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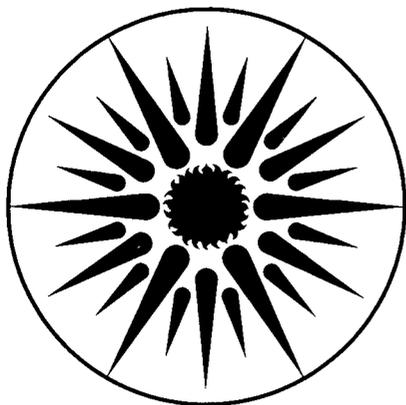
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**APPLYING THE TWO-RESISTANCE THEORY
TO CONTAMINANT VOLATILIZATION
IN SHOWERS**

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Abstract

The two-resistance theory is applied to the transfer of volatile contaminants from shower water to indoor air by means of two transient mass balance models. Mass transfer coefficients are calculated from reported experimental data for four full-scale shower systems. Both liquid- and gas-phase coefficients appear to increase rapidly with water flowrate, but the results are confounded by substantial variations among the different shower systems. The influence of water temperature on mass transfer coefficients is generally smaller than the experimental uncertainty. The measured mass transfer coefficients enable predictions to be made of the accumulation of volatile contaminants in shower and bathroom air during a typical shower. Exposures are calculated for volatile organic compounds representative of the entire range of volatilities found in water supply systems.

Introduction

The major sources of human exposure to volatile organic compounds (VOCs) occur indoors rather than in the outdoor environment (1). For example, levels of certain VOCs present in indoor air have been found to be more than ten times higher than outdoors (2). One potential source of VOCs in indoor air is transfer from contaminated tap water during residential water use in, for example, showers, dish washers and washing machines. McKone (3) has shown that the daily indoor inhalation exposure attributable to contaminated tap water may be as much as six times higher than that incurred by consuming 2 L of the same water. Of the total inhalation exposure, more than one-half was projected to occur in the shower stall with an additional one-third occurring in the bathroom (3).

Andelman (4) recently reviewed exposure to VOCs in potable water via pathways other than ingestion; namely inhalation and uptake through skin contact. He points out the need for refining present estimates of indoor air exposure to VOCs derived from potable water sources by, *inter alia*, more accurately accounting for the chemical characteristics that affect the rate and extent of volatilization. In order to account for the different properties of VOCs, McKone (3,5,6) proposed a relationship which adjusts the measured transfer

efficiency (the fraction volatilized) for radon (7,8) to that for any VOC using the Henry's law constant and liquid and gas diffusivities. Although the relationship was only intended to be approximate it does not adequately account for gas-phase resistance (9). More recently, however, the results of four experimental studies on full-scale showers have become available (6,10,11,12). These results present an opportunity to determine mass transfer coefficients for the various shower systems and then to use these to account in a consistent fashion for variation in contaminant volatility.

In this paper, the classic two-resistance mass transfer theory (13) is applied to the volatilization of contaminants from showers. Experimental data from four full-scale shower systems are used to calculate liquid- and gas-phase mass transfer coefficients using transient mass balance models. These models account for variation in volatility, mass transfer driving force, water and air flowrates and volume of the shower stall and bathroom. The results from the four studies are compared, and measured mass transfer coefficients are used to predict shower stall and bathroom exposures during a typical shower.

Theoretical Development

Using Henry's law and the two-resistance theory, transient mass balance models are developed which describe volatilization from showers in terms of an overall mass transfer coefficient. A procedure is outlined for separating the overall coefficient into individual liquid- and gas-phase coefficients and the influence of diffusivity on these mass transfer coefficients is discussed.

The version of Henry's law used to describe equilibrium between water and air is

$$y = mc \tag{1}$$

where y is the gas phase contaminant concentration in equilibrium with c the aqueous phase contaminant concentration and m is a dimensionless Henry's law constant. The temperature dependence of m is commonly described (14) by the expression

$$m \propto \frac{1}{T} 10^{(-J/T)} \quad (2)$$

where J is a temperature correction coefficient and T is absolute temperature.

The mass transfer flux between two fluid phases can be expressed as a concentration driving force divided by an overall resistance to mass transfer. The two-resistance theory (13,15) gives the overall resistance as the sum of two resistances in series, one for each of the phases, or

$$\frac{1}{K_{OL}} = \frac{1}{K_L} + \frac{1}{mK_G} \quad (3)$$

where K_{OL} , K_L and K_G are the overall, liquid-phase and gas-phase mass transfer coefficients, respectively. For very volatile compounds (large m) the liquid-phase resistance controls while gas-phase resistance becomes significant as volatility decreases.

An idealized and schematic representation of an experimental shower stall is given in Figure 1a. The volumetric flowrates of water (Q_L) and air (Q_{G_s}) are assumed to be constant with time and the shower air volume (V_s) is assumed to be well mixed. The air entering the shower has constant contaminant concentration y_{sin} (usually, $y_{sin} = 0$) and at time $t = 0$ the concentration of the contaminant in the water entering the shower changes from zero to c_{in} . As the water falls through the shower stall, it loses contaminant at a rate proportional to the concentration driving force existing between the water and the air, or

$$\frac{dc}{dt} = -K_{OL}(A/V_L)(c - y_s/m) \quad (4)$$

where A is the interfacial area available for mass transfer between the water and the air and V_L is the volume of water present in the shower. Assuming that the water passes through the stall in plug flow and that the shower air contaminant concentration y_s is constant during the relatively short residence time of the water, eq 4 may be integrated to yield

$$c_{out} = c_{in} \exp(-N) + (y_s/m)(1 - \exp(-N)) \quad (5)$$

where $N = (K_{OL}A)/Q_L$ is a dimensionless overall mass transfer coefficient. In reality, the water will not pass through the stall in perfect plug flow and there will be some distribution

of residence times. This liquid phase dispersion will be incorporated into the values of N (or K_{OLA}) estimated from the experimental data. A transient mass balance on the air in the shower stall results in

$$\frac{dy_s}{dt} V_s = Q_L (c_{in} - c_{out}) - Q_G (y_s - y_{sin}) \quad (6)$$

Substituting eq 5 into eq 6 and integrating from an initial concentration y_{si} at $t = 0$, gives on rearrangement

$$y_s = \frac{a}{b} + (y_{si} - \frac{a}{b}) \exp(-bt) \quad (7)$$

where $a = (Q_L c_{in} (1 - \exp(-N)) + Q_{Gs} y_{sin})/V_s$

and $b = ((Q_L/m)(1 - \exp(-N)) + Q_{Gs})/V_s$

Eqs 5 and 7 simplify under certain limiting conditions. When $t \rightarrow \infty$, $y_s \rightarrow a/b$ which is the steady-state concentration in the shower air. Also, when $y_s = 0$, $c_{out} = c_{in} \exp(-N)$.

Eqs 5 and 7 give c_{out} and y_s as functions of time, a single overall mass transfer coefficient, and experimentally measurable parameters. The mass transfer coefficient (K_{OLA}) may therefore be determined by measuring c_{in} and either c_{out} or y_s . A more reliable estimate may be obtained by measuring both c_{out} and y_s over a time period and then determining K_{OLA} by means of a least squares fit to both data sets in turn. Since the model assumes a perfect mass balance, any discrepancy in the experimental mass balance will result in different values of the mass transfer coefficient being obtained from the water and air data. A check of the experimental transient mass balance may be obtained for any time period t_1 to t_2 using the following equation

$$Q_L c_{in} (t_2 - t_1) - Q_L \int_{t_1}^{t_2} c_{out} dt = V_s (y_{s2} - y_{s1}) + Q_{Gs} \int_{t_1}^{t_2} y_s dt - Q_{Gs} y_{sin} (t_2 - t_1) \quad (8)$$

where the left hand side represents the amount of contaminant volatilized from the water and the right hand side represents the net amount of contaminant transferred to the air. The two integrals may be evaluated by numerical integration of the experimental data.

Figure 1b shows a schematic representation of the same shower stall located inside a bathroom where the volumetric flowrate of bathroom air (Q_{Gb}) is also constant and the bathroom air volume (V_b) is assumed to be well mixed. A transient mass balance on the air in the shower stall now results in

$$\frac{dy_s}{dt} V_s = Q_L (c_{in} - c_{out}) - Q_{Gs} (y_s - y_b) \quad (9)$$

where y_b is the contaminant concentration in the bathroom air. A similar balance on the bathroom air yields:

$$\frac{dy_b}{dt} V_b = Q_{Gb} (y_{bin} - y_b) - Q_{Gs} (y_b - y_s) \quad (10)$$

Rearranging eq 10 and substituting eq 5 into eq 9 yields

$$\frac{dy_s}{dt} = A_1 + A_2 y_b + A_3 y_s \quad (11)$$

$$\frac{dy_b}{dt} = B_1 + B_2 y_s + B_3 y_b \quad (12)$$

where $A_1 = (Q_L c_{in})(1-\exp(-N))/V_s$

$$A_2 = Q_{Gs}/V_s$$

$$A_3 = ((-Q_L/m)(1-\exp(-N)) - Q_{Gs})/V_s$$

$$B_1 = (Q_{Gb} y_{bin})/V_b$$

$$B_2 = Q_{Gs}/V_b$$

and $B_3 = (-Q_{Gb}-Q_{Gs})/V_b$.

These two differential equations may be solved simultaneously by means of Laplace transforms using the initial conditions at $t = 0$ of y_{si} and y_{bi} . The solution (outlined in an Appendix) is

$$\frac{y_s}{y_{si}} = \left(\frac{a_2}{r_1 r_2}\right) - \frac{(r_1^2 + a_1 r_1 + a_2)}{r_1(r_2 - r_1)} \exp(r_1 t) + \frac{(r_2^2 + a_1 r_2 + a_2)}{r_2(r_2 - r_1)} \exp(r_2 t) \quad (13)$$

$$\frac{y_b}{y_{bi}} = \left(\frac{b_2}{r_1 r_2}\right) - \frac{(r_1^2 + b_1 r_1 + b_2)}{r_1(r_2 - r_1)} \exp(r_1 t) + \frac{(r_2^2 + b_1 r_2 + b_2)}{r_2(r_2 - r_1)} \exp(r_2 t) \quad (14)$$

where $a_1 = (A_1 + A_2 y_{bi} - B_3 y_{si})/y_{si}$

$$a_2 = (A_2 B_1 - A_1 B_3)/y_{si}$$

$$b_1 = (B_1 + B_2 y_{si} - A_3 y_{bi})/y_{bi}$$

$$b_2 = (A_1 B_2 - A_3 B_1)/y_{bi}$$

$$\text{and } r_{1,2} = \frac{1}{2}(A_3 + B_3) \pm \frac{1}{2}((A_3 + B_3)^2 - 4(A_3 B_3 - A_2 B_2))^{0.5}$$

The value of c_{out} is calculated from eq 5 as before. When y_{si} and/or y_{bi} are exactly zero, they should be set to a finite, but very small number. Also, if Q_{Gb} is set equal to a very large number, then eq 13 gives the same results as eq 7. Finally, the steady state values are:

$$y_s = (A_2 B_1 - A_1 B_3)/(A_3 B_3 - A_2 B_2) \quad (15)$$

$$y_b = (A_1 B_2 - A_3 B_1)/(A_3 B_3 - A_2 B_2) \quad (16)$$

The above transient mass balance models describe the volatilization of VOCs from a shower in terms of measurable experimental parameters and an overall mass transfer coefficient N (or K_{OLA}). The two resistance theory given by eq 3 relates the overall mass transfer coefficient to individual liquid-phase and gas-phase mass transfer coefficients by means of the Henry's constant, m . Dividing eq 3 through by A , the interfacial area available for mass transfer, gives:

$$\frac{1}{K_{OLA}} = \frac{1}{K_{LA}} + \left(\frac{1}{K_{GA}}\right) \frac{1}{m} \quad (17)$$

It is common practice in mass transfer studies to lump the intrinsic mass transfer coefficient and the interfacial area into a single coefficient which is determined experimentally. Mass transfer coefficients determined in this fashion are typically found to vary with liquid and gas flowrates (which influence the degree of turbulence in the liquid and gas "films" as well as the interfacial area), temperature and the liquid and gas diffusivities of the transferring chemicals. If two or more chemicals of differing volatility are transferred under identical hydrodynamic and temperature conditions and through the same interfacial area then all of these variables remain constant except for the diffusivities. This provides a basis for separating the liquid- and gas-phase mass transfer coefficients (16,17,18).

Mass transfer coefficients typically depend on diffusivity according to a power relationship (16,17):

$$K_L \propto D_L^p \quad (18)$$

$$K_G \propto D_G^q \quad (19)$$

where D_L and D_G are the liquid and gas diffusivities, respectively. Factoring the dependence on diffusivities into eq 17 gives, with some rearrangement

$$\frac{1}{(K_{OLA})_i} \left(\frac{D_{Li}}{D_{Lr}} \right)^p = \frac{1}{(K_{LA})_r} + \frac{1}{(K_{GA})_r} \frac{1}{m_i} \left(\frac{D_{Gr}}{D_{Gi}} \right)^q \left(\frac{D_{Li}}{D_{Lr}} \right)^p \quad (20)$$

where i represents the individual VOCs studied and r a selected reference compound.

When compounds are chosen with similar air and water diffusivities, eq 20 reduces to eq 17. Then, if the transfer of two or more VOCs of widely differing volatility is measured simultaneously, the individual mass transfer coefficients K_{LA} and K_{GA} can be evaluated from the intercept and slope of a plot of $1/K_{OLA}$ vs $1/m$ for the various compounds. Alternately, the influence of liquid and gas diffusivities must be taken into account. If the exponents p and q are known, the more cumbersome eq 20 can still be used to find K_{LA} and K_{GA} for the reference compound.

Mass transfer coefficients have not yet been measured for shower systems, let alone their dependence on diffusivity. However, earlier work on spray-type mass transfer equipment suggests that there are four regions of mass transfer: drop formation, a period of drop acceleration to terminal velocity, the fall of the drop at terminal velocity and coalescence on impact (19). There is considerable evidence that internal circulation within drops, and hence the mass transfer rate, is large during drop formation, release and acceleration (19). Also, a theoretical analysis shows that K_L should be proportional to the $1/2$ power of D_L during drop formation from orifices (19). For drops falling at terminal velocity, K_L will be strongly dependent on drop size and the degree of internal circulation. Correlations for gas-phase mass transfer from a drop to a gas show that K_G also will be most strongly influenced by drop size and the rate of fall, however, K_G appears to vary according to the $2/3$ power of D_G (19).

Interpretation of Experimental Data

Tancrede et al. (12), Giardino and Andelman (11), Hodgson et al. (10) and McKone and Knezovich (6) (also referred to as studies T, G, H and M) have all obtained experimental data from full-size shower systems. The main parameters of these four studies are listed in Table I while complete experimental details may be obtained from the original references. ACH_s and ACH_b are the air exchange rates in the shower and bathroom, respectively, expressed as a number of volume changes per hour. The physical properties of the various VOCs examined in the four studies are given in Table II and were obtained from a compilation of such constants (14). The studies of Tancrede et al. and Giardino and Andelman were performed in specially constructed experimental shower units with the shower air mixed by means of an air fan. The studies of Hodgson et al. and of McKone and Knezovich were done in shower stalls located in residential bathrooms.

Tancrede et al. (12) measured the simultaneous volatilization of five VOCs in four experimental runs at varying water flowrate and temperatures. The data from the runs at 33 and 42°C were selected for analysis here with salient details reported in Table III. The value of c_{in} is the average of measurements at 2, 6 and 11 minutes, while that of c_{out} is the average of measurements at 8 and 12 minutes. The contaminant air concentration y_s was measured after 10 minutes of shower operation. Using these data, the percentage recovery is calculated (see eq 8) as the ratio of the mass of VOC accounted for in the air to the mass volatilized from the water during the first ten minutes of operation, and reported in Table III. In calculating the masses leaving in the water and air streams (the two integrals in eq 8) the value of c_{out} was assumed to be constant with time while that of y_s was assumed to be increasing linearly with time from zero. The validity of these assumptions will be checked in a later section. The water data were first used to estimate N as follows: a value for N was guessed and eqs 7 and 5 were then used to calculate c_{out} at 8 and 12 minutes. The two calculated values of c_{out} were averaged and then compared to the observed value given in Table III. This process was repeated until the calculated and observed values converged. The contaminant concentration in the air, y_s , taken at 10 minutes, was also used to calculate N now using only eq 7. The values of N obtained from the water and the air data (expressed as K_{OLA}) are reported in Table III together with their ratio. Note that y_{si} and y_{sin} are both zero in these calculations.

Giardino and Andelman (11) report data for the volatilization of three VOCs in an experimental shower system and details of the three runs are given in Table IV. The contaminant concentration in the outlet water was calculated from the percentage volatilization quoted in the original reference and represents an average c_{out} for the 11 minute shower period. The mass balance could be checked for TCE and $CHCl_3$ as measurements of the air concentration with time were given (11) for these two compounds. As before, N was estimated in an iterative fashion for the water data (using eqs 7 and 5). However in this case, an average value for c_{out} was calculated for the entire 11 minute shower period and then compared to the observed value given in Table IV. The air data given for TCE and $CHCl_3$ also enabled an estimate of N to be obtained (using eq 7) by a least squares fit to all the data points. The percentage recovery, the values of K_{OLA} determined from the water and the air data and their ratio are also given in Table IV.

Hodgson et al. (10) measured the volatilization of VOCs in a residential shower within a bathroom and selected results are given in Table V. The air exchange rate between the house and the bathroom was measured using SF_6 as a tracer, however, the exchange rate between the shower stall and the bathroom was not determined. Two ten minute runs were performed, one with and one without a showering individual and measurements of the bathroom air were made rather than of the air inside the shower stall. The values of c_{out} and y_b represent average values of the outlet water and bathroom air during the course of each ten minute shower. The initial contaminant concentration in the bathroom air, y_{bi} , (attributed to the background VOC level in the house) was also determined and is reported in Table V. For the present calculations, the initial shower concentration, y_{si} , and the concentration entering the bathroom, y_{bin} , were assumed equal to y_{bi} . An estimate of the air flowrate between the bathroom and the shower was initially obtained by finding the values of N and Q_{GS} which resulted in the best fit (using eqs 13, 5 and 14) to the values of c_{out} and y_b in Table V. The objective function was calculated as the sum of the squares of the normalized differences between the observed and calculated values. The data for TCE were not used for this purpose since gas-phase concentrations were not determined. Q_{GS} was found to be 110 ± 50 L/min (mean \pm standard deviation) and was then fixed at 110 L/min for all the data and the values of N recalculated using only c_{out} . The recomputed values of N did not change from those estimated initially and are listed, together with those for TCE, in Table V (expressed as K_{OLA}).

McKone and Knezovich (6) measured the transfer of TCE during eight 20 minute showers at two water temperatures. The inlet contaminant concentration c_{in} was about

100ug/L throughout and the transfer efficiency (%) was found to be 58 ± 11 at 22°C and 63 ± 9 at 37°C. No statistical difference was found in the transfer efficiency with time or with temperature. Eqs 13 and 5 were used to find N values for each of the average transfer efficiencies quoted above. For the purposes of the present calculations, c_{in} was set at 100ug/L and c_{out} was set at 42 and 37ug/L, respectively, for the two temperatures. Note that the value of N is independent of c_{in} since the mass transfer model assumes that volatilization is a first order process. The values of Q_{Gs} and Q_{Gb} given in Table I are used in the calculation even though they are derived from what appear to have been only estimates of the residence times (6). These results are presented in Table VI.

Discussion of Results

The mass balances shown in Table III range from 43 to 93% indicating that, for all experimental runs, more VOC was volatilized from the water than was recovered in the air. This discrepancy is reflected in the ratio of K_{OLA} values which varies from 2.5 at 43% recovery to 1.2 at 93% recovery. The reasons for the fairly low recovery are unclear, but could be due to unidentified sinks for the VOCs (12), imperfect mixing of the shower air or inaccuracies in experimental measurement. Notice, however, that the steady state mass balances used by Tancrede et al. (12) account for only 9 to 19% recovery with accumulation in the shower air accounting for the major portion of the difference. In contrast to the data of Tancrede et al., the recovery for the data of Giardino and Andelman (Table IV) tends to be greater than 100% and again this is reflected in the ratio of the values of K_{OLA} determined from the water and air data.

The values of K_{OLA} determined from the water data of study T, and shown in Table III, decrease as the volatility of the VOCs decrease. Neglecting the influence of diffusivities for the moment, these data are plotted according to eq 17 in Figure 2. The intercept and slope of the two lines are used to find values for K_{LA} of 18 and 17 L/min and for K_{GA} of 320 and 380 L/min at 33°C and 42°C, respectively. Earlier workers have found that the K_G/K_L ratio appears to be reasonably constant under similar conditions for a given mass transfer system (for example see ref 17) and once known, it may be used to obtain an estimate of K_{GA} or K_{LA} when only the other is known. This ratio is found to be 17 and 22 for the runs at 33°C and 42°C, respectively. An overall, but irregular, decrease with m is also observed for K_{OLA} obtained from the air data of study T as shown in Table III. It appears that at least some of the irregularity may be explained by the

variation in recovery suggesting that measurements of the VOC concentrations in water were more reliable than those in air. The K_{OLA} values for the air data of study G shown in Table IV together with the value for DBCP are also plotted according to eq 17 in Figure 2. Even though the data were obtained at different air flow rates and water temperatures, the points again appear to be linear. The slope and intercept give values for K_{GA} of 130 L/min and for K_{LA} of 9.5 L/min with a K_G/K_L ratio of 13.

In using eq 17 to calculate the individual mass transfer coefficients, the influence of D_L and D_G have been neglected. Even though the exact dependence of K_L and K_G on diffusivity is unknown for shower systems, a rough check of the validity of neglecting changes in diffusivity may be obtained by assuming that K_L and K_G vary according to the 1/2 and the 2/3 power of the diffusivity, respectively. Using the values of D_L and D_G given in Table II, the terms in eq 20 involving diffusivity are found to vary from 1.00 to 1.13 for $(D_{Li}/D_{Lr})^{0.5}$ and from 0.76 to 1.00 for $((D_{Gr}/D_{Gi})^{0.67} (D_{Li}/D_{Lr})^{0.5})$ where DBCP is the reference compound. Neglecting these terms would introduce an error of approximately $\pm 12\%$ which appears to be justified when compared with the relatively large uncertainties associated with the experimental measurements (12).

The values of K_{OLA} obtained from the data of Hodgson et al. are all for fairly volatile VOCs suggesting a small gas-phase resistance. The average value for K_G/K_L obtained from studies T and G is 17 and assuming that this holds for study H, eq 17 can be used to show that the gas-phase resistance amounts to no more than about 8% of the total resistance for TCE, the least volatile VOC examined. This means that the K_{OLA} values in Table V are all essentially equivalent to K_{LA} values which, if the influence of liquid diffusivity is neglected, should all be the same. Averaging gives $K_{LA} = 28 \pm 4$ L/min (mean \pm standard deviation) with a coefficient of variation of 14%. This variation is about two times higher than the influence of gas-phase resistance and the variation arising as a result of differences in D_L . One surprising and useful result demonstrated by Hodgson et al. (10) is the statistically insignificant influence on mass transfer when a person is standing under the shower spray. This is reflected in the mass transfer coefficients given in Table V and lends confidence to exposure predictions based on mass transfer coefficients determined from experiments without a showering individual present.

If the K_G/K_L ratio of 17 is assumed to hold for the shower system of McKone and Knezovich (study M), then gas-phase resistance accounts at most for about 15% of the overall resistance in their studies. Therefore, the error introduced by neglecting K_{GA} is

about the same as the variation in experimental precision (6), and the K_{OLA} values in Table VI are essentially equivalent to K_{LA} values.

A summary of the mass transfer coefficients determined from the four studies is given in Table VII. The two major influences on mass transfer coefficients are shower type and water flowrate. In general, the mass transfer coefficients appear to increase with increasing water flowrate, but this influence is confounded by the considerable variation with the type of shower system. The influence of water temperature on mass transfer coefficients appears to be smaller than the variation in experimental precision as observed by Tancrede et al. (12).

Behavior of Transient Mass Balance Models

The experimental parameters of the study by Hodgson et al. (10) comprise the most complete set of conditions representative of an actual residential shower. These parameters will be used as a basis for examining the behavior of the mass balance models. In addition to the parameters listed in Table I, y_{bin} , y_{bi} and y_{si} are all set to zero. All results are normalized with respect to c_{in} since the models are first order and hence independent of initial concentration. K_{LA} is taken as 28 L/min since this is the average value found from the data of study H. Using the ratio $K_G/K_L = 17$ results in an estimate for K_GA of 480 L/min. Eq 17 is used to calculate K_{OLA} from which the appropriate value of N is calculated, and hence contaminant concentrations in the air and water streams. The effect of increasing the shower air exchange rate is also examined by increasing ACHs from 2.4 to 12 h^{-1} , the value used in study M.

Figures 3a, 3b and 3c show the influence of volatility (m) and shower air exchange rate (ACH_s) on water, shower air and bathroom air concentrations with time. CCl_3F , $CHCl_3$ and DBCP are chosen as representative VOCs since they cover the entire range of volatilities examined. The most obvious impact of the decrease in m is the dramatic reduction in mass transfer which results in a substantially higher c_{out} and lower y_s and y_b . Also of interest is the change with time in both air and water contaminant concentrations. For CCl_3F , the most volatile VOC, c_{out} is practically constant with time while for DBCP, the VOC of lowest volatility, c_{out} increases fairly substantially with time. The curtailment of volatilization which occurs at low m is due to the reduced driving force for mass transfer (see eq 4) resulting from the increase in y_s and the low m . The effect of increasing ACH_s

from 2.4 to 12 h⁻¹ has little influence on the water concentration, but a strong influence on both shower and bathroom air contaminant concentrations. Finally, the assumptions of linear increase in y_s and constant c_{out} with time, used in the analysis of the data of Tancrede et al., appear to be excellent for all compounds except TCPA, the least volatile VOC used in that study. By assuming a constant c_{out} , the amount of TCPA in the outgoing water was overestimated by about 10% which means that the recoveries for TCPA tend to be overestimated. The amount of TCPA in the outgoing air is so small that any error introduced by the assumption of linear increase in y_s is negligible.

One final comment should be made concerning the use of the shower models to estimate mass transfer coefficients. The steady state solutions can also be used to estimate N from experimental data; however, for lower volatility VOCs, the steady state concentrations become relatively insensitive to the value of N . Therefore, it is important to use the earlier transient data when estimating N for compounds of low volatility such as TCPA and DBCP. The models developed here should provide a useful tool for determining suitable experimental conditions in future research.

Assessment of Potential Exposure

The set of reference parameters is now used to estimate the average shower stall and bathroom exposure during a typical ten minute shower. These reference conditions represent an upper bound for the potential exposure because they include the highest water flowrate and mass transfer coefficients for the four shower systems. The influence is also shown of increasing ACH_s from 2.4 to 12 h⁻¹ and of decreasing the water flowrate from 13.7 to 5 L/min, the value used in study G. In the latter case, K_{LA} and K_{GA} were taken as 9.5 and 130 L/min, respectively, since the mass transfer coefficients depend on water flowrate. Figures 4a and 4b show the average normalized concentrations in the shower and bathroom air during the 10 minute shower period. The influence of volatility on exposure is dramatic with the average normalized concentration for CCl_3F being about three times that for the least volatile DBCP in both the shower and bathroom air. Assuming a breathing rate of 20 m³ per day (3) and considering only the most volatile compounds, the inhalation exposure during a single 10 minute shower is equivalent to about 1.5 times the ingestion exposure incurred by drinking 2 L of the same water. Decreasing the water flowrate to 5 L/min results in an exposure which is about one third that at a flowrate of 13.7 L/min for all volatilities examined. At a shower air exchange rate of 2.4 h⁻¹ the

shower exposure is about 20 times higher than the bathroom exposure. Increasing the exchange rate to 12 h^{-1} results in a reduced shower exposure, but an increase in the average bathroom concentration.

The influence of volatility on exposure will be even more dramatic if the shower is left running for a long period. The low volatility compounds reach steady state rapidly, but the highly volatile VOCs take a long time to reach steady state during which the concentration in air builds up to comparatively high levels. For example, under the reference conditions, the normalized steady state shower and bathroom air concentrations for CCl_3F are 0.39 and 0.29, respectively, taking about 16 hours to be achieved. The equivalent values for DBCP are 0.016 and 0.012, in this case taking only about 3 hours to attain steady conditions. The high contaminant concentration for the more volatile VOCs has serious implications for institutional shower facilities such as health clubs where showers may be operated intermittently for periods of up to 16 hours at a time.

Summary and Conclusions

The two-resistance theory was applied to contaminant volatilization in showers by means of two transient mass balance models. Overall mass transfer coefficients were calculated using previously reported data from two experimental and two residential, full-scale shower systems. The simultaneous volatilization of VOCs of widely varying volatility in the two experimental systems enabled individual liquid- and gas-phase mass transfer coefficients to be determined. This provides a means of accounting for variation in contaminant volatility more accurately than has previously been achieved. The results are strongly influenced by inconsistencies in the mass balance between the amount of VOC volatilized from the water and that recovered in the air.

Measured liquid-phase mass transfer coefficients, K_{LA} , range between 8 and 28 L/min while the gas-phase coefficients, K_{GA} , vary from 130 to 380 L/min. Until more reliable data become available, a ratio of gas-phase to liquid-phase mass transfer coefficients of 17 is recommended for shower systems. This ratio can be used to estimate K_{GA} when only K_{LA} is known. The mass transfer coefficients appear to vary strongly with water flowrate, but variation among shower systems prohibits firm conclusions from being drawn. Allowing for the variation in the Henry's law constant, the influence of water temperature on the mass transfer coefficients is smaller than the observed experimental precision. More

accurate and precise data are needed as well as data more evenly spread over the entire range of contaminant volatilities found in water supply systems. Also, the influence of water flowrate, type of shower system and water temperature should be more closely examined.

The average exposure occurring during a 10 minute shower period in a typical residential shower stall and bathroom is calculated for the entire range of representative volatilities. Shower stall exposures for the most volatile VOCs are higher by a factor of 3 than those for the VOC of lowest volatility. For the most volatile compounds, the inhalation exposure in the shower stall is equivalent to about 1.5 times that incurred through ingestion of 2 L of the same water.

Acknowledgments

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Appendix

A simultaneous solution to the following two differential equations is required:

$$\frac{dy_s}{dt} = A_1 + A_2 y_b + A_3 y_s \quad (E1)$$

$$\frac{dy_b}{dt} = B_1 + B_2 y_s + B_3 y_b \quad (E2)$$

Taking the Laplace transform of eqs E1 and E2 and using the initial conditions at $t = 0$ of y_{si} and y_{bi} gives:

$$sY_s - y_{si} = \frac{A_1}{s} + A_2 Y_b + A_3 Y_s \quad (E3)$$

$$sY_b - y_{bi} = \frac{B_1}{s} + B_2 Y_s + B_3 Y_b \quad (E4)$$

where s represents the transform of the variable t , and where Y_s and Y_b are the transforms of y_s and y_b , respectively. Rearranging eq E3 yields:

$$Y_b = \frac{(s - A_3)}{A_2} Y_s - \frac{A_1}{sA_2} - \frac{y_{si}}{A_2} \quad (E5)$$

which is substituted into eq E4. Following rearrangement and collection of terms, an expression for Y_s is obtained:

$$\frac{Y_s}{y_{si}} = \frac{(s^2 + a_1 s + a_2)}{s(s - r_1)(s - r_2)} \quad (E6)$$

where $a_1 = (A_1 + A_2 y_{bi} - B_3 y_{si})/y_{si}$

$a_2 = (A_2 B_1 - A_1 B_3)/y_{si}$

and $r_{1,2} = \frac{1}{2}(A_3 + B_3) \pm \frac{1}{2}((A_3 + B_3)^2 - 4(A_3 B_3 - A_2 B_2))^{0.5}$

The inverse transform of the right hand side of eq E6 is listed by Roberts and Kaufman (20) and gives eq 13 in the text. Eq 14 is obtained in an analogous fashion.

Glossary

Dimensions of variables are given in parentheses: L is a unit of length, M is a unit of mass, T is a unit of time and Θ denotes temperature.

a	constant defined in eq 7
a ₁ , a ₂	constants defined in eq 13
A	effective air/water interfacial area (L ²)
A ₁ , A ₂ , A ₃	constants defined in eq 11
ACH _b	air changes per hour in bathroom (1/T)
ACH _s	air changes per hour in shower (1/T)
b	constant defined in eq 7
B ₁ , B ₂ , B ₃	constants defined in eq 12
c	concentration of contaminant in water (M/L ³)
c _{in}	concentration of contaminant in inlet water (M/L ³)
c _{out}	concentration of contaminant in outlet water (M/L ³)
D _G	diffusion coefficient for contaminant in air (L ² /T)
D _L	diffusion coefficient for contaminant in water (L ² /T)
J	temperature correction coefficient for Henry's law constant (Θ)
K _G	gas-phase mass transfer coefficient (L/T)
K _L	liquid-phase mass transfer coefficient (L/T)
K _{OL}	overall mass transfer coefficient (liquid phase basis) (L/T)
m	Henry's law constant (dimensionless)
N	overall mass transfer coefficient (dimensionless)
Q _{Gb}	volumetric air flowrate in bathroom (L ³ /T)
Q _{Gs}	volumetric air flowrate in shower (L ³ /T)
Q _L	volumetric water flowrate (L ³ /T)
r ₁ , r ₂	constants defined in eqs 13 and 14
t	time (T)
T	absolute temperature (Θ)
V _L	volume of water in shower (L ³)
V _b	volume of air in bathroom (L ³)
V _s	volume of air in shower (L ³)
y	concentration of contaminant in air (M/L ³)
y _b	concentration of contaminant in bathroom air (M/L ³)

y _{bi}	initial concentration of contaminant in bathroom air (M/L ³)
y _{bin}	concentration of contaminant in influent bathroom air (M/L ³)
y _s	concentration of contaminant in shower air (M/L ³)
y _{si}	initial concentration of contaminant in shower air (M/L ³)
y _{sin}	concentration of contaminant in influent shower air (M/L ³)

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Tables

Table I. Experimental parameters of four full-scale shower studies.

Parameter	Tancrede et al. (12)	Giardino & Andelman (11)	Hodgson et al. (10)	McKone & Knezovich (6)
V_s (L)	1481	1200	2800	2300
V_b (L)	-	-	8100	9600
Q_L (L/min)	13.5	5	13.7	9.5
ACH_s (1/h)	1.4	2.1-3.3	2.4*	≥12
Q_{Gs} (L/min)	34.8	42-66	110*	≥460
ACH_b (1/h)	-	-	0.28	~3
Q_{Gb} (L/min)	-	-	37.8	~480
T_w (°C)	33,42	42,46	40	22,37
Height (m)	1.7	1.8	1.6	1.6
Duration (min)	12	11	10	20

* Calculated, not measured.

Table II. Physical properties of volatile organic chemicals (20°C).

VOC name (abbreviation)	m	J (K)	$D_L \times 10^9$ (m^2/s)	$D_G \times 10^5$ (m^2/s)
Trichlorofluoromethane (CCl ₃ F)	3.0	1030	0.90	0.84
Carbon tetrachloride (CCl ₄)	0.88	1820	0.92	0.72
1,1,1-Trichloroethane (TCA)	0.57	1770	0.90	0.80
Tetrachloroethylene (PCE)	0.55	1990	0.85	0.77
Trichloroethylene (TCE)	0.32	1960	0.94	0.84
Chloroform (CHCl ₃)	0.12	1930	0.97	1.01
1,2,3-Trichloropropane (TCPA)	0.012	1510	0.79	0.73
1,2-Dibromo-3-chloropropane (DBCP)	0.0056	2350	0.76	0.56

Table III. K_{OLA} values calculated from the data of Tancrede et al. (12).

VOC	T_w (°C)	Q_L (L/min)	c_{in} (ug/L)	c_{out} (ug/L)	y_s (ug/L)	Recov (%)	K_{OLA}^* (L/min)	$K_{OLA}^\#$ (L/min)	Ratio (*/#)
CCl ₄	33	13.5	.104	.025	.0046	72	20.9	10.9	1.9
PCE	33	13.5	.26	.086	.0083	60	16.3	7.2	2.3
TCE	33	13.5	3.1	1.2	.118	77	15.4	9.3	1.7
CHCl ₃	33	13.5	1.5	.70	.050	81	14.6	8.4	1.7
TCPA	33	13.5	90	71	.66	43	4.3	1.7	2.5
CCl ₄	42	13.4	.094	.022	.0043	74	21.0	11.4	1.8
PCE	42	13.4	.24	.078	.0078	60	16.2	7.1	2.3
TCE	42	13.4	2.8	1.0	.129	93	14.7	12.3	1.2
CHCl ₃	42	13.4	1.4	.67	.056	91	12.9	9.9	1.3
TCPA	42	13.4	89	73	1.03	82	6.0	3.1	2.0

*Calculated from water data, #Calculated from air data

Table IV. K_{OLA} values calculated from the data of Giardino & Andelman (11).

VOC	T_w (°C)	Q_{Gs} (L/min)	c_{in} (ug/L)	c_{out} (ug/L)	Recov (%)	K_{OLA}^* (L/min)	$K_{OLA}^\#$ (L/min)	Ratio (*/#)
TCE	46	66	920	170	102	8.9	9.2	0.97
$CHCl_3$	42	52	580	260	128	4.4	7.4	0.60
DBCP	42	42	1680	1300	-	1.9	-	-

$Q_L = 5$ L/min, *Calculated from water data, #Calculated from air data

Table V. K_{OLA} values calculated from the data of Hodgson et al. (10).

VOC	Person present	c_{in} (ug/L)	c_{out} (ug/L)	y_{bi} (ug/L)	y_b (ug/L)	K_{OLA}^* (L/min)
CCl_3F	No	11	1.0	.0040	.011	34
CCl_3F	Yes	9.4	1.8	.0045	.012	25
TCA	No	3.4	0.5	.0014	.0066	29
TCA	Yes	3.1	0.8	.0066	.0096	21
PCE	No	18	3.2	.0060	.025	26
PCE	Yes	29	4.2	.0036	.022	27
TCE	No	2.7	0.4	nd [#]	nd	30
TCE	Yes	3.0	0.4	nd	nd	31

$Q_L = 13.7$ L/min, *Calculated from water data, # not determined

Table VI. K_{OLA} values calculated from the data of McKone & Knezovich (6).

VOC	T_w (°C)	c_{in} (ug/L)	c_{out} (ug/L)	K_{OLA}^* (L/min)
TCE	22	100	42#	8.6
TCE	37	100	37#	9.7

$Q_L = 9.5$ L/min, *Calculated from water data, # average of 4 runs

Table VII. Individual mass transfer coefficients calculated from the data of four studies.

Study	Q_L (L/min)	T_w (°C)	K_{LA} (L/min)	K_{GA} (L/min)	K_G/K_L
G	5	42-46	9.5	130	13
M	9.5	22	8.6	-	-
M	9.5	37	9.7	-	-
T	13.4	42	17	380	22
T	13.5	33	18	320	17
H	13.7	40	28	-	-

Figures

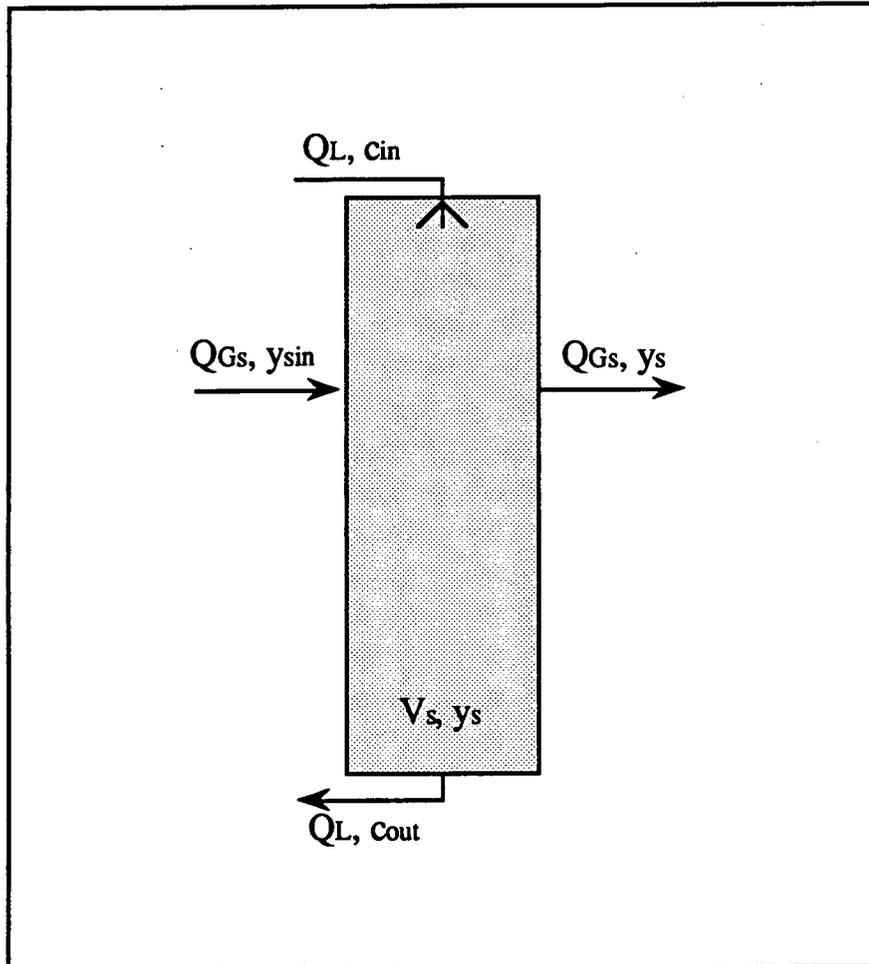


Figure 1a. Idealized schematic representations of shower stall showing air and water flows. Symbols described in text.

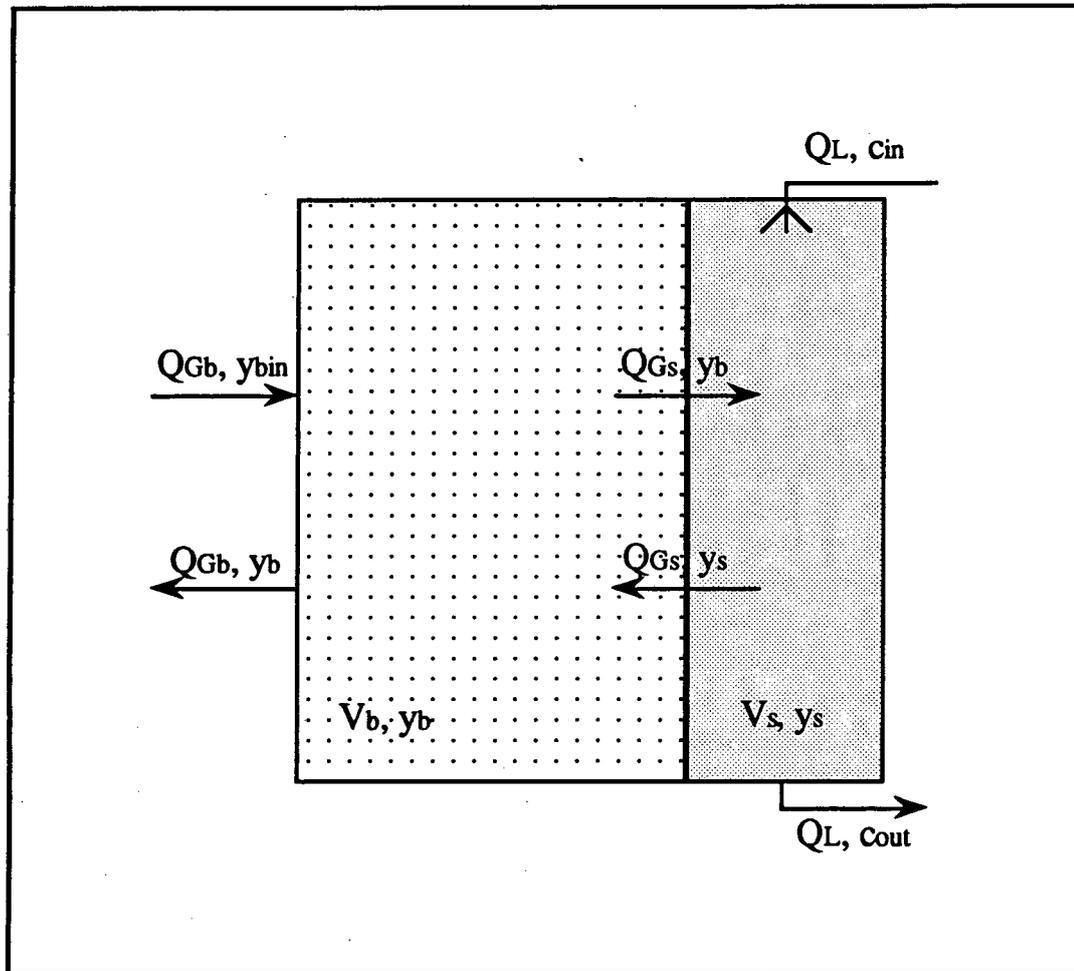


Figure 1b. Idealized schematic representations of shower stall and bathroom showing air and water flows. Symbols described in text.

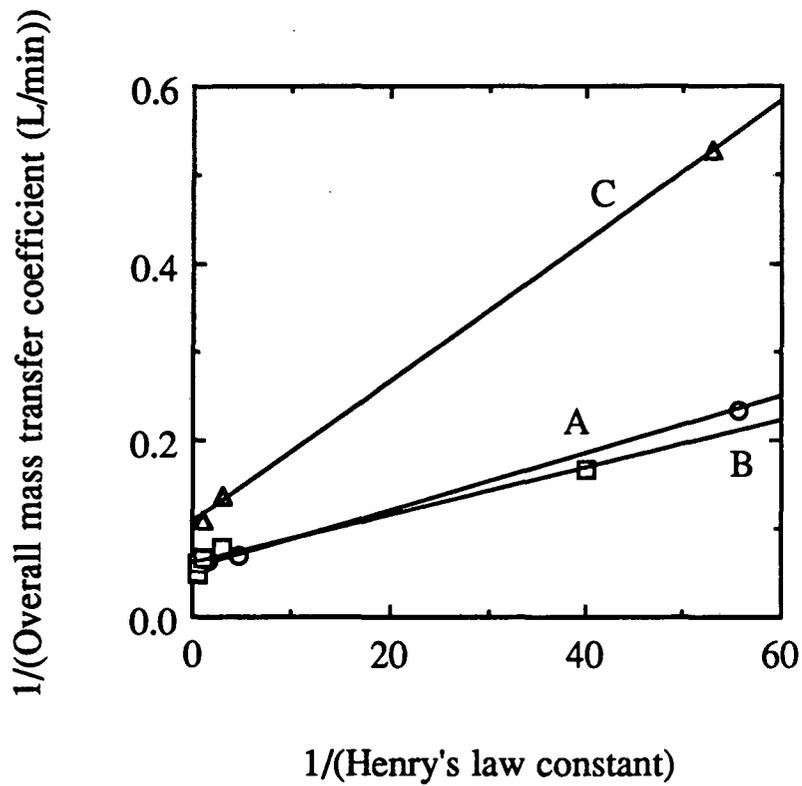


Figure 2. Plots of $1/K_{OLA}$ vs $1/m$ where plot A is for study T at 33°C , plot B is for study T at 42°C and plot C is for study G.

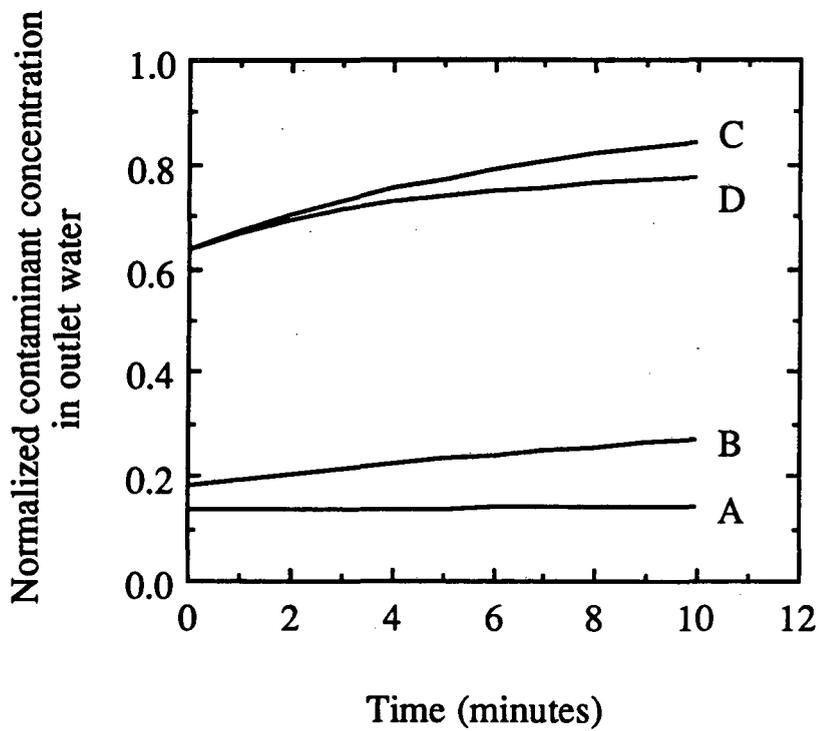


Figure 3a. Normalized contaminant concentrations in outlet water with time at reference conditions. Concentrations are normalized with respect to the contaminant concentration in the inlet water. Plots A, B and C are for CCl_3F , CHCl_3 and DBCP at reference conditions, respectively, and plot D shows the effect on the DBCP concentration of increasing the shower air exchange rate from the reference level of 2.4/h to 12/h.

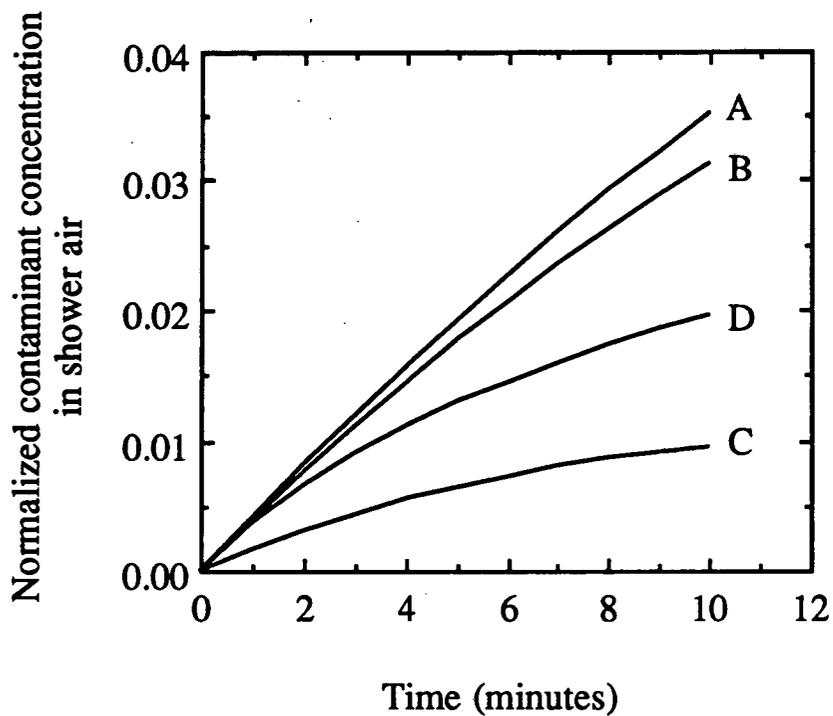


Figure 3b. Normalized contaminant concentrations in shower air with time at reference conditions. Concentrations are normalized with respect to the contaminant concentration in the inlet water. Plots A, B and C are for CCl_3F , CHCl_3 and DBCP at reference conditions, respectively, and plot D shows the effect on the CHCl_3 concentration of increasing the shower air exchange rate from the reference level of 2.4/h to 12/h.

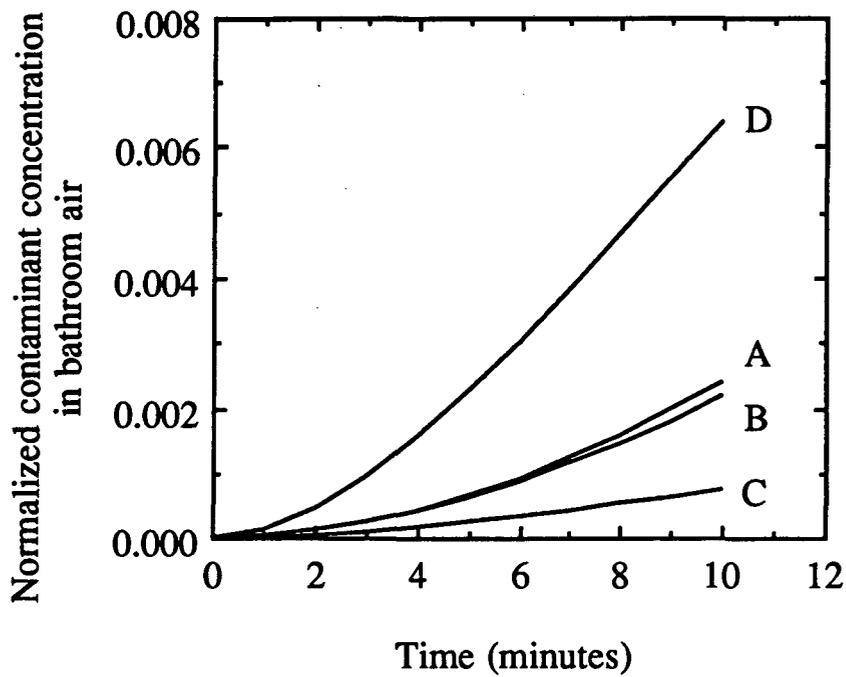


Figure 3c. Normalized contaminant concentrations in bathroom air with time at reference conditions. Concentrations are normalized with respect to the contaminant concentration in the inlet water. Plots A, B and C are for CCl_3F , CHCl_3 and DBCP at reference conditions, respectively, and plot D shows the effect on the CHCl_3 concentration of increasing the shower air exchange rate from the reference level of 2.4/h to 12/h.

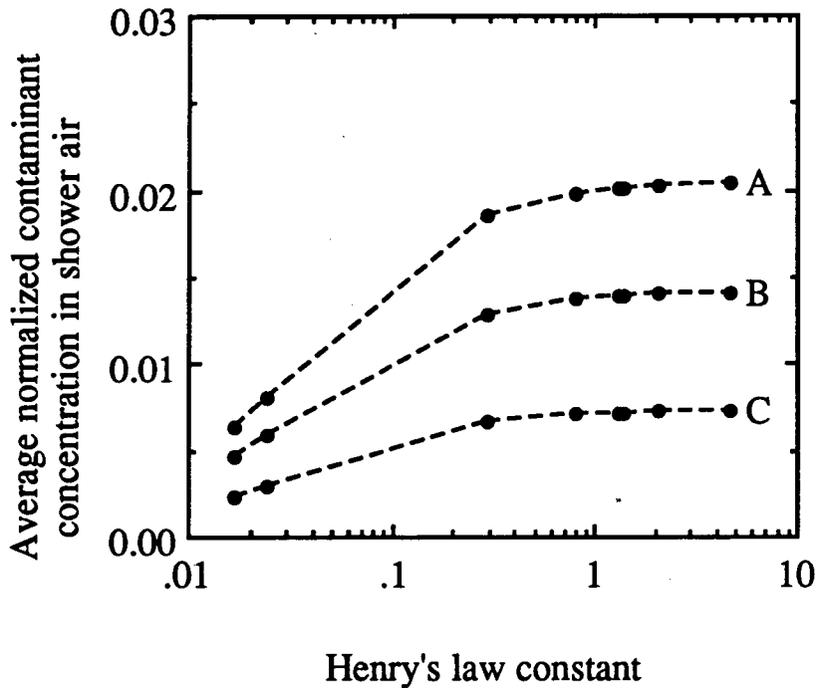


Figure 4a. Estimate of potential exposure showing the influence of volatility on the average contaminant shower air concentration during a 10 minute shower. Concentrations are normalized with respect to the concentration of the inlet water. Plot A shows all eight VOCs given in Table II and uses the reference conditions, plot B shows the effect of increasing the shower air exchange rate from the reference level of 2.4/h to 12/h and plot C shows the effect of decreasing the water flowrate from the reference level of 13.7 L/min to 5 L/min.

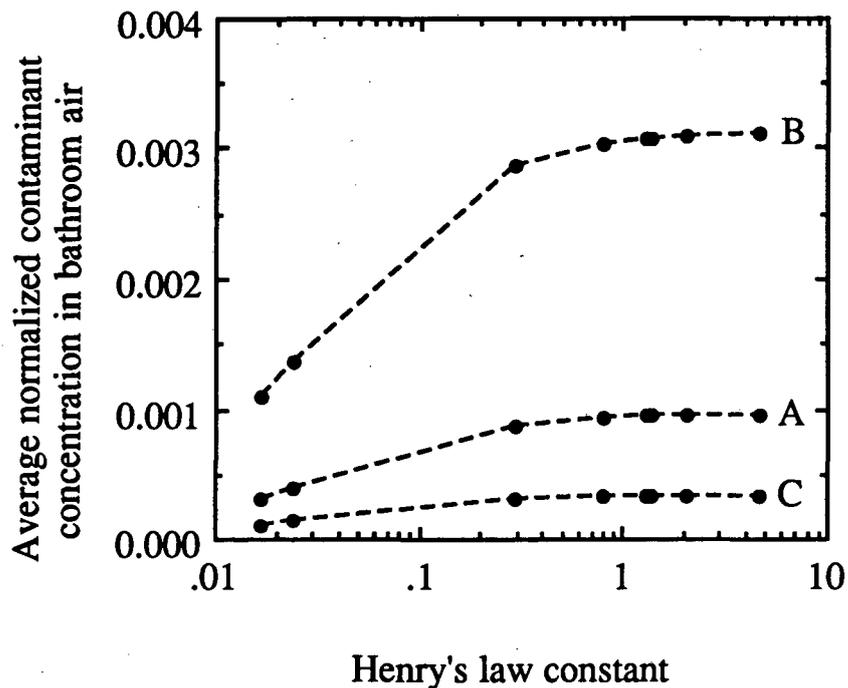


Figure 4b. Estimate of potential exposure showing the influence of volatility on the average contaminant bathroom air concentration during a 10 minute shower. Concentrations are normalized with respect to the concentration of the inlet water. Plot A shows all eight VOCs given in Table II and uses the reference conditions, plot B shows the effect of increasing the shower air exchange rate from the reference level of 2.4/h to 12/h and plot C shows the effect of decreasing the water flowrate from the reference level of 13.7 L/min to 5 L/min.

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