5. DISCUSSION OF RESULTS

A discussion of predicted VOC emission rates for the reference treatment units and sequence, summaries of the mass transfer coefficient models used to estimate VOC emissions, and sensitivity analyses on removal efficiencies by reference primary treatment processes are presented below.

EMISSION RATES

Range of Oxygen and VOC Mass Transfer Rates Used for the Reference Treatment Processes

A summary of mass transfer coefficient models used in the emissions model to estimate VOC mass transfer for the reference primary treatment units is listed in Table 5-1.

Minimum and maximum oxygen and VOC volatilization mass transfer rates, K_La_{O2} and K_La_{VOC}, respectively, and minimum and maximum percent-removed of an influent VOC concentration estimated for the reference treatment processes are presented in Table 5-2. The Roberts et al. model was used to predict K_La_{O2} and K_La_{VOC} for diffused aeration units. These values for the reference aerated grit chambers were 2.9 and 1.8 hr^{-1}, respectively, and the values for the reference aerated conveyance channels were 0.5 and 0.3 hr^{-1}, respectively. Mass transfer coefficients predicted by the Roberts et al. model were constant for the range of flows and concentrations studied, and therefore were not included in Table 5-2. Minimum and maximum percent-removed values were a summation of mass transferred via gas stripping and volatilization.

Caveats associated with estimated emission rates for each reference treatment unit are listed below.

1. Oxygen reaeration rates, and therefore VOC mass transfer rates, for bar screens, comminutors, Parshall flumes, and weirs were a function of headloss and detention time.

Table 5-1. Gas Stripping and Volatilization Mass Transfer Models Used in This Study

Treatment unit	Gas stripping model	Volatilization model
Bar screen	____	Cascade waterfall aerator or Tsivoglou-Neal
Comminutor	____	Cascade waterfall aerator or Tsivoglou-Neal
Parshall flume	____	Cascade waterfall aerator or Tsivoglou-Neal
Grit chamber	Roberts et al.	Tsivoglou-Neal or Parkhurst-Pomeroy
Sedimentation Basin	____	Parkhurst-Pomeroy
Conveyance channels	Roberts et al.	Tsivoglou-Neal or Parkhurst-Pomeroy
Weirs	____	Cascade waterfall aerator or Tsivoglou-Neal

Table 5-2. Oxygen and VOC Volatilization Mass Transfer Rates and Percent Removed Estimated for the Reference Treatment Units

Treatment unit	Volatilization K_La_{O2}, hr^{-1} Min.	Volatilization K_La_{O2}, hr^{-1} Max.	Volatilization K_La_{VOC}, hr^{-1} Min.	Volatilization K_La_{VOC}, hr^{-1} Max.	Total percent removed [a] Min.	Total percent removed [a] Max.
Bar screen	270	513	162	308	0.9	1.7
Comminutor	36.0	68.4	21.6	41.0	0.6	1.1
Parshall flume	54.6	360	32.7	216	2.8	10.2
Weirs	360	2280	223	1410	0.6	19.1
Grit chambers	0	0	0	0	6.1	7.7
Sedimentation basins	$1.7 \cdot 10^{-7}$	$1.2 \cdot 10^{-4}$	$1.2 \cdot 10^{-7}$	$7.2 \cdot 10^{-5}$	<0.05	<0.05
Conveyance channels	$2.1 \cdot 10^{-3}$	$9.6 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$5.9 \cdot 10^{-3}$	1.4	1.9

[a] Total percent removed is a summation of mass transferred via stripping and volatilization.

2. Volatilization losses from the water surfaces of sedimentation basins and conveyance channels were estimated to be negligible.

3. The surface area available for volatilization from an aerated grit chamber (G = 1330 m^3/hr) was estimated to be zero, but the entire surface area of an aerated conveyance channel (G = 150 m^3/hr) was estimated to be available for volatilization.

4. Gas-stripping losses dominated volatilization losses from aerated conveyance channels. Minimum percent removed reported for the reference aerated grit chambers and reference aerated conveyance channels was for TCM (H_C = 0.131 at 20^oC), and maximum percent removed was for CT (H_C = 0.947 at 20^oC).

Overview of the Estimated Emission Rates

A reference primary treatment sequence, particularly headworks, aerated grit chambers, aerated conveyance channels, and weirs, was demonstrated to be a source of VOC emissions. For example, an influent CT (H_C = 0.947 at 20^oC) load of 61.5 kg/d was reduced to 45.3 kg/d by the reference primary treatment sequence. Volatilization losses from water surfaces of sedimentation basins and conveyance channels were estimated to be negligible. Predicted losses for headwork units and the reduction of an influent VOC from the reference primary treatment train (approximately 5 and 25%, respectively) were consistent with preliminary results of a current tracer study conducted by East Bay Municipal Utility District (EBMUD) (Hellier, 1989).

Estimated VOC losses from the reference primary treatment sequence were a result of diffused aeration, and also a result of drops at bar screens, comminutors, Parshall flumes, and weirs. Emission rates for CT (H_C = 0.947) from the reference primary treatment train decreased approximately 28 percent (16.2 to 11.6 kg/d) when grit chambers and conveyance channels were not aerated (see Tables 4-15 and 4-16). Reported headloss values for headwork processes were typical values in the literature, and predicted emission rates (kg/d) are probably common to most MWTPs. However, weir drops are not only plant specific but also

vary with flow rate, i.e. minimum headloss at maximum flow rate. Because weir heights differ among facilities, estimated emissions of VOCs for a range of heights were presented. For the reference treatment sequence, approximate effluent weir heights for the grit chambers and sedimentation basins were based on visits to MWTPs, and a constant percent-reduction used in the overall system emissions model was estimated from results presented for weirs in Table 4-11.

The Tsivoglou-Neal stream reaeration model and an oxygen transfer rate for a cascade waterfall aerator were believed to predict conservative values for the oxygen mass transfer coefficient, K_La_{O2}, at weirs. Nakasone (1987) observed that entrained air bubbles in a downstream pool were responsible for approximately 95 percent of oxygen transfer at weirs. Because both the Tsivoglou-Neal and the cascade waterfall aerator models are functions of weir height and drop time, emission losses from weirs were probably under estimated. An equation developed by Nakasone (1987) to estimate oxygen transfer rates at weirs was used to predict K_La_{O2} for weir heights of 0.3, 1.0, and 2.0 m (see Appendix E for a detailed calculation). These values are presented in Table 5-3.

Table 5-3. Estimated Values of K_La_{O2} for Weirs Using an Equation Developed by Nakasone (1987)

Weir height, m	K_La_{O2}, hr^{-1}		
	Nakasone	CWA [a]	Tsivoglou [b]
0.3	2980	1030	540
1.0	7470	1710	900
2.0	9850	2280	1200

[a] Cascade waterfall aerator model.
[b] Tsivoglou-Neal model.

As shown in Table 5-3, the Nakasone method estimate of K_La_{O2} for weirs is 3 to 4 times larger than predicted by the cascade waterfall aerator model, and 5 to 8 times larger than that of the Tsivoglou-Neal model. Emission losses would follow a similar trend.

The magnitude of estimated VOC emission rates are unique to the reference treatment units and reference primary treatment facility designed for this study. Variation in plant design and treatment practices, e.g.. circular clarifiers, non-aerated processes, make VOC emission rates site-specific, but regardless of treatment facility, one concludes that a primary treatment train is a potential source of VOC emissions.

Comparison With Studies in the Literature

Four researchers, Bell et al. (1988), Berglund and Whipple (1987), Petrasek et al. (1983), and Lurker et al. (1982), studied VOC emissions from primary wastewater treatment processes. A summary of the findings of each researcher is presented below.

Bell et al. (1988) - Bell et al. studied emission of VOCs from aerated grit chambers and secondary aeration basins at four MWTPs in Ontario, Canada. The researchers reported total VOC emissions for measured compounds ranged from 0.0015 to 0.075 g of VOCs per m^3 of wastewater treated.

Berglund and Whipple (1987) - Berglund and Whipple reported an average 12 percent decrease of volatile compounds from a full scale primary treatment sequence at an industrial wastewater treatment plant. Noted sources of emissions included an aerated pH adjustment tank, a splitter box with a 1.4 m (4.5 ft) drop, a well-mixed equalization basin, and the basin weir. The authors reported that emissions from the surface of a 122 m (400 ft) waste transfer ditch were insignificant.

Petrasek et al. (1983) - Petrasek et al. reported an average 24 percent decrease for both semi-volatile and volatile compounds from a pilot scale primary clarifier. Mentioned as potential

sources of VOC emissions were the clarifier surface, overflow weir, and effluent channel.

Lurker et al. (1982) - Lurker et al. reported measured emissions of TCM, CT, and PERC from grit chamber weirs at a MWTP.

PEEP and BAAT (1991) - Recently, results of the Pooled Emission Estimation Program (PEEP) and the Bay Area Air Toxics (BAAT) Group became available. Although the reference treatment train modeled did not match the sources tested by the PEEP and BAAT exactly, it was still possible to compare the range of model results with the experimental data from a grit chamber at the JWPCP and the headworks at the EBMUD. Details of the comparison are contained in Appendix I.

The average of three rounds of 8-hr sampling at the JWPCP yielded an estimated stripping efficiency of 1.5% for the three compounds DCM, TCM and BZ based upon the liquid influent and the difference of the measured inlet and outlet gas concentrations to the grit chamber. The measured stripping efficiencies compare with a range of from about 1% to 3% (TCM to BZ)) for the Namkung and Rittman mass transfer model formulation to about 6% (TCM to BZ) for the Roberts et al. model formulation. Considering that the possible effects of partitioning to solids or to a separate organic phase have not been taken into account, and the uncertainty introduced by the presence of an ice bath impinger in the PEEP sampling train (discussed in greater detail in Appendix I), the model predictions' agreement with the experimental data are considered satisfactory. The "headworks" processes at the EBMUD that are believed to have been measured consist of bar screens, an influent pump and non-aerated grit chambers. Measured emissions ranged from 1.4% to 6.3% for the three compounds DCM, TCM, and BZ. Model estimates of emissions through bar screens and comminutors range from 0.9% to 1.7% and 0.6% to 1.1%, respectively, over the range of values assumed. Thus emissions from these processes would be expected to range from about 1.5% to 2.8% of the influent mass. Again the agreement appears to be satisfactory given the limited ability to model such processes.

These studies at full scale and pilot scale facilities', headworks, aerated grit chambers, aerated conveyance channels, and weirs demonstrate their potential as sources of VOC emissions. Using the emission values reported by Bell et al. (1988), the total VOC emission load from aerated grit chambers and aeration basins for an influent flow of 6.6 m^3/s would be in the range of 0.9 to 42.8 kg/d (Bell et al., 1988). Total emissions estimated from the reference primary treatment sequence varied from 11.6 to 18.4 kg/d (0.02 to 0.03 g of VOCs per m^3 of wastewater treated), within the approximate range measured by Bell et al. (1988).

A source of controversy is whether volatilization from water surfaces of clarifiers and conveyance channels significantly contributes to a VOC emission load. Petrasek et al. (1983) reported significant VOC emissions from a pilot scale sedimentation basin water surface. Berglund and Whipple (1987) reported insignificant emissions from a water surface of a 122 m (400 ft) transfer ditch. Models used in this study estimated negligible (<0.05 kg/d) volatilization emissions from water surfaces of reference primary clarifiers and conveyance channels.

OVERALL MASS TRANSFER COEFFICIENT MODELS

Summaries of models that predict overall mass transfer coefficients for diffused aeration and natural reaeration used in the emissions model are presented in this section.

Diffused Aeration Models

Three models, that predict K_La_{VOC} for diffused aeration systems were studied: Roberts et al. (1984), Truong-Blackburn (1984), and Namkung-Rittman (1987). The Roberts et al. model, which approximates K_La_{VOC} as 62% of K_La_{O2}, was preferred for diffused aeration systems for the following reasons: 1) the model was developed for high volatility compounds; 2) degree of exit

gas saturation is taken into account; 3) the model has been shown to be applicable to both submerged and surface aeration devices.

The VOC emission model proposed by Namkung and Rittman (1987) assumed exit gas saturation. Infinite dilution in a rising air bubble was also indirectly assumed because a gas phase concentration was not included in the concentration gradient, i.e. $C_g = 0$ (see Eq. 2-3). Thus the concentration gradient was always maximized, and the effect of the magnitude of VOC mass transfer coefficient, K_La_{VOC}, was suppressed when Namkung and Rittman modelled VOC emissions from a municipal wastewater treatment plant.

High volatility compounds can be classified as compounds having a Henry's law constant, H_c, greater than 0.12 at 20°C (Roberts et al., 1984). When Henry's law constant is defined in this manner, liquid phase resistance dominates mass transfer. So although the volatility of a compound is directly proportional to H_c, the likelihood of the "exit gas" achieving saturation is diminished, i.e. for short bubble residence times, exit gas saturation is approached more closely for low volatility compounds.

Exit gas saturation was assumed in the development of the Namkung-Rittman emissions model. The Truong-Blackburn model was derived from studies of lower volatility compounds, i.e. toluene with $H_c = 0.25$ at 25°C (Petrasek et al., 1983) was the most volatile compound studied. Because high volatility compounds are less likely to be saturated with respect to exit gas, the ability of the Namkung-Rittman and Truong-Blackburn models to accurately predict K_La_{VOC} for high volatility compounds is questionable. To demonstrate the inability of the Truong-Blackburn and Namkung-Rittman models to accurately estimate mass transfer coefficients for high volatility compounds, predicted values for K_La_{O2} at 20°C by the three models for two diffused aeration systems are presented in Table 5-4.

Table 5-4. Predicted Values for K_La_{O2} at 20°C by Diffused Aeration Models

Volume, m^3	Air flow rate, m^3/s	H_c, oxygen [a]	K_La_{O2}, hr^{-1} Truong [b]	Namkung [c]	Roberts [d]
133	0.09	30.02	137	69.0	4.7
840	0.37	30.02	94.9	47.6	2.9

[a] Roberts et al., 1984.
[b] Truong-Blackburn model.
[c] Namkung-Rittman model.
[d] Roberts et al. model.

As shown in Table 5-4, values for the overall oxygen mass transfer coefficient predicted by the Truong-Blackburn and Namkung-Rittman models are not reasonable for diffused aeration devices.

Natural Reaeration

Two models that predict K_La_{O2} for naturally aerated streams, Tsivoglou-Neal (1976) and Parkhurst-Pomeroy (1972), were studied. Both models estimated K_La_{O2} in the same order of magnitude (approximately 10^{-3}) for streams representative of a conveyance channel, i.e. velocities approximately equal to 0.3 m/s. When velocity was decreased to 0.02 m/s (sedimentation basin horizontal velocity), variation between the Tsivoglou-Neal and Parkhurst-Pomeroy predicted values for K_La_{O2} increased to three orders of magnitude, i.e. 10^{-7} versus 10^{-4}, respectively. Because of difficulty determining a slope of a sedimentation basin water surface (the Manning equation assuming uniform flow was used to approximate the slope), a Reynolds number versus K_La_{O2} relationship was developed from data for conveyance channels. A Reynolds number-K_La_{O2} relationship was developed because Reynolds number is indicative of the amount of turbulence in a system, and turbulence enhances oxygen transfer at a water-atmosphere interface. Extrapolation of the linear relationship

between Reynolds number and K_La_{O2} to sedimentation basins resulted in an estimation of K_La_{O2} of approximately 10^{-3} hr^{-1}. Because of the small magnitude of the oxygen mass transfer rate coefficient, and therefore K_La_{VOC}, resulting from all three model formulations, volatilization losses from sedimentation basin and conveyance channel water surfaces were estimated to be negligible.

SENSITIVITY ANALYSES

To demonstrate effects of input parameters on emission estimates for diffused aeration and surface reaeration processes, sensitivity analyses were performed on models that predicted losses from an aerated grit chamber and a non-aerated conveyance channel. Results of those analyses are discussed below.

Aerated Grit Chamber

Input parameters to the Roberts et al., Truong-Blackburn, and Namkung-Rittman mass transfer coefficient models were varied to demonstrate sensitivity to percent-removal from an aerated grit chamber. Air flow rate, tank volume, and oxygen transfer efficiency were individually changed to demonstrate the effect on influent VOC percent-removal. Sensitivity of Henry's law constant was not studied because influent percent-removal was previously estimated for three VOCs of various volatility (see Table 4-6). Results of the analyses are presented in Table 5-5.

Estimated percent-removal for each diffused aeration model was insensitive to air flow rate and tank volume, with removal percentages similar to values presented for an aerated grit chamber in Table 4-6. Improved oxygen transfer efficiency increased percent-removal for similar systems, i.e. air flow rate and tank volume equivalent. This result may be superficial because an introduction of smaller bubbles usually permits a reduction of air flow rate, which then decreases percent-removal. Predicted percent-removal by the Roberts et al. model demonstrated the effect of an increased oxygen transfer efficiency, with percent-removal ranging from 6.4 (coarse bubble)

to 14.5 (fine bubble) for similar systems. However, when air flow rates were adjusted for increased oxygen transfer efficiency, percent-removal was approximately constant, ranging from 6.4 (coarse bubble) to 6.9 (medium bubble), i.e. air flow rates for coarse, medium, and fine bubble aerators were 1330, 800, and 530 m^3/hr, respectively. In primary wastewater treatment, aeration is generally used to facilitate particle suspension and enhance grit removal, oxygenation of wastewater in grit chambers and conveyance channels is typically a side benefit. For that reason, air is usually supplied through sub-surface coarse bubble diffusers.

Predicted percent-removal by the Namkung-Rittman and Truong-Blackburn models would be expected to be greater than percent-removal by the Roberts et al. model because exit gas saturation was assumed by Namkung and Rittman and the Truong-Blackburn model closely approximates an equilibrium predictor (Truong and Blackburn, 1984). As stated previously though, the assumption of exit gas saturation, and the indirect assumption of infinite dilution in a rising gas bubble, maximizes the concentration gradient and suppresses the magnitude of K_La_{VOC}, a VOC mass transfer coefficient.

Non-Aerated Conveyance Channel

The slope of a non-aerated conveyance channel was varied to demonstrate sensitivity to percent-removal predicted by the Tsivoglou-Neal and Parkhurst-Pomeroy oxygen reaeration models. Results of the analyses are presented in Table 5-6.

For a steep slope of 0.0024 (an increase of two orders of magnitude from the design slope of the conveyance channel), and a velocity of 1.2 m/s, volatilization losses estimated from both models were still negligible. Only when the slope was increased to an unreasonable value (for a conveyance channel) of 0.24 were volatilization losses significant.

Table 5-5. Parameter Sensitivity on removal from an Aerated Grit Chamber

Diffused aeration model	H_c of VOC	Air flow rate, m^3/hr	Volume, m^3	Oxygen transfer efficiency[a]	K_La_{O2}, hr^{-1}	K_La_{VOC}, hr^{-1}	Percent removal
Roberts et al.[b]	0.392	2000	840	0.06	4.4	2.7	9.3
	0.392	1330	840	0.06	2.9	1.8	6.4
	0.392	1330	840	0.10	5.0	3.1	9.1
	0.392	1330	840	0.15	7.7	4.8	14.5
	0.392	1330	500	0.06	4.9	3.1	6.4
	0.392	800	840	0.10	3.0	1.9	6.9
	0.392	530	840	0.15	3.1	1.9	6.6
	0.392	500	840	0.06	1.1	0.7	2.5
Truong-Blackburn	0.392	2000	840	0.06	—	1.6[c]	6.1
	0.392	2000	840	0.06	—	0.9[d]	4.1
	0.392	1330	840	0.06	—	1.0[c]	4.2
	0.392	1330	840	0.06	—	0.6[d]	2.8
	0.392	1330	500	0.06	—	1.7[c]	4.2
	0.392	1330	500	0.06	—	1.0[d]	2.8
	0.392	500	840	0.06	—	0.4[c]	1.6
	0.392	500	840	0.06	—	0.2[d]	1.1
Namkung-Rittman	0.392	2000	840	0.06	—	0.9	4.3
	0.392	1330	840	0.06	—	0.6	2.9
	0.392	1330	500	0.06	—	1.0	2.9
	0.392	500	840	0.06	—	0.2	1.1

[a] Oxygen transfer efficiency for fine bubbles is 0.15, medium bubbles is 0.10, and coarse bubbles is 0.06 (Roberts et al.,1984).
[b] Roberts et al. model estimates K_La_{VOC} as 62 percent of K_La_{O2} for VOCs with $H_c > 0.12$.
[c] $b = 3.7 \cdot 10^{-3}$ and $m = 1.04$.
[d] $b = 9.3 \cdot 10^{-3}$ and $m = 0.87$.

Table 5-6. Slope Sensitivity on Percent-removal from a Non-Aerated Conveyance Channel

Natural reaeration model	Slope, m/m	Velocity, m/s	K_La_{O2}, hr^{-1}	K_La_{VOC}, hr^{-1}	Percent removal
Tsivoglou-Neal	2.4 E-3	1.2	1.0	0.6	1
	0.24	5.2	446	276	67
Parkhurst-Pomeroy	2.4 E-3	1.2	0.4	0.2	1
	0.24	5.2	72.9	45.2	21

6. CONTROL STRATEGIES

Results from this and other emission studies (Bell et al., 1988; Berglund and Whipple, 1987; Petrasek et al., 1983; Lurker et al., 1982) indicate that significant amounts of volatile organic compounds (VOC) can be emitted during primary wastewater treatment. Existing options for controlling VOC emissions during initial stages of treatment include collection and treatment of off-gases from headworks and other covered primary treatment units, and modification of design of primary treatment operations to minimize mass transfer. Selection of an appropriate alternative should be based on knowledge of the types and quantities of VOCs emitted and sensitivity of emission rates to operating parameters, information which is just becoming available as a result of AB 2588 reporting requirements. Sources and methods of release of VOCs from primary treatment processes to the atmosphere are recorded in Table 6-1.

Options to control VOC emissions from primary treatment units include capture and treatment of exhaust gases or minimization of VOC mass transfer, i.e. keep compounds in an aqueous form. Recommendations to control VOC emissions and recommendations to reduce VOC mass transfer from primary treatment processes are discussed below.

Control VOC Emissions

1. Cover the headworks - Covering the headworks and removing VOCs from the exhaust gas will control emissions from headworks. Two problems associated with covered processes are corrosion and subsequent removal of VOCs from exit gas. Corrosion can be minimized by proper structural design, adequate supplemental aeration, routine cleaning and maintenance of the structure. Removal of VOCs from a gas stream by adsorption onto granular activated carbon (GAC) is possible but operating data are limited. Chang et al. (1989) measured removal efficiencies of VOCs from an aerated grit chamber exhaust stream by adsorption to GAC. Because the carbon bed was designed for odor control and not sized for the organic load, complete breakthrough of 23 VOCs for virgin GAC occurred in less than 60 days. Breakthrough of some compounds occurred

in less time, e.g. DCM and TCM were detected within about one and three weeks of operation, respectively.

2. Cover the entire primary treatment sequence - To reduce VOC transfer to the atmosphere from other treatment processes, covering and treating the exhaust gas is an alternative. The problems with this control strategy are analogous to covering the headworks. One benefit of covered processes, however, is odor control. A significant number of wastewater treatment plants in California have covered primary works, including the Joint Water Pollution Control Plant (County Sanitation Districts of Los Angeles County) and the city of Fairfield's wastewater treatment facility.

Reduce VOC Mass Transfer

1. Reduce headloss at bar screens, comminutors, and Parshall flumes - Emission of VOCs from bar screens, comminutors, and Parshall flumes is directly related to the headlosses associated with these treatment units. Suggestions to minimize mass transfer from headworks include use of in-line enclosed comminutors and use of an alternative flow measuring device to the Parshall flume.

2. Reduce drops at weirs - Emission of VOCs from weirs are a function of weir height, and weir heights fluctuate with flow rate, with the minimum drop occurring at peak flow rate. Regulating flow rate through grit chambers and sedimentation basins to simulate peak flow conditions will minimize VOC emissions from weirs. However, if an equalization basin or a wet well is used to regulate flow rates, VOC emissions from these processes must be evaluated to determine applicability of this control measure. Another option is to use submerged weirs which will decrease turbulence, and therefore decrease VOC emissions.

3. Reduce diffused aeration rates - A reduction in aeration rate will decrease VOC emissions from aerated processes because VOC mass transfer rates vary directly with air flow rate. To maintain particle suspension and decrease VOC emissions, an increase in velocity will compensate for a decreased rate of diffused air. Volatilization losses from water surfaces were estimated to be negligible (<0.05 kg/d) for conveyance channels with velocities approximately equal to 1.0 m/s and an invert slope of 0.0025.

Table 6-1. Sources and Methods of Release of VOCs from Primary Wastewater Treatment Units to the Atmosphere

Source	Method of release
Bar screen	Volatilization due to turbulence.
Comminutor	Volatilization due to turbulence.
Parshall flume	Volatilization due to turbulence.
Grit chamber	Volatilization due to turbulence in conventional horizontal-flow grit chambers. Volatilization and air stripping in aerated grit chambers.
Equalization basin	Volatilization from water surface enhanced by local turbulence. Air stripping where diffused air is used.
Primary sedimentation basin	Volatilization from water surface.
Weir	Volatilization from overflow weirs at grit chambers and sedimentation tanks.
Conveyance channel	Volatilization from water surface enhanced by local turbulence. Volatilization and air stripping in aerated conveyance channels.

A summary of strategies for the control of VOCs released from primary wastewater treatment processes is listed in Table 6-2. Whether one chooses to reduce or enhance stripping and volatilization at the headworks depends upon overall control system strategy. If the VOCs of concerns are biodegradable, e.g. benzene, then preventing the VOC from leaving the aqueous phase can result in control through biodegradation in secondary treatment processes. However, if for example, the secondary treatment process is a trickling filter, or if the VOCs are non-degradable, there may be advantages to stripping the compounds at the headworks for routing to a centralized pollution control device and to minimize total airflow that must be handled. Control strategies to be employed will be plant specific and depend upon whether retrofit or new plant design is under consideration.

Table 6-2. Strategies for the Control of VOCs Released from Primary Wastewater Treatment Units to the Atmosphere

Source	Control strategy
Bar screen	Cover existing units. Reduce headloss through bar screens.
Comminutor	Cover existing units. Use in-line enclosed comminutors.
Parshall flume	Cover existing units. Use alternative flow measuring device.
Grit chamber	Cover existing aerated grit chambers. Reduce turbulence in conventional horizontal-flow grit chambers; cover if necessary. Decrease or eliminate the use of diffused aeration.
Equalization basin	Cover existing unit. Reduce air flow.
Primary sedimentation basin	Cover existing units.
Weir	Cover existing weirs. Simulate peak flow conditions to reduce weir height. Replace conventional weirs with submerged weirs.
Conveyance channel	Cover existing units or use enclosed channels. Reduce or eliminate the use of diffused aeration.

7. CONCLUSIONS

Volatile organic compound (VOC) emission rates from reference primary wastewater treatment processes and a reference primary treatment sequence, influent flow rate 6.6 m^3/s (150 Mgal/day), were estimated. Conclusions obtained from this study are presented in this section. Conclusions regarding estimated emission rates for treatment units, diffused aeration models, natural reaeration (volatilization) models, and models used to predict losses from weirs are discussed in separate sections.

Estimated Emission Rates for Treatment Processes

1. Emission of VOCs during primary wastewater treatment can be significant. Approximately 16.3 kg/d (or 25% of an influent VOC load) of highly volatile carbon tetrachloride was emitted from the reference primary treatment sequence studied.

2. Emission of VOCs from treatment processes with drops (bar screens, comminutors, Parshall flumes, weirs), and diffused aeration processes (aerated grit chambers and aerated conveyance channels), contributed the bulk of the total VOC load emitted from the reference treatment sequence.

3. A reduction in weir height, e.g. through the use of submerged weirs or control of water depth in launders, will minimize mass transfer and effectively decrease VOC emissions. Grit chamber weirs and sedimentation weirs were the major sources of VOC emissions from the reference treatment sequence, contributing about 50% (7.8 kg/d) of the estimated 16.2 kg/d of carbon tetrachloride emitted.

4. Predicted emission losses from the headworks and the overall reduction of an influent VOC by the reference primary treatment sequence (approximately 5 and 25%, respectively) are consistent with preliminary results of a current tracer study at a municipal wastewater treatment facility (Hellier, 1989).

Diffused Aeration Models

1. For aerated processes, e.g. aerated grit chambers and aerated conveyance channels, gas stripping losses dominated volatilization emissions.

2. Estimated emission rates by the diffused aeration models for the reference aerated grit chamber were insensitive to air flow rate and tank volume.

3. Estimated emission rates by the Roberts et al. model were insensitive to Henry's law constant. Emission rates of three VOCs predicted by the Roberts et al. model for the reference aerated grit chamber varied from 1.8 to 2.3 kg/d, while values for Henry's law constant ranged by a factor of seven from 0.131 to 0.947. In contrast to the Roberts et al. model, emission estimates using both the Truong-Blackburn and the Namkung-Rittman models were sensitive to a compound's H_c. Estimated VOC emission rates for the reference aerated grit chamber ranged from 0.4 to 2.9 kg/d using the Truong-Blackburn model, and from 0.3 to 2.0 kg/d using the Namkung-Rittman model, for the same three compounds.

4. Namkung and Rittman (1987) indirectly assumed infinite dilution in a rising gas bubble in the development of their emissions model, and probably underestimated the magnitude of a VOC mass transfer coefficient, K_La_{VOC}, because the concentration gradient was always maximized.

Natural Reaeration Models

1. Volatilization losses from water surfaces of primary wastewater treatment units, e.g. sedimentation basins, are negligible with respect to emissions from other primary treatment processes. Volatilization losses from the reference sedimentation basins and reference conveyance channels were estimated to be negligible (<0.05 kg/d).

2. The Parkhurst-Pomeroy and Tsivoglou-Neal models estimate similar oxygen mass transfer rates for conveyance channels. For the reference conveyance channels, both reaeration models predicted K_La_{O2} to be approximately equal to 0.001 hr^{-1}.

3. The Parkhurst-Pomeroy and Tsivoglou-Neal stream reaeration models are believed to be relatively inaccurate for prediction of oxygen mass transfer rates for processes with low horizontal velocities, e.g. sedimentation basin.

Models Used to Predict Emissions at Weirs

1. Because of turbulence created when wastewater flows over a weir and into a downstream pool, transfer of

VOCs into entrained air bubbles caused by the falling wastewater is expected to occur. Oxygen mass transfer rates, and therefore VOC mass transfer rates, predicted by the cascade waterfall aerator model as well as the Tsivoglou-Neal model were based only on weir height, and the models are believed to underestimate VOC mass transfer rates.

2. A model developed by Nakasone (1987) to predict oxygen transfer rates at weirs that included weir height and accounted for oxygen transfer from entrained air bubbles in a downstream pool estimated the magnitude of K_La_{O2} as approximately 3 to 4 times larger than the cascade waterfall aerator model, and 5 to 8 times larger than the Tsivoglou-Neal model.

3. Emission of VOCs from weirs and other drops dominated losses in a primary treatment sequence. Approximately 50% of the emissions of an influent VOC load to the reference treatment train was emitted from the grit chamber weirs and the sedimentation basin weirs. The percentage emitted from the reference weirs is a conservative estimate because oxygen mass transfer rates, and therefore VOC mass transfer rates, were predicted using the cascade waterfall aerator model and the Tsivoglou-Neal stream reaeration model.

Literature Values of Henry's Law Constants

1. Literature values of the Henry's law constants for C1 C2, and C6 chlorinated hydrocarbons were evaluated and compared. The values recently presented by Gosset appear to be most valid. (See Appendix H.)

2. Use of molecular connectivity indices appeared to be promising in correlating and predicting certain physico-chemical properties, but the data set evaluated was too small to draw definitive conclusions regarding its future utility for the purposes of predicting physico-chemical properties for a wider range of compounds.

3. Recent evidence obtained by the County Sanitation Districts of Los Angeles (Caballero, 1990) indicates that separation of an oil phase can occur in certain portions of the treatment sequence, e.g. grit chamber and primary sedimentation basin. In such a case, partitioning of VOC to the organic phase can occur and simple aqueous Henry's Law Constants will over-predict emissions.

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APPENDICES

APPENDIX A

AN EQUATION TO DETERMINE THE SATURATION CONCENTRATION OF A VOLATILE ORGANIC COMPOUND IN A RISING BUBBLE

A derivation of an equation to estimate a VOC saturation concentration in a rising bubble for a submerged diffused aeration process is presented below.

A materials balance on a VOC in a single bubble, assuming an average bubble area and bubble volume, is shown below. Liquid within a system was assumed to be well-mixed and that the mass transfer rate to a bubble was assumed to be rapid relative to changes in the liquid concentration.

$$V_b \frac{dC_b}{dt} = k_L A_{sb}(C-Cs) \qquad \text{(A-1)}$$

where

V_b	=	average bubble volume, m^3
$\frac{dC_b}{dt}$	=	time rate of change of a VOC concentration in a bubble, $\mu g/m^3 * hr$
k_L	=	VOC mass transfer coefficient, m/hr
A_{sb}	=	average bubble surface area, m^2
C	=	liquid VOC concentration, $\mu g/m^3$
C_s	=	saturation concentration of a VOC, $\mu g/m^3$

Assume local equilibrium.

$$C_s = \frac{C_b}{H_c} \qquad \text{(A-2)}$$

where

C_b	=	VOC concentration in bubble, ug/m3
H_c	=	Henry-s law constant, unitless

Substitute Eq. A-2 into Eq. A-1, and simplify.

$$\frac{dC_b}{C-(C_b/H_c)} = \frac{k_L A_{sb}}{V_b} dt \qquad \text{(A-3)}$$

Integrate Eq. A-3 with limits Cb=0 to Cb=Cb and t=0 to t=t.

$$-H_c\{\ln[(C-C_b/H_c)/C]\} = k_L A_{sb} t/V_b \qquad \text{(A-4)}$$

Simplify Eq. A-4 and solve for Cb.

$$C_b = H_c C[1-\exp(-k_L A_{sb} t/H_c V_b)] \qquad \text{(A-5)}$$

Substitute Eq. A-2 into Eq. A-5, and rearrange, yields an expression for C_s at time t.

$$C_s = \frac{C_b}{H_c} = C[1-\exp(-k_L A_{sb} t/H_c V_b)] \qquad \text{(A-6)}$$

APPENDIX B

A MATERIALS BALANCE EQUATION FOR A VOLATILE ORGANIC COMPOUND IN A CONTINUOUS-FLOW STIRRED-TANK REACTOR

A derivation of a materials balance equation for a volatile organic compound (VOC) in a continuous-flow stirred tank reactor (CFSTR) is shown below.

Accumulation = Inflow - Outflow + Generation

$$VdC/dt = QC_i - QC + rV \qquad \text{(B-1)}$$

where

dC/dt = rate of change of the reactor (and effluent) liquid VOC concentration, $\mu g/m^3 \cdot hr$

Q = liquid flow rate, m^3/s

V = reactor volume, m^3

C_i = influent liquid VOC concentration, $\mu g/m^3$

C = effluent (and reactor) liquid VOC concentration, $\mu g/m^3$

r = VOC mass rate of reaction, $\mu g/m^3 \cdot s$

Divide Eq. B-1 by a liquid flow rate, Q.

$$\frac{V}{Q}\frac{dC}{dt} = C_i - C + r(V/Q) \qquad \text{(B-2)}$$

Define the hydraulic detention time, θ_H, as shown below.

$$\theta_H = V/Q \qquad \text{(B-3)}$$

Divide Eq. B-2 by the hydraulic detention time, Eq. B-3.

$$\frac{dC}{dt} = \frac{Ci - C}{\theta_H} + r\theta_H \qquad \text{(B-4)}$$

If gas transfer is assumed to be the only mechanism of VOC depletion in a CFSTR, then r, the VOC mass rate of reaction, is defined as

$$r = -K_L a_{VOC}(C - C_s) \qquad \text{(B-5)}$$

where

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

C = liquid VOC concentration in a CFSTR, $\mu g/m^3$

C_s = VOC saturation concentration, $\mu g/m^3$

Convert $K_L a_{VOC}$ for hr^{-1} to s^{-1} to be consistent with the defined units of r, the VOC mass rate of reaction.

A materials balance expression for a VOC, assuming gas transfer to be the only mechanism of VOC depletion, is shown below. Liquid within a CFSTR was assumed to be well-mixed and that the mass transfer rate was assumed to be rapid relative to changes in the liquid concentration.

$$\frac{dC}{dt} = \frac{C_i - C}{jH} - K_L a_{VOC}(C - C_s) \qquad \text{(B-6)}$$

The saturation concentration of a gas in a liquid is proportional to the atmospheric gas concentration, and is related by the Henry's law constant.

$$C_s = C_g/H_c \qquad \text{(B-7)}$$

where

C_s = saturation concentration, $\mu g/m^3$

C_g = gas phase concentration, $\mu g/m^3$

H_c = Henry's law constant, unitless

For volatilization from a water surface or stripping using surface aerators, infinite dilution was assumed, i.e. $C_g = 0$, and Eq. B-6 was reduced to the following expression.

$$\frac{dC}{dt} = \frac{C_i - C}{\theta_H} - K_L a_{VOC} C \qquad \text{(B-8)}$$

For submerged diffused aeration, gas phase concentration within an air bubble increases and the liquid concentration gradient decreases, as a bubble moves vertically. The corresponding liquid saturation concentration of a VOC at time t is given by Eq. A-6.

$$C_s = \frac{C_b}{H_c} = C[1 - \exp(-k_L A_{sb} t/H_c V_b)] \qquad \text{(A-6)}$$

An emission rate of a VOC from a system can be estimated by either considering either an entire process or a summation of all bubbles as a control volume.

$$M_E = K_L a_{VOC} V_L (C - Cs) = k_L A_{sb} N (C - C_s) \qquad \text{(B-9)}$$

where

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

VL = liquid volume, m^3

k_L = VOC mass transfer coefficient, m/hr

A_{sb} = bubble surface area, m^2

N = total number of bubbles in a system, unitless

Solve Eq. B-9 for $k_L A_{sb}$.

$$k_L A_{sb} = K_L a_{VOC} V_L / N \qquad \text{(B-10)}$$

Substitute Eq. B-10 into the exponential term in Eq. A-6.

$$\frac{-k_L A_{sb} t}{H_c V_b} = \frac{-K_L a_{VOC} V_L t}{H_c V_b N} = \frac{-K_L a_{VOC} V_L}{H_c G} \qquad \text{(B-11)}$$

where

G = NV_b/t; air flow rate, m^3/hr

Assume an effective saturation concentration equivalent to half the saturation concentration at the water surface.

$$C_{se} = C_s/2 \qquad \text{(B-12)}$$

Substitute Eq. B-12 into the saturation concentration term in Eq. B-6, and simplify, yields the following materials balance expression for a VOC in a submerged diffused aeration process.

$$\frac{dC}{dt} = \frac{C_i - C}{\theta_H} - K_L a_{VOC}[C - \frac{C}{2}(1 - \exp(-K_L a_{VOC} V_L / H_c G))]$$

$$\frac{dC}{dt} = \frac{C_i - C}{\theta_H} - \frac{K_L a_{VOC} C}{2}[1 + \exp(-K_L a_{VOC} V_L / H_c G)] \qquad \text{(B-13)}$$

APPENDIX C

A METHOD TO DETERMINE AN OVERALL OXYGEN MASS TRANSFER COEFFICIENT FOR SUBMERGED DIFFUSED AERATION PROCESSES

Roberts et al. (1984) presented a method to estimate an overall oxygen mass transfer coefficient, K_La_{O2}, for submerged diffused aeration processes. The method is presented below.

$$\exp(\Phi Z) = \frac{(C_{ge} - H_cC)}{(C_{gi} - H_cC)} \qquad \text{(C-1)}$$

where

ΦZ = saturation factor, unitless

Z = depth of process, m

C_{gi} = oxygen concentration in a bubble at the aeration inlet, g/m3

C = oxygen concentration in liquid, g/m3

H_c = Henry's law concentration for oxygen, unitless

Determine the oxygen concentration in a bubble at the aeration inlet.

$$C_{gi} = P_{O2}M_{O2}(0.209)/RT \qquad \text{(C-2)}$$

where

P_{O2} = absolute pressure, atm (1 atm = 10.33 m H_2O)

M_{O2} = molecular weight of oxygen, 32.0 g/mole

R = universal gas constant, $82.05 \cdot 10^{-6}$ atm.m^3/g-mole·K

T = absolute temperature of wastewater, K

Because hydrostatic pressure is linearly proportional to water depth, oxygen concentration in a bubble at the aeration inlet is estimated using the hydrostatic pressure at mid-depth of a system.

Determine the oxygen concentration in a bubble at the water surface.

$$C_{ge} = (1 - \eta)C_{gi} \qquad \text{(C-3)}$$

where

η = oxygen transfer efficiency, 0.06 of coarse bubble diffusers

Roberts et al. (1984) defined the saturation factor to be a function of mass transfer, liquid volume, diffused air flow rate, and Henry's law constant.

$$\Phi Z = K_L a_{O2} V_L / H_C G \qquad \text{(C-4)}$$

Rearranging Eq. C-4 yields an expression for KLaO2.

$$K_L a_{O2} = \Phi Z H_C G / V_L \qquad \text{(C-5)}$$

where

$K_L a_{O2}$ = overall oxygen mass transfer coefficient, hr^{-1}

V_L = liquid volume of a system, m^3

Hc = Henry's law constant for oxygen, unitless

G = air flow rate, m^3/hr

APPENDIX D

DERIVATION OF AN OVERALL OXYGEN MASS TRANSFER COEFFICIENT FOR A CASCADE WATERFALL AERATOR

A derivation of an overall oxygen mass transfer coefficient, K_La_{O2}, for a cascade waterfall aerator is presented below. Bar screens, comminutors, Parshall flumes, and weirs were modelled as cascade waterfall aerators. An oxygen transfer rate, OTR, for a cascade waterfall aerator varies between 0.2 to 0.6 kg-O_2/kW*hr (Tchobanoglous and Schroeder, 1987).

Determine K_La_{O2} from the OTR.

$$K_La_{O2} = \frac{(OTR)(\gamma_{ww})(h)(10^{-3}kW/W)}{(\beta)(C_s)(t)(10^{-3}kg/g)} \qquad \text{(D-1)}$$

$$K_La_{O2} = \frac{(OTR)(\gamma_{ww})(h)}{(\beta)(C_s)(t)} \qquad \text{(D-2)}$$

where

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

OTR = oxygen transfer rate for a cascade waterfall aerator, kg-O_2/kW·hr

γ = specific weight of wastewater (assumed to be equivalent to specific weight of water), 9803 N/m^3 at 20°C.

h = headloss, m

C_s = saturation concentration of oxygen in water, g/m^3

β = correction factor for solubility difference between wastewater and water, 0.95 (Tchobanoglous and Schroeder, 1987)

t = hydraulic detention time, hr

APPENDIX E

AN EQUATION TO ESTIMATE AN OVERALL OXYGEN MASS TRANSFER COEFFICIENT FOR WEIRS

Nakasone (1987) stated that 95 percent of oxygen transfer at weirs occurred in entrained air bubbles in a downstream pool. Equations developed by Nakasone (1987) to model oxygen transfer at weirs were used to estimate overall oxygen mass transfer coefficients, K_La_{O2}, for grit chamber weirs. An example of these calculations is presented below. Dimensions of a reference grit chamber are listed in Table E-1.

Table E-1. Dimensions of a Reference Grit Chamber

Flow rate, m3/s	Depth, m	Length, m	Width, m	Volume, m3
3.3	4.0	35.0	6.0	840

ft=m*0.3048

Determine a weir loading rate, q. Assume weirs extend across the width of a grit chamber, i.e. weir length is 6.0 m.

$$q = \frac{Q}{L} = \frac{3.3\ m3/s}{35.0\ m} \cdot 3600\ s/hr = 339\ m3/m.hr \qquad (E-1)$$

A mass balance for oxygen transfer from air to water is expressed in Eq. E-2.

$$\frac{dC}{dt} = K_La_{O2}(C_s - C) \qquad (E-2)$$

where

$\frac{dC}{dt}$ = time rate of change of oxygen concentration in water, $mg/m^3 \cdot hr$

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

C_s = oxygen saturation concentration, $\mu g/m^3$

C = oxygen concentration in liquid, $\mu g/m^3$

Integrate Eq. E-2 with limits $C = C$ to $C = C_t$ and $t = 0$ to $t = t$.

$$\ln\{(Cs-Ct)/(Cs-C)\} = KLaO2t \qquad (E-3)$$

where

(Cs-Ct)/(Cs-C) = oxygen deficit, unitless

t = hydraulic detention time, hr

Nakasone (1987) developed the following equations to estimate an oxygen deficit at weirs.

For $(D + Hc) \leq 1.2$ m and $q > 235$ $m^3/m \cdot hr$,

$$\ln r_{20} = 5.39(D + H_c)^{1.31} q^{-0.363} H^{0.310} \quad \text{(E-4)}$$

For $(D + Hc) > 1.2$ m and $q > 235$ m3/m.hr,

$$\ln r_{20} = 5.92(D + H_c)^{0.816} q^{-0.363} H^{0.310} \quad \text{(E-5)}$$

where

$\ln r_{20}$ = oxygen deficit at 20°C, unitless

D = weir drop height, m

H_c = critical water depth on a weir, m

H = tailwater depth for downstream channel having a horizontal bed, m

Rearrange Eq. E-3 and solve for $K_L a_{O2}$.

$$K_L a_{O2} = \frac{\ln r_{20}}{\theta_H} \quad \text{(E-6)}$$

where

θ_H = hydraulic detention time, hr

Assume Hc = 0.13 m (5.1 in.) and H = 1.0 m. For weir heights of 0.3, 1.0, and 2.0 m, respective hydraulic detention times were 0.2, 0.4, and 0.6 s (see Table 4-11). Oxygen deficits and oxygen mass transfer coefficients, calculated using the appropriate Nakasone (1987) equation, are recorded in Table E-2.

Table E-2. Oxygen Deficits and Mass Transfer Coefficients for Various Weir Heights

Weir height, m	Detention time, s	Oxygen deficit	Mass transfer coefficients, hr-1
0.3	0.2	0.2	2980
1.0	0.4	0.8	7470
1.5	0.6	1.6	9850

APPENDIX F

DERIVATION OF AN EQUATION TO DETERMINE BUBBLE DIAMETERS IN A DIFFUSED AERATION SYSTEM

A derivation of an equation to determine a diameter of a rising bubble in a submerged diffused aeration process is shown below. Rising bubbles are assumed to be spatially equivalent.

Assume the ideal gas law holds and temperature is uniform throughout a system.

$$P_I V_I = nRT = P_z V_z \qquad \text{(F-1)}$$

where

P_I = absolute pressure at aeration inlet, atm

V_I = bubble volume at aeration inlet, m^3

P_z = absolute pressure at depth z, atm

V_z = bubble volume at depth z, m^3

n = number of moles, unitless

R = universal gas constant, $atm.m^3/g\text{-}mol \cdot {}^oK$

T = absolute temperature of system, ^oK

Assume bubbles are spherical to determine a bubble volume.

$$V_b = \pi d_b^3/6 \qquad \text{(F-2)}$$

where

V_b = bubble volume, m^3

d_b = bubble diameter, m

Substitute Eq. F-2 into Eq. F-1, and simplify, yields the following expression for a bubble diameter as a function of depth, z.

$$P_I \pi d_{bI}^3/6 = P_z \pi d_{bz}^3/6$$

$$P_I d_{bI}^3 = P_z d_{bz}^3$$

$$d_{bz}^3 = d_{bI}^3 (P_I/P_z)$$

$$d_{bT} = d_{bI} (P_I/P_T)^{1/3} \qquad \text{(F-3)}$$

APPENDIX G

DERIVATION OF AN EQUATION TO ESTIMATE AVAILABLE WATER SURFACE AREA FOR VOLATILIZATION FROM A SUBMERGED DIFFUSED AERATION PROCESS

A derivation of an equation to estimated available surface area for volatilizatin from a submerged diffused aeration process is developed below.

Use Eq. D-3 to determine a diameter of an air bubble at the water surface system.

$$d_{bz} = d_{bI}(P_I/P_z)^{1/3} \quad \text{(G-1)}$$

where

d_{bT} = bubble diameter at water surface, m

d_{bI} = bubble diameter at aeration inlet, m

P_I = absolute pressure at aeration inlet, atm

P_T = absolute pressure at water surface, atm

Determine volume of a bubble at aeration inlet, and volume and area of a bubble at the water surface of a system.

$$V_{bI} = \pi d_{bI}^3/6 \quad \text{(G-2)}$$

$$V_{bT} = \pi d_{bT}^3/6 \quad \text{(G-3)}$$

$$A_{bT} = \pi d_{bT}^2/4 \quad \text{(G-4)}$$

Determine the number of bubbles entering a system per second.

$$q_b = G/V_{bI}$$

where

q_b = number of bubbles entering a system, bubbles/s

G = diffused air flow rate, m^3/s

Determine total bubble area at the water surface.

$$A_{bs} = q_b A_{b2} \quad \text{(G-6)}$$

$$A_s = W \cdot L \quad \text{(G-7)}$$

$$SDR = [1-(A_{bs}/A_s)] \quad \text{(G-8)}$$

where

A_{bs}	=	total bubble area at water surface, m^2
A_s	=	surface area of process, m^2
W	=	width of process, m
L	=	length of process, m
SDR	=	surface reduction factor, unitless

APPENDIX H
LITERATURE VALUES OF SOLUBILITY AND HENRY'S LAW CONSTANTS

Solubility

Solubility is defined as the dissolved concentration of a solute in the solvent in two phase equilibrium, e.g., aqueous phase and the phase containing the component. In this study, water is used as solvent for the solubility data. The solubility of a substance is clearly of importance in determining the environmental fate of a compound, as it embodies information about the free energy of a molecule in solution. It is an useful parameter for predicting the partitioning behavior of compounds from aqueous solutions. Solubility is a difficult property to measure accurately for either very slightly soluble or gaseous compounds. As a result, up to order-of-magnitude discrepancies exist in solubility data.

Nirmalakhandan and Speece (1988a) have recently reported a regression equation for solubility using parameters such as modified connectivity indices, atom count and polarizability to correlate and predict solubilities of compounds. The following regression equation for 95 hydrocarbons and chlorinated hydrocarbon compounds in aqueous solution was determined to be:

$$\log S = 1.512 - 0.619\ {}^{0}X' + 0.99\ \Phi\ (-0.131\ (\#\text{ of C}) + 0.082\ (\#\text{ of H}))\quad (r^2=0.89) \qquad \text{(H-1)}$$

It should be noted that the above equation really uses three free parameters in predicting the solubility. (The parameter Ò is fitted by accounting for the number of carbon and hydrogen atoms in the molecule.) On the other hand, in this study the regression analysis was conducted with non-modified connectivity indices as defined by Kier and Hall (1985) and restricted the analysis to chlorinated organic compounds.

From values listed in Table H-1, it was possible to compile solubility data for several groups of compounds, C1 and C2 halocarbons and chlorinated organic rings. These data were then

Table H-1 The Experimental Data for Regression Analysis

Compd.	S (wt.%)	log S	D-less Henry's log Ha Constant (Ha)	
CM	0.74	-0.1308	0.4076	-0.3898 *
	0.627	-0.2027	0.3609	-0.4426 #
	0.725	-0.1397		
	0.5325	-0.2737		
	0.535	-0.2716		
DCM	1.3206	0.1208	0.1101	-0.9582 *
	1.9409	0.2880	0.1215	-0.9154 *
	1.981	0.2969	0.1305	-0.8844 *
	1.62	0.2095 *	0.0933	-1.0301 *
			0.0896	-1.0477 #
TCM	0.8	-0.0969 *	0.1301	-0.8857 *
	0.82	-0.0862	0.1387	-0.8579 *
	0.77	-0.1135 *	0.178	-0.7496 *
	0.79	-0.1024 *	0.1735	-0.7607 *
	0.795	-0.0996 *	0.1752	-0.7565 *
			0.1502	-0.8233 #
CT	0.08	-1.0969 *	0.8717	-0.0596
	0.0784	-1.1057 *	1.2359	0.0920 *
	0.078	-1.1079 *	1.1745	0.0699
	0.116	-0.9355 *	1.2441	0.0949 #
	0.08	-1.0969 *		
MCA	0.571	-0.2434	0.3466	-0.4602
	0.47	-0.3279	0.4342	-0.3428 #
1,1-DCA	0.55	-0.2596 *	0.223	-0.6517 *
	0.51	-0.2924 *	0.2398	-0.6202 *
	0.5	-0.3010 *	0.23	-0.6383 #
1,2-DCA	0.8	-0.0969	0.04	-1.3979 *
	0.87	-0.0605 *	0.045	-1.3448 *
	0.88	-0.0555 *	0.0536	-1.2708 *
	0.8	-0.0969		
	0.86	-0.0655 *		
1,1,1-TCA	0.073	-1.1367 *	0.2018	-0.6951
	0.048	-1.3188 *	0.6605	-0.1801 *
	0.072	-1.1427 *	0.7039	-0.1525 #
	0.1495	-0.8254		
	0.1301	-0.8857		

Compd.	S (wt.%)	log S	D-less Henry's log Ha Constant (Ha)	
1,1,2,2-TetraCA	0.2999	-0.5230 *	0.0186	-1.7305
	0.3199	-0.4950 *		
	0.29	-0.5376 *		
VC	0.009	-2.0458	2.292	0.3602
	0.27	-0.5686	1.1377	0.0560 #
1,1-DCE	0.04	-1.3979	0.6138	-0.2120
	0.55	-0.2596	1.0681	0.0286 #
	0.04	-1.3979		
1,2-DCE	0.35	-0.4559 *	0.2754	-0.5600
	0.77	-0.1135	0.167	-0.7773 #
	0.63	-0.2007	0.2177	-0.6621
	0.63	-0.2007	0.3839	-0.4158 #
TCE	0.11	-0.9586 *	0.4788	-0.3198
	0.11	-0.9586 *	0.4788	-0.3198
	0.1	-1.0000 *	0.406	-0.3915 *
	0.13	-0.8861 *	0.4215	-0.3752 *
			0.392	-0.4067 #
PERC	1.19E-02	-1.9245	0.4911	-0.3088
	1.49E-02	-1.8268	1.1745	0.0699
	1.39E-02	-1.8570	0.4993	-0.3016
	4.00E-02	-1.3979 *	0.7243	-0.1401 #
CB	4.72E-02	-1.3261 *	0.1269	-0.8965 *
	5.00E-02	-1.3010 *	0.1608	-0.7937 *
	4.90E-02	-1.3098 *	0.1821	-0.7397 *
	5.03E-02	-1.2984 *	0.1543	-0.8116 *
	4.98E-02	-1.3028 *		
o-DCB	1.45E-02	-1.8386 *	0.0782	-1.1068 *
	1.45E-02	-1.8386 *	0.0794	-1.1002 *
	1.51E-02	-1.8210 *	0.0999	-1.0004 *
	9.26E-03	-2.0334 *		
m-DCB	1.23E-02	-1.9101 *	0.1076	-0.9682 *
	1.23E-02	-1.9101 *	0.1907	-0.7196
	1.21E-02	-1.9172 *		
	1.23E-02	-1.9101 *		

Compd.	S (wt.%)	log S	D-less Henry's log Ha Constant (Ha)	
p-DCB	8.38E-03	-2.0768 *	0.097	-1.0132 *
	8.67E-03	-2.0620 *	0.0794	-1.1002 *
	7.94E-03	-2.1002 *	0.0982	-1.0079 *
	7.64E-03	-2.1169 *		
	9.11E-03	-2.0405 *		
	8.97E-03	-2.0472 *		
1,2,3-TCB	1.66E-03	-2.7799 *	0.0513	-1.2899 *
	3.15E-03	-2.5017 *	0.0512	-1.2907 *
	3.16E-03	-2.5003 *		
1,2,4-TCB	2.50E-03	-2.6021 *	0.0581	-1.2358 *
	3.46E-03	-2.4609 *		
1,3,5-TCB	2.50E-03	-2.6021 *		
	6.60E-04	-3.1805		
1,2,3,4-TetraCB	4.32E-04	-3.3645 *		
	4.32E-04	-3.3645 *		
1,2,3,5-TetraCB	3.50E-04	-3.4559 *	0.0642	-1.1925 *
	3.52E-04	-3.4535 *	0.0655	-1.1838 *
1,2,4,5-TetraCB	5.96E-05	-4.2248		
	5.96E-05	-4.2248		

Notes : *'s and #'s indicate data for the second step analysis without the gas nor outliers.
#'s are the Gossett's experimental data.
D-less means dimensionless.

subjected to a stepwise multiple regression analysis using the methodology of Kier and Hall (1985), a computer program, MOLCONN2, to compute connectivity indices (Hall, 1989), and the SAS statistical package.

The multiple regression analyses were repeated for each physico-chemical property studied. The first regression was carried out with all of the experimental data regardless of quality, the second regression was repeated without the apparent outlying data points. The resulting regression equation of the overall data set, a total of 85 solubility measurements for 24 compounds, using molecular connectivity indices was

$$\log S = -1.295\ {}^{0}X + 1.394\ {}^{1}X^{v} + 1.504 \quad (r^2=0.86) \qquad \text{(H-2)}$$

After removing the outliers, the stepwise regression was re-run and the result became,

$$\log S = -0.719\ {}^{0}X + 2.322 \quad (r^2=0.93) \qquad \text{(H-3)}$$

With one fewer parameter, the unexplained variance was reduced by about 7%. Figure (H-1) shows the result of the second regression analysis (64 data points for 19 chemicals). The line in Figure H-1 indicates the line along which all data would fall if the correlation was ideal (r^2=1.0). Again the hypothesis is that by removing the outliers, one is eliminating poorer quality experimental data or compound classes whose properties cannot be simply represented by the connectivity indices. Justification for removing outliers can also be obtained by recognition of the physico-chemical characteristics of the compounds eliminated. For example, chloromethane, chloroethene, and 1,2,4,5-tetrachlorobenzene existed in the outlier region (greater than a factor of two difference from the full regression equation). As can be seen in Table (H-1), the first two compounds, actually exist in the gas phase at room temperature. As a result a relatively poorer correlation was obtained when they were included in the regression. Chloroethane is also a gas, and although the discrepancy between its measured and predicted

$$\log S = -0.719\ {}^{0}X + 2.322\ (r^2=0.94)$$

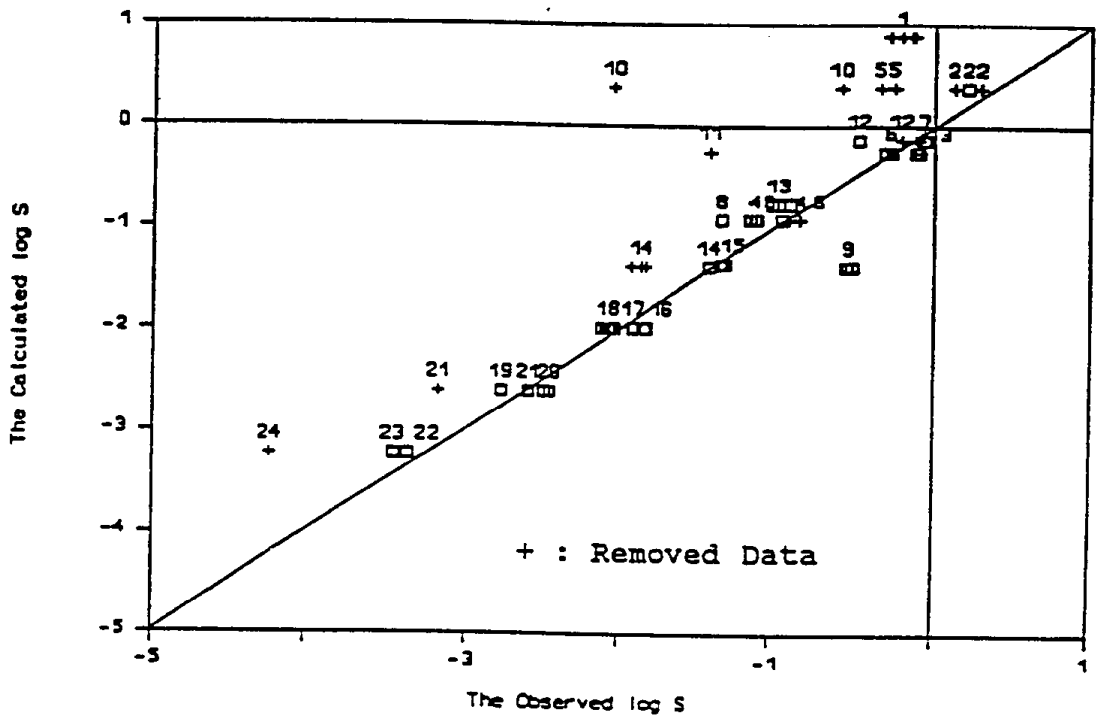


Figure (H-1) Comparison of experimental with calculated values for solubility (after elimination of outliers)

Notes :

1. CM*	2. DCM*	3. TCM
4. CT	5. MCA*	6. 1,1-DCA
7. 1,2-DCA	8. 1,1,1-TCA*	9. 1,1,2,2-TetraCA
10. VC	11. 1,1-DCE*	12. 1,2-DCE
13. TCE	14. PERC	15. CB
16. o-DCB	17. m-DCB	18. p-DCB
19. 1,2,3-TCB	20. 1,2,4-TCB	21. 1,3,5-TCB
22. 1,2,3,4-TetraCB	23. 1,2,3,5-TetraCB	24. 1,2,4,5-TetraCB*

(* indicates the eliminated compound from a regression analysis)

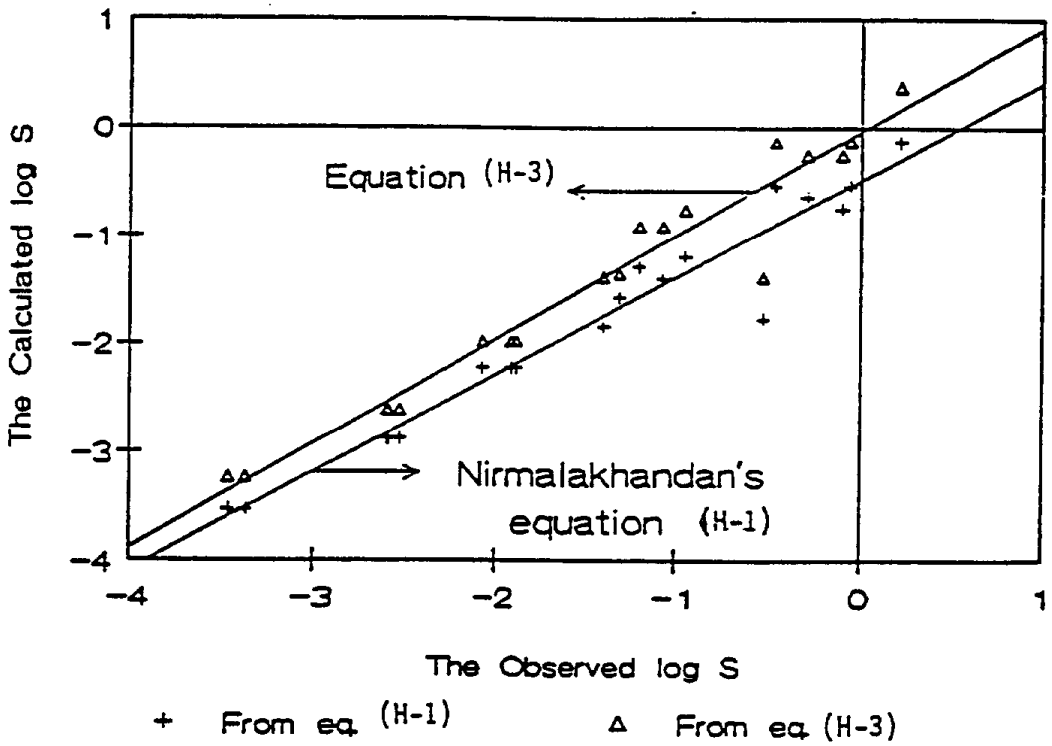
values was smaller, it was also removed. The solubility of all these compounds depends upon the total pressure at which the experiment was conducted and are inherently less reliable if a headspace analysis was performed. The 1,2,4,5-tetrachlorobenzene exhibits anomalous behavior because of its much higher melting point than that of the other tetra-isomers. Apparently, that property could not be captured adequately with the simple chi indices, but is reported to be better characterized when melting point is included as a regression variable.

Comparison of solubility between the Nirmalakhandan and Speece's equation (H-1) and equation (H-3) is shown in Figure (H-2). The lines in the figure are the linear regression lines. The calculated solubilities from equation (H-1) tended to underestimate solubility, especially for chlorinated aliphatics, the differences were larger. Because Nirmalakhandan and Speece used data including non-chlorinated species for their regression analysis it is recommended that equation (H-3) be used to estimate solubility of the chlorinated hydrocarbons listed.

Henry's Law Constant

Henry's law constant, also called Henry's law coefficient, air-water partition coefficient, or absorption equilibrium constant, has been used to represent the relationship between a substance's partial pressure and its solubility in <u>dilute</u> solutions. As with solubility, difficulties are encountered in estimating the fate of compounds in the environment because of the range of values cited in the literature for the same organic compounds. A critical review of the available Henry's coefficients was undertaken by Mackay and Shiu (1981). More recently, Roberts et al., under U.S. EPA sponsorship, and Gossett (1987) under U.S. Air Force sponsorship, undertook measurements of Henry's coefficients for several compounds that are in common with ones reviewed by Mackay and Shiu. These results are shown in Figures (H-3a) and (H-3b). Clearly there is a systematic bias between Gossett's and Roberts et al.'s data set (only five common

Figure (H-2) Comparison of solubility between equation (H-1) and (H-3)



compounds), and some of Mackay and Shiu's recommended values differ substantially from the more recent measurements (total of eight compounds). Some of Mackay and Shiu's recommendations are based on calculations, using solubility and pure compound vapor pressure. However, no obvious explanation for the small systematic differences between the data of Roberts et al. and Gossett could be discerned. Roberts et al.'s experimental methodology required application of mass transfer theory and average bubble parameter data in order to compute Henry's constants, whereas Gossett's method did not and was more direct. Gossett's values are in good agreement with those recommended by Mackay and Shiu for low values of Henry's constant, whereas for high values, Gossett's data agree well with those of Roberts et al. Furthermore, Gossett determined Henry's coefficients for a larger number of chlorinated compounds of interest than Robert et al. Because of the importance of Henry's law constants in estimating mass transfer and partitioning between phases, we recommend that Gossett's values be used when available.

Similar procedures to those described above for solubility were carried out for correlation of the Henry's constant data which are given in Table H-1. On the basis of molecular structure and melting point, the regression equation shown below was obtained for the overall experimental data set (62 values for 21 chemicals):

$$\log H_a = 0.474\ {}^0X + 0.737\ {}^0X^v - 2.65\ {}^1X^v - 0.133 \quad (r^2=0.81) \qquad \text{(H-4)}$$

The result of removing "outliers" was,

$$\log H_a = 0.466\ {}^0X + 0.743\ {}^0X^v - 2.653\ {}^1X^v - 0.119 \quad (r^2=0.85) \qquad \text{(H-5)}$$

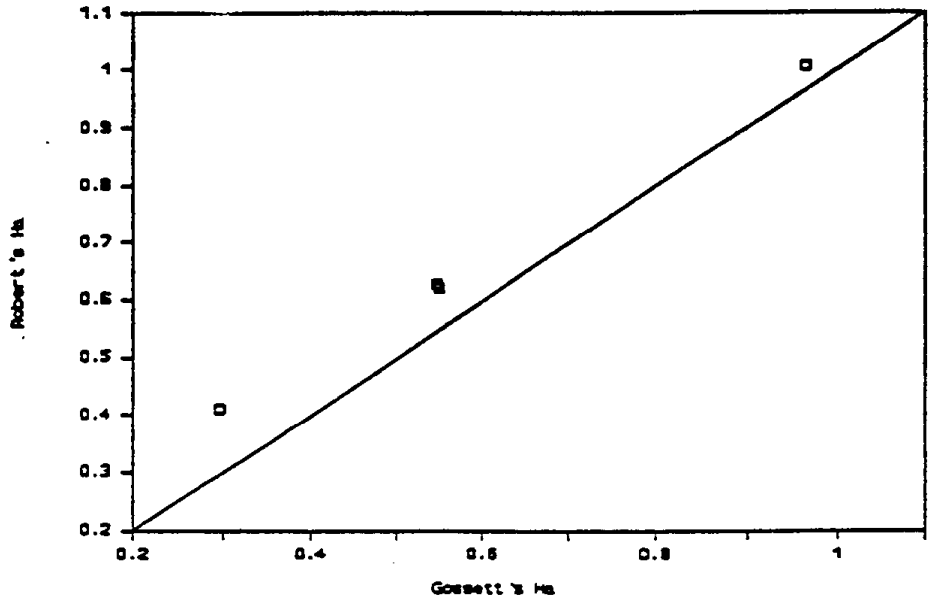


Figure (H-3a) **Comparison of Henry's constants at 20 °C**
Roberts et al. vs. Gossett

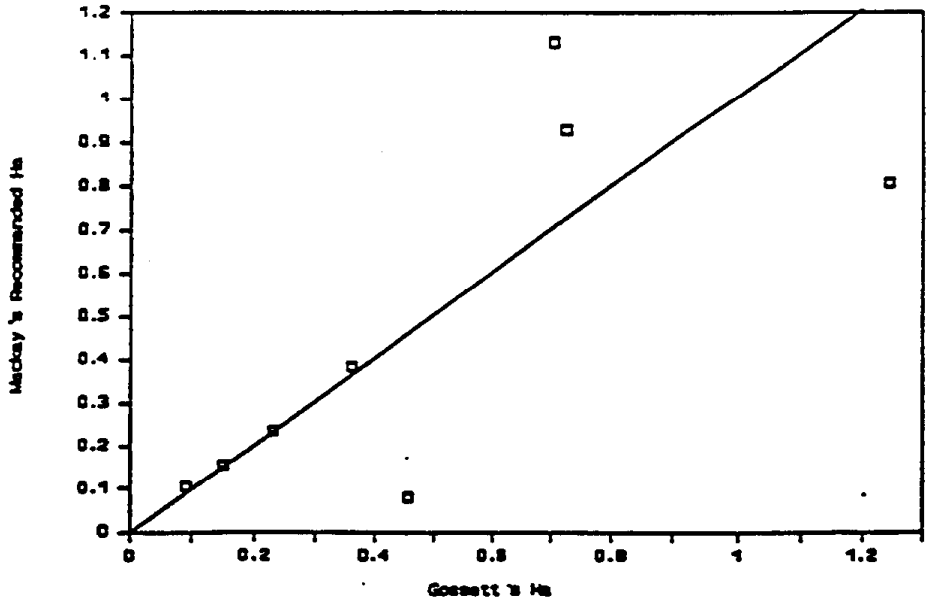


Figure (H-3b) **Comparison of Henry's constants at 25 °C**
Mackay vs. Gossett

In this case, because Gossett's data were felt to reflect accurate experimental data, his points were not removed even if they appeared to be outliers. His data points are denoted as the solid squares in Figure (H-4). The physico-chemical reasons for the relatively low correlation coefficient is not known other than that the experimental data set used appear to have an inherently greater uncertainty. It is not recommended that the compound range be extended to use equation H-5 in a "predictive" sense. The general utility of using molecular connectivity indices for prediction of Henry's coefficients, while initially attractive, was not demonstrated in this study.

Temperature Effects

The effect of temperature on the Henry's law coefficient has been discussed by Pierotti (1963) as presented by Nirmalakhandan and Speece (1988b). Pierotti proposed that the potential of a nonelectrolytic solute, μ_2^L, is given by the expression

$$\mu_2^L = G_c + G_i + kT \cdot \ln(x_2/v_1) - kT \cdot \ln \epsilon \qquad \text{(H-6)}$$

where G_c is the free energy associated with the formation of a cavity in the solvent, G_i is the free energy associated with interaction between the solute and the solvent, T is absolute temperature, x_2 is the mole fraction of the solute, v_1 is the molar volume of the solvent, Ÿ is the partition function for the translational and internal degrees of freedom of the solute, and the subscripts 1 and 2 are used to denote solvent and solute, respectively.

In the vapor phase the potential of the gas becomes,

$$\mu_2^G = -kT \cdot \ln(\epsilon) + kT \cdot \ln(P_2/kT) \qquad \text{(H-7)}$$

where P_2 is the partial pressure of the gas.

Combining equations (H-6) and (H-7) yields,

$$\ln (P_2/x_2) = G_c/kT + G_i/kT + \ln(kT/v_1) \qquad \text{(H-8)}$$

Figure H-4. Comparison of Experimental With Calculated Values for Henry's Constant (After Elimination of Outliers)

$$\log H_a = 0.466\ {}^0X + 0.743\ {}^0X^v - 2.653\ {}^1X^v - 0.119\ (r^2=0.85)$$

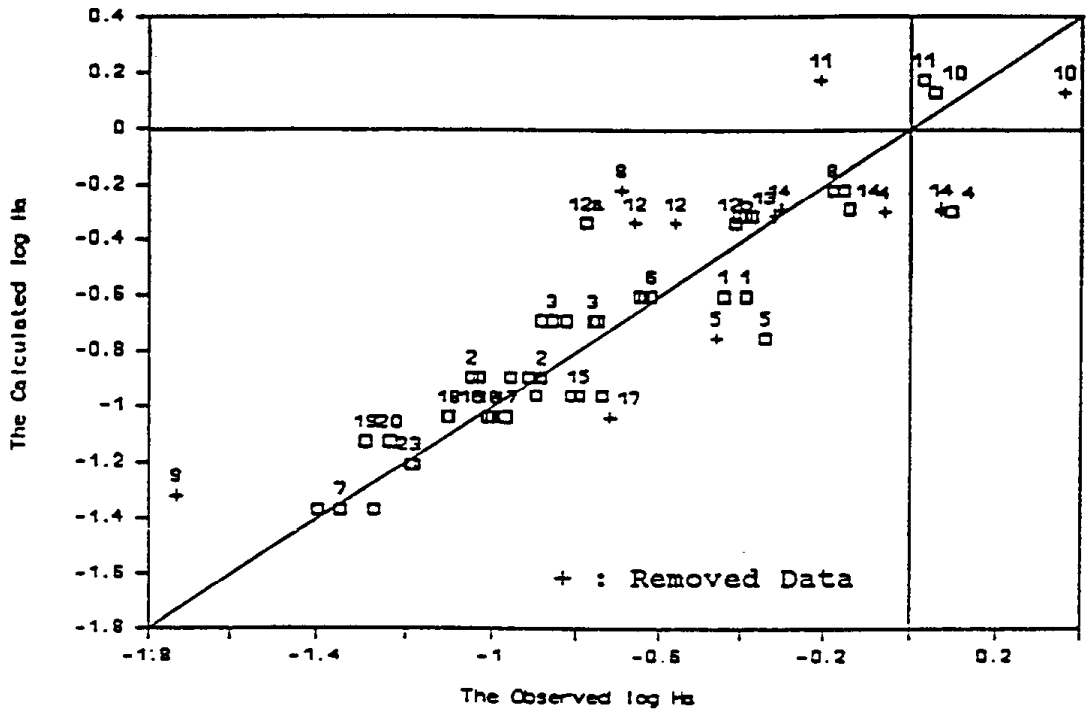


Figure (H-4) Comparison of experimental with calculated values for Henry's constant (after elimination of outliers)

Notes :

1. CM	2. DCM	3. TCM
4. CT	5. MCA	6. 1,1-DCA
7. 1,2-DCA	8. 1,1,1-TCA	9. 1,1,2,2-TetraCA*
10. VC	11. 1,1-DCE	12. 1,2-DCE
13. TCE	14. PERC	15. CB
16. o-DCB	17. m-DCB	18. p-DCB
19. 1,2,3-TCB	20. 1,2,4-TCB	21. 1,3,5-TCB*
22. 1,2,3,4-TetraCB*	23. 1,2,3,5-TetraCB	24. 1,2,4,5-TetraCB*

(A : * indicates no data available)
(B : The solid squares are Gossett's data)
(12a : cis-1,2-DCE; 12b : trans-1,2-DCE)

Finally, if Henry's law constant, H, is taken to be the ratio of P_2 to x_2,

$$\ln H = G_c/kT + G_i/kT + \ln(kT/v_1) \qquad \text{(H-9)}$$

Therefore, a theoretically based general form for the temperature dependence of the Henry's law coefficient is

$$\ln H = C_1 + C_2/T + C_3 \cdot \ln(T) \qquad \text{(H-10)}$$

where C_1, C_2 and C_3 are constants. For a small temperature range, as might be encountered in environmental applications ($\approx 10^{o}$ C), the last term can be neglected because of its weaker logarithmic temperature dependence (Gossett, 1987). Table (H-2) shows the estimation equations for Henry's constant from experiments at temperatures from 10 to 35 ^{o}C by Gossett (1987). (Note that the units of H are m^3-atm/mol.) Nevertheless, even for such a small temperature range, the change in the Henry's coefficient can be substantial. For example, for tetrachloroethene (PERC), from 20 to 30 ^{o}C the effect of temperature on Henry's constants is shown below:

$H = 0.0131\ m^3$-atm/mol $\qquad T = 293$ K

$H = 0.0228\ m^3$-atm/mol $\qquad T = 303$ K.

If the temperature correction for Henry's constant is not given by Gossett, the effect of temperature on Henry's constant can be obtained approximately by using equation (16) and noting that the variation of solubility with temperature between 0 and 40 ^{o}C is negligibly small for most chlorinated hydrocarbons (Horvath, 1982). The influence of vapor pressure dominates the temperature variation, and the pure compound vapor pressure temperature dependence can be used instead.

Table (H-2) Regression equations of Henry's constant

Compound	Coefficients of C_1 and C_2	r^2
PERC	H = exp(12.45 - 4918/T)	0.996
TCE	H = exp(11.37 - 4780/T)	0.996
1,1-DCE	H = exp(8.845 - 3729/T)	0.994
cis-1,2-DCE	H = exp(8.479 - 4192/T)	0.979
t-1,2-DCE	H = exp(9.341 - 4182/T)	0.994
VC	H = exp(7.385 - 3286/T)	0.987
1,1,1-TCA	H = exp(9.777 - 4133/T)	0.995
MCA	H = exp(5.974 - 3120/T)	1.0
CT	H = exp(11.29 - 4411/T)	0.995
TCM	H = exp(9.843 - 4612/T)	0.996
DCM	H = exp(6.653 - 3817/T)	0.951
CM	H = exp(9.358 - 4215/T)	0.99

(T in Kelvins, H in m^3-atm/mol)
Source : Gossett, J.M. (1987)

It should be noted that Henry's Law strictly applies only to dilute two-component mixtures. If a third separable phase occurs, as recently observed by Caballero (1990), the Henry's coefficient for aqueous solution would need to be supplemented by a Henry's coefficient for the separate phase with air, as well as an aqueous phase partition coefficient. Appropriate mass transfer relationships would also need to be developed.

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APPENDIX I
EMISSIONS FROM HEADWORKS PROCESSES

Subsequent to the completion of the preliminary and primary processes modeling study, additional emissions data for some headworks processes became available from the Pooled Emissions Estimation Program (PEEP, 1991) and the Bay Area Air Toxics (BAAT, 1991) Study. An attempt has been made to compare the measured emissions with the general range of predictions from the modeling effort.

Data for a grit chamber at the JWPCP are presented in Table I-1. These data were extracted from Appendix G of the PEEP report. Although the grit chamber in question was not the same as the reference process discussed in Chapter 3, coarse bubble diffusers were applied for both, and the gas-to-liquid ratios (G/L) and detention times are of comparable magnitude (G/L = 0.11, θ_H = 4.2 min, reference process; G/L = 0.17, θ_H = 10 min, JWPCP). The higher gas-to-liquid ratio at the JWPCP would be expected to result in slightly lower concentrations in the gas phase, hence less efficient stripping than for the reference process.

The average of three rounds of 8-hr sampling at the JWPCP yielded an estimated stripping efficiency of 1.5% for the three compounds DCM, TCM and BZ based upon the liquid influent and the difference of the measured inlet and outlet gas concentrations to the grit chamber. In Volume 3 of this report, higher gas phase concentrations of BZ were reported as having been observed at Grit Chamber #6 during four days of continuous sampling (roughly 500 ppbv to 10,000 ppbv with a mean of about 3000 ppbv) than reported during the PEEP testing. The reason for this large difference is not known with certainty, but as discussed in greater detail in Volume 3, may be related to the use of a midget impinger, immersed in an ice bath, ahead of the Tedlar® bags used to contain the gas samples. Such an impinger could have resulted

in condensation of a film of semi-volatile compounds and subssequent sorption of VOCs.

The measured stripping efficiencies compare with a range of from about 1% to 3% (TCM to BZ)) for the Namkung and Rittman mass transfer model formulation to about 6% (TCM to BZ) for the Roberts et al. model formulation. Considering that possible effects of partitioning to solids or to a separate organic phase, e.g. oil or grease, have not been taken into account, and the uncertainty introduced by the ice bath impinger in the PEEP sampling, the model predictions' agreement with the experimental data are considered satisfactory.

Measured data for the "headworks" at the EBMUD WWTP were also found in BAAT report. The report did not detail the exact process points sampled. However, the "headworks" processes at the EBMUD that are vented through a stack are believed to consist of bar screens, an influent pump and non-aerated grit chambers. As can be seen in Table I-2, emissions ranged from 1.4% to 6.3% for the three compounds DCM, TCM, and BZ. As shown in Tables 4-2 and 4-3, estimates of emissions through bar screens and comminutors range from 0.9% to 1.7% and 0.6% to 1.1%, respectively, over the range of values assumed. Thus emissions would be expected to range from about 1.5% to 2.8% of the influent mass. Again the agreement appears to be satisfactory given the limited ability to model such processes.

Table I-1 JWPCP/PEEP Grit Chamber#6 Results

Comp'd	MW	Test Round [#]	Air Flow [cfm]	Liq Flow [Mgd]	Liq In [μg/L]	Liq Out [μg/L]	Avg Air In [ppbv]	Avg Air Out [ppbv]	Calc Loss Air/Liq [%]
		1	2267	70.7					
DCM	85				60.0	56.0	20.5	110.5	0.2%
TCM	119				8.0	7.0	0.0	22.5	0.5%
BZ	78				39.0	38.0	24.5	500.0	1.4%
		2	2868	73.9					
DCM	85				0.0	28.0	23.5	380.0	3.7%
TCM	119				8.0	7.0	2.6	120.0	3.2%
BZ	78				27.0	28.0	18.0	655.0	3.1%
		3	3368	65.0					
DCM	85				14.0	13.0	20.5	110.5	1.3%
TCM	119				7.0	7.0	0.0	22.5	0.9%
BZ	78				33.0	31.0	24.5	500.0	2.6%
		Average		70.0					1.5%

Table I-2 EBMUD/BAAT Headworks Emissions

Comp'd	MW	Liq Flow [Mgd]	Liq Conc In [μg/L]	Mass In [kg/yr]	Headworks Rept'd Emission [kg/yr]	Headworks %-Est. Emission [%]	%-In Emitted [%]
		80					
DCM	85		19	2097	956	3%	1.4%
TCM	119		28	3091	842	5%	1.4%
BZ	78		2	221	175	8%	6.3%

Appendix I REFERENCES

Pooled Emission Estimation Program (1991). "PEEP for POTWs." James Montgomery Consulting Engineers, Pasadena, CA.

Bay Area Air Toxics (BAAT) Group (1991). "AB 2588 Emissions Inventory Guidelines for POTWs." CH2M Hill, Emeryville, CA.