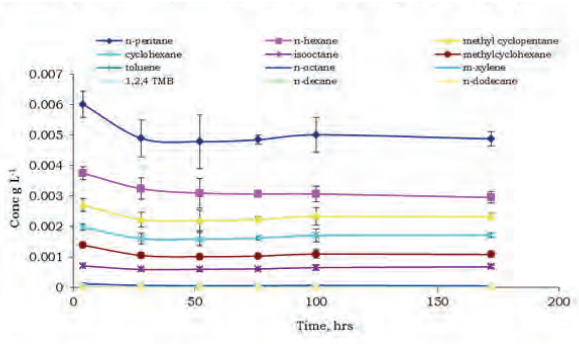


Fig.1. Comparison of fuel vapour-phase concentration in the autoclaved sand batches, as a function of time. Error bars: ±1 standard deviation (SD, n=3).

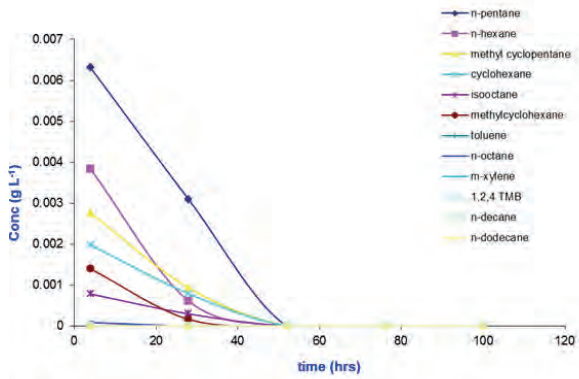


Fig. 2. Vapour-phase concentration of VPHs in live sand batches.

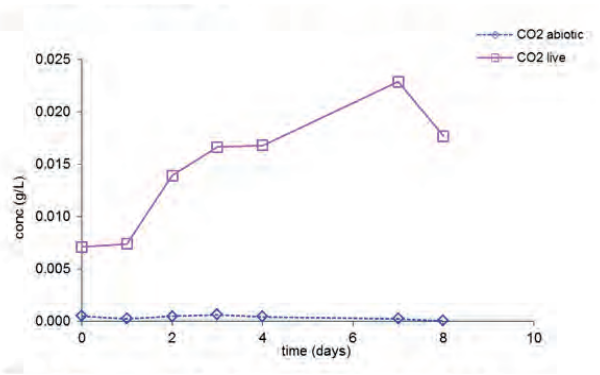


Fig. 3. Concentration profiles of CO2 in the live and autoclaved sand.

estimate the half-life rate for each constituent. From the measured half-life, the first order apparent biodegradation rate was estimated.

This approach assumes first order decay and it does not allow for an initiation or lag period during which the microbial community becomes activated or acclimated. First-order kinetics has been found to be a good approximation for most of the VPHs studied in both batch and column experiments. For all highly-volatile VPHs, the concentration decreased in the live sand was significantly different to that in abiotic sand within the first 7 days, indicating rapid biodegradation has occurred. For less-volatile VPHs constituents, the concentration decreased even faster than the highly VPHs in the live sand, in particular the aromatics (this decrease was significantly different in comparison with that in abiotic sand within the first 3 days).

For the was significantly different in comparison with that in abiotic sand highly VOCs the apparent half-lives are in the order of 0.5-1.2 days, which translates into an apparent first-order biodegradation rate kapp of 1.2 to 0.6 per day, and for the aromatic VOCs the concentration decreases and biodegradation rates are even faster. This is comparable to the biodegradation rates determined by (Providenti *et al*, 1993; Pasteris *et al*, 2002) for sand in a lysimeter.

Oxygen and Carbon dioxide

Profiles of the concentrations of CO_2 in the batches for both live and abiotic sands are shown in Fig. 3. CO_2 plots in the abiotic control were relatively stable through the incubation period and the concentration remained within 82 ± 26 % from its initial concentration. For the live sand batches a CO_2 production increase was clearly seen in the headspace (Fig. 3). From the plots it can be seen that CO_2 production started immediately after vapour

injection without any significant lag phase period. On day 0 the CO_2 concentration in the live sand increased significantly from 0.0070g/L, to reach a concentration of 0.017g/L on day 7. The increasing of CO_2 in the live sand batches which were observed after the vapour injection illustrates metabolic activity of soil microorganisms and demonstrates the active biodegradation process. Both, VOCs biodegradation and background soil respiration contribute to the observed increase in CO_2.

Analytical model results using experimental data

Results of the analytical model based on measured first order apparent biodegradation rates and solid-water distribution coefficients are shown in (Fig. 2). The results show the concentration attenuation of VPHs as they diffuse away from the source zone. Fig. 4, illustrates the rapid attenuation of the concentration of the VPHs as a result of biodegradation, and eventually the pollutant levels reach near zero concentration within a very short distance. The no biodegradation data in the plot confirms that the VPHs concentrations also decrease with distance solely as a result of the dilution process.

Fig. 5 illustrates the distance $(r_{95\%})$, ranged from 75cm to 350cm away from the source. 75-100cm distance from the source zone illustrates the 95% attenuation of toluene and n-octane respectively. While the attenuation distance of cyclohexane and methylcyclopentane was 200 and 250cm respectively, n-pentane and n-hexane and iso-octane have 95% attenuation distances of 350, 200 and 225cm respectively. These data suggest that the significant differences in the attenuation distance from the source zone between the laboratory data and field data was related to the difference in the apparent biodegradation rates, which were faster for the soil investigated in the laboratory in this study.

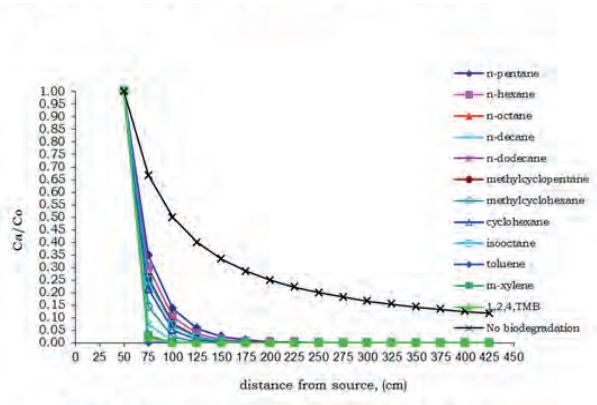


Fig. 4. Attenuation of VPHs released from a 50cm source zone.

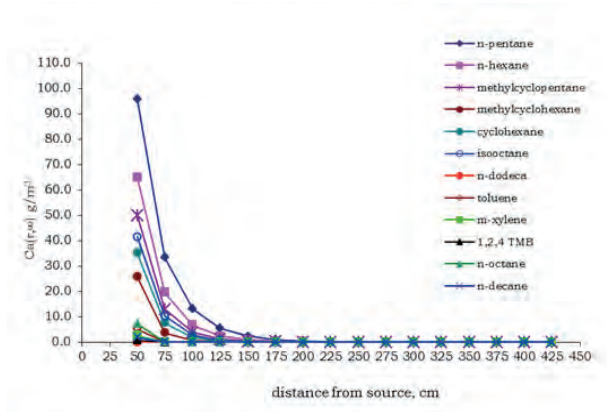


Fig. 5. Attenuation distance of VPHs from the source zone.

Analytical model results comparison between experimental batches and field lysimeter data

To validate and fine-tune numerical models for comparison reason, comprehensive data sets are required from a field experiment. Here, the data from a lysimeter test performed to quantify biodegradation of VOCs of an artificial fuel mixture are used for a comprehensive understanding of the attenuation distance from a source zone in a real field scenario. Data from the lysimeter experiment include apparent biodegradation rates and solid-water distribution coefficient (Pasteris *et al*, 2002). Data have been applied to the analytical model in order to compare the batches results and the field data model results.

The analytical results of how far a constituent can migrate from a 50cm source zone before its attenuation, based on the field lysimeter data are shown in (Fig. 7). Fig. 8 illustrates the distance (r_ (95%)), ranged from 75cm to 350 cm away from the source. 75-100 cm distance from the source zone illustrates the 95% attenuation of toluene and n-octane respectively. While the attenuation distance of cyclohexane and methylcyclopentane was 200 and 250cm respectively, n-pentane and n-hexane and iso-octane have 95% attenuation distances of 350, 200 and 225cm respectively. These data suggest that the significant differences in the attenuation distance from the source zone between the laboratory data and field data was related to the difference in the apparent biodegradation rates, which were faster for the soil investigated in the laboratory in this study.

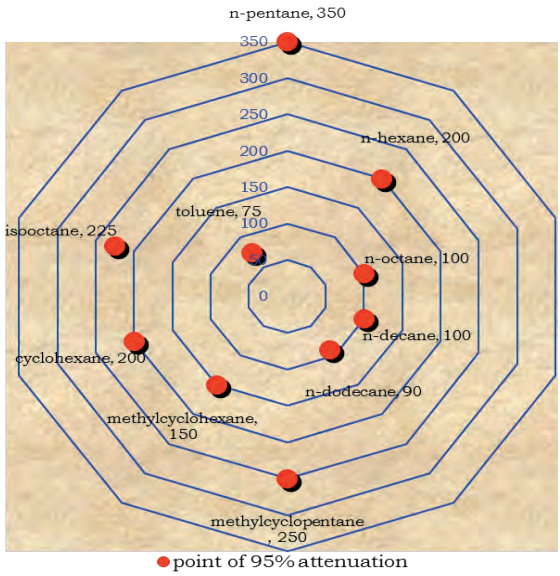


Fig. 6. VPHs attenuation from a 50 (cm) source zone (Lysimeter data).

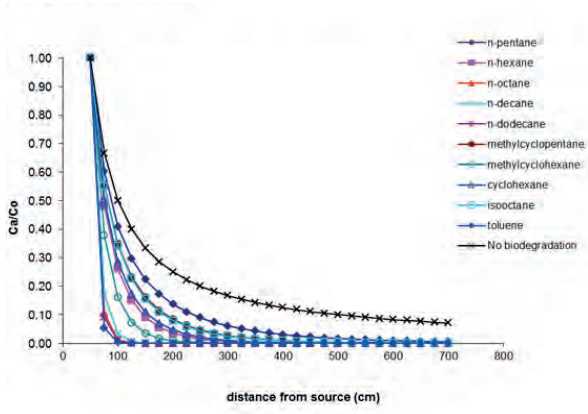


Fig. 7. Attenuation distance of VPHs released from a 50cm source zone.

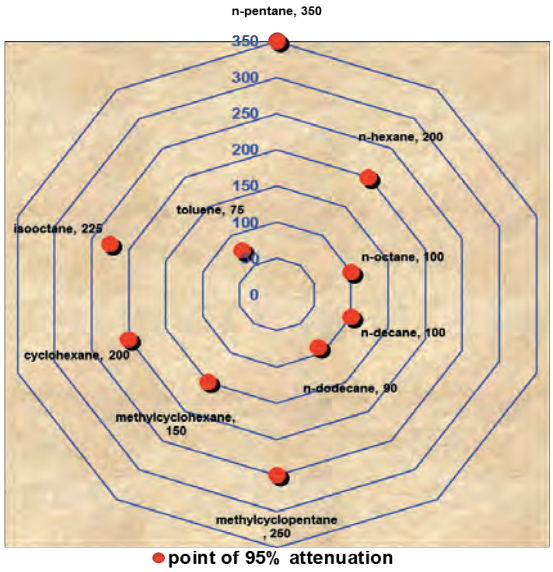


Fig. 8. VPHs attenuation from a 50 (cm) source zone (Lysimeter data).

Analytical risk assessment of VPHs source in the subsurface

Based on the lysimeter data for the 50cm source zone (Fig. 4) one could assume as a scenario that a groundwater table is just 100cm in the vertical direction (r_1) and a residential or industrial property basement just 200cm (r_2) away from the source zone. In this case (r_1) is shorter than (r_2). As a result the receptor at (r_1), which is the groundwater table, will be significantly affected, because it is within the reach of most VPHs, except toluene which has been attenuated at 80 cm. The contaminants when they reach the groundwater table are reduced to less harmful concentrations of approximately 5% of their initial concentration. Similarily, n-octane, n-decane, n-dodecane, methylcyclopentane, toluene and 1, 2, 4 TMB will not reach the (r_2) receptors.

CONCLUSIONS

In summary the data presented in this part illustrate the phenomenon of biodegradation and sorption of VPHs in the unsaturated zone and the analytical model analyses data results demonstrate the VOCs extent of migration from source zone under different scenarios (source zone radius, biodegradation rate and sorption distribution coefficients). All data show that biodegradation by indigenous microorganisms is the key parameter controlling the fate and transport of contaminants in the subsurface, and in the absence of effective biodegradation another parameter may become most important in particular sorption and partitioning (Schwarzenbach and Westall, 1981).

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