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Removal of Refractory Organics from Water by Aeration. I. Methyl Chloroform

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Abstract

A mathematical model for the removal of volatile organics from water by aeration and by solvent sublation into an organic phase is presented. The model includes the effect of the finite rate of solute mass transfer from the aqueous into the vapor phase. Results are calculated for the removal of 1,1,1-trichloroethane (TCE) chloroform, and benzene from water with 1-octanol, anisole, or kerosene as the organic phase. Experimental data on the aeration of TCE and on its solvent sublation into 1-octanol are in good agreement with the model. Small bubbles and long water columns greatly reduce the inefficiency of the process caused by mass transfer rate limitations.

INTRODUCTION

In 1972 the EPA reported that potentially toxic organic compounds were present in drinking water from the Mississippi River in Louisiana; in 1974 they reported 82 organic compounds which had been identified in New Orleans' drinking water (*1*). This and similar reports led EPA to prepare the National Organics Reconnaissance Survey in 1974, in which raw and finished drinking waters were sampled in 80 cities throughout the United States (*2*). Trihalomethanes were common in chlorinated waters, and a large number of organics from industrial and agricultural sources were found. There has been some impetus for limiting exposure to these compounds because of the association of such exposure and increased risk of cancer (*3*–*5*). Chlorinated organics were formed by the reactions of chlorine with organic precursers, such as humic and fulvic acids, and a broad spectrum of organics occur as a result of industrial wastewater disposal and the migration of material from chemical waste disposal sites.

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These facts have motivated our interest in the development and improvement of techniques for the removal of trace organic compounds from aqueous systems. Biological treatment has long been the standard method from the degradation of organics vulnerable to microbial attack, with activated carbon commonly used for the removal of refractory organics. Macroreticular resins also show promise for removal of refractor organics (*6–8*). We here discuss two closely related aeration techniques into which we were led by previous work on adsorptive bubble separation methods for the removal of inorganic compounds (*9*, *10*). Both of these involve the bubbling of air through a countercurrent flow column. In one instance (solvent sublation), the organic solute is surfaceactive and is transported from the water to an overlying layer of nonvolatile organic liquid on the air–water interfaces of the bubbles rising through the column. In the other (aeration), a volatile organic solute is first stripped from the water column as vapor in the bubbles; it may then be stripped from the bubbles by passage through an overlying layer of nonvolatile organic solvent. Evidently these two modes of removal are not necessarily exclusive—one may have compounds which are both surface active and volatile in aqueous solution which may be removed simultaneously by both modes of separation.

Although the use of surface activity for ore concentration is of relatively long standing. Sebba was the first to systematically exploit surface activity for a wider range of solutes and suspensions (*11*). Lemlich has edited a comprehensive book on the various adsorptive bubble separation methods (*12*), and a number of comprehensive review articles on the subject have been written (*13*).

Sebba developed solvent sublation techniques mainly for the removal of inorganic ions, but noted that ionizable dyes and indicators could be readily and selectively removed by appropriate adjustment of conditions and use of suitable surfactants (*11*). Caragay, Karger, and Lee investigated the solvent sublation of methyl orange and rhodamine B (*14*, *15*). The solvent sublation of Fe(III), Co(II), Ni(II), Th(IV), Pa(V), and U(VI) from aqueous solution was reported by Bittner et al. (*16*), and Elhanan and Karger examined the sublation of $FeCl_4^-$ (*17*). Karger, Pinfold, and Palmer investigated the mechanism of the solvent sublation of methyl orange–hexadecyltrimethylammonium (HTA) (*18*), Spargo and Pinfold studied the sublation of $Fe(CN)_6^{4-}$-dodecylpyridinium (*19*), and Sheiham and Pinfold carried out a study of the sublation of HTA chloride (*20*).

Szeglowski and his co-workers carried out solvent sublation of europium, thulium, and ytterbium (*21*) and of americium and curium (*22*). Stachurski carried out a theoretical treatment of solvent sublation in terms of a random Markov process (*23*, *24*). Grieves and his co-workers examined the removal of phenol from water by solvent extraction, solvent sublation, and foam fractionation, concluding that solvent sublation was most effective (*25*). Kotsuji and his co-workers published a solvent sublation procedure for the spectrophotometric determination of Fe(II) (*26*).

Removal of volatile organics from water by air sparging has long been practiced; it is crucial to the "purge and trap" technique introduced in 1974 by Bellar and Lichtenberg for the determination of volatile organics in the parts per billion (*27*) and even the parts per trillion (*28*) range. Closed-loop stripping is also based on gas sparging (*29*, *30*).

In 1976 EPA issued a report (*31*) indicating that granulated activated carbon (GAC) had several advantages over aeration for removal of trihalomethanes (THSs); THM precursors were not removed by aeration, relatively large volumes of air were required, THMs were regenerated during subsequent storage of the water, and THMs were released to the atmosphere. The National Research Council agreed with EPA that GAC treatment was preferable to aeration, noting that an air:water ratio of 30:1 was necessary to remove 90% of the THMs, but concluded that aeration appeared to be a technically feasible method of control (5).

In a series of papers Rook reported on the chemistry of THM formation and compared THM stripping by aeration with GAC (*32–34*); he obtained 80% THM removal with an air:water ration of 11:1, and 50% removal with an air:water ratio of 3.2:1, both in lab scale and pilot-plant scale apparatus. He concluded that air stripping for volatile organics removal was promising. Trussell and Trussell (*28*) noted that, of all the treatment alternatives for synthetic organics removal, aeration was the least adequately evaluated. They mentioned that (a) stripping in packed towers was found to be quite efficient; (b) reasonable minimum air:water ratios were required for removal of chloroform, 1,2-dichloroethane, and *cis*-1,2-dichloroethylene; and (c) high air:water ratios had been used by McCarty et al. (*35*) to remove a variety of synthetic organics.

We note that equilibrium calculations indicate that aeration should be a quite efficient process even from a simple stirred tank, and that inclusion of a nonvolatile organic solvent layer over the water should eliminate or at least greatly reduce the objectionable discharge of volatile organics to the atomosphere. Failure of the process to meet the promise of the equilibrium calculations indicates that it is limited by the rate of mass transfer between the liquid and the gas phase. This, in turn, suggests some design modifications of the apparatus which should markedly improve its performance.

In the following we present a rather straightforward mathematical model of an aerator apparatus for removing volatile organics with a supernatant nonvolatile organic liquid layer, and we examine the dependence of the model's output on the physical parameters describing the system being modeled. Experimental data on the removal of 1,1,1-trichloroethane (methyl chloroform) are then reported and used as a test of the mathematical model.

THEORY

In this section we analyze the operation of a batch-type aeration apparatus containing an aqueous column topped by a layer of organic liquid. We assume that mass transfer of solute from the liquid to the vapor phase is first-order in the difference between the actual vapor concentration of the solute and the local equilibrium vapor solute concentration. We assume that the aqueous column is formally partitioned into N slabs, and that the organic layer is contained within the $(N+1)$th slab. The mass balance equations for the solute in the vapor and liquid phases in the ith slab are given by

$$\frac{dC_w(i,t)}{dt} = \frac{1}{V_{ai}}\left\{\frac{4\pi N_b}{3}[r_{i-1}^3 C_w(i-1,t) - r_i^3 C_w(i,t)] + k_w S_i[c_w(i,t) - K_w C_w(i,t)]\right\} \qquad (1)$$

and

$$\frac{dc_w(i,t)}{dt} = \frac{k_w S_i}{V_{wi}}[K_w C_w(i,t) - c_w(i,t)], \qquad i = 1, 2, \ldots, N \qquad (2)$$

where $C_w(i,t)$ = concentration of solute in the vapor phase in the ith slab of the water layer
$c_w(i,t)$ = concentration of solute in the ith slab in the water layer
V_{ai} = volume of air in the ith slab
N_b = number of bubbles discharged per second
$= \frac{3Q_a}{4\pi r_t^3}$, Q_a = air flow rate at 1 atm pressure
r_t = bubble radius at 1 atm pressure
r_i = radius of bubble in the ith slab
k_w = mass transfer rate coefficient for vapor–water transfer of solute
S_i = total air–water interface in the ith slab
$K_w = \frac{c_w(\text{eq})}{C_w(\text{eq})}$, Henry's law constant, essentially
V_{wi} = volume of water in the ith slab

We calculate K_w from the equilibrium vapor pressure and water solubility of the solute at the temperature of interest as follows:

$$K_w = \frac{6.23 \times 10^3 T c_s}{(\mathrm{MW})_s P_s^\circ} \tag{3}$$

where T = temperature, °K
c_s = solute solubility in water, g/mL
$(\mathrm{MW})_s$ = solute molecular weight
P_s° = vapor pressure of pure solute, mmHg

We assume that the solute is miscible in the organic layer, and that its vapor pressure is determined by Raoult's law,

$$P_s = P_s^\circ X_s \tag{4}$$

where X_s = solute mole fraction in the organic layer
P_s = vapor pressure of the solute in equilibrium with the solution
P_s° = vapor pressure of pure solute

After use of the definition of mole fraction, the ideal gas law, and noting that for an ideal solution

$$\frac{c_s}{D_s} + \frac{c_o}{D_o} = 1 \text{ mL} \tag{5}$$

we obtain for the solute vapor concentration in the organic layer

$$C_s = \frac{(\mathrm{MW})_s P_s^\circ c_s}{6.23 \times 10^3 T \left[c_s \left(\frac{(\mathrm{MW})_s}{(\mathrm{MW})_o} - \frac{D_s}{D_o} \right) + D_s \right]} \tag{6}$$

where C_s = solute vapor concentration, g/mL
c_s = solute concentration in the organic liquid, g/mL
$(\mathrm{MW})_o$ = organic liquid molecular weight
D_o = organic liquid density, g/mL
D_s = solute density, g/mL

At any instant the total mass of solute in the organic layer is the sum of that in the organic liquid itself and that in the air bubbles passing through this layer.

Thus

$$m_o = V_o c_s + V_{oa} C_s \tag{7}$$

where V_o = volume of organic liquid
V_{oa} = volume of air in the organic layer
m_o = total solute mass in the organic layer

The change in m_o with time is due to the difference in solute concentration of the air entering and leaving this layer,

$$\frac{dm_o}{dt} = Q_{ao}(C_w(N, t) - C_s(t)) \tag{8}$$

The mass of solute in the organic phase at time $t + dt$ is found by integrating Eq. (8) forward one time increment. The new value of m_o is substituted into Eq. (7), which is then solved for C_s, yielding

$$C_s = \frac{m_o(t + dt) - V_o c_s}{V_{oa}} \tag{9}$$

This in turn is substituted into Eq. (6) to give, on rearrangement, a quadratic equation for $c_s(t + dt)$,

$$c_s^2 \left[- V_o \left(\frac{(\mathrm{MW})_s}{(\mathrm{MW})_o} - \frac{D_s}{D_o} \right) \right] + c_s \left[m_o \left(\frac{(\mathrm{MW})_s}{(\mathrm{MW})_o} - \frac{D_s}{D_o} \right) \right.$$
$$\left. - V_o D_s - \frac{(\mathrm{MW})_s p_s^\circ V_{oa}}{6.23 \times 10^3 T} \right] + m_o D_s = 0 \tag{10}$$

The positive root of Eq. (10) gives the new solute concentration, $c_s(t + dt)$, in the organic solvent. $C_s(t + dt)$ can then be calculated from Eq. (9).

The flow rate and bubble radius are defined at 1 atm pressure; these need to be corrected for the hydrostatic pressure in the various slabs into which the column is partitioned. The slabs are numbered from the bottom of the column, and for the ith slab we have approximately

$$P_i = P_{\mathrm{atm}} g + h_o D_o g + h_w D_u g(N + 0.5 - i)/N \tag{11}$$

where P_i = pressure in the ith slab, dyn/cm^2
P_{atm} = (1 atm) × (76.0 cmHg/atm) × (13.6 g Hg/cm^3)
g = 980 cm/s^2
h_o = height of organic layer

D_o = density of organic layer
h_w = height of water column
D_w = density of water layer
N = number of slabs into which the water column is partitioned

The air flow rate in the ith slab is then given by multiplying Q_a (1 atm) by the factor $P_{\text{atm}}g/P_i$; the bubble radius in the ith slab is given by multiplying the bubble radius at 1 atm, r_t, by the cube root of this factor.

In the organic layer the pressure is approximately

$$P_{\text{org}} = P_{\text{atm}}g + 0.5h_oD_og \tag{12}$$

The airflow rate in the organic layer is corrected for pressure by the factor $P_{\text{atm}}g/P_{\text{org}}$; the bubble radius, by the cube root of this factor.

The rise velocity u_i of a bubble in the ith layer was calculated from (*36*)

$$u_i = \frac{2gDr_i^2}{9\eta}\left[1 + \frac{1}{4}\left(\frac{Dr_iu_i}{2\eta}\right)^{1/2} + \frac{0.34Dr_iu_i}{12\eta}\right] \tag{13}$$

where $D = D_w$ or D_o, as appropriate
η = water or organic solvent viscosity

This equation is used iteratively, using $2gDr_i^2/9\eta$ as a starting value for u_i. The rise velocity is then combined with the number of bubbles discharged/s (N_b) and the thickness of the water or organic layer to calculate the number of bubbles in a slab at one time, which is given by $N_b(\Delta h)/u_i$, where Δh is the thickness of the slab. This is needed to calculate V_{ai}, S_i, V_{wi}, V_{oa}, and V_o.

$$V_{ai} = \frac{4}{3}\pi r_i^3 \frac{N_b\Delta h}{u_i} \tag{14}$$

$$S_i = 4\pi r_i^2 \frac{N_b\Delta h}{u_i} \tag{15}$$

$$V_{wi} = V_{\text{slab}} - V_{ai} \tag{16}$$

$$V_{oa} = \frac{4}{3}\pi r_0^3 \frac{N_bh_o}{u_i} \tag{17}$$

$$V_o = (\text{total organic solvent layer}) - V_{oa} \tag{18}$$

We choose as initial conditions at time zero a solute water concentration of c_w^0 in all the slabs representing the water column, and zero solute concentrations in the bubbles and the organic layer. Equations (1), (2), and (8) are then integrated forward in time by means of a standard predictor-corrected method (*37*). A typical run, simulating the removal of 1,1,1-trichloroethane from water with 2-octanol as the supernatant organic phase, is shown in Fig. 1. The parameters for this run are given in Table 1.

The general appearance of the plots of the quantities of solute in the water and organic phases suggest that this model could be fitted by the rate

TABLE 1

Standard Input Parameters

Parameter	Value
Organic layer height	2.0 cm
Aqueous column height	50.0 cm
Column radius	2.5 cm
Bubble radius at 1 atm	0.05 cm
Flow rate	3.0 mL/s
Number of aqueous column slabs	5
Initial solute concentration	2.0×10^{-5} g/mL = 20 ppm
Aqueous mass transfer rate coefficient	1.0×10^{-3} cm/s
Density of water[a,b]	0.998203 g/mL
Density of *n*-octanol[a,b]	0.8270 g/mL
Density of 1,1,1-trichloroethane[a,b]	1.3390 g/mL
Solubility of 1,1,1-trichloroethane in water[a,b]	1.32×10^{-3} g/mL
Viscosity of water[a,b]	0.01002 poise
Viscosity of *n*-octanol[a,d]	0.10 poise
Vapor pressure constants:[a,b]	
A (molar heat of vaporization)	8012.7 cal/g·mol
B	7.955902
Molecular weight of 1,1,1-trichloroethane	133.41 g/mol
Molecular weight of water	18.016 g/mol
Molecular weight of *n*-octanol	130.22 g/mol
Acceleration due to gravity	980 cm^2/s^2
Temperature	293.15 K
Δt	0.20 s
Column run duration	20,000 s

[a] At 20°C.

[b] Source: R. C. Weast (ed.) *CRC Handbook of Chemistry and Physics*, 51st ed., Chemical Rubber Co., Cleveland, 1970.

[c] Source: A. Seidell, *Solubilities of Organic Compounds*, Vol. 2, 3rd ed., Van Nostrand, New York, 1941, p. 84.

[d] Source: R. H. Perry and C. H. Chilton (eds.), *Chemical Engineers' Handbook*, 5th ed., McGraw-Hill, New York, 1973, p. 3–212.

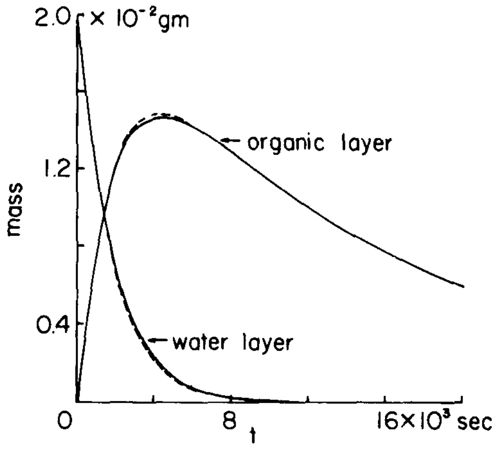

FIG. 1. Solvent sublation, standard conditions. 1,1,1-Trichloroethane (20 ppm) in H_2O, octanol as organic phase, air flow rate of 3.0 mL/s. Other parameters are given in Table 1. Total solute masses in the aqueous and organic phases are plotted. The dotted lines show the approximations obtained using simple first-order kinetics.

equations describing two consecutive irreversible first-order processes—solute moving from water to organic phase, followed by solute moving from the organic phase to the atmosphere. The differential equations for this are

$$dm_w/dt = -k_w m_o \tag{19}$$

and

$$dm_o/dt = k_w m_w - k_o m_o \tag{20}$$

which integrate to give

$$m_w = m_w^{\circ} \exp(-k_w t) \tag{21}$$

and

$$m_o = \frac{k_w m_w^{\circ}}{k_w - k_o} \exp(-k_o t)\{1 - \exp[(k_o - k_w)t]\} \tag{22}$$

Equation (22) cannot be solved for k_o so a nonlinear least squares method was used to estimate the value of k_o. Values for m_w^0 and k_w were obtained by linear least squares, and a starter value for k_o was obtained by fitting the plot of $m_o(t)$ in the time interval following the point of inflection. Numerical least squares minimization was then performed to obtain k_o; the International

Mathematics and Statistical Libraries program ZXXSQ was used (*38*). This is a modified Levenberg-Marquardt algorithm for finding the minimum of the sum of squares of M functions of N variables. The fit obtained is shown by the dashed lines in Fig. 1, and appears to be quite good in this particular case. The reason for this is apparent in Fig. 2; the parameters are such that the rates of removal from the individual slabs representing the water column are quite similar, and appear to be essentially exponential decays.

THEORETICAL RESULTS

The first eight parameters in Table 1 were varied to observe their effects on solute loss from the water layer and on solute gain and loss in the organic layer. With the exception of the mass transfer rate coefficient for solute movement from the aqueous to the vapor phase, these quantities are experimentally variable. (N, the number of slabs into which the water column is partitioned, is related to the axial dispersion in the column, decreasing as axial mixing increases.)

The effects of varying the thickness of the organic layer are shown in Fig. 3. As we expect, the thickness of the organic layer has no effect on the rate of removal from the water column. We see that the retention of solute in the organic phase improves as the thickness of the organic layer increases.

The influence of the height of the water column is exhibited in Fig. 4. We see that, in terms of mass of solute removed per unit volume of air, the longer

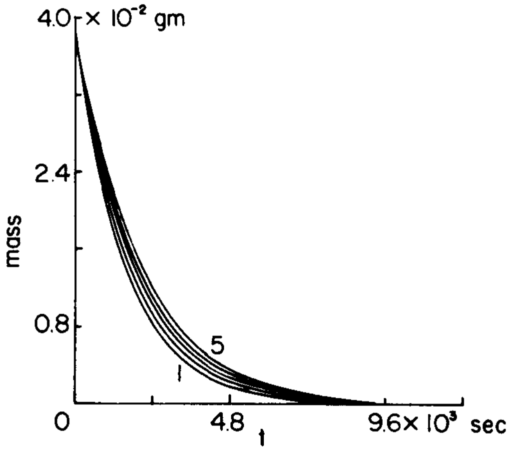

FIG. 2. Aqueous solute behavior in each of the five slabs used to represent the aqueous phase in the column. See Table 1 for parameters. The top curve corresponds to the top slab; the bottom curve to the bottom slab, etc.

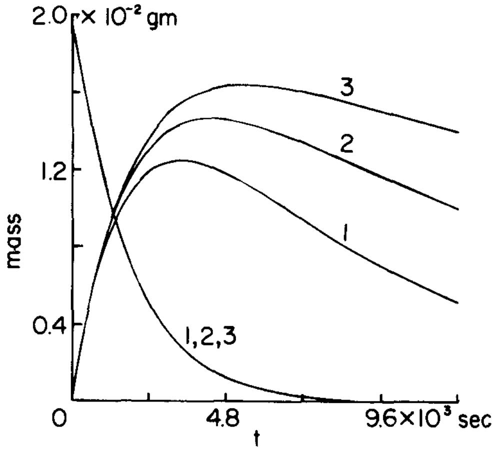

FIG. 3. The effect of the thickness of the organic layer. From top to bottom, $h_0 = 4$, 2, and 1 cm. Other parameters as in Table 1.

the water column the better. This trend reaches a limit, however, when the contact time of the bubbles in the water is long enough to permit a close approach to equilibrium of the distribution of solute between the aqueous and vapor phases. This, as we shall see, is favored by small bubbles.

The effects of increasing column radius are shown in Fig. 5, and are what one would expect. Since the air flow rates are the same in all three runs, the fractional removal rates decrease proportionally to 1/(column radius)^2.

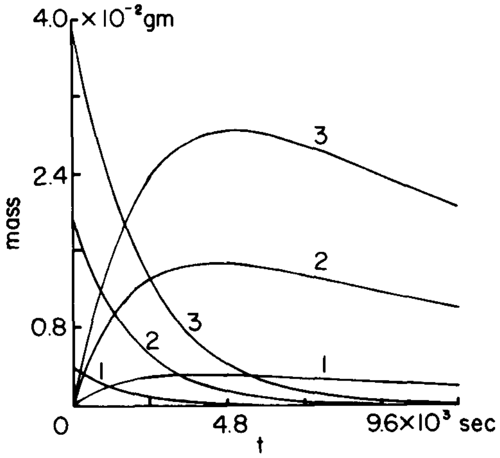

FIG. 4. The effect of the height of the aqueous phase. From top to bottom, $h_w = 100$, 50, and 10 cm. Other parameters as in Table 1.

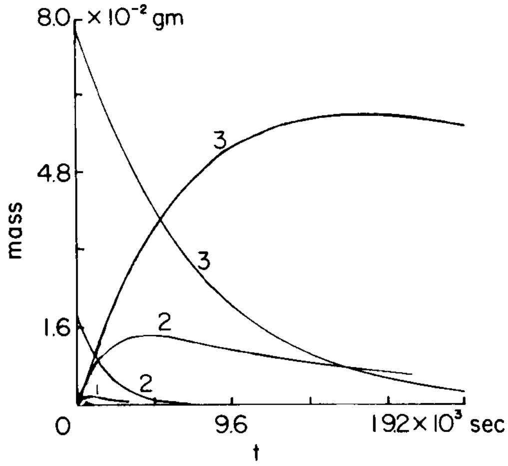

FIG. 5. Effect of column radius. From top to bottom, column radius = 5.0, 2.5, and 1.0 cm. Other parameters as in Table 1.

Bubble radius is a very important parameter, as shown in Fig. 6. The increased contact times and surface-to-volume ratios of small bubbles permit them to come much closer to achieving equilibrium solute concentration (with respect to the aqueous phase) than is possible for larger bubbles. Figure 6 makes it quite apparent that the key to efficient removal of volatile solutes by aeration is the use of small bubbles if the process is mass transfer limited.

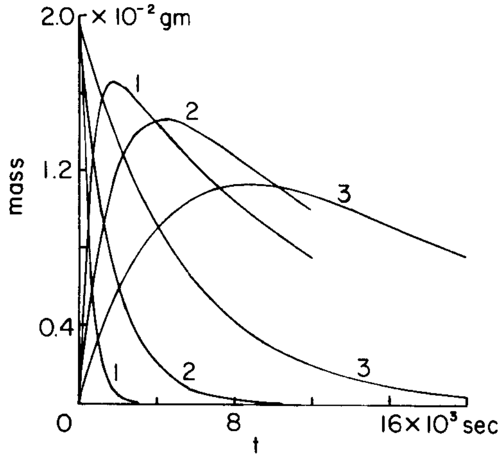

FIG. 6. Effect of bubble radius. Bubble radius = 0.02 (1), 0.05 (2), and).10 (3) cm. Other parameters as in Table 1.

We note that small bubbles result in less loss of solute to the atmosphere in this model.

The effects of air flow rate are shown in Fig. 7. In essence, changing air flow rates in this model simply changes the time scale of the process inversely, as can be seen by noting that N_b and S_i are proportional to the airflow rate and that $V_{ai}\, dC_{w'}(i, t)/dt$ is the rate of change of solute mass in the vapor phase in the ith slab. Equation (8), governing the organic layer, exhibits explicitly its similar dependence on airflow rate. We note that this conclusion is unrealistic at high flow rates, since bubble size increases with a given gas dispersion device as pressure is increased. One also would expect that axial dispersion would increase greatly at high air flow rates, which is not taken into account in these results.

We next examine the effects of varying the number of slabs into which the water column is formally partitioned; this also represents the effects of axial dispersion. Axial dispersion can be controlled by baffles in the column and by dispersal of air uniformly across the cross-sectional area of the column. Axial dispersion also decreases bubble–water contact times, since portions of the water which are relatively rich in bubbles are low in density and therefore tend to rise. The effects of the partitioning of the column into slabs was studied by representing the water column by 1, 2, 5, 10, 20, or 30 slabs (Fig. 8). This of course increases proportionally the number of differential equations which must be integrated, and also decreases the size of the maximum time increment which can be used in the numerical integration.

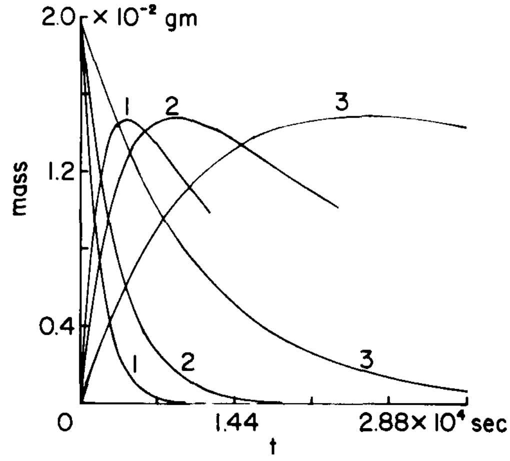

FIG. 7. Effect of airflow rate. Airflow rate = 3.0 (1), 1.5 (2), and 0.5 (3) mL/s. Other parameters as in Table 1.

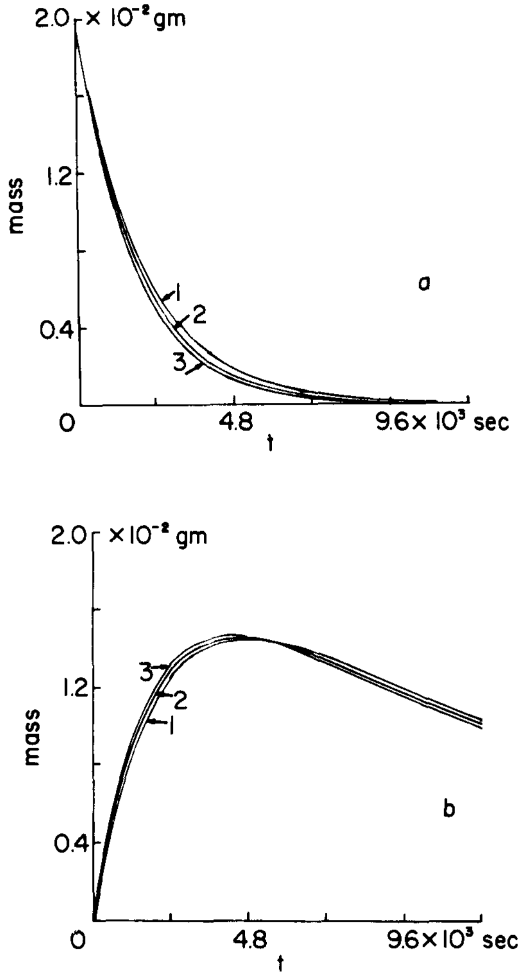

FIG. 8. Effect of the number of aqueous slabs on solute masses in the aqueous (a) and organic (b) phases. Number of slabs = 1 (1), 2 (2), 5, 10, 20, and 30 (3). Other parameters as in Table 1.

The computer time requirements therefore increase roughly as the square of the number of slabs. In view of this it is fortunate that increasing the number of slabs above about 5 has very little effect on the behavior of the model. For $1 \leq N \leq 5$ we find that increasing the number of slabs (decreasing axial dispersion) increases the efficiency of removal by a modest amount (about 20% in going from 1 to 5).

These results were compared with best fits to Eqs. (21) and (22), our

TABLE 2

Comparison between the Model and the Results of Eqs. (21) and (22)

N	Maximum % discrepancy
30	4.9
20	4.8
10	4.7
5	4.2
2	2.7
1	0.5

simple consecutive first-order processes model. The results are given in Table 2.

The initial solute concentration in the water column does not affect the shapes of the plots of m_w versus t, since our assumption of Henry's law and first-order mass transfer kinetics guarantee that the vaporization of solute is directly proportional to its weight concentration in the water phase. This is not true in the organic layer, for which we have assumed Raoult's law; the solute concentration in the organic layer at high initial aqueous solute concentrations also shows marked departures from the simple consecutive first-order model.

The parameter having the most uncertainty is certainly the rate coefficient for mass transfer of solute from the aqueous to the vapor phase, k_w. This includes the effects of turbulent diffusion and of molecular diffusion through the boundary layer. Runs made with values of k_w of 5×10^{-4}, 1×10^{-3}, and 5×10^{-3} cm/s are plotted in Fig. 9. Further increase of k_w causes the curves to approach the equilibrium-controlled limit. The failure of aeration to live up to the promise of equilibrium-based calculations must be due to the process being mass transfer limited. The mass transfer parameter in this model must be selected to fit experimental data. A small mass transfer rate coefficient may be compensated for by increasing the length of the water column and/or decreasing the bubble size.

Most of our simulation runs involved 1,1,1-trichloroethane and 2-octanol. We next examine some results for other volatile solutes and organic solvents. Trichloroethane, chloroform, and benzene were used as solutes; and 2-octanol, kerosene, and anisole were used as organic solvents to give a total of nine combinations. The physical constants needed for chloroform, benzene, kerosene, and anisole are listed in Table 3; those for trichloroethane and 2-octanol were given in Table 1. Other factors being equal, one would like to use a nonvolatile organic solvent which retained the maximum fraction of the volatile solute being removed from the aqueous phase.

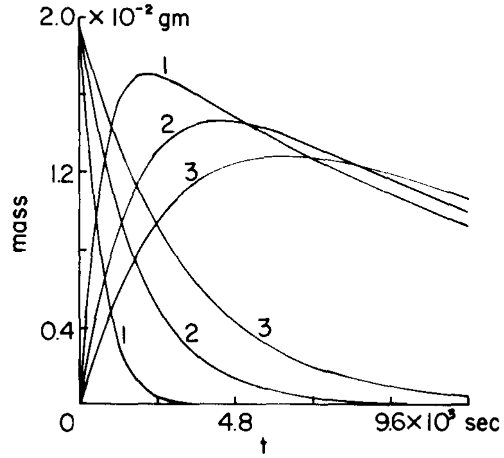

FIG. 9. Effect of aqueous-vapor mass transfer rate coefficient. Coefficient = 5 × 10^{-3} (1), 1 × 10^{-3} (2), and 5 × 10^{-4} (3) cm/s. Other parameters as in Table 1.

TABLE 3

Physical Constants

Solute parameter	Chloroform	Benzene
Density (g/mL)[a,b]	1.4832	0.87865
Solubility in water (g/mL)[a,b]	8.22 × 10^{-3}	1.75 × 10^{-3}
Vapor pressure constants:[a,b]		
A (cal/g·mol)	7500.5	8146.5
B	7.735083	7.833714
Molecular weight (g/mol)[b]	119.38	78.12
Solvent parameter	**Kerosene**	**Anisole**
Density (g/mL)[b]	0.82	0.9961[a]
Viscosity (poise)[a,b]	0.0245	0.0110
Molecular weight (g/mol)	184[e]	108.13[b]

[a] At 20°C.

[b] Source: R. C. Weast (ed.), *CRC Handbook of Chemistry and Physics*, 51st ed., Chemical Rubber Co., Cleveland, 1970.

[c] Source: A. Seidell, *Solubilities of Organic Compounds*, Vol. 2, 3rd ed., Van Nostrand, New York, 1941, p. 84.

[d] Source: R. H. Perry and C. H. Chilton (eds.), *Chemical Engineers' Handbook*, 5th ed., McGraw-Hill, New York, 1973, p. 3–212.

[e] Average of a mixture of C_{10} to C_{16} alkanes (*Merck Index*, 9th ed., Merck & Co., Rahway, New Jersey, 1976, No. 5146).

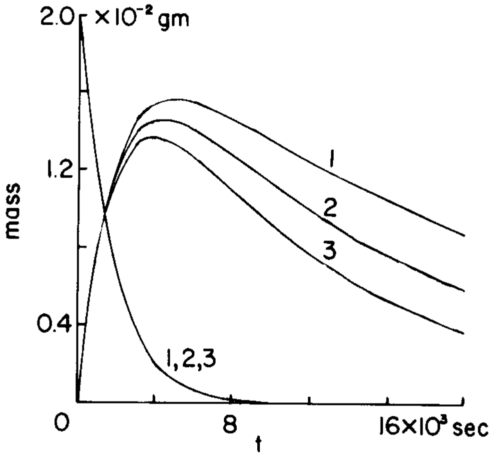

FIG. 10. Sublation of TCE into anisole (1), octanol (2), and kerosene (3). Parameters given in Tables 1 and 3.

Figure 10 shows plots simulating the removal of 1,1,1-trichloroethane from water with anisole, 2-octanole, and kerosene as the organic solvent. The differences in the plots of concentration in the organic layer as a function of time are due solely to differences in the molecular weights of the organic solvents which affect the equilibrium between organic liquid and vapor through Raoult's law. In a more sophisticated model one could take departures from ideality into account too. Figure 11 shows a similar set of plots for chloroform removal, and Fig. 12 simulates the removal of benzene. Generally, the lower the molecular weight of the organic solvent, the more effective it is in trapping the volatile solute. One is limited in capitalizing on this by the requirements that the solvent be of quite low volatility and solubility in water, and that it be less dense than water.

Figure 13 compares the removals of trichloroethylene, chloroform, and benzene into 2-octanol. The removal rates of these solutes from water are governed by their Henry's law constants. Their removal rates from octanol, however, are governed by the vapor pressures of the pure solutes and by their molecular weights. This is responsible for the cross-over we see in the curves for trichloroethane and benzene.

The performance of the apparatus can be assessed in a number of ways. We define V_M as the volume of air per unit volume of water at which the solute concentration in the organic layer is a maximum. We define the percent efficiency, E, as the ratio of the maximum mass of solute in the organic layer divided by the initial solute mass in the water times 100%. Percent residual efficiency, E_R, we define as 100% × $m_w^*/m_{w(0)}$, where m_w^* is

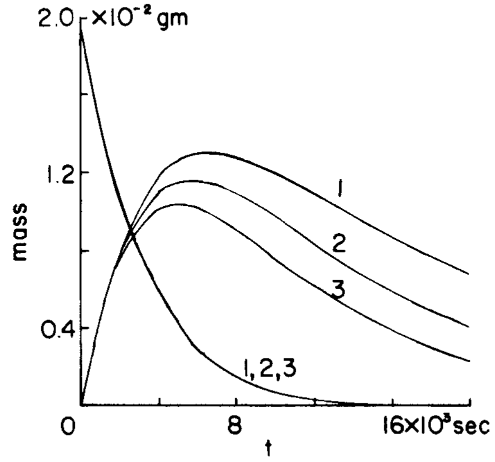

FIG. 11. Sublation of chloroform into anisole (1), octanol (2), and kerosene (3). Parameters given in Tables 1 and 3.

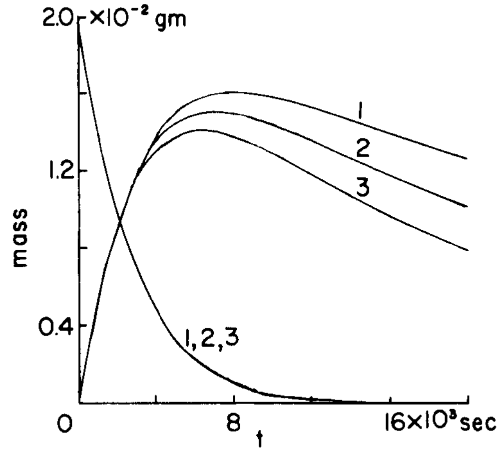

FIG. 12. Sublation of benzene into anisole (1), octanol (2), and kerosene (3). Parameters given in Tables 1 and 3.

the mass of solute in the water layer when m_o is at a maximum. $V_{1\%}$ is the volume of air required per volume of water to reduce the aqueous solute concentration to 1% of its initial value. $E_{1\%}$ is the percent of the initial solute which is retained in the organic layer when the solute concentration in the

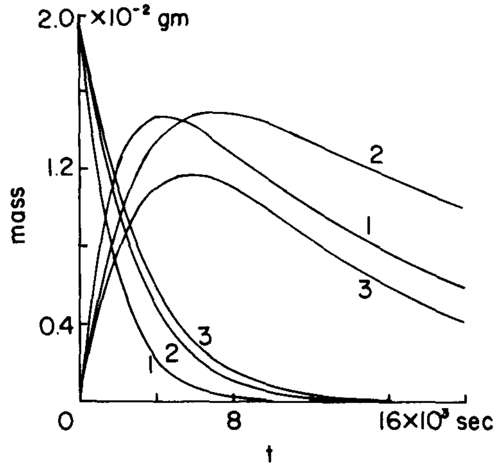

FIG. 13. Sublation of TCE (1), benzene (2), and chloroform (3) into octanol. Parameters given in Tables 1 and 3.

aqueous layer has been reduced to 1% of its initial value. These separation criteria are listed in Table 4 for the runs previously described.

EXPERIMENTAL PROCEDURES

A lab-scale solvent sublation apparatus was built for studying the removal of volatile and surface-active solutes from water; this is diagrammed in Fig. 14. The column was made from a piece of Pyrex glass tubing with a "fine" fritted glass disk sealed in near the bottom. The distance from the glass frit to the top of the column is 116 cm, and the internal diameter of the column is 5.2 cm. Stopcocks are sealed into the column at 1, 54, and 110 cm from the frit. A larger outlet port 1.5 cm above the frit permits rapid draining of the column and could be used in continuous flow operation. The column is wrapped with 50 ft of Tygon tubing connected to a controlled temperature bath which circulates a mixture of ethylene glycol and water through the tubing. A thermometer is inserted through the large rubber stopper closing the top of the column; a piece of glass tubing inserted through this stopper provides connection to a soap film flowmeter. House air is used after filtration through 15 cm of glass wool; its flow is measured with the soap film flowmeter and a stopwatch, and is controlled by a micrometer needle valve. Experiments are timed with an electric timer.

Solutions were prepared with Fisher Certified 1,1,1-trichloroethane and deionized water. Aldrich 1-octanol, 99%, was used as the organic layer.

TABLE 4

Efficiency of Sublation

Value of indicated parameter	V_M	E (%)	E_R (%)	$V_{1\%}$	$E_{1\%}$ (%)
		Organic Layer Height			
1 cm	10.25	64.4	14.4	24.34	43.6
2 cm	13.08	75.5	8.4	24.35	65.2
4 cm	16.28	83.8	4.6	24.37	80.0
		Aqueous Layer Height			
10 cm	56.76	77.6	7.8	102.6	69.3
50 cm	13.08	75.4	8.4	24.35	65.2
100 cm	7.54	73.0	9.2	14.53	60.7
		Column Radius			
1.0 cm	11.52	72.4	8.5	21.54	59.8
2.5 cm	13.08	75.4	8.4	24.35	65.2
5.0 cm	13.82	76.0	8.2	24.57	66.4
		Bubble Radius			
0.02 cm	5.46	87.9	1.0	5.49	87.9
0.05 cm	13.08	75.4	8.4	24.35	65.2
0.10 cm	26.21	57.5	19.5	73.79	30.4
		Flow Rate			
3.0 mL/s	13.08	75.4	8.4	24.35	65.2
1.4 mL/s	13.27	75.8	8.2	24.49	66.0
0.5 mL/s	13.36	76.1	8.2	24.60	66.6
		Aqueous Column Slabs			
30	12.83	75.7	8.1	23.56	65.8
20	12.90	75.6	8.1	23.64	65.7
10	12.94	75.5	8.2	23.87	65.5
5	13.11	75.4	8.4	24.35	65.2
2	13.55	74.8	8.9	25.85	64.0
1	14.32	73.8	9.9	28.45	62.2
		Solute Concentration			
2×10^{-6} g/mL	13.09	75.4	8.4	24.35	65.2
2×10^{-5} g/mL	13.08	75.4	8.4	24.35	65.2
2×10^{-4} g/mL	13.9	75.4	8.3	24.35	65.3
2×10^{-3} g/mL	13.37	75.9	8.0	24.35	66.2

(continued)

TABLE 4 (continued)

Value of indicated parameter	V_M	E (%)	E_R (%)	$V_{1\%}$	$E_{1\%}$ (%)
		Mass Transfer Rate Coefficient			
5×10^{-3}	6.41	88.6	1.3	6.85	88.1
1×10^{-3}	13.08	75.4	8.4	24.35	65.2
5×10^{-4}	19.08	65.9	13.8	44.42	46.5
		TCE/Solvent			
Anisole	14.92	80.8	5.7	24.02	75.1
Octanol	13.08	75.6	8.1	24.02	65.7
Kerosene	11.74	70.8	10.5	24.01	56.3
		Chloroform/Solvent			
Anisole	19.86	68.8	9.3	38.52	53.0
Octanol	17.23	61.9	12.7	38.51	39.5
Kerosene	15.21	55.8	16.2	38.51	28.2
		Benzene/Solvent			
Anisole	23.88	82.3	4.1	34.53	77.9
Octanol	21.35	77.4	5.8	34.53	69.5
Kerosene	19.22	72.9	7.7	34.53	60.9

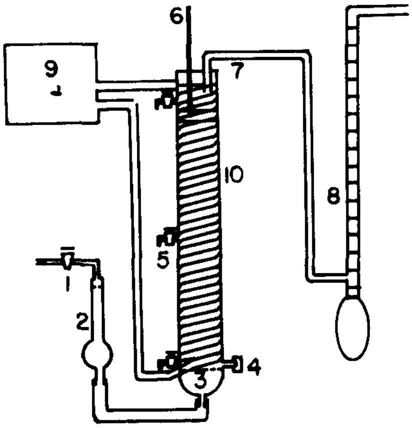

FIG. 14. The apparatus: (1) air needle valve, (2) glass wool column, (3) fritted glass disk, (4) outlet port, (5) sampling tap, (6) thermometer, (7) vent, (8) soap film flowmeter, (9) controlled temperature bath, (10) wrapped Tygon tubing.

Trichloroethane concentrations were measured with an F and M Model 700 gas chromatograph equipped with a Tracor nickel-63 high temperature electron capture detector and a Tracor solid state electrometer. The prepurified nitrogen carrier gas was passed through a Matheson XF-100 gas chromatography scrubber before reaching the column. Six-foot glass columns were used, packed with 3% DC-200 on 60/80 Chromosorb P, or with 4% SE-30 and 6% SP-2401 on 100/120 Supelcoport. Samples were stored in 2.3 mL Pierce Reacti-Vials with Pierce Reacti-Vials with Pierce Tuf-Bond Teflon-silicone, disk septum caps lined with aluminum foil.

A stock solution of 200 mg/L of trichloroethane in deionized water was prepared before each run. It was diluted to prepare 2250 mL of 20 mg/L trichloroethane solution. Standards containing 10, 5, 4, and 2 mg/L of trichloroethane were prepared for the 20 mg/L solution. The airflow rate through the column (filled with deionized water) was adjusted, generally to 120 or 60 mL/min, and the column was then emptied, rinsed, and filled to a height of 100 cm (a volume of 2124 mL) with the 20 mg/L trichloroethane solution. A 4-cm layer (85 mL) of 1-octanol was then poured on top. Runs were made at 20°C. One milliliter samples were taken from the middle stopcook during the course of the run. After each run octanol was pipetted off and the column drained rinsed, scrubbed with Alconox, rinsed, and filled with deionized water.

Trichloroethane analyses of the samples in the vials were carried out by equilibrating the samples at 21°C for at least half an hour and then sampling the headspace gas. The gas chromatograph column was run at 90°C. Samples and standards were injected alternately. Peak areas were calculated as the product of peak height and peak width at half-height.

EXPERIMENTAL RESULTS

Three solvent sublation runs of an airflow rate of 120 mL/min, two aeration runs at 120 mL/min, and two aeration runs at 60 mL/min were carried out. (In the aeration runs, no octanol layer was present.) The mass of solute remaining in the water layer is shown for each of these runs in Figs. 15–22. It was found that the initial rate of removal was anomalously rapid; this was due to the fact that the solutions were not precooled to 20°C and solute was removed more rapidly from the solution when it was warm. The initial data point was therefore omitted in fitting computer simulations to the experimental data. In simulating these runs a value of 1.0×10^{-3} cm/s was used for the mass transfer rate coefficient; the effect of changing the mass transfer rate coefficient is shown in Fig. 22, and it is evident that the curves

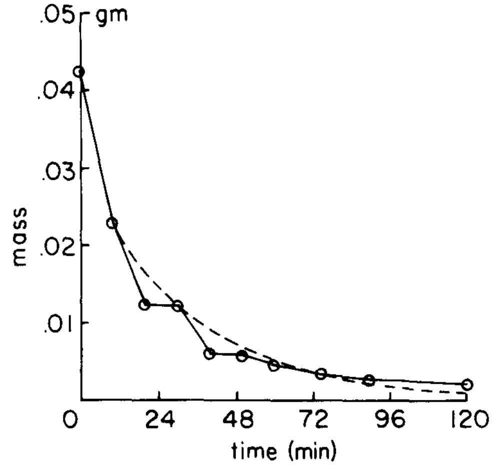

FIG. 15. Comparison of experimental results and computer fit (dashed line) for first TCE solvent sublation. The computed curve was generated using an initial solute concentration of 1.1 × 10^{-5} g/mL, a bubble radius of 0.01 cm, and a mass transfer rate coefficient of 1.0 × 10^{-3} cm/s. Experimental conditions were 20 ppm TCE, 20°C, airflow rate 2.0 mL/s, $h_w = 100$, and $h_0 = 4$ cm.

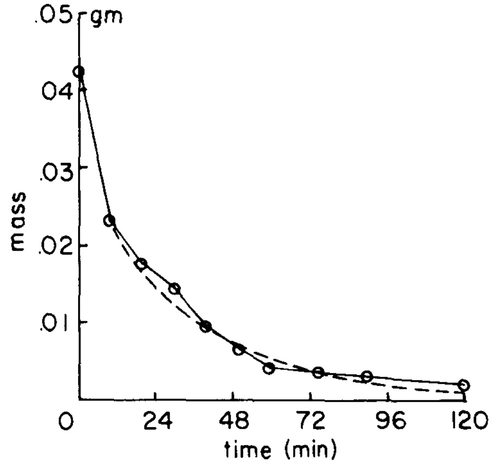

FIG. 16. Comparison of experimental data and computer fit (dashed line) for second TCE solvent sublation. Computer and experimental parameters as in Fig. 15.

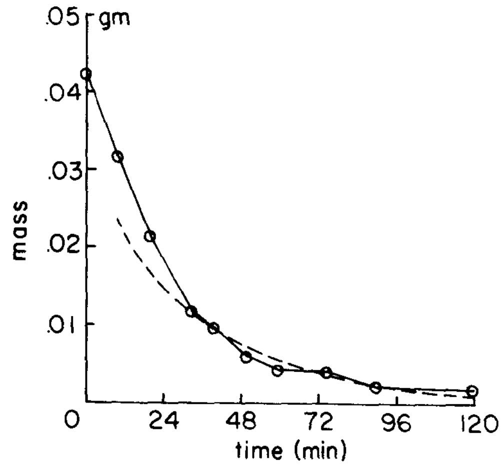

FIG. 17. Comparison of experimental data and computer fit (dashed line) for third TCE solvent sublation. Computer and experimental parameters as in Fig. 15.

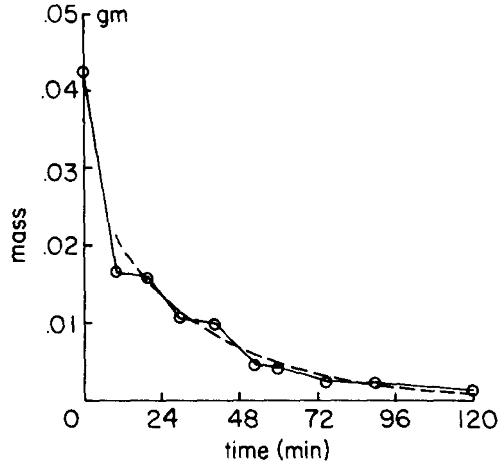

FIG. 18. Comparison of experimental data and computed results (dashed line) for first TCE aeration run. Computer parameters were: initial solute concentration 1.0×10^{-5} g/mL and bubble radius 0.01×10^{-3} cm/s. Experimental conditions as in Fig. 15, except that $h_0 = 0$ cm.

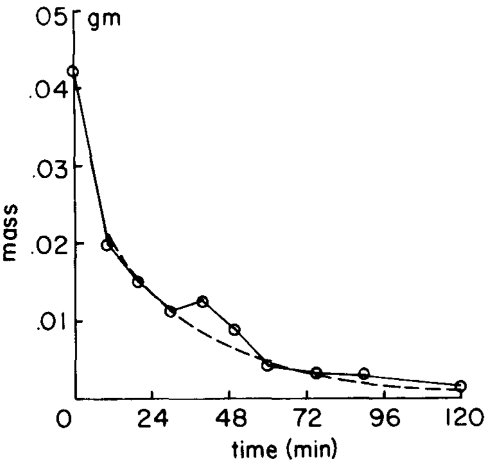

FIG. 19. Comparison of experimental data and computed results (dashed line) for second TCE aeration run. All parameters as in Fig. 18.

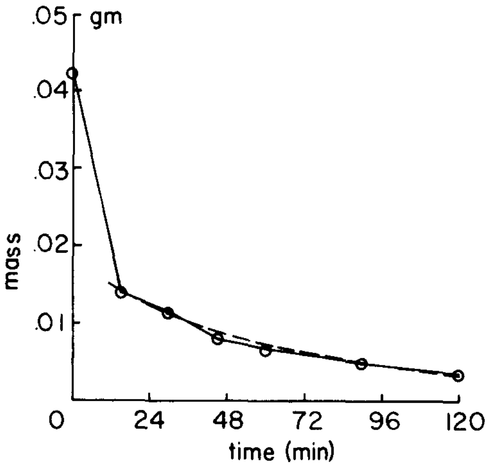

FIG. 20. Comparison of experimental data and computed results (dashed line) for third TCE aeration run. All parameters as in Fig. 18, except that airflow rate = 1.0 mL/s.

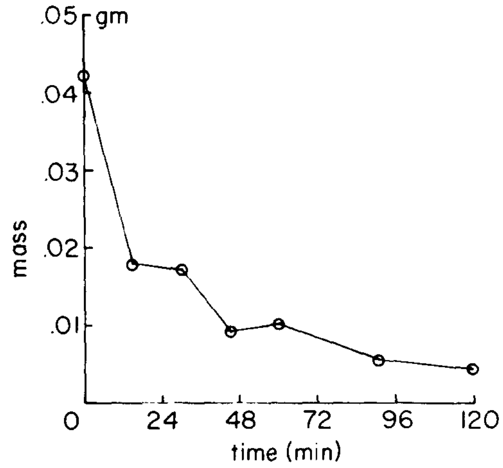

FIG. 21. Comparison of experimental data and computed results (dashed line) for fourth TCE aeration run. Parameters as in Fig. 18, except that airflow rate = 1.0 mL/s and bubble radius = 0.0075 cm.

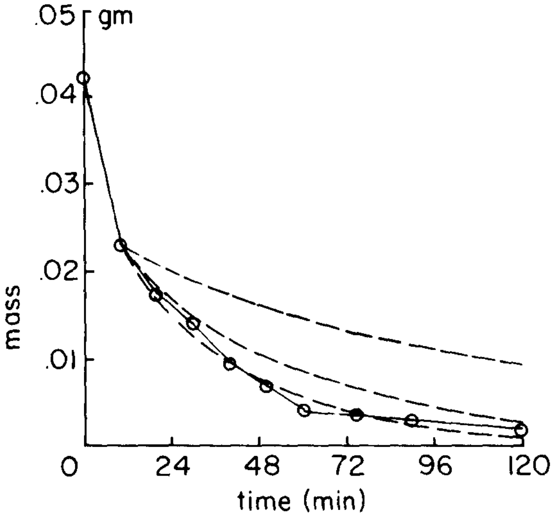

FIG. 22. Comparison of experimental data for the second solvent sublation run with computed results for various mass transfer rate coefficients. Computed curves were made using an initial solute concentration of 1.1 × 10^{-5} g/mL, a bubble radius of 0.01 cm, and mass transfer rate coefficients of 1.0 × 10^{-3}, 5.0 × 10^{-4}, and 1.0 × 10^{-4} cm/s. Experimental conditions as in Fig. 15.

depend markedly on the assignment of this parameter. The bubble radius used was 0.01 cm in all cases. This was based on photographic data on bubbles rising from "fine" frits.

CONCLUSIONS

The agreement between the observed results and the calculated curves is fairly good. The main discrepancies appear to be associated with uncertainties in the gas chromatographic analysis and with the decrease in temperature during the initial stages of the runs. We conclude that these data support the mathematical model, and note that the only parameter in the model which is adjustable is the mass transfer rate coefficient.

The experimental results are rather encouraging in terms of the application of the technique for wastewater and drinking water treatment. (Trichloroethane was selected because of a local wastewater problem involving this compound.) From Fig. 16, for example, we calculate that 3.39 volumes of air per volume of water removes about 91% of the trichloroethane when the airflow rate is 120 mL/min. From Fig. 20 we find that 3.39 volumes of air per volume of water removes about 92% of the trichloroethane at an air-flow rate of 60 mL/min. On the basis of Fig. 13 we expect that the situation will not be quite so favorable for chloroform; about 6.0 volumes of air should be required to remove 90% of the chloroform from water with this apparatus. We note that no mention of bubble size is made in the *Interim Treatment Guide* (*31*), but small columns and contact times of only 10 min were used. These conditions did not permit adequate mass transfer and were insufficient for trihalomethanes removal. Our results indicate the importance of having fairly small bubbles and long columns, which provide large bubble surface-to-volume ratios and long bubble–water contact times, both of which favor increased mass transfer. It would appear that a reinvestigation of trihalomethane removal by aeration may be in order.

We note that solvent sublation is also able to remove nonvolatile materials from water provided that they are suface-active. Simple aeration is not effective for these, since axial dispersion back-mixes the enriched upper portion of the water column. Work is currently in progress on testing this technique for the removal of chlorinated benzenes, chlorinated organic pesticides, and PCB's from aqueous systems.

Acknowledgment

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