

Toxchem V4.3

Modeling the Fate of Toxics in Wastewater Treatment Plants



TECHNICAL GUIDE

Copyright ©1992-2014

Hydromantis Environmental Software Solutions, Inc. (HESS, Inc.)

All rights reserved

No part of this work covered by copyright may be reproduced in any form or by any means - graphic, electronic or mechanical, including photocopying, recording, taping, or storage in an information retrieval system - without the prior written permission of the copyright owner.

The information contained within this document is subject to change without notice. HESS, Inc. makes no warranty of any kind with regard to this material, including, but not limited to, the implied warranties of merchantability and fitness for a particular purpose. HESS, Inc. shall not be liable for errors contained herein or for incidental consequential damages in connection with the furnishing, performance, or use of this material.

Trademarks

Toxchem and all other Hydromantis trademarks and logos mentioned and/or displayed are trademarks or registered trademarks of HESS, Inc. in Canada and in other countries.

Adobe and Acrobat are trademarks of Adobe Systems Incorporated

JAVA is a trademark of Sun Microsystems, Inc.

Microsoft, Windows, Windows NT, Windows 98, Windows 2000, Windows ME, and Windows XP, Windows 7 and Windows 8 are trademarks of Microsoft Corporation.



Contents

Contents.....	3
1. TOXCHEM MODELS.....	5
1.1 Fate and Transport Mechanisms.....	5
Liquid-Gas Mass Transfer.....	5
Sorption.....	22
Biodegradation.....	26
Temperature Correction of Sensitive Parameters.....	31
1.2 Flow/Mass Distribution in Process Streams.....	43
1.3 Contaminant Mass Balances in Unit Processes.....	46
Open Versus Closed/Covered Unit Processes.....	46
Sewer Reaches - Closed.....	46
Sewer Reaches - Open.....	48
Drop Structures – Closed.....	49
Drop Structures – Open.....	51
Process Drain.....	52
Lift Stations.....	52
Bar Screen Process.....	53
Grit Chambers.....	54
Primary Clarifier/Secondary Clarifier/Sludge Thickener.....	55
Weir Process.....	57
Equalization Basins.....	57
Equalization – Mixed/Aerated.....	58
Closed Surge Tank.....	59
Floating Roof Tank.....	60
Channels.....	61
API Separator.....	63
Dissolved Air Flotation.....	65
Activated Sludge – Anaerobic/Anoxic.....	67
Diffused Bubble Aeration Basins.....	68

Mechanical Aeration Basins	70
Combined Diffused and Mechanical Aeration Basins.....	71
High Purity Oxygen (HPO) Reactor.....	73
Sequencing Batch Reactor (SBR)	75
Membrane Bioreactor	78
Aerated Lagoon	79
Trickling Filters.....	80
Rotating Biological Contactors	83
Cooling Towers.....	86
Polishing Ponds.....	87
Chlorine Disinfection.....	88
Anaerobic Digestion.....	91
Aerobic Digestion	91
Water Scrubber.....	93
Generic Sludge Dewatering.....	94
Centrifuge	94
Belt Filter Press	95
Sludge Drying Bed	95
Concentrator	96
Sludge Drying	98
Conveyor	103
Incinerator.....	104
Fly ash / Dust removal.....	104
Settling Pond.....	104
1.4 Metals Modeling.....	104
Influent mass balance.....	105
Biological Processes Mass Balances.....	106
Digester Processes Mass Balances.....	107
Solid Handling Processes Mass Balances.....	108
Stream mixing	109
Glossary of Terms.....	110
References	119

1. TOXCHEM MODELS

The Toxchem models incorporate a number of fate mechanisms for toxic contaminants into process specific mass balance equations. In the following sections the relationships defining the individual fate and transport mechanisms are initially presented. The process-specific mass balance equations are presented subsequently.

1.1 Fate and Transport Mechanisms

Liquid-Gas Mass Transfer

Volatile contaminants may be removed from wastewater by volatilization into the atmosphere. Volatilization of contaminants to the atmosphere may occur wherever air-water interfaces exist, such as from the surface of open tanks and process vessels or in aeration processes.

Mass transfer is discussed for a number of systems including:

- volatilization from surfaces
- air stripping (mechanical and diffused aeration)
- volatilization at weirs
- volatilization in sewer reaches
- volatilization at drops
- volatilization at process drains

In general there are two forms in which the overall mass transfer is expressed, K_L and $K_L a$. K_L is the mass transfer coefficient in the unit of meters per hour [m/hr]. The parameter 'a' is the specific interfacial area [m^2/m^3] and, therefore, the $K_L a$ expression is expressed in units of the inverse of time [1/hr]. In experiments where mass transfer was determined, the value $K_L a$ is most often reported. In systems where the 'a' value can be estimated by dividing the surface area [m^2] by the volume [m^3], the value of $K_L a$ value can be easily separated into a value for K_L and a value for 'a'. An example for such a system is a rectangular tank with a quiescent surface. For systems where it is difficult to determine the value of 'a' (e.g. mechanical aeration), the value of $K_L a$ is used to represent mass transfer from the system. It has become common practice to separate the K_L and the 'a' even for systems where it is not physically possible. Under these systems, the 'a' value is determined as if the surface of the water were quiescent.

Volatilization from Surfaces

The rate of volatilization from the surface of a process vessel is given by:

$$r_v = K_L a (C \cdot f_{non} - C^*) V \quad (1)$$

where,

r_v = rate of volatilization, mg/h

K_L = overall mass transfer coefficient, m/h

a = specific interfacial area for mass transfer, m^2/m^3

C = concentration of volatile compound in the water, mg/m^3

C^* = equilibrium concentration of compound in water, mg/m^3

V = volume of process vessel, m^3

f_{non} = pH dependent fraction of non-dissociated compound, -

The specific interfacial area for surface volatilization is taken to be the liquid surface area divided by the tank volume or, equivalently, the inverse of the tank depth. For low contaminant concentrations equilibrium between the liquid and gas phases can be represented by Henry's law:

$$C_g = H C^* \quad (2)$$

where,

H = Henry's law coefficient, m^3 liquid/ m^3 gas.

Combining Equations (1) and (2):

$$r_v = k_v \left(C f_{non} - \frac{C_g}{H} \right) \times V \quad (3)$$

where,

k_v = $K_L a = K_v a$ = volatilization rate constant, 1/h

K_v = volatilization mass transfer coefficient, m/h.

For a system open to the atmosphere, it is assumed that the air movement above the basin is sufficient to carry the volatilized compounds away so that their bulk concentration in the air phase is negligible. In that case the equilibrium water phase concentration will also be negligible. Therefore Equation (3) becomes:

$$r_v = k_v C_{f_{non}} V \quad (4)$$

The mass transfer coefficients for surface volatilization can be estimated using the following correlations developed by Mackay and Yeun (1983):

$$k_G = 10^{-3} + 46.2 \times 10^{-3} U^* S_{c_G}^{-0.67} \quad (5)$$

$$k_L = 10^{-6} + 34.1 \times 10^{-4} U^* S_{c_L}^{-0.5} \quad (U^* > 0.3) \quad (6)$$

$$k_L = 10^{-6} + 144 \times 10^{-4} U^{*2.2} S_{c_L}^{-0.5} \quad (U^* < 0.3) \quad (7)$$

$$U^* = 10^2 (6.1 + 0.63 U_{10})^{0.5} U_{10} \quad (8)$$

where,

k_G = gas film mass transfer coefficient, m/s

k_L = liquid film mass transfer coefficient, m/s

U^* = air side friction velocity, m/s

U_{10} = wind velocity 10 m above the water surface, m/s

S_{c_G} = gas phase Schmidt number, -

S_{c_L} = liquid phase Schmidt number, -.

The Schmidt numbers are calculated as follows:

$$S_{c_G} = \frac{\nu_a}{D_G \times d_a} \quad (9)$$

$$v_a = 1.8 \times 10^{-4} \quad (10)$$

$$D_G = 0.0067T_k^{1.5} \frac{\left(0.034 + \frac{1}{M}\right)^{0.5}}{M^{0.17} \left\{ \left(\frac{M}{2.5d_c}\right)^{0.33} + 1.81 \right\}^2} \quad (11)$$

$$d_a = 1.2928 \times 10^{-3} \frac{273.16 (760 - 0.08694h)}{T_k \quad 760} \quad (12)$$

$$S_{CL} = \frac{v_w}{D_L d_w} \quad (13)$$

$$v_w = \frac{1}{2.1482 \left\{ (T_c - 8.435) + \left[8078.4 + (T_c - 8.435)^2 \right]^{0.5} \right\} - 120.0} \quad (14)$$

$$D_L = 5.06 \times 10^{-9} \times \frac{T_k \times d_c^{0.6}}{M^{0.6} \times v_w} \quad (15)$$

$$d_w = 0.9982 \quad (16)$$

where,

d_c = density of compound at the compound normal boiling point, g/cm³

d_a = density of air, g/cm³

d_w = density of water, g/cm³

v_a = viscosity of air, g/cm/s

v_w = viscosity of water, g/cm/s

D_G = diffusion coefficient of compound in air, cm²/s

D_L = diffusion coefficient of compound in water, cm²/s

h = elevation above sea level, m

- T_k = temperature, °K
 T_c = temperature, °C
 M = molecular weight of compound, g/mol.

The overall mass transfer coefficient can be obtained from the liquid film and gas film mass transfer coefficients based on two-film theory (Lewis and Whitman, 1924). The overall mass transfer coefficient is calculated as follows:

$$K_L = \left\{ \frac{1}{k_L} + \frac{1}{Hk_G} \right\}^{-1} \quad (17)$$

where,

- K_L = overall mass transfer coefficient, m/h
 k_L = liquid phase mass transfer coefficient, m/h
 k_G = gas phase mass transfer coefficient, m/h.

Stripping in Aerated Vessels

Mechanical Aeration

Process vessels may be aerated either by submerged diffusers or by mechanical surface aerators. The equation describing the contaminant removal rate by stripping for mechanical aeration is similar to Equation (1) or Equation (3):

$$r_s = K_L a (C_{f_{non}} - C^*) V = k_s \left(C_{f_{non}} - \frac{C_g}{H} \right) V \quad (18)$$

where,

- r_s = stripping rate for mechanical aeration, mg/h
 k_s = $K_L a$ = $K_s a$ = stripping rate constant for mechanical aeration, h^{-1}
 K_s = K_L = overall mass transfer coefficient for mechanical aeration, m/h.

For mechanical aeration systems open to the atmosphere, the equilibrium concentration, C^* , is assumed to be zero since the atmosphere around the aerator is considered to be free of the volatilizing compound. Equation (18) can then be rewritten as:

$$r_s = k_s C_{f_{non}} V \quad (19)$$

The overall mass transfer coefficient can be obtained from the liquid film and gas film mass transfer coefficients (Equation (17)). The liquid film mass transfer coefficient for surface aeration can be related to the oxygen transfer coefficient, assuming that oxygen mass transfer is liquid phase controlled:

$$k_L = K_L^{oxy} \left(\frac{D_c}{D_{oxy}} \right)^n = K_L^{oxy} \Psi \quad (20)$$

where,

$$\Psi = \left(\frac{D_c}{D_{oxy}} \right)^n \quad (21)$$

and,

K_L^{oxy} = oxygen transfer coefficient, m/h

D_c = diffusion coefficient of compound in water, cm^2/s

D_{oxy} = diffusion coefficient of oxygen in water, cm^2/s

n = proportionality parameter between 0.5 and 1.0 (0.5 used by Toxchem) -.

The diffusion coefficient of oxygen in water is calculated using Equation (22).

$$D_{oxy} = 2.5 \times 10^{-5} \frac{T_k}{298.15} \quad (22)$$

where,

D_{oxy} = diffusion coefficient of oxygen in water, cm^2/s

T_K = temperature, $^{\circ}K$

Combining Equation (20) with a correlation for the oxygen transfer rate constant, the following equation, proposed by Thibodeaux (1979), is used to estimate the liquid phase mass transfer coefficient for mechanical surface aeration:

$$k_L a = 109.39 N_{oxy} EP \alpha (1.024)^{(T-20)} \left(\frac{D_c}{D_{oxy}} \right)^{0.5} \left(\frac{I}{V} \right) \quad (23)$$

where,

$k_L a$ = liquid phase mass transfer constant, 1/hr

N_{oxy} = standard oxygen transfer rate for aerator, $(kg O_2)/(kW \cdot h)$

E = power delivery efficiency for aerator (fixed at 0.85), -

α = dirty water/clean water conversion factor-

P = aerator power, kW

T = temperature, $^{\circ}C$

V = volume of aeration basin, m^3 .

To determine the overall mass transfer coefficient the gas phase mass transfer coefficient must be estimated. Equation (17) can be rewritten as:

$$K_L a = K_s a = k_L a \frac{\frac{k_G H}{k_L}}{\frac{k_G H}{k_L} + 1} \quad (24)$$

Munz and Roberts (1989) suggest a value of 40 for the ratio of the gas and liquid film mass transfer coefficients, i.e.:

$$\frac{k_G}{k_L} = 40 \quad (25)$$

Combining Equations (24) and (25) yields:

$$K_L a = K_s a = k_L a \frac{40H}{40H + 1} \quad (26)$$

Diffused Bubble Aeration

For diffused bubble aeration, the rate of stripping is equal to the contaminant concentration in the air bubbles times the air flow rate:

$$r_d = Q_a C_g \quad (27)$$

where,

r_d = diffused aeration stripping rate, mg/h

Q_a = air flow rate, m³/h

C_g = contaminant concentration in air bubbles, mg/m³.

Equation (27) can be rewritten in terms of the contaminant concentration in the wastewater:

$$r_d = Q_a f H C_{f_{non}} = k_d C_{f_{non}} V \quad (28)$$

where,

f = fractional saturation of gas bubbles, -

k_d = diffused aeration stripping constant = $Q_a f H / V$, h⁻¹.

The fractional saturation can be estimated using the following equation proposed by Matter-Muller *et al.* (1981):

$$f = 1 - \exp\left(\frac{-K_L a V}{Q_a H}\right) \quad (29)$$

For subsurface aeration the value of $K_L a$ for the volatile compound can be estimated from Equation (20) using the $K_L a$ for oxygen under the same conditions. For subsurface aeration a value of $n = 0.5$ is used in Equation (20). The overall mass transfer coefficient for the compound is then calculated from Equation (24). Hsieh *et al.* (1992) observed k_G/k_L ratios ranging from 2.2 to 3.6 for diffused aeration systems. Therefore a k_G/k_L ratio of 3.0 is used for diffused aeration.

The $K_L a$ for oxygen for a diffused air system can be related to the oxygen transfer efficiency according to the following equation given by Redmon *et al.* (1983):

$$K_L a_{oxy} = \frac{Q_a d_{oxy} (OTE) Y_{oxy}}{(C_{oxy}^* - C_{oxy}) V} \quad (30)$$

where,

- $K_L a_{oxy}$ = oxygen transfer rate constant, h^{-1}
- d_{oxy} = density of oxygen at mid-depth in basin, mg/L
- OTE = oxygen transfer efficiency as a decimal fraction, -
- Y_{oxy} = mole fraction of oxygen in air, moles of oxygen/mole of air, -
- C_{oxy}^* = equilibrium oxygen concentration in water at mid-depth, mg/L
- C_{oxy} = oxygen concentration in water at mid-depth, mg/L.

For aerated grit chambers and channels the oxygen transfer efficiency is generally not known. In the program an OTE value of 0.02 (2%) is assumed for these processes.

Mechanical Mixing

The following expression as postulated by Peng *et al.* (1995) is used to estimate the volatilization rate from the water surface due to subsurface mechanical mixing in anaerobic and anoxic activated sludge tanks.

$$k_M = \frac{22.1}{24.0} D^{\frac{1}{2}} G^{\frac{1}{3}} \frac{1 + e^{-0.0131.D^{-\frac{1}{2}} G^{\frac{1}{3}}}}{1 - e^{-0.0131.D^{-\frac{1}{2}} G^{\frac{1}{3}}}} \cdot \frac{A}{V} \quad (31)$$

where:

- k_M = volatilization rate due to mixing, 1/h
- D = diffusivity of contaminant in water, m²/d
- G = shear rate, 1/s
- A = surface area of reactor, m²
- V = Volume of reactor, m³.

The G value is estimated by the following expression.

$$G = \sqrt{\frac{P_V}{\mu}} \quad (32)$$

where,

- P_V = Specific power input, W/m³
- μ = Dynamic viscosity, N.s/m²

Volatilization at Weirs

The mass transfer from a film of water falling over a weir can be described by the following differential equation:

$$\frac{dC}{dt} = -K_L a \left(C_{f_{non}} - \frac{C_g}{H} \right) \quad (33)$$

where,

- t = travel time of water from point of spilling over weir, h
- C = liquid phase contaminant concentration, mg/m³
- C_g = gas phase contaminant concentration, mg/m³.

If this equation is integrated over the total time for the water to fall from the weir to the receiving trough (t_o), the following relationship can be derived:

$$\ln \left\{ \frac{Cf_{non} - \frac{C_g}{H}}{C_o f_{non} - \frac{C_g}{H}} \right\} = -K_L a t_o \quad (34)$$

where,

C_o = contaminant concentration entering weir, mg/m^3

C = contaminant concentration leaving weir, mg/m^3 .

A similar relationship can be defined for oxygen mass transfer as follows:

$$\ln \left\{ \frac{C_s^{oxy} - C^{oxy}}{C_s^{oxy} - C_o^{oxy}} \right\} = -K_L a_{oxy} t_o \quad (35)$$

where,

C_s^{oxy} = oxygen saturation concentration, mg/m^3

C_o^{oxy} = oxygen concentration entering weir, mg/m^3

C^{oxy} = oxygen concentration leaving weir, mg/m^3 .

Pincince (1991) has defined an empirical relationship between the term on the left of Equation (35) and process variables such as overflow rate and drop height. From Equations (34) and (35) it is apparent that the terms on the left side of the equations are proportional to the mass transfer coefficients; however, the ratio of mass transfer coefficients is related to the ratio of diffusion coefficients:

$$\frac{K_L a}{K_L a_{oxy}} = \left(\frac{D_c}{D_{oxy}} \right)^1 \left(\frac{\frac{k_G H}{k_L}}{\frac{k_G H}{k_L} + 1} \right) \quad (36)$$

Using a ratio of gas phase to liquid phase film coefficients of 100, Equation (36) becomes:

$$\frac{K_L a}{K_L a_{oxy}} = \left(\frac{D_c}{D_{oxy}} \right)^1 \frac{100H}{100H + 1} \quad (37)$$

Therefore, Equations (34), (35) and (37) can be combined to yield:

$$\ln \left\{ \frac{C_{f_{non}} - \frac{C_g}{H}}{C_{o_{f_{non}}} - \frac{C_g}{H}} \right\} = -A \left[\frac{D_c}{D_{oxy}} \right]^1 \left\{ \frac{100H}{100H + 1} \right\} \quad (38)$$

where,

A = empirical relationships defined by Pincince (1991) for primary and secondary clarifiers as follows:

Primary Clarifier Weirs:

$$A = 0.042h^{0.872}q^{0.509} \quad (39)$$

Secondary Clarifier Weirs:

$$A = 0.077h^{0.623}q^{0.66} \quad (40)$$

where,

h = weir drop height, m

q = weir loading rate, $m^3/h \cdot m$.

Equation (38) can be rearranged to solve for the effluent concentration in terms of the influent concentration and the gas concentration:

$$C = \left(C_0 f_{non} - \frac{C_g}{H} \right) \exp \left[-A \frac{D_c}{D_{oxy}} \left(\frac{100H}{100H + 1} \right) \right] + \frac{C_g}{H} \quad (41)$$

The mass rate of volatilization from a weir can then be calculated as:

$$r_v = Q (C_0 f_{non} - C) \quad (42)$$

where,

r_v = rate of volatilization from the weir, mg/h

Q = wastewater flow rate, m^3/h .

The model used for primary clarifiers is also used to estimate emissions from weirs for Dissolved Air Flotation (DAF) unit processes.

Volatilization in Sewer Reaches

Parkhurst and Pomeroy (1972) published a model to predict oxygen transfer along sewer reaches. According to their model:

$$K_L^{oxy} = 2.67 \times 10^{-4} (1 + 0.17 F^2) \gamma (US)^{3/8} \quad (43)$$

$$\gamma = (1.0212)^{(T_c - 20)} \quad (44)$$

where,

K_L^{oxy} = oxygen liquid phase mass transfer coefficient, m/s

F	= Froude number = $U/(gd)^{1/2}$, -
g	= gravitational acceleration = 9.81 m/s ²
d	= hydraulic depth of flow (cross-sectional area of water divided by surface width), m
U	= wastewater mean velocity, m/s
γ	= temperature correction factor, -
S	= slope of the energy grade line, m/m
T _c	= temperature, °C.

The depth of flow (d) is obtained by application of Manning's equation (pipe assumed circular). Wastewater mean velocity (U) is calculated by dividing wastewater flow rate by wastewater cross-sectional area. The value of S is assumed to be equal to channel slope (i.e., uniform flow conditions).

Using the value of K_L^{oxy} estimated from Equation (43), the liquid mass transfer coefficients for volatile contaminants are obtained from Equation (20), assuming a value of $n = 0.5$. Several researchers have tested and verified the application of Equations (20) and (43) using volatile tracers in sewers with a wide range of operating conditions (Jensen and Hvitved-Jacobsen, 1991; Corsi *et al.*, 1992; Whitmore and Corsi, 1994).

There are currently no published models for estimating values of k_g in confined sewer (closed reach) environments. In Toxchem values of k_g are estimated using the relationship published by Mackay and Yeun (1983) (Equation (5)). The overall mass transfer coefficient (K_L) is estimated using Equation (17). For closed reaches, the wind speed is taken to be the gas velocity in the sewer. For open reaches, the ambient wind speed is taken to be the gas velocity in the sewer.

Volatilization at Drops

Gas-liquid mass transfer at drop structures can occur as a result of three primary mechanisms: 1) transfer to/from the falling film, 2) transfer across an agitated tailwater surface, and 3) transfer to/from air bubbles which become entrained in a drop structure's tailwater pool. Based on computational studies completed by Burnham *et al.*, (1993), gas-liquid mass transfer due to entrained air bubbles is likely to be the dominant transfer mechanism for a wide range of drop structures. Similar assumptions and findings were published by McLachlan *et al.*, (1990) and Nakasone (1987). Thus, Toxchem includes an assumption that all contaminant emissions which occur at drop structures are due entirely to air entrainment and associated diffused bubble stripping.

The liquid-phase contaminant concentration downstream of a drop is estimated by relating contaminant to oxygen transfer deficit ratios:

$$r_o = \frac{C_s^{oxy} - C_o^{oxy}}{C_s^{oxy} - C^{oxy}} \quad (45)$$

$$r_v = \frac{C_o f_{non} - \frac{C_g}{H}}{C f_{non} - \frac{C_g}{H}} \quad (46)$$

$$r_v = r_o^{\Psi_m} \quad (47)$$

where,

r_o = oxygen deficit ratio, -

r_v = contaminant deficit ratio, -

C_s^{oxy} = saturation dissolved oxygen concentration, mg/m^3

C_o^{oxy} = dissolved oxygen concentration upstream of drop, mg/m^3

C^{oxy} = dissolved oxygen concentration downstream of drop, mg/m^3

C_o = Contaminant concentration upstream of drop, mg/m^3

C = contaminant concentration downstream of drop, mg/m^3

C_g = contaminant concentration in headspace of drop, mg/m^3

Ψ_m = ratio of contaminant-to-oxygen overall mass transfer coefficients, -.

The oxygen deficit ratio (r_o) is estimated using an empirical model which accounts for variations in drop height, wastewater discharge, and tailwater depth (Nakasone, 1987):

$$\ln r_{o20} = A d^B q^D z^F \quad (48)$$

where,

r_{o20} = oxygen deficit ratio at 20 °C

d = drop height, m

q = flow rate per width of stream, m³/m·h

z = tailwater depth, m

A, B, D, and F are adjustable parameters obtained from the following table:

d	q	A	B	D	F
≤1.2	≤235	0.0785	1.31	0.428	0.31
>1.2	≤235	0.0861	0.816	0.428	0.31
≤1.2	>235	5.39	1.31	-0.363	0.31
>1.2	>235	5.92	0.816	-0.363	0.31

Estimates of r_o are adjusted to temperatures other than 20°C using a relationship developed by Gameson *et al.* (1958):

$$\ln r_o = \ln r_{o20} [1 + 0.0168(T_c - 20)] \quad (49)$$

Combining Equations (46), (47), (48) and (49) yields:

$$\frac{C_o f_{non} - \frac{C_g}{H}}{C f_{non} - \frac{C_g}{H}} = [\exp(A d^B q^D z^F [1 + 0.0168(T_c - 20)])]^{\Psi_m} \quad (50)$$

The parameter Ψ_m is related to Ψ (Ψ defined by Equation (21)), but accounts for gas-phase resistance to mass transfer (Hsieh *et al.*, 1992).

$$\Psi_m = \frac{\Psi}{1 + \frac{1}{H \left(\frac{k_G}{k_L} \right)}} \quad (51)$$

The mechanism of volatilization at a drop structure is considered to be similar to that at the weir. Therefore, a default k_G/k_L value of 100.0 is used in Toxchem for wastewater drops.

Volatilization at Process Drains

An empirical relationship that was developed by Enviromega (1993) for the Chemical Manufacturers Association (CMA) has been incorporated into Toxchem for estimating the emissions from process drains. The model was developed based on the assumption that the majority of emissions occur during the period when the vertically discharged stream is exposed to the atmosphere. That is, the time interval in which a slice of water leaves the pipe outlet to the time it crosses the plane for the top of the drain hub. Emissions are assumed to occur from the cylindrical column of contaminated water and that the surrounding air has a zero contaminant concentration, thus, maximizing the driving force for volatilization.

The expressions for the gas and liquid phase mass transfer coefficients are presented in Equations (52) and (53). The mass transfer coefficients were based on experimental work and were determined based on the results of toluene at 25°C. The data used to determine the expressions are presented in the CMA report "Comments of the Chemical Manufacturers Association on Proposed Hazardous Organic NESHAP". The data are presented in Volume II of the appendices.

(52)

$$k_g = 0.0899 \left(\frac{D_g}{0.1225} \right)^{0.66}$$

(53)

$$k_l = 0.00192 v \left(\frac{D_l}{0.0000103} \right)^{0.66}$$

where,

v = drain discharge velocity, cm/s.

The gas phase diffusion coefficient, D_g , and the liquid phase diffusion coefficient, D_l , are calculated using Equations (11) and (15) (units: cm^2/s). The gas and liquid phase mass transfer coefficients are in units of m/s. The overall mass transfer coefficient (K_L) is calculated using Equation (17).

The fraction of the mass flow emitted to the air, based on a mass balance of the system, is calculated using Equation (54).

$$f_{air} = f_{non} \left[1 - e^{-\frac{K_L A}{Q}} \right] \quad (54)$$

where,

A = exposed surface area of the cylindrical discharge, m²

Q = discharge flow rate, m³/s.

Sorption

Contaminants can be transported from the liquid phase by sorption onto biomass or other solid particles. In a liquid/solid system, at equilibrium, the concentration of a contaminant on a solid sorbent can be expressed by:

$$C_x = K_p C \quad (55)$$

where,

C_x = concentration of contaminant in solid phase, mg/kg (ug/g)

K_p = sorption partition coefficient, m³/kg (L/g)

C = concentration of contaminant in liquid phase, mg/m³ (ug/L).

Equation (55) is generally valid at low contaminant concentrations. The sorption partition coefficient for a given compound can be related to the octanol/water partition coefficient of that compound. The following correlation reported by Dobbs *et al.*, (1989) is used to estimate the sorption partition coefficients where experimentally determined coefficients are not available:

$$\log K_p = 0.58 \log K_{ow} + 1.14 \quad (56)$$

where,

K_p = sorption partition coefficient, L/kg

K_{ow} = octanol/water partition coefficient, -.

The partition coefficient obtained from Equation (56) provides the solid phase contaminant concentration on a volatile solids basis for primary solids, activated sludge, and digested sludge.

Sorption and desorption of contaminants by wastewater treatment plant solids has been observed to be a relatively rapid process. Toxchem therefore assumes that, as far as sorption is concerned, the system is always in equilibrium. In other words, it is assumed that sorption equilibrium is attained instantaneously in all parts of the system.

The portion of the total concentration of a contaminant which is sorbed onto solids is:

$$C_{ss} = K_p XC = S_{ss} C \quad (57)$$

where,

C_{ss} = concentration of contaminant in wastewater sorbed on solids, mg/m³

X = volatile suspended solids (VSS) concentration, kg/m³

S_{ss} = sorption coefficient for solids, dimensionless.

Contaminants can also sorb into oils present in the wastewater. Sorption of contaminants into oil is handled similarly to sorption onto solids. It is also assumed that sorption and desorption by oil is a rapid process and that the system is always in equilibrium with respect to sorption into oil. Note that for drops/weirs this process is considered to be a two step process: volatilization from liquid then re-equilibrate before the wastewater is passed to the following connected processes.

Partitioning of contaminants between oil and water has been represented by the octanol/water partition coefficient (Barbari and King, 1982). Therefore, in an oil/water system at equilibrium, the concentration of a contaminant in the oil can be expressed by:

$$C_{oil} = K_{ow} C \quad (58)$$

where,

C_{oil} = concentration of contaminant in oil phase, mg/kg.

The portion of the total concentration of a contaminant which is sorbed into oil is:

$$C_{so} = K_{ow} \frac{O}{d_o} C = S_{oil} C \quad (59)$$

where,

C_{so} = concentration of contaminant in wastewater sorbed in oil, mg/m³ (ug/L)

O = oil concentration in wastewater, kg/m³ (g/L)

d_o = density of oil, kg/m³ (g/L)

S_{oil} = sorption coefficient for oil, -.

The density of the oil is assumed to be 870 kg/m³.

Sorption to Powdered Activated Carbon

Powdered activated carbon can also be added to the wastewater (typically the activated sludge process) which will enhance the sorption of the contaminant. The Freundlich isotherm for the contaminant is used to estimate the sorption to carbon as described by equation (60).

$$C_{pac} = K_c C^{1/n} X_c \quad (60)$$

where,

C_{pac} = concentration sorbed to the powdered activated carbon, mg contaminant/L

C = Final concentration of the solution at equilibrium, mg/L

X_c = Concentration of PAC in solution, g/L

K_c = K from Freundlich carbon isotherm, mg/g

$1/n$ = 1/n from Freundlich carbon isotherm, -.

Sorption to Dissolved Organic Carbon

The adsorption of contaminant on the Dissolved Organic Carbon is modeled using the following expression.

$$C_{DOC} = K_{doc} \cdot C_{doc} \cdot C \quad (61)$$

where,

C_{DOC} = concentration of contaminant sorbed onto DOC, mg/L

K_{doc} = adsorption partition coefficient for DOC, L/g DOC

C_{doc} = concentration of DOC, mg DOC/L

C = concentration of contaminant in effluent, mg/L.

An adsorption parameter of K_{doc} is added in the database for each compound. The unit of this parameter is L/g DOC. For the user defined compounds, the user can choose to directly enter the value of K_{doc} instead of calculating it using the LFER relationships based on log octanol – water partition coefficient.

When the value of K_{doc} is not provided, the value of the adsorption coefficient is estimated based on the following relationship (Kim and Kwon, 2010).

$$\log K_{\text{doc}'} = A \cdot \log K_{\text{ow}} + B \quad (62)$$

$$K_{\text{doc}} = \frac{K_{\text{doc}'}}{1000} \quad (63)$$

Where:

$K_{\text{doc}'}$ = adsorption partition coefficient for DOC, L/kg DOC

K_{doc} = adsorption partition coefficient for DOC, L/g DOC

K_{ow} = octanol-water partition coefficient, L H_2O /L Oct

A = empirical coefficient relating adsorption partition coefficient for DOC and octanol-water partition coefficient (a default value of 0.82 is used), -

B = empirical coefficient relating adsorption partition coefficient for DOC and octanol-water partition coefficient (a default value of 0.31 is used), -

The total concentration of a contaminant in wastewater is presented in following Equation.

$$C_{tot} = C + C_{sorb} = C + \left[K_p \cdot X + K_{ow} \cdot \frac{X_{oil}}{d_o} + K_c \cdot C^{\left[\frac{1}{n}-1\right]} \cdot X_{pac} + K_{doc} \cdot C_{doc} \right] \cdot C \quad (64)$$

where,

C_{tot} = total concentration of contaminant in wastewater, mg/m³ (µg/L).

Substituting the sorption coefficients and rearranging terms gives the expression below:

$$C_{tot} = \left(1 + K_p X + K_{ow} \frac{O}{d_o} + K_c X_c \frac{C^{1/n}}{C} \right) C = (1 + S)C \quad (65)$$

where,

$$S = K_p X + K_{ow} \frac{O}{d_o} + K_c X_c \frac{C^{1/n}}{C} \quad (66)$$

Where the separation of oil is not specified in a process, the oil concentration in the effluent and sludge streams are taken to be equal to the concentration in the influent stream. In suspended growth biological treatment processes, the oil is assumed to be completely biodegraded. Contaminants sorbed to the oil are accounted for in the mass balance equations. The concentration of powdered activated carbon is assumed to behave like other suspended solids in the mass balance equations.

Biodegradation

Suspended Growth Processes

In Toxchem suspended growth processes, biodegradation is assumed to be represented by the Monod expression, as presented in Equation (67).

$$r_b = \frac{\mu_m}{Y} \left(\frac{C}{K_s + C} \right) XV \quad (67)$$

where,

- r_b = biodegradation rate, mg/h
 μ_m = maximum specific growth rate, 1/h
 Y = maximum yield coefficient, g biomass/g substrate
 X = biomass concentration (volatile fraction of total suspended solids), g/m³ (mg/L)
 K_s = half saturation constant, mg/L
 C = contaminant liquid phase concentration, mg/L
 V = vessel volume, L.

Equation (67) is rearranged and then reproduced in Equation (68).

$$r_b = \frac{\mu_m}{YK_s} \left(\frac{C}{1 + \frac{C}{K_s}} \right) XV \quad (68)$$

If the contaminant concentration is small and or the value of the half saturation constant is large, the mass removal rate due to biodegradation can be simplified to Equation (69).

$$r_b = \frac{\mu_m}{YK_s} CXV = k_b CXV \quad (69)$$

where,

- k_b = first order biodegradation rate coefficient, m³/kg VSS/h, (L/mg VSS/h),

Substituting k_b into Equation (68), results in Equation (70).

$$r_b = k_b \left(\frac{C}{1 + \frac{C}{K_s}} \right) XV \quad (70)$$

Toxchem uses Equation (70) to model biodegradation. If the half saturation constant is not known or the user selects that only first order biodegradation be used, Equation (69) is used.

Biofilm Processes

In processes such as trickling filters and rotating biological contactors (RBCs) the biomass is attached to surfaces as a biofilm. Usually, toxics in wastewater are present at trace concentrations in an aqueous media which contains higher concentrations of other organics that act as a primary substrate. It is assumed that biofilm thickness and density will be defined by the primary substrate and therefore, the biodegradation kinetics of the trace contaminants are assumed first order with respect to concentration as indicated below:

$$r_b = k_b X_f CV \quad (71)$$

where,

- r_b = rate of biodegradation, mg/hr
- k_b = biodegradation rate coefficient, m^3/kg VSS/h (L/mg VSS/h)
- X_f = biofilm density, g/m^3 (mg/L)
- C = contaminant concentration, mg/L.

An effective diffusion layer is assumed to exist between the bulk liquid phase and the biomass surface. The following terms are defined:

- C_b = contaminant concentration in bulk liquid layer, mg/m^3
- C_s = contaminant concentration at outer edge of biofilm, mg/m^3
- L_f = biofilm thickness, m
- z = distance in biofilm as measured from liquid interface, m.

In Toxchem L_f is assigned a value of 1.0 mm. The following boundary conditions are assumed for the biofilm:

$$C = C_s \text{ at } z = 0$$

$$dC/dz = 0 \text{ at } z = L_f$$

The governing equation for diffusion and biodegradation in the biofilm at steady state is:

$$D_e \frac{\partial^2 C}{\partial z^2} = k_b X_f C \quad (72)$$

where,

D_e = contaminant diffusion coefficient in biofilm, m^2/h .

In the program D_e is assigned a value of 80% of the contaminant's water phase diffusion coefficient.

Solving Equation (72) with the previously stated boundary conditions yields:

$$C = C_s \frac{\cosh[r_1(L_f - z)]}{\cosh(r_1 L_f)} \quad (73)$$

where,

$$\cosh(u) = 0.5(e^u + e^{-u}) \quad (74)$$

and,

$$r_1 = \sqrt{\frac{X_f k_b}{D_e}} \quad (75)$$

The contaminant mass flux at the biofilm-stagnant layer boundary ($z = 0$) is defined as:

$$N_s = D_e \frac{dC}{dz} \quad (76)$$

where,

N_s = mass flux into biofilm, $\text{mg}/\text{m}^2 \cdot \text{h}$.

Differentiating Equation (73) and substituting into Equation (76) yields:

$$N_s = D_e r_1 \tanh(r_1 L_f) C \quad (77)$$

The flux through the stagnant layer (external resistance) must equal the flux into the biomass and therefore:

$$D_e r_1 \tanh(r_1 L_f) C_s = k_L (C_b - C_s) \quad (78)$$

where,

k_L = external mass transfer coefficient, m/hr .

The external mass transfer coefficient might be approximated by:

$$k_L = \frac{D_c}{L} \quad (79)$$

where,

D_c = contaminant diffusion coefficient in water, m^2/h

L = thickness of stagnant layer, m .

In Toxchem, L is assigned a value of 0.05 mm. Equation (78) can be solved for C_s and the resulting equation can be substituted into:

$$N_s = k_L(C_b - C_s) \quad (80)$$

to yield:

$$N_s = k_L \frac{D_e r_l \tanh(r_l L_f)}{D_e r_l \tanh(r_l L_f) + k_L} C_b \quad (81)$$

This equation relates the mass flux into the biofilm to the bulk phase concentration and does not require iterative solutions. When k_L is very large it reduces to:

$$N_s = D_e r_l \tanh(r_l L_f) C_b \quad (82)$$

When k_L is very small it reduces to:

$$N_s = k_L C_b \quad (83)$$

Temperature Correction of Sensitive Parameters

Industrial and municipal wastewater treatment plants are subject to variations in wastewater temperature. The wastewater temperature can significantly influence the fate of trace contaminants in wastewater treatment plants. To account for temperature effects Toxchem incorporates temperature correction for the Henry's Law coefficient and the biodegradation rate coefficients.

Henry's Law Coefficient

The following relationship has been used to estimate Henry's Law coefficients at different temperatures:

$$H = \frac{\exp(A - \frac{B}{T})}{RT} \quad (84)$$

where,

- H = Henry's Law coefficient, m³ liquid/m³ gas
 A = compound specific Van't Hoff parameter, -
 B = compound specific Van't Hoff parameter, -
 T = temperature, °K
 R = gas constant = 8.2057 x 10⁻⁵ atm· m³/mole·°K.

Unfortunately, the Van't Hoff parameters A and B are not available for all compounds of interest. However, Henry's Law coefficients have been determined for a large number of compounds at 25 °C. If the Henry's Law coefficient is known at 25 °C the following relationship can be used to estimate the coefficient at a different temperature:

$$H = H_{25} \Theta^{(T - 25)} \quad (85)$$

where,

- H = Henry's Law coefficient at T°C, m³ liquid/m³ gas
 H₂₅ = Henry's Law coefficient at 25°C, m³ liquid/m³ gas
 T = temperature, °C
 Θ = temperature correction factor, -.

The data of Gossett (1987) were examined to evaluate the applicability of this relationship to a number of compounds. In the Gossett study, the influence of temperature on the Henry's Law coefficients of 13 compounds was evaluated. The modified van't Hoff relationship was linearly regressed with all of the Gossett data to estimate Θ. The results of this regression indicated a best fit value for Θ of 1.044 with 95% confidence limits of 0.0035. From the narrow confidence limits of the estimated Θ value it was apparent that Equation (85) can reasonably predict the temperature influence on Henry's Law coefficients and was therefore incorporated into Toxchem as:

$$H = H_{25} 1.044^{(T - 25)} \quad (86)$$

Toxchem uses Equation (84) to estimate the Henry's Law coefficient for compounds with available Van't Hoff A and B parameters. For other compounds, Equation (86) is used to correct the database value to temperatures other than 25°C.

Biodegradation Rate Constants

The effect of temperature on biological processes is usually expressed in the form:

$$k_b = k_{b20} \Theta^{(T - 20)} \quad (87)$$

where,

k_b = biodegradation rate coefficient at T°C, m³/kg·h

k_{b20} = biodegradation rate coefficient at 20°C, m³/kg·h

Θ = temperature correction factor, -

T = temperature, °C.

A typical value reported for Θ in activated sludge systems is 1.04 (Metcalf and Eddy, 1991). As there is little information on the influence of temperature on the biodegradation rate of trace organics, the following relationship is incorporated into Toxchem to adjust the aerobic biodegradation rate coefficients:

$$k_b = k_{b20} 1.04^{(T - 20)} \quad (88)$$

The biodegradation rate in activated sludge systems can be further corrected by applying a correction factor for the system SRT. It is well established that the specific active biomass (quantity of active biomass per unit VSS) in activated sludge decreases as the SRT of the system increases. Without any considerations to the system SRT, the amount of measured VSS in both the low and high SRT are treated as equivalent, which theoretically is not a valid assumption. To provide users some flexibility to account for the change in the active biomass concentration depending on SRT, a SRT based correction factor is applied to the biodegradation rates.

$$k_{b,srt} = k_{b20} \cdot 1.04^{(T-20)} \cdot f_{srt} \quad (89)$$

Where,

f_{SRT} = SRT correction factor, -.

The estimation procedure for the SRT based correction factor, f_{SRT} , is as described in following sections.

The correction factor, f_{SRT} , is estimated based on the relative change in the specific active biomass at a given SRT relative to a reference SRT. The reference SRT is the SRT at which the biodegradation rates in the Toxchem database are assumed to be valid. In the present calculations, a reference SRT of 10 days is considered. The yield of active biomass per unit substrate removed (Y_{active}) (kg solid/kg substrate) at a given SRT may be estimated using the following expression.

$$Y_{active} = \frac{Y}{(1 + k_d \cdot SRT)} \quad (90)$$

Where,

Y = maximum yield of active biomass (a default value of 0.66 is used), kg solid/kg substrate

k_d = endogenous decay rate of active biomass (a default value of 0.25 is used, 1/d)

SRT = system SRT, d.

The yield of endogenous solid production per unit substrate removed (Y_{endo}) (kg solid/kg substrate) at a given SRT is calculated using the following expression.

$$Y_{endo} = \frac{Y \cdot f_u \cdot k_d \cdot SRT}{(1 + k_d \cdot SRT)} \quad (91)$$

Where,

f_u = endogenous fraction from active biomass decay (a default value of 0.2 is used), -.

The yield of inert solid per unit substrate removed (Y_{inert}) (kg solid/kg substrate) at a given SRT is estimated as below.

$$Y_{inert} = \frac{f_{xi}}{\gamma_{BOD}(1 - f_{xi} - f_{si})} \quad (92)$$

where,

f_{xi} = fraction of particulate inert COD in influent (a default value of 0.2 is used), -

f_{si} = fraction of soluble inert COD in influent (a default value of 0.05 is used), -

Y_{BOD} = BOD_U removal efficiency (a default value of 0.95 is used), -.

The fraction of active biomass in a given system at a given SRT may be estimated using the following expression.

$$f_{active} = \frac{Y_{active}}{Y_{active} + Y_{endo} + Y_{inert}} \quad (93)$$

Using the same expression as above, the fraction of active biomass in system at a reference SRT (SRT_{ref}) may be estimated as below.

$$f_{active,ref} = \frac{Y_{active,ref}}{Y_{active,ref} + Y_{endo,ref} + Y_{inert,ref}} \quad (94)$$

The SRT based biodegradation rate correction factor is then estimated as below.

$$f_{bio,corr} = \frac{f_{active}}{f_{active,ref}} \quad (95)$$

where,

SRT_{ref} = Reference SRT, d.

The above procedure is not a comprehensive way to account for many different mechanisms which may affect the biodegradation at different SRT. However, it is an attempt to improve the

VSS based estimation procedure used until now. This method provides users a way to assess the relative effect of SRT by estimating the relative fraction of active biomass in sludge. The estimation procedure for biodegradation in activated sludge in previous versions did not make any differentiation in the biodegradation potential of two sludges having the same VSS concentration, but originating from two different SRT systems. If the user chooses not to apply the SRT based correction, then they should leave the system SRT value to 10 days in the user input form of the activated sludge processes.

For biodegradation in anaerobic digesters, the same Θ value is used as for aerobic biodegradation except that the rate coefficients in the database are entered at 35°C. The SRT correction is not applied to anaerobic biodegradation rates ($f_{SRT} = 1.0$). Therefore, the following relationship is used for temperature correction of anaerobic biodegradation rate coefficients:

$$k_b = k_{b35} 1.04^{(T - 35)} \quad (96)$$

pH dependent non-dissociated fraction

The effect of pH on weak acids and bases is included in Version 4 by considering the concentration of non-dissociated compound in the gas-liquid mass transfer equation. For example, a form of equation as shown below is used. The total soluble concentration (dissociated + non-dissociated) is multiplied by, f_{non} , a fraction estimated based on the dissociation constants on the compound. The estimation procedure for, f_{non} , is as described in following sections.

$$r_v = k_v \left(C f_{non} - \frac{C_g}{H} \right) V \quad (97)$$

The estimation procedure for f_{non} , requires two inputs. The first input is regarding the acid/base nature of the non-dissociated compound. For example, the non-dissociated form of ammonia is a base while non-dissociated form of acetic acid is an acid. The second required input is the value of dissociation constant, expressed as the negative logarithmic value, i.e., pK. Depending on the compound, first and second dissociation constant can be specified. It shall be noted that the dissociation constants are always for dissociation of the acid form of the compound. The following expressions are used for estimating the non-dissociated fraction of the compound.

Non-dissociated form is an acid

The non-dissociated fraction is estimated for the following two cases.

Case 1: When both pKa1 and pKa2 are specified (diprotic)

$$f_{non} = \frac{1}{1 + \frac{10^{-pka1}}{10^{-pH}} + \frac{10^{-pka1} \cdot 10^{-pka2}}{10^{-2 \cdot pH}}} \quad (98)$$

Case 1: When only pKa1 is specified (monoprotic)

$$f_{non} = \frac{1}{1 + \frac{10^{-pka1}}{10^{-pH}}} \quad (99)$$

When non-dissociated form is a base

The non-dissociated fraction is estimated for the following two cases.

Case 1: When both pKa1 and pKa2 are specified (dibasic)

$$f_{non} = \frac{1}{1 + \frac{10^{-pH}}{10^{-pka2}} + \frac{10^{-2 \cdot pH}}{10^{-pka1} \cdot 10^{-pka2}}} \quad (100)$$

Case 2: When only pKa1 is specified (monobasic)

$$f_{non} = \frac{1}{1 + \frac{10^{-pH}}{10^{-pka1}}} \quad (101)$$

The estimated value of non-dissociated fraction, f_{non} , is used in the gas-liquid mass transfer equation. In the event of following exceptions, the value of f_{non} is assigned to 1.

1. Compound is neither classified as acid or base
2. Compound is classified as acid or base, but no values are provided for both of the dissociation constants pKa1 and pKa2
3. Compound is classified as acid or base, but no value of pKa1 is provided.

Modeling emissions from an oil film overlying a water surface

The issue of modeling of air emissions of organic compounds from a non-aqueous layer floating on a water surface is of growing concern. In certain specific industries, such as petroleum refining, however, it is possible that the surface of the wastewater in collection or treatment process units may be covered by a floating layer of oil, assumed to be of hydrocarbon origin.

When the solubility of dissolved oil in water is exceeded, a separate layer of oil begins to form. Because the density of the oil layer is less than that of water, the oil layer will float on the water surface. Contaminants present in the two phases will tend to equilibrate between the layers, depending on their solubility in water and in oil, as represented by the K_{ow} [octanol water coefficient] value. Many non-polar and higher molecular weight compounds are very sparingly soluble in water, but are readily soluble in oil. As a result, the concentration of a specific hydrocarbon (e.g., hexane) in the oil layer can be orders of magnitude higher than in the water layer. Conversely, polar organic compounds such as alcohols and phenols do not readily dissolve in oil, but remain at higher concentrations in the aqueous phase. It seems intuitive that higher emissions of organics would result when the concentrations may be orders of magnitude higher in an oil layer than in the aqueous phase; because the solubility of the compound in oil is so much higher than in water, however, it may not tend to partition to the air from the oil layer as readily as from the aqueous phase.

TOXCHEM includes four procedures for estimating emissions of organic contaminants from a floating oil layer. The default approach is based on mass transfer principles similar to volatilization from a water surface, while additional procedures are provided based on an EPA approach as defined in the document “ Air Emission Models for Waste and Wastewater (EPA, 1994).

Mantis Method [Default Method]

The science on mass transfer of organic compounds from an oil layer floating on a water surface is not well-developed. The default approach in TOXCHEM for estimating emission rates from an oil-covered surface is based on the mass transfer models of emissions due to volatilization from an open water surface (Mackay-Yeun, 1983). This procedure involves the calculation of Schmidt numbers, from which liquid and gas phase mass transfer coefficients are calculated. Users are directed to section on volatilization from a water surface for more details on the mathematical models.

In the Mackay-Yeun (1983) model, the Schmidt numbers are derived from physical-chemical properties of the liquid and gas (air) phases, including density, viscosity and diffusion coefficients. In the Toxchem Technical Manual, expressions are provided for the density and dynamic viscosity of water, the presumed liquid phase involving most wastewater treatment. No similar expressions or values are provided for “oil”. Because the Schmidt numbers for air are based on air density and viscosity values that are independent of the liquid phase (either water or oil), they are identical for either liquid phase. Schmidt numbers for the liquid phase are calculated using density and viscosity measurements for each type of liquid, and thus will be different for water and oil. The calculation method, however, is identical.

For calculation of the liquid phase Schmidt number for “oil”, viscosity can be related to temperature by the Walther (or Ubbelohde-Walther equation) (Speight and Exall, 2014). This is a complex mathematical relationship, however. For simplicity with this evaluation, values for viscosity and density of light mineral oil were selected, namely a specific gravity of 0.85 at 25 °C, and a viscosity of 15.3 cP at 40 °C (California Air Resources Board, 2014), corrected to a value of 62.4 cP at 25 °C using a graphical procedure outlined in Perry’s Chemical Engineers’ Handbook (5th ed., 1973).

The Mackay-Yeun (1983) procedure estimates an overall mass transfer coefficient between water and air using a two-film mass transfer model involving liquid and gas phase resistances, according to following Equation:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{K_{eq} * k_g} \quad (102)$$

where :

- K_L = overall mass transfer coefficient, m/s
- k_l = liquid phase mass transfer coefficient (water or oil), m/s
- k_g = gas phase mass transfer coefficient (air), m/s
- K_{eq} = equilibrium coefficient between liquid and gas phases, L_{liq}/L_{gas} .

The system studied by Mackay and Yeun (1983) was evaporation of organic compounds from a water surface, and thus the equilibrium coefficient K_{eq} was represented by Henry's Law coefficient, applied for compounds in a dilute aqueous solution. The units of Henry's law coefficient are thus L_{water}/L_{air} .

A corresponding equilibrium coefficient is needed for transfer of organic compounds between a floating oil layer, and the overlying air. No such coefficient has been defined in any technical literature reviewed. In the default procedure, a value of this equilibrium is calculated using Henry's law coefficient and the octanol-water partition coefficient (K_{ow}). The latter is an equilibrium coefficient for organic compounds partitioned between water and n-octanol phases. It is regularly employed as a surrogate partition coefficient between various types of oils and lipids.

The units of measurement for an oil:air equilibrium coefficient (K_{oa}) analogous to Henry's law coefficient (H) would be L_{oil}/L_{air} . The units of measurement for the octanol:water partition coefficient can be expressed as L_{water}/L_{oil} . Assuming that the concentrations of an organic compound are in equilibrium in all three phases, the required coefficient can be estimated by dividing Henry's law coefficient by the octanol:water coefficient, as indicated in following Equation:

$$K_{oa} = H/K_{ow} \quad (103)$$

When estimating air emission losses due to volatilization from a thin oil surface, the equilibrium coefficient K_{oa} can then be used in the two film mass transfer equation, rather than H (for a water surface). The equation for overall mass transfer coefficient from oil ($K_{L,oil}$) can be derived as below.

$$\frac{1}{K_{L,oil}} = \frac{1}{k_l} + \frac{1}{K_{oa} * k_g} \quad (104)$$

It is assumed in this approach is that the Mackay-Yeun (1983) procedure is applicable to volatilization from an oil surface as it is for a water surface when calculating and using Schmidt numbers for derivation of mass transfer coefficients.

EPA Method

The expression provided by the U.S. EPA (1994) for calculating emissions of organic compounds from an oil film overlying water makes use of a Raoult's Law-type of expression involving vapor pressure, and molecular weights and densities of oil and air. The EPA equation is defined as:

$$K_{eq} = \frac{P^* \rho_a MW_{oil}}{P_o \rho_{oil} MW_{air}} \quad (105)$$

where:

K_{eq} = dimensionless equilibrium constant between oil and air, -

P^* = vapor pressure of the organic compound of interest, atm

P_o = total pressure = 1 atm

ρ_a = density of air, g/cm³

ρ_{oil} = density of oil, g/cm³

MW_{air} = molecular weight of air = 28.8 g/g-mol

MW_{oil} = molecular weight of oil, g/g-mol.

The EPA approach then defines the overall mass transfer coefficient K as the product of the gas phase mass transfer coefficient k_g and the value of K_{eq} as calculated by Equation (105). This relationship is expressed as

$$K_{L,oil} = k_g * K_{eq} \quad (106)$$

The EPA calculation for the gas phase mass transfer coefficient k_g uses an empirical mass transfer relationship involving wind speed, gas phase Schmidt numbers and air viscosity developed by Mackay and Matsugu (1973). In TOXCHEM, however, for consistency, the gas phase mass transfer coefficient will be calculated by the expression of Mackay and Yeun (1983), as shown in the section on Surface Volatilization.

Inherent in this assumption of Equation (106) is that mass transfer of a contaminant between the oil and air is controlled by the gas phase resistance, which will not be valid for all of the organic contaminants in the TOXCHEM database. Also, the vapor pressure of the contaminant in the oil layer is based on the assumption of vapor pressure exerted by a pure compound. The EPA approach may therefore result in substantially higher emissions of some organic compounds, compared to the default approach adopted for TOXCHEM.

Modified EPA Method

The Method listed by EPA in the preceding Section does not accurately follow Raoult's Law, which states that the vapor pressure exerted by a mixture of components is the sum of vapor pressures of individual components multiplied by the mole fraction of each individual component in the mixture.

Consequently, the EPA procedure has been modified to account for the mole fraction of a contaminant in an oil layer. In this modification, it is assumed that the mole fraction of oil (the solvent) is far greater than the mole fraction of the contaminant, and thus the mole fraction of oil is considered to be equal to 1.

The mole fraction of contaminant i (mf_i) in oil is expressed as:

$$mf_i = \frac{\text{moles}_i}{\text{moles}_i + \text{moles}_{oil}} \quad (107)$$

Equation (107) can be re-written in the form:

$$mf_i = \frac{\frac{C_{i,oil}}{MW_i}}{\frac{C_{i,oil}}{MW_i} + \frac{C_{oil,oil}}{MW_{oil}}} \quad (108)$$

Where:

$C_{i,oil}$ = concentration of contaminant i in oil, mg/L

$C_{oil,oil}$ = concentration of oil in oil, mg/L

MW_i = molecular weight of contaminant i , g/g-mol

MW_{oil} = molecular weight of oil, g/g-mol.

The expression for the equilibrium constant K_{eq} in Equation (105) is then modified by inclusion of the mole fraction term from Equation (108), as indicated in Equation (109):

$$K'_{eq} = \frac{mf_i P^* \rho_a MW_{oil}}{P_0 \rho_{oil} MW_{air}} \quad (109)$$

The modified constant K'_{eq} is then multiplied by the gas phase mass transfer coefficient as described in the non-modified EPA procedure.

Addition of the mole fraction according to Raoult's Law is considered to provide a more correct approach to the EPA procedure for estimation of air emissions from an oil layer.

Correction Factor Method

A correction factor method is provided to the user so that they can input a constant experimental factor to correct for the emissions from the oil layer. Since the correction factor could be different for different contaminant, the correction factor is set as a compound property in the chemical database. In the absence of experimental correction factors, the default values of the correction factors are calculated based on the following approach.

$$f_{oil,correction} = \frac{K_{L,oil}}{K_{L,water}} \quad (110)$$

Where:

$f_{oil,correction}$ = correction factor for emissions from oil layer, -

$K_{L,oil}$ = overall mass transfer coefficient from oil layer, m/hr

$K_{L,water}$ = overall mass transfer coefficient from water layer, m/hr.

The $K_{L,oil}$ is determined according to the Mantis method and $K_{L,water}$ based on the Mackay and Yeun (1983), as shown in the section on Surface Volatilization. It shall be noted that the air emissions calculations from the oil layer are based on the concentration of the contaminant in the oil phase as shown in following Equation.

$$M_{emission,oil} = K_{L,oil} \cdot \left[\frac{K_{OW} \cdot X_{oil}}{\rho_{oil}} \right] \cdot C = K_{L,water} \cdot f_{oil,correction} \left[\frac{K_{OW} \cdot X_{oil}}{\rho_{oil}} \right] \cdot C \quad (111)$$

Comparing the mass emissions from the oil layer with that estimated from the water surface, the

net correction factor, thus becomes equivalent to $f_{oil,correction} \left[\frac{K_{OW} \cdot X_{oil}}{\rho_{oil}} \right]$.

The oil layer emission model is implemented in the unit processes of Primary Clarifier, API Separator, DAF, Equalization tank, Equalization tank-mixed/aerated, Floating roof tank, Grit Chamber and Bar Screen.

1.2 Flow/Mass Distribution in Process Streams

For each process unit in Toxchem, the flow and mass distribution in outlet streams is estimated based on the user specified input values. Depending on the nature of the process unit, it may have a combination of wastewater outlet stream, air stream, oil stream or sludge stream outlets. Flow and mass distribution algorithms are described for some selected process units.

DAF and API Separator unit processes

The process units of DAF and API Separator contain the outlet streams of wastewater, oil and sludge. The flow rate and the oil and solids concentrations in each stream are estimated using the following expressions.

$$Q_w = \frac{Q \cdot X_{in} \cdot R_{TSS}}{100 \cdot X_w} \quad (112)$$

$$Q_f = \frac{Q \cdot O_{in} \cdot R_{oil}}{100 \cdot O_f} \quad (113)$$

$$Q_e = Q - Q_w - Q_f \quad (114)$$

Where,

Q_w = waste sludge (underflow) flow rate, m³/h

Q_f = oil float flow rate, m³/h

Q_e = effluent flow rate, m³/h

R_{TSS} = Removal efficiency of TSS, %

R_{oil} = Removal efficiency of oil, %

X_w = concentration of solid in waste sludge underflow, g/m³

O_f = concentration of oil in float, g/m³.

Unit processes involving Powdered Activated Carbon

If the influent stream contains PAC, the concentration of PAC in different output streams is estimated by assuming that the PAC removal efficiency is same as the solid removal efficiency.

Primary Clarifier unit process

The underflow rate in the primary clarifier process unit is estimated using the following equation. Removal of oil in the underflow is now allowed in Version 4; it was not in earlier versions.

$$Q_u = \frac{Q_{in} \cdot (X_{in} - X_e)}{(X_u - X_e)} \quad (115)$$

$$Q_e = Q_{in} - Q_u \quad (116)$$

$$O_u = \frac{Q_{in} O_{in} \cdot R_{oil}}{100 \cdot Q_u} \quad (117)$$

where,

Q_u = underflow rate, m³/h

Q_e = effluent flow rate, m³/h

R_{oil} = Removal efficiency of oil, %

X_w = concentration of solid in underflow, g/m³

X_e = concentration of solid in effluent, g/m³

O_u = concentration of oil in underflow, g/m³.

Secondary Clarifier unit process

The flow and mass distribution in the secondary clarifier process unit is performed using the same set of equations as used for primary clarifier (except that no removal of oil is considered in secondary clarification). In a secondary clarifier process unit, if a waste activated sludge (WAS) stream is connected to the underflow, then two different ways of estimating the flow rate of WAS stream are possible. The flow rate of WAS stream can be estimated based on the pre-set split

fraction or based on the SRTs specified in activated sludge process units. Following equations are used for each method.

Method 1- Based on a specified split fraction

$$Q_{was} = f_{was} Q_u \quad (118)$$

Where,

Q_{WAS} = waste activated sludge flow rate, m³/d

f_{WAS} = fraction of total underflow rate split to waste activated sludge, -

Method 2- Based on SRT in selected activated sludge tanks

$$Q_{was} = \frac{1}{24 \cdot X_u} \left[\sum_{i=1}^n \frac{V_i \cdot X_i}{SRT} \right] \quad (119)$$

Where,

X_U = underflow SS concentration, mg/L

V_i = volume of activated sludge tank i which is selected in SRT based WAS flow calculation, m³

X_i = SS concentration in activated sludge tank i which is selected in SRT based WAS flow calculation, mg/L

SRT = SRT, d.

n = total number of activated sludge tanks, -

The following situations will lead to negative underflow rates. These situations should be avoided by making sure that the set values in the input forms are appropriate.

1. The solid concentration in the underflow (X_u) is set to a value lower than the influent solid concentration (X_{in}).
2. The effluent solid concentration (X_e) is set to a value higher than the influent solid concentration (X_{in}).
3. In the SRT based WAS flow rate calculation, the estimated flow rate is higher than the underflow rate or influent flow rate due to inappropriate values of reactor volumes or SRT.

1.3 Contaminant Mass Balances in Unit Processes

In the Toxchem models, the fate of toxic organics is simulated in a number of unit processes. The mathematical basis for the toxic contaminant process simulation is based upon mass balances on the contaminant around each unit process. Three main removal mechanisms are considered in mass balance equations: (1) volatilization (including air stripping and surface volatilization), (2) sorption onto solids, and (3) biodegradation. The mass balance equations for all of the unit processes in the treatment system are solved simultaneously by the Toxchem program to determine the fate of the contaminants. The following sections provide details on the process unit model formulations and discuss underlying assumptions.

Open Versus Closed/Covered Unit Processes

Toxchem contains many process units typically used in the conveyance, primary, secondary and tertiary treatment of wastewater. Some of these process units are explicitly modeled as closed or open e.g. Sewer Reach – Open and Sewer Reach – Closed. Conversely, other unit processes may be modeled both as open/covered by appropriate selection in the input form. In modeling the open process units, it is assumed that these process units are infinitely ventilated and the gas phase contaminants are continuously swept away from the water surface. Therefore, the gas phase concentration for the open (infinitely ventilated) system is assumed to be zero. In the case of closed/covered process units, the head space ventilation flow rate are explicitly specified and used to define the mass balance equation for the gas phase. For covered/closed systems, the gas and liquid mass balance equations are simultaneously solved to estimate the gas and liquid phase concentration.

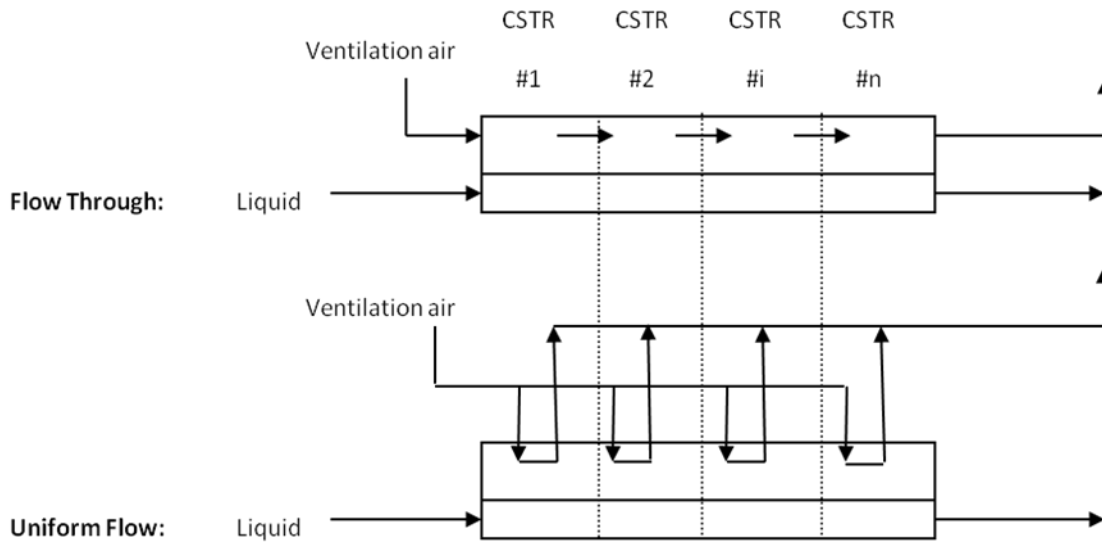
The following sections document the derivation of the models present in Toxchem software.

Sewer Reaches - Closed

Sewer reaches are modeled as a user prescribed number of continuous-flow stirred tank reactors (CSTRs). The number of specified CSTRs divides the sewer in equal size reactors for both the liquid and gas phases. For each CSTR, the contents are assumed to be completely mixed. For the closed sewer reach, there are two possible conditions that can be modeled with respect to ventilation gas flow, flow-through and uniform flow. In the flow-through mode, all of the air entering the reach travels through all of the reach. In the uniform flow mode, the head space of each CSTR is separately ventilated i.e. the ventilation air is divided equally by the number of CSTRs. The schematic below illustrates both the flow-through and uniform flow modes.

The possible conditions under which Toxchem models the closed reach as a flow through system include:

- the influent air connection is connected to a air outlet stream from another unit process
- the influent air connection is connected to the forced air unit process
- the effluent air stream is split and directed to two or more separate unit processes.



In all other conditions, Toxchem models the closed reach as a uniform flow. For the uniform flow system, the gas concentration displayed on the screen is the average of the gas concentrations for each of the CSTRs.

The steady state mass balance equations for contaminant transport in each CSTR are:

Liquid Phase:

$$Q(I + S_{i-1})C_{i-1} - Q(I + S_i)C_i - K_L \left(C_i f_{non} - \frac{C_{gi}}{H} \right) A_i = 0 \quad (120)$$

gas phase:

$$Q_g (C_g^* - C_{gi}) + K_L \left(C_i f_{non} - \frac{C_{gi}}{H} \right) A_i = 0 \quad (121)$$

where,

C_i = contaminant concentration in liquid CSTR i , mg/m^3

C_{i-1} = contaminant concentration in liquid CSTR $i-1$, i.e., CSTR immediately upstream of i , mg/m^3

C_{gi} = contaminant concentration in gaseous CSTR i , mg/m^3

C_{g^*} = ambient contaminant concentration if uniform ventilation, or C_{gi-1} if flow-through type ventilation, mg/m^3

C_{gi-1} = contaminant concentration in gaseous CSTR i-1, i.e., CSTR immediately upstream of i, mg/m^3

S_{i-1} = influent sorption term, -

S_i = effluent sorption term, -

Q = wastewater flow rate, m^3/h

Q_g = headspace ventilation rate, m^3/h

K_L = overall mass transfer coefficient, m/h

H = Henry's Law coefficient, $\text{m}^3 \text{ liquid}/\text{m}^3 \text{ gas}$

A_i = interfacial surface area for each CSTR, m^2

f_{non} = pH dependent non-dissociated fraction of a contaminant, -

The wastewater flow rate (Q) and headspace ventilation rate (Q_g) (air flow rate) are prescribed by the user. The wastewater flow rate and user-prescribed reach characteristics (channel slope, diameter and roughness coefficient) are used in conjunction with Manning's equation to solve for depth of water flow. This in turn is used to calculate interfacial surface area (A_i) for each CSTR. The total headspace ventilation rate is either entered as a user-prescribed fraction of the liquid flow rate or is calculated from the specified air influent streams. For uniform ventilation the total headspace ventilation rate is divided equally between the gas phase CSTRs. The overall mass transfer coefficient (K_L) is estimated as described in Section on Volatilization from Surfaces.

Sewer Reaches - Open

Open Sewer Reaches are modeled as a user prescribed number of continuous-flow stirred tank reactors (CSTRs). The number of specified CSTRs divides the sewer in equal size reactors for both the liquid and gas phases. For each CSTR, the contents are assumed to be completely mixed. The Open Sewer Reaches are modeled as infinitely ventilated system. Therefore, the gas phase concentrations are assumed to be zero.

The steady state mass balance equations for contaminant transport in each CSTR are:

$$Q(I + S_{i-1})C_{i-1} - Q(I + S_i)C_i - K_L C_i f_{non} A_i = 0 \quad (122)$$

$$M_{g,i} = K_L C_i f_{non} A_i \quad (123)$$

$$M_g = \sum_{i=1,n} M_{g,i} \quad (124)$$

where,

C_i = contaminant concentration in liquid CSTR i , mg/m^3

C_{i-1} = contaminant concentration in liquid CSTR $i-1$, i.e., CSTR immediately upstream of i , mg/m^3

S_{i-1} = influent sorption term, -

S_i = effluent sorption term, -

Q = wastewater flow rate, m^3/h

K_L = overall mass transfer coefficient, m/h

A_i = interfacial surface area for each CSTR, m^2

$M_{g,i}$ = mass of contaminant in gas phase from CSTR i , mg/h

M_g = total mass of contaminant in from all the CSTR, mg/h

f_{non} = pH dependent non-dissociated fraction of a contaminant, -.

The wastewater flow rate (Q) and headspace ventilation rate (Q_g) (air flow rate) are prescribed by the user. The wastewater flow rate and user-prescribed reach characteristics (channel slope, diameter and roughness coefficient) are used in conjunction with Manning's equation to solve for depth of water flow. This in turn is used to calculate interfacial surface area (A_i) for each CSTR. The overall mass transfer coefficient (K_L) is estimated as described in Section on Volatilization from Surfaces.

Drop Structures – Closed

The closed drop structure unit process object is modeled by assuming that the headspace in the drop structure is well-mixed and finitely ventilated. The relationship using the influent, effluent contaminant concentration in liquid and gas phase concentration as developed in the Volatilization at Drops section is used along with the gas-phase steady state mass balance, to estimate the liquid and gas phase concentrations.

$$\frac{C_o f_{non} - \frac{C_g}{H}}{C_{f_{non}} - \frac{C_g}{H}} = [\exp (A d^B q^D z^F [1 + 0.0168(T_c - 20)])]^{\Psi_m} \quad (125)$$

$$Q_g (C_{go} - C_g) + Q C_o - Q C = 0 \quad (126)$$

where,

Q_g = air flow rate through drop structure, m³/h

C_{go} = contaminant concentration in air influent, mg/m³

C_g = contaminant concentration in air effluent, mg/m³

Q = wastewater flow rate, m³/h

C_o = wastewater influent contaminant concentration, mg/m³

C = estimated wastewater effluent contaminant concentration, mg/m³

f_{non} = pH dependent non-dissociated fraction of a contaminant, -

and other terms as have been defined previously

If the influent air connection is not connected or the influent air flow rate is zero then the ventilation air flow rates are considered to be equal to the sewer ventilation rate specified in the input form. In making the gas phase mass balance, it is assumed that the sorbed contaminant in influent is unavailable for volatilization. The estimated soluble liquid contaminant concentration from the mass balance equation is corrected using the following equation.

$$C_{eff} (1 + S_{eff}) = C + C_o S_o \quad (127)$$

$$C_{eff} = \frac{C + C_o S_o}{(1 + S_{eff})} \quad (128)$$

where,

C = estimated wastewater effluent contaminant concentration, mg/m³

C_{eff} = corrected wastewater effluent contaminant concentration, mg/m³

S_o = influent sorption term, -

S_{eff} = effluent sorption term, -.

Drop Structures – Open

The open drop structure unit process object is modeled by assuming that the headspace in the drop structure opens to atmosphere and is infinitely ventilated. The relationship using the influent, effluent contaminant concentration in liquid and gas phase concentration as developed in the Volatilization at Drops section is used along with the assumption that the gas phase concentrations are zero. The following equation is used to estimate the expected soluble concentration in effluent.

$$\frac{C_o}{C} = [\exp (A d^B q^D z^F [1 + 0.0168(T_c - 20)])]^{\psi_m} \quad (129)$$

$$M_g = Q \cdot (C_o - C) \quad (130)$$

where,

Q = wastewater flow rate, m³/h

C_o = wastewater influent contaminant concentration, mg/m³

C = estimated wastewater effluent contaminant concentration, mg/m³

M_g = mass flow rate of contaminant in gas phase, mg/h

and other terms as have been defined previously

In drop structures, it is assumed that the sorbed contaminant in influent is unavailable for volatilization. The effluent soluble liquid contaminant concentration is corrected using the following mass balance equation.

$$C_{eff} (1 + S_{eff}) = C + C_o S_o \quad (131)$$

$$C_{eff} = \frac{C + C_o S_o}{(1 + S_{eff})} \quad (132)$$

where,

C = estimated wastewater effluent contaminant concentration, mg/m³

C_{eff} = corrected wastewater effluent contaminant concentration, mg/m³

S_o = influent sorption term, -

S_{eff} = effluent sorption term, -

Process Drain

The Process Drain process unit is modeled by considering that the water surface is in contact with atmospheric air and the process unit is infinitely ventilated. Based on these assumptions, the gas phase concentrations are assumed to be zero and only the total mass of the contaminant emitted from the process is estimated.

The general mass balance for the liquid stream around the process drain is presented below:

$$Q(1 + S_o)C_o - Q(1 + S)C - f_{air}Q(1 + S_o)C_o = 0 \quad (133)$$

where,

Q = wastewater flow rate, m³/h

S_o = influent sorption term, -

C_o = Influent liquid phase contaminant concentration, ug/L

C = effluent liquid phase contaminant concentration, ug/L

S = effluent sorption term, -

f_{air} = fraction of total influent contaminant mass volatilized, -.

Equation (133) is rearranged in Equation (134) to solve for the effluent liquid phase contaminant concentration.

$$C = \frac{Q(1 + S_o)(1 - f_{air})C_o}{Q(1 + S)} \quad (134)$$

This fraction, f_{air}, is dependent on the overall mass transfer coefficient, the wastewater flow and the exposed surface area of the liquid at the drain. The estimation method of, f_{air}, is described in the section on Volatilization at Process Drain.

Lift Stations

The lift station model is used to estimate emissions from the wet-well of a covered lift station that is filled over a period of time and then pumped out. The emissions from the process occur as air is displaced from above the wet-well. The Lift Station model results in a finite gas flow

rate. The gas emitted from the wet-well is considered to be in equilibrium with the liquid phase. The mass balance of the contaminant around the wet-well can be written as follows to estimate the gas and liquid phase concentrations:

$$Q_l C_0 (1 + S_o) - Q_l (1 + S) C - f_{non} Q_g H C = 0 \quad (135)$$

Where, Q_g is given by:

$$Q_g = \frac{Q_l t}{24} \quad (136)$$

The gas phase concentration is estimated using the following expression:

$$C_g = f_{non} H C \quad (137)$$

where,

C_0 = influent concentration to the lift station, ug/L

Q_g = gas flow rate, m³/h

Q_l = liquid flow rate, m³/h

C_l = contaminant concentration in liquid leaving the lift station, ug/L

C_g = contaminant concentration in gas phase, ug/L

S = overall sorption coefficient which includes solids, oil and PAC, -

H = Henry's Law coefficient, m³_{liq}/m³_{gas}

t = amount of time per day the pump is off, h

f_{non} = pH dependent non-dissociated fraction of a contaminant, -

Bar Screen Process

As wastewater flows through the bar screen, the metal bars offer resistance to the water passing through. This resistance can result in turbulence and eddies, which dissipate some of the energy in the wastewater flow. The head loss through the bar screen racks is calculated using equation below (Metcalf and Eddy, 1991).

$$h_L = \frac{1}{7} * \left(\frac{v^2 - v_0^2}{2 * g} \right) \quad (138)$$

where:

h_L = head loss, m

0.7 = empirical discharge coefficient to account for turbulence and eddy losses, -

v = velocity of flow through the openings on the bar rack, m/s

v_o = approach velocity in upstream channel, m/s

g = acceleration constant due to gravity = 9.81 m/s^2 .

It may then be possible to relate the emission rates to the head loss, or energy dissipation. The head loss is then used in an expression that translates the head loss to an equivalent power loss as indicated in equation below:

$$P_L = \left(\frac{Q}{86,400} \right) * (h_L * g) \quad (139)$$

where:

P_L = Power loss, kW

Q = wastewater flow, m^3/d

86,400 = conversion of day to seconds per day

g = acceleration constant due to gravity = 9.81 m/s^2 .

The power loss is then converted to a specific Power loss by dividing the Power loss value by the volume of wastewater in the structure enclosing the bars of the screen. The units of measurement of specific power loss are kW/m^3 .

Once the specific Power loss is computed, the mass transfer coefficient for surface volatilization is calculated in the same manner as for volatilization from a tank with subsurface mechanical mixing developed by Peng et al. (1995).

Grit Chambers

The grit chamber is assumed to be a completely mixed continuous flow stirred tank reactor (CSTR). Depending on the process configuration, the grit chambers can be modeled as open (infinitely ventilated or closed (finitely ventilated). The surface volatilization and the volatilization and stripping to process air bubbles, when applicable, are assumed to be the only removal mechanisms. The mass balance equations for the grit chamber are:

Liquid Phase:

$$Q(I+S_o)C_o - Q(I+S)C - V[k_v(Cf_{non} - \frac{C_g}{H}) + k_d C] = 0 \quad (140)$$

Gas Phase:

$$V [k_v(Cf_{non} - \frac{C_g}{H}) + k_d C] - Q_g C_g = 0 \quad (141)$$

where,

Q = wastewater flow rate, m³/h

C_o = influent contaminant concentration, mg/m³

C = effluent contaminant concentration, mg/m³

C_g = gas phase contaminant concentration, mg/m³

H = Henry's Law coefficient, m³ liquid/m³ gas

V = volume of process vessel, m³

k_v = surface volatilization rate constant, h⁻¹

k_d = diffused aeration stripping rate constant, h⁻¹

f_{non} = pH dependent non-dissociated fraction of a contaminant, -.

The surface volatilization rate constant, k_v, is estimated as described in the section on Volatilization from surfaces. For aerated grit chambers, the air stripping rate constant, k_d, is estimated as described in the section on stripping in Diffused Bubble Aeration. For grit chambers, the oxygen transfer efficiency is generally not known. An oxygen transfer efficiency of 6% is assumed for the grit chamber.

Primary Clarifier/Secondary Clarifier/Sludge Thickener

The bulk volume of the clarifier is modeled as a CSTR. The liquid phase contaminant concentration in the sludge waste stream is assumed to be equal to the clarifier influent liquid phase contaminant concentration. Contaminants entering the clarifier can undergo liquid-gas mass transfer from the quiescent surface and from the weirs.

The mass balance equations for the clarifier are:

Liquid Phase:

$$Q(I + S_o)C_o - Q_w(I + S_w)C - Q_e(I + S)C - V k_v \left(C f_{non} - \frac{C_g}{H} \right) = 0 \quad (142)$$

Gas Phase:

$$V k_v \left(C f_{non} - \frac{C_g}{H} \right) + Q_e C - Q_e C_{eff} - Q_g C_g = 0 \quad (143)$$

where,

Q_w = wasting flow rate, m³/h

Q_e = effluent flow rate, m³/h, = $Q - Q_w$

C_o = contaminant concentration in clarifier influent, mg/m³

C = contaminant concentration in clarifier prior to weir, mg/m³

C_{eff} = contaminant concentration in clarifier effluent after weir, mg/m³

S_w = waste sludge sorption term, -

S = effluent sorption term before weir, -

S_{eff} = effluent sorption term after weir, -

f_{non} = pH dependent non-dissociated fraction of a contaminant, -.

It should be noted that the loss of contaminant due to volatilization across the weir is assumed to be due to the soluble concentration only, therefore no sorption term is included in the gas phase equation. The surface volatilization rate constant is estimated according to the procedure described in Volatilization from Surface section.

The concentration change across the weir is determined by applying Equation (41):

$$\left(C f_{non} - \frac{C_g}{H} \right) \exp \left[-A \frac{D_c}{D_{oxy}} \left(\frac{100H}{100H + 1} \right) \right] + \frac{C_g}{H} - C_e f_{non} = 0 \quad (144)$$

The concentrations of the contaminant in the clarifier contents, the clarifier effluent and the vent gas are determined by solving Equations (142), (143) and (144). The estimated effluent concentration is corrected for the sorbed influent mass to estimate the corrected effluent concentration using the following expression.

$$C_{e,cor}(1 + S_{e,cor}) = C_e + CS \quad (145)$$

$$C_{e,cor} = \frac{C_e + CS}{(1 + S_{e,cor})} \quad (146)$$

where,

C_e = estimated wastewater effluent contaminant concentration, mg/m³

$C_{e,cor}$ = corrected wastewater effluent contaminant concentration, mg/m³

S = influent sorption term, -

$S_{e,cor}$ = corrected effluent sorption term, -.

Weir Process

The weir process is provided as a unit for estimating air emission losses of organic compounds as water drops over a V-notch (saw-tooth) weir. [For estimating mass air emissions from water falling over a rectangular weir, use of the drop structure process unit is recommended.] The weir model is one of two volatilization mechanisms in primary and secondary clarifiers, surface volatilization being the other mass transfer mechanism.

In the weir model, a user may choose to estimate emissions from either a primary effluent or a secondary effluent weir, according to the equations established by Pincince (1991). Pincince (1991) developed empirical coefficients involving weir loading rates and waterfall drop heights that are used in the mass transfer equations of the process [See sub-section "Volatilization at Weirs" for more details].

Equalization Basins

The Equalization Basin is modeled as a single completely mixed reactor with surface volatilization as the only removal mechanism. The Equalization Basin can be modeled as an open or covered basin. For the covered basin (finitely ventilated), the mass balance equations are prepared both for the liquid and gas phase to estimate the liquid and gas phase concentrations. The mass balance equations for the covered equalization basin are:

Liquid Phase:

$$Q(1 + S_o)C_o - Q(1 + S)C - V k_v \left(C_{f_{non}} - \frac{C_g}{H} \right) = 0 \quad (147)$$

Gas Phase:

$$V k_v (C_{f_{non}} - \frac{C_g}{H}) - Q_g C_g = 0 \quad (148)$$

The surface volatilization rate constant is estimated as described in the section on Volatilization from Surface.

For the open Equalization basin, only the liquid phase equation, with the assumption that C_g is close to zero, is used to solve for the concentration in the effluent. The mass of contaminant in the air is then estimated by the difference of contaminant masses between influent and effluent.

Equalization – Mixed/Aerated

Equalization basins employing diffused and/or mechanical aeration are modeled as a user specified number of CSTRs in series in both the liquid and gas phases. The mixed/aerated equalization basin can be modeled either as an open or close basin. The mechanisms of surface volatilization and air stripping are assumed to be the only removal mechanisms. The model for equalization basins that employ both mechanical and diffused aeration has stripping rate coefficients associated with each of these aeration mechanisms. With respect the air flow rates, the equalization basin is considered as a uniform flow system (each basin having its own head space). The mass balance equations for the i^{th} CSTR for a closed equalization basin are:

Liquid Phase:

$$Q[(1 + S_{i-1})C_{i-1} - Q[(1 + S_i)C_i - \frac{V}{N}[(k_v + k_s)(C_i f_{non} - \frac{C_{vi}}{H})] + Q_{gi0}C_{gi0} - Q_{gi}C_{gi} = 0 \quad (149)$$

Gas Phase:

$$\frac{V}{N}[(k_v + k_s)(C_i f_{non} - \frac{C_{vi}}{H})] + Q_{gi}C_{gi} - Q_{vi}C_{vi} = 0 \quad (150)$$

where,

- Q = wastewater flow rate, m³/h
- C_{i-1} = contaminant concentration in liquid CSTR i-1, mg/m³
- S_{i-1} = influent sorption term, -
- C_i = contaminant concentration in liquid CSTR i, mg/m³
- S_i = effluent sorption term, -

- V = total volume of reactors, m^3
 N = number of CSTRs, -
 k_v = surface volatilization rate constant, h^{-1}
 k_s = stripping rate constant for mechanical aeration, h^{-1}
 f_{non} = pH dependent non-dissociated fraction of a contaminant, -
 Q_{gi0} = influent air flow rate into tank i, m^3/h
 C_{gi0} = contaminant concentration in influent air, mg/m^3
 Q_{gi} = Diffused air flow rate from tank i, m^3/h , maximum of process air flow rate and influent air flow rate
 C_{gi} = contaminant concentration in effluent diffused air by equation (151), mg/m^3
 Q_{vi} = headspace ventilation air flow rate in tank i, m^3/h
 C_{vi} = contaminant concentration in the ventilation air in tank i, mg/m^3 .

where C_{gi} is given by :

$$C_{gi} = HC_i f_{non} - (HC_i f_{non} - C_{gi0}) e^{\frac{-K_L a V}{NQ_{gi0}}} \quad (151)$$

The diffused air flow rate, Q_{gi0} , in tank i is considered to be the maximum of the process air flow rate specified in the process unit inputs and the forced air flow rate fed to the forced air influent connection. If the input process air flow rate is higher than the forced air flow from the air connection, then the influent contaminant concentration, C_{gi0} in diffused air is recalculated using the process air flow rate.

The vent flow rate (Q_v) is assumed to be the higher of the specified vent flow rate and the diffused air flow rate, Q_{gi0} . The surface volatilization rate constant is estimated as described in the Fate & Transport Mechanisms section under Volatilization from Surfaces. The air stripping rate constants are estimated as described in the Fate & Transport mechanisms section under Air Stripping Mechanical/Diffused Aeration. The N liquid phase mass balance equations are solved simultaneously with the N gas phase equations.

For the open Equalization basin, only the liquid phase equation, with the assumption that C_{vi} is close to zero, is used to solve for the concentration in effluent. The mass of contaminant in the air is then estimated by the difference of contaminant masses between influent and effluent.

Closed Surge Tank

The closed surge tank is a vessel to which wastewater is discharged over the course of a day. Although in reality the flow may be sporadic during this daily time interval, because Toxchem is a steady-state simulator, the flow is considered to be at a consistent rate. As the wastewater volume fills the tank during the specified time period, an equivalent volume of headspace air is expelled through an opening in the cover, such as a vent stack or open grate. In this way, the tank does not become pressurized. The model for this process unit assumes that the headspace air inside the tank is at equilibrium with the water phase. This assumption is consistent with the emission model for the lift station process. For mathematical details of the model, please refer to the section on “Lift Station”.

Floating Roof Tank

The emission model for floating roof tank is based on the assumption that the main source of emission from this tank is the clingage of water/oil layer adhering to the periphery of the floating roof tank exposed to the atmosphere. The exposed clingage arises when the floating roof moves down due to withdrawal of liquid in the tank. The composition of the clingage is assumed to be same as the average composition of the influent. The model uses exposed clingage height, clingage thickness and exposure time to estimate the amount of emissions. Following equations are used in estimating the emissions from the floating roof tank. At first, the concentration of contaminant is calculated in the clingage after a specified time of exposure.

$$C_{clingage} = C_{in} e^{(-K_L \cdot T \cdot f_{non})} \quad (152)$$

where,

$C_{clingage}$ = concentration of contaminant in clingage, mg/L

C_{in} = concentration of contaminant in influent

K_L = mass transfer rate, 1/hr

T = exposure time, hr

f_{non} = non-dissociated fraction, -

The total mass air emission rate $M_{emission}$ is then estimated using the following expression.

$$M_{emission} = [S_o \cdot C_o - S_{clingage} \cdot C_{clingage}] \cdot V_{clingage} \quad (153)$$

where,

S_o = sorption term for the influent, -

$S_{clingage}$ = sorption term for the clingage, -

$V_{clingage}$ = volume of the clingage, m³.

The volume of the clingage is estimated by using the following expressions.

$$V_{clingage} = A_{clingage} \cdot d_{clingage} \quad (154)$$

$$A_{clingage} = \pi \cdot D \cdot h_{clingage} \quad (155)$$

Where,

$A_{clingage}$ = area of clingage, m²

$d_{clingage}$ = depth (thickness) of clingage, m

D = diameter of tank, m

$h_{clingage}$ = height of clingage, m.

Channels

Channels are modeled as ten CSTRs in series in the liquid and gas phases to simulate plug flow. The channel can be modeled either as a closed or open system. In the case of closed system, the gas ventilation is modeled as uniform flow (i.e. each reactor is assumed to have its own headspace with ventilation air. The channel can be either diffused bubble aerated or non-aerated. The removal mechanisms are surface volatilization and stripping by diffused bubble aeration when applicable. The program solves a mass balance equation for each CSTR. The mass balance equations for the i^{th} CSTR are:

Liquid Phase:

$$Q(I + S_i)C_i - Q(I + S_{i-1})C_{i-1} - \frac{V}{N} [k_v(C_i f_{non} - \frac{C_{gi}}{H}) + k_d C_i f_{non}] = 0 \quad (156)$$

Gas phase:

$$\frac{V}{N} \left[k_v \left(C_i f_{non} - \frac{C_{gi}}{H} \right) + k_d C_i f_{non} \right] - Q_{gi} C_{gi} = 0 \quad (157)$$

$$Q_g = \sum_{i=1,10} Q_{gi} \quad (158)$$

$$C_g = \frac{\sum_{i=1,10} C_{gi} Q_{gi}}{\sum_{i=1,10} Q_{gi}} \quad (159)$$

where,

Q = wastewater flow rate, m³/h

C_{i-1} = contaminant concentration in liquid CSTR i-1, mg/m³

S_{i-1} = influent sorption term, -

C_i = contaminant concentration in liquid CSTR i, mg/m³

S_i = effluent sorption term, -

V = total volume of reactors, m³

N = number of CSTRs, -

k_v = surface volatilization rate constant, h⁻¹

k_d = stripping rate constant for diffused aeration, h⁻¹

f_{non} = pH dependent non-dissociated fraction of a contaminant, -

Q_{gi} = Diffused air flow rate in tank i, m³/h

C_{gi} = contaminant concentration in effluent diffused air by equation (151), mg/m³

Q_g = total ventilation air flow rate, m³/h

C_g = concentration in the ventilation air, mg/m³.

The surface volatilization rate constant is estimated based on the method described in Section on Volatilization from Surface. For aerated channels the air stripping rate constant is estimated as described in Section on Diffused Bubble Aeration. For channels, the oxygen transfer efficiency is generally not known. An oxygen transfer efficiency of 6% is assumed for the channels.

API Separator

The API Separator is modeled as a process to remove oil and suspended solids from the waste stream. The process can be modeled either as open or covered process. The oil and solid concentrations in the respective streams are estimated based on the mass balance of oil and solids. The contaminants entering and leaving the API basin in the liquid are assumed to be partitioned in equilibrium in liquid, solid and oil phases. The contaminants leaving the basin in the float oil and settled solids are assumed to be partitioned in equilibrium with the water phase contaminant concentration in the tank prior to the weir. The surface area of the basin is divided into two regions e.g. oil-free surface and oil-covered surface. The relative fraction of the each surface area is estimated by employing a user specified input. The surface volatilization rate from the oil-free surface is estimated using the method described in the Volatilization from Surfaces. The surface volatilization rate from the oil-covered surface is estimated by multiplying the volatilization rate from the oil-free surface by a user-specified empirical factor. The gas phase concentrations of the contaminants in the air evolved in the API Separator are assumed to be in equilibrium with respect to the liquid phase concentration in the tank and the compound's Henry's Law coefficient.

It is assumed that the water leaving the API Separator passes over a weir. The volatilization from the weir is estimated in the same manner as for a primary clarifier. It is also assumed that the contaminant concentrations sorbed to particulates do not change when going over the weir, only the liquid phase concentration changes.

The mass balance equations for the API Separator are as below:

Liquid Phase:

$$Q(I + S_o)C_o - Q_w(I + S_w)C - Q_f(I + S_f)C - Q_e(I + S_e)C - V \cdot (1 - f_{A,oil}) \cdot k_v \left(C f_{non} - \frac{C_g}{H} \right) - V \cdot f_{A,oil} \cdot k_v \cdot f_{kv,oil} \left(C f_{non} - \frac{C_g}{H} \right) = 0 \quad (160)$$

Gas Phase:

$$V \cdot (1 - f_{A,oil}) \cdot k_v \left(C f_{non} - \frac{C_g}{H} \right) + V \cdot f_{A,oil} \cdot k_v \cdot f_{kv,oil} \left(C f_{non} - \frac{C_g}{H} \right) + Q_e(C - C_e) - Q_g C_g = 0 \quad (161)$$

where,

Q_w = waste sludge flow rate, m³/h

Q_f = oil float flow rate, m³/h

Q_e = effluent flow rate, m³/h

- C_o = contaminant concentration in influent, mg/m^3
 C = contaminant concentration in tank prior to weir, mg/m^3
 C_e = contaminant concentration in effluent after weir, mg/m^3
 k_v = mass transfer rate from surface, 1/hr
 f_{non} = pH dependent non-dissociated fraction of a contaminant, -
 $f_{k_v, \text{oil}}$ = empirical mass transfer factor for oil-covered surface, -
 $f_{A, \text{oil}}$ = fraction of water surface covered with oil, -
 R_{TSS} = Removal efficiency of TSS, %
 R_{oil} = Removal efficiency of oil, %.

The surface volatilization rate constant, k_v , is estimated as described in Section on volatilization from surfaces. The weir constant, A, is determined using the primary clarifier parameters.

The concentration change across the weir is determined by applying the following Equation.

$$\left(C f_{\text{non}} - \frac{C_g}{H} \right) \exp \left[-A \frac{D_c}{D_{\text{oxy}}} \left(\frac{100H}{100H + 1} \right) \right] + \frac{C_g}{H} - C_e f_{\text{non}} = 0 \quad (162)$$

The effluent soluble liquid contaminant concentration is corrected using the following mass balance equation.

$$C_{\text{eff}} (1 + S_{\text{eff}}) = C_e + CS \quad (163)$$

$$C_{\text{eff}} = \frac{C_e + CS}{(1 + S_{\text{eff}})} \quad (164)$$

where,

C_e = estimated wastewater effluent contaminant concentration, mg/m^3

C_{eff} = corrected wastewater effluent contaminant concentration, mg/m^3

S = before weir sorption term, -

S_{eff} = effluent sorption term, -.

Dissolved Air Flotation

Dissolved air flotation (DAF) is commonly employed to either separate oils from wastewater streams or for thickening of waste activated sludge. The dissolved air flotation model can simulate either of these scenarios. The partitioning of contaminants between oil and aqueous phases is assumed to be represented by the compound's octanol-water partition coefficient (Barbari and King, 1982). Contaminants entering and leaving the flotation basin in the liquid phase are assumed to be partitioned in equilibrium between the water and oil phases. Contaminants leaving the basin in the float are assumed to be partitioned in equilibrium with the water phase contaminant concentration in the tank prior to the weir. Surface volatilization is assumed to be equivalent to that observed in aqueous systems. Gas phase concentrations of the contaminants in the air evolved in the flotation basin are assumed to be in equilibrium with respect to the liquid phase concentration in the tank and the compound's Henry's Law coefficient.

It is assumed that the water leaving the DAF passes over a weir. The volatilization from the weir is estimated in the same manner as for a primary clarifier. It is also assumed that the contaminant concentrations sorbed to particulates do not change when going over the weir, only the liquid phase concentration changes.

The mass balance equations for the dissolved air flotation process are:

Liquid Phase:

$$Q(I + S_o)C_o - Q_w(I + S_w)C - Q_e(I + S_e)C - Q_a fHCf_{non} - V k_v \left(C - \frac{C_g}{H}\right) = 0 \quad (165)$$

Gas Phase:

$$V k_v \left(C - \frac{C_g}{H}\right) + Q_a fHCf_{non} + Q_e(I + S_e)(C - C_e) - Q_g C_g = 0 \quad (166)$$

where,

Q_w = waste float flow rate, m³/h

Q_e = effluent flow rate, m³/h

C_o = contaminant concentration in influent, mg/m³

C = contaminant concentration in tank prior to weir, mg/m³

C_e = contaminant concentration in effluent after weir, mg/m³

- k_v = mass transfer rate from surface, 1/hr
 f_{non} = pH dependent non-dissociated fraction of a contaminant, -
 Q_a = flotation air flow rate, m³/h
 Q_g = ventilation air flow rate, m³/h
 C_o = contaminant concentration in influent, mg/m³
 f = fractional saturation of gas bubbles, -.

The concentration change across the weir is determined by applying Equation (41):

$$\left(C f_{non} - \frac{C_g}{H} \right) \exp \left[-A \frac{D_c}{D_{oxy}} \left(\frac{100H}{100H + 1} \right) \right] + \frac{C_g}{H} - C_e f_{non} = 0 \quad (167)$$

The surface volatilization rate constant, k_v , is estimated as described in the section on Volatilization from Surfaces. The fractional saturation of gas bubble is estimated using the procedure described in the section on Diffused Bubble Aeration. The weir constant, A , is determined using the primary clarifier parameters. The concentration of the contaminants in the DAF contents, the DAF effluent, and the vent gas are determined by solving simultaneously Equations (165), (166) and (167).

The effluent soluble liquid contaminant concentration is corrected using the following mass balance equation.

$$C_{eff} (1 + S_{eff}) = C_e + CS \quad (168)$$

$$C_{eff} = \frac{C_e + CS}{(1 + S_{eff})} \quad (169)$$

where,

C_e = estimated wastewater effluent contaminant concentration, mg/m³

C_{eff} = corrected wastewater effluent contaminant concentration, mg/m³

S = before weir sorption term, -

S_{eff} = effluent sorption term, -.

Activated Sludge – Anaerobic/Anoxic

The anaerobic and anoxic activated sludge process units are added in Toxchem V4 to model the fate of contaminants in the nutrient removal activated sludge processes. The anaerobic and anoxic basins are considered to be mechanically mixed. The gas-liquid mass transfer rate due to mechanical mixing are estimated using the equation developed by Peng *et al.* (1995). The anaerobic and anoxic basins are modeled as a user specified number of CSTRs in series in both the liquid and gas phases. The basins may be modeled both as open or covered basins. The surface volatilization, stripping due to mixing, and biodegradation are assumed to be the only removal mechanisms. The biodegradation rate under anaerobic and anoxic basins is considered to be lower than that under aerobic conditions. A default value for the reduction factors under anaerobic and anoxic conditions are provided in the database. Because the information regarding anoxic and anaerobic biodegradation factors is limited, the current default values are set to 0.6 and 0.1 for anoxic and anaerobic reduction factors. The user shall change these values if better information is available. The mass balance equations for the i^{th} CSTR for the anaerobic/anoxic basin are:

Liquid Phase:

$$Q[(1 + S_{i-1})C_{i-1} - (1 + S_i)C_i] - \frac{V}{N} [(k_v + k_m)(C_i f_{non} - \frac{C_{gi}}{H}) + k_b f_{an} X_m C_i] = 0 \quad (170)$$

Gas Phase:

$$\frac{V}{N} (k_v + k_s)(C_i f_{non} - \frac{C_{gi}}{H}) - Q_{gi} C_{gi} = 0 \quad (171)$$

where,

- Q = wastewater flow rate, m³/h
- C_{i-1} = contaminant concentration in liquid CSTR i-1, mg/m³
- S_{i-1} = influent sorption term, -
- C_i = contaminant concentration in liquid CSTR i, mg/m³
- S_i = effluent sorption term, -
- V = total volume of reactors, m³
- N = number of CSTRs, -
- k_v = surface volatilization rate constant, h⁻¹
- k_m = volatilization rate due to mixing, h⁻¹

- k_b = biodegradation rate constant, $m^3/kg/h$
 f_{non} = pH dependent non-dissociated fraction of a contaminant, -
 Q_{gi} = headspace ventilation air flow rate, m^3/h
 C_{gi} = concentration in the ventilation air, mg/m^3
 f_{an} = reduction factor under anaerobic and anoxic conditions, -.

The surface volatilization rate constant, k_v is estimated as described in the section on Volatilization from Surface. The air stripping rate constant, k_m , is estimated as described in the section on volatilization due to mixing. The biodegradation rate constant, k_b and reduction factor f_{an} are obtained from the compound database. If Monod kinetics are utilized, the value of k_b is modified as described the section on suspended growth processes.

The N liquid phase mass balance equations are solved simultaneously with the N gas phase equations.

Diffused Bubble Aeration Basins

Diffused bubble aeration basins are modeled as a user specified number of CSTRs in series in both the liquid and gas phases. The basin can be modeled as an open or covered tank. The surface volatilization, stripping to air bubbles and biodegradation are assumed to be the only removal mechanisms. The mass balance equations for the i th CSTR in the diffused bubble aeration basin are:

Liquid Phase:

$$Q[(1 + S_{i-1})C_{i-1} - (1 + S_i)C_i] - \frac{V}{N} \left[k_v \left(C_i f_{non} - \frac{C_{vi}}{H} \right) + k_b X_m C_i \right] + Q_{gio} C_{gio} - Q_{gi} C_{gi} = 0 \quad (172)$$

Gas Phase:

$$\frac{V}{N} \left[k_v \left(C_i f_{non} - \frac{C_{vi}}{H} \right) \right] + Q_{gi} C_{gi} - Q_{vi} C_{vi} = 0 \quad (173)$$

where,

- Q = wastewater flow rate, m^3/h
 C_{i-1} = contaminant concentration in liquid CSTR $i-1$, mg/m^3
 S_{i-1} = influent sorption term, -

- C_i = contaminant concentration in liquid CSTR i, mg/m³
 S_i = effluent sorption term, -
 V = total volume of reactors, m³
 N = number of CSTRs, -
 k_v = surface volatilization rate constant, h⁻¹
 k_b = biodegradation rate constant, m³/kg/h
 f_{non} = pH dependent non-dissociated fraction of a contaminant, -
 Q_{gi0} = Diffused air flow rate into tank i, m³/h
 C_{gi0} = contaminant concentration in influent diffused air, mg/m³
 Q_{gi} = Diffused air flow rate from tank i, m³/h
 C_{gi} = contaminant concentration in effluent diffused air, mg/m³
 Q_{vi} = headspace ventilation air flow rate, m³/h
 C_{vi} = concentration in the ventilation air, mg/m³.

where C_{gi} is given by :

$$C_{gi} = HC_i f_{non} - (HC_i f_{non} - C_{gi}) e^{\frac{-K_L a V}{HQ_{gi}}} \quad (174)$$

The diffused air flow rate, Q_{gi0} , in tank i is considered to be the maximum of the process air flow rate specified in the process unit inputs and the forced air flow rate fed to the forced air influent connection. If the input process air flow rate is higher than the forced air flow from the air connection, then the influent contaminant concentration, C_{gi0} in diffused air is recalculated using the process air flow rate.

The vent flow rate (Q_{vi}) is assumed to be the higher of the specified vent flow rate and the diffused air flow rate, Q_{gi0} . The surface volatilization rate constant is estimated as described in the Fate & Transport Mechanisms section under Volatilization from Surfaces. The air stripping rate constants are estimated as described in the Fate & Transport mechanisms section under Diffused Aeration. The N liquid phase mass balance equations are solved simultaneously with the N gas phase equations.

For the open Diffused Aeration Basin, only the liquid phase equation, with the assumption that C_{vi} is close to zero, is used to solve for the concentration in effluent. The mass of contaminant in the air is then estimated by the difference of contaminant mass in influent and effluent.

Mechanical Aeration Basins

Aeration basins employing mechanical aerators are modeled as a user specified number of CSTRs in series in both the liquid and gas phases. The mechanical air basins may be modeled as open or covered basins. The surface volatilization, air stripping, and biodegradation are assumed to be the only removal mechanisms. The mass balance equations for the i^{th} CSTR in a mechanical aeration basin are:

Liquid Phase:

$$Q[(I + S_{i-1})C_{i-1} - (I + S_i)C_i] - \frac{V}{N} [(k_v + k_s)(C_i f_{non} - \frac{C_{gi}}{H}) + k_b X_m C_i] = 0 \quad (175)$$

Gas Phase:

$$\frac{V}{N} (k_v + k_s)(C_i f_{non} - \frac{C_{gi}}{H}) - Q_{gi} C_{gi} = 0 \quad (176)$$

where,

- Q = wastewater flow rate, m³/h
- C_{i-1} = contaminant concentration in liquid CSTR i-1, mg/m³
- S_{i-1} = influent sorption term, -
- C_i = contaminant concentration in liquid CSTR i, mg/m³
- S_i = effluent sorption term, -
- V = total volume of reactors, m³
- N = number of CSTRs, -
- k_v = surface volatilization rate constant, h⁻¹
- k_s = volatilization rate constant for mechanical aeration, h⁻¹
- k_b = biodegradation rate constant, m³/kg/h
- f_{non} = pH dependent non-dissociated fraction of a contaminant, -
- Q_{gi} = headspace ventilation air flow rate, m³/h
- C_{gi} = concentration in the ventilation air, mg/m³.

The surface volatilization rate constant, k_v is estimated as described in the section on Volatilization from Surfaces. The air stripping rate constant, k_s , is estimated as described in the section on Mechanical Aeration. The biodegradation rate constant, k_b , is obtained from the compound database. If Monod kinetics are utilized, the value of k_b is modified as described the section on suspended growth processes.

The N liquid phase mass balance equations are solved simultaneously with the N gas phase equations.

Combined Diffused and Mechanical Aeration Basins

Aeration basins employing both diffused and mechanical aeration are modeled as a user specified number of CSTRs in series in both the liquid and gas phases. The mechanical air basins may be modeled as open or covered basins. The surface volatilization, air stripping, and biodegradation are assumed to be the only removal mechanisms. The model for aeration basins that employ both mechanical and diffused aeration has stripping rate coefficients associated with each of these aeration mechanisms. Therefore, the mass balance equations for the i^{th} CSTR are:

Liquid Phase:

$$Q[(I + S_{i-1})C_{i-1} - (I + S_i)C_i] - \frac{V}{N}[(k_v + k_s)\left(C_i f_{non} - \frac{C_{vi}}{H}\right) + k_b X_m C_i] + Q_{gio}C_{gio} - Q_{gi}C_{gi} = 0 \quad (177)$$

Gas Phase:

$$\frac{V}{N}\left[(k_v + k_s)\left(C_i f_{non} - \frac{C_{vi}}{H}\right)\right] + Q_{gi}C_{gi} - Q_{vi}C_{vi} = 0 \quad (178)$$

where,

- Q = wastewater flow rate, m^3/h
- C_{i-1} = contaminant concentration in liquid CSTR i-1, mg/m^3
- S_{i-1} = influent sorption term, -
- C_i = contaminant concentration in liquid CSTR i, mg/m^3
- S_i = effluent sorption term, -
- V = total volume of reactors, m^3

- N = number of CSTRs, -
- k_v = surface volatilization rate constant, h^{-1}
- k_s = stripping rate constant for mechanical aeration, h^{-1} ,
- k_b = biodegradation rate constant, $m^3/kg/h$
- f_{non} = pH dependent non-dissociated fraction of a contaminant, -
- Q_{gi0} = Diffused air flow rate into tank i, m^3/h
- C_{gi0} = contaminant concentration in influent diffused air, mg/m^3
- Q_{gi} = Diffused air flow rate from tank i, m^3/h
- C_{gi} = contaminant concentration in effluent diffused air by equation (151), mg/m^3
- Q_{vi} = headspace ventilation air flow rate, m^3/h
- C_{vi} = concentration in the ventilation air, mg/m^3 .

where C_{gi} is given by :

$$C_{gi} = HC_i f_{non} - (HC_i f_{non} - C_{gi0}) e^{\frac{-K_L a V}{N} \frac{1}{HQ_{gi0}}} \quad (179)$$

The diffused air flow rate, Q_{gi0} , in tank i is considered to be the maximum of the process air flow rate specified in the process unit inputs and the forced air flow rate fed to the forced air influent connection. If the input process air flow rate is higher than the forced air flow from the air connection, then the influent contaminant concentration, C_{gi0} in diffused air is recalculated using the process air flow rate.

The vent flow rate (Q_{vi}) is assumed to be the higher of the specified vent flow rate and the diffused air flow rate, Q_{gi0} . The surface volatilization rate constant is estimated as described in the Fate & Transport Mechanisms section under Volatilization from Surfaces. The air stripping rate constants are estimated as described in the Fate & Transport mechanisms section under Diffused Aeration. The N liquid phase mass balance equations are solved simultaneously with the N gas phase equations.

For the open Diffused Aeration Basin, only the liquid phase equation, with the assumption that C_{vi} is close to zero, is used to solve for the concentration in effluent. The mass of contaminant in the air is then estimated by the difference of contaminant masses between influent and effluent.

The surface volatilization rate constant, k_v , is estimated as described in the Section on Volatilization from Surfaces. The air stripping rate constant, k_s , is estimated as described in the Section on stripping due to mechanical aeration. The value for C_g is calculated the same as it is for aerated equalization. The biodegradation rate constant is obtained from the compound database. If Monod kinetics is utilized, the value of k_b is modified as described in section on Biodegradation.

The N liquid phase mass balance equations are solved simultaneously with the N gas phase equations.

High Purity Oxygen (HPO) Reactor

HPO reactor uses in-situ oxygenation method to transfer the pure oxygen into the biological reactor. These reactors are normally open, but could also be covered. The HPO reactor can be modeled as a user specified number of CSTRs in series in both the liquid and gas phases. The in-situ oxygenation method dissolves the pure oxygen into the liquid. The oxygen transfer takes place across the boundary of the dissolved oxygen bubble. This oxygenation method results in very high oxygen transfer efficiencies ranging from 70% - 95%. To model the VOC emission from HPO, the mechanism of surface volatilization and stripping to oxygen bubbles is considered. The VOC's are also removed by biodegradation in the reactor. The mass balance equations for the ith CSTR in the HPO basin are:

Liquid Phase:

$$Q[(1 + S_{i-1})C_{i-1} - (1 + S_i)C_i] - \frac{V}{N} [k_v(C_i f_{non} - \frac{C_{vi}}{H}) + k_b X_m C_i] - Q_{gi} C_{gi} = 0 \quad (180)$$

Gas Phase:

$$\frac{V}{N} \left[k_v \left(C_i f_{non} - \frac{C_{vi}}{H} \right) \right] + Q_{gi} C_{gi} - Q_{vi} C_{vi} = 0 \quad (181)$$

where,

- Q = wastewater flow rate, m³/h
- C_{i-1} = contaminant concentration in liquid CSTR i-1, mg/m³
- S_{i-1} = influent sorption term, -
- C_i = contaminant concentration in liquid CSTR i, mg/m³
- S_i = effluent sorption term, -
- V = total volume of reactors, m³
- N = number of CSTRs, -
- k_v = surface volatilization rate constant, h⁻¹
- k_b = biodegradation rate constant, m³/kg/h
- X_m = biomass concentration, mg VSS/m³

- f_{non} = pH dependent non-dissociated fraction of a contaminant, -
 Q_{gi} = oxygen gas flow rate in tank i, m³/h
 C_{gi} = contaminant concentration in effluent gas, mg/m³
 Q_{vi} = headspace ventilation air flow rate, m³/h
 C_{vi} = concentration in the ventilation air, mg/m³.

where C_{gi} is given by :

$$C_{gi} = HC_i f_{non} - (HC_i f_{non} - C_{gi0}) e^{\frac{-K_L a V}{HQ_{gi0}}} \quad (182)$$

The use of pure oxygen and relatively high oxygen transfer efficiencies in HPO reactor make the oxygen gas flow rate an order of magnitude lower than the diffused air flow rates for the same organic loading. For estimation of the oxygen gas flow rate, either of two methods may be used in the HPO model. In the first method, the required oxygen gas flow rate is estimated based on the information on the total oxygen demand in the aeration basin. In the second method, the model estimates required oxygen gas flow rate based on the air flow rate information for an equally loaded diffused aeration system. The calculations performed in both methods are shown below.

Method 1 - HPO total gas flow estimation from oxygen demand

$$Q_g = \frac{O_D}{d_{oxy}(OTE_{HPO})Y_{oxy,HPO}} \quad (183)$$

Method 2- HPO total gas flow estimation based on the air flow rate from diffused aeration

$$O_D = Q_{g,air} d_{oxy}(OTE_{air})Y_{oxy,air} \quad (184)$$

$$Q_g = \frac{O_D}{d_{oxy}(OTE_{HPO})Y_{oxy,HPO}}$$

where,

- Q_g = oxygen gas flow rate, m³/d
 O_D = oxygen demand, g O₂/d
 d_{oxy} = density of oxygen at mid-depth in basin, mg/L

OTE_{HPO}	= oxygen transfer efficiency in HPO, -
$Y_{oxy,HPO}$	= mole fraction of oxygen in HPO gas, moles of oxygen/mole of air
$Q_{g,air}$	= diffused air flow needed to meet the oxygen demand, m^3/d
OTE_{air}	= oxygen transfer efficiency in diffused aeration-
$Y_{oxy,air}$	= mole fraction of oxygen in diffused air [a value of 0.209 is used], moles of oxygen/mole of air.

The total HPO gas flow rate (Q_g) is divided equally in all the CSTR's to get the air flow rate in each tank (Q_{gi})

The vent flow rate (Q_{vi}) is assumed to be the higher of the specified vent flow rate and the HPO gas flow rate, Q_{gi} . The surface volatilization rate constant is estimated as described in the Fate & Transport Mechanisms section under Volatilization from Surfaces. The gas stripping rate constants for the HPO process are estimated as described in the Fate & Transport Mechanisms section under Diffused Aeration. The N liquid phase mass balance equations are solved simultaneously with the N gas phase equations.

For the open HPO Basin, only the liquid phase equation, with the assumption that C_{vi} is zero, is used to solve for the concentration in effluent.

Sequencing Batch Reactor (SBR)

The Sequencing Batch Reactor (SBR) is an alternative treatment technology that combines mixing, biological reaction and settling in one reactor. There is widespread interest in this technology and there are many practical installations. Due to the time-based and intermittent operation of the reactor, it is not straight forward to estimate the air-emissions from this reactor.

A new model has been developed and implemented in Toxchem to estimate the emissions from the different stages of the SBR operational cycle. At present, the software only manages a SBR open to the atmosphere. The new model allows user to construct the operational cycle by selecting the appropriate stages in a desired order. The drop model is used to estimate the volatilization losses during the SBR fill stage. The parameters in the drop model are estimated using the following equations.

Tail-water depth

$$h_{tail} = \frac{[h_{min} + h_{max}]}{2}$$

Drop height

$$h_{drop} = \max[0, h_{feed} - h_{tail}]$$

Stream Width

$$D_c = D_{feed}$$

where:

- h_{min} = minimum water height in SBR, m
- h_{max} = maximum water height in SBR, m
- h_{feed} = height of feed discharge point above tank floor, m
- h_{tail} = tail water depth in drop model, m
- h_{drop} = drop height in drop model, m
- D_{feed} = diameter or the width of the feed inlet to SBR tank, m
- D_c = width of the channel in drop model, m.

The feed concentration of the contaminant is adjusted for the volatilization losses during the feed stage. This loss reduces the mass loading of contaminant in the SBR.

The loss of contaminant in the SBR is estimated using the following mass balance equation.

$$\frac{dV_t \cdot (1 + S_t) \cdot C_t}{dt} = Q_{feed,t} \cdot (1 + S_{in,t}) \cdot C_{in,t} - Q_{out,t} \cdot (1 + S_{eff,t}) \cdot C_t - Q_{sl,t} \cdot (1 + S_{sl,t}) \cdot C_t - r_{rem,t} \quad (185)$$

The above mass balance equation is integrated in time to estimate the contaminant concentration during each stage of the cycle. The feed flow rates, effluent flow rate and the sludge flow rates are only active during the filling, decanting and desludging phases respectively. The integration of the equation can be controlled by the time step value provided by the user. Higher integration time step will increase the error in estimation. By default an integration time step value of 1 min is used.

where,

- $Q_{feed,t}$ = feed wastewater flow rate, m³/h
- $C_{in,t}$ = contaminant concentration in feed, mg/m³
- $S_{in,t}$ = influent sorption term, -

$Q_{out,t}$	= effluent wastewater flow rate, m ³ /h
C_t	=contaminant concentration in effluent, mg/m ³
$S_{eff,t}$	= effluent sorption term, -
$Q_{sl,t}$	= WAS flow rate, m ³ /h
C_t	=contaminant concentration in effluent, mg/m ³
$S_{sl,t}$	= WAS sorption term, -
$r_{rem,t}$	= contaminant removal rate, mg/h
V_t	= total volume of reactor, m ³

The 't' subscript in the variable name shows the time dependency of these variables.

The $r_{rem,t}$ in the mass balance equation is estimated using the following relationship.

$$r_{rem,t} = r_{v,t} + r_{s,t} + r_{d,t} + r_{m,t} + r_{b,air,t} + r_{b,ano,t} + r_{b,ana,t}$$

$$r_{v,t} = k_v \cdot C_t \cdot f_{non} \cdot V_t$$

$$r_{d,t} = k_d \cdot C_t \cdot f_{non} \cdot V_t$$

$$r_{m,t} = k_m \cdot C_t \cdot f_{non} \cdot V_t$$

$$r_{b,air,t} = k_b \cdot C_t \cdot V_t \quad \rightarrow \text{First order biodegradation}$$

$$= \frac{k_b}{(1 + C_t/K_s)} C_t \cdot V_t \quad \rightarrow \text{Monod Kinetics}$$

$$r_{b,ana,t} = r_{b,air,t} \cdot f_{ana}$$

$$r_{b,ano,t} = r_{b,air,t} \cdot f_{ano}$$

where:

$$k_v \quad = \text{surface volatilization rate, h}^{-1}$$

$$k_s \quad = \text{stripping rate constant for mechanical aeration, h}^{-1}$$

$$k_d \quad = \text{stripping rate constant for diffused aeration, h}^{-1}$$

$$k_m \quad = \text{stripping rate constant for mixing, h}^{-1}$$

- k_b = first order biodegradation rate constant, $m^3/mg/h$
 f_{non} = pH dependent non-dissociated fraction of a contaminant, -
 f_{ana} = anaerobic reduction factor for biological rate, -
 f_{ano} = anoxic reduction factor for biological rate, -
 K_s = half rate constant, mg/m^3 .

The volatilization rate constant, k_v , k_s , k_d and k_m are estimated as described in the Section on compound volatilization. The biodegradation rate constant is obtained from the compound database. During integration, only the rates that are relevant for the active stage are considered. The other rates are set to zero. The rates applicable to each phase are as listed in Table below.

Table - The switches for different removal rates in different stages of the operational cycle

Phase	r_{sv}	r_{df}	r_{mech}	$r_{b,ana}$	$r_{b,ano}$	$r_{b,air}$
Feed unmixed, no react	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Feed mixed anaerobic	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Feed mixed anoxic	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
Feed aerated	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Mixed anaerobic	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Mixed anoxic	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
Aerated	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Settling	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Decanting	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Sludge Withdrawal	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Idle	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Membrane Bioreactor

A new air emission model has been developed for a membrane bioreactor (MBR) considering the effect of the coarse bubble backwash of membranes. The process estimates air emissions from both normal aeration and coarse bubble backwash. The total air emissions from the unit process are then calculated based on the frequency of the coarse bubble backwash.

The net emission from the process is estimated based on the following equation.

$$E_{total} = [1 - f_{BW}]E_{aeration} + f_{BW}E_{aeration+BW} \quad (186)$$

where:

E_{total} = total emission rate of contaminant from MBR, g/d

$E_{aeration}$ = emission rate of contaminant during aeration of MBR, g/d

f_{BW} = frequency of backwash of MBR membranes, hr/d

$E_{aeration+BW}$ = emission rate of contaminant during aeration and backwashing, g/d

The mass transfer rates for coarse bubble backwash are calculated based on the procedures outlined in the stripping in aerated vessels [diffused aeration]. The estimated mass transfer rates of fine bubble aeration and coarse bubble aeration are used to estimate the air emissions during the aeration and backwashing processes.

Aerated Lagoon

Aerated Lagoons are large shallow surface impoundments which are normally aerated using surface mechanical aerators. The aerated lagoon model is modeled similar to the mechanical surface aerated activated sludge process. Aerated lagoons are normally open, however, the option of covered lagoon is also provided in the model. The hydrodynamics in the aerated lagoon can be accounted by modeling the lagoon as a series of CSTRs. The surface volatilization, air stripping, and biodegradation are assumed to be the only removal mechanisms in aerated lagoons. Since the specific aerator power input are much smaller in aerated lagoon than the mechanically aerated activated sludge, the mass transfer coefficient for gas-liquid transfer are lower for aerated lagoon. However, the large surface area of the lagoon leads to increased mass transfer rates. The mass balance equations for the i^{th} CSTR in a mechanical aeration lagoon are:

Liquid Phase:

$$Q[(I + S_{i-1})C_{i-1} - (I + S_i)C_i] - \frac{V}{N} [(k_v + k_s)(C_i f_{non} - \frac{C_{gi}}{H}) + k_b X_m C_i] = 0 \quad (187)$$

Gas Phase:

$$\frac{V}{N} (k_v + k_s)(C_i f_{non} - \frac{C_{gi}}{H}) - Q_{gi} C_{gi} = 0 \quad (188)$$

where,

- Q = wastewater flow rate, m^3/h
 C_{i-1} = contaminant concentration in liquid CSTR i-1, mg/m^3
 S_{i-1} = influent sorption term, -
 C_i = contaminant concentration in liquid CSTR i, mg/m^3
 S_i = effluent sorption term, -
 V = total volume of reactors, m^3
 N = number of CSTRs, -
 k_v = surface volatilization rate constant, h^{-1}
 k_s = volatilization rate constant for mechanical aeration, h^{-1}
 k_b = biodegradation rate constant, $m^3/kg/h$
 f_{non} = pH dependent non-dissociated fraction of a contaminant, -
 Q_{gi} = headspace ventilation air flow rate, m^3/h
 C_{gi} = concentration in the ventilation air, mg/m^3 .

The surface volatilization rate constant, k_v is estimated as described in the section on Volatilization from Surfaces. The air stripping rate constant, k_s , is estimated as described in the section on Mechanical Aeration. The biodegradation rate constant, k_b , is obtained from the compound database. If Monod kinetics are utilized, the value of k_b is modified as described the section on suspended growth processes.

The N liquid phase mass balance equations are solved simultaneously with the N gas phase equations.

Trickling Filters

Trickling filters consist of a packed bed which has a biofilm layer growing on it. Various packing such as rock, Raschig rings, etc. have been employed, however, at present most trickling filters are constructed of modular sheet packing. Wastewater is spread over the surface of the bed and allowed to trickle down over the biofilm. If the wastewater is not distributed over 100% of the bed, neither biodegradation nor volatilization can occur in the unwetted surfaces. The contaminants in the wastewater diffuse into the biofilm where they are biodegraded. Excess biomass will slough off and be carried away by the wastewater stream. The oxygen supply to the process is generally provided by natural advection which is created by temperature differences between the surrounding air and the wastewater stream. In some cases air is supplied by forced ventilation.

The volatile contaminants may be transferred from wastewater to air as the wastewater trickles over the packing material. The airborne contaminants are then carried out of the reactor by the same movement of gas which is responsible for oxygen supply.

The model for the trickling filter process employs the following considerations:

- steady state with respect to time,
- the wastewater flows down the media in a plug flow regime,
- the air stream flows co-current or counter-current to the liquid stream in a plug flow regime,
- the gas phase contaminant concentration is considered,
- the biofilm is modeled as follows:
 - a stagnant liquid layer between the bulk liquid and the biofilm provides an external mass transfer resistance,
 - the rate of biodegradation is first order with respect to biomass and contaminant concentrations,
 - there is an internal diffusion resistance through the biofilm,
 - the biofilm is of constant thickness and density for the entire process.

The trickling filter is modeled as 10 reactors in series. The liquid phase and gas phase mass balance equations for each reactor may be written as below:

Liquid Phase:

$$QdC = -(N_v + N_b)aA_x dz \quad (189)$$

$$Q(I + S_{i-1})C_{i-1} + Q_r(I + S_n)C_n - (Q + Q_r)(I + S_i)C_i - [N_v + N_b]aV_i = 0 \quad (190)$$

$$Q(I + S_{i-1})C_{i-1} + Q_r(I + S_n)C_n - (Q + Q_r)(I + S_i)C_i - \left[K_v \left(C_i f_{non} - \frac{C_{gi}}{H} \right) + N'_b C_i \right] aV_i = 0 \quad (191)$$

Gas Phase (counter-current flow):

$$Q_g dC_g = -N_v aA_x dz \quad (192)$$

$$Q_g C_{gi+1} - Q_g C_{gi} + N_v aV_i = 0$$

$$Q_g C_{gi+1} - Q_g C_{gi} + K_v \left(C_i f_{non} - \frac{C_{gi}}{H} \right) aV_i = 0$$

Gas Phase (co-current flow):

$$Q_g dC_g = N_v a A_x dz \quad (193)$$

$$Q_g C_{gi-1} - Q_g C_{gi} + N_v a V_i = 0$$

$$Q_g C_{gi-1} - Q_g C_{gi} + K_v \left(C_i f_{non} - \frac{C_{gi}}{H} \right) a V_i = 0$$

where,

N_v = mass flux out of slice due to volatilization, $\text{mg}/\text{m}^2 \cdot \text{h}$

N_b = mass flux out of slice due to biodegradation, $\text{mg}/\text{m}^2 \cdot \text{h}$

a = specific interfacial area of trickling filter media, m^2/m^3

A_x = cross-sectional area of the trickling filter, m^2

z = depth of the trickling filter, m

Q_r = internal recirculation, m^3/h .

The term representing the mass flow due to internal recirculation is added to the mass balance equation for the first reactor. It is assumed that the internal recirculation takes place from the last tank to the first tank. For estimating the sorption term in each reactor, it is assumed that the concentration of solids concentration flowing from one reactor to the next is equal to the effluent solid concentration as specified in the user input. The oil is assumed to be completely degraded in trickling filter and therefore the effluent concentration is set to zero.

The mass transfer flux due to volatilization is:

$$N_v = K_v \left(C_i f_{non} - \frac{C_g}{H} \right) \quad (194)$$

where,

K_v = volatilization mass transfer coefficient, m/h .

The mass transfer flux due to biodegradation is defined as (see Section on biofilm growth):

$$N_b = k_L \frac{D_e r_l \tanh(r_l L_f)}{D_e r_l \tanh(r_l L_f) + k_L} C = N'_b C \quad (195)$$

where,

$$r_l = \sqrt{\frac{X_f k_b}{D_e}} \quad (196)$$

and,

k_L = stagnant layer mass transfer coefficient, m/h

X_f = biomass density, kg/m³

k_b = biodegradation rate constant, m³/kg·h

D_e = diffusion coefficient in biofilm layer, m²/h

L_f = biofilm thickness, m.

A default value for the oxygen mass transfer coefficient of 0.2 m/d is included in the trickling filter process input parameters. The value is based on pilot plant trickling filter experiments. A different value may be specified by the user. The volatilization mass transfer coefficient, K_v , is calculated from the oxygen mass transfer coefficient using Equations (22) and (23) in the Section on Volatilization from Surfaces. For the trickling filter a k_G/k_L ratio of 40 is used assuming that the principal mechanism of gas liquid transfer is similar to mechanical aeration in which liquid droplets come in contact with air.

The biodegradation rate coefficient (first order with respect to contaminant liquid phase concentration) is obtained from the compound database. If no fixed film bio rate is available, the suspended solids aerobic biodegradation rate constant (first order) is used. Contaminants sorbed onto solids or oil in the influent are assumed to not be available for volatilization or biodegradation in the trickling filter.

An analytical solution obtained by solving simultaneous equations is used to estimate the concentrations of contaminants through the depth of the filter in each phase.

Rotating Biological Contactors

The Rotating biological contactors (RBCs) consist of biofilm-covered discs rotating in a basin through which a wastewater stream flows. The discs are only partially submerged in the wastewater and wastewater is picked up as the revolving disc leaves the water and is carried around by the rotation of the disc. This allows a transfer of oxygen into the wastewater to occur on the non-submerged portion of the disc. A majority of the organic contaminant removal is

expected to result from diffusion of the contaminants into the biofilm followed by subsequent biodegradation. Biodegradation of contaminants by suspended biomass in the basin is assumed to be negligible.

The RBC process is typically separated into a series of cells by baffles which segregate the wastewater basin. The headspace of the process can be either open to the atmosphere or covered. Forced ventilation of the headspace is not commonly employed.

In the RBC model, volatilization from the surface of the wastewater in the basin is assumed to be negligible with emissions dominated by volatilization from the film of wastewater that covers the rotating discs while not submerged in the wastewater basin.

The model for the RBC process employs the following assumptions:

- steady state with respect to time,
- each section of the wastewater basin is a CSTR,
- the headspace of the entire RBC is connected and considered as one CSTR,
- the background gas phase concentrations of the contaminants are negligible,
- the biofilm is modeled as follows:
 - a stagnant liquid layer between the bulk liquid and the biofilm provides external mass transfer resistance,
 - biodegradation rate is first order with respect to biomass and contaminant concentrations,
 - there is an internal diffusion resistance through the biofilm,
 - the biofilm is of constant thickness and density for the entire process.

The mass balance equation for the liquid phase of the i^{th} basin is:

$$Q(1 + S_{i-1})C_{i-1} - Q(1 + S_i)C_i - N_{vi}A_{ei} - N_{bi}A_{si} = 0 \quad (197)$$

where,

N_{vi} = mass flux due to volatilization from i^{th} CSTR, $\text{mg}/\text{m}^2 \cdot \text{h}$

N_{bi} = mass flux due to biodegradation in i^{th} CSTR, $\text{mg}/\text{m}^2 \cdot \text{h}$

A_{ei} = exposed surface area of disks in i^{th} CSTR, m^2

A_{si} = total surface area of disks in i^{th} CSTR, m^2 .

The mass flux due to volatilization from each basin is described as:

$$N_{vi} = K_v \left(C_i f_{non} - \frac{C_{gi}}{H} \right) \quad (198)$$

where,

K_v = surface volatilization mass transfer coefficient, m/h.

The relationship defining mass flux due to biodegradation is the same as for a trickling filter (Equation (195)). The surface area over which this mass flux occurs is assumed to be the total area of the discs that are present in the RBC basin.

The concentration in the gas phase is estimated using the following relationship:

$$C_v = \frac{\sum_{i=1}^N N_{vi}}{Q_v} \quad (199)$$

where,

N = number of CSTRs, dimensionless

Q_v = total headspace ventilation air flow rate, m³/h

C_v = average concentration in the ventilation air, mg/m³.

A default value for the oxygen mass transfer coefficient of 0.2 m/d is included in the RBC process input parameters. The value is based on pilot plant RBC experiments. The user may specify a different value. The volatilization mass transfer coefficient is calculated from the oxygen mass transfer coefficient using Equations (20) and (24). For the RBC a k_G/k_L ratio of 40 is used assuming that the principal mechanism of gas liquid transfer is similar to mechanical aeration in which liquid droplets come in contact with air.

The biodegradation rate coefficient (first order with respect to contaminant liquid phase concentration) is obtained from the compound database. If no fixed film bio rate is available, the suspended solids aerobic biodegradation rate constant (first order) is used.

The N liquid phase mass balance equations are solved simultaneously with Equation (199) to determine the liquid and gas phase concentrations of contaminants in the RBC.

Cooling Towers

Cooling towers are occasionally employed to cool wastewater prior to biological treatment. Contaminants may be transferred from wastewater to air as the wastewater trickles over the packing material. The contaminants are then carried out of the reactor by the same movement of gas responsible for wastewater cooling.

The model for the cooling tower process employs the following considerations:

- steady state with respect to time,
- the wastewater flows down the media in a plug flow regime,
- the air stream flows co-current or counter-current to the liquid stream in a plug flow regime,
- the gas phase contaminant concentration is considered,

Cooling towers are modeled similarly to trickling filters except that it is assumed that no biodegradation takes place. Therefore, the liquid and gas phase mass balance equations for a horizontal differential slice of the reactor are:

Liquid Phase:

$$QdC = -N_v a A_x dz \quad (200)$$

Gas phase (counter-current flow):

$$Q_g dC_g = -N_v a A_x dz \quad (201)$$

Gas Phase (co-current flow):

$$Q_g dC_g = N_v a A_x dz \quad (202)$$

where,

N_v = mass flux out of slice due to volatilization, $\text{mg}/\text{m}^2 \cdot \text{h}$

a = specific interfacial area of cooling tower media, m^2/m^3

A_x = cross-sectional area of the cooling tower, m^2

z = depth of the cooling tower, m .

The mass transfer flux due to volatilization is defined as:

$$N_v = K_v \left(C f_{non} - \frac{C_g}{H} \right) \quad (203)$$

where,

K_v = volatilization mass transfer coefficient, m/h.

A value for the liquid film mass transfer coefficient of 0.8 m/d (for all contaminants) is used in the cooling tower process. The volatilization mass transfer coefficient is calculated from the oxygen mass transfer coefficient using Equations (20) and (24). For the cooling tower a k_G/k_L ratio of 40 is used assuming that the principal mechanism of gas liquid transfer is similar to mechanical aeration in which liquid droplets come in contact with air. The value of K_v is determined, therefore, by the Henry's Law coefficient (H) value of the compound. The temperature used to correct the compound H value is that of the cooling tower influent.

Contaminants sorbed onto solids or oil in the influent are assumed to not be available for volatilization in the cooling tower.

Equations (200) and (201) are solved simultaneously to predict the concentrations of contaminants through the depth of the tower in each phase.

Polishing Ponds

Polishing ponds are modeled as completely mixed reactors with surface volatilization as the only removal mechanism. The effluent suspended solids from the pond are specified by the user. Solids removed (settled) in the pond are assumed to be degraded. The contaminants associated with the solids are thus available for volatilization or discharge in the effluent. The mass balance equations for an equalization basin are:

Liquid Phase:

$$Q[(1 + S_o)C_o - (1 + S)C] - V k_v \left(C f_{non} - \frac{C_v}{H} \right) = 0 \quad (204)$$

Gas Phase:

$$V k_v \left(C f_{non} - \frac{C_g}{H} \right) - Q_v C_v = 0 \quad (205)$$

where,

Q = wastewater flow rate, m³/h

C_o	= contaminant concentration in influent, mg/m^3
S_o	= influent sorption term, -
C	= contaminant concentration in effluent, mg/m^3
S	= effluent sorption term, -
V	= total volume of reactors, m^3
k_v	= surface volatilization rate constant, h^{-1}
f_{non}	= pH dependent non-dissociated fraction of a contaminant, -
Q_v	= headspace ventilation air flow rate, m^3/h
C_v	= concentration in the ventilation air, mg/m^3 .

The surface volatilization rate constant is estimated as described in the section on Volatilization from Surfaces.

Chlorine Disinfection

The disinfection of wastewater effluents (principally municipal) by chlorination can result in formation of trihalomethanes (THMs); however, the formation only proceeds if the effluent is nearly or completely nitrified. This is because the chlorine will react preferentially with ammonia before reacting with the humic acids that are the precursors to THM formation.

According to Sawyer and McCarty (1967) free residual chlorine is only available for chloramine production after two moles of Cl_2 are added per mole of ammonia-N. Therefore, the minimum required chlorine equals 144 g (71 g/mole) and the minimum required ammonia equals 14 grams. Therefore, 144g/14g equals 10.3 grams of chlorine per gram $\text{NH}_3\text{-N}$. If Cl_2 required for chloramine production is greater than the applied chlorine dosage then no THM formation occurs. The model for THM formation is described in following equations (Robinson and Desing, 1995).

$$TRC = C_{cl2} - 10.3 \times C_{m,NH3} \quad (206)$$

$$C_{THMs} = a + b[\log T_C] - TRC \quad (207)$$

where,

C_{THMs} = total THMs formed at the end of the contact basin, ug/L

a, b = model constants, -

Tc	= contact time, minutes
TRC	= total residual chlorine in the contact basin, mg/L
C _{cl2}	= applied chlorine dose, mg/L
C _{in,NH3}	= ammonia-N concentration in contact basin influent, mg/L.

The value of empirical constants a and b are 40.3 and 4.64 respectively. The following expressions from Robinson and Desing (1995) are used for compounds speciation:

CHCl ₃ (chloroform)	= 0.92 THMs	CAS NUM. 67-66-3
CHCl ₂ Br (bromodichloromethane)	= 0.06 THMs	CAS NUM. 75-27-4
CHClBr ₂ (dibromochloromethane)	= 0.02 THMs	CAS NUM. 124-48-1

The Chlorine Disinfection unit is modeled as a 10 reactor system i.e. plug flow condition. The reactors can be modeled as open or closed system. For the closed system, a common headspace is considered with one single gas phase concentration. The liquid is assumed to pass over a weir. The volatilization over the weir is considered only for the soluble contaminant and it is assumed that the sorbed contaminant does not contribute to volatilization.

The mass balance equations for the chlorine disinfection unit process are as shown below.

The mass balance in liquid phase for ith tank,

Liquid Phase:

$$Q[(1 + S_{i-1})C_{i-1} - Q(1 + S_i)C_i + \frac{QC_{THM}}{N} - \frac{V}{N}[k_v(C_i f_{non} - \frac{C_v}{H})] = 0 \quad (208)$$

Gas Phase:

$$\sum_{i=1,N} \frac{V}{N} k_v \left(C_i f_{non} - \frac{C_v}{H} \right) + QC_N - QC_e - Q_v C_v = 0 \quad (209)$$

$$\sum_{i=1,N} V_i k_v C_i f_{non} - \frac{V k_v C_v}{H} + QC_N - QC_e - Q_v C_v = 0 \quad (210)$$

where,

Q	= wastewater flow rate, m ³ /h
C _{i-1}	= contaminant concentration in liquid CSTR i-1, mg/m ³
S _{i-1}	= influent sorption term, -
C _i	= contaminant concentration in liquid CSTR i, mg/m ³

- C_N = concentration in last tank, mg/m^3
 C_e = concentration after weir, mg/m^3
 S_i = effluent sorption term, -
 V = total volume of reactors, m^3
 N = number of CSTRs, -
 k_v = surface volatilization rate constant, h^{-1}
 f_{non} = pH dependent non-dissociated fraction of a contaminant, -
 Q_v = headspace ventilation air flow rate, m^3/h
 C_v = concentration in the ventilation air, mg/m^3
 C_{THM} = concentration of THM formed, mg/m^3 .

The concentration change across the weir is determined by applying Equation (41):

$$\left(C_N f_{\text{non}} - \frac{C_v}{H} \right) \exp \left[-A \frac{D_c}{D_{\text{oxy}}} \left(\frac{100H}{100H + 1} \right) \right] + \frac{C_v}{H} - C_e f_{\text{non}} = 0 \quad (211)$$

The surface volatilization rate constant, k_v , is estimated as described in the section on Volatilization from Surfaces. The weir constant, A , is determined using the primary clarifier parameters. The concentration of the contaminants in each reactor, effluent and the vent gas are determined by solving the set of above equations simultaneously.

The effluent soluble liquid contaminant concentration is corrected using the following mass balance equation.

$$C_{\text{eff}} (1 + S_{\text{eff}}) = C_e + C_N S_N \quad (212)$$

$$C_{\text{eff}} = \frac{C_e + C_N S_N}{(1 + S_{\text{eff}})} \quad (213)$$

where,

C_e = estimated wastewater effluent contaminant concentration, mg/m^3

C_{eff} = corrected wastewater effluent contaminant concentration, mg/m^3

S_N = before weir sorption term, -

C_N = concentration in the last tank before weir, mg/m³

S_{eff} = effluent sorption term, -

Anaerobic Digestion

Anaerobic digesters are assumed to be completely mixed reactors with volatilization and biodegradation as the removal mechanisms. The biomass concentration in the digester is calculated as the influent volatile suspended solids (VSS) concentration minus the VSS reduction observed in the reactor. The model assumes that the off-gas from the digestion process is in equilibrium with the digester liquid concentration and Henry's Law. The off-gas flow is computed from the VSS reduction at a rate of 1.0 m³ of off-gas per kg of VSS removed. The mass balance equation for the anaerobic digester is:

$$Q[(1 + S_o)C_o - (1 + S_d)C] - V k_b X_d C - Q_g HCf_{non} = 0 \quad (214)$$

where,

Q = wastewater flow rate, m³/h

S_o = sorption term in influent, -

C_o = contaminant concentration in influent, mg/m³

S = sorption term in digester, -

C = contaminant concentration in digester, mg/m³

X_d = volatile suspended solids concentration in digester, kg/m³

k_b = first order anaerobic biodegradation rate, m³/kg·h

Q_g = biogas flow rate, m³/h.

First order biodegradation with respect to concentration is considered in the anaerobic digester. The biodegradation rate constant is obtained from the compound database.

Aerobic Digestion

The aerobic digester is modeled as a user specified number of completely mixed reactors in series in both the liquid and gas phases. The digester may have mechanical and/or diffused bubble aeration. The biomass concentration in the digester is calculated as the influent volatile

suspended solids (VSS) concentration minus the VSS reduction observed in the reactor. Contaminants are assumed to be removed by surface volatilization, air stripping, sorption and biodegradation. The mass balance equations for the i^{th} CSTR are:

Liquid Phase:

$$Q[(1 + S_{i-1})C_{i-1} - (1 + S_i)C_i] - \frac{V}{N} [(k_v + k_s)(C_i f_{\text{non}} - \frac{C_{vi}}{H}) + k_b X_m C_i] + Q_{gio}C_{gio} - Q_{gi}C_{gi} = 0 \quad (215)$$

Gas Phase:

$$\frac{V}{N} [(k_v + k_s)(C_i f_{\text{non}} - \frac{C_{vi}}{H})] + Q_{gi}C_{gi} - Q_{vi}C_{vi} = 0 \quad (216)$$

where,

- Q = wastewater flow rate, m³/h
- C_{i-1} = contaminant concentration in liquid CSTR i-1, mg/m³
- S_{i-1} = influent sorption term, -
- C_i = contaminant concentration in liquid CSTR i, mg/m³
- S_i = effluent sorption term, -
- V = total volume of reactors, m³
- N = number of CSTRs, -
- k_v = surface volatilization rate constant, h⁻¹
- k_s = stripping rate constant for mechanical aeration, h⁻¹,
- k_b = biodegradation rate constant, m³/kg/h
- f_{non} = pH dependent non-dissociated fraction of a contaminant, -
- Q_{gio} = Diffused air flow rate into tank i, m³/h
- C_{gio} = contaminant concentration in influent diffused air, mg/m³
- Q_{gi} = Diffused air flow rate from tank i, m³/h
- C_{gi} = contaminant concentration in effluent diffused air by equation (151), mg/m³
- Q_{vi} = headspace ventilation air flow rate, m³/h

C_{vi} = concentration in the ventilation air, mg/m³.

where C_{gi} is given by :

$$C_{gi} = HC_i f_{non} - (HC_i f_{non} - C_{gi0}) e^{\frac{-K_L a V}{HQ_{gi0}}} \quad (217)$$

The diffused air flow rate, Q_{gi0} , into tank i is considered to be the maximum of the process air flow rate specified in the process unit inputs and the forced air flow rate fed to the forced air influent connection. If the input process air flow rate is higher than the forced air flow from the air connection, then the influent contaminant concentration, C_{gi0} in diffused air is recalculated using the process air flow rate.

The vent flow rate (Q_{vi}) is assumed to be the higher of the specified vent flow rate and the diffused air flow rate, Q_{gi0} . The surface volatilization rate constant is estimated as described in the Fate & Transport Mechanisms section under Volatilization from Surfaces. The air stripping rate constants are estimated as described in the Fate & Transport mechanisms section under Diffused Aeration. The N liquid phase mass balance equations are solved simultaneously with the N gas phase equations.

For the open Diffused Aeration Basin, only the liquid phase equation, with the assumption that C_{vi} is close to zero, is used to solve for the concentration in effluent. The mass of contaminant in the air is then estimated by the difference of contaminant mass in influent and effluent.

The surface volatilization rate constant is estimated as described in the section on Volatilization from Surfaces. The air stripping rate constant is estimated as described in the section on Stripping due to Diffused Aeration. The biodegradation rate constant is obtained from the compound database. If Monod kinetics are utilized, the value of k_b is modified as described in section on Biodegradation.

The above set of Equations is solved simultaneously for both the liquid and gas phase concentrations.

Water Scrubber

The water scrubber is an air treatment process intended to remove contaminants in the gas phase (e.g. headspace air from a ventilated process vessel) The conceptual scrubber consists of a packed tower through which water is distributed at the top and trickles downward through the scrubber packing elements, which are specified as having a specific surface area per volume of packing. The influent air stream can be modeled as entering the scrubber either from the bottom of the tower (counter-current flow) or from the top of the tower (co-current flow).

Based on this conceptual model, the water scrubber behaves in the same manner as the cooling tower process. The difference between the two processes, in terms of mass transfer is

that the water scrubber is intended to remove contaminants from the gas phase to the water phase, whereas in the cooling tower process, contaminants are inadvertently transferred from the water phase to the gas phase (usually air).

Generic Sludge Dewatering

The generic sludge dewatering process is assumed to be a solids separation process without any volatilization, stripping or biodegradation. The mass balance equation for sludge dewatering is as follows:

$$[Q(I + S_o) - Q_f(I + S_f) - Q_s(I + S_s)]C_o = 0 \quad (218)$$

where,

Q_f = flow rate of filtrate or supernatant, m³/h

S_f = sorption term for filtrate or supernatant, -

Q_s = flow rate of dewatered sludge, m³/h

S_s = sorption term for dewatered sludge, -

Centrifuge

The centrifuge is used for sludge dewatering. This process accounts for loss of contaminants due to volatilization from the sludge. An emission factor is computed for each compound as a function of the Henry's Law coefficient for the compound. The relationship between the Henry's Law coefficient and the emission factor was obtained from research sponsored by the Water Environment Research Federation (WERF, 1998). The emission factors for the centrifuge are computed from the following relationship:

$$E = [1 - \exp(-0.0056H)]f_{non} \quad (219)$$

where,

E = fraction of contaminant emitted from process, -

f_{non} = pH dependent non-dissociated fraction of a contaminant, -

The rate of volatilization from the centrifuge is given by:

$$r_v = EQ C_o \quad (220)$$

where,

r_v = rate of volatilization, mg/h.

Belt Filter Press

The belt filter press is used for sludge dewatering. This process accounts for loss of contaminants due to volatilization from the sludge. An emission factor is computed for each compound as a function of the Henry's Law coefficient for the compound. The relationship between the Henry's Law coefficient and the emission factor was obtained from research sponsored by the Water Environment Research Foundation (WERF, 1998). The emission factors for the belt filter press are computed from the following relationship:

$$E = [1 - \exp(-0.00587H)] f_{non} \quad (221)$$

The rate of volatilization from the belt filter press is given by:

$$r_v = EQ C_o \quad (222)$$

Sludge Drying Bed

The sludge drying bed is used for sludge dewatering. This process accounts for loss of contaminants due to volatilization from the sludge. An emission factor is computed for each compound as a function of the Henry's Law coefficient for the compound. The relationship between the Henry's Law coefficient and the emission factor was fitted from the PEEP study (Montgomery, 1990). The emission factors for the sludge drying bed are computed from the following relationship:

$$E = [1 - \exp(-1.07H)] f_{non} \quad (223)$$

The rate of volatilization from the sludge drying bed is given by:

$$r_v = EQ C_o \quad (224)$$

Concentrator

The concentrator is used to generate two streams, purified effluent and concentrate, resulting from treatment of the incoming flow to the unit. For the concentrator, information supplied by the user is the fraction of the influent flow directed to the purified effluent and the fraction of the influent contaminant mass flow directed to the concentrate. These mathematical relationships are presented in Equations (225) and (226).

$$Q_f = \frac{Q_{out}}{Q_{in}} \quad (225)$$

$$M_f = \frac{Q_{conc} C_{conc,tot}}{Q_{in} C_{in,tot}} \quad (226)$$

where,

- Q_f = fraction of influent flow directed to the effluent, -
- Q_{out} = effluent flow from concentrator, m³/d
- Q_{in} = influent flow to concentrator, m³/d
- M_f = fraction of influent contaminant mass flow directed to the concentrate, -
- Q_{conc} = concentrate flow, m³/d
- $C_{conc,tot}$ = concentrate total contaminant concentration (liquid plus non-aqueous concentrations), mg/m³
- $C_{out,tot}$ = influent total contaminant concentration, mg/m³.

The assumptions made in developing the concentrator are:

- oil, solids and activated carbon do not pass through to the effluent

- the concentrate and effluent phases are in equilibrium with respect to solid and liquid phase concentrations
- no biodegradation occurs
- no emissions occur

In addition to the flow split and mass flow split equations presented previously, three more equations are utilized to describe the concentrator system. These are the flow balance, solids mass balance and the contaminant mass balance equations (Equations (227), (228) and (229)).

$$Q_{in} = Q_{out} + Q_{conc} \quad (227)$$

$$Q_{in} C_{in,ss} = Q_{conc} C_{conc,ss} \quad (228)$$

$$Q_{in} (1 + S_{in}) C_{in,l} = Q_{conc} (1 + S_{conc}) C_{conc,l} + Q_{out} C_{out,l} \quad (229)$$

where,

$C_{in,ss}$ = influent suspended solids concentration, mg/L

$C_{conc,ss}$ = concentrate suspended solids concentration, mg/L

S_{in} = influent sorption term, -

$C_{in,l}$ = influent contaminant liquid phase concentration, ug/L

S_{conc} = concentrate sorption term, -

$C_{out,l}$ = purified effluent liquid phase concentration (same as total concentration), ug/L.

Combining the flow balance and solids mass balance equations, the concentrate suspended solids concentration can be calculated. The resulting equation is presented in Equation (230).

$$C_{conc,ss} = \frac{1}{(1 - Q_f)} C_{in,ss} \quad (230)$$

Similar relationships can be developed for oil and PAC. The equations are presented below (Equations (231) and (232)).

$$C_{conc,oil} = \frac{1}{(1-Q_f)} C_{in,oil} \quad (231)$$

$$C_{conc,PAC} = \frac{1}{(1-Q_f)} C_{in,PAC} \quad (232)$$

where:

- $C_{in,oil}$ = influent oil concentration, mg/L
 $C_{conc,oil}$ = concentrate oil concentration, mg/L
 $C_{in,PAC}$ = influent PAC concentration, mg/L
 $C_{conc,PAC}$ = concentrate PAC concentration, mg/L.

Using the flow fraction and mass fraction equations, relationships for the liquid phase purified effluent and concentrate contaminant concentrations can be calculated. The results are presented in Equations (233) and (234).

$$C_{out,l} = \frac{Q_{in}(1+S_{in})C_{in,l}(1-M_f)}{Q_{out}} \quad (233)$$

$$C_{conc,l} = \frac{M_f Q_{in}(1+S_{in})C_{in,l}}{Q_{conc}(1+S_{conc})} \quad (234)$$

It should be noted that the concentrator was developed for the use with chemicals and that the mass split is not applicable to metals modeling.

Sludge Drying

The amount of VOC volatilized during sludge drying is assumed to be proportional to the ratio of the partial pressure exerted by the contaminant and water vapor. The model is originally described in Goel (2013).

The molar rate of contaminant volatilized is expressed using the following equation.

$$m_{c,v} = m_{w,v} \frac{p_c}{p_w} \quad (235)$$

Where:

$m_{c,v}$ = mole of contaminant vaporized, mole/d

$m_{w,v}$ = mole of water vaporized, mole/d

p_c = partial pressure of contaminant, atm

p_w = partial pressure of water vapor, atm.

For the mass removal of contaminant, the equation is transformed as below.

$$\frac{M_{c,v}}{\pi_c} = \frac{M_{w,v}}{\pi_w} \frac{p_c}{p_w} \quad (236)$$

Where:

$M_{c,v}$ = mass of contaminant vaporized, g/d

$M_{w,v}$ = mass of water vaporized, g/d

π_c = molecular weight of contaminant, g/mole

π_w = molecular weight of water, g/mole.

The partial pressure of contaminant and water vapor can be correlated to the mole fractions of each compound in the dried sludge. The equations for the partial pressure of each compound are expressed as below:

$$p_c = \frac{\alpha_c f_{m,c}}{P_{atm}} \quad (237)$$

$$p_w = \frac{\alpha_w f_{m,w}}{P_{atm}} \quad (238)$$

where:

α_c = vapor pressure of pure contaminant at dryer temperature, mm Hg

α_w = vapor pressure of water at dryer temperature, mm Hg

$f_{m,c}$ = mole fraction of contaminant in the dried sludge, -

$f_{m,w}$ = mole fraction of water in the dried sludge, -

P_{atm} = atmospheric pressure, mm Hg.

and,

$$f_{m,c} = \frac{m_{c,s}}{m_{c,s} + m_{w,s}} \quad (239)$$

$$f_{m,w} = \frac{m_{w,s}}{m_{c,s} + m_{w,s}} \quad (240)$$

where:

$m_{c,s}$ = mole of contaminant in water phase of dried sludge, mole/L

$m_{w,s}$ = mole of water in in water phase of dried sludge, mole/L.

The following equation is used to estimate the molar concentration of contaminant in the water phase of the dried sludge:

$$m_{c,s} = \frac{C_c \cdot f_{non}}{\pi_c} \quad (241)$$

where:

f_{non} = the fraction of non-dissociated compound and is pH dependent, -

C_c = concentration of contaminant in liquid phase of dry sludge, mg/L.

The molar concentration of water in the water phase of the dried sludge is estimated by the following expression:

$$m_{w,s} = \frac{10^6 - C_c \cdot f_{\text{non}}}{\pi_w} \cong \frac{10^6}{\pi_w} \quad (242)$$

Combining equations, we can write the following expression for the expected mass of VOC volatilized during the drying operation.

$$M_{c,v} = M_{w,v} \frac{\alpha_c C_c \cdot f_{\text{non}}}{\alpha_w 10^6} \quad (243)$$

Now the concentration of contaminant in liquid of dried sludge depends on the mass of incoming contaminant and mass of contaminant removed during drying. The concentration in dried sludge can be expressed with the following equation.

$$C_c = \frac{M_{c,\text{in}} - M_{c,v}}{Q_{w,\text{out}}} \quad (244)$$

where:

$M_{c,\text{in}}$ = mass of contaminant in the feed sludge stream, g/d

$M_{c,v}$ = mass of contaminant vaporized, g/d

$Q_{w,\text{out}}$ = volumetric flow of water in dried sludge, m³/d

Combining equations, the mass of contaminant vaporized is estimated as below.

$$M_{c,v} = M_{w,v} \frac{\alpha_c}{\alpha_w} f_{\text{non}} \frac{M_{c,\text{in}}}{\left[M_{w,v} \frac{\alpha_c}{\alpha_w} f_{\text{non}} + 10^6 Q_{w,\text{out}} \right]} \quad (245)$$

The mass of water evaporated is estimated based on the %DS in the incoming and outgoing sludge. The vapor pressure of pure contaminant at drying temperature is estimated using the

data of vapor pressure (VP) and boiling point (BP) of the compound. The VP and BP of the compound is used in the Clausius-Clapeyron equation to estimate the heat of vaporization.

The Clausius-Clapeyron equation can be expressed as:

$$\frac{d \ln P}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2} \quad (246)$$

where:

P = vapor pressure, atm

T = temperature, °K

ΔH_{vap} = heat of vaporization of compound, cal/mol

R = ideal gas constant = 1.9872 cal/(mol-°K)

The above equation can be integrated to derive the following expression:

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (247)$$

Equation 247 can be re-arranged to provide an expression of the heat of vaporization.

$$\Delta H_{\text{vap}} = R * \left(\frac{1}{\frac{1}{T_2} - \frac{1}{T_1}} \right) * \ln \left(\frac{P_1}{P_2} \right) \quad (248)$$

The boiling point at atmospheric pressure provide (P_1 , T_1) and the vapor pressure at 25 °C provide another point (P_2 , T_2) to allow estimation of ΔH_{vap} . The estimated value is then used to find the vapour pressure at dryer temperature.

The amount of dust emission from the sludge drying process is estimated as a percentage of solid loading rate to the dryer. The amount of dust is estimated using the following expression.

$$M_{\text{dust}} = \frac{Q_{\text{in}} \cdot X_{\text{in}} \cdot f_{\text{dust}}}{100.0} \quad (249)$$

where:

M_{dust} = mass rate of dust in dryer exhaust air, g/d

Q_{in} = feed flow rate to dryer, m³/d

X_{in} = solid concentration in the feed, g/m³

f_{dust} = dust generation percentage, %.

For the covered and ventilated drying process, the mass of dust emitted is converted to solid concentration in air stream using the following expression.

$$C_{\text{dust}} = \frac{M_{\text{dust}}}{Q_{\text{air}}} \quad (250)$$

where:

C_{dust} = concentration of dust in dryer exhaust air, g/m³

Q_{air} = ventilation flow rate, m³/d.

Conveyor

During conveying process, the loss of organic contaminant is assumed to be mainly due to loss of sorbed contaminant on the dust particles.

$$M_c = \frac{Q_{\text{in}} \cdot C_{\text{sorb}} \cdot f_{\text{dust}}}{100.0} \quad (251)$$

where:

M_c = mass rate of contaminant emission, g/d

Q_{in} = feed flow rate to dryer, m³/d

C_{sorb} =sorbed contaminant concentration, g/m^3 .

The dust emission and metal emission estimation procedures for the conveyor process are same as for the dryer process.

Incinerator

The VOC in the incinerator are assumed to be completely degraded thermally and therefore the VOC air emissions from this unit are set to zero.

Fly ash / Dust removal

The fly ash/dust removal object removes contaminant, metal and solids from an air stream. In the empirical model, the user sets the removal efficiencies of each component from the air stream. The unit allows the user to have a wet or a dry process. The compounds removed from the air stream are available from the waste stream and can be transferred to other downstream treatment processes.

Settling Pond

The settling pond is modeled as completely mixed reactors with surface volatilization as the only removal mechanism. The effluent suspended solids from the pond are specified by the user. Solids removed (settled) in the pond are assumed to be accumulated in the pond. The contaminants associated with the solids are thus available for volatilization or discharge in the effluent. The mass balance equations for settling ponds are similar to polishing pond. The only difference is that the volumetric flow rate of the effluent stream is estimated based on water content in the incoming concentrated solid stream.

1.4 Metals Modeling

Toxchem models metals by simulating the sorption of metals to bio-solids and the precipitation of metals based on the solubility of the metal in influent, effluent and digester effluent. The model will consider influent to the wastewater system to have a influent sorption and solubility coefficient. Sludge influent, biological processes (activated sludge processes, aerobic digestion, trickling filter, rotating biological contactors and polishing ponds) will have an effluent sorption and solubility coefficient. Anaerobic digestion will have a digester solubility coefficient. All other processes in the Toxchem model are assumed to have no effect on the sorption or solubility of the metal. In the case where multiple streams are mixed before entering a process, the model will calculate new sorption and solubility coefficients for the mixed stream based on a mass flow-weighted basis. A

new metals liquid concentration will then be calculated on this value. If the liquid concentration is above the newly calculated solubility level then the metal will form a precipitate. Once a precipitate is formed Toxchem assumes that the precipitate will not re-dissolve.

Influent mass balance

The influent metals concentration is partitioned into soluble, sorbed and precipitate fractions by initially calculating:

$$C_{Test} = \frac{C_{in}}{(1 + K_{P1}X_o)} \quad (252)$$

where,

C_{Test} = current liquid concentration of the metal, mg/m³

C_{in} = influent metal concentration (total liquid, sorbed and precipitate), mg/m³

K_{P1} = primary sorption coefficient, m³/kg

X_o = influent volatile suspended solids concentration, kg/m³.

If C_{Test} is greater than the metal's primary solubility limit, the soluble concentration is set to the influent solubility and the concentration of metal present as precipitate is calculated as:

$$C_{P0} = C_{in} - (1 + K_{P1}X_o)C_{soli} \quad (253)$$

where,

C_{P0} = concentration of the metal precipitate, mg/m³

C_{soli} = solubility limit of the metal, mg/m³.

If C_{Test} is less than the metal's primary solubility limit, the concentration of metal present as precipitate (C_{P0}) is zero and the soluble concentration (C_{S0}) is equal to C_{Test} . The total metal concentration at any point in the treatment process is calculated as the sum of the soluble, sorbed and precipitate fractions.

Each stream leaving an influent unit process will be assigned a value for the metal solubility and sorption. For influent processes the value of K_p for the stream is set equal to K_{p1} and the value of C_s is set equal to C_{soli} .

The metals models were assembled in a similar fashion to the organics models and therefore the assumptions previously stated also hold for the metals models. Additional assumptions include:

- In each unit operation precipitated metals behave in the same manner as all other suspended solids.
- Precipitated metals do not re-dissolve once precipitated

Biological Processes Mass Balances

The effluent leaving a biological process is considered to have different characteristics (sorption and solubility) from the influent to the process. To calculate the metals concentrations leaving a biological process the following equations are used:

$$C_{Test} = \frac{C_{in}}{(1 + K_{p2}X_b)} \quad (254)$$

where,

C_{in} = concentration of the metal in the influent to the biological process, mg/m³

K_{p2} = sorption coefficient of the metal to biological solids, m³/kg

X_b = concentration of volatile suspended solids in the biological process, kg/m³.

If C_{Test} is greater than the solubility of the metal in secondary effluent, then following equations are used:

$$C_p = C_{pin} + C_{Test} - C_{Sole} \quad (255)$$

$$C_{out} = C_{sole}(1 + K_{p2}X_b) \quad (256)$$

where,

C_p = precipitate concentration leaving the biological process, mg/m³

C_{pin} = precipitate concentration entering the biological process, mg/m³

C_{Sole} = solubility of the metal in the effluent of the biological process, mg/m³

C_{out} = effluent liquid concentration of the metal including the sorbed fraction, mg/m³.

If C_{Test} is less than or equal to the C_{Sole} , then the value for C_p is set equal to the value of C_{pin} , and C_{out} is set equal to C_{Test} .

Each stream leaving a biological process will be assigned a value for the metal solubility and sorption when leaving the process. For biological processes the value of K_p for the stream is set equal to K_{P2} and the value of C_s is set equal to C_{Sole} .

Digester Processes Mass Balances

The effluent leaving an anaerobic digester is considered to have a different solubility value than the influent to the process. To calculate the metals concentrations leaving a biological process the following equations are used:

$$C_{Test} = \frac{C_{in}}{(1 + K_p X_d)} \quad (257)$$

where,

C_{in} = concentration of the metal in the influent to the biological process, mg/m³

K_p = sorption coefficient of the metal in the influent stream, m³/kg

X_d = concentration of volatile suspended solids in the anaerobic digester process, kg/m³.

If C_{Test} is greater than the solubility of the metal in Digester effluent, then the following equations are used:

$$C_p = C_{pin} + C_{Test} - C_{Sold} \quad (258)$$

$$C_{out} = C_{sold}(1 + K_p X_d) \quad (259)$$

where,

C_p = precipitate concentration leaving the anaerobic digester process, mg/m^3

C_{pin} = precipitate concentration entering the anaerobic digester process, mg/m^3

C_{Solid} = solubility of the metal in the effluent from the digester process, mg/m^3

C_{out} = effluent liquid concentration of the metal including the sorbed fraction, mg/m^3 .

If C_{Test} is less than or equal to the C_{Solid} , then the value for C_p is set equal to the value of C_{pin} , and C_{out} is set equal to C_{Test} . Each stream leaving an anaerobic digester process will be assigned a value for the metal solubility. The sorption coefficient is considered to remain constant through the anaerobic digester process. For the anaerobic digester process the value of C_s in the stream is set to C_{Solid} .

Solid Handling Processes Mass Balances

The metal emission in the air stream is assumed to be mainly due to the mass of metal lost along with dust generation. The precipitated metal and the adsorbed metal are lost with dust. The mass metal emission is estimated using the following expression.

$$M_{\text{metal}} = Q_{\text{in}} \cdot [C_{\text{sorb,metal}} + C_{\text{ppt,metal}}] \cdot f_{\text{dust}} \quad (260)$$

where,

M_{metal} = mass rate of metal emission, g/d

Q_{in} = feed flow rate to dryer, m^3/d

$C_{\text{sorb,metal}}$ = sorbed metal concentration, g/m^3

$C_{\text{ppt,metal}}$ = precipitated metal concentration, g/m^3 .

For the covered and ventilated drying process, the mass of metal in dust emitted is converted to solid concentration in air stream using the following expression.

$$C_{\text{metal}} = \frac{M_{\text{metal}}}{Q_{\text{air}}} \quad (261)$$

where,

C_{metal} = concentration of metal in dust in ventilation air, g/m³

Q_{air} = ventilation flow rate, m³/d

Stream mixing

Toxchem modifies the value for K_p and C_s for metals modeling whenever multiple streams are combined into a unit process. The model assumes that the new value of K_p and C_s will be based on a flow-weighted average of the value in the streams that are combined together. An example of a mixing of two streams is shown in the equation below:

$$K_p = \frac{K_{p1}Q_1 + K_{p2}Q_2}{Q_1Q_2} \quad (262)$$

where,

K_p = the new sorption coefficient of the mixed stream, m³/kg,

K_{p1} = the sorption coefficient of the first stream, m³/kg

Q_1 = the flow of the first stream, m³/day,

K_{p2} = the sorption coefficient of the second stream, m³/kg,

Q_2 = the flow rate of the second stream, m³/day

The same technique is used for calculating new values for C_s .

Glossary of Terms

α_c	vapor pressure of pure contaminant at dryer temperature [mm Hg]
α_w	vapor pressure of water at dryer temperature [mm Hg]
γ	temperature correction factor (sewer reach) [-]
μ_m	maximum specific growth rate [1/h]
ΔH_{vap}	heat of vaporization of compound [cal/mol]
Θ	temperature correction factor [-]
π_c	molecular weight of contaminant [g/mole]
π_w	molecular weight of water [g/mole]
ρ_a	density of air [g/cm ³]
ρ_{oil}	density of oil [g/cm ³]
Ψ	ratio of diffusion coefficients of contaminant to oxygen raised to an exponent between 0.5 and 1 [-]
Ψ_μ	ratio of overall mass transfer coefficients of contaminant to oxygen [-]
a	specific interfacial area [m ² /m ³]
a	empirical parameter in trihalomethane formation in chlorine disinfection [-]
A	surface area [m ³]
A	empirical parameter in clarifier weir relationships [-]
A	empirical coefficient relating adsorption partition coefficient for DOC and octanol-water partition coefficient (a default value of 0.82 is used) [-]
A	empirical parameter in oxygen deficit ratio for drop structures [-]
A	van't Hoff parameter used to estimate Henry's law coefficient [-]
A_{clingage}	area of clingage in floating roof tank model [m ²]
A_{ei}	exposed surface area of RBC disks in i_{th} CSTR [m ²]
A_{si}	total surface area of RBC disks in i_{th} CSTR [m ²]
A_x	cross-sectional area of trickling filter [m ²]
b	empirical parameter in trihalomethane formation in chlorine disinfection [-]
B	empirical parameter in oxygen deficit ratio for drop structures [-]
B	empirical coefficient relating adsorption partition coefficient for DOC and octanol-water partition coefficient (a default value of 0.31 is used) [-]
B	van't Hoff parameter used to estimate Henry's law coefficient [-]
C	concentration of volatile compound in water (typically effluent) [ug/L]
C^{oxy}	oxygen concentration in wastewater leaving weir [mg/L]
C_o	wastewater influent contaminant concentration [ug/L]
C_o^{oxy}	oxygen concentration in wastewater entering weir [mg/L]
C^*	liquid phase equilibrium concentration in equilibrium with a gas phase concentration [ug/L]
C_b	contaminant concentration in bulk liquid layer [mg/m ³]
C_c	concentration of contaminant in liquid phase of dry sludge [mg/L]

C_{Cl_2}	applied chlorine dose [mg/L]
$C_{clingage}$	concentration of contaminant in clingage in floating roof tank model [mg/L]
$C_{conc,oil}$	concentrate oil concentration (concentrator) [mg/L]
$C_{conc,PAC}$	concentrate PAC concentration (concentrator) [mg/L]
$C_{conc,ss}$	concentrate suspended solids concentration (concentrator) [mg/L]
$C_{conc,tot}$	concentrate total contaminant concentration [ug/L]
C_{DOC}	concentration of contaminant sorbed onto DOC [mg/L]
C_{doc}	concentration of DOC [mg DOC/L]
C_{dust}	concentration of dust in dryer exhaust air [g/m ³]
C_e	wastewater effluent contaminant concentration after clarifier weir [ug/L]
$C_{eff,l}$	unit process effluent liquid phase contaminant concentration [ug/L]
C_f	concentration of compound in water at equilibrium with powdered activated carbon [mg/L]
C_g	concentration of volatile compound in gas phase [ug/L]
C_{go}	concentration of volatile compound in influent gas phase [ug/L]
C_{qi0}	contaminant concentration in influent diffused air to activated sludge tank i [mg/m ³]
C_{gi}	gas phase contaminant concentration in CSTR i [mg/m ³]
C_{gi-1}	gas phase contaminant concentration in CSTR i-1 [mg/m ³]
C_{q^*}	ambient gas phase contaminant concentration in uniform ventilation [mg/m ³]
C_i	liquid phase contaminant concentration in CSTR i [mg/m ³]
C_{i-1}	liquid phase contaminant concentration in CSTR i-1 [mg/m ³]
C_{in}	influent metal concentration (total of soluble, sorbed, precipitate) [mg/m ³]
$C_{in,oil}$	influent oil concentration [mg/L]
C_{in,NH_3}	ammonia-N concentration in chlorine contact basin influent [mg/L]
$C_{in,PAC}$	influent PAC concentration [mg/L]
$C_{in,l}$	influent contaminant liquid phase concentration [ug/L]
$C_{in,ss}$	influent suspended solids concentration [mg/L]
$C_{i,oil}$	concentration of contaminant i in oil [mg/L]
C_{metal}	concentration of metal with dust in ventilation air from solids handling process [g/m ³]
$C_{oil,oil}$	concentration of oil in oil [mg/L]
C_{out}	effluent metal concentration (total of soluble, sorbed, precipitate) [mg/m ³]
$C_{out,l}$	effluent liquid phase contaminant concentration [ug/L]
$C_{out,tot}$	effluent total contaminant concentration [ug/L]
C_{oxy}^*	liquid phase equilibrium oxygen concentration in equilibrium with a gas phase oxygen concentration at aeration tank mid-depth [mg/L]

C_{oxy}	oxygen concentration at aeration tank mid-depth [mg/L]
C_p	concentration of metal precipitate leaving secondary treatment or digester processes [mg/m ³]
C_{pac}	concentration of compound sorbed to powdered activated carbon [mg/L]
C_{P0}	concentration of metal precipitate in primary treatment processes [mg/m ³]
C_{pin}	concentration of metal precipitate entering secondary treatment or digester processes [mg/m ³]
$C_{ppt,metal}$	precipitated metal concentration in solids handling process dust [g/m ³]
C_s	contaminant concentration at outer edge of biofilm [mg/m ³]
C_s	soluble metal concentration [mg/m ³]
C_s^{oxy}	oxygen saturation concentration in wastewater (weir model) [mg/L]
C_{so}	concentration of compound in wastewater sorbed to oil [mg/m ³]
C_{sold}	solubility limit of metal in anaerobic digester [mg/m ³]
C_{sole}	solubility limit of metal in secondary treatment processes [mg/m ³]
C_{soli}	solubility limit of metal in primary treatment processes [mg/m ³]
$C_{sorb,metal}$	sorbed metal concentration in solids handling process dust [g/m ³]
C_{ss}	contaminant concentration adsorbed on wastewater solids [mg/m ³]
C_{THMs}	total THM concentration at end of contact basin [ug/L]
C_{tot}	sum of liquid phase and particulate phase compound concentrations in water [ug/L]
C_{vi}	contaminant concentration in the ventilation air in activated sludge tank i [mg/m ³]
C_x	concentration of contaminant in solid phase (mg/kg)
CSTR	continuous stirred tank reactor
d	water drop height [m]
d_a	density of air [g/cm ³]
d_c	density of compound [g/cm ³]
$d_{clingage}$	depth (thickness) of clingage in floating roof tank model [m]
d_o	density of oil [kg/m ³]
d_{oxy}	density of oxygen at mid-depth point in basin [mg/L]
d_w	density of water [g/cm ³]
D	empirical parameter in oxygen deficit ratio for drop structures [-]
D	diameter of tank [m]
D_c	width of the channel in drop model [m]
D_{feed}	diameter or the width of the feed inlet to SBR [m]
D_e	diffusion coefficient of compound in biofilm [m ² /h]
D_G	diffusion coefficient of compound in air [cm ² /s]
D_L	diffusion coefficient of compound in water [cm ² /s]

D_{oxy}	diffusion coefficient of oxygen in water [cm^2/s]
E	surface aerator power delivery efficiency factor [-]
E	fraction of contaminant emitted from process [-]
$E_{aeration}$	emission rate of contaminant during aeration of MBR [g/d]
$E_{aeration+BW}$	emission rate of contaminant during aeration and backwash of MBR [g/d]
E_{total}	Total emission rate of contaminant from MBR [g/d]
f	fractional saturation of gas bubbles [-]
f_{active}	fraction of active biomass in a given system at a given SRT [-]
$f_{active,ref}$	fraction of active biomass in system at a reference SRT [-]
f_{air}	fraction of contaminant mass flow emitted to air [-]
f_{ana}	reduction factor applied to value of aerobic biodegradation rate coefficient under anaerobic conditions (default value set to 0.1) [-]
f_{ano}	reduction factor applied to value of aerobic biodegradation rate coefficient under anoxic conditions (default value set to 0.6) [-]
$f_{A,oil}$	fraction of water surface covered with oil [-]
$f_{bio,corr}$	SRT-based biodegradation rate correction factor [-]
f_{bw}	duration of backwash of MBR membranes [hr/d]
f_{dust}	dust generation percentage in sludge dryer [%]
$f_{kv,oil}$	empirical mass transfer factor for oil-covered surface [-]
$f_{m,c}$	mole fraction of contaminant in the dried sludge [-]
$f_{m,w}$	mole fraction of water in the dried sludge [-]
f_{non}	pH dependent non-dissociated fraction of a contaminant [-]
$f_{oil,correction}$	correction factor for emissions from oil layer [-]
f_{SRT}	SRT correction factor [-]
f_{si}	fraction of soluble inert COD in influent (a default value of 0.05 is used) [-]
f_u	endogenous fraction from active biomass decay (a default value of 0.2 is used) [-]
f_{WAS}	fraction of total underflow rate split to waste activated sludge [-]
f_{xi}	fraction of particulate inert COD in influent (a default value of 0.2 is used) [-]
F	Froude number [-]
F	empirical parameter in oxygen deficit ratio for drop structures [-]
g	acceleration due to gravity [m/s^2]
h	elevation above sea level [m]
$h_{clingage}$	height of clingage in floating roof tank model [m]
h_L	head loss [m]
h_{feed}	height of feed discharge point above SBR tank floor [m]
h_{min}	minimum water height in SBR [m]
h_{max}	maximum water height in SBR [m]
h_{tail}	tail water depth in drop model [m]
h_{drop}	drop height in drop model [m]
H	Henry's law coefficient [m^3_{liq} / m^3_{gas}]

k_b	first order biodegradation rate coefficient [L/mg VSS/h]
k_{b20}	biodegradation rate coefficient at 20°C [m ³ /kg·h]
k_{b35}	biodegradation rate coefficient at 35°C [m ³ /kg·h]
$k_{b,SRT}$	biodegradation rate coefficient adjusted for active biomass at SRT [m ³ /kg·h]
k_d	diffused aeration stripping constant [1/h]
k_d	endogenous decay rate of active biomass (a default value of 0.25 d ⁻¹ is used) [1/d]
k_g	gas phase mass transfer coefficient [m/h]
k_L	liquid phase mass transfer coefficient [m/h]
k_m	volatilization rate due to mixing [h ⁻¹]
k_v	volatilization rate constant for a quiescent surface [1/h]
k_s	stripping rate constant for mechanical aeration [1/h]
K_c	Freundlich isotherm parameter for powdered activated carbon [mg/g]
K_{DOC}	adsorption partition coefficient for DOC [L/g DOC]
K_{eq}	equilibrium coefficient between liquid and gas phases [L_{liq}/L_{gas}]
K'_{eq}	equilibrium coefficient between liquid and gas phases modified by multiplication with mole fraction [L_{liq}/L_{gas}]
$K_{La_{oxy}}$	oxygen transfer rate constant [1/h]
K_L	overall mass transfer coefficient [m/h]
K_L^{oxy}	overall oxygen mass transfer coefficient [m/h]
$K_{L,oil}$	overall mass transfer coefficient from oil layer [m/h]
$K_{L,water}$	overall mass transfer coefficient from water layer [m/h]
K_{oa}	equilibrium coefficient between oil and air [L_{oil}/L_{air}]
K_{ow}	octanol/water partition coefficient [$(mg_{octanol}/L)/(mg_{water}/L)$]
K_p	general sorption partition coefficient [L/g]
K_{P1}	primary wastewater sorption partition coefficient for metals [L/g]
K_{P2}	sorption partition coefficient for metals to biological process solids [L/g]
K_s	Monod half saturation rate constant [mg/L]
K_S	overall mass transfer coefficient due to stripping in mechanical aeration [m/h]
K_v	volatilization mass transfer coefficient [m/h]
L	thickness of stagnant layer at biofilm surface [m]
L_f	biofilm thickness [m]
$m_{c,s}$	moles of contaminant in water phase of dried sludge [mole/L]
$m_{w,s}$	moles of water in in water phase of dried sludge [mole/L]
$m_{c,v}$	moles of contaminant vaporized [mole/d]
$m_{w,v}$	moles of water vaporized [mole/d]
mf_i	mole fraction of contaminant i [-]
M	compound molecular weight [g/mole]

M_f	fraction of influent mass flow directed to concentrate (concentrator) [fraction]
$M_{c,v}$	mass of contaminant vaporized in sludge drying process [g/d]
$M_{w,v}$	mass of water vaporized in sludge drying process [g/d]
$M_{c,in}$	mass of contaminant in the feed sludge stream [g/d]
M_{dust}	mass rate of dust in dryer exhaust air [g/d]
$M_{emission}$	mass emission rate of contaminant [mg/h]
$M_{emission,oil}$	mass emission rate of contaminant from oil layer [mg/h]
$M_{g,i}$	mass of contaminant in gas phase from CSTR i [mg/h]
M_g	total mass of contaminant in from all the CST, [mg/h]
M_{metal}	mass rate of metal emission from solids handling process [g/d]
MW_{air}	molecular weight of air = 28.8 [g/g-mol]
MW_i	molecular weight of contaminant i [g/g-mol]
MW_{oil}	molecular weight of oil [g/g-mol]
$mass_{in}$	unit process influent mass flow [mg/h]
$1/n$	Freundlich isotherm parameter [-]
N	number of CSTRs in series [-]
N_b	contaminant mass flux out of trickling filter slice due to biodegradation [mg/m ² .h]
N_{bi}	contaminant mass flux due to biodegradation from i_{th} CSTR [mg/m ² /h]
N_{oxy}	standard oxygen transfer rate of surface aerator [kg O ₂ /kWh]
N_s	contaminant mass flux into biofilm [mg/m ² .h]
N_v	contaminant mass flux out of trickling filter slice due to volatilization [mg/m ² /h]
N_{vi}	contaminant mass flux due to volatilization from i_{th} CSTR [mg/m ² /h]
O	oil concentration in wastewater [kg/m ³]
O_D	oxygen demand [g O ₂ /d]
O_f	concentration of oil in float [g/m ³]
O_u	concentration of oil in underflow [g/m ³]
OTE	oxygen transfer efficiency [-]
OTE_{HPO}	oxygen transfer efficiency in HPO [-]
p_c	partial pressure of contaminant [atm]
p_w	partial pressure of water vapor [atm]
pKa	negative logarithmic value (base 10) of weak acid dissociation constant [-]
P	surface aerator power [kW]
P^*	vapor pressure of the organic compound of interest [atm]
P_{atm}	atmospheric pressure [mm Hg]
P_L	power loss [kW]
P_o	total atmospheric pressure (a default value of 1 is used) [atm]
q	flow rate per width of stream [m ³ /m/h]
Q	wastewater flow rate [m ³ /h]

Q_a	air flow rate [m^3/h]
Q_{conc}	concentrate flow rate (concentrator) [m^3/h]
Q_e	process effluent flow rate [m^3/h]
Q_{out}	process effluent flow rate [m^3/h]
Q_f	flow rate of filtrate or supernatant [m^3/h]
Q_f	oil float flow rate in DAF an API Separator models [m^3/h]
Q_f	fraction of influent flow directed to effluent (concentrator) [fraction]
Q_g	gas flow rate [m^3/h]
Q_{gi0}	diffused air flow rate into activated sludge tank i [m^3/h]
Q_{gi}	diffused air flow rate from activated sludge tank i [m^3/h]
Q'_g	headspace ventilation rate [m^3/h]
Q_{in}	process influent flow rate [m^3/h]
Q_s	flow rate of dewatered sludge [m^3/h]
Q_u	underflow rate [m^3/h]
Q_{vi}	headspace ventilation air flow rate in activated sludge tank i [m^3/h]
Q_w	clarifier wasting flow rate [m^3/h]
$Q_{w,out}$	volumetric flow of water in dried sludge [m^3/d]
Q_{WAS}	waste activated sludge flow rate [m^3/h]
r_b	rate of biodegradation [mg/h]
r_d	rate of contaminant stripping by diffused aeration [mg/h]
r_{o20}	oxygen deficit ratio at 20 °C [-]
r_s	rate of stripping from a take through either mechanical or diffused aeration [mg/h]
r_v	rate of volatilization from a quiescent surface or weir [mg/h]
R	ideal gas law constant = $8.2057 * 10^{-5} \text{ atm}\cdot\text{m}^3/\text{mol}\cdot\text{K}$
R	ideal gas law constant = $1.9872 \text{ [cal}/(\text{mol}\cdot\text{K})]$
R_{TSS}	Removal efficiency of TSS [%]
R_{oil}	Removal efficiency of oil [%]
S	slope of energy grade line [m/m]
S	overall sorption coefficient which includes solids, oil and PAC in a given system [$(\text{mg}_{\text{sorbed to material}}/\text{L})/(\text{mg}_{\text{in liquid phase}}/\text{L})$]
$S_{clingage}$	sorption term for the clingage in floating roof tank model [-]
S_{conc}	concentrate sorption term (concentrator) [$(\text{mg}_{\text{sorbed to material}}/\text{L})/(\text{mg}_{\text{in liquid phase}}/\text{L})$]
S_{i-1}	influent sorption term for CSTR i [-]
S_i	effluent sorption term for CSTR i [-]
S_{in}	influent sorption term [-]
S_{eff}	unit process effluent sorption term, [$(\text{mg}_{\text{sorbed to material}}/\text{L})/(\text{mg}_{\text{in liquid phase}}/\text{L})$]

S_o	influent overall sorption coefficient which may includes solids, oil and PAC [[$(mg_{\text{sorbed to material}}/L)/(mg_{\text{in liquid phase}}/L)$]
S_{cg}	gas phase Schmidt number [-]
S_{cl}	liquid phase Schmidt number [-]
S_d	sorption coefficient to digester (similar to S_{ss}),[[$(mg_{\text{sorbed to material}}/L)/(mg_{\text{in liquid phase}}/L)$]
S_e	sorption coefficient to effluent wastewater from a unit process
S_f	sorption coefficient to filtrate or supernatant [[$(mg_{\text{sorbed to material}}/L)/(mg_{\text{in liquid phase}}/L)$] sorption coefficient to mixed liquor (similar to S_{ss}), [[$(mg_{\text{sorbed to material}}/L)/(mg_{\text{in liquid phase}}/L)$]
S_m	phase/L]
S_{oil}	sorption coefficient to oil [[$(mg_{\text{sorbed to material}}/L)/(mg_{\text{in liquid phase}}/L)$]
S_s	sorption coefficient to dewatered sludge [[$(mg_{\text{sorbed to material}}/L)/(mg_{\text{in liquid phase}}/L)$]
S_{ss}	sorption coefficient to suspended solids [[$(mg_{\text{sorbed to material}}/L)/(mg_{\text{in liquid phase}}/L)$]
S_{pac}	sorption coefficient to activated carbon [[$(mg_{\text{sorbed to material}}/L)/(mg_{\text{in liquid phase}}/L)$] sorption coefficient to waste activated sludge (similar to S_{ss}), [[$(mg_{\text{sorbed to material}}/L)/(mg_{\text{in liquid phase}}/L)$]
S_w	material/L)/($mg_{\text{in liquid phase}}/L)$]
SRT	system solids retention time [d]
SRT_i	SRT in selected tank i [d]
SRT_{ref}	reference system SRT [d]
t	time [h]
T_c	contact time in chlorine contactor [min]
T_K	temperature [kelvin]
T_c	temperature [°C]
TRC	total residual chlorine concentration [mg/L]
U^*	air side friction velocity [m/s]
U_{10}	wind velocity (10m above surface) [m/s]
v	water velocity [m/s]
v_a	viscosity of air [g/cm/s]
v_o	approach velocity in upstream channel [m/s]
v_w	viscosity of water [g/cm/s]
V	volume of process vessel [m ³]
$V_{clingage}$	volume of the clingage in the floating roof tank model [m ³] volume of activated sludge tank i which is selected in SRT based WAS flow calculation [m ³]
V_i	calculation [m ³]
X	volatile suspended solids (VSS) concentration [kg/m ³]
X_b	volatile suspended solids concentration in biological process [kg/m ³]
X_c	concentration of powdered activated carbon in solution [g/L]
X_d	volatile suspended solids concentration in digester [kg/m ³]
X_f	fixed film /biomass density [kg/m ³] SS concentration in activated sludge tank i which is selected in SRT based WAS
X_i	flow calculation [mg/L]

X_o	influent volatile suspended solids concentration [kg/m ³]
X_U	underflow SS concentration [mg/L]
Y	maximum yield coefficient [g VSS/g compound utilized]
Y_{active}	yield of active biomass per unit substrate removed at a given SRT [kg solid/kg substrate]
$Y_{active,ref}$	yield of active biomass per unit substrate removed at a reference SRT [kg solid/kg substrate]
Y_{BOD}	BOD _U removal efficiency (a default value of 0.95 is used) [-]
Y_{endo}	yield of endogenous solid production per unit substrate removed at a reference SRT [kg solid/kg substrate]
$Y_{endo,ref}$	yield of endogenous solid production per unit substrate removed at a reference SRT [kg solid/kg substrate]
Y_{inert}	yield of inert solid per unit substrate removed at a given SRT [kg solid/kg substrate]
$Y_{inert,ref}$	yield of inert solid per unit substrate removed at a reference SRT [kg solid/kg substrate]
Y_{oxy}	mole fraction of oxygen in supply air [(moles of oxygen)/(mole of air)]
$Y_{oxy,HPO}$	mole fraction of oxygen in HPO gas [moles of oxygen/mole of air]
z	distance in biofilm as measured from liquid interface [m]
z	tailwater depth [m]
z	depth of trickling filter or cooling tower [m]

References

- Barbari, T., and C. King (1982). Equilibrium Distribution Coefficients for Extraction of Chlorinated Hydrocarbons and Aromatics from Water into Undecane. *Environ Sci. Technol.*, 16, 624.
- Burnham, N.L., R.L. Corsi, R.G. Zytner and W.H. Stiver (1993). Model of VOC Emissions at Hydraulic Drop Structures. Proceedings of the 1993 Joint CSCE-ASCE National Conference on Environmental Engineering, Montreal, Quebec.
- California Air Resources Board (2014). "Mineral Oil". Accessed at http://www.arb.ca.gov/db/solvents/solvent_pages/Hydrocarbon-HTML/Mineral_Oil.htm. April 11.
- Corsi, R.L., D.P.Y. Chang and E.D. Schroeder (1992). A Modeling Approach for VOC Emissions from Sewers. *Water Environment Research*, 64, 734.
- Dobbs R.A., L.Wang, R.Govind (1989). Sorption of Toxic Organic Compounds on Wastewater Solids: Correlation with Fundamental Properties. *Environ. Sci. Technol.*, 23, 1092.
- Enviromega Ltd. (1993). Measurement of Hazardous Air Pollutant Emissions from Wastewater Collection System Components. Report to Chemical Manufacturers Association, Washington, D.C. April.
- Gameson, A.L. *et al.* (1958). The Effect of Temperature on Aeration at Weirs. *Water and Wastes Engineering*, 489.
- Goel R. (2013) Modeling of VOC emission from sludge dryer, Technical Memorandum, Hydromantis ESS, Inc.
- Gossett, J.M. (1987). Measurement of Henry's Law Constants for C1 and C2 Chlorinated Hydrocarbons. *Environ. Sci. Technol.*, 21, 1092.
- Hsieh, C.C., R.W. Babcock and M.K. Stenstrom (1992). Estimating Semi-Volatile Organic Compound Emission Rates and Oxygen Transfer Coefficients in Diffused Aeration. Presented at the 65th Annual Conference of the Water Environment Federation, New Orleans, Louisiana.
- Jensen, N.A., and T. Hvitved-Jacobsen (1991). Method of Measurement of Reaeration in Gravity Sewers using Radiotracers. *Research Journal of the Water Pollution Control Federation* 63, 758.
- Kim, S.-J., Kwon, J.-H., 2010. Determination of partition coefficients for selected PAHs between water and dissolved organic matter. *CLEAN-Soil, Air, Water* 38, 797-802.
- Lewis, W.K., and W.G. Whitman (1924). Principles of Gas Absorption. *Industrial and Engineering Chemistry* 16, 1215.
- Mackay D., and T.K. Yeun (1983). Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water. *Environ. Sci. Technol.*, 17, 211.
- Mackay, D., and R. S. Matsugu (1973). Evaporation Rates of Liquid Hydrocarbon Spills on Land and Water. *Can. J. Chem. Eng.* 51:434-439.

- Matter-Muller C., W. Gujer, W. Giger (1981). Transfer of Volatile Substances from Water to the Atmosphere. *Water Res.*, 15, 1271.
- McLachlan, M., D. Mackay and P.H. Jones (1990). A Conceptual Model of Organic Chemical Volatilization at Waterfalls. *Environmental Sci. and Technol.* 25, 252.
- Metcalf & Eddy, Inc. (1991). *Wastewater Engineering*. McGraw-Hill, New York.
- Montgomery, James M., Consulting Engineers, Inc. (1990). Final Report for Publicly Owned Treatment Works (POTW's). Joint Powers Agencies for Pooled Emission Estimation Program (PEEP), Pasadena, California.
- Monteith 2014? Munz C. and P.V. Roberts (1989). Gas- and Liquid Phase Mass Transfer Resistances of Organic Compounds During Mechanical Surface Aeration. *Wat. Res.*, 23, 589.
- Nakasone, H. (1987). Study of Aeration at Weirs and Cascades. *Journal of Environmental Engineering, ASCE* Vol. 113, No.1 p. 64.
- Parkhurst, J.D., and R.D. Pomeroy (1972). Oxygen Absorption in Streams. *Journal of the Sanitary Engineering Division, ASCE* 98, 101.
- Peng J., Bewtra J. K., Biswas N. (1995) Effect of turbulence on volatilization of selected organic compounds from water, *Water Environ. Res.*, 67, 000, pp 101-107
- Perry's Chemical Engineers' Handbook, 5th edition.* (1973). Edited by R.H. Perry and C.H. Chilton. McGraw-Hill, Toronto. P. 3-247.
- Pincince, A.B. (1991). Transfer of Oxygen and Emissions of Volatile Organic Compounds at Clarifier Weirs. *Res. J. Water Poll. Control Fed.*, 63, 114.
- Redmon D., W.C. Boyle, L. Ewing (1983). Oxygen Transfer Efficiency Measurements in Mixed Liquor Using Off-Gas Techniques. *J. Water Poll. Control Fed.*, 55, 1338.
- Robinson, M. and W. Desing (1995). Formation and Air Emissions of Trihalomethanes from Chlorine Wastewater Disinfection, Proceedings of the Water Environment Federation, 68th Annual Conference and Exposition. Management & Facility Operation, Miami Beach, FL., Oct. 21-25, 5, 341-346.
- Sawyer, C.N. and P.L. McCarty (1967). McGraw-Hill Series in Sanitary Science and Water Resources Engineering, McGraw-Hill, Inc., New York.
- Speight, J and Exall, D.I. (2014). *Refining Used Lubricating Oils*, CRC Press, Boca Raton, FL. pp. 56-57.
- Thibodeaux, L.J. (1979). *Chemodynamics*, John Wiley and Sons, New York.

U.S. Environmental Protection Agency (1994). Air Emission Models for Waste and Wastewater. Report No. EPA-453/R-94-080A. Office of Air Quality Planning and Standards, Research Triangle Park, NC. November.

Water Environment Research Foundation (WERF) (1998). Modeling the Stripping and Volatilization of VOCs in Wastewater Collection and Treatment Systems. Project 91-TFT-1, 1998.

Whitmore, A., and R.L. Corsi (1994). Measurement of Gas-Liquid Mass Transfer Coefficients for Volatile Organic Compounds in Sewers. Environ. Prog., 13, 114.