

Simulating Fate and Transport of Volatile Organic Compounds inside Sewer Systems

Supporting Material

I.1 Calculating Liquid-Gas Mass Transfer

Interfacial VOCs mass transfer flowrate between liquid phase and gas phase can be estimated by the two-film theory equation:

$$R_{liquid-gas} = -K_T \cdot (C_l - \frac{C_g}{H_c}) \cdot A \quad (I.1)$$

$R_{liquid-gas}$ = mass transfer rate of VOC between liquid and gas phase, (mg/s);

K_T = overall mass-transfer coefficient for chemical “i”, (m/s);

C_l = concentration of the chemical “i” in the liquid phase, (mg/m³);

C_g = concentration of the chemical “i” in the gas phase, (mg/m³);

H_c = Henry's law constant for the chemical “i”, (m³ liquid/m³ gas);

A = interfacial contact area between wastewater and air, (m²).

The equilibrium concentration is defined based on this partitioning. K_T can be calculated by equation below:

$$\frac{1}{K_T} = \frac{1}{K_l} + \frac{1}{K_g \times H_c} \quad (I.2)$$

Which k_l is the liquid phase mass transfer coefficient (m/s) and k_g is the gas phase mass transfer coefficient (m/s). Parkhurst and Pomeroy (1972) developed a semi-empirical model for oxygen mass transfer coefficient. They tested 12 operating municipal sewer systems and by applying the mass balance equations, they calculated the mass transfer coefficients for oxygen in different conditions. Based on the results they developed a numerical model by using a non-linear regression:

$$K_{lo} = 2.6 \times 10^4 \times (1 + 0.17Fr^2) \cdot \delta \cdot (S \cdot U)^{3/8} \quad (I.3)$$

K_{lo} = the liquid mass transfer coefficient for oxygen, (m/s);

S = slope of the energy gradient, (m/m);

U = average velocity of wastewater, (m/s);

δ = temperature correction factor, dimensionless;

Fr = Froude number.

The Froude number is a dimensionless number. It is defined as the ratio between inertial forces and gravitational forces and calculated by the equation below:

$$Fr = \frac{U_l}{(g \cdot d)^{0.5}} \quad (I.4)$$

U_l = the liquid (wastewater) velocity, (m/s);

g= gravitational constant, 9.81 (m/s²);
d= depth of the liquid (wastewater) flow, (m).

The empirical Manning's equation that has been used for uniform flows in channels since 1889, is used in the model to estimate correlation between the sewer liquid velocity and the depth of the liquid inside the sewer system, shown in Equation I.5.

$$U_l = \left(\frac{k}{n}\right) \cdot \left(\frac{A}{P}\right)^{\frac{2}{3}} \cdot S^{0.5} \quad (I.5)$$

k = conversion factor, (1.49 for English units and 1.0 for SI units).
n = Manning's roughness coefficient.
A =flow area of the pipe, culvert, or channel, (m²);
P =wetted perimeter (portion of the circumference that is in contact with water), (m);
S =downward (longitudinal) slope of the culvert, (m/m).

It has been shown that for chemicals with H_c>0.1, the liquid mass transfer coefficients are proportional to the liquid molecular diffusion coefficients (Higbie, 1935 & Lewis and Whitman, 1924).

$$\frac{K_{l,1}}{K_{l,2}} = \left(\frac{D_1}{D_2}\right)^n \quad (I.6)$$

Which D_i is the molecular diffusion coefficient for chemical "i" (m²/s) and "n" is the power constant, theoretically varies between 0.5 and 1. In a well-mixed system "n" is normally assumed to be 0.5. The sewer system due to its nature can be consider as a mixed system and therefore "0.5" has been used as the value for "n" in the sewer systems (Parker and Yu, 2001). The liquid mass transfer coefficient for any VOC in this model is estimated by calculating the oxygen liquid mass transfer coefficient (Equation I.3) and applying Equation I.6 for converting this value to the targeted VOC's liquid-gas mass transfer coefficient.

I.2 Calculating Vapor Diffusion

This diffusive flow can be calculated by using equation below:

$$R_{diffusion,in} = D_{effective} \cdot A_{pipe} \cdot F_{cracked} \cdot \left(\frac{dc}{dx}\right)_{groundwater-ground} \quad (I.7)$$

R_{diffusion, in} = VOC mass flow through diffusion, (mg/s);
D_{effective} = effective diffusive coefficient of VOC, (m²/s);
A_{pipe}= area of the pipe, (m²);
F_{cracked} = average cracked ratio of the pipe, (m²/m²);
 $\left(\frac{dc}{dx}\right)_{groundwater-ground}$ = VOC concentration gradient form groundwater to the ground surface, ((mg/m³)/m).

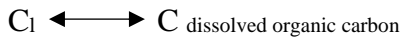
Accumulation of VOCs inside the sewer system through different mechanisms, creates an elevated concentration of VOC inside the sewer system compare to the surrounding soil gas and atmosphere. This contaminated sewer gas can act a new source of VOC. VOC vapors can also leave the sewer system through cracks of the sewer pipe by diffusion due to the VOC concentration gradient. This diffusive mass transfer leaving the sewer system can be estimated by using equation below.

$$R_{diffusion,out} = D_{effective} \cdot A_{pipe} \cdot F_{cracked} \cdot \left(\frac{dc}{dx}\right)_{sewer\ gas-ground\ surface} \quad (I.8)$$

Which $\left(\frac{dc}{dx}\right)_{sewer\ gas-ground\ surface}$ is the average gradient of the soil gas VOC concentration from the sewer gas to the ground surface.

I.3 Calculating Sorption

Partitioning of VOCs in the aqueous phase between dissolved organic carbon and liquid phase can be described as:



$$K_{oc} = \frac{C_{dissolved\ organic\ carbon}}{C_l} = \frac{\frac{C_d}{S_d}}{C_l} \quad (I.9)$$

K_{oc} = dissolved organic carbon-water partitioning coefficient, (L water/Kg DOC);

$C_{dissolved\ organic\ carbon}$ = VOC concentration adsorbed on DOC, (g VOC/ Kg doc);

C_d = concentration of VOC that bound on DOC, (g VOC/L water);

S_d = dissolved organic compound concertation in sewer liquid, (Kg doc/L water);

C_l = sewer liquid VOC concentration, (g VOC/L water).

In a sewer system containing active sludge, VOC adsorption on the surface of sludge is a possible scenario. Biological cells adsorb VOCs and partition between a specific VOC on aqueous phase and biological suspended solids can be described by:



$$K_p = \frac{C_{suspended\ solid}}{C_l} = \frac{\frac{C_s}{S_s}}{C_l} \quad (I.10)$$

K_p = suspended solid-water partitioning coefficient (L water/Kg SS);

$C_{suspended\ solid}$ = VOC concentration sorbed on SS, (g VOC/ Kg SS);

C_s = concentration of VOC that bound on suspended solid, (g VOC/ L water);

S_s = suspended solid concertation in sewer liquid (Kg SS /L water).

Suspended solid-water partitioning coefficient (K_p), can be calculated by using the organic carbon-water partitioning coefficient (K_{oc}) (USEPA, 1993).

$$K_p = f_{oc} \times K_{oc} \quad (I.11)$$

$$K_{oc} = \frac{\text{VOC concentration sorbed on organic carbon}(\frac{g}{kg})}{\text{VOC concentration in water}(\frac{g}{L})}$$

f_{oc} = fraction of organic carbon in the solids, (g/g).

The K_{oc} values for several VOCs are available in the table provided by USEPA (USEPA, 1996). There are also few equations available for estimating K_{oc} value for different compounds. These equations typically use the octanol-water partitioning coefficient value (K_{ow}) of the compound to estimate K_{oc} . Equation below is one of the equations that has been suggested for VOCs (Weiner, 2012). The K_{oc} value calculated by this equation has the unit of liter per kilogram (L/kg).

$$\log K_{oc} = 0.7919 \log K_{ow} + 0.0784 \quad (I.12)$$

Karickhoff et al. (1979) suggested Equation I.13 for estimating the K_p value for hydrophobic pollutants. Namkung and Rittmann (1987), used this equation for VOC's adsorption in wastewater studies to calculate VOC emission rate at water treatment plants. They consider $C_5H_7O_2N$ as the representative formula for biological cells in a wastewater system and based on this assumption calculated the organic carbon fraction (f_{oc}) = 0.531. Equation I.14 is calculated based on this estimation for f_{oc} and is used to calculate K_p .

$$K_p = 6.3 \times 10^{-7} f_{oc} \cdot K_{ow} \quad (I.13)$$

$$K_p = 3.345 \times 10^{-7} \cdot K_{ow} \quad (I.14)$$

The rate of the VOC adsorption on dissolved organic carbon ($R_{adsorption-DOC}$ (g/s)) and suspended solid ($R_{adsorption-SS}$ (g/s)) can be calculated by applying Equations I.15 and I.16 respectively.

$$R_{adsorption-DOC} = Q_l \cdot C_l \cdot S_d \cdot K_{oc} \quad (I.15)$$

$$R_{adsorption-SS} = Q_l \cdot C_l \cdot S_s \cdot K_p \quad (I.16)$$

By assuming that VOCs inside a sewer system, only can be adsorbed on the suspended solid and dissolved organic carbon, the total VOC adsorption rate can be calculated by applying Equation I.17. It worth to note that non-dispersible materials such as wet wipes that exist inside the sanitary sewer systems could be another potential adsorbent for VOCs. They are not considered in this model due to the lack of information about their typical concentrations inside the sewer system.

$$\begin{aligned}
R_{adsorption} &= R_{adsorption-DOC} + R_{adsorption-SS} = Q_l \cdot C_l \cdot (S_d \cdot K_{oc} + S_s \cdot K_p) \\
&= Q_l \cdot C_l \cdot K_{oc} \cdot (S_d + S_s \cdot f_{oc})
\end{aligned}
\tag{I.17}$$

I.4 Calculating Biodegradation

The biological degradation rate can be estimated by using Monod kinetics model (Monod, 1949).

$$R_{biodegradation} = \frac{K_{max} S_s C_l V_l}{K_s + C_l} \tag{I.18}$$

$R_{biodegradation}$ = biological reaction rate, (g/s);

S_s = biological suspended solid concentration in the wastewater, (g VSS/m³);

K_{max} = maximum specific substrate utilization, (g/s. g bio);

K_s = half saturation constant, (g/m³);

C_l = Sewer liquid VOC concentration (g/m³);

V_l = Sewer liquid phase volume (m³).

VOC's water solubility is limited and its concentration in wastewater and sewer liquid is relatively low (Corsi and Card, 1991; Yaghmei and Rashidkhani, 2005), so $C_l \ll K_s$ and therefore Equation I.18 can be simplified as:

$$R_{biodegradation} = K_l S_s C_l V_l \tag{I.19}$$

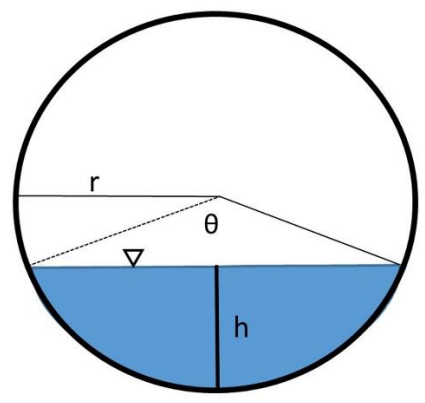
K_l = apparent first-order biological reaction constant ($= \frac{K_{max}}{K_s}$), (m³/g VSS.s).

I.5 Calculating Sewer Liquid Information

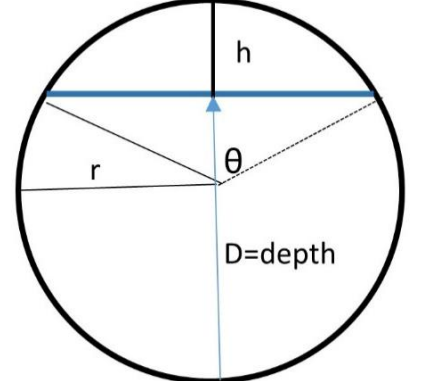
The first step for the modeling of VOC mass transfer within a sewer system is to define the hydraulic properties for the system. The sewer liquid depths, sewer liquid velocities and the total liquid volume all over the sewer system need to be calculated based on the given information. Depth of the sewer liquid (or flowrate of the sewer liquid) on the upstream boundaries of the sewer system and any tributaries flows should be defined. Based on the system's information such as pipes diameters, pipe's material and sewer system slopes, sewer liquid velocity and the sewer depth all over the system will be calculated by using equations in Table I.1.

Table 1 Sewer Liquid Calculation

a) For sewer liquid depth < Sewer pipe radius

	h = depth of the sewer liquid	
	Central angle (θ): $2 \cdot \arccos(\frac{r-h}{r})$	(I.20)
	Flow area (A_l): $\frac{r^2 \cdot (\theta - \sin(\theta))}{2}$	(I.21)
	Wetted perimeter (P_w)= $r \times \theta$	(I.22)
	Hydraulic radius (R_h)= $\frac{A_l}{P_w}$	(I.23)
	$U_l = (\frac{1}{n}) \cdot (R_h)^{2/3} \cdot (S)^{0.5}$	(I.5)
	Liquid flow rate (Q_l)= $U_l \cdot A_l$	(I.24)
	Total flow rate(Q_t) = $Q_l + Q_{tributary}$	(I.25)
	Liquid Volume V_l = $A_l \cdot L$	(I.26)

b) For sewer liquid depth > Sewer pipe radius

	$h = (2r) - (\text{depth of the sewer liquid})$	(I.27)
	Central angle (θ): $2 \cdot \arccos(\frac{r-h}{r})$	(I.20)
	Flow area (A_l): $\pi r^2 - (\frac{r^2 \cdot (\theta - \sin(\theta))}{2})$	(I.28)
	Wetted perimeter (P_w)= $2\pi - (r \cdot \theta)$	(I.29)
	Hydraulic radius (R_h)= $\frac{A_l}{P_w}$	(I.23)
	$U_l = (\frac{1}{n}) \cdot (R_h)^{2/3} \cdot (S)^{0.5}$	(I.5)
	Q_l, Q_t and V_l are calculated by Equations I.24, I.25 and I.26 respectively.	

L = length of the each sewer pipe between two manhole(m).

r =sewer pipe radius (m);

I.6 Calculating Sewer Headspace Velocity

The sewer headspace velocity needs to be calculated for each sewer section. It is assumed that Equation I.30 dictates the relation between the sewer liquid velocity and sewer headspace velocity all over the sewer system. For using this equation, we need to calculate width of the water surface and headspace perimeter for each section. Equations below shows how these parameters are calculated.

Table 2 Sewer Headspace Calculations

a) For sewer liquid depth < Sewer pipe radius

$U_g = 0.397(W \cdot U_l / P_{air})^{0.7234}$	(I.30)
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$W(\text{width of the water surface}) = 2.r.\sin\left(\frac{\theta}{2}\right)$	(I.31)
$P_{\text{air}}(\text{headspace perimeter}) = r.(2\pi - \theta)$	(I.32)
$\text{Headspace area } (A_H) = \pi r^2 - \left(\frac{r^2.(\theta - \sin(\theta))}{2}\right)$	(I.33)
$\text{Sewer gas flow rate } (Q_g) = U_g \cdot A_H$	(I.34)
$V_g = A_H.L$	(I.35)

b) For sewer liquid depth > Sewer pipe radius

$W (\text{width of the water surface}) = 2. r. \sin\left(\frac{\theta}{2}\right)$	(I.31)
$P_{\text{air}}(\text{headspace perimeter}) = r.(\theta)$	(I.36)
$\text{Headspace area } (A_H) = \left(\frac{r^2.(\theta - \sin(\theta))}{2}\right)$	(I.37)
Q_g and V_g are calculated by Equations I.34 and I.35 respectively.	

θ (central angle) is calculated using Equation I.20.

L = length of the sewer pipe between two manholes (m).

r =sewer pipe radius (m);

I.7 Calculating Diffusion Coefficient of VOCs in Soil

The diffusion coefficient in a porous media such as soil can be calculated using both the VOC-water diffusion coefficient (D_w) and the VOC-air diffusion coefficient (D_a) by applying Millington quirk equation (1961):

$$D_{\text{effective}} = D_a \left(\frac{\theta_a^{10/3}}{\theta_t^2} \right) + \frac{D_w}{H_c} \left(\frac{\theta_w^{10/3}}{\theta_t^2} \right) \quad (\text{I.38})$$

θ_a = air porosity (volumetric soil gas content), (m^3/m^3)

θ_w = water porosity (volumetric water content), (m^3/m^3)

θ_t = total porosity of the soil ($\theta_t = \theta_w + \theta_a$)

Equation I.38 is used in this model to calculate soil's diffusion coefficient for the targeted VOC based on soil characteristics such as soil total porosity and water content.

I.8 Drop Structure Equations

Rahme et al. (1997) used the equations below based on a non-regression analysis performed on 48 different oxygen transfer experiments. Equations I.39-I.42 suggested by their study are used to calculate VOCs mass transfer between liquid and gas phases in a drop structure.

$$\text{Fraction Emitted} = \frac{r_v - 1}{r_v + B \cdot r_v - B} \quad (\text{I.39})$$

$$\ln(r_0) = 1.081 \times h^{0.784} \times Q_l^{-0.139} \quad (\text{I.40})$$

$$r_v = r_0^{F \cdot \alpha \cdot \Psi} \quad (\text{I.41})$$

$$B = \frac{Q_l}{Q_g \cdot H_c} \quad (\text{I.42})$$

r_o = oxygen deficit ratio, dimensionless;

r_v = VOC deficit ratio, dimensionless;

h = drop height, (m);

Q_l = liquid flow rate (m^3/min);

$$\Psi = \frac{k_{l,\text{VOC i}}}{k_{l,\text{O}_2}} = \left(\frac{D_{\text{VOC i}}}{D_{\text{O}_2}} \right)^n$$

α = effect of contamination in the water on VOC diffusion in water;

F = correction coefficient.

Ψ is the diffusion coefficient of VOC in water relative to the diffusion coefficient of oxygen in the water and “ n ” is typically considered= 0.5 in a sewer system. The F value depends on several parameters such as H_c and liquid-gas mass transfer coefficient. This value is assumed to be 1 unless there is a significant stripping due to air entrainment. The value of α is typically assumed to be 1 (Labocha et al., 1994).