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Modeling Volatilization Flux of Semi-Volatile Organic Compounds from Soil.

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ABSTRACT

Volatilization of organic pollutants due to their disposal or leaks and spills is one of the important contributors to their presence in the atmosphere. The transport of chemicals through porous soil occurs: (1) vapor diffusion; (2) liquid diffusion; and (3) mass transfer during upward liquid water flow. Because of their toxicity, volatilization of poly aromatic hydrocarbons (PAHs) from crude oil and poly-chlorinated biphenyls (PCBs) from PCB mixture into the atmosphere is a significant issue. In this paper, the volatilization fluxes of semi-volatile organic compounds (SVOCs), specifically PAHs and PCBs are estimated. The mathematical model accounts for pore water movement upward towards the surface, biodegradation of the organics and a stagnant air boundary layer across which diffusion occurs, at the surface. Assuming a certain depth of contamination due to leaks and spills, the volatilization flux was predicted as a function of time. The results showed that lower ringed PAHs and less chlorinated PCBs tend to volatilize faster, compared to higher changed PAHs. It was also observed that volatilization rates decreased over time. Factors significantly affecting flux including soil moisture content, pore water flow and depth of contamination were varied to determine changes in volatilization flux.

Key words: Volatilization, Diffusion, Henry's Law, PAHs, PCBs

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds with two or more fused aromatic rings [1-3]. They are ubiquitous environmental contaminants, and sediments in and soils are often contaminated with a mixture of PAHs both from point and non-point sources. PAHs released in the environment from non-point sources include : (1) surface run-off from roads, highways; (2) treatment plant sewage effluent; (3) accidental petroleum and gasoline spills, and (4) atmospheric soot from combustion sources [1-5]. Similarly, Polychlorinated biphenyls (PCBs) is not a single chemical, but a group of molecules that have varying numbers of chlorine atoms attached to the carbon atoms of the biphenyl rings. There are 209 discrete PCB compounds, called congeners, in which one to 10 chlorine atoms are attached to the biphenyl rings. Homolog groups include all congeners that have equal number of chlorines attached to the biphenyl ring, thus 209 congeners or isomers are classified into 10 homologs [5-6]. Starting in the 1930s, PCBs were produced for use in transformers, capacitors, carbonless copy paper, printing inks, hydraulic fluids, and other applications. During their production and handling, PCBs and PAHs inadvertently released into the environment, particularly soils [5-6]. Because of their persistence in their environment and toxicity, PCB and PAHs concentrations are monitored and regulated.

Once these semi-volatile organic compounds (SVOCs) are released to the environment, their fate and transport is largely influenced by various reaction pathways, notably vaporization (i.e., evaporation), solubilization, and biodegradation [5-9]. The volatilization of these chemicals into the atmosphere contributes significantly to the increase in organic pollutants in air. The volatilization of PCBs and PAHs is largely dependent of the chemical properties of the chemical. PAHs and PCBs exhibit low vapor pressure, low water solubilities and high octanol water partitioning coefficient, suggesting that these SVOCs would preferably bind to soils than move along with water. Additionally, due to their extremely high biodegradable half-lives, they are persistent in the environment. To put this in perspective, it would require about a half minute for complete vaporization of 1 gallon of gasoline spilled on the ground. Under the same conditions, complete PCB vaporization would occur in approximately 1,200 to 1,850 years, depending upon the congener. Because of their persistent presence in the environment, and despite their low volatility, PCBs and PAHs contribute significantly to the atmospheric pollution due to the volume spill during production and handling [5-6].

Therefore, the purpose of this study is to employ chemical reaction and transport models to estimate the extent of volatilization of these SVOCs to the atmosphere from soil. The specific objectives are: (1) estimate volatilization flux as a function of time; and (2) evaluate the effect of soil properties on the volatilization flux.

MODELING OF VOLATILIZATION FLUX

Volatilization of organic compounds from contaminated soil was modeled using a complex equation developed by Jury et al., known as the *Jury equation* [7-9]. The Jury equation (Equation 1) is based on Fick's second law of chemical transport, and assumes the incorporation of chemicals in soil to a certain depth. Figure 1 provides a conceptual illustration of the Jury equation.

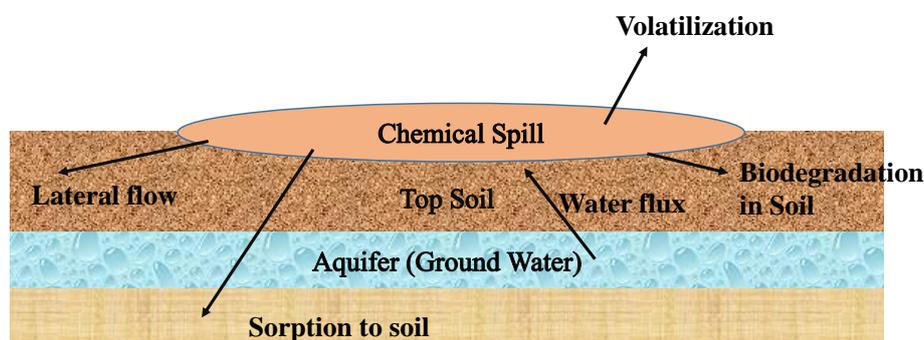


Figure 1. Fate and Transport Mechanisms of Chemicals in Soil

The transport of a contaminant through porous soil occurs via three specific pathways, as shown in the illustration: (a) vapor diffusion; (b) liquid diffusion; and (c) convective mass transfer during upward liquid water flow. The *Jury equation* assumes an idealized soil column of uniform properties throughout the depth of the column (porosity, water content, bulk density, fractional organic carbon content, and vertical water flux). For an

assumed initial concentration of the chemical present in the soil, the transport of the chemical via the three mechanisms is modelled. Over time, the chemical moves upward or downward (depending on the direction of water flux), degrades, diffuses and volatilizes from the surface of the soil. Due to evaporation of water at the surface, a steady flow of water, in the upward direction (i.e., towards the soil surface) occurs to replace evaporative loss from the soil surface. This process, also known as "wicking," results in the movement of the contaminant to the surface along with water. Once the contaminant reaches the surface, vaporization of the chemical occurs. In the sub-surface, the contaminant diffuses through the porous soil, due to concentration gradient. The model considers both sorption of the chemical to the soil and biodegradation of the chemical over time. The Jury equation is a conservative model because it assumes that: (1) vaporization of a contaminant from soil and the movement of water from the subsurface are continuous; and (2) soil properties are constant in time and space. Near the air-soil-water interface, there is relatively little or no movement of air. Therefore the movement of the chemical to the atmosphere is mostly diffusion controlled [7-9]. The governing equations used to determine the flux are:

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_S}{\partial z} + \mu C_T = 0$$

$$J_S = -D_G \frac{\partial C_G}{\partial z} - D_L \frac{\partial C_L}{\partial z} + J_w C_L$$

Solving the governing equations and accounting for air and water diffusivity, boundary layer thickness, water flux etc., the Jury equation for volatilization flux of the chemical at the surface of soil is [6-7]:

$$J_S(t, L) = +\frac{1}{2} C_0 \exp(-\mu t) V_E \left[\operatorname{erfc} \left(\frac{V_E t}{2\sqrt{D_E t}} \right) - \operatorname{erfc} \left(\frac{L + V_E t}{2\sqrt{D_E t}} \right) \right] \quad (1)$$

$$+ \frac{1}{2} C_0 \exp(-\mu t) (2H_E + V_E) \exp \left(\frac{H_E (H_E + V_E) t}{D_E} \right)$$

$$\times \left[\exp \left(\frac{H_E L}{D_E} \right) \operatorname{erfc} \left(\frac{L + (2H_E + V_E) t}{2\sqrt{D_E t}} \right) - \operatorname{erfc} \left(\frac{(2H_E + V_E) t}{2\sqrt{D_E t}} \right) \right]$$

Where V_E is Effective solute velocity and D_E is Effective diffusion coefficient.

$$V_E = \frac{J_w}{\rho_b f_{oc} K_{oc} + \theta + a K_H} \quad (2)$$

$$D_E = \frac{\left(\frac{10}{a^3} D_g a K_H + \theta^{\frac{10}{3}} D_l^w \right)}{\phi^2 (\rho_b f_{oc} K_{oc} + \theta + a K_H)} \quad (3)$$

The term H_E in Equation (1) represents the mass transfer coefficient of the chemical across a defined boundary layer. Considering zero water evaporation (i.e., $V_E = 0$) and with near zero boundary layer thickness, the above equation becomes:

$$J_S = C_0 e^{-\mu t} \left(\frac{D_E}{\pi t} \right)^{\frac{1}{2}} \left[1 - \exp \left(\frac{-L^2}{4D_E t} \right) \right] \quad (4)$$

For an infinitesimal boundary layer thickness, the value of $H_E \rightarrow \infty$ and therefore the second term in the equation 1 almost goes to zero. Consideration upward flow of water, and water evaporation (i.e., $V_E \neq 0$) and $H_E \rightarrow \infty$, Equation 1 becomes:

$$J_S(0, t; L) = \frac{1}{2} C_0 \exp(-\mu t) V_E \frac{L}{\sqrt{\pi D_E t}} \quad (5)$$

C_T	Total concentration in micro grams per cubic centimeter of soil.
C_S	Adsorbed phase concentration in micrograms per gram of soil.
C_l	Dissolved phase concentration in micrograms per cubic centimeter of soil solution.
C_g	Gas phase concentration in micrograms per cubic centimeter of soil air.
ρ_b	Soil bulk density (g/cm^3)
θ	Volumetric water content.
a	Volumetric air content.
J_g	Gaseous diffusion coefficient in soil.
D_g	Gaseous diffusion coefficient in soil.
D_g^a	Gaseous diffusion coefficient in air.
ξ_g	Factor accounting for vapor diffusion porosity and tortuosity effects.
J_l	Dissolved solute flux.
D_l	Liquid diffusion coefficient in soil.
J_w	Volumetric Soil water flux.
ξ_l	Factor accounting for liquid diffusion porosity and tortuosity.
D_l^w	Liquid diffusion coefficient in pure water.
μ	Rate constant for first order chemical degradation in soil.
τ	Effective half-life.
V_E	Effective solute velocity.
D_E	Effective diffusion coefficient.
K_H	Dimensionless Henry's Law Constant
k_{oc}	Fractional Organic Carbon in soil
K_{ow}	Soil Organic Carbon-Water Partitioning Coefficient

Chemical properties for the 10 PCB homologs and 16 priority pollutant PAHs was collected and used to determine the volatilization flux using both equations (4) and (5). The effect of different properties on the flux rates was also determined.

RESULTS AND DISCUSSION

Table 2 presents the properties of 10 PCB homologs and 16 priority pollutant PAHs [10-11]. As seen in the table, Henry's law constant decreased with the number of aromatic rings in the PAHs (from naphthalene – a 3 ringed PAH to dibenz (a,h) anthracene – a 5 ringed PAH [1]. Similarly, as the number of aromatic rings increase, the octanol water partitioning coefficient increased, suggesting that higher order PAHs would preferentially adsorb onto soil and the organic matter in soil, compared to being soluble in water. Similar trends were observed for PCBs. The properties of the PCB congeners are largely influenced by the number of chlorines attached to the biphenyl ring [5]. For example, as chlorine content increases, the vapor pressure of PCBs decreases significantly from mono-CB to hexa-CB. Tri-PCBs have almost two orders of magnitude higher vapor pressures compared to hexa-PCBs, and six orders of magnitude higher compared to deca-PCB at room temperature. Lower chlorinated congeners have much higher solubility in water than the more chlorinated congeners, and are more biodegradable.

Volatilization Flux for Zero water evaporation

The data from Table 2 was used to determine the volatilization flux of the PAHs and PCBs when the evaporation of water is zero. The soil conditions assumed were unit chemical concentration ($C_0 = 1 \text{ kg/m}^3$), soil organic fraction of 0.0075, soil porosity of 0.5, soil water content of 0.3 (air content = 0.2), soil density of 1.6 g/cc, water flux in the upward direction of 0.1 m/day and a depth of contamination of 0.1 m. These values were based upon the average of the parameters observed for sandy soils [8].

The volatilization flux decreased with time, as seen in Figures 2 (PCBs) and 3 (PAHs). Initially, the concentration at the surface of soil is high and therefore the diffusion of the chemicals is high. As surficial concentration decreases, flux is also decreased. Expectedly, higher order PAHs and PCBs showed lower volatility compared to their lower order chemicals.

Table 2. Properties of PAHs and PCBs.

Chemical	Mol. Wt	Henry's Law Const.	Diffusivity in Air x 10 ⁻²	Diffusivity in Water x 10 ⁻⁶	Bio-degradation Half-life (t _{1/2})	Soil Organic Carbon-Water Partitioning Coefficient (K _{ow} x 10 ³)
		(Pa m ³ /mol)	(cm ² /s)	(cm ² /s)	(hr)	(L/Kg)
Polyaromatic Hydrocarbons						
Naphthalene	128.2	43	5.9	7.5	775	7.1
Acenaphthalene	150.2	8.4	4.4	7.5	1372	2.8
Acenaphthene	154.2	12.2	4.2	7.7	1372	7.1
Fluorene	166.2	7.9	3.6	7.9	1104	13.8
Anthracene	178.2	3.96	3.2	7.7	6120	29.5
Phenanthrene	178.2	3.24	3.3	7.5	5500	26.5
Fluoranthene	202.3	0.96	3.0	6.4	17000	107.0
Pyrene	202.3	0.92	2.7	7.2	17000	105.0
Benzo[a]anthracene	228.3	0.58	5.1	9.0	17000	398.0
Chrysene	228.3	0.065	2.5	6.2	17000	7.1
Benzo[b]fluoranthene	252.3	0.069	2.6	5.6	17000	1230.0
Benzo[k]fluoranthene	252.3	0.016	2.6	5.6	17000	1230.0
Benzo[a]pyrene	252.3	0.046	4.3	9.0	17000	1020.0
Dibenz(a,h)anthracene	278.3	0.0017	2.0	5.2	17000	3800.0
Benzo(ghi)perylene	276.3	0.0014	2.0	5.3	14880	3860.0
Indeno(1,2,3-ed)pyrene	276.3	0.16	1.9	5.7	14880	3470.0
Polychlorinated Biphenyls						
Mono-CB	188.7	62.7	5.9	6.5	17000	18.1
Di-CB	223.1	60.7	5.6	6.4	26000	86.9
Tri-CB	257.5	68.5	5.4	6.2	55000	233.3
Tetra-CB	292.0	150.8	5.2	6.1	55000	514.2
Penta-CB	326.4	189.5	5.0	6.1	87600	1430.8
Hexa-CB	360.9	179.0	4.8	6.1	165000	5699.8
Hepta-CB	395.3	178.7	4.8	6.1	330000	11193.3
Octa-CB	429.8	128.1	4.8	6.1	330000	41241.4
Nona-CB	462.2	32.1	4.8	6.1	330000	36030.2
Deca-CB	498.7	20.8	4.8	6.1	330000	112201.8

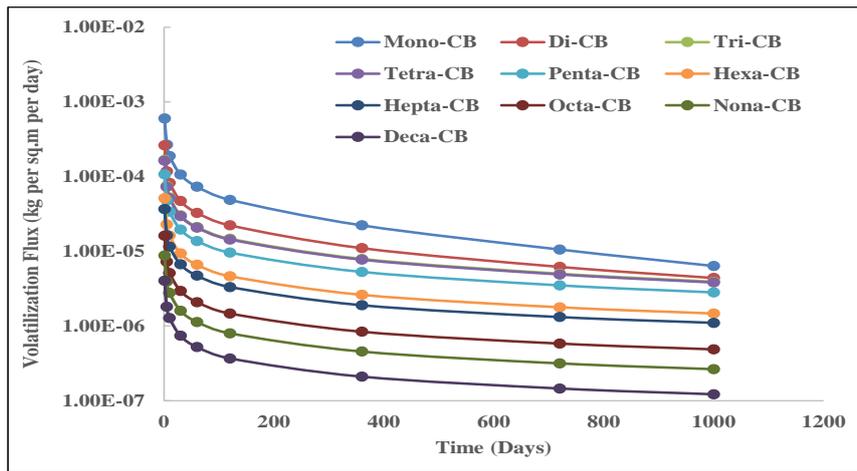


Figure 2. Volatilization flux of PCBs from soil vs. time in the absence of water evaporation.

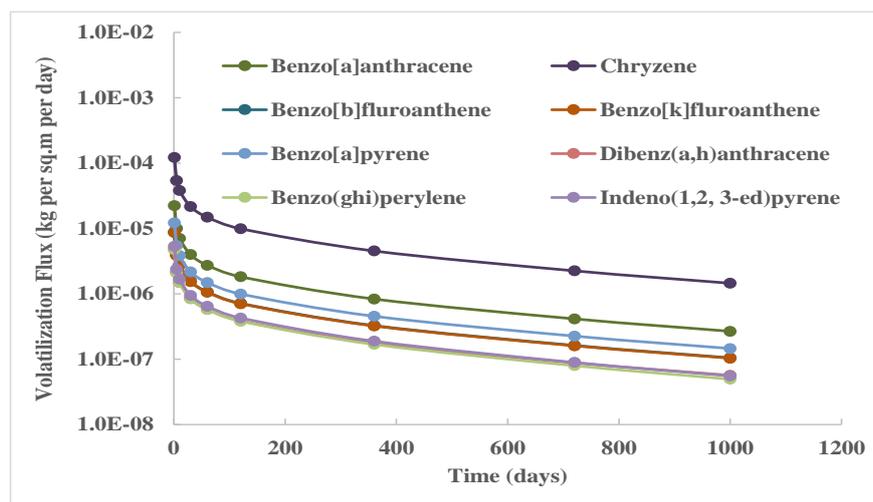
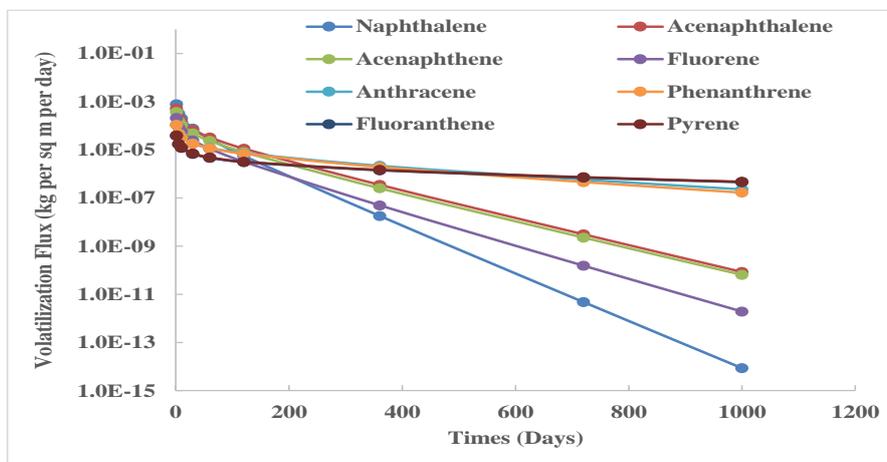


Figure 3. Volatilization flux of PAHs from soil vs. time in the absence of water evaporation.

Chiarenzelli *et al.* investigated the vaporization of PCBs from subaqueous sand and sediments for different Aroclors (composed of the PCB homologs) [12-13]. It was noted that 90% of lower chlorinated congeners in Aroclors vaporized, and almost none of the higher congeners. PCB vaporization rate, reported in several studies for contaminated river sediment ranged from 2×10^{-7} to 18×10^{-5} g/m²/hr [12-14]. The

vaporization rate is significantly lower than that observed for volatile organics, such as gasoline. Data for PAH volatilization for comparison is not available.

Volatilization Flux with Water Evaporation

As noted earlier, evaporation of water from the surface results in wicking process, which results in the movement of the chemical from the sub-surface soil to the surface. Using Equation (3), the volatilization flux of PCBs and PAHs was determined as a function of time (Figures 4 and 5).

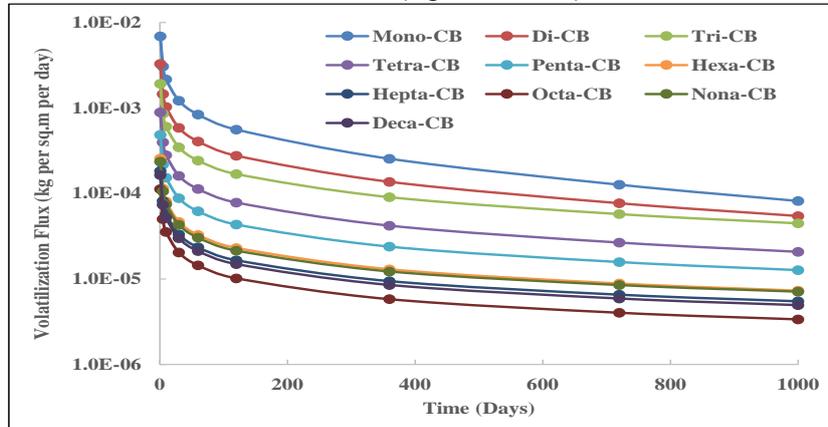


Figure 4. Volatilization of PCBs vs. time in the presence of water evaporation.

Despite PCBs being sparingly soluble in water, movement of water due to wicking and its subsequent evaporation increased the volatilization fluxes of PCBs. For example, the flux for mono-CB was almost 10 times higher (6×10^{-3} kg/m²/day) with water evaporation than without water evaporation (7×10^{-4} kg/m²/day). Similar trends was observed for PAHs as well. A comparison of Figures 4 & 5 with Figures 3 and 4 clearly indicate the water evaporation contributes significantly to the movement of the chemicals, despite their low solubilities.

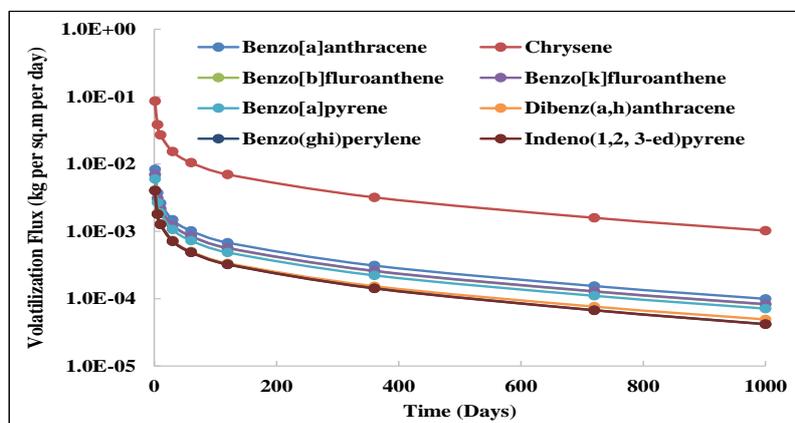
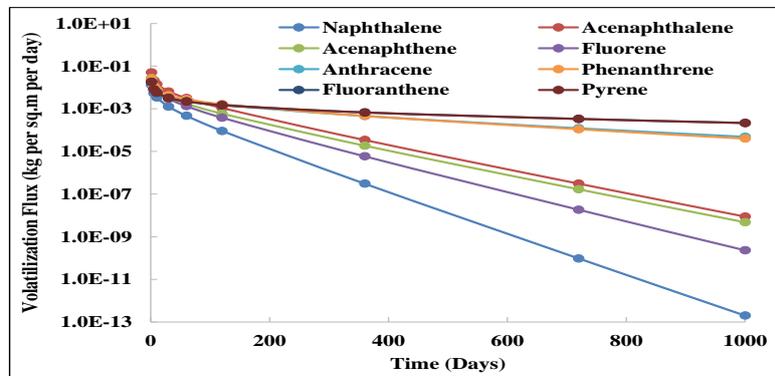


Figure 5. Volatilization flux of PAHs from soil vs. time in the presence of water evaporation.

Effect of Soil Properties on Volatilization Flux

Vaporization of PAHs and PCBs from soil is greatly influenced by soil properties such as organic carbon content, moisture, and porosity. Eduljee [15] reported reduced PCB evaporation rates in high organic matter-containing soils. PCB adsorption to soil organic matter reduces the activity of free PCBs, resulting in lower evaporation rates. Park et al. noted that volatilization of lower ringed PAHs accounted for their 20-30% loss from soils, and volatility of higher ringed PAHs was relatively low. In this study, the effect of soil organic carbon fraction, water content and soil porosity on volatilization flux was determined. Since the behavior of PAHs was largely dependent on the number of aromatic rings, select PAHs (i.e., a 3, 4, 5 and 6 ringed PAH) was selected. The soil conditions assumed were unit chemical concentration ($C_0 = 1 \text{ kg/m}^3$), soil density of 1.6 g/cc , soil porosity of 0.5, soil water content of 0.3 (air content = 0.2), water flux in the upward direction of 0.1 m/day and a depth of contamination of 0.1 m . If the soil porosity is varied, the soil water content is kept at 0.3, and therefore variation in soil porosity will result in variation in soil air content.

The effect of these soil properties was more profound on lower chlorinated PCB homologs compared to the higher chlorinated homologs (Figure 6). Volatilization flux decreased with increased soil organic carbon fraction because of increased binding of the SVOCs with the soil, and thereby decreasing flux. The effect of soil porosity was determined by varying soil porosity, and keeping the water content constant (i.e., air content increases with increasing soil porosity). A decrease in flux of PCBs with increasing soil porosity (and air content) strongly indicated that water flux and evaporation of water played a significant role in PCB evaporation. This was confirmed in the increase in vaporization flux observed with increased soil water content.

Volatilization flux of PAHs also behaved similarly to that of PCBs in that lower ringer aromatics volatilized faster than higher ringed PAHs. Similar to PCBs, increasing soil organic carbon decreased flux due to binding of PAHs to the soil. However, interesting behavior of the PAHs was observed with changes in soil porosity and water content. As soil porosity (or air content) increased, naphthalene flux decreased, while that of other higher ringed PAHs increased. Conversely, when soil water content increased, naphthalene flux increased while that of other higher ringer PAHs decreased. Both these findings suggest that naphthalene is more preferentially solubilized in water, and unlike PCBs, volatilization flux of PAHs is largely due its diffusion in air, rather than water flux evaporation.

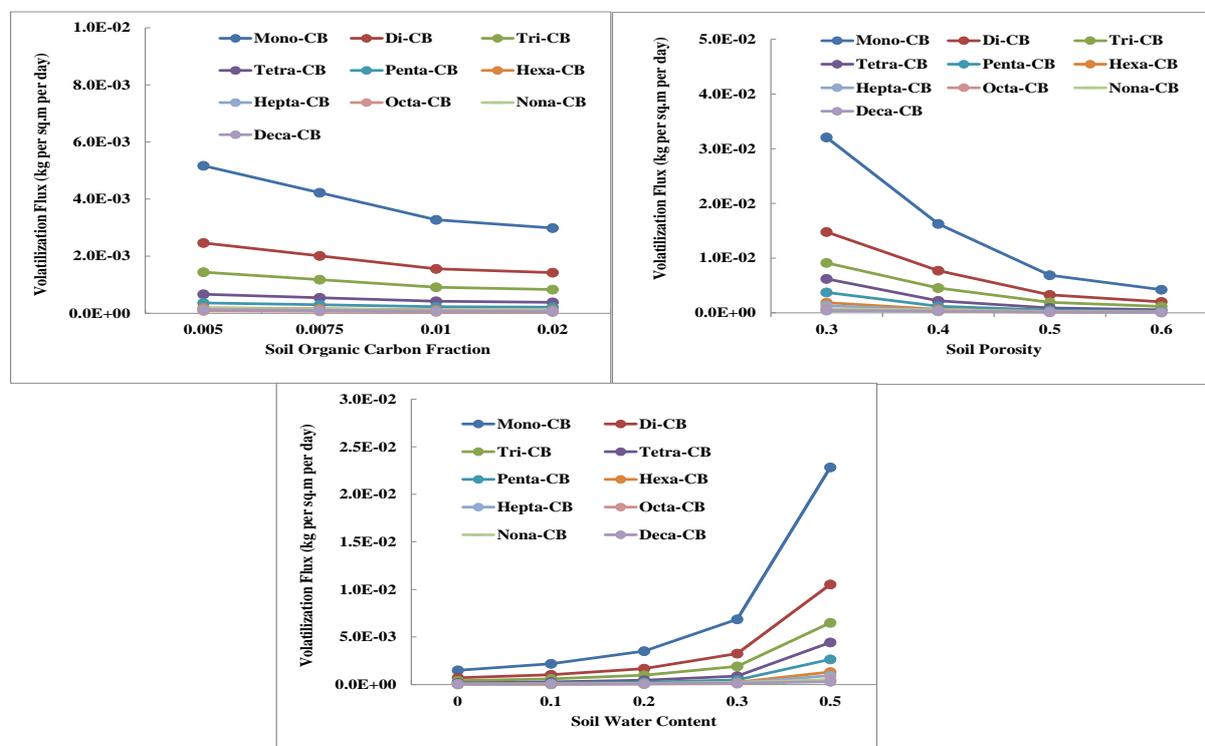


Figure 6. Volatilization flux of PCBs from soil as a function of various soil parameters.

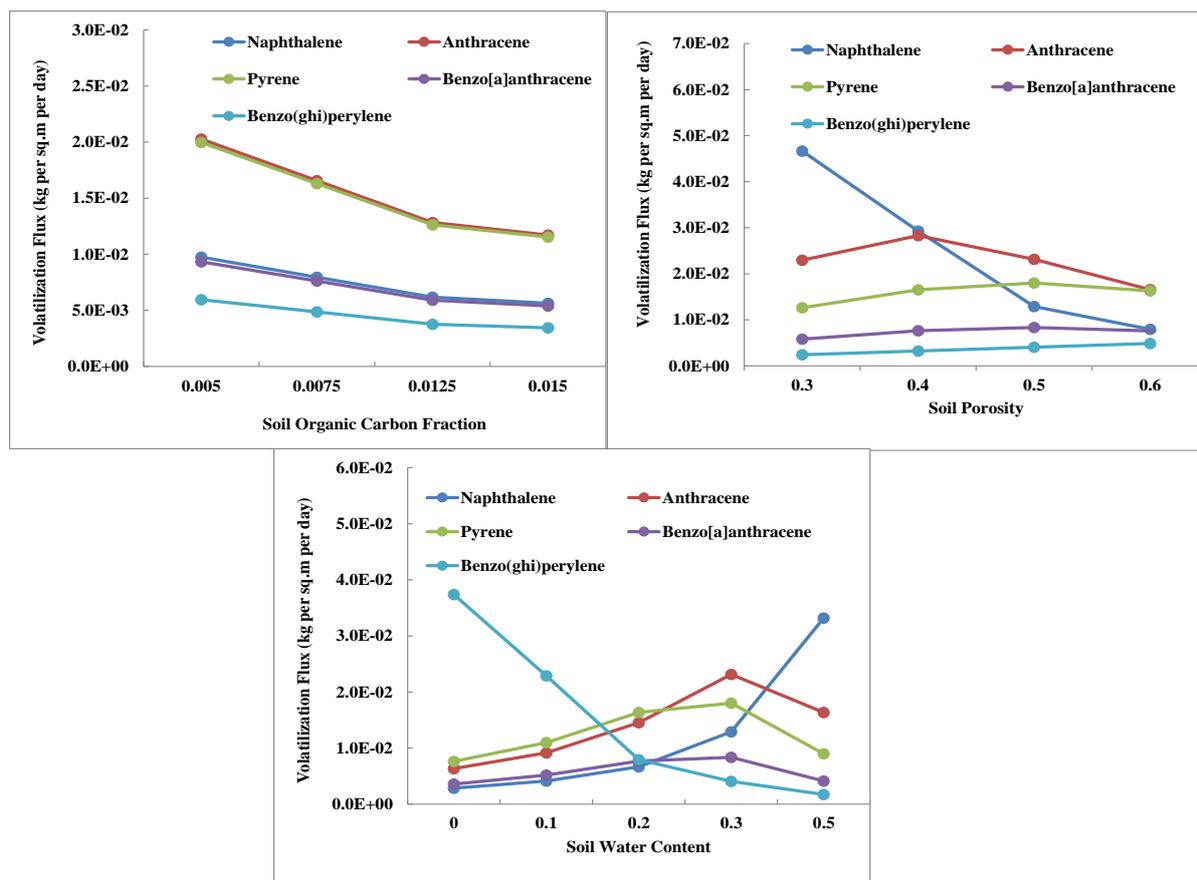


Figure 7. Volatilization flux of PAHs from soil as a function of various soil parameters.

CONCLUSIONS

The volatilization of semi-volatile organic compounds, PCBs and PAHs, was estimated using a modeling equation, which combines mass transport due to diffusion in air, diffusion in water, convective mass transport, evaporation, sorption and biodegradation of chemicals in soil. It was observed that volatilization flux decreased with time for both PCBs and PAHs. Lower molecular weight compounds and lower isomers of PAHs and PCBs have higher fluxes compared to higher molecular weight compounds. The effect of soil properties was also studied and it was observed that:

- Increase in soil organic matter decreased PAH and PCB fluxes due to increasing binding of the organic chemical to the soil.
- Increase in soil porosity generally decreased flux.
- Increased water flux and increased water evaporation will result in increased volatilization.

The results from this study can be used to estimate concentration of these SVOCs in the atmosphere from crude oil spills, and also to determine their rate of natural purification.

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