

## Groundwater Pollution Risks For Ethanol-Blended Fuel.

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**ABSTRACT:** *The processes of diffusion, sorption and biodegradation greatly impacts on the efficiency of natural attenuation. Central to this, is information on microbial biodegradation kinetics in order to predict the natural attenuation of volatile organic compounds in unsaturated zone. This study aimed both at determining the first-order rate coefficients for aerobic biodegradation of 12 volatile petroleum hydrocarbons (VOCs) with ethanol and the sorption-affected diffusion coefficient of these compounds in unsaturated homogenous sand. Data obtained were fitted in an inverse analytical modelling approach assuming a diffusive gas transport at steady state to estimate the lateral attenuation of the VOCs. The modelling approach is a tool used for degradation rate assessment. Outcome of the results were than used to carry out a hypothetical risk assessment to predict the likely effect of the VOCs at a source zone in the subsurface. Batch experiments were performed at room temperature using Biotic (Live) and Abiotic (Autoclaved) soil by injecting synthetic ethanol – fuel mixture into the headspace of the batches. Generally, aerobic biodegradation of the all fuel compounds to CO<sub>2</sub> started after a lag phase of 5 hrs. Ethanol vapor remain below detection throughout the duration of the experiment. The study showed that isooctane vapours possess the most risk from a contaminated source zone in the subsurface.*

**KEYWORDS:** *Ethanol, biodegradation, headspace, VOCs, diffusion and sorption.*

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### I. INTRODUCTION

Environmental pollution and the health hazard associated with it, is increasingly becoming a major political and health issue globally today. Comingled stream of industrial development, population growth, rapid urbanization and other human activities all contribute to the modern pollution situation with far reaching consequences on the environment. Of the industries, the petroleum industry is a major contributor of organic pollutant to the environment, releasing hydrocarbon contaminants in a number of ways. Groundwater and soil contamination due to organic pollutant has resulted to public health concern about the toxic compounds transferred from the soil to groundwater aquifers used for drinking (Johnson et.al.,2000). These occur via leakage of underground storage tanks, pipelines, spills and seepages at production wells, distribution terminals and spills of gasoline from motorist, accidents or tanker trucks and frequent users at filling stations. The discontinued use of Methyl tert-butyl ether (MTBE) as a fuel additive because of its high strength of groundwater contamination by companies and ban in most countries (Squillace, et.al.,1999); bioadditives such as ethanol is increasing becoming popular as an alternative additive (Powers et.al., 2001)with several countries adopting legislation requiring certain content of bioadditive in fuels; the Federal Reformulated Fuels Acts of 2001, the Clean Air and Water Preservation Act of 2001, the Clean and Renewable Fuels Act of 2001 and the Ethanol Energy Promotion Act of 2001 (Williams et.al., 2003). Biofuels degrade easily in the environment (Powers, 2001; Alvarez and Craig. 2002) and has been found to cause little groundwater pollution risk after spill and also because they are carbon neutral. But there are concerns that the bioadditive components in blended fuels may inhibit the microbial degradation of the petroleum hydrocarbons, causing risk to groundwater pollution. These substances of concern are some volatile organic hydrocarbons (VOCs) found in petroleum derivatives as gasoline such as the BTEX group which is an acronym that stands for the monoaromatic hydrocarbons, Benzene, Toluene, Ethylbenzene and the three isomers of Xylenes (Alvarez and Craig. 2002). Also changes in fuel polarity with the addition of bioadditives will alter the properties of the Non-aqueous phase liquid (NAPL) which may increase risk of NAPL dissolution and migration in the subsurface (Hermann and Powers, 1998). The aim of this paper is to investigate the effect of ethanol a bioadditive, on the fate and transport of blended fuels, looking at microbial degradation and fuel leaching risk. The objectives of the study includes; To form a defined unsaturated zone in a batch microcosm container (mesocosm) to obtain a homogeneous source zone with residual NAPL saturation using a mixture of 12 fuel components with ethanol; To monitor and quantify the vapour phase transport (volatilization rate) of the fuel compounds to the atmosphere and to groundwater using tracer; To monitor Aerobic Biodegradation rates using first –order kinetics in the unsaturated zone for the individual fuel components; To determine the sorption-affected diffusion coefficient of these compounds in unsaturated homogenous sand.

### 1.1 Materials and Methods

**Synthetic gasoline:** An artificial gasoline with ethanol (8%) and 12 typical major constituents of gasoline (Johnson et al., 2000, Cline et al., 1991) was mixed from products of purities > 99% (Table 1). Their weight percentages were chosen according to typical fuel composition (Pasteris et al 2002; Dakhel et al., 2003). The batch experiments were performed with vapors concentrations coming from the mixture of the composition as given in (Table 1). Sulphur hexafluoride (SF<sub>6</sub>) was chosen as non-volatile gas-phase tracer which is recalcitrant under aerobic condition and is non-absorbable to soil.

**Table 1. 8% Ethanol - Fuel Mixture, tracer and calculated initial vapour phase concentration.**

Compound	formula	weight in mixture, %	Moles	Moles fraction	initial vapor concn. (25 °C)	Total mass injected (g)
Fuel Compounds		92%	mol		g / cm <sup>3</sup>	(g)
n-pentane	C <sub>5</sub> H <sub>12</sub>	2.94	0.04	0.05	9.51 E -05	9.51 E-05
n-hexane	C <sub>6</sub> H <sub>14</sub>	6.81	0.01	0.09	6.40 E -05	6.40 E-05
n-octane	C <sub>8</sub> H <sub>18</sub>	7.73	0.07	0.08	7.11 E -06	7.11 E-06
n-decane	C <sub>10</sub> H <sub>22</sub>	16.5	0.12	0.14	1.91 E -06	1.90 E-06
n-dodecane	C <sub>12</sub> H <sub>26</sub>	8.74	0.05	0.06	1.3 E -07	1.26 E-07
methylcyclopentane	C <sub>6</sub> H <sub>12</sub>	5.80	0.07	0.08	4.89 E-05	4.89 E-05
methylcyclohexane	C <sub>7</sub> H <sub>14</sub>	9.66	0.10	0.12	2.51 E -05	2.51 E-05
cyclohexane	C <sub>6</sub> H <sub>12</sub>	5.80	0.07	0.08	3.44 E -05	3.44 E-05
Isooctane (2,2,4-trimethylpentane)	C <sub>8</sub> H <sub>18</sub>	14.5	0.13	0.15	4.06 E -05	4.06 E-05
toluene	C <sub>7</sub> H <sub>8</sub>	2.94	0.03	0.04	5.11 E -06	5.11 E-06
m-xylene	C <sub>8</sub> H <sub>10</sub>	4.88	0.05	0.05	2.56 E -06	2.56 E-06
1,2,4-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	5.80	0.05	0.06	8.4 E -07	8.38E-07
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	8 %	0.17	1	1.45 E -04	0.000145
Tracer						Total Volume injected (uL)
Sulphur Hexafluoride	SF <sub>6</sub>					170

**Sand:** Moist sand with an indigenous microorganism population was used in setting up the homogeneous unsaturated zone for the batches in this study. The sand obtained was used as an infill by construction site workers. No further microbial organism was added before or during the experiment.

#### Laboratory batch microcosm experiments (Biotic and Abiotic Soils)

Batch microcosm experiments were carried out with the fuel mixture using a normal soil (Biotic) and an Autoclaved soil (Abiotic). Bottles of 40ml volume (H × Ø = 10cm × 1.2 cm) closed with a Teflon Mininert valves were used. The sand was filled into the bottle with a spoon and packed leaving a headspace of 8.3cm. In all the soil types before adding the ethanol fuel mixtures (EtOHVOCs) the microcosms were stored at 25 °C for 24 hrs and the oxygen concentration was measured. Thereafter, 1mL of the EtOHVOCs-saturated headspace of a bottle containing the synthetic fuel mixture at 25 °C were injected by using a Teflon plunger fitted into a gas-tight syringe. The injection was directed at the center of the bottle in the sand. Hohener, et al., (2003) stated that homogenization of vapour concentrations in a microcosm is through the process of diffusion and because diffusion is fast over short distances, homogenous distribution was expected within few minutes of EtOHVOCs vapor additions. Hence, it is assumed there is an instantaneous equilibration of the EtOHVOCs between the soil, air and water (Hohener, et al., 2003). The abiotic soil was prepared by autoclaving the soil three times at 120°C for 20 minutes at an interval of 24 hrs. The processes carried out for each batch soil is described below.

#### Normal soil (Biotic microcosm)

The glass viral bottle container (40 ml) with mininert valve, was packed tightly with uncontaminated soil up to 7cm. Resulted soil volumetric water content (θ<sub>w</sub>) was 0.17 and a total porosity of 0.29. The weight of the glass bottle before and after filling was noted to determine the soil weight. Subsequent to contamination, headspace sample (40uL) was drawn from the batch for analysis of both CO<sub>2</sub> and O<sub>2</sub> concentration. This was followed by removing 1mm Headspace volume from the batch before injection of 1 mL of the synthetic ethanol-gasoline mixture (EtOHVOCs) and 170 uL of the tracer gas (SF<sub>6</sub>). The first and second headspace measurement

was taken after 2 and 5 hours, hereafter measured daily for a period of 126 hours (Figure 1), to monitor the first-order biodegradation rates of each individual fuel components using gas chromatography flame ionization detector (GC-FID) and CO<sub>2</sub>, O<sub>2</sub> and SF<sub>6</sub> concentration profiles using gas chromatography–mass spectrometry (GC-MS).

**Autoclaved Soil (Abiotic microcosm)** Also used was the glass viral bottle (40 ml) with mininert valve packed tightly with uncontaminated soil up to 7cm before autoclaving. Resulted volumetric water content  $\theta_w$  was 0.16 and a total porosity of 0.33. The same process applied to the normal soil was employed to determine the soil weight and the injection of both the synthetic ethanol gasoline mixture (EtOHVOCs) and tracer gas into the batch.

The first headspace measurement was taken 5 hours, hereafter measured daily for a period of 221 hours (Figure 2), to monitor the concentration stability and estimate the partition or distribution coefficient ( $K_d$ ) of each individual fuel components using GC-FID and CO<sub>2</sub>, O<sub>2</sub> and SF<sub>6</sub> concentration profiles using GC-MS.

## 1.2 Analytical methods: Soil Gas Sampling and Analysis

Soil gas from the batch experiments (normal and autoclaved soil) were analysed for vapor concentrations of the synthetic gasoline compounds and ethanol by GC-FID, as explained by Pasteris et al., (2002) and for CO<sub>2</sub>, O<sub>2</sub> and SF<sub>6</sub>, using the hyphenated GC-MS technique a method outlined by Grobs(1985). Partial pressures of CO<sub>2</sub> and O<sub>2</sub> in laboratory experiments have been previously analysed by gas chromatography (Hohener et al.,2003). The soil gases were collected by a 100 uL syringe with locking device and a plunger to prevent sample losses. The gas concentration of the hydrocarbons (VOCs) and ethanol were analysed by injecting 40uL into a HP-7890 A Series Gas Chromatograph (Agilent Technologies, China) equipped with a HP-5 capillary column (30 m \* 0.25 mm) and FID. The injector used a split ratio of 10 and was heated to 200 °C. The column temperature was held at 30 °C for 5 minutes, increased to 120 °C at a rate of 10 °C min<sup>-1</sup> and then held constant for 6 min. Carrier gas was hydrogen at a flow rate of 2 mL min<sup>-1</sup>. GC-MS analysis of vapour concentration for CO<sub>2</sub>, O<sub>2</sub> and SF<sub>6</sub> was performed on a Fisons 8060 GC using a split injection linked to a Fisons Trio1000 MS (electron voltage 70Ev, filament current 4.2 A, source current 1000 uA, source temperature 250 °C, multiplier voltage 250 V and interface temperature 250 °C). The acquisition was controlled by a TVM 486 computer using mass-lab software. Identification of molecular masses of the individual compounds and their relative abundance according to their m/z (mass to charge ratio) from the soil gas was analysed by injecting between 20-100 uL into a Agilent HP-PLOT-Q capillary column (30m \* 0.32 mm) packed with 20um Q phase. The injector used a split mode of 100 mLs min<sup>-1</sup> at pressure of 65 kPa. The column temperature was held at 35 °C for 60 minutes. Carrier gas was helium at a flow rate of 1mL min<sup>-1</sup>.

### 1.2.1 Biodegradation kinetics

The basic assumptions underlying this work are that in the unsaturated zone microorganisms live in the aqueous phase, that VOC vapors needs to dissolve in the aqueous phase before biodegradation can occur (Hohener et al., 2003) and that biodegradation follows a first order-rate kinetics and is aerobic. Jin et al., (1994) pointed out that the first-order reactions assume a constant biomass and is normally observed in short incubation studies conducted at low concentrations.

An expression for first order biodegradation rate is given as; (Wiedemeier et.al.1999; Alvarez and Craig., 2002)

$$C = COe^{-kt} \text{Equation 1}$$

Where C = biodegraded concentration of the chemical [gcm<sup>-3</sup>], CO = initial concentration [gcm<sup>-3</sup>], k = rate of decrease of the chemical [T<sup>-1</sup>].

The relationship between k and t is expressed in terms of the half-life of the chemical;

$$t_{1/2} = \ln(2) = 0.693 / k \quad \text{Equation 2}$$

$t_{1/2}$  = half-life and k = [s<sup>-1</sup>] rate constant.

Partition of the VOC between the soil and aqueous phase as described by; (Yong and Mulligan., 2004)

$$\text{The distribution coefficient} = \frac{\text{Concentration in the soil}}{\text{Concentration in aqueous phase}} = \frac{C_s}{C_w} = [\text{cm}^{-3}/\text{g}] \quad \text{Equation 3}$$

Hohener et al., (2003) noted the difficulty with measurement of VOCs concentrations in soil water. Hence, it is assumed  $C_w$  is proportional to the concentration in soil air using the relationship; (Hohener et al., 2003)

$$H = \frac{C_{\text{air}}}{C_w} \quad \text{Equation 4}$$

H = is the dimensionless form of Henry's law constant (g cm<sup>-3</sup> air / g cm<sup>-3</sup> water).

## 1.3 Results and Discussion

**1.3.1 Vapour phase concentration of Fuel compounds and Tracer gas – Biotic and Abiotic Soils** Measured data from the gaseous concentrations of the fuel compounds for both biotic and abiotic microcosm are shown together in Figure 1. The compounds showed fast decrease in the biotic microcosm compared to the sterile (autoclaved). Both the tracer SF<sub>6</sub> and CO<sub>2</sub> and O<sub>2</sub> concentrations profiles are shown in Figure 2. The vapour concentrations of ten compounds in Figure 1 completely disappeared from the biotic microcosm before day 5.

Decane and 1, 2, 4-trimethylbenzene (TMB) were not detected in any of the measurement. In a previous laboratory microcosm experiment, Hohener et al., (2006), n-Dedocane was not detected in any of their measurements. Throughout the duration of the experiments the concentration of ethanol vapors remain below detection for both batches. Generally, vapor concentration started decreasing 5 hrs (lag-time) after EtOHVOCs injection following first- order rate, ranging between  $0.31 \text{ day}^{-1}$  for isooctane to  $1.11 \text{ day}^{-1}$  for toluene (Table 2). The lag-time reflects the acclimation phase when the VOCs concentration shows no decrease or is relatively constant compared to the sterile soil (Moreels et al., 2004).

In abiotic soil, vapor concentration of five of the more volatile components; n-Hexane, cyclohexane, methylcyclohexane, methylcyclopentane and isooctane all showed steady concentration profile against time and stayed within 70% of initial concentration during the 7-day period (Figure 1). Pentane, concentration versus time profile differed slightly from the rest but also remained within the initial concentration injected. The gaseous concentration of the least volatile components of m-xylene, n-dodecane, n-decane, 1, 2, 3 –TMB, and to a lesser extent, toluene, n-octane, all showed decrease in an erratic manner that is prone to scatter. These concentration trends can be attributed to condensation and sorption of these compounds (Hohener et al., 2003). Values for sorption distribution coefficient  $K_d$  are given in (Table 2). Total losses in the sterile soil within the 7 days ranged between 17 % for toluene and 70% for dedocane (Figure 1). The relative steady concentration profile of the  $\text{SF}_6$  in the abiotic batch give an indication that VOCs concentration measured was relatively steady and that the batch was tight while the output for the biotic soil was erratic with a decrease of about 32% from the initial concentration measured showing occasional leaks in the biotic batch using the  $\text{SF}_6$  data. Hohener et al., (2003) has identified leaks in stoppers using CFC tracer data.

**1.3.2 Discussion** Basically, in all the batch experiments vapor concentration was monitored and modelling of the soil physical properties was designed to be close as possible to that in real soils.

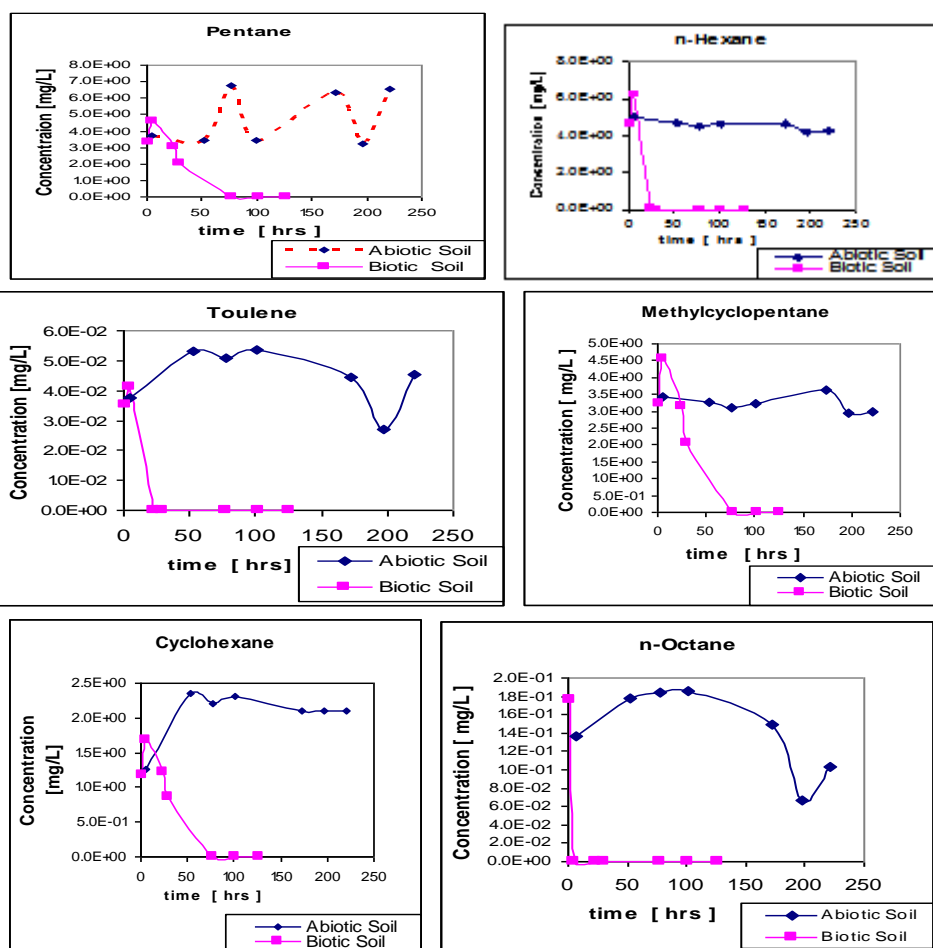
**Batch experiments: Biotic and Abiotic Soils** The complete VOCs removal in the viable microcosm but not in the sterile microcosm provided evidence of biodegradation. Biodegradation of the fuel compounds to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by the indigenous microorganism started after a lag phase of about 0.2 days with toluene and octane showing higher first –order rate at 1.11 and  $6.65 \text{ day}^{-1}$  for the 7 days duration (Table 2). The quantification of the first-order coefficients  $k$  depended on best fittings (Hohener., et al., 2006; Pasteris et al., 2002). Rapid degradation of toluene at low concentration has been reported by (Jin et al., 1994) and findings from a laboratory study using mixed a culture of bacteria from uncontaminated soil lag phases for degradation of toluene and xylenes were found to be between 0.02 and 1.55 days (Greene, et al., 2000). Pasteris et al., (2002) reported first-order biodegradation rates for a mixture of 13 fuel compounds in an unsaturated zone lysimeter experiment with the highest rate for toluene and the long chain alkanes, octane, decane and dodecane ranging from  $2.5 \text{ day}^{-1}$  to  $8.7 \text{ day}^{-1}$ . Decane and 1, 2, 4-TMB were completely degraded under 2 hours of the first measurement in this study. Slow rates of  $0.31 - 0.98 \text{ day}^{-1}$  were estimated for the short chain alkanes, cyclic alkanes with isooctane being the lowest. Rates between  $0.1 - 1.2 \text{ d}^{-1}$  have been reported for these compounds (Pasteris et al., 2002). Microbial activity is reported to be hindered by the short chains alkanes by their solvent effect (Atlas, 1981) while branched chains alkanes slow degradation results from steric problems imposed by the side chains (Watkinson and Morgan, 1990). Under favourable conditions, Ostendorf and Kampbell., (1991) and Lahvis et al., (1999) have all observed the rapid and complete biodegradation of some petroleum hydrocarbon in the unsaturated zone.

Prediction of microcosm biodegradation rate coefficient rely on knowledge of sorption and partitioning into the soil water since laboratory measurement entails short period during which slow sorption kinetics are observed (Hohener, et al., 2003). Contrast to the above, ethanol vapor were not detected for both batches and is said to be completely attenuated, a fact attributed to; ethanol partitioning into the soil water and subsequent biodegradation for the biotic microcosm (Dakhel et al., 2003), as reflected by it's extremely low henry's constant,  $H_k = 0.00024$  (Lahvis, 2003); insignificant sorption due to its low octanol- water partitioning constant (Hansch et al ., 1995), hence the low affinity for soil organic matter (Schwarzenbach et al ., 1993 )in both the biotic and abiotic microcosms. This suggests biodegradation as the sole ethanol removal mechanism (Pasteris et al., 2002). Ethanol does not sorb to sediments or soils and because of its polar and hydrophilic nature, ethanol extraction from water is extremely difficult (NEIWPC, 2001). The polarity of the ethanol compound as results of the alcohol functional group makes it act as a cosolvent in an aqueous phase; this reduces the extent of sorption as compared to the gasoline constituents (Powers et al., 2001). In a study on small volume releases of gasoline in the vadose zone, using MtBE and ethanol as an additive, Dakhel et al., (2003) observed that ninety-seven percent of ethanol partitioned into the aqueous phase in the unsaturated zone with 1 out of 2000 molecules present in the soil air phase from a buried residual gasoline source.

**Table 2: Results of Fuel compounds, tracer and calculated model parameters**

Compound	Formula	weight in mixture, %	Initial conc. <sup>a</sup> (g/cm <sup>3</sup> )	vapour k <sup>c</sup> (day <sup>-1</sup> )	K <sub>d</sub> <sup>d</sup> (cm <sup>3</sup> / g)
Fuel Compounds		<b>92%</b>			
n-pentane	C <sub>5</sub> H <sub>12</sub>	2.944	9.506 E -05	0.52	7.5
n-hexane	C <sub>6</sub> H <sub>14</sub>	6.808	6.398 E -05	0.98	1.3
n-octane	C <sub>8</sub> H <sub>18</sub>	7.728	7.114 E -06	6.65	91
n-decane	C <sub>10</sub> H <sub>22</sub>	16.468	1.905E-06	e	502
n-dedocane	C <sub>12</sub> H <sub>26</sub>	8.74	1.3 E -07	f	-
methylcyclopentane	C <sub>6</sub> H <sub>12</sub>	5.796	4.888 E-05	0.48	0.44
methylcyclohexane	C <sub>7</sub> H <sub>14</sub>	9.66	2.514 E-05	0.76	0.17
cyclohexane	C <sub>6</sub> H <sub>12</sub>	5.796	3.435 E -05	0.42	0.39
isooctane (2,2,4-trimethylpentane)	C <sub>8</sub> H <sub>18</sub>	14.536	4.063 E -05	0.31	2.1
toluene	C <sub>7</sub> H <sub>8</sub>	2.944	5.108 E-06	1.11	0.41
m-xylene	C <sub>8</sub> H <sub>10</sub>	4.876	2.561 E -06	1.19	0.33
1,2,4-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	5.796	8.4 E -07	e	0.24
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	<b>8 %</b>	1.453 E -04	b	b
<b>Tracer</b>					
Sulphur Hexafluoride	SF <sub>6</sub>	1% v/v			

<sup>a</sup> Calculated based on initial mole fraction and Raoult's law. <sup>b</sup> below detection. <sup>c</sup> Calculated according to first-order rates. <sup>d</sup> Calculated as K<sub>d</sub> = henry's law relationships. <sup>e</sup> Compound was not present. <sup>f</sup> No fitting was possible because steady state was not reached, and data did not match.



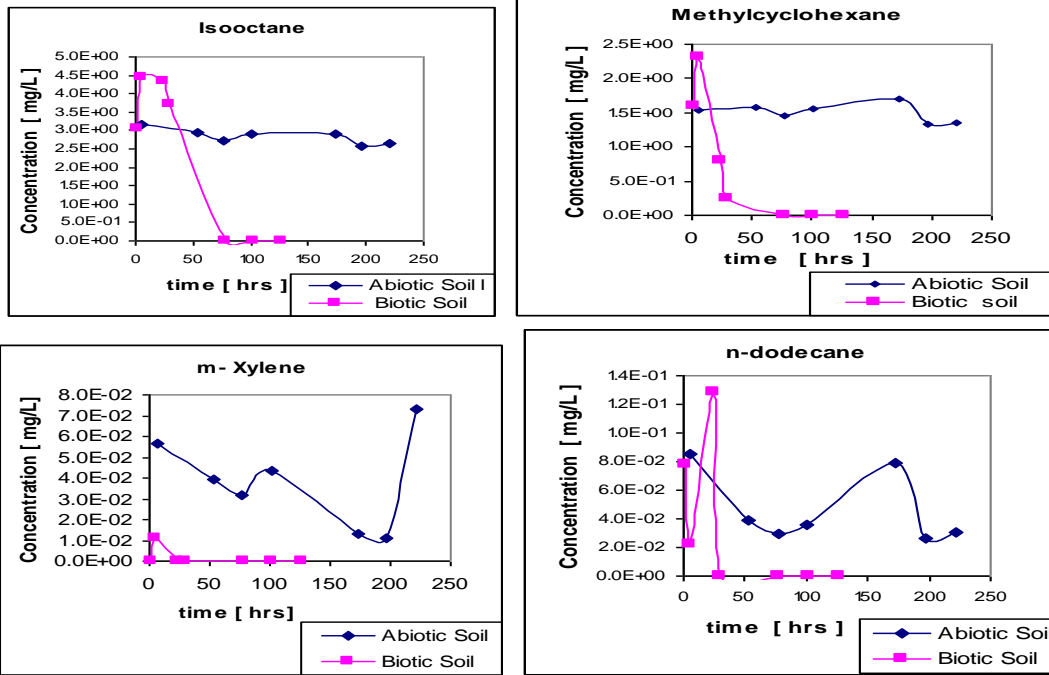
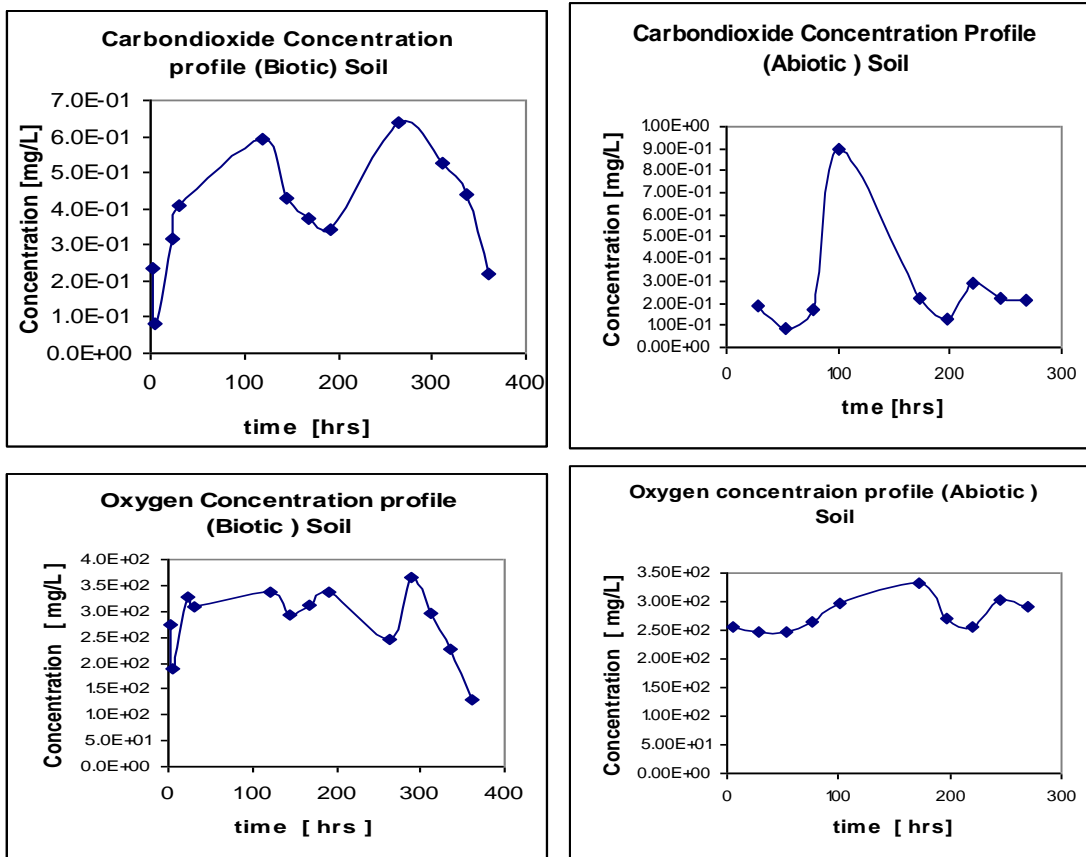
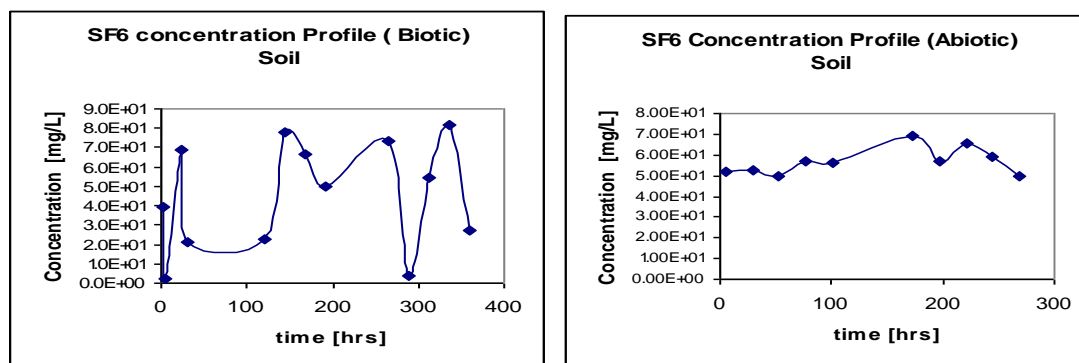


Figure 1: Result of microcosm experiments: Squares: Biotic soil; Diamonds: Abiotic soil.







**Figure 2:** CO<sub>2</sub>, O<sub>2</sub> and SF<sub>6</sub> concentration vs time profile for Batches (Biotic and Abiotic Soil)

One factor attributed to support the rapid degradation process of the VOC vapor is that the diffusion time into the liquid from the gas phase is not significantly limiting the process (Jin et al., 1994). This is consistent with finding of Schwarzenbach et al., (1993) using a two-film model, calculated diffusion times on the order of seconds to few minutes for gas molecules to move to the air-water interface, dissolve and move through the liquid films typically found in soils.

Results of the  $K_d$  (Table 2) shows high values for the more volatile compounds with high vapour pressure for example pentane (7.5), n-hexane (1.3) and isooctane (2.1). This implies they volatilize into the air phase where they spread fast and are carried away to farther distance from the source of the contaminant. Their preference for the gas phase is also reflected by their high Henry's constant, hence their reduction in an NAPL source is preferentially through volatilization before been attenuated. Iso-octane has been reported as a slowly degrading or recalcitrant VOC (Pasteris, et al., 2002).

The probability of sorption is directly related to the size of a molecule, with larger size molecule having greater tendency to be sorbed, (Testa and Winegardner., 2000). Nash, (1987) stated that Octanol-water partitioning coefficient ( $k_{ow}$ ) values can be used to estimate the tendency of an organic compound to become or remain adsorbed in soils. Organic compounds with low solubility  $S$  and high  $k_{ow}$  have the greatest tendency for attachment with soil or sediment matrix (Kenaga and Goring, 1980). From their high Henry constant and  $k_{ow}$  values,  $K_d$  obtained for the least volatile components, of n-decane and n-octane suggest these compounds are sorbed into the soil organic matter but are still able to be degraded easily by the microorganism. n-dodecane has been stated to partition into the soil organic matter (Pasteris et al., 2002), due to its hydrophobic nature (Hohener et al 2003). The high degradation rates of the toluene, xylene, 1,2,4 TMB all reflects their partitioning into the soil water (low Henry constant) and therefore bio-available for microbial degradation. The compounds of n-octane, n-decane, m-xylene, 1, 2, 4 TMB have all been reported as fast degrading compounds. (Hohener et al., 2006). Among the least volatile compound the aromatic groups can exhibit both the solid and water partitioning process (Pasteris, et al., 2002) an example is toluene (Hohener et al., 2006) which partitions into the soil water and organic matter (Pasteris et al., 2002). The scatter data for dodecane makes it impossible to obtain its degradation rates as fitting was not possible.

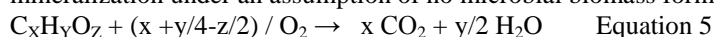
A look at the abiotic soil concentration profile (Figure 1), the erratic scatter trend of the compounds with low volatility (Hohener, et al., 2006) or high boiling temperatures (Hohener, et al., 2003); n-dodecane (216 °C), n-decane (174 °C), 1,2,4-TMB (169 °C) can be associated with analytical problems created by exhaustive sorption and or condensation of the vapors either in the batch bottles, with the syringes used for sampling or during the transfer from the microcosm batch to the GC system (Hohener, et al., 2006; 2003), factors also seen with xylene (139 °C), octane (125.3 °C) and toluene (110.6 °C). In two laboratory studies by Hohener et al., (2006) n-Dodecane could not be unambiguously assessed due to the above listed reasons. Ostendorf and co-workers (2000) performed microcosm experiment with Teflon mininert valves immersed in a water bath where they obtained data with less scatter for the high volatile constituent but could not avoid scatter for the less volatile VOCs.

The relative steady profile of the high volatile compounds in the abiotic microcosm shows no biodegradation taking place. Concentration variances can be attributed to two phases of disappearance that can be observed in a abiotic batch microcosm; rapid abiotic losses due to sorption and partitioning taking place, followed by slower sorption (Hohener, et al., 2003). The slower continuous sorption in the abiotic batches may be explained in terms of intraparticle diffusion-limited approach of equilibrium between the soil water and soil particles (Hohener, et al., 2003). Grathwohl and Reinhard., (1993) attributed the characteristics of the intraparticle diffusion to its dependency on the particle radius  $a$  with coarser materials obtaining faster sorption kinetics. In an abiotic batch experiment using sieved sand fraction, Hohener, et al., (2003) showed that rapid initial decline in VOC concentration occurred, followed by more pronounced abiotic losses with first-order

kinetics in fraction  $500 < a < 1000 \mu\text{m}$  while in sieved fraction  $150 < a < 200\mu\text{m}$  sorption dominated reaching equilibrium quickly. Result from a similar abiotic batch experiment with poisoned sand, Allen –king et al., (1994), the vapour of toluene was found to decrease rapidly initial, before slowly and finally remaining constant. These finding suggests that intraparticle diffusion is a likely mechanism for abiotic loss of VOC during short-term batch experiments (Hohener, et al., 2003).

Studying the influence of ethanol on BTX degradation, Corseuil et al., (1998) noted that in all the experimental cases carried out ethanol was preferentially utilized over all BTX compounds with a lag phase generally observed before substantially BTX degradation occurred. The preferential degradation of ethanol over the BTX is related to the degradable substrate nature of ethanol which is easily oxidized by constitutive enzymes through central metabolic pathways. (Corseuil et al., 1998).

**Oxygen and Carbon dioxide concentration profiles**The general stoichiometry equation of aerobic mineralization under an assumption of no microbial biomass formation is given as; (Grathwohl et.al., 2003)



From the theoretical stoichiometry of the compound using toluene to represent the weighted average of all the fuel compound, 0.45 mg of oxygen is needed for complete mineralisation 0.35 mg of the total carbon from fuel compounds injected into the live batch. Before, expose of the soil to the VOCs vapour the theoretical calculated amount of oxygen in biotic soil was 0.76 mg of  $O_2$ . On the basics of the stoichiometry of equation 5, for every mole of  $O_2$  consumed, 0.77 mole of  $CO_2$  is produced, this ratio correlates closely with stoichiometry of hydrocarbon degradation of 0.67 vol. % of  $CO_2$  formed per vol.%  $O_2$  consumed ( Pasteris et al., 2002 ) rather than that of soil organic matter, where a ratio of 1 vol. % of  $CO_2$  per vol.%  $O_2$  is expected (Wood et al., 1993). Comparing the amount needed to completely mineralise the hydrocarbons, it is reasonable to assume that aerobic biodegradation was prevalent in the batch. Wiedemeier et al., (1999) stated that another method to estimate the amount of oxygen needed by the aerobic bacteria to degrade the VOCs is to average the amount of oxygen consumed during the biodegradation of each compound separately. Salanitro, (1993) and Brown et al., (1995) stated all components of the BTEX degrade rapidly when the oxygen is present at concentration of 2 mg/L in water or 5% in the Vadose zone. The relatively steady concentration profile for both  $O_2$  and  $CO_2$  in the sterile soil gives an indication that no biodegradation is taking place (Figure 2). The trend of the curve might be due to some uncertainty in the sampling process.

**1.4 Conclusion**Microorganism can degrade hydrocarbons that are dissolved, sorbed or volatilized. In laboratory batch experiments conducted at low concentration, first –order rate laws are employed to estimate the biodegradation rate of the microorganisms. This proves true for all the VOCs except n-dedocane that were degraded. The partitioning of ethanol to the aqueous phase and its easy biodegradable nature suggest it is preferential degradation by the indigenous organisms. A process that can result to depletion of oxygen and other electron acceptors which could hinder the biodegradation of other VOCs constituents, this is not pronounced at the concentration used in this study. In the absence of pressure gradients, conditions prevalent in the batch experiments, gas –phase diffusion dominates migration of volatile pollutants in the unsaturated zone. At transient diffusion described by the sorption- affected diffusion coefficient, compounds with higher vapour pressure as isooctane, n-hexane, methylpentane showed higher mass fraction in soil gas, a phenomenon that accounts for their higher diffusion rate hence longer distance attained before attenuated. From the inverse analytical model employed, this study showed that toluene, octane and m-xylene will poses the less risk to groundwater and the atmosphere from a contaminated source in the subsurface. Abiotic losses associated with the least volatile constituents in the autoclaved batch can be attributed to sorption and condensation of the VOCs, these possess a great problem in correctly predicting their sorption coefficient. Generally, the rate coefficient was found within a range of certain uncertainty. Drawbacks includes gas leaks, sorption to glass and stoppers and possible sampling error and measurements.

This study confirms the recalcitrance nature of isooctane vapor; unlike toluene and m-xylene vapors it has the lowest biodegradation rate kinetics.

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