

Natural Transport of Volatile Organic Compounds Due to Annual Variation of Soil Temperature

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ABSTRACT

A theoretical investigation of factors affecting gas phase transport of volatile organic compounds in unsaturated zone is presented. Studying annual soil temperature variation with time and depth declares that there is a considerable temperature variation in the upper few meters that may affect the overall natural mass transport of volatile organic compounds. A one-dimensional mathematical model is used to study the effect of soil temperature variation on diffusive mass transport. From the analytical solution, it is clear that there is a significant net mass transport upward direction and a stimulated spatial oscillation of contaminant concentration in soil. The magnitude of these two modes of mass transport is higher as the contaminant is more volatile.

KEYWORDS: VOC, Soil temperature, Mass transfer.

INTRODUCTION

Volatile organic compounds (VOCs) were identified as one of the more ubiquitous groups of hazardous chemicals present in contaminated groundwater due to widespread uses of VOCs in the manufacturing of pesticides, plastics, paints, pharmaceuticals and textiles. These contaminants may enter the ground as separate phase liquid due to chemical spill or leaking storage tanks (Ding et al., 1999).

During migration of these liquids through the unsaturated zone, a certain amount of the liquid will be retained in the soil by capillary forces. This trapped fraction is known as the residual saturation, and may occupy about 2-20% of available pore space. The fate of this trapped liquid in the unsaturated zone is determined

by the degree of evaporation and transport in the gas phase, dissolution and transport in aqueous phase, and chemical and biological reactions (Falta et al., 1989).

Although researches directed toward remediation of VOC contaminated sites have led to the development of a variety of *in-situ* cleanup technologies, including soil vapor extraction and bioremediation, soil heterogeneities or geologic formation with low air permeability can however cause serious limitations to the applicability of these technologies. Contaminant transport through the formation is thus limited to diffusion, which is a very slow transport mechanism (Ho and Udell, 1992; Reddy et al., 1999; U.S. Army Corps of Eng., 2002; Schulenberg and Reeves, 2002; Hoier et al., 2007).

Gas diffusion is the dominant mechanism of VOC transport in many situations. Under natural conditions, the transport of contaminants in the gas phase is due to both advection and diffusion. Natural gas phase advection

may result from gas density gradient. In order for density driven flow to be significant, the gas phase permeability (in a homogeneous porous medium) should be at least in the order of $1 \times 10^{-11} \text{ m}^2$ (≈ 10 darcy) (Falta et al., 1989). Otherwise in less permeable soils, the contribution of advection to overall gas transport becomes negligible.

Fick's Law is traditionally used to evaluate the diffusion process. The diffusive flux is proportional to contaminant concentration gradient in the gas phase. For typical organic contaminants at common environmental conditions, contaminant vapor pressure and consequently the contaminant concentration in the gas phase is a strong function of temperature. In soil containing residual saturation of contaminants a temperature-driven diffusive flux may be stimulated in presence of a temperature gradient.

The general behavior of soil temperature has been studied by many researchers. According to Williams and Gold (1976), Hillel (1982), Marshall and Holms (1988) and Wu and Nofziger (1999), for ground with constant thermal properties, the annual variation of daily average soil temperature at different depths is described with a sinusoidal function whose amplitude decreases exponentially with the depth from the soil surface. In soil containing residual saturation of contaminants, this temperature variation with time and depth may stimulate a spatial oscillation in contaminant concentration especially in the few meters depth from the soil surface.

Previous studies simulate VOC gas phase transport in soil with isothermal mathematical models assuming constant soil temperature (Falta et al., 1989; Mendoza and Frind, 1990; Grathwohl and Maier, 2002). This study focuses on diffusive transport of VOC driven by soil temperature variation with time and depth using a single component non-isothermal mathematical model.

MATHEMATICAL MODEL

Soil Temperature: The properties of soil that determine its response to temperature changes at the

surface are volumetric heat capacity, C_v , thermal conductivity, K , and water content. The ratio, K/C_v , known as thermal diffusivity, is important in calculating rate of heat flow in the soil.

Detailed simulation of soil temperature includes complex interrelationships. Fortunately, in nature many factors tend to compensate each other so that it is usually possible to use relatively simple formulae to estimate the limits within which soil temperatures will fluctuate.

The principal features of air and ground surface temperature variations can usually be described by an equation of the form (Williams and Gold, 1976):

$$T_s(t) = T_{av} + X \cdot \cos(At) \quad (1)$$

$$A = \frac{2\pi}{t_o} \quad (2)$$

where $T_s(t)$ is the ground surface temperature at a given time, T_{av} is the average temperature for a period involving one or more complete cycles of variation, X is the difference between the maximum and average temperatures for the period, t is time, and t_o is time for one complete cycle.

If the ground has constant thermal properties, the temperature induced in it by cyclical variation is given by (Hillel, 1982):

$$T(z, t) = T_{av} + X \cdot \exp(-Bz) \cdot \cos(At - Bz) \quad (3)$$

where

$$B = \sqrt{\frac{\pi}{\alpha t_o}} \quad (4)$$

and z is the depth below the surface (L), and α is the thermal diffusivity (K/C_v).

Mass Transport Model: The following assumptions are made (commonly employed in transport models in an unsaturated zone):

- 1- The soil contains single-component contaminant.
- 2- Vapor phase behaves as an ideal gas.
- 3- Initial non-aqueous phase liquid (NAPL) saturation is uniform throughout the soil.
- 4- NAPL is immobile.
- 5- NAPL density is constant.
- 6- Equilibrium between NAPL and gas phase concentration is described by Raoult's Law.
- 7- Dissolution and sorption species are ignored.
- 8- The gas phase is in thermal equilibrium with solid phase. This assumption has been shown to be reasonable in other numerical investigations of more severe cases (Adenekan et al., 1993; Yoon et al., 2003).
- 9- Energy changes due to contaminant evaporation or condensation are neglected. This assumption has been shown to be reasonable in other experimental and numerical investigations of more severe cases (Ho et al., 1994).
- 10- Soil gas permeability is relatively low, so that the contribution of density-driven advection to overall gas transport is negligible and the use of a standard diffusion model to describe the gas phase transport would be appropriate (Falta et al., 1989).

The mass balance equation will be:

$$\frac{\partial C}{\partial t} = \nabla \cdot (nS_a D^* \nabla \rho_a) \quad (5)$$

where C is the total contaminant concentration in the soil, n is the soil porosity, S_a is the gas saturation, D^* is the effective gas phase soil molecular diffusion coefficient and ρ_a is the mass concentration of the contaminant in the gas phase.

The effective soil molecular diffusion coefficient is given by Millington (1959) as follows:

$$D^* = \left(\frac{(nS_a)^{10}}{n^2} \right) D \quad (6)$$

where D is the unobstructed gas phase molecular

diffusion coefficient.

The total contaminant concentration is made up of contributions from the gas and the liquid phase, as expressed in Eqn. (7):

$$C = nS_a \rho_a + nS_o \rho_o \quad (7)$$

where S_o is the liquid phase saturation, and ρ_o is the liquid phase density.

Totality condition states that the fluid phase saturations sum up to unity at all time:

$$S_a + S_o = 1 \quad (8)$$

As a numerical solution cannot be used to study all possible cases, an analytical solution is useful and further model simplification is needed. Since air saturation S_a is the secondary dependent variable, it is assumed to be constant with time and depth (error estimation due to this assumption to be discussed later) and Eqn. (5) becomes:

$$\frac{\partial C}{\partial t} = nS_a D^* \nabla^2 \rho_a \quad (9)$$

and for a one-dimensional system, the above equation becomes:

$$\frac{\partial C}{\partial t} = nS_a D^* \frac{\partial^2 \rho_a}{\partial z^2} \quad (10)$$

Then

$$\Delta C(z, t) = nS_a D^* \int_0^t \frac{\partial^2 \rho_a}{\partial z^2} dt \quad (11)$$

The partial derivative term inside the integral can be defined as a function of time and depth as follows:

The mass concentration of the contaminant in the gas phase ρ_a is the contaminant saturated vapor concentration that can be calculated from the ideal gas law as:

$$\rho_a = \frac{MP}{RT} \quad , T \text{ in } (^{\circ}\text{K}) \quad (12)$$

where M is the contaminant molecular weight, R is

the universal gas constant, P is the contaminant vapor pressure calculated as a function of temperature (Ho et al., 1994):

$$P(Pa) = a_0 + a_1 T(^{\circ}C) + a_2 T^2(^{\circ}C) + a_3 T^3(^{\circ}C) \quad (13)$$

values for a_0 , a_1 , a_2 and a_3 are given in Table 1 for different VOCs.

Table (1): Saturated vapor pressure parameters for different VOCs. (Ho et al., 1994).

	a_0	a_1	a_2	a_3
Benzene	3390	227	3.01	0.111
Toluene	833	72.8	0.492	0.054
o-Xylene	192	15.3	0.0214	0.019

Differentiating Eqn. (12) with respect to depth gives:

$$\frac{\partial^2 \rho_a}{\partial z^2} \approx \frac{\partial}{\partial z} \left[\left(\frac{M}{RT} \right) \frac{\partial P}{\partial T} \frac{\partial T}{\partial z} \right] \approx \frac{M}{RT} \left[\frac{\partial^2 P}{\partial T^2} \left(\frac{\partial T}{\partial z} \right)^2 + \frac{\partial P}{\partial T} \frac{\partial^2 T}{\partial z^2} \right] \quad (14)$$

From Eqn. (13)

$$\frac{\partial P}{\partial T} = a_1 + 2a_2 T + 3a_3 T^2, \quad T \text{ in } (^{\circ}C) \quad (15)$$

and

$$\frac{\partial^2 P}{\partial T^2} = 2a_2 + 6a_3 T, \quad T \text{ in } (^{\circ}C) \quad (16)$$

Combining Eqn. (3), Eqn. (11), Eqn. (14), Eqn. (15) and Eqn. (16) gives:

$$\begin{aligned} \Delta C(z,t) \approx nS_a D^* \frac{M}{RT} [& \{b_0 \cdot \exp(-2Bz)\}t + b_1 \cdot \exp(-Bz) \\ & \{ \cos(At - Bz) - \cos(Bz) \} + \\ & b_2 \cdot \exp(-3Bz) \{ \sin(At - Bz) + \sin(Bz) \} + b_3 \cdot \exp(-2Bz) \\ & \{ \cos(2At - 2Bz) - \cos(2Bz) \} + \\ & b_4 \cdot \exp(-3Bz) \{ \cos(3At - 3Bz) - \cos(3Bz) \}] \quad (17) \end{aligned}$$

where

$$\begin{aligned} b_0 &= (2a_2 + 6a_3 T_{av}) B^2 X^2 \\ b_1 &= (1/A) (2a_1 + 4a_2 T_{av} + 6a_3 T_{av}^2) (B^2 X) + \\ & \quad (3/A) a_3 B^2 X^3 \cdot \exp(-2Bz) \\ b_2 &= (6/A) a_3 B^2 X^3 \\ b_3 &= (1/A) (a_2 + 3a_3 T_{av}) B^2 X^2 \\ b_4 &= (1/A) a_3 B^2 X^3 \end{aligned}$$

The first term in Eqn. (17) represents a net increase in contaminant concentration at a steady rate m^* :

$$m^* = nS_a D^* \frac{M}{RT} (2a_2 + 6a_3 T_{av}) B^2 X^2 \cdot \exp(-2Bz) \quad (18)$$

Equation (18) shows that m^* is a function of contaminant vapor pressure parameters a_2 and a_3 . It has a maximum value at soil surface and decreases exponentially with the depth from the soil surface.

The other four terms in Eqn. (17) represent sinusoidal functions, fundamental and two harmonics, whose amplitudes decrease exponentially with depth with phase lags Bz , $2Bz$, $3Bz$, respectively. These phase lags increase linearly with depth.

APPLICATION

Figures 1 and 2 show the variation of contaminant concentration with time and depth from the soil surface for a hypothetical system. Benzene and Toluene are considered as contaminants, respectively. Table 1 shows typical system parameters, while Table 2 shows contaminants physical properties. Time range is chosen to be 0-1200 days. This range has shown to be reasonable for common contaminants which still exist in the soil after spill although there are several natural attenuation mechanisms (El-Beshry et al., 2001).

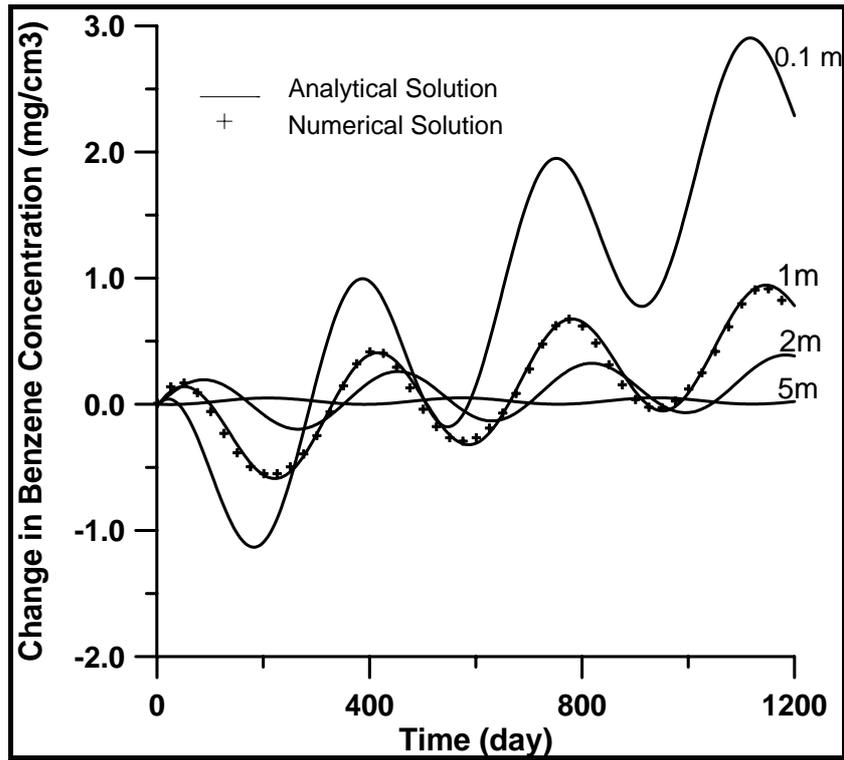


Figure (1): Change in benzene concentration with time for different depths from soil surface.

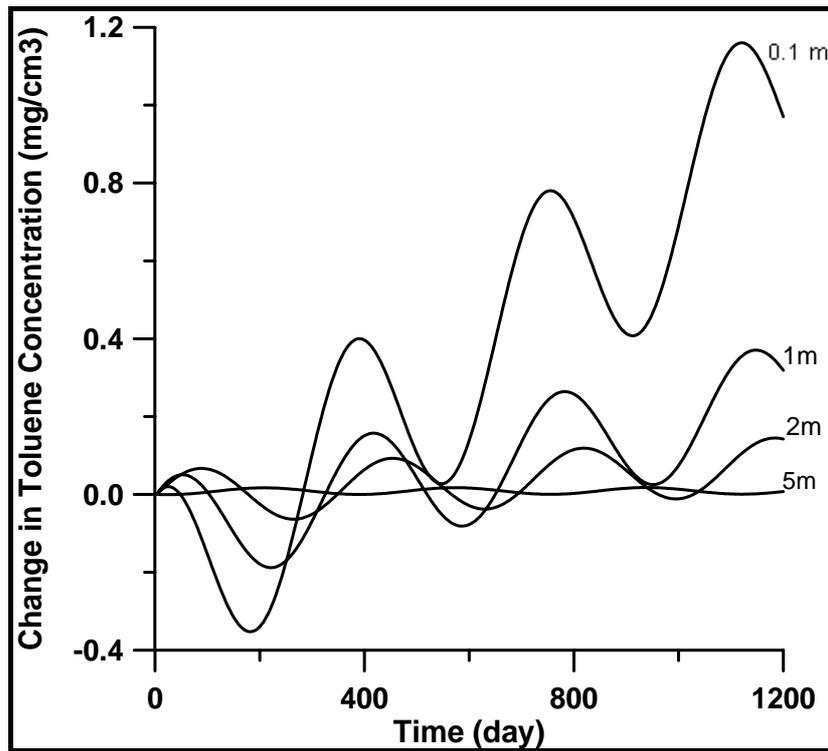


Figure (2): Change in toluene concentration with time for different depths from soil surface.

Table (2): Parameters used in application.

Soil porosity, n (-)	0.4
Initial NAPL saturation, S_o (%)	1
Average soil surface temperature, T_{av} (°C)	20
Amplitude of soil surface temperature, X (°C)	10*
Time for one complete cycle, t_o (sec)	$365 \times 24 \times 3600$
Thermal diffusivity, α (m ² /sec)	2×10^{-7} *

(*) (Williams and Gold, 1976).

Table (3): Physical properties of contaminants used in application. (Rathfelder et al., 1991).

	benzene	toluene
Molecular weight (kg/kmole)	78.1	92.1
Binary diffusion coefficient in air (20°C) (m ² /sec)*	8.8×10^{-6}	0.077
Liquid density (at 20°C) (kg/m ³)	879	867

(*) $D = D_{(20^\circ C)} \left(\frac{T}{20 + 273} \right)^{3/2}$, T in (°K) (Bird et al., 1960).

Both Figures 1 and 2 show a net contaminant mass transport upward direction and a stimulated sinusoidal variation of the contaminant concentration in soil. These two modes of mass transport are more pronounced for benzene than for toluene as benzene is more volatile than toluene (larger values for a_2 and a_3). The net increase in contaminant concentration for the region near the soil surface is higher than that for deeper soil. At depth of 0.1 m from the soil surface, the change in benzene and toluene concentration reaches a maximum magnitude of 3 mg/cm³ and 1.2 mg/cm³, respectively. These magnitudes of mass transport may have significant contribution and may play a role in natural attenuation remediation process in the upper few meters from the soil surface when they are compared with mass transport magnitudes mentioned in other studies which dealt with natural attenuation of

soil contaminants in the absence of NAPL (Jury et al., 1990; Shoemaker et al., 1990).

The sinusoidal variations of the contaminant concentration in the lower depth are lagged by about 180° from that near the soil surface, so that any concentration increase in one region results in a concentration decrease in the other region and *vice versa*. This means that there is a stimulated spatial oscillation of contaminant concentration in the soil. The amplitude of the oscillation is higher as the contaminant is more volatile.

Equation (5) has been numerically solved using the finite difference method with air saturation S_a as a function of depth and time. Comparison of the solution obtained from the approximate analytical solution with that obtained from the numerical solution is shown in Fig.1. It is clear that there is a negligible difference between the two solutions. This is an evidence on that the assumption of constant air saturation S_a in the derivation of Eqn. (9) has a negligible effect on the accuracy of the analytical solution.

CONCLUSIONS

The analytical model presented in this paper provides a conceptually clear and computationally simple way to examine the impact on VOC transport resulting from annual soil temperature variation with time and depth from the soil surface.

The analytical solution states that in soil containing residual saturation of VOC contaminant, a temperature-driven diffusive mass transport is stimulated as a result of soil temperature variation with time and depth from the soil surface. Two modes of mass transport occur; a net mass transport upward direction and a stimulated spatial oscillation of contaminant concentration in soil. The magnitudes of these two modes of mass transport are higher as the contaminant is more volatile.

Application of the analytical solution to a hypothetical volatilization system of common VOCs shows that the

modes of mass transport mentioned above may have significant contribution and may play a role in natural attenuation remediation in the upper few meters from the soil surface. This is especially important for

heterogeneous soil or formation with low air permeability where the applicability of *in-situ* cleanup technologies is limited.

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