

## Modelling Attenuation of Volatile Petroleum Hydrocarbons in the Unsaturated Zone

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### Abstract

We applied the measured  $K_{app}$  and  $K_d$  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 50 cm source zone before its attenuation, based on the field lysimeter data, the distance ( $r_{95\%}$ ) ranged from 75 cm to 350 cm away from the source zone. 75 to 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 250 cm respectively, n-pentane, n-hexane and iso-octane have 95% attenuation distance of 350, 200 and 225 cm 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 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.

*Keywords:* Volatile hydrocarbons; biodegradation; attenuation distance; lysimeter experiment.

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### 1. 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 [1].

### 2. 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, 1 ml of the headspace gas of a vial containing the fuel mixture at 25 °C was injected into the batches and VOC 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 includ-

ing 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 (2.1) from Hohener *et. al* [2] is applied.

For a constant spherical source with radius  $r_0$  in a homogenous infinite porous medium, the attenuation of the vapour concentration  $C_a$  with radial distance  $r$  is:

$$C_a(r, \infty) = \frac{(C_{a0}r_0)}{r} e^{-\sqrt{\frac{k_{app}}{D'}}(r-r_0)} \quad (2.1)$$

Where;  $C_a(r, \infty)$ : the steady-state vapour concentration as a function of distance from the source;  $C_{a0}$ : the concentration near the source [cm];  $r_0$ : the radius of the source [cm];  $r$ : the distance from the source [cm];  $K_{app}$ : the apparent biodegradation rate in the batch experiments [ $s^{-1}$ ]; and  $D'$ : the sorption-affected gas-phase diffusion coefficient can be calculated as:

$$D' = f_a \tau_a D_a \quad (2.2)$$

Where  $\tau_a$ : denotes the tortuosity factor  $\tau$  described by the model of [3]:

$$\tau_a = \frac{\theta_a^{2.33}}{n_{tot}^2} \quad (2.3)$$

$D_a$ : the molecular diffusion coefficient in air can be calculated according to the method of Fuller as outlined in [4], [ $cm^2/s$ ]; and  $f_a$ : the mass fraction of the compound in the soil air can be calculated according to the method of [5]:

$$f_a = \frac{1}{1 + \frac{\rho_s(1-\theta_t)}{K_s\theta_a} + \frac{\theta_w}{H\theta_a}} \quad (2.4)$$

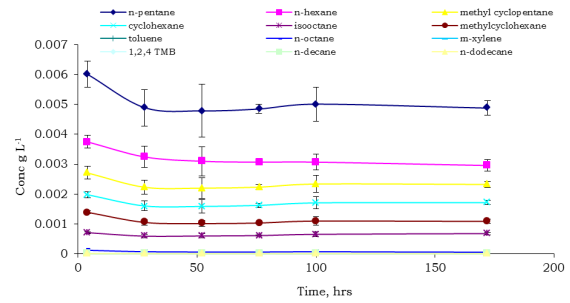
Where  $\theta_a$ ,  $\theta_w$  and  $\theta_t$ , and denote the air-filled, the water filled, and total porosity respectively, and  $\theta_s$  denotes the density of the solids; and  $K_s$  denotes the air-solid partitioning coefficient [ $\frac{mol\ cm^{-3}(air)}{mol\ g^{-1}(solid)}$ ], which can be defined as the ratio between the Henry's law constant and the solid-water partitioning coefficient  $K_d$ .

### 3. Results and Discussion

#### 3.1. Solid-water distribution coefficient determination

The measured  $K_d$  values ranged from  $0.90 \pm 0.6$  for m-xylene to  $377 \pm 103$  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 [6, 7].



**Figure 3.1:** Comparison of fuel vapour-phase concentration in the autoclaved sand batches, as a function of time. Error bars:  $\pm 1$  standard deviation (SD,  $n = 3$ ).

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.

#### 3.2. 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 Figure 3.2. The results show the concentration attenuation of VOCs as they diffuse away from the source zone. Figure 3.3, illustrates the rapid attenuation of the concentration of the VOCs 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 VOCs concentrations also decrease with distance solely as a result of the dilution process.

Figure 3.4 illustrates the distance  $r_{95\%}$ , ranged from 75 cm 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.

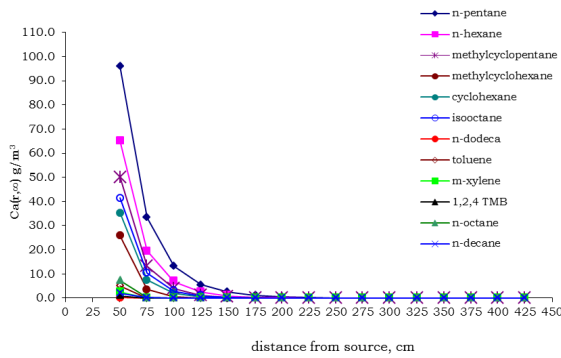


Figure 3.2: Attenuation of VOCs released from a 50 cm source zone.

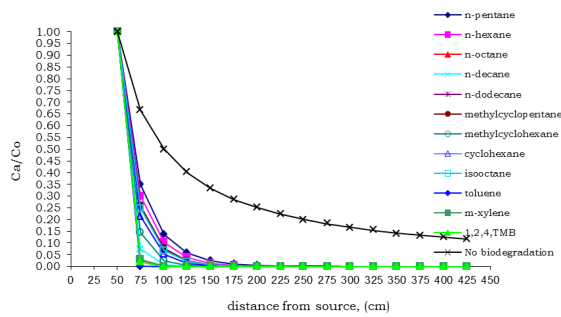


Figure 3.3: Attenuation distance of VOCs from the source zone.

While the attenuation distance of cyclohexane and methylcyclopentane was 200 and 250 cm respectively, n-pentane and n-hexane and iso-octane have 95% attenuation distances of 350, 200 and 225 cm 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.

### 3.3. Analytical risk assessment of VPHs source in the subsurface

Based on the lysimeter data for the 50 cm source zone, Figure 3.4 one could assume as a scenario that a groundwater table is just 100 cm in the vertical direction ( $r_1$ ) and a residential or industrial property basement just 200 cm ( $r_2$ ) 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

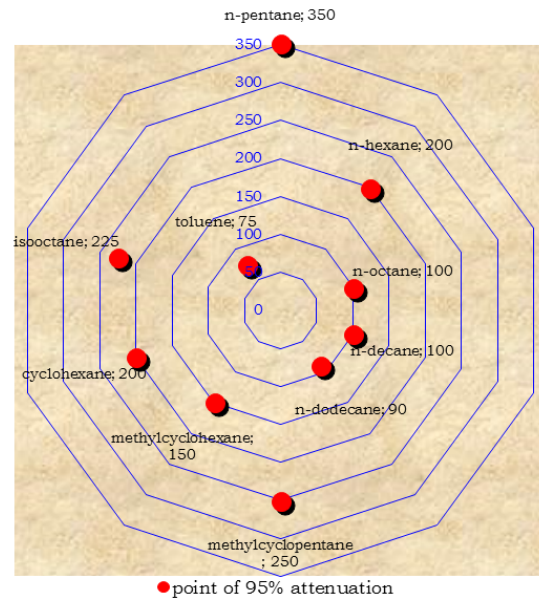


Figure 3.4: VPHs attenuation from a 50 (cm) source zone (Lysimeter data) [8].

groundwater table, will be significantly affected, because it is within the reach of most VOCs, 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. Similarly, n-octane, n-decane, n-dodecane, methylcyclopentane, toluene and 1,2,4 TMB will not reach the ( $r_2$ ) receptors.

## 4. Conclusion

In summary the data presented in this part illustrate the phenomenon of biodegradation and sorption of VOCs 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 [9].



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