Diffusive-Gas Transport of Volatile Organic Carbons from a Source in an Unsaturated (Vadose) Zone

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Abstract: *In the absence of pressure gradients, conditions prevalent in the batch experiments, gas –phase diffusion dominates migration of volatile pollutants in the unsaturated zone. Gas –phase diffusion in the unsaturated zone is affected by partitioning into soil-water, onto air-water and into or onto solid. The process spreads only the contaminants in the gas phase where contaminants with low mass fraction fa in the soil gas diffuse more slowly depending on the soil and chemical properties on the diffusing substance. This study shows Non-aqueous phase liquids (NAPL) compounds with higher mass fraction (Isooctane (0.82), n-hexane (0.78), methylcyclopentane (0.54)) diffuse to a longer distance (1.75m, 1.30m, 1.50m) than those with low mass fraction (toluene (0.04), m-xylene (0.04), octane (0.09), (60m, 60m and 51 m respectively) from a source zone. The diffusion coefficient D' calculated was also higher for these compounds; 0.05, 0.05, 0.05 and 0.00, 0.00 and 0.001 respectively. 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 phenomena that accounts for their higher diffusion rate hence longer distance attained before attenuated. The results obtained shows isooctane travel the most distance (1.3 m) before been attenuated to 1 % of the original concentration of a source zone, a reason attributed to it recaltricant and slow degradation nature.*
Keywords: *Non-aqueous phase liquids, Diffusion, VOCs, Unsaturated zone, Mass fraction*

I. Introduction

Non-aqueous phase liquids are liquids that are not readily miscible with water [1], but are generally sparingly soluble in water and exist as a separate fluid phase in an aqueous environment [2]. Petroleum mixtures exist as a non-aqueous phase liquids (NAPLs) contaminants and can be a persistent source of groundwater contamination [3], and soil pollution [4]. NAPLs are organic, non-dissolved liquids in the subsurface [5]. They are distinguished in terms of their density greater than or less than water [2]. The Lighter- than-water (LNAPLs) include gasoline, kerosene, heating oil, jet fuel and aviation gas while the Denser than water (DNAPLs) are chlorinated hydrocarbons such as carbon tetrachloride, chlorophenols, 1,1,1-trichloroethane, carbon tetrachloride, chlorobenzenes, tetrachloroethylene and polychlorinated biphenyls (PCBs) [2]. The nature of subsurface environment is usually divided into unsaturated and saturated zone and consist of unconsolidated porous and granular mineral material overlying a solid rock bed sometimes termed regolith [6]. The upper portion of the unsaturated zone is also known as the vadose `zone with the uppermost layers typically of few tens of centimeters in depth called soil [6]. Both air and water are present in the pore spaces between the mineral grains and the soil is characterized by intense biological activities [6]. The soil water pressure in this zone is less than that of the atmosphere (negative) and is referred to as the matric potential [7]. The saturated zone is formed by porous materials where all the pore spaces are always completely filled with water at greater than atmospheric pressure (www.toxic.usgs.gov). The water table with a thickness above the saturated zone is called the capillary fringe and defined as the depth at which the porewater pressure equals atmospheric pressure [6]. For instance, a hole dug down to the saturated zone, the water table is the depth at which water accumulates in the hole [6]. The unsaturated zone is inclusive of the capillary fringe [6, 8]. An understanding of how NAPL contaminant released from various point sources migrate through the subsurface environment is important in critically evaluating their impact. Separate phase of residual LNAPL or DNAPL often with constituents of high vapour pressure are sources for spreading of volatile pollutant by volatilization from a source zone and gas transport away from the source by diffusion and advection processes [9]. A conceptual model of these processes governing pollutant transport and degradation (attenuation) at a hydrocarbon source in the vadose zone has been reported [9].

As hydrocarbons are lost by biodegradation, they are replaced to an extent by desorption bound material [10], while during the gas transport, some are dissolved into soil moisture content, sorbed to the soil and attenuated. These are carried by recharge water through infiltration and percolation precipitation forming leachates that continue to migrate under the influence of gravity to the water table [5, 11]. The leaching process of the soluble contaminant by the infiltrating water creates an area of contamination much larger than the source [9]. Physical properties of the fluid which affect initial distribution of NAPLs in the subsurface are density of the NAPL, viscosity of the NAPL and interfacial tension between the NAPL and the water or vapour phase [3]. Others are vapour pressure, hydrophobic nature of NAPL and the nature of the subsurface environment; the geology, aquifer mineralogy, organic matter and hydrology [12]. A density difference as small as 1% can induce fluid flow in the subsurface [13]. This determines whether an NAPL will remain at water table or sink lower into the aquifer [3]. Predicting the effects of volatile organic compounds (VOCs) transport in the unsaturated zone using modelling approach are associated with difficulties. The zone contains multiple fluid phases through which VOCs movement and mass transfer is controlled.

Generally, VOCs mixture composition may have profound effect on each individual component constituent as described by Raoult's Law for dissolution and volatilization [9]. The mixture composition also change with time due to mass transfer rates from the pure NAPL phase to the aqueous and liquid phases [9]. As a rule described by [9], modelling of the transport and fate of each individual component of a NAPL without the effect of the mixture composition on the transport processes results in overestimation of the maximum concentrations and spreading of the gas and aqueous plumes in the vadose zone. This study look at the diffusion rate of vapour phase transport of mixed fuel compounds in a subsurface.

II. Materials And Methods

1.1 SYNTHETIC GASOLINE

An artificial gasoline with ethanol (8%) and 12 typical major constituents of gasoline [14, 15], was mixed from products of purities > 99% as described in Membere, (2018). Their weight percentages were chosen according to typical fuel composition [17, 18]. Batch experiments as described in [16] were performed with vapors concentrations coming from the mixture of the composition. Sulphur hexafluoride (SF_6) was chosen as non-volatile gas-phase tracer which is recalcitrant under aerobic condition and is non-absorbable to soil.

1.2 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.

1.3 ANALYTICAL METHODS: SOIL GAS SAMPLING AND ANALYSIS

Soil gas from the batch experiments (normal and autoclaved soil) were analyzed for vapor concentrations of synthetic gasoline compounds and ethanol by GC-FID, as explained by [17] and for CO_2, O_2 and SF_6 using the hyphenated GC-MS technique a method outlined by [19–21]. Partial pressures of CO_2 and O_2 in laboratory experiments have been previously analyzed by gas chromatography [22]. 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 analyzed by injecting 40 uL 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 ^{o}C. The column temperature was held at 30 ^{o}C for 5 minutes, increased to 120 ^{o}C at a rate of 10 ^{o}C min^{-1} and then held constant for 6 mins. Carrier gas was hydrogen at a flow rate of 2 mL min^{-1}.

GC-MS analysis of vapour concentration for CO_2, O_2 and SF_6 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 ^{o}C, multiplier voltage 250 V and interface temperature 250 ^{o}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^{-1} at pressure of 65 kPa. The column temperature was held at 35 ^{o}C for 60 minutes. Carrier gas was helium at a flow rate of 1 mL min^{-1}.

1.4 THEORY
1.4.1 Partitioning of gaseous tracers in soil
Tracers are used for the detection of non-aqueous phase liquid (NAPL) distribution in the vadose zone [23] and they are added to ensure correct evaluation of the transport processes in soil [24], other applications of the tracer gas are in remediation effectiveness and impacts of remediation evaluation [25]. Soil pore space has been described as a three-phase system consisting of air, water and NAPL and assuming an instantaneous linear equilibrium between these three phases and the solid, Werner and Höhener, (2002) described partitioning of a gaseous tracer in the soil pore using the air-solid partitioning coefficient k_s, air-water partitioning coefficient or Henry coefficient H and the air – NAPL portioning coefficient k_n , shown in Figure 1.
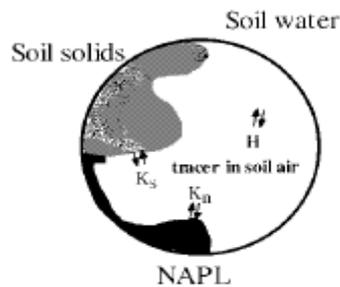

Figure 1. Equilibrium consideration for the soil gas tracers in an NAPL-contaminated soil [23].

Naturally occurring gasses such as [222]Rn may be used as partitioning tracers [26] or a variety of harmless organic chemicals [25] with differing affinities for an NAPL [23]. Using SF_6 as the sole tracer, [27] has reported the determination of an in-situ effective vapor-phase diffusion coefficient. Mariner *et al.*, (1999) stated that chromatography is the general principle for partitioning tracer determination.

1.4.2 Partitioning of gaseous compounds in soil
Werner and Höhener, (2003) described partitioning of a gaseous compound in the soil pore using the air-solid partitioning coefficient k_s, air-water partitioning coefficient or Henry coefficient H and the air-solid partitioning coefficient k_d.
The mass fraction f_a of the compound in soil air is calculated as; [23]

$$F_a = 1/1 + ((\theta_w/\theta_a) *(1/H)) + (((1-\theta_t) * \rho_s/\theta_a) *k_d/H) \qquad \text{---- Equation 1}$$

Where
θ_a, θ_w, θ_t denotes the air-filled, water-filled and total porosity.
ρ_s [g / cm^3] is the density the solids, kd [cm^3/g].

The relationship between f_a and mass fraction in water is given as; [23]

$$F_w = (\theta_w / H\theta_a) *F_a \qquad \text{----- Equation 2}$$

The fraction in solid is given as $\quad F_s = (\theta_s * \rho_s / \theta_a) * K_d/H * F_a.$ $\qquad \text{----- Equation 3}$

1.4.3 Evaluation of degradation rate Coefficient
The basic assumptions underlying this work are that in the unsaturated zone microorganisms live in the aqueous phase, Figure 2, that VOC vapors needs to dissolve in the aqueous phase before biodegradation can occur and that biodegradation follows a first order-rate kinetics and is aerobic [9].
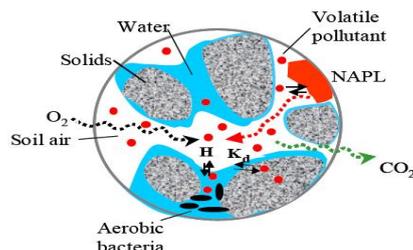

Figure 2: Conceptual model for a VOC biodegradtion in unsaturated porous media

H: Air-water equilibrium partitioning (Henry coefficient); **K$_d$**: Water-solid equilibrium partitioning, **broken arrows**: vapour-phase diffusion. Source: [9]

Apparent First-order biodegradation rate coefficient obtained are reported in Membere, 2018, Table 2 were calculated from the vapor concentration decline in the biotic sand filled vial using the half-life of the EtOHVOCs compounds. A general model equation for gaseous compounds undergoing first order-degradation in the aqueous phase, assuming a diffusive –dominated transport in a porous medium with uniform and constant properties can be written as; [24].

$$\partial/\partial t \; C_a = \; f_a \, \zeta_a \, D_m. \; \Delta \; C_a - f_w k_w \, C_a \qquad \text{------- Equation 4}$$

where Δ stands for Laplace operator, ζ_a tortuosity factor and D_m [cm^2.s^{-1}] molecular diffusion coefficient. k_w is the first order degradation rate constant, f_w mass fraction in the water phase, f_a mass fraction in the air phase and C_a [g/m^3] is the vapour concentration in the soil air.

From (4) above, parameters accounting for degradation can be lumped into a single apparent first –order degradation constant $k_{app} = f_w \, k_w$ [24].

For a spherical symmetry, having a constant spherical VOCs source with radius r$_o$ in a homogeneous infinite porous medium, equation 4 can be rewritten for the attenuation of vapor concentration C_a with radial distance r as; [29].

$$Ca \; (r, \infty) = ((C_{a0}r_0)/r) \; exp \; [\; -\sqrt{(K_{app}/D')} \; (r-r_0)] \qquad \text{-------- Equation 5}$$

where K_{app} [s^{-1}] apparent degradation rate, r [cm] distance from source, ro [cm] radius of the source, Cao vapor concentration near the source, C$_a$ (r, ∞) vapor concentration as a function of distance from the source, D' [cm^2.s^{-1}] is modified diffusion coefficient for the gaseous and dissolved phases; Hohner, et al., 2003)

$$D' = fa * \zeta_a * D_m \qquad \text{-------- Equation 6} \qquad [22]$$

where $\qquad Tourtisity, \zeta_a = \theta_a^{2.33} / \theta t^2 \qquad \text{------- Equation 7} \qquad [30]$

where $D_m = \; 10^{-3} * T^{\wedge 1.75}[(1/M_{air})+(1+M_i)]^{\wedge 0.5}/P[V_{air}^{\wedge 1/3}+V_i^{\wedge 1/3}]^{\wedge 2} \qquad \text{-----Equation 8}$

(A method of Fuller as outlined in [31]

where T is the absolute temperature [k], m$_{air}$ is the average molecular mass of air [28.97 g.mol^{-1}], m is the organic chemical molecular mass [g.mol^{-1}], P is the gas phase pressure [atm], V_{air} is the average molar volume of gases in air [~ 20.1 cm^3. mol], V_i is the molar volume of the chemical of interest [cm^3.mol^{-1}].

It should be noted that known *D'* is used to fit the apparent k_{ap} from lateral attenuation (vapor plume extension) of C$_a$ at steady state, this does not reply on sorption to soil particles and partitioning into the soil water, because f_a is cancelled out in the division of K_{app}/D' [29].

Hence, since the f_a accounts for the sorption coefficient k$_d$, the resulting apparent first-order degradation rate is applied to the gaseous phase as obtained in [17, 22].

2 RESULTS AND DISCUSSION

2.1.1 Degradation rate Coefficient

Using equation (1), the mass fraction *fa* was determined based on the partition coefficient K_d [16] and the diffusion coefficient D' was calculated as a function of f_a and the molecular diffusion coefficient.

Table 1: Mass fractions of compounds in air, water and solid phase, diffusion coefficient D' *calculated*.

Fuel Compounds	Fs	Fa	D$_a$ (25^{0}C) [cm^2/s]	Fw	D'
n-pentane	0.662	0.329	0.082	0.009	0.003
n-hexane	0.202	0.783	0.076	0.015	0.005
n-octane	0.910	0.089	0.067	0.001	0.001
n-decane	0.959	0.041	0.060	0.000	0.000
methylcyclopentane	0.272	0.667	0.081	0.061	0.005
methylcyclohexane	0.293	0.537	0.075	0.170	0.004
cyclohexane	0.379	0.525	0.082	0.096	0.004
isooctane (2,2,4-trimethylpentane)	0.176	0.816	0.066	0.008	0.005
toluene	0.776	0.036	0.082	0.187	0.000
m-xylene	0.736	0.043	0.076	0.221	0.000
1,2,4-trimethyl-benzene	0.669	0.055	0.071	0.276	0.000

2.1.2 Estimating the vapor concentration as a function of distance from the source

Substituting the modified diffusion coefficient *D'* into equation 5 as a function of distance in an inverse analytical modelling method calculates; Ca (r, ∞) vapor concentration as a function of distance from the vapour source, Figure 3. This method is used as a degradation rate assessment tool.

Assumption used: A source radius r$_o$ of 50 cm and r (distance from source) between 1 -6 m was used.

III. Discussion

2.1.3   *Degradation rate assessment*

The presence of NAPLs which are associated with high VOC concentrations defines the so-called source zone [5], from where the contaminant evaporates and forms gaseous and aqueous plumes [23]. Vapors are also released in the subsurface from residual saturation of an NAPL [32], held by capillary forces in the soil during migration [17, 29]. The constituents of NAPL like gasoline often have high vapour pressure, leading to volatilization form the source to the soil air and spreads by diffusion or pressure driven gas advection [9, 33]. In the absence of pressure gradients advection, Werner and Höhener, (2003) pointed out that gas-phase diffusion dominates the migration of these volatile pollutant in the vadose zone. Diffusive spreading and or gaseous transport of these fuel constituents (VOCs) through the unsaturated zone has been identified as a serious threat to groundwater quality [17, 34] and also potential health threat to individuals living within the vicinity of the emission sources from volatilized vapors to the atmosphere [35]. Predicting, the natural attenuation of the VOCs in the unsaturated zone requires information about the microbial biodegradation rates and kinetics [24, 29]. Hence, knowledge of these kinetics is a prerequisite for groundwater risk assessment [29].

In this study, an assumption of gas phase diffusion process using calculated diffusion coefficient (D')   and first-order degradation rate of the various EtOHVOCs constituent measured from the decline in soil gas concentration forms the basis of the batch (Abiotic soil) VOC attenuation using the inverse analytical modelling equation (5), Figure 3. Falta *et al.*, (1989) carried out a survey for subsurface gasoline contamination using soil-gas monitoring method. The method has been a widely used tool to observe the migration of volatile organic compounds at contaminated sites [37]. Measured vapour concentration profiles are then used to approximate location of source and description of lateral or vertical extension of its emanating vapour plume [17, 38, 39].

2.1.4   ***Compound specific biodegradation***

At field site O_2 and CO_2 data can reflect well the temporal evolution and partial spatial distribution of biodegradation but lacked information on which compounds were degraded, the degradation information is only obtained by-compound –specific lateral spreading [29], as shown in Figure 3.
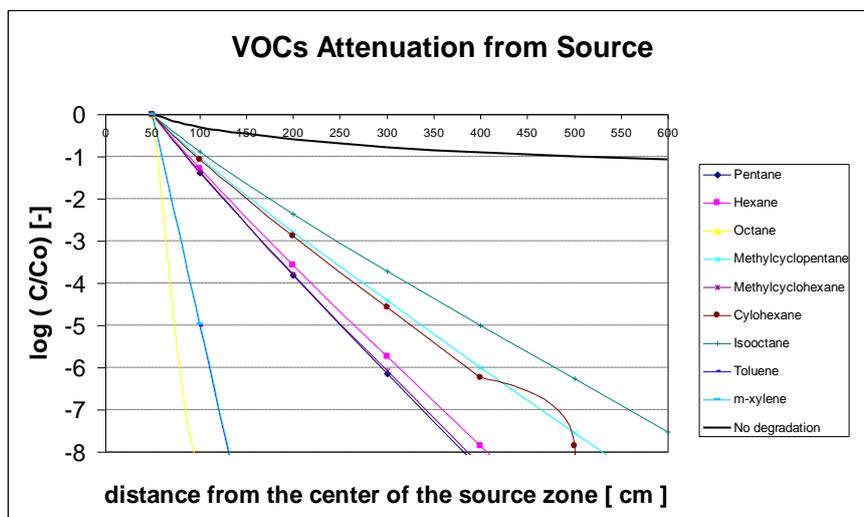
Figure 3: Gas-phase concentration of the VOC. Concentrations are divided by the initial concentration of the source zone.

From the plot of Figure 3, vapor concentration log [C/C_O] as a function of distance from the vapour source, the concentration profiles indicates that compound –specific attenuation mechanism were active resulting in maximum lateral migration distances from the source of less than 0.2 m (toluene, xylene) to about 1.2 m (iso-octane) assuming 99% degradation has occurred relative to their initial concentration, Table 2, defined by Ca (r,∞) = 0.01C_O of the distances attenuated [29]. The shape of the concentration profile in Figure 3 clearly shows the assume source of contamination has a radius of 50 cm.

Since, steady- state diffusion do not reply on sorption and partitioning into the soil water [40], thus at steady state, lateral migration is controlled by degradation [29]. This is can be seen for n-hexane and isooctane which are higher volatile compounds with close calculated K_d values [16], having clearly different vapor attenuation distances at log (- 2) concentration (99%); n-hexane (0.8 m) and iso-octane (1.3 m).

Gas –phase diffusion in the unsaturated zone is affected by partitioning into soil-water, onto air-water and into or onto solid [40]. The process spreads only the contaminants in the gas phase where contaminants with

low mass fraction *fa* in the soil gas diffuse more slowly depending on the soil and chemical properties on the diffusing substance. Since, the soil used in this study is homogenous, this fact also explains the reasons why compounds with higher mass fraction (Isooctane, n-hexane, methylcyclopentane) diffuse to a longer distance than those with low mass fraction (toluene, m-xylene, octane), (Table 1 and 2). Biodegradation may have considerably reduced the compounds with greater aqueous solubility as m-xylene and toluene while the compounds with higher vapour pressure having higher k_d values as pentane, *n*-hexane, methylcyclopentane are depleted from the source at a much faster rate than the less volatile mixture compounds hence the longer distances attained before attenuation. Grathwohl *et al.*, (2003) stated that high aqueous solubility enhances the effect of biodegradation, the simple reason why comparism between toluene a least volatile component with lower vapour pressure is depleted before methylcyclopentane having a higher vapour pressure. It can be inferred from Figure 3 that relative to the state when non biodegradation is taking place (Black curve) from the source, isooctane travel the most distance (1.3 m) before been attenuated to 1% of the original concentration of the source, a reason attributed to it recalcitrant and slow degradation nature [17].

An important factor affecting the time to depletion from NAPL source of all VOC constituents is the location of the source zone relative to the ground surface or water table. A source zone placed 1 m closer to the water table, the time of depletion is increased by one order of magnitude [9].

Table 2 Lateral distances from source at Attenuation factor 0.01 (99%)

Compound	Distance at Log C/C$_a$ from graph (cm)	Source radius	Distance attenuated at 99% from Source (cm)	Reduction (m)
Fuel Compounds				
n-pentane	120	50	70	0.7
n-hexane	130	50	80	0.8
n-octane	51	50	1	0.01
methylcyclopentane	150	50	100	1
methylcyclohexane	125	50	70	0.7
cyclohexane	145	50	95	0.95
isooctane (2,2,4-trimethylpentane)	175	50	125	1.3
toluene	60	50	10	0.1
m-xylene	60	50	10	0.1

Assuming hypothetically that a house is situated 3m at ground surface (above) and a groundwater table at 3 m (below) from the source of contamination in the subsurface, then using data obtained in Table 2, isooctane possess greatest health risk through lateral vapor migration / spreading to the house and ground water before natural attenuated at factor 0.01 used in this approach. Other compounds with significant risk are methylcyclopentane and cyclohexane while toluene and m-xylene posses little or no risk with octane being the least. At these assumed distances the vapour of the VOCs will be attenuated before getting to the potential receptors (Household and groundwater table). Pasteris *et al.*, (2002) has reported isooctane is a slowly degrading compounds which persisted much longer in groundwater and fast degradation rate for octane.

The maximum extension x$_{max}$ of a vapor plume from the source zone at time t after pollution can be estimated with; [37].

$$x_{max} = 2 (0.66 \, D_m t)^{1/2} \qquad \text{----Equation 9}$$

This uses the Penman relationship [41] for the tortuosity factor and assumes vapor migration by diffusion.
Using typical valves of D_m = 0.1 cm^2 / s, x$_{max}$ after 24 hours
$$= 2 (0.66 \times 0.1 cm^2 / s \times 86400 \, s)^{1/2} = 151 \, cm = 1.5 \, m$$

From data in Table 2, isooctane will likely attain this maximum distance in 24 hours before other contaminants. Several factors influence the contaminant vapor concentration in the subsurface as; the mole fraction of a constituent in the liquid phase [42], the physical and chemical properties of the soil [40], biodegradation rate [43] and the duration of the vapor migration [37], hence the quantification of diffusive transport from a source zone or the liquid contaminant phase cannot be based on vapor / soil gas measurement solely. Tracer methods base on gas –phase diffusion from a point source are used to overcome these gap [37].

IV. Conclusion

Transport in an unsaturated porous media is sufficiently complex when only two fluid phases air and water are present but becomes even more complicated with the presence of an NAPL fluid phase [6]. The migration of an NAPL contaminants depends primarily on the quantity released, the structure of the soil through which it moves and the physical properties of the subsurface [2]. In order to quantitatively predict the

mechanism of gaseous transport of the VOCs in the unsaturated zone, natural attenuation processes such as biodegradation, volatilization, sorption and partitioning into phases such as soil water or soil organic matter needs to be understood [17]. The sources of vapour from a an NAPL after volatilisation can be from the free-phase LNAPL pool, product adsorbed onto soil particles in the vadose or dissolved in groundwater. The movement of the evolved vapour upward from the groundwater through the vadose zone is by diffusion [44]. The volatilized vapour from the soil atmosphere to the soil surface is through dispersion gradient from areas of higher to lower concentration, ultimately reaching the surface [8].

This study shows from a contaminated source zone toluene, octane and m-xylene will diffuse and or travel a lesser distance before been attenuated, hence pose a less risk to groundwater and the atmosphere compared to iso-octane followed by methylcyclopentane which diffuse to longer distance before attenuation. One factor attributed to support the rapid degradation process of these VOCs (toluene, octane and m-xylene) vapor is that the diffusion time into the liquid from the gas phase is not significantly limiting the process [35]. This is consistent with finding of Schwarzenbach, Gschwend and Imboden, (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. The more volatile compounds with high vapour pressure for example pentane (7.5), n-hexane (1.3) and isooctane (2.1) 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.

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