

Chapter 6. Volatilization

- transfer of chemicals from solids or liquids to the gaseous phase
- one of the loss mechanisms of contaminants from soil or water
- air pollution problem

1. The Governing Variables: Vapor Pressure and Henry's Law (p. 304)

1) Vapor pressure

- volatility of a pure compound
- the pressure exerted by a chemical on the atmosphere
- ranges from 10^{-10} mm Hg to 760 mm Hg at 20°C
- increases with temperature
- boiling point; the temperature at which a compound's vapor pressure reaches atmospheric pressure (760 mm Hg)

2) Henry' law

- volatility of a compound from the aqueous phase where the compound is dissolved (esp. a dilute contaminant)
- "the concentration of a compound in the aqueous phase is directly proportional to its partial pressure in the gaseous phase"

$$P = H \cdot X$$

P; partial pressure (atm)

H; Henry's law constant (atm·m³/mole)

X; concentration of the compound in water (mole/m³)

$$P = (P^0 - P_{\text{water}}) \cdot m$$

P; partial pressure

P⁰; atmospheric pressure (1 atm)

P_{water}; vapor pressure of water

m; mole fraction the compound in the air

- Henry's law constant; a partition coefficient between air and water

$$H = \frac{VP}{S_w}$$

H; Henry's law constant (atm·m³/mole)

VP; vapor pressure (atm)

S_w; water solubility (mole/m³)

- both vapor pressure and water solubility affect H

e.g) DDT vs. methanol

- chemicals with H less than 10⁻⁷

-> essentially non-volatile because water molecules evaporate faster than the chemical

-> become more concentrated (Fig. 6.1)

e.g.) dieldrin, benz(a)anthracene, 2,3,7,8-TCDD

e) influenced significantly by temperature, and an empirical equation available;

$$H = \exp\left(A - \frac{B}{T}\right)$$

A, B; empirical constants (Table 6.2)

T; temperature (°K)

f) dimensionless Henry's law constant;

$$H' = \frac{H}{RT} \quad (\doteq 41H)$$

g) Table 6.1 and Appendix J for VP and H

2. Volatilization from Open Containers (p. 306)

2.1. Volatilization fluxes across liquid surfaces

a) open system

b) vaporization rate is proportional to the difference between the chemical's vapor pressure and its steady state partial pressure

$$Q \propto (P_{\text{sat}} - P)$$

Q; evaporation rate (mass/time)

P_{sat} ; vapor pressure of the compound (atm)

P; partial pressure of the compound above the liquid (atm)

$$Q = \frac{MKA (VP - P)}{RT}$$

Q; evaporation rate (g/sec)

M; molecular weight of the compound (g/mole)

K; mass transfer coefficient per area A (m/sec)

since open system is considered $P \rightarrow 0$ (partial pressure = 0),

$$Q = \frac{MKA \cdot VP}{RT}$$

c) estimating mass transfer rate (K_1) using a reference (water, K_2); Example 6.1

$$\frac{K_1}{K_2} = \left(\frac{D_1}{D_2}\right)^{2/3}$$

K_1, K_2 ; mass transfer coefficients for compound 1 and 2

D_1, D_2 ; corresponding gas diffusion coefficients

$$\frac{D_1}{D_2} = \sqrt{\frac{M_2}{M_1}}$$

M_1, M_2 ; corresponding molecular weights

finally,

$$K_1 = K_2 \left(\frac{M_2}{M_1}\right)^{1/3} \quad (K_2; 0.83 \text{ cm/sec}, M_2; 18 \text{ g/ mole})$$

2.2. Saturation concentration in an enclosed area

a) mass balance on the enclosed space (Fig. 6.3)

$$\frac{VdC}{dt} = Q_m - kQ_vC$$

C; vapor phase conc. of the compound (g/m³)

V; volume of the enclosed area (m³)

Q_m; volatilization rate of the compound (g/sec); Q in open system

Q_v; ventilation rate for the enclosed area (m³/sec)

k; a factor accounting for incomplete mixing (0.1 - 0.5)

assuming steady state, $\frac{VdC}{dt} = 0$

therefore, $C = \frac{Q_m}{kQ_v}$

b) if necessary, convert C into C_{ppm}

$$C_{ppm} = \frac{Q_m RT}{kQ_v PM} \times 10^6$$

P; absolute pressure (atm)

M; molecular weight (g/mole)

c) Example 6.2

3. Volatilization from Soils (p. 316)

- volatilization calculations are inherently prone to error

3.1. Environmental and chemical properties affecting volatilization from soils

- Fig. 6.4

- governing variables; sorption, soil water content, diffusion, temperature, wind

a) sorption

- the most important mechanism affecting transport, transformation, toxicity
- also greatly influences volatilization of contaminants
- "Conceptually, sorbed compounds need to be desorbed and dissolved into the aqueous phase first before the compounds are volatilized"
- vapor phase conc. related to surface area, organic carbon content

b) volumetric water content (*mainly for VOCs on mineral surfaces*)

- at low moisture content, contaminants (mainly nonpolar, slightly polar) are sorbed on soil (esp. mineral surfaces) -> less volatile
- as moisture content increases, water molecules compete with the sorbed contaminants for available sorption sites
 - > contaminants desorbed
 - > become more volatile
- also, ample amount of water itself works as a partitioning medium for the contaminants (i.e., at least to the water solubility)

c) diffusion

- "diffusion through pore space is usually a rate-limiting process for contaminant volatilization"
- diffusion can occur through gaseous phase and aqueous phase (aqueous phase diffusion < gas phase diffusion, app. 10^{-4} times difference)
- volumetric water content affects aqueous phase diffusion
- bulk density (porosity) affects gaseous phase diffusion

d) temperature

- not much temperature change -> insignificant variable

e) wind and atmospheric turbulence

- creates higher conc. gradients -> more volatilization
- only near the soil surface

3.2. Volatilization from soil surfaces

- assumes to follow first-order kinetics

$$-\frac{dC}{dt} = kC \quad \rightarrow \quad C_t = C_0 \cdot e^{-kt}$$

$$t_{1/2} = \frac{0.693}{k}$$

- volatilization rates increase with vapor pressure and decrease as a function of K_{OC} and water solubility

$$k \text{ (volatilization rate constant, day}^{-1}\text{)} = 4.4 \times 10^7 \frac{VP}{K_{OC} \cdot S_w}$$
$$\text{(} = 4.4 \times 10^7 \frac{H}{K_{OC}} \text{)}$$

3.3. Volatilization from deep soil contamination

- Hartley equation
- Hamaker equation

4. Volatilization of Metals and Inorganic Nonmetals (p. 327)

- generally, metals and inorganic nonmetals show low volatilities
- once methylated, volatility increases (e.g., methylated As & Hg)
- hydrogen cyanide most volatile among inorganic nonmetals

■ 토양포화농도와 포화증기농도

1. 토양포화농도 (Soil Saturation Concentration)

어떤 토양에서 오염물질이 NAPL로 존재하는가는 오염물질의 토양 내 포화한계농도 (soil saturation limit)를 기준으로 판단할 수 있다. 토양포화농도 (soil saturation concentration, C_{sat})는 토양입자에 흡착된 농도, 토양 공극수에 용해된 농도, 토양 공극 내 공기 중의 농도의 합이므로 만약 토양에 존재하는 오염물질의 농도가 그 합을 초과한다면 그 초과된 부분이, 액상 오염물질인 경우는 NAPL 상태로, 고체상 오염물질의 경우는 고체로 존재한다고 간주할 수 있다. 오염물질의 토양포화농도는 다음 식으로 계산할 수 있다.

$$C_{sat} = (S/\rho_b) * (K_d\rho_b + \Theta_w + H'\Theta_a)$$

Parameter/Definition (unit)	Nature	Default value
C_{sat} /soil saturation concentration (mg/kg)	site-specific	calculated
S/solubility in water (mg/L-water)	chemical-specific	-
ρ_b /dry soil bulk density (kg/L)	site-specific	1.5
K_d /soil-water partition coefficient (L/kg)	site-specific	$K_{oc} \times f_{oc}$
K_{oc} /soil organic carbon-referenced K_d (L/kg)	chemical-specific	-
f_{oc} /fraction organic carbon of soil (g/g)	site-specific	0.006 (0.6%)
Θ_w /water-filled soil porosity (L_{water}/L_{soil})	site-specific	0.15
H' /dimensionless value of H	chemical-specific	$H \times 41$
H/Henry's Law constant ($atm \cdot m^3/mol$)	chemical-specific	-
Θ_a /air-filled soil porosity (L_{air}/L_{soil})	site-specific	0.28 ($n - \Theta_w$)
n /total soil porosity (L_{pore}/L_{soil})	site-specific	0.43 ($1 - \rho_b/\rho_s$)
ρ_s /soil particle density (kg/L)	site-specific	2.65

토양포화농도 (C_{sat})는 토양의 특성, 오염물질의 종류 등에 따라서 그 값이 변하게 되며 오염물질의 총 농도가 C_{sat} 수준을 넘어서게 되면 위 계산의 기본 전제가 되는 Henry's Law가 더 이상 적용되지 않는다.

◎ 평균토양함수율

평균토양함수율 (average soil moisture content, Θ_w)은 토양의 총 공극 중 물이나 공기로 채워진 부분으로 정의되며 다음 식을 이용하여 계산할 수 있다.

$$\Theta_w = n * (I/K_s)^{1/(2b+3)}$$

- n; total soil porosity
- I; infiltration rate (m/yr)
- K_s ; saturated hydraulic conductivity (m/yr)
- b; soil-specific exponential parameter (unitless)

평균토양함수율은 일년을 기준으로 오염지역에서의 평균적인 토양함수율을 뜻하는 것이며 따라서 현장조사 시 시료채취를 통하여 직접 측정한 토양의 함수율과는 다를 수 있다. 따라서 평균토양함수율은 반드시 위 식을 이용하여 구한 값을 사용하여야 하는데 그 이유는 시료채취 이전의 기후조건에 의해 토양의 함수율은 가변적이므로 특정 시점에 측정한 현장의 함수율을 그 토양의 평균토양함수율로는 볼 수는 없기 때문이다. 평균토양함수율을 구하기 위하여서는 K_s 와 b값이 필요한데 토양의 입자구성에 따른 토양조직별 대표값은 다음과 같다 (US EPA 자료).

Soil texture	K_s (m/yr)	$1/(2b+3)$
sand	1,830	0.090
loamy sand	540	0.085
sandy loam	230	0.080
silt loam	120	0.074
loam	60	0.073
sandy clay loam	40	0.058
silt clay loam	13	0.054
clay loam	20	0.050
sandy clay	10	0.042
silt clay	8	0.042
clay	5	0.039

(* 참고: 위 표에는 'silt'는 포함되어 있지 않음)

토양의 총 공극성 (total soil porosity, n)은 토양건조밀도 (dry soil bulk density, ρ_b)로부터 아래의 식을 이용하여 구할 수 있다.

$$n = 1 - (\rho_b/\rho_s)$$

현장 특이적 계수인 침투율 (infiltration rate, I)은 HELP (hydrological evaluation of landfill performance) 모델을 이용하여 예측하거나 자연적인 재충전율 (recharge)과 동일하다고 가정할 수 있는데 ASTM (American Standards for Testing and Materials)에서는 보수적인 기본값으로서 토지이용용도에 상관없이 30 cm/yr를 이용하고 있다.

2. 포화증기농도

포화증기농도는 특정 온도에서 열역학적 평형이 이루어진 상태에서 어떤 순수한 물질이 공기 중에 존재할 수 있는 최대농도이며 포화증기압 (vapor pressure, V_p)으로부터 다음과 같이 계산된다.

$$C_{\text{sat-vap}} \text{ (mg/m}^3\text{-air)} = \left(\frac{V_p}{760 \text{ mmHg/atm}} \right) \left(\frac{MW}{RT_{\text{amb}}} \right) (1,000,000 \frac{\text{mg/m}^3}{\text{g/L}})$$

Parameter (unit)	Definition	Default value
MW (g/g-mol)	molecular weight	chemical-specific
R (atm-L/g-mol-K)	ideal gas constant	0.08206
T_{amb} (K)	ambient temperature	293
V_p (mm Hg)	saturated vapor pressure	chemical-specific

☞ 오염물질의 토양포화농도, 포화증기농도는 각 매질 (토양, 대기)에 최대 존재할 수 있는 오염물질의 농도임 (물에 대한 용해도의 개념과 유사).