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Emissions of Volatile and Potentially Toxic Organic Compounds from Wastewater Treatment Plants and Collection Systems (Phase II)

Volume 4:

Modeling Volatile Organic Compound Emissions during Preliminary and Primary Treatment

State of California
AIR RESOURCES BOARD
Research Division

EMISSIONS OF VOLATILE AND POTENTIALLY TOXIC ORGANIC COMPOUNDS FROM WASTEWATER TREATMENT PLANTS AND COLLECTION SYSTEMS (PHASE II)

VOLUME 4 - MODELING VOLATILE ORGANIC COMPOUND EMISSIONS DURING PRELIMINARY AND PRIMARY TREATMENT

Final Report
Contract No. A732-085

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ABSTRACT

The purpose of this phase of the study was to develop models of VOC emissions that can be used to determine the importance of individual stages in the preliminary and primary operations sequence. Included in the study was selection of candidate operations for design or operational modification to minimize emission rates.

Preliminary and primary treatment steps considered include bar screens, comminuters and Parshall flumes in the headworks, grit removal, primary sedimentation, flow over weirs at unit effluent points, and emissions from conveyance channels. Emission models for each unit were constructed and evaluated using time varying inputs that simulated typical diurnal loading rate variations. Individual models of unit operations were then combined in a treatment sequence and the overall effect determined for the time varying input. The importance of non-linearities in the system was examined.

Individual steps in a treatment sequence were assumed to be well mixed. Where appropriate, units were treated as cascades of ideally mixed tanks. The conventional two-film mass transfer model was used in all cases. Mass transfer occurring in diffused air systems, such as aerated grit chambers and aerated conveyance channels, was described using aeration type models. Mass transfer in non-aerated operations, such as primary sedimentation tanks and non-aerated conveyance channels, was described using modified forms of expressions developed for mass transfer in streams and collection systems. Losses in high headloss steps, such as weirs, screens and comminuters, were described using expressions similar to those used for waterfall aerators.

Overall emissions predicted during preliminary and primary treatment were approximately 25% of influent VOC load and varied from 0.02 to 0.03 g-VOCs/m^3 of wastewater treated, depending on the method of plant operation selected. Major losses occurred in aerated grit chambers and at weirs. Losses from non-aerated tanks and conveyance channels were negligible relative to other

units. Emissions predicted for headworks steps were small, but not negligible.

Options to covering treatment units and collection of off-gases are clearly available in many cases. Submerged weirs, launder depth controls, and elimination of aeration are examples of modifications that can be used to effectively decrease VOC emissions. Incorporation of such techniques will, in many cases, allow treatment plants to operate without off-gas collection and treatment.

In order to utilize mass-transfer models, certain compound-specific physico-chemical data are needed. An assessment of small chlorinated hydrocarbon partition coefficients, e.g. Henry's coefficients and solubility was undertaken. A tabular summary of values is included. A methodology for correlating and predicting such coefficients, i.e. molecular connectivity indices, was also examined for its possible utility.

DISCLAIMER

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Several individuals contributed valuable suggestions for the modeling efforts described herein: Dr. Richard Corsi provided much of the background for the current effort; Mssrs. Chip Hellier of the East Bay Municipal Utilities District, Ross Caballero of the County Sanitation Districts of Los Angeles County and Mr. Randall Guensler provided data.

The California Air Resources Board and their staff have been supportive of our efforts over the past years. In particular, we will always remember the friendship and efforts of our former research project manager Mr. Joseph R. Pantalone. Mr. Ralph Propper has capably taken over that task and we are thankful for his assistance and patience in completing it.

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LIST of ACRONYMS

ARB - California Air Resources Board
CFSTR - Continuous flow stirred-tank reactor
CSDLAC - County Sanitation Districts of Los Angeles County
EBMUD - East Bay Municipal Utilities District
GC/MS - Gas chromatography/Mass spectrometry
HTP - Hyperion Treatment Plant
JWPCP - Joint Water Pollution Control Plant
MGD - Million gallons per day
mTPY - Metric ton (tonne) per year
MWTP - Municipal wastewater treatment plants
PTOC - Volatile and potentially toxic organic (inorganic) compounds - 16 selected in Phase I:
    ACY - 2-propenenitrile (acrylonitrile)
    BZ - benzene
    BDCM - bromodichloromethane
    CT - tetrachloromethane (carbon tetrachloride)
    ClBZ - chlorobenzene
    TCM - trichloromethane (chloroform)
    DBCM - dibromochloromethane
    EDC - 1,2-dichloroethane
    DCE - 1,1-dichloroethene (vinylidene chloride)
    ETBZ - ethylbenzene
    DCM - dichloromethane
    PERC - tetrachloroethene
    TOL - methylbenzene (toluene)
    TCA - 1,1,1-trichloroethane (methyl chloroform)
    TCE - trichloroethene (trichloroethylene)
    VC - chloroethene (vinyl chloride)
  additional compound acronyms
    CM - chloromethane
    DCB - dichlorobenzene(s)
    LIM - limonene
    MCA - monochloroethane
    UND - undecane

T-BACT	-	Toxics best available control technology
TPY	-	Tons per year (English)
UCD	-	University of California, Davis - Civil Engineering
VOC	-	Volatile organic compound - for the purposes of this study any compound in the wastewater captured in an air sample
WWTP	-	Wastewater Treatment Plant

1. INTRODUCTION

Volatile organic compounds (VOCs), such as organic solvents, are characteristic constituents of influent streams to municipal wastewater treatment plants (MWTPs). In previous volumes of this report, emissions from the collection system and actual in plant measurement have been discussed. Little information was available on emissions of VOCs from MWTPs at the time this project was initiated, and both modeling and experimental studies were needed to develop control strategies. In this volume, modeling of emissions within the preliminary and primary treatment processes of a hypothetical MWTP was performed.

Within the treatment train, VOCs are removed through gas-stripping, volatilization, adsorption, and biodegradation. Mass transfer theory and previously reported work relating mass transfer rates of selected organics to that of reference compounds were used to develop an approach for predicting VOC emissions from headworks, grit chambers, primary sedimentation tanks, weirs, and primary conveyance channels.

PURPOSE

The purpose of this study was to develop a method of estimating emission rates, of VOCs during primary wastewater treatment. A three-step process was implemented: development of a mathematical model for estimating emission rates of VOCs; comparison of the results of the mathematical model to reported emissions from several MWTPs to determine model accuracy; recommendation of control strategies to limit release of VOCs to the atmosphere.

Use of mass transfer models also requires inputs of partition coefficients for species of interest among other physico-chemical data. Uncertainties in the values of these coefficients was determined to be relatively large for several of the compounds of interest, and the data base for many other compounds was sparse. For that reason, an attempt was made to evaluate Henry's coefficient and solubilities. A recent methodology for correlating and predicting physico-chemical properties, i.e. molecular connectivity indices, was evaluated for its potential value for such purposes.

SCOPE

A materials balance method, assuming gas transfer to be the dominant mechanism of VOC depletion, was used to estimate VOC emission rates from reference primary wastewater treatment processes. A continuous-flow stirred-tank reactor (CFSTR) was used as the unit process in modeling each treatment process. A series of CFSTRs was used to model processes that resembled plug flow. Oxygen and VOC overall mass transfer coefficients, K_La_{O2} and K_La_{VOC} respectively, were predicted by models developed by other researchers. Because only high volatility compounds were studied, liquid phase resistance was assumed to dominate interphase mass transfer.

2. BACKGROUND

Previous studies have demonstrated that wastewater treatment plants are sources of VOC emissions (Bell et al., 1988; Chang et al., 1987; USEPA, 1986; California Air Resources Board, 1985). After conducting off-gas sampling and analysis at four Ontario MWTPs, Bell et al. (1988) determined total VOC emissions from aerated grit chambers and activated sludge basins to range from approximately 0.0015 to 0.075 g-VOC/m^3 of wastewater treated. During the period roughly corresponding to 1983 to 1985, 730 metric tons of potentially toxic organic compounds (PTOCs) were estimated as the maximum potential annual emissions from MWTPs throughout California (Chang et al., 1987). Applying the higher bound reported by Bell et al. for Ontario wastewater plants to an estimated 3.9 X 10^9 m3 of wastewater generated annually in California during the years 1983 to 1986, an emission rate of 290 mTPY results. The following treatment processes were listed in a report to Congress in 1986 as expected sources of VOC emissions: flumes, grit chambers, sumps, equalization basins, pH adjustment stations, nutrient addition stations, clarifiers, oxidation basins, open storage tanks, wastewater transfer lines, pipes, and ditches (USEPA, 1986). From a study at two large MWTPs, the California Air Resources Board (1985) determined that emissions of PTOCs from aerated grit chambers, digester tanks, and aerated channels are potentially significant with respect to emissions from other treatment processes.

In primary treatment of raw wastewater, emission to the atmosphere is the dominant mechanism of VOC depletion; adsorption and biodegradation are believed to be ineffective in reducing influent VOC concentrations (Pellizzari, 1981; Petrasek et al., 1983). Pellizzari (1981) studied the fate of six volatile compounds (benzene, chlorobenzene, chloroform, toluene, trichloroethylene, and carbon tetrachloride) at MWTPs and concluded:

1. Significantly higher concentrations of VOCs are generally in raw wastewater than in activated sludge influent, thus vaporization has probably occurred.

2. Adsorption to solids in the activated sludge may be a significant removal mechanism for some VOCs, while adsorption to raw wastewater solids is negligible.

3. Sorption to biomass is negligible in raw wastewater.

For compounds with large octanol/water partition coefficients ($K_{OW} > 10^3$) adsorption of as much as 33% of a compound such as ethylbenzene to primary sludge has been estimated (Dixon and Bremmen, 1984). However, because adsorption and biodegradation are not prominent methods of VOC depletion in primary wastewater treatment, transfer of VOCs from wastewater to the atmosphere was assumed to be the only source of VOC losses in the modeling conducted for the current study.

INTERPHASE MASS TRANSFER

Interphase mass transfer, either from gas to liquid or liquid to gas, is divided into three steps: gas phase transport, absorption at the gas-liquid interface, and liquid phase transport. Common models used to predict interfacial mass transfer are the two-film (Lewis and Whitman, 1924), the penetration (Higbie, 1935), and the surface renewal (Dankwerts and Kennedy, 1954) theories.

Interfacial Mass Transfer Rate

An overall expression to determine interfacial mass transfer rates can be derived, and is only presented below.

$$M_A = K_L a \cdot (C_{LA}^* - C_{LA}) \qquad (2\text{-}1)$$

where

M_A = mass transfer rate of solute A from liquid, $g/m^3 \cdot hr$

K_L = mass transfer rate coefficient, m/hr

a = specific surface area, m^2/m^3

C_{LA}^* = liquid concentration of solute A in equilibrium with gas phase concentration, g/m^3

C_{LA} = bulk liquid concentration of solute A, g/m^3

Interfacial mass transfer is a function of both liquid and gas phase resistance. However, liquid phase resistance usually controls mass transfer for compounds with a Henry's law constant greater than about 0.10 (Roberts et al., 1984). Because only high volatility compounds were studied, liquid phase resistance was assumed to dominate mass transfer.

Liquid and gas phase mass transfer coefficients and specific interfacial areas are usually difficult to determine, thus researchers commonly express an overall mass transfer rate coefficient, K_La, for a solute with units of hr^{-1}.

Henry's Law

Henry's Law is used to define the partitioning relationship for a compound between the vapor and liquid states. The relationship, expressed mathematically, is shown below.

$$H = Yi/Xi \tag{2-2}$$

where

H = Henry's Law constant based on mole fraction, unitless

Y_i = mole fraction of solute i in vapor phase at equilibrium, unitless

X_i = mole fraction of solute i in liquid phase at equilibrium, unitless

Inherent assumptions with Henry's law are that a vapor behaves as an ideal gas and that a solution is very dilute.

A number of expressions of Henry's law are in fairly widespread use with the result that the Henry's law constant is not limited to the ratio of mole fractions in vapor and liquid phases. Other relationships, e.g. ratio of the concentrations in gas and liquid phases, can cause confusion about units of a Henry's law constant. Henry's law constant conversion factors assuming dilute solutions in water at 25°C are presented in Table 2-1. A further discussion of literature values for Henry's constant is provided in Appendix H. Symbols used to express Henry's law constant are arbitrary. Fair et al. (1968) referred to Henry's law constant as the "coefficient of absorption", labelled k_s with units of mL/L. Strictly speaking, the coefficient of absorption is not limited to dilute solutions. Because Table 2-1 was taken directly from Fleming (1988), symbols used for Henry's law constant in this report are, for convenience, consistent with that reference.

Table 2-1: Henry's Law Constant Conversion Factors

To Obtain	Multiply	By (units)
H	H_i	$1/P_T$ (atm^{-1})
H	H_A	$55556/P_T$
H	H_B	$4.559 \cdot (T/P_T)$ (unitless)
H	H_C	1343 (unitless)

Note: All conversion factors assume dilute solutions in water at 25°C.

Source: Fleming, 1988.

H = Henry's constant; Y_i/X_i, unitless
H_i = Henry's constant; P_i/X_i, atm
H_A = Henry's constant; P_i/C,
H_B = Henry's constant; $P_i/(C \cdot R \cdot T)$, unitless
H_C = Henry's constant concentration ratio; C_g/C_l, unitless
P_T = total pressure, atm
P_i = partial pressure of organic vapor "i ", atm
T = temperature, K
C_g = gas concentration of solute "i" at equilibrium, g/m^3
C_l = liquid concentration of solute "i" at equilibrium, g/m^3
Y_i = mole fraction of solute "i" in vapor phase at equilibrium, unitless
X_i = mole fraction of solute "i" in liquid phase at equilibrium, unitless
R = universal gas constant, 0.082057

EMISSION OF VOCs DURING PRIMARY WASTEWATER TREATMENT

Total emission of VOCs and possible emission sources during primary wastewater treatment are discussed in this section.

Total Emissions

In the wastewater literature, volatilization differs from gas-stripping based on the mode of transfer at a gas-liquid interface. Volatilization is defined as mass transferred at a water surface-atmosphere interface, while stripping is defined as mass transferred at a water-diffused air bubble interface. Thus, total emissions of VOCs from a unit is a summation of mass transferred via volatilization and stripping.

Volatilization - At a wastewater-atmosphere interface, oxygen will naturally diffuse from the atmosphere into the wastewater because of an oxygen deficit between the wastewater and the atmosphere. Conversely, volatile compounds present in the wastewater will transfer to the atmosphere if they are below their equilibrium concentrations in the air. Turbulence in the wastewater facilitates the transfer process (turbulence in the atmosphere also facilitates mass transfer but liquid phase resistance was assumed to dominate gas phase resistance). Those primary treatment processes, e.g. sedimentation basins and equalization basins, with large water surface areas are conducive to VOC volatilization.

Gas stripping - Aeration may be used in grit chambers, conveyance channels, equalization basins, and neutralization basins to facilitate primary wastewater treatment. Air is generally supplied to grit chambers and conveyance channels through sub-surface coarse bubble diffusers, while surface aerators are generally used for aeration of equalization and neutralization basins. Because wastewater generally has a low dissolved oxygen concentration, oxygen is transferred from diffused air to wastewater, and correspondingly VOCs transfer from wastewater to diffused air.

Possible Sources of Emissions During Primary Wastewater Treatment

Possible sources of VOC emissions during primary wastewater treatment are discussed in this section. Principal primary treatment processes include bar screens, comminutors, Parshall flumes, grit chambers, equalization basin, sedimentation basins, and conveyance channels.

Bar screens - Bar screens are located at the front of a treatment facility to remove large debris in incoming wastewater. Turbulence created by bar screens facilitates VOC emissions.

Comminutors - To prevent damage to pumps, comminutors reduce the size of large suspended material that pass through bar screens. Turbulence created by comminutors enhances VOC transfer to the atmosphere.

Parshall flume - A Parshall flume is a critical flow measuring device. Turbulence associated with a hydraulic jump created by a Parshall flume contributes to VOC emissions.

Grit chamber - Grit chambers are used to remove large suspended particles (e.g. sand, gravel, and coffee grounds) from wastewater while leaving less dense organic particles in suspension. Specific gravity of material removed is in the range of 2.5 to 2.6, which allows for significant levels of turbulence while providing efficient grit removal. In non-aerated grit chambers turbulence is developed hydraulically, and in aerated grit chambers diffused aeration causes turbulence. A typical hydraulic detention time and horizontal water velocity for grit chambers are 3 to 5 minutes and 0.3 m/s (1.0 ft/sec), respectively. If a grit chamber is aerated, a typical air flow rate is 0.3 m^3/m of length-min (Metcalf and Eddy, 1979), and diffused air is generally supplied via submerged coarse bubble diffusers. Emission sources include volatilization from the water surface, transfer at overflow weirs, and, if applicable, stripping by diffused air.

Equalization basin - An equalization basin is used to equalize flow rates to subsequent treatment processes. To prevent deposition of solids and anaerobic conditions, diffused air is usually applied by surface aerators. Typical air flow rates are 0.01 to 0.015 m^3/m^3 of wastewater-min (1.25 to 2.0 $ft^3/10^3$ gal-min) (Metcalf and Eddy, 1979). Analogous to aerated grit chambers, emission sources include volatilization from the water surface, transfer at effluent weirs, and stripping by diffused air.

Primary sedimentation tanks - In sedimentation tanks suspended material is removed by gravity settling. Typical detention times of primary clarifiers are 90 to 150 min (Metcalf and Eddy, 1979). Emission sources include volatilization from the water surface and transfer at overflow weirs.

Conveyance channels - Conveyance channels are used to distribute wastewater to primary treatment processes and convey primary effluent to secondary treatment. Channels may be aerated to keep solids in suspension and minimize odors. Typical air flow rates in conveyance channels are 0.02 to 0.05 m^3/lin m-min (2 to 5 ft^3/linear ft-min) (Metcalf and Eddy, 1979). Emission sources include volatilization from the water surface, and, if applicable, stripping by diffused air.

MODELING APPROACH

Each primary treatment process was modelled as either a single continuous-flow, stirred-tank reactor (CFSTR), or, when necessary, as a cascade of CFSTRs. A CFSTR was chosen as the basic model unit because individual primary treatment processes with short hydraulic detention times, i.e. approximately less than 10 minutes, best resemble a single CFSTR. Included in this category were bar screens, comminutors, Parshall flumes, grit chambers, and weirs. A series of CFSTRs was used to model treatment processes that resembled a plug flow reactor. Included in this category were rectangular primary sedimentation basins and conveyance channels. A distribution channel could have a hydraulic detention time less than 10 minutes, but a cascade of CFSTRs was still used to model the process to account for dispersion.

A simplified mass balance expression for a VOC in a CFSTR, assuming gas transfer to be the only mechanism of VOC depletion, is given below (See Appendix 4-B for a detailed derivation of Eq. 2-3).

$$dC/dt = [(C_i - C)/\theta_H] - [K_L a_{voc} \cdot (C - C_g/H_c)] \qquad (2\text{-}3)$$

where

dC/dt = rate of change of a reactor (or effluent) liquid VOC concentration, $mg/m^3 \cdot hr$

C_i = influent liquid VOC concentration, mg/m^3

C = effluent (or reactor) liquid VOC concentration, mg/m^3

θ_H = hydraulic detention time, hr

$K_L a_{voc}$ = overall VOC mass transfer coefficient, hr^{-1}

C_g = atmospheric VOC gas phase concentration, mg/m^3

H_c = Henry's law constant, unitless

Assuming infinite dilution, the partial pressure of a VOC is 0 atm, i.e. $C_g = 0$. If the water surface of a CFSTR is open to the atmosphere, infinite dilution is a valid assumption when estimating volatilization losses. For submerged diffused aeration processes, VOC concentration accumulates in a bubble as a bubble rises, and infinite dilution is not a valid assumption when estimating stripping losses. Appendix A contains a detailed explanation and an equation to determine VOC gas concentration in a bubble as a function of bubble residence time.

Mass Transfer Rate Models

To estimate VOC emissions using Eq. 2-3, an overall VOC mass transfer coefficient, $K_L a_{voc}$, must be known. A number of approaches have been developed to estimate $K_L a_{voc}$, and relationships suggested by Roberts et al. (1984), Namkung and Rittman (1987), and Truong and Blackburn (1984) for diffused aeration systems were considered. Two researchers, Tsivoglou and Neal (1976), and Parkhurst and Pomeroy (1972), have developed methods to determine the overall oxygen mass transfer coefficient, K_La_{O2}, for naturally aerated systems. A model developed by Nakasone (1987) was used to estimate oxygen reaeration rates at weirs. For high volatility compounds ($H_c >= 0.12$), Roberts et al. (1984) has shown KLavoc to be proportional to K_La_{O2}. These methods are discussed below.

Diffused Aeration Models

Models developed by previous researchers to estimate an overall VOC mass transfer coefficient for diffused aeration systems are presented in this section.

Roberts et al. (1984) - Roberts et al. monitored emissions of six compounds from a bench scale reactor. Both surface and sub-surface (coarse and fine bubble) diffused aeration conditions were studied. Compounds used in the experiments were CCl_2F_2 (dichlorodifluoromethane (Freon 12)), $CHCl_3$ (chloroform), CH_3CCl_3 (1,1,1-trichloroethane), CCl_4 (tetrachloroethane), $CHCl{=}CCl_2$ (trichloroethene), and $CCl_2{=}CCl_2$ (tetrachloroethene). These six compounds were chosen because Hc for each compound is greater than 0.12 ($3.0 \cdot 10^{-3}$ atm m^3/g-mole) at 20^oC and each is considered highly volatile. Henry's law constants used by Roberts et al. in their analysis of experiments covered a range of 2.5 orders of magnitude; $0.13 < H_c < 62.1$. Roberts et al. experimentally determined K_La_{voc} to be proportional to K_La_{O2}, for compounds with H_c larger than 0.12. The coefficient of proportionality, Ψ_{voc}, is defined below.

$$\Psi_{voc} = K_La_{voc}/K_La_{O2} \qquad (2\text{-}4)$$

Ψ_{voc} is in the range 0.55 to 0.65 for organic solutes in the molecular weight range of 100 to 200. Roberts et al. (1984) suggested a general value of 0.62 for high volatility compounds. The ratio of VOC to oxygen overall transfer rate constants was virtually the same in filtered secondary wastewater effluent and in clean water. Values for Ψ determined in surface aeration experiments in clean water and filtered secondary effluent at

20°C are listed in Table 2-2. Experimental values for Henry's law constant in clean water and filtered secondary effluent are presented in Table 2-3.

Table 2-2. Values of the Overall Mass Transfer Constant Ratio Ψ in Clean Water and Filtered Secondary Effluent

		Ψ		Difference	
Compound	H_c	Clean water	Filtered secondary effluent	$D\Psi$	%
CCl_2F_2	62.11	0.661	0.668	0.007	1.1
CCl_4	0.947	0.617	0.627	0.010	1.6
$CCl_2=CCl_2$	0.847	0.608	0.625	0.107	2.8
$CHCl=CCl_2$	0.392	0.615	0.626	0.011	1.8
CH_3CCl_3	0.166	0.607	0.619	0.012	2.0
$CHCl_3$	0.131	0.560	0.584	0.024	4.3

Source: Roberts et al., 1984.

Table 2-3. Theoretical and Experimental Values for Henry's Law Constant

	Henry's law constant, $(g/m^3)/(g/m^3)$		
Compound	Theoretical [a]	Clean water	Filtered secondary effluent
CCl_4	0.947	0.977	0.980
$CCl_2=CCl_2$	0.847	0.605	0.698
$CHCl=CCl_2$	0.392	0.388	0.507
CH_3CCl_3	0.166	0.594	0.693
$CHCl_3$	0.131	0.203	0.326

[a] "Theoretical" values for H_c were calculated from vapor pressure and solubility data.

Source: Roberts et al., 1984.

Truong and Blackburn (1984) - Truong and Blackburn developed an equation to calculate K_La_{VOC} from experimental results. A bench scale batch reactor, 1.82 m (6.0 ft) high with a diameter of 0.15 m (6.0 in), with coarse bubble diffusers was used to perform experiments. The expression developed by Truong and Blackburn is given below.

$$K_La_{VOC} = (G/V)\cdot b\cdot (H_T)^m \qquad (2\text{-}5)$$

where

K_La_{VOC} = overall VOC mass transfer coefficient, hr^{-1}
G = volumetric air flow rate, L/min
V = liquid volume, L
H_T = Henry's law constant,
b, m = empirical constants

Conversion of K_La_{VOC} from min^{-1} to hr^{-1} is contained in the empirical constants (Truong, 1989).

Truong and Blackburn performed experiments with toluene (TOL), 1,4-dichlorobenzene (DCB), and methylethylketone (MEK) in both pure water and water containing a contaminant (surfactant Triton DF-12). Experiments with phenol in pure water were also performed. Toluene was the most volatile compound studied with H_C = 0.151 (a corresponding temperature was not given, but Petrasek et al. (1983) reported H_C = 0.25 at 25°C). Empirical constants for pure water and for contaminated water based on experimental studies are listed in Table 2-4.

Namkung and Rittman (1987) - Namkung and Rittman developed a theoretical volatilization model to quantify measured VOC emissions from a MWTP. Exit gas saturation was assumed, i.e. partial pressure of an exit gas of interest was assumed to be in equilibrium with the liquid solute concentration. The volatilization model, expressed mathematically, is shown below.

$$R_{vol} = (G\cdot H_A\cdot C)/(R\cdot T) \qquad (2\text{-}6)$$

where

R_{vol} = volatilization rate of compound, mg/d
G = volumetric air flow rate, L/d

H_A = Henry's law constant,
R = universal gas constant, $8.206 \cdot 10^{-5}$
T = temperature, K
C = reactor VOC liquid concentration, mg/L

Table 2-4. Empirical Constants for Truong and Blackburn's Overall Mass Transfer Coefficient Equation

Water condition	b	m	Data points	Regression coefficient, r^2
Pure[a]	3.71 · 10-3	1.045	11	0.991
Contaminated[b]	9.30 · 10-3	0.872	11	0.997

[a] Toluene, 1,4-DCB, and MEK in pure water at air flow rates of 2, 4, and 8 L/min and phenol in pure water at air flow rates of 2 and 4 L/min.

[b] Toluene, 1,4-DCB, and MEK in Triton DF-12 (0.01 %) at air flow rates of 2, 4, 5, 6, and 8 L/min.

Source: Truong and Blackburn, 1984.

If the volatilization rate, R_{vol}, in Eq. 2-6 is divided by liquid volume, V, reactor VOC liquid concentration, C, and appropriate conversion factors, K_La_{voc} can be calculated using the following equation.

$$K_La_{voc} = (G \cdot H_A)/(R \cdot T \cdot V) \qquad (2\text{-}7)$$

where

K_La_{voc} = overall mass transfer coefficient, hr^{-1}
V = liquid volume, L

Comparison of diffused aeration models - The fundamental difference between the three diffused aeration models is their dependency on exit gas saturation. Exit gas saturation was assumed for the Namkung-Rittman model; the equation developed by Truong and Blackburn closely approximates an equilibrium predictor (Truong and Blackburn, 1984); the Roberts et al. model is applicable to both saturated and unsaturated systems. In primary wastewater treatment, diffused air is generally supplied via coarse bubble diffusers or surface aerators, thereby decreasing the likelihood of bubbles becoming saturated. Because of a possibility of exit gases not being saturated, the model developed by Roberts et al. (1984) was preferred and was used in this study.

Namkung and Rittman (1987) assumed exit gas saturation, and also indirectly assumed infinite dilution in a rising gas bubble ($C_g = 0$), in the development of their volatilization model. Because the VOC saturation term (C_s in Eq. 2-3) was assumed to be zero, the concentration gradient was maximized and the VOC mass transfer coefficient, K_La_{VOC}, was effectively suppressed when modeling stripping rates.

Truong and Blackburn (1984) conducted emission experiments in a bench scale reactor with lower volatility compounds; the most volatile compound studied was benzene with $H_c = 0.25$ at 25°C (Petrasek et al., 1983). Because aeration tends to dominate bench scale experiments, and lower volatility compounds were studied, applicability of the VOC mass transfer coefficient equation developed by Truong and Blackburn to full scale systems is questionable.

Natural Reaeration Models

Models developed by researchers to estimate a natural oxygen reaeration mass transfer coefficient are presented in this section.

Tsivoglou and Neal (1976) Tsivoglou and Neal estimated reaeration of streams based on transfer of a tracer gas (krypton-85) from a stream to the atmosphere. From laboratory experiments, the ratio of krypton-85 to oxygen overall mass transfer constants was determined to be 0.83.

$$K_La_{Kr}/K_La_{O2} = 0.83 \qquad (2\text{-}8)$$

Tsivoglou and Neal reported that reaeration of a stream was a function of two hydraulic properties: change of water surface elevation and time of flow of a water surface of a stream segment. The expression developed by Tsivoglou and Neal to calculate the overall oxygen mass transfer constant is given below.

$$K_La_{O2} = C(\Delta h/t_f) \qquad (2\text{-}9)$$

where

K_La_{O2} = overall oxygen mass transfer coefficient, hr^{-1}

C = constant of proportionality, m^{-1}

Δh = change in water surface elevation between two locations, m

t_f = time of flow between two locations, hr

Tsivoglou and Neal defined C as an escape coefficient; a function of quality and intensity of mixing of a stream. Some parameters that affect the magnitude of the escape coefficient include abrupt changes of channel slope, channel obstructions, and changes in a channel's cross-sectional geometry. A value of 0.177 m^{-1} at 20°C for streams that are moderately polluted, reasonably well mixed, and with flows larger than 0.7 m^3/s (16.0 Mgal/day) was recommended. Tsivoglou and Neal suggested that the magnitude of the escape coefficient should be decreased to a limiting value in the range of 0.08 to 0.10 m^{-1} at 20°C for heavily polluted streams with flows larger than 0.7 m^3/s. For heavily polluted flows smaller than 0.28 m^3/s (7.5 Mgal/day), Tsivoglou and Neal suggested a magnitude for the escape coefficient of approximately 0.20 m^{-1}.

To incorporate the Tsivoglou and Neal reaeration constant into the mathematical model used in this study, Eq. 2-9 was modified. If the right side of Eq. 2-9 is multiplied by (L/L), where L is a length of a stream segment, Eq. 2-9 becomes

$$K_La_{O2} = C(\Delta h/L)\cdot(L/t_f) = C\cdot S\cdot v \qquad (2\text{-}10)$$

where

S = slope of the stream segment, m/m
v = average stream velocity, m/hr
L = length of the stream segment, m

Assuming K_La_{VOC} is proportional to K_La_{O2} (Roberts et al., 1984), K_La_{O2} can then be multiplied by an appropriate Ψ factor to determine K_La_{VOC}.

Parkhurst and Pomeroy (1972) - Parkhurst and Pomeroy studied oxygen reaeration of raw wastewater in sewers. The empirical equation developed by Parkhurst and Pomeroy predicts an oxygen exchange coefficient, f, in m/hr, and is given below.

$$f = a \cdot C_f \cdot C_A \cdot a \cdot b \cdot g \cdot (S \cdot v)^{3/8} \qquad (2\text{-}11)$$

where

f = oxygen exchange coefficient, m/hr

a = 1.0 if "f" is expressed as m/hr and v as m/s, unitless

C_f = a general constant having a value probably between 2.5 and 3.0, unitless

C_A = a function of the increase of surface area due to turbulence, approaching 1.0 in quiet streams, unitless

a = ratio of the oxygen exchange coefficient in wastewater to the exchange coefficient in clean water, 0.3 to 0.4 for raw wastewater, unitless

b = a function of the geometry of the stream; 1.0 for fairly regular cross-sections, unitless

g = ratio of the exchange coefficient at the actual temperature to the exchange coefficient at 20°C, unitless

S = invert slope of the stream segment, m/m

v = average stream velocity, m/s

Further definition of variables, and subsequent substitution, is required to enable the use of Eq. 2-11 to predict K_La_{O2}. The oxygen exchange coefficient, f, is defined as

$$f = K_La_{O2} \cdot d_m$$

where

d_m = mean hydraulic depth, m (area of a cross section of a stream divided by a surface width).

The term C_A is calculated empirically as

$$C_A = 1 + 0.17 \cdot F^2$$

where

F = Froude number = $v \cdot (g \cdot d_m)^{-0.5}$, unitless.

The term g is calculated empirically as

$$g = q \cdot (T - 20)$$

where

q = 1.042

T = temperature of wastewater, °C

Substituting the above definitions into Eq. 2-11 results in the following expression for K_La_{O2}:

$$K_La_{O2} = \{a \cdot C_f \cdot a \cdot b \cdot (1+0.17 \cdot F^2) \cdot (1.042)^{(T-20)} \cdot (S \cdot v)^{3/8}\}/d_m \qquad (2\text{-}12)$$

To obtain a maximum value for K_La_{O2}, i.e. conservative estimate with respect to VOC emissions, let a = 1.0, C_f = 3.0, a = 0.4, b = 1.0, and substitute into Eq. 2-12.

$$K_La_{O2} = \{1.2 \cdot 1+0.17 \cdot F^2) \cdot (1.042)^{(T-20)} \cdot (S \cdot v)^{3/8}\}/d_m \qquad (2\text{-}13)$$

To obtain K_La_{VOC}, K_La_{O2} is multiplied by an appropriate Ψ factor (Roberts et al., 1984).

Comparison of natural reaeration models - Both natural reaeration models predicted similar values (same order of magnitude) for K_La_{O2}, and therefore K_La_{VOC}. Possible beneficial and detrimental aspects of the models are discussed briefly. The tracer technique implemented by Tsivoglou and Neal (1976) is analogous to the method used by Roberts et al. (1984) for diffused aeration. A drawback to the krypton-oxygen transfer coefficient ratio determined by Tsivoglou and Neal (1976) is the applicability of the ratio from laboratory experiments to actual stream measurements. The East Bay Municipal Utility District (EBMUD) has successfully using deuterated chloroform as a tracer to estimate VOC emissions from a wastewater treatment facility in Oakland, CA.

The Parkhurst-Pomeroy model is appealing because reaeration in raw wastewater was studied. Because the model was developed from sewer studies, a drawback may be the applicability of the model to units open to the atmosphere. Corsi (1989) has verified the accuracy of the Parkhurst-Pomeroy model with preliminary results of tracer studies in operating sewers. Details of those studies are presented in Volume 2 of this report.

PREVIOUS STUDIES ESTIMATING VOC EMISSIONS

Previous studies estimating VOC emissions from primary wastewater treatment are discussed in this section. Studies were conducted at actual WWTPs and pilot scale facilities.

Predictive Modeling of Organic Emissions

Berglund and Whipple (1987) studied volatile and semi-volatile organic compound losses from a WWTP that receives wastewater from a large petrochemical plant. Four volatile compounds were studied: benzene, toluene, 1,2-dichloroethane, and ethylbenzene. Physical parameters of the primary treatment system, equalization basin, and waste transfer ditch are shown in Table 2-5.

Liquid samples were collected from the plant influent, effluent from the primary sedimentation tanks, and effluent from the equalization basin. Observed emission losses for individual VOCs from each unit process are presented in Table 2-6.

Table 2-5. Physical Parameters of the Primary Treatment Processes, Equalization Basin, and Waste Transfer Ditch

Process units	Parameters	Detention time, hr
Inlet box and pH adjustment tanks	Two 60640 L (16,000 gal.) uncovered tanks; 4.6 m (15 ft) diameter, 3.7 m (12 ft) high; Each mixed with 10-hp, 45-rpm agitator 0.9 m (3 ft) wide, 3.7 m (12 ft) long	0.5
Splitter box	Open-top, rectangular; Water drops 1.4 m (4.5 ft)	—
Primary sedimentation tanks	Three in parallel with two usually in operation; 13.7 m (45 ft) diameter, 2.4 m (8 ft) deep	2.7
Equalization basin	13.6 M L (3.6 M gal) basin; wastewater flows over a weir and drops 0.6 m (2 ft) from a discharge pipe into a waste transfer ditch	50
Waste transfer ditch	122 m (400 ft) long open ditch, 0.6-1.5 m (2-5 ft) deep, 1.2-3.0 m (4-10 ft) wide	—[a]

[a] No detention time was given for the waste transfer ditch.
Source: Berglund and Whipple, 1987.

Table 2-6. Observed Emission Losses of the Influent Load from the Primary Treatment Processes and Equalization Basin

VOC	H_c[a]	Influent load, kg/d	Percent loss of influent load: Primary processes	Percent loss of influent load: Equalization basin
1,2-Dichloroethane	0.05	15.4	22.0	28
Benzene	0.23	88.9	12.7	37
Toluene	0.25	18.1	10.2	31
Ethylbenzene	0.27	41.7	15.7	29

[a] Petrasek et al. (1983) at 25°C, except for 1,2-Dichloroethane. H_c for 1,2-Dichloroethane from Chang et al. (1987).
Source: Berglund and Whipple, 1987.

Percent removed from the primary processes for 1,2-dichloroethane was not consistent with the reported percent removed for the other VOCs, based on the magnitude of Henry's law constant. However, H_C for 1,1-dichloroethane is 0.21.

Emission of VOCs from individual processes comprising the primary treatment system (inlet box, two pH adjustment tanks, splitter box, and two primary sedimentation tanks), equalization basin, basin overflow weir, and waste transfer ditch were estimated using short-term air analyses for benzene, toluene, and ethylbenzene; no liquid samples were withdrawn from specific processes. Transfer of VOCs from the primary treatment processes to the atmosphere are shown in Table 2-7. Based on short term sampling measurements, 55% of air emissions from the area constituting the equalization basin, overflow weir, discharge pipe, and waste transfer ditch were estimated to be from the weir and discharge pipe. Some 45% were estimated to be from the basin water surface. Emissions from the waste transfer ditch were negligible. The authors described the estimates as "crude at best" (Berglund and Whipple, 1987).

Adsorption of VOCs to primary sedimentation sludge was also monitored. Underflow of the primary solids represented 11% of the influent wastewater flow. The underflow was directed to a settling basin, where the sludge settled, and the supernatant was removed and included in the influent to secondary treatment. The amount of VOCs contained in the primary influent, effluent, and underflow are presented in Table 2-8.

Berglund and Whipple obtained the following results which relate to Y:

1. Disappearance of VOCs in the equalization basin corresponded to approximately 60 percent of the estimated overall oxygen transfer rate.

2. If volatilization is the sole removal mechanism, removal of VOCs from the aerated stabilization basin is in the range of 15 to 50 percent of the estimated overall oxygen transfer rate.

Table 2-7. Estimated VOC Transfer from the Primary Treatment Processes

Treatment process	Percent loss of influent load
Inlet Box	0.8
pH Tank #1	0.5
pH Tank #2	0.25
Splitter Box	1.7
Primary Sedimentation #1 (center take off)	9.4
Primary Sedimentation #2 (peripheral take off)	2.5

Source: Berglund and Whipple, 1987.

Table 2-8. Amount of VOCs in the Primary Influent, Effluent, and Underflow

	Primary			
			Underflow load	
VOC	Influent load, kg/d	Effluent load, kg/d	kg/d	Percent[a]
1,2-Dichloroethane	15.4	10.9	1.1	7.1
Benzene	88.9	66.2	10.2	11.5
Toluene	18.1	13.2	2.2	12.0
Ethylbenzene	41.7	28.8	5.3	12.6

[a] Percent = underflow load/influent load

Source: Berglund and Whipple, 1987.

Removal and Partitioning of Volatile Organic Priority Pollutants in Wastewater Treatment

Petrasek et al. (1983) evaluated removal and partitioning of 16 VOCs from a pilot-scale conventional wastewater treatment sequence. Two parallel systems were operated, each consisting of a primary sedimentation tank, an aeration basin, and a secondary clarifier. Raw wastewater, degritted and comminuted, from a nearby WWTP served as influent to each system. One process was operated as a control to monitor typical VOC removal. Influent to the other treatment sequence was continuously spiked with a methanol solution containing known amounts of the compounds of interest. Design flow for the pilot system was $2.2 \cdot 10^{-3}$ m^3/s (35 gal/min).

Specifications of the treatment processes are shown in Tables 2-9 and 2-10. Total percentage of the compounds removed by the primary clarifier for both sequences is presented in Table 2-10. Percentage of the influent concentration contained in primary sludge is shown in Table 2-11.

Among the conclusions of Petrasek et al. (1983) were that

1. Appreciable removals of VOCs occurred in the primary clarifiers.
2. Partitioning to solids during primary sedimentation was not a significant removal mechanism for the majority of VOCs studied.

Table 2-9. Specifications of the Primary Sedimentation Tanks

Diameter, m	Weir diameter, m	Water height, m	Volume, m^3	Detention time, hr
3.0	2.8	3.7	24.9	3.1

Source: Adapted from Petrasek et al., 1983.

Table 2-10. Total Percentage Removed by the Primary Clarifier

		Treatment sequence	
Compound	Hc,[a]	Experimental[b]	Control
Methylene Chloride	0.13	25	27
1,1-Dichloroethene	0.62	57	65
Chloroform	0.16	0	33
Carbon Tetrachloride	1.26	47	47
1,2-Dichloropropane	0.12	5	0
Trichloroethylene	0.49	36	31
1,1,2-Trichloroethane	0.03	0	83
Dibromochloromethane	0.03	16	50
Benzene	0.23	16	0
1,1,1-Trichloroethane	0.20	27	48
Bromodichloromethane	0.09	28	0
Chlorobenzene	0.16	17	14
Tetrachloroethylene	1.19		
and		0	88
1,1,2,2-Tetrachloroethane	0.16		
Toluene	0.25	22	29
Ethylbenzene	0.27	16	70

[a] H_c at 25°C.

[b] Influent to the experimental sequence contained the spiked solution.

Source: Petrasek et al., 1983.

Table 2-11. Percentage Removed by the Primary Sludge

Compound	Percentage removed
Methylene Chloride	1.4
1,1-Dichloroethane	<0.7
Chloroform	2.0
Carbon Tetrachloride	<0.3
1,2-Dichloropropane	<2.0
Trichloroethylene	4.7
1,1,2-Trichloroethane	2.1
Dibromochloromethane	<0.2
Benzene	2.3
1,1,1-Trichloroethane	2.1
Bromodichloromethane	<0.4
Chlorobenzene	<6.6
Tetrachloroethylene	
and	10.7
1,1,2,2-Tetrachloroethane	
Toluene	5.1
Ethylbenzene	12.3

Source: Petrasek et al., 1983.

Atmospheric Release of Chlorinated Organic Compounds From the Activated Sludge Process

Lurker et al. (1982) studied the fate of chlorinated compounds at a MWTP. Only results pertaining to high volatility compounds, chloroform (TCM), carbon tetrachloride (CT), and tetrachloroethene (PERC), during primary treatment will be presented.

Primary treatment consisted of a wet well, coarse screens, pump house, fine screens, and grit chambers. Dimensions of the unit processes were not given. Design flow of the MWTP was 2.2 m^3/s (100 Mgal/day). Liquid concentrations of TCM, CT, and PERC in the wet well and grit chambers, and airborne concentrations above the grit chamber weir, are listed in Table 2-12. Unitless Henry's law constants for TCM, PERC, and CT at 25°C are 0.16, 1.16, and 1.26, respectively (Petrasek et al., 1983). Airborne concentrations were based upon 4-hour time-weighted averages, and liquid concentrations were based upon a single grab sample collected during the midpoint of the air sampling survey.

Table 2-12. Liquid and Airborne Concentrations of $CHCl_3$, CCl_4, and C_2Cl_4in the Primary Treatment Processes

	Wastewater concentration, µg/L		
Sampling location	$CHCl_3$	CCl_4	C_2Cl_4
Wet well	19	160	7
Grit chamber effluent	15	140	9
	Airborne concentration, $\mu g/m^3$		
Grit chamber weir	19	230	24
Grit chamber drag-out	15	44	4.7

Source: Lurker et al., 1983.

3. METHODS AND PROCEDURES

Components of an emission model for individual primary treatment units, an overview of an emissions model for a primary treatment sequence, and specifications of reference primary treatment processes are presented in this section.

EMISSION MODEL COMPONENTS

A model formulation and the computer software used to estimate volatile organic compound (VOC) emissions from reference primary wastewater treatment processes are discussed below.

Model Formulation

Continuous-flow stirred-tank reactors (CFSTRs) were the basic units of the emissions model. Primary treatment processes with short hydraulic detention times, i.e. approximately less than 10 minutes, were assumed to behave as a single CFSTR. Included in this category were bar screens, comminutors, Parshall flumes, grit chambers, and weirs. Treatment processes that resembled plug flow, such as rectangular sedimentation basins and conveyance channels, were modelled as a cascade of CFSTRs.

A mass balance for a VOC in a CFSTR, assuming gas transfer to be the only mechanism of depletion, was given previously in Eq. 2-3.

$$dC/dt = [(Ci-C)/\theta_H] - [K_La_{voc} \cdot (C-C_g/H_C)] \qquad (2\text{-}3)$$

where

dC/dt = rate of change of a reactor (or effluent) liquid VOC concentration, $mg/m^3 \cdot hr$

C_i = influent liquid VOC concentration, mg/m^3

C = effluent (or reactor) liquid VOC concentration, mg/m^3

θ_H = hydraulic detention time, hr

K_La_{voc} = overall VOC mass transfer coefficient, hr^{-1}

C_g = atmospheric VOC gas phase concentration, mg/m^3

H_c = Henry's law constant, unitless

If an influent VOC liquid concentration and hydraulic detention time of a system are known, and an overall mass transfer coefficient for a compound can be estimated, an effluent concentration of a compound of interest, with respect to time, can be estimated by solving Eq. 2-3. For those processes that required a series of CFSTRs, Eq. 2-3 was repeated for each reactor in a cascade with the effluent of a preceding reactor serving as influent to the following reactor.

Modeling Software

A simulation modeling program was used to write the emissions model (Richmond et al., 1987). The program is time dependent, that allows the operator to select from Euler's, second order Runge Kutta, or fourth order Runge Kutta numerical integration methods to solve differential equations. Second Order Runge Kutta was used in the emission models. Using the simulation program to model VOC emissions permitted non-steady state modeling of systems, input of flow rate and concentration curves, and flexibility to easily add and/or delete treatment components.

EMISSIONS MODEL

A completed emissions model for a primary treatment train required connecting individual treatment processes. Following a treatment sequence, effluent from a treatment process was influent to a successive treatment process. For example, effluent from grit chambers served as influent to sedimentation tanks, and effluent from sedimentation basins served as influent to conveyance channels. If a unit was modelled as a cascade of CFSTRs, this effluent-influent linking was performed within a treatment process. Therefore, an entire primary treatment sequence was modelled as a series of connected CFSTRs.

Headwork processes (bar screens, comminutors, Parshall flumes) and weirs required small time steps for an accurate numerical solution, and inclusion of these units in the emissions model for the reference treatment sequence made the numerical solution impractical with respect to time. Losses from these processes reach steady state in less than one hydraulic detention time, and predicted percentage removed was virtually constant for the range of flows and concentrations studied. To reduce computation time, a constant reduction factor was applied to influent flows to headwork processes and to weirs in the overall systems emissions model.

Time steps used when solving the materials balance differential equation, Eq. 2-3, for each treatment unit are presented in Table 3-1. If a time step greater than a unit hydraulic detention time was used, the numerical solution of Eq. 2-3 would become unstable.

Table 3-1. Time Steps Used for Each Treatment Process

Treatment process	Detention time, hr [a]	Time step	
		hr	min
Bar screens	$5.6 \cdot 10^{-5}$	10^{-6}	$6 \cdot 10^{-5}$
Comminutors	$2.8 \cdot 10^{-4}$	10^{-6}	$6 \cdot 10^{-5}$
Parshall flume	$5.3 \cdot 10^{-4}$	10^{-6}	$6 \cdot 10^{-5}$
Grit chamber	0.07	0.05	3.0
Sedimentation tank	1.4	0.05	3.0
Weirs	$2.8 \cdot 10^{-5}$	10^{-6}	$6 \cdot 10^{-5}$
Conveyance channels	0.09	0.035	2.1
Entire primary treatment sequence	—	0.035	2.1

[a] Detention times listed for bar screens, comminutors, Parshall flumes, and weirs represent the minimum detention times for the respective processes.

SPECIFICATIONS OF REFERENCE PRIMARY WASTEWATER TREATMENT PROCESSES

To estimate emissions from a primary treatment sequence, sizes of reference primary treatment processes were based on the Hyperion wastewater treatment facility (HTP) in El Segundo, CA. Influent design flow was 6.60 m^3/s (150 Mgal/day). Reference primary treatment processes are detailed below. A schematic of the reference primary treatment sequence is shown in Fig. 3-1.

Primary treatment processes consisted of bar screens, comminutors, Parshall flumes, two aerated grit chambers, four rectangular sedimentation basins, and two aerated conveyance channels. Specifications of the reference bar screens, comminutors, and Parshall flumes are listed in Table 3-2.

Table 3-2. Specifications of Bar Screens, Comminutors, and Parshall Flumes

Primary process	Headloss, m	Wastewater velocity, m/s	Length of influence, m [a]	Detention time, s [b]
Bar Screen [c]	0.15	0.6 - 1.0	0.2	0.33 - 0.20
Comminutor [d]	0.05 - 0.10	0.6 - 1.0	1.0	1.7 - 1.0
Parshall Flume [e]	0.5	1.2 - 2.1	4.0	3.3 - 1.9

[a] Length of influence values for all processes were estimated.

[b] Detention time = (length of influence)/(wastewater velocity)

[c] Headloss and wastewater velocity values for a bar screen are from Metcalf and Eddy (1979).

[d] Headloss value from Tchobanoglous and Schroeder (1987) ; wastewater velocity assumed equivalent to bar screen wastewater velocity.

[e] Headloss and wastewater velocity values for a Parshall flume are from Qasim (1985).

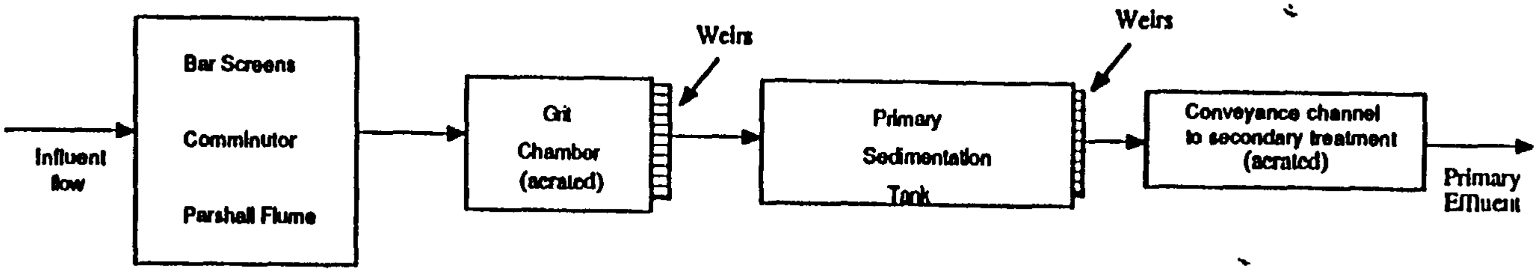

Figure 3-1. Schematic of the Reference Primary Wastewater Treatment Sequence

Design flow for the reference aerated grit chambers was 3.30 m^3/s (75 Mgal/day), thus two grit chambers were required to treat an influent flow of 6.60 m^3/s (150 Mgal/day). Dimensions for both aerated grit chambers are shown in Table 3-3.

Table 3-3. Dimensions of Aerated Grit Chambers

Depth, m	Length, m	Width, m	Volume, m^3
4.0	35.0	6.0	840

Flow dependent specifications, i.e. detention time, air flow rate, settling velocity, horizontal velocity, for the aerated grit chambers are listed in Table 3-4 for a flow of 3.30 m^3/s.

Design flow for the reference rectangular primary sedimentation basins was 1.65 m^3/s (37.5 Mgal/day), thus four sedimentation basins were required for an influent design flow of 6.60 m^3/s. Dimensions for all four sedimentation tanks are shown in Table 3-5.

Flow dependent specifications, i.e. detention time, overflow rate, settling velocity, horizontal velocity, are listed in Table 3-6 for a flow of 1.65 m^3/s.

Aerated conveyance channels transported effluent wastewater from primary sedimentation basins to secondary treatment processes of a treatment train. Design flow for the reference aerated conveyance channels was 3.30 m^3/s, thus two channels were required to convey the influent wastewater flow rate. The Manning equation was used to size rectangular channels for a wastewater velocity of 0.30 m/s (1.0 ft/sec). Dimensions for the two aerated conveyance channels for a wastewater velocity of 0.30 m/s are shown in Table 3-7.

Table 3-4. Specifications of Aerated Grit Chambers [a]

Detention time, min	Air flow rate, m^3/s	Settling velocity, m/s [b]	Horizontal velocity, m/s [c]
4.2	0.37	$1.6 \cdot 10^{-2}$	0.14

---

[a] The air is supplied via coarse bubble diffusers.
[b] Settling velocity = depth / detention time
[c] Horizontal velocity = wastewater flow/(depth·width)

Table 3-5. Dimensions of Primary Sedimentation Basins

Depth, m	Length, m	Width, m	Volume, m^3
4.0	100	20.8	8320

Table 3-6. Specifications of Primary Sedimentation Basins

Detention time, hr	Overflow rate, m^3/m^2 [a]	Settling velocity, m/s [b]	Horizontal velocity, m/s [c]
1.4	68.3	0.02	0.02

---

[a] Overflow rate = wastewater flow / (width·length)
[b] Settling velocity = depth / detention time
[c] Horizontal velocity = wastewater flow / (depth·width)

Table 3-7. Dimensions of Aerated Rectangular Conveyance Channels

Wastewater						
Velocity, m/s	Depth, m	Area, m^2	Width, m	Air flow,[a] m^3/lin m-min	Roughness coefficient	Slope, m/m
0.30	1.6	11.0	7.0	0.02 to 0.05	0.018	$2.4 \cdot 10^{-5}$

---

[a] Metcalf and Eddy (1979).
lin m = linear meter of channel

4. RESULTS

Estimated emission rates for three volatile organic compounds (VOCs) from reference primary treatment processes and a reference primary treatment sequence are presented in this section. The three compounds studied were chloroform (H_c = 0.131 at 20^oC), trichloroethene (H_c = 0.392), and carbon tetrachloride (H_c = 0.947). Emission rates for VOCs were assumed to be independent, with a total VOC emission load equivalent to a summation of individual VOC emission rates. Daily emission rates were estimated from typical flow and concentration curves that were converted to annual emission rates with no consideration for seasonal flow and possible concentration variation.

INFLUENT FLOW AND VOC CONCENTRATION CONDITIONS

Emission rates for VOCs were estimated for a range of influent flow, Q, and concentration, C_i, conditions. A list of the operating pairings used is presented below.

1. Q = daily average ; C_i = daily average
2. Q = daily average ; C_i = variable
3. Q = variable ; C_i = variable

Percent removal of an influent VOC, i.e. $[1 - (C/C_i)]\cdot 100\%$, was predicted for a constant influent flow and concentration (pairing 1), and daily and annual emission estimates were based on the other two flow-concentration combinations (pairings 2 and 3). The daily influent flow and concentration values are listed in Table 4-1 and shown graphically in Figure 4-1. Daily averages for influent flow and VOC concentration were 6.6 m^3/s (150 Mgal/day) and 100 $\mu g/L$, respectively. Emission estimates for the three VOCs studied were based on identical influent flow and concentration conditions.

Table 4-1. Daily Variation of Influent Flow and Concentration

Time	Flow, [a] m^3/s	Concentration, $\mu g/L$
12 midnight	6.59	85
2 a.m.	5.93	20
4 a.m.	5.38	15
6 a.m.	5.60	30
8 a.m.	6.04	140
10 a.m.	6.81	200
12 noon	7.14	120
2 p.m.	6.70	130
4 p.m.	6.37	135
6 p.m.	7.03	130
8 p.m.	8.13	110
10 p.m.	7.47	100
12 midnight	6.59	85

[a] Modified flow values from Tchobanoglous and Schroeder (1985).

PRIMARY TREATMENT PROCESSES

Emission rate estimates for VOCs for primary treatment processes are presented in this section. These included headworks (bar screens, comminutors, Parshall flumes), grit chambers, weirs, sedimentation basins, and conveyance channels.

Headworks

Headworks at a MWTP usually include bar screens, comminutors, and Parshall flumes. Estimates of VOC emissions from these processes were based on oxygen reaeration models. Losses from distribution channels within the headworks were considered negligible.

Oxygen reaeration was modelled using the Tsivoglou-Neal model. For comparison, a reaeration rate was also predicted from a modified expression for cascade waterfall aerators (Tchobanoglous and Schroeder, 1987; see Appendix D for derivation). A similar expression for K_La_{O2}, the overall oxygen mass transfer rate coefficient, was developed using either method, and is shown in Eq. 4-1. An overall VOC mass transfer rate coefficient, K_La_{VOC}, was approximated as 62% of K_La_{O2} (Roberts et al., 1984).

$$K_La_{O2} = C \cdot (\Delta_h / t_f) \qquad (4\text{-}1)$$

where

K_La_{O2} = overall oxygen mass transfer coefficient, hr^{-1}

C = constant of proportionality, m^{-1}

Δ_h = change in water elevation between two locations, m

t_f = time of flow between two locations, hr

Losses of VOCs from bar screens, comminutors, and Parshall flumes were predicted to reach steady state in less than one hydraulic detention time. Because headwork processes system volume was difficult to determine and because steady state VOC losses were approached rapidly, a range of hydraulic detention times and a constant influent VOC concentration of 100 µg/L were used to estimate emission losses. Daily and annual emission rates were estimated for one set of flow and concentration conditions, i.e. $Q = 6.6\ m^3/s$, $C_i = 100\ \mu g/L$, and were assumed constant for the range of flows and concentrations studied. Percent removal and daily and annual VOC emission rates for bar screens, comminutors, and Parshall flumes are shown in Tables 4-2 through 4-4. Details of each process are listed in Tables 3-2 through 3-4.

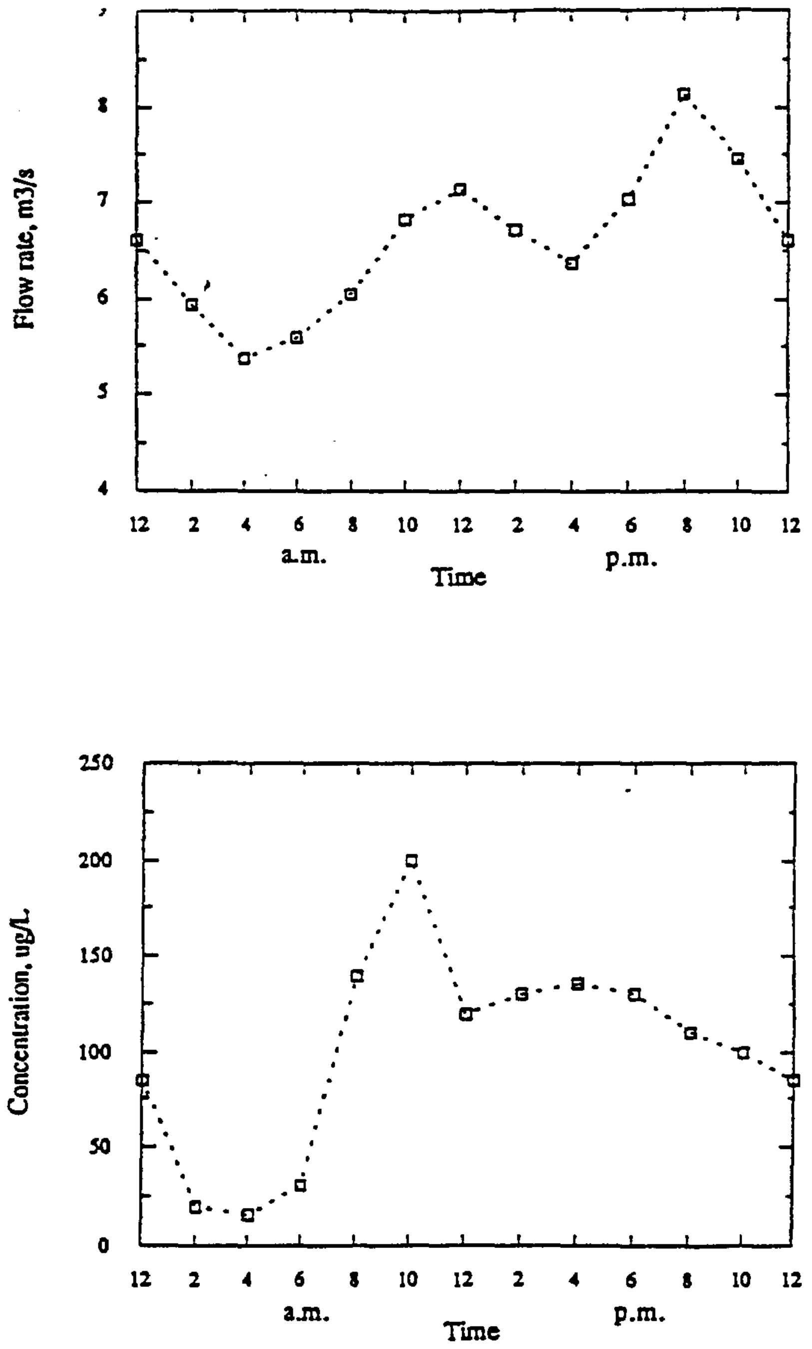

Figure 4-1. Daily Flow Rate and Concentration Distributions Used to Estimate VOC Emissions from the Reference Primary Treatment Sequence

Table 4-2. VOC Emission Estimates for Bar Screens

Constant m^{-1}	Detention time, s	Headloss m	K_La_{O2} hr^{-1}	K_La_{VOC} hr^{-1}	Percent removal	Emission rate kg/d	Emission rate mTPY
0.10	0.2	0.15	270	162	0.9	0.5	0.2
0.19	0.2	0.15	513	308	1.7	0.9	0.3
0.19	0.3	0.15	342	205	1.7	0.9	0.3

Table 4-3. VOC Emission Estimates for Comminutors

Constant m^{-1}	Detention time, s	Headloss m	K_La_{O2} hr^{-1}	K_La_{VOC} hr^{-1}	Percent removal	Emission rate kg/d	Emission rate mTPY
0.10	1.0	0.10	36.0	21.6	0.6	0.3	0.1
0.19	1.0	0.10	68.4	41.0	1.1	0.7	0.3
0.19	1.7	0.10	39.9	24.0	1.1	0.7	0.3

Table 4-4. VOC Emission Estimates for Parshall Flumes

Constant m^{-1}	Detention time s	Headloss m	K_La_{O2} hr^{-1}	K_La_{VOC} hr^{-1}	Percent removal	Emission rate kg/d	Emission rate mTPY
0.10	3.3	0.5	54.6	32.7	2.8	1.6	0.6
0.19	3.3	0.5	104	62.2	5.3	2.9	1.1
0.10	1.9	1.0	190	114	5.7	3.2	1.2
0.19	1.9	1.0	360	216	10.2	5.6	2.0
0.19	3.3	1.0	207	124	10.2	5.6	2.0

mTPY = metric tonne per year

Grit Chamber

A single CFSTR was used to model grit chambers. Mass transfer coefficients for a VOC for gas-stripping were estimated using the Roberts et al. (1984), Truong-Blackburn (1984), and Namkung-Rittman (1987) models. In the case of the Namkung-Rittman model, an "effective" value of K_La_{VOC} was derived (Equation 2-7). For aerated grit chambers, the available surface area for volatilization was estimated from incoming bubble diameter and air flow rate (see Appendix F and G), and volatilization losses were estimated using the Tsivoglou-Neal model. Dimensions for the aerated grit chamber studied are shown in Table 4-5. Detailed specifications of the grit chamber are presented in Table 3-4. Losses from the overflow weir are presented in a separate section.

Predicted VOC percent removal and estimated daily and annual emission rates for the reference aerated grit chamber by the three models are presented in Tables 4-6 and 4-7, respectively. Both the Truong-Blackburn and Namkung-Rittman models directly predict a value for K_La_{VOC}, with the magnitude of a VOC mass transfer coefficient directly proportional to H_C. Because the Roberts et al. model (1984) approximates K_La_{VOC} as 62% of K_La_{O2}, the magnitude of K_La_{VOC} was insensitive to a compound's H_C. For the Truong-Blackburn equation, the values suggested for the empirical constants, b and m, were $3.71 \cdot 10^{-3}$ and 1.045, respectively (Truong and Blackburn, 1984).

Table 4-5. Dimensions of the Aerated Grit Chamber

Design flow, m^3/s	Air flow rate, m^3/s	Depth, m	Length, m	Width, m	Volume, m^3
3.30	0.37	4.0	35.0	6.0	840

m3/s = Mgal/day . 0.044

Table 4-6. Predicted VOC Percent Removal for the Aerated Grit Chamber

Model	H_c[a]	Concentration, μg/L Influent	Concentration, μg/L Effluent	Percent removal
Roberts et al.	0.131	100	93.9	6.1
	0.392	100	93.6	6.4
	0.947	100	92.3	7.7
Truong-Blackburn	0.131	100	98.6	1.4
	0.392	100	95.8	4.2
	0.947	100	90.2	9.8
Namkung-Rittman	0.131	100	99.0	1.0
	0.392	100	97.1	2.9
	0.947	100	93.2	6.8

[a] Roberts et al. (1984) at 20°C.

Table 4-7. Estimated Daily and Annual VOC Emission Rates for the Aerated Grit Chamber

						K_La_{VOC}, hr^{-1}		Emission rate	
Model	H_c, [a]	Q, m^3/s	C_i, mg/L	θ_H, min	K_La_{O2}, hr^{-1}	stp.	vol.	kg/d	mTPY
Roberts et al.	0.131	var.	var.	3.4-5.2	2.9	1.8	0.0	1.8	0.7
	0.392	var.	var.	3.4-5.2	2.9	1.8	0.0	1.9	0.7
	0.947	var.	var.	3.4-5.2	2.9	1.8	0.0	2.3	0.8
	0.131	con.	var.	4.2	2.9	1.8	0.0	1.8	0.7
	0.392	con.	var.	4.2	2.9	1.8	0.0	1.9	0.7
	0.947	con.	var.	4.2	2.9	1.8	0.0	2.3	0.8
Truong-Blackburn	0.131	var.	var.	3.4-5.2	—	0.3	0.0	0.4	0.1
	0.392	var.	var.	3.4-5.2	—	1.0	0.0	1.2	0.4
	0.947	var.	var.	3.4-5.2	—	2.6	0.0	2.9	1.1
	0.131	con.	var.	4.2	—	0.3	0.0	0.4	0.1
	0.392	con.	var.	4.2	—	1.0	0.0	1.2	0.4
	0.947	con.	var.	4.2	—	2.6	0.0	2.9	1.1
Namkung-Rittman	0.131	var.	var.	3.4-5.2	—	0.2	0.0	0.3	0.1
	0.392	var.	var.	3.4-5.2	—	0.6	0.0	0.8	0.3
	0.947	var.	var.	3.4-5.2	—	1.5	0.0	2.0	0.7
	0.131	con.	var.	4.2	—	0.2	0.0	0.3	0.1
	0.392	con.	var.	4.2	—	0.6	0.0	0.9	0.3
	0.947	con.	var.	4.2	—	1.5	0.0	2.0	0.7

[a] Roberts et al. (1984) at 20°C.

var. = variable con. = constant stp. = stripping

vol. = volatilization

Sedimentation Basin

Rectangular sedimentation basins were assumed to behave as plug flow reactors, and were modelled as a series of CFSTRs. Seven reactors were used to model rectangular sedimentation basins in the reference treatment facility. The number of reactors in a cascade was chosen based on results of several model runs, each trial with a different number of reactors in the cascade, i.e. 3, 5, 7, 9. Seven CFSTRs were chosen to model the reference sedimentation basin because seven and nine CFSTRs in series estimated similar emission losses. Surface reaeration rates were predicted using the Tsivoglou-Neal and Parkhurst-Pomeroy models. Losses from the overflow weir are presented in a separate section.

Dimensions for the sedimentation basin studied are shown in Table 4-8. Detailed specifications of the sedimentation basin are listed in Tables 3-5 to 3-7. The slope of the sedimentation tank was estimated using the Manning equation, assuming uniform flow and a roughness coefficient of 0.018.

Predicted VOC percent removal and daily and annual emission rates for the sedimentation tank are presented in Tables 4-9 and 4-10, respectively. Both the Tsivoglou-Neal and Parkhurst-Pomeroy models have similar expressions for the oxygen mass transfer coefficient, i.e. $K_La_{O2} = C'(Sv)^n$. For the Tsivoglou-Neal equation, $n = 1.0$, and for the Parkhurst-Pomeroy equation, $n = 3/8$. Estimated percent removal for the reference sedimentation basin was less than 0.05 percent. Estimated daily and annual emission rates were less than 0.05 kg/d.

Table 4-8. Dimensions of the Sedimentation Basin

Design flow, m^3/s	Slope, m/m	Depth, m	Length, m	Width, m	Volume, m^3
1.65	$3.2 \cdot 10^{-8}$	4.0	100	20.8	8320

Table 4-9. Predicted VOC Percent Removal for the Sedimentation Basin

	Concentration, mg/L		Percent
Model	Influent	Effluent	removal
Tsivoglou-Neal	100	~100	<0.05
Parkhurst-Pomeroy	100	~100	<0.05

Table 4-10. Estimated Daily and Annual VOC Emission Rates for the Sedimentation Basin

						Emission rate	
Model	Q, m^3/s	C_i, mg/L	q_H, hr	K_La_{O2}, hr^{-1}	K_La_{VOC}, hr^{-1}	kg/d	mTPY
Tsivoglou-Neal	var.	var.	1.1-1.7	1.9-2.8 E-7	1.2-1.7 E-7	<0.05	<0.02
	con.	var.	1.2	2.3 E-7	1.4 E-7	<0.05	<0.02
Parkhurst-Pomeroy	var.	var.	1.1-1.7	1.0-1.2 E-4	6.1-7.2 E-5	<0.05	<0.02
	con.	var.	1.2	1.1 E-4	6.6 E-5	<0.05	<0.02

var. = variable con. = constant
mTPY = metric tonnes per year

Weirs

Weirs were modelled as a single CFSTR. Analogous to headwork processes, oxygen reaeration rates were predicted using the Tsivoglou-Neal model and an expression for cascade waterfall aerators (see Eq. 4-1). Losses of VOCs were predicted to reach steady state in less than a weir's hydraulic detention time. Because a system volume for a weir was difficult to determine and a rapid approach to steady state VOC losses occurred, a range of hydraulic detention times and a constant influent VOC concentration of 100 mg/L were used to estimate emission losses. Daily and annual emission rates were estimated for one set of flow and concentration conditions, i.e. $Q = 6.6\ m^3/s$, $C_i = 100$ mg/L, and were assumed constant for the range of flows and concentrations studied. Percent removal and daily and annual VOC emission rates for the weirs are shown in Table 4-11.

Later in the study, a model developed by Nakasone (1987) that estimates oxygen reaeration at weirs was found in the literature. Nakasone (1987) stated that approximately 95 percent of oxygen transfer at weirs occurred in bubbles in a downstream pool. Oxygen mass transfer rate coefficients, K_La_{O2}, estimated by the Nakasone (1987) model were 3 to 4 times larger than estimates using the cascade waterfall aerator model, and 5 to 8 times larger than estimates using the Tsivoglou-Neal model.

Conveyance Channels

Conveyance channels were assumed to behave as a plug flow reactor, and modelled as a cascade of CFSTRs. Two reactors in series were selected to model the reference conveyance channel, using a trial and error procedure (detailed in the sedimentation basin section). If a channel was aerated, stripping losses were estimated using the Roberts et al. model. For aerated conveyance channels, the available surface area for volatilization was estimated from incoming bubble diameter and air flow rate, and volatilization losses were estimated using the Tsivoglou-Neal and Parkhurst-Pomeroy models.

Dimensions for the aerated conveyance channel studied are shown in Table 4-12. Detailed specifications of the channel are listed in Table 3-7.

Predicted VOC percent removal and estimated daily and annual emission rates for the aerated conveyance channel are presented in Tables 4-13 and 4-14, respectively. Values presented for percent removal and daily and annual emission rates are a summation of stripping and volatilization losses. Gas stripping losses were estimated using the Roberts et al. model.

Table 4-11. VOC Emission Estimates for the Weirs

Constant m^{-1}	Detention time, s	Headloss, m	K_La_{O2}, hr^{-1}	K_La_{VOC}, hr^{-1}	Percent removal	Emission rate kg/d	Emission rate mTPY
0.10	0.1	0.1	360	223	0.6	0.3	0.1
0.19	0.1	0.1	684	424	1.2	0.7	0.3
0.10	0.2	0.3	540	335	1.8	1.0	0.4
0.19	0.2	0.3	1030	636	3.4	1.9	0.7
0.10	0.4	1.0	900	558	5.8	3.3	1.2
0.19	0.4	1.0	1710	1060	10.5	6.0	2.2
0.10	0.6	2.0	1200	744	11.0	6.2	2.3
0.19	0.6	2.0	2280	1410	19.1	10.9	4.0

1 tonne = 1000 kg

Table 4-12. Dimensions of the Aerated Conveyance Channel

Design flow, m^3/s	Air flow rate, $m^3/m\text{-}hr$[a]	Velocity, m/s	Slope, m	Depth, m	Length, m	Width, m	Volume, m^3
3.30	3.0	0.30	$2.4 \cdot 10^{-5}$	1.6	100	7.0	1120

[a] Because the conveyance channel was modelled as two CFSTRs, the air flow rate used was 150 m^3/hr per CFSTR.

Table 4-13. Predicted VOC Percent Removal for the Aerated Conveyance Channel

Model	H_c[a]	Concentration, mg/L Influent	Concentration, mg/L Effluent	Percent removal
Tsivoglou-Neal	0.131	100	98.6	1.4
	0.392	100	98.5	1.5
	0.947	100	98.1	1.9
Parkhurst-Pomeroy	0.131	100	98.5	1.5
	0.392	100	98.4	1.6
	0.947	100	98.1	1.9

[a] Roberts et al. (1984) at 20°C.

Table 4-14. Estimated Daily and Annual VOC Emission Rates for the Aerated Conveyance Channel

Model	H_c[a]	Q, m^3/s	C_i, mg/L	q_H, min	K_La_{O2}, hr^{-1}		K_La_{VOC}, hr^{-1}		Emissions	
					stp.	vol.(E-3)	stp.	vol.(E-3)	kg/d	mTPY
Tsivoglou-Neal	0.131	var	.var.	4.6-6.8	0.5	2.1-3.2	0.3	1.3-2.0	0.4	0.1
	0.392	var	.var.	4.6-6.8	0.5	2.1-3.2	0.3	1.3-2.0	0.5	0.2
	0.947	var	.var.	4.6-6.8	0.5	2.1-3.2	0.3	1.3-2.0	0.6	0.2
	0.131	con	.var.	5.6	0.5	2.6	0.3	1.6	0.5	0.2
	0.392	con	.var.	5.6	0.5	2.6	0.3	1.6	0.5	0.2
	0.947	con	.var.	5.6	0.5	2.6	0.3	1.6	0.6	0.2
Parkhurst-Pomeroy	0.131	var	.var.	4.6-6.8	0.5	8.2-9.6	0.3	5.1-5.9	0.5	0.2
	0.392	var	.var.	4.6-6.8	0.5	8.2-9.6	0.3	5.1-5.9	0.5	0.2
	0.947	var	.var.	4.6-6.8	0.5	8.2-9.6	0.3	5.1-5.9	0.6	0.2
	0.131	con	.var.	5.6	0.5	8.9	0.3	5.5	0.5	0.2
	0.392	con	.var.	5.6	0.5	8.9	0.3	5.5	0.5	0.2
	0.947	con	.var.	5.6	0.5	8.9	0.3	5.5	0.6	0.2

[a] Roberts et al. (1984) at 20°C.

var. = variable con. = constant stp. = stripping

vol. = volatilization

mTPY = metric tonne per year

PRIMARY TREATMENT SEQUENCE

Estimated VOC emissions from the reference primary treatment train are presented in this section. Processes included in primary treatment were headworks (bar screens, comminutors, Parshall flumes), aerated grit chambers, grit chamber weirs, sedimentation tanks, sedimentation basin weirs, and aerated conveyance channels. A schematic of the complete primary treatment sequence was shown in Fig. 3-1.

Estimated VOC emission rates from the reference treatment train were determined using the flow and concentration curves in Fig. 4-1. Total influent VOC load was 61.5 kg/d (22.4 TPY). Emission estimates for the reference primary treatment sequence are divided into three categories: non-infinite dilution in rising bubbles, infinite dilution in rising bubbles, and unaerated. Estimated emission rates for CT (H_c = 0.947 at 20°C), TCE (H_c = 0.392), and TCM (H_c = 0.131) when infinite dilution in a rising bubble is not assumed, i.e. $C_g \neq 0$ in a rising bubble, are reported in Table 4-15. Estimated maximum and minimum emission rates for the primary treatment train are listed in Table 4-16. A maximum rate of VOC emission estimates are obtained based on the assumption of infinite dilution within a rising air bubble in both the aerated grit chambers and aerated conveyance channels, i.e. $C_g = 0$ in a rising air bubble. A minimum emission rate for the treatment sequence was estimated by assuming the grit chambers and conveyance channels were not aerated. The estimated maximum and minimum emission rates presented in Table 4-16 are for any VOC because a gas concentration in a rising bubble, C_g, was not included in emission rate calculations.

As removal of an influent VOC decreased for grit chambers, the magnitude of volatilization losses from grit chamber and sedimentation weirs increased.

Table 4-15. Estimated VOC Emission Rates for the Primary Treatment Sequence
(total influent load was 61.5 kg/d)

	Value, kg/d (mTPY)						
H_C,[a]	Head-works	Aerated grit chambers[b]	Grit chamber weirs	Sed. basin	Sed. basin weirs	Aerated convey. channels[c]	Total emissions
0.947[d]	3.1 (1.1)	4.4 (1.6)	5.4 (2.0)	<0.05 (<0.02)	2.4 (0.9)	0.9 (0.3)	16.2 (5.9)
0.392[e]	3.1 (1.1)	3.6 (1.3)	5.5 (2.0)	<0.05 (<0.02)	2.5 (0.9)	0.7 (0.3)	15.4 (5.6)
0.131[f]	3.1 (1.1)	3.5 (1.3)	5.5 (2.0)	<0.05 (<0.02)	2.4 (0.9)	0.7 (0.3)	15.2 (5.4)

[a] Roberts et al. (1984) at 20°C.
[b] Aerated grit chamber; G = 1330 m^3/hr.
[c] Aerated conveyance channel; G = 150 m^3/hr per CFSTR.
[d] Carbon tetrachloride (CT).
[e] Trichloroethene (TCE).
[f] Chloroform (TCM).

Table 4-16. Estimated Maximum and Minimum VOC Emission Rates for the Primary Treatment Sequence
(total influent load was 61.5 kg/d)

	Value, kg/d (mTPY)						
Estimation	Head-works	Grit chambers	Grit chamber weirs	Sed. basins	Sed. basin weirs	Convey. channels	Total emissions
Maximum	3.1 (1.1)	6.5[a] (2.4)	5.2 (1.9)	<0.05 (<0.02)	2.3 (0.8)	1.3[b] (0.5)	18.4 (6.7)
Minimum	3.1 (1.1)	0.0[c] (0.0)	5.9 (2.2)	<0.05 (<0.02)	2.6 (0.9)	0.0[c] (0.0)	11.6 (4.2)

[a] Aerated grit chamber; G = 1330 m^3/hr; (infinite dilution assumed).
[b] Aerated conveyance channel; G=150 m^3/hr per CFSTR; (infinite dilution assumed).
[c] Non-aerated process.

Important caveats used in estimating VOC emissions from the reference primary treatment sequence are listed below.

1. The flow and concentration curves in Fig. 4-1 (p. 36) were used as influent conditions for all three VOCs.

2. Specifications of individual treatment processes are presented in the Methods and Procedures section (Section 3, p. 26 ff.).

3. Stripping and volatilization parameters, i.e. K_La_{O2}, K_La_{VOC}, q_H, air flow rate, for the respective processes are presented in the preceding sub-section.

4. A grit chamber was modelled as a single CFSTR incorporating the Roberts et al. model to predict K_La_{O2} for diffused air and the Tsivoglou-Neal equation to estimate oxygen reaeration. To determine K_La_{VOC}, K_La_{O2} was multiplied by 0.62 (Roberts et al., 1984). For an aerated grit chamber, the available surface area unaffected by the rising bubbles was determined to predict volatilization losses.

5. A rectangular sedimentation basin was modelled as a seven CFSTR cascade, implementing the Parkhurst-Pomeroy model to predict a surface K_La_{O2}.

6. A conveyance channel was modelled as a two CFSTR cascade, incorporating the Tsivoglou-Neal model to predict K_La_{O2} for volatilization and the Roberts et al. model to predict K_La_{O2} for stripping. To determine K_La_{VOC}, K_La_{O2} was multiplied by 0.62 (Roberts et al., 1984). The entire surface area was determined available for volatilization, i.e. air flow rate did not appreciably disrupt the water surface.

7. Headwork processes and weirs required small time steps to obtain accurate numerical solutions, and inclusion of these units in the emissions model for the reference treatment sequence made the numerical solution impractical with respect to time. Losses from these processes reached steady state in less than one hydraulic detention time, and the percentage removed was virtually constant for the range of flows and concentrations studied. To reduce computational time, a constant reduction factor was applied to influent flows to headwork processes and weirs in the overall systems emissions model. The reduction factors were based on percent removal results presented for headwork processes and weirs in Tables 4-2, 4-3, 4-4, and 4-11. Reduction factors for headworks and weirs used in the emissions model are presented in Table 4-17.

Table 4-17. Reduction Factors for Headworks and Weirs

Process	Reduction factor
Headworks	0.95
Grit chamber weir	0.90
Sedimentation basin weir	0.95