

Volatilization of Chemicals from Tap Water to Indoor Air from Contaminated Water Used for Showering

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Volatile organic compounds (VOCs) may enter indoor air during the use of contaminated tap water. When this occurs, occupants can become exposed to potentially toxic VOCs via the inhalation route. The propensity for VOCs to volatilize into indoor air during the routine use of showers was investigated. A series of mass transfer experiments were conducted while a shower was operated within an enclosed chamber. Acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane were used as volatile tracers. Chemical-specific stripping efficiencies and mass transfer coefficients were determined. An assessment of the importance of gas-phase resistance to mass transfer from water to air was also completed. Chemical-specific stripping efficiencies ranged from 6.3% (for acetone) to 80% (for cyclohexane) for household showers used under normal conditions. As described in this paper, data resulting from this study allow for the determination of overall mass transfer coefficients, and corresponding volatilization rates, for any showering event and chemical of interest. As such, the information presented herein should lead to improved estimates of human inhalation exposure to toxic chemicals that volatilize from water to indoor air.

Introduction

Most people perceive that pollution occurs primarily in the open (outdoor) environment. However, the indoor microenvironment can also become contaminated with harmful pollutants. In fact, the concentrations of many volatile organic compounds (VOCs) and pesticides in indoor air have been observed to far exceed those in outdoor air (1). One potential source of pollution within the home is chemically contaminated tap (drinking) water. It is commonly assumed that exposure to toxic contaminants in tap water is mainly via the ingestion pathway. However, many VOCs can volatilize appreciably during normal water use in the home. Examples of VOCs commonly found in potable water include chloroform and methyl *tert*-butyl ether (MTBE).

Previous researchers have focused on showering as a potential source of indoor air pollution, and it has been shown

that showering increases the likelihood that a VOC will volatilize and become an indoor air pollutant subject to human inhalation exposure (2-6). However, only a few researchers have successfully quantified the amount of chemical in both the gas phase and the liquid phase to accurately determine the percent of mass recovery (5). In addition, previous researchers have focused only on highly volatile chemicals, thus precluding estimates of gas-phase resistance to mass transfer. The purpose of our research was to assess and quantify the mass transfer of VOCs from water to air during showering with contaminated tap water. A series of mass transfer experiments were conducted while a shower was operated within an enclosed chamber. Five tracer chemicals (acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane) were dissolved in tap water and metered through the shower. This paper reports on the results of the shower experiments, with an emphasis on practical applications involving the extrapolation of experimental results to any chemical of interest.

Background

There are many factors that can affect the volatilization process for showers. These factors include chemical properties, water temperature, water flow rate, nozzle design, and the ventilation rate of the shower stall. The mass transfer mechanisms that characterize the emissions from a given source are often quantified using an overall mass transfer coefficient (K_L). In accordance with two-film theory (7), the inverse of the overall mass transfer coefficient for any chemical dissolved in water can be expressed as the reciprocal of the sum of the resistance to the exchange between the liquid and gas phases. However, it is often difficult to separate mass transfer coefficients and the interfacial area (A) over which mass transfer occurs. This interfacial area corresponds to the film surface between the liquid and the adjacent air through which molecules must pass by the process of diffusion to vaporize into air. Therefore, the inverse of the overall mass transfer coefficient for any chemical dissolved in water can be expressed as in

$$\frac{1}{K_L A} = \frac{1}{k_l A} + \frac{1}{k_g A H_c} \quad (1)$$

where K_L = overall mass transfer coefficient (L/T), A = interfacial area (L²), k_l = liquid-phase mass transfer coefficient (L/T), k_g = gas-phase mass transfer coefficient (L/T), and H_c = Henry's law constant (L³_{liq}/L³_{gas}).

Hence, $1/K_L$ represents a chemical's overall resistance to mass transfer from the liquid phase to the gas phase. The term $1/k_l$ represents the liquid-phase resistance to mass transfer, and $1/(k_g H_c)$ is referred to as the gas-phase resistance to mass transfer. For $(k_g H_c) \gg k_l$, gas-phase resistance to mass transfer is small and the overall mass transfer coefficient is approximately equal to the liquid-phase mass transfer coefficient. This condition is generally true for highly volatile compounds such as radon or trichloroethene.

On the basis of two-film theory, liquid- and gas-phase mass transfer coefficients are directly related to molecular diffusion coefficients for the chemical of interest and the hypothetical film thickness. In dilute aqueous solutions, hydrodynamic factors that define the film thickness are independent of chemical concentrations. Therefore, the film thickness is independent of the chemical of concern, and the ratio of liquid-phase mass transfer coefficients for two compounds can be expressed as

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$$\Psi_1 = \frac{k_{li}}{k_{lj}} = \frac{k_{li}A}{k_{lj}A} = \left(\frac{D_{li}}{D_{lj}}\right)^{n_1} \quad (2)$$

where Ψ_1 = liquid-phase mass transfer relational parameter (dimensionless), k_{li} = liquid-phase mass transfer coefficient for chemical i (L/T), k_{lj} = liquid-phase mass transfer coefficient for chemical j (L/T), A = interfacial area (L²), D_{li} = liquid-phase molecular diffusion coefficient for chemical i (L²/T), D_{lj} = liquid-phase molecular diffusion coefficient for chemical j (L²/T), and n_1 = liquid-phase power constant (dimensionless).

Similarly, the ratio of gas-phase mass transfer coefficients for two compounds can be expressed as

$$\Psi_g = \frac{k_{gi}}{k_{gj}} = \frac{k_{gi}A}{k_{gj}A} = \left(\frac{D_{gi}}{D_{gj}}\right)^{n_2} \quad (3)$$

where Ψ_g = gas-phase mass transfer relational parameter (dimensionless), k_{gi} = gas-phase mass transfer coefficient for chemical i (L/T), k_{gj} = gas-phase mass transfer coefficient for chemical j (L/T), A = interfacial area (L²), D_{gi} = gas-phase molecular diffusion coefficient for chemical i (L²/T), D_{gj} = gas-phase molecular diffusion coefficient for chemical j (L²/T), and n_2 = gas-phase power constant (dimensionless).

The power constants, n_1 and n_2 , vary between 0.5 for penetration theory (8) and 1.0 for two-film theory (7). A value of 0.67 is commonly applied (9–11).

Using eq 1, and assuming k_{gj}/k_{lj} is equal to k_{gi}/k_{li} (12), the ratio of overall mass transfer coefficients for chemicals i and j can be expressed as (see Supporting Information for details about the derivation of this equation)

$$\Psi_m = \frac{K_i}{K_j} = \Psi_1 \Psi_g \left(\frac{H_{ci}}{H_{cj}}\right) \left[\frac{1 + \left(\frac{k_{gj}}{k_{lj}}\right) H_{cj}}{\Psi_1 + \Psi_g H_{ci} \left(\frac{k_{gj}}{k_{lj}}\right)} \right] \quad (4)$$

where Ψ_m = ratio of overall mass transfer coefficients for chemicals i and j (dimensionless), K_i = overall mass transfer coefficient for chemical i (L/T), K_j = overall mass transfer coefficient for chemical j (L/T), k_{gi} = gas-phase mass transfer coefficient for chemical i (L/T), k_{gj} = gas-phase mass transfer coefficient for chemical j (L/T), A = interfacial area (L²), H_c = Henry's law constant (L³_{liq}/L³_{gas}), k_{li} = liquid-phase mass transfer coefficient for chemical i (L/T), and k_{lj} = liquid-phase mass transfer coefficient for chemical j (L/T).

A common assumption made when in the relation of overall mass transfer coefficients between two chemicals is that $K_{li}/K_{lj} = \Psi_1$. This relationship is valid only when gas-phase resistance to mass transfer is negligible for each compound, that is, when both compounds are highly volatile. In this case, the relationship requires knowledge of only the liquid molecular diffusion coefficients for each compound.

Mass transfer occurs in several regions within the shower system. These regions include water droplet formation, droplet acceleration to terminal velocity, fall of droplet at terminal velocity, and impact of droplet on shower surfaces. Little (11) developed equations to predict the rate of mass transfer from liquid droplets to surrounding air (see Supporting Information for Little's equations).

If C_g is assumed to be constant for the relatively short residence time of a shower droplet, the equation derived by Little (11) may be solved in terms of the outlet liquid concentration.

$$C_{l,out} = C_{l,in} \exp\left(-\frac{K_L A}{Q_1}\right) + \left(\frac{C_g}{H_c}\right) \left[1 - \exp\left(-\frac{K_L A}{Q_1}\right)\right] \quad (5)$$

where $C_{l,out}$ = outlet chemical concentration in water (M/L³), $C_{l,in}$ = inlet chemical concentration in water (M/L³), K_L = overall mass transfer coefficient (L/T), A = interfacial area between water stream and adjacent air (L²), Q_1 = volumetric flow rate (L³/T), C_g = chemical concentration in air adjacent to water (M/L³), and H_c = Henry's law constant (L³_{liq}/L³_{gas}).

Similarly, Little (11) developed a mass balance model to characterize the change in gas-phase concentration during shower operation (see Supporting Information for details).

The equations developed by Little (11) for both liquid and gas-phase concentrations can be solved simultaneously to yield

$$C_g = \frac{B}{D} + \left(C_{g,0} - \frac{B}{D}\right) \exp(-Dt) \quad (6)$$

$$B = \frac{\left[Q_1 C_{l,in} \left(1 - \exp\left(-\frac{K_L A}{Q_1}\right)\right) + Q_g C_{g,in}\right]}{V_g} \quad (7)$$

$$D = \frac{\left[\left(\frac{Q_1}{H_c}\right) \left(1 - \exp\left(-\frac{K_L A}{Q_1}\right)\right) + Q_g\right]}{V_g} \quad (8)$$

where $C_{l,out}$ = outlet chemical concentration in water (M/L³), $C_{l,in}$ = inlet chemical concentration in water (M/L³), A = interfacial area between water stream and adjacent air (L²), Q_1 = volumetric flow rate (L³/T), $C_{g,0}$ = initial chemical concentration in air (M/L³), $C_{g,in}$ = inlet chemical concentration in air (M/L³), Q_g = gas flow rate (L³/T), H_c = Henry's law constant (L³_{liq}/L³_{gas}), V_g = headspace volume (shower stall volume) (L³), K_L = overall mass transfer coefficient (L/T), t = showering time (T), and C_g = chemical concentration in air adjacent to water (M/L³).

The chemical stripping efficiency for a flow-through system with a constant volumetric flow rate of water and no chemical reactions is defined as

$$\eta = 1 - (C_{l,out}/C_{l,in}) \quad (9)$$

where η = stripping efficiency (fractional), $C_{l,out}$ = outlet chemical concentration in water (M/L³), and $C_{l,in}$ = inlet chemical concentration in water (M/L³).

Experimental Approach

A series of experiments were completed to determine volatilization rates from showers. The purpose of this study was to develop and evaluate improvements to existing extrapolation methods for relating mass transfer coefficients and volatilization rates between chemicals.

Experiments were conducted within a stainless steel exposure chamber. The use of an enclosed chamber allowed for the measurements of both liquid- and gas-phase concentrations and volumetric flow rates, which resulted in a mass closure assessment. A cocktail of five tracer chemicals representing a wide range of Henry's law constants was used in each experiment. The chemicals included acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane. Table 1 provides a summary of the physicochemical properties for the selected tracers. Henry's law constants for experiments completed at temperatures other than 25 °C were adjusted to reflect the temperature change (12).

The water used in each experimental system was spiked with a multitracer solution containing the five tracers. The tracer solutions were prepared using Tedlar bags (volume of 3 L) fitted with a stainless steel hose/valve with locking screw and replaceable Teflon-lined septum with a stainless steel cap. The bags were filled with tap water, and excess air was removed by the agglomeration and collection of bubbles near the bag's valve immediately after water injection. Known amounts of each chemical were injected into the bags using syringes adequately cleaned with methanol and water. To

TABLE 1. Physicochemical Properties^a of Selected Chemicals (12, 17, 18, 19)

chemical	H_c at 25 °C ($\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$)	D_l at 24 °C (cm^2/s)	D_g at 24 °C (cm^2/s)	T_b (°C)	ρ (kg/L)	S (mg/L)	P_v° (mmHg)
acetone	0.0015	1.1E-05	0.11	56.5	0.79	miscible	270
ethyl acetate	0.005	9.5E-06	0.092	77	0.89	64000	115
toluene	0.27	9.1E-06	0.085	111	0.87	515	22
ethylbenzene	0.33	8.4E-06	0.077	136	0.87	152	7
cyclohexane	7.2	9.0E-06	0.088	80.7	0.77	58	77

^a H_c = Henry's law constant; D_l = liquid-phase diffusion coefficient; D_g = gas-phase diffusion coefficient; T_b = normal boiling point at 1 atm; ρ = pure-chemical density at 25 °C; S = solubility in water at 25 °C; P_v° = pure-chemical vapor pressure at 25 °C.

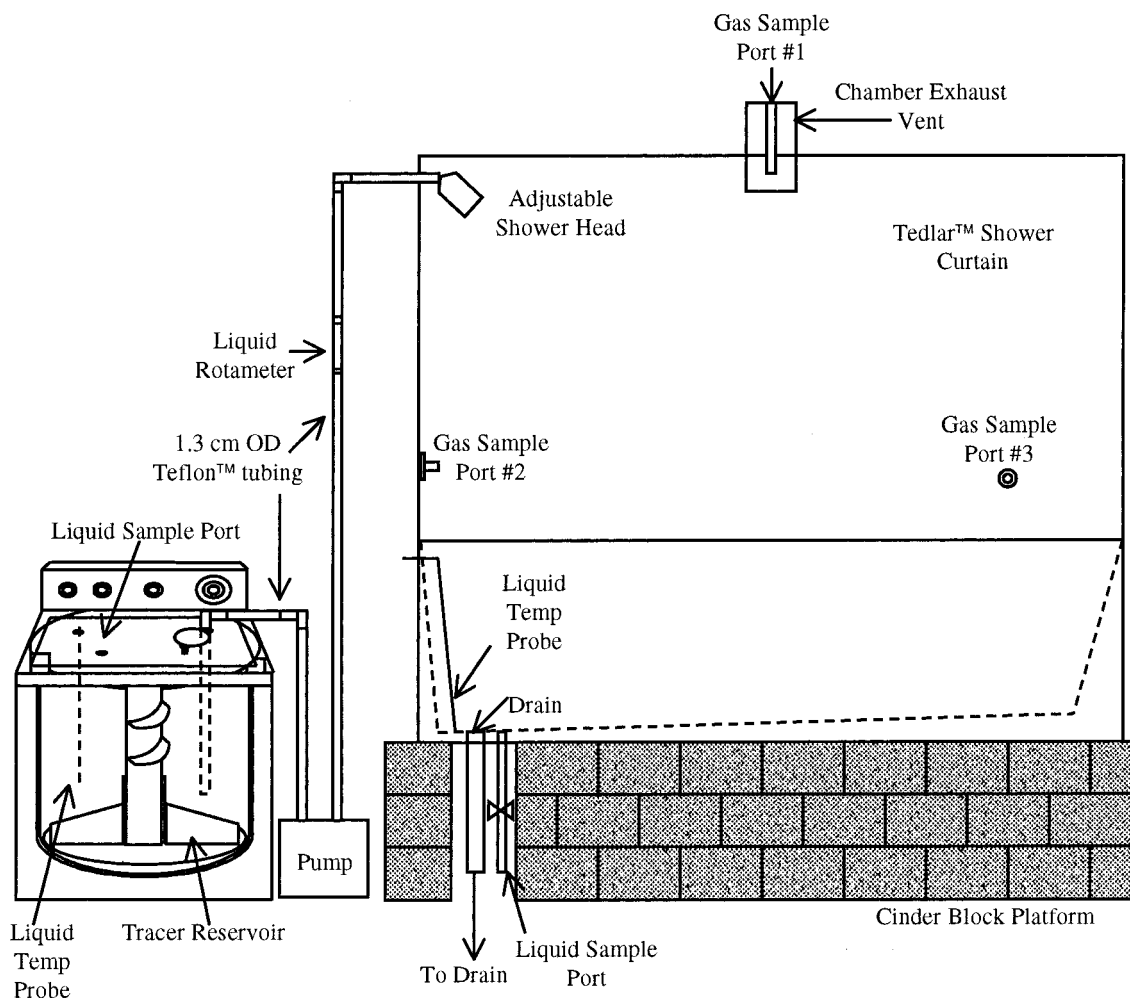


FIGURE 1. Shower experimental system.

facilitate dissolution, bags were manually agitated and allowed to sit for periods over 24 h prior to use in any experiments. This predissolved solution was added to the experimental system using a peristaltic pump with Teflon tubing.

A shower with bathtub stall (1.7 m³ total volume) was installed on a 58 cm high cinder block platform within the stainless steel chamber (Figure 1). A washing machine placed outside the chamber was used as the water supply for the shower experiments. The mixture of tracer chemicals from the Tedlar bags were added to the washing machine as it filled. The reservoir's contents were further mixed by using wash cycle agitation. An adjustable low-flow (9.5 L/min maximum) shower head was used for all experiments. The shower head could be adjusted between fine and coarse spray. The experimental flow rates were selected on the basis of typical uses and the restrictions of the shower head.

Liquid samples were collected from the washing machine reservoir at the beginning and end of each experiment. Three

gas sample ports were installed in the shower system to better understand the gas-phase chemical concentration distribution in the stall.

A liquid temperature probe was submerged in the tracer reservoir, and a second probe was inserted in the shower stall near the drain. Liquid temperatures at these two locations were continuously measured using a thermocouple and digital monitor.

Shower experiments were conducted by varying the shower operating conditions including water temperature, liquid flow rate, and shower spray type. A total of eight experiments involving a 2³ factorial design were completed with two additional experiments serving as replicates. Liquid temperature ranged from 21 to 36 °C. Liquid flow rate was set to either 6.1 L/min to represent a low flow rate or 9.1 L/min to represent a high flow rate. Gas flow rate ranged from 343 to 379 L/min. The shower system was characterized by air exchange rates ranging from 12 to 13 air changes per hour (ACH). The effects of the spray type was studied by

TABLE 2. Mass Transfer Coefficients and Stripping Efficiencies for Individual Experiments

expt	k_g/k_l	K_LA (L/min)/stripping efficiency (%)				
		acetone	ethyl acetate	toluene	ethylbenzene	cyclohexane
1	153	1.8/6.3	2.9/15	8.8/61	8.9/62	9.6/65
2	223	3.0/8.4	4.0/15	11/68	11/68	12/73
3	200	1.4/9.1	2.3/20	6.2/63	6.0/63	6.5/66
4	195	1.5/9.3	2.5/20	6.4/64	6.2/63	6.7/66
5	111	2.8/13	5.5/27	11/68	11/68	13/75
6	131	3.4/11	6.9/28	13/75	13/75	14/77
6-replicate	153	3.7/12	6.7/29	12/74	12/74	13/77
7	110	2.2/16	3.8/32	8.4/74	8.2/73	8.6/76
8	143	2.3/14	4.7/33	8.1/73	7.9/72	8.4/75
8-replicate	138	2.5/15	5.3/36	9.2/77	8.8/75	9.9/80
av	156	2.5/11	4.5/26	9.4/70	9.3/69	10/73

using the coarse or fine settings in the shower head. (Experimental conditions for each experiment can be found in the Supporting Information.)

Shower experiments lasted 8 min, during which time five liquid-phase samples were collected from both the tracer reservoir and the shower stall. The experimental system was retrofitted with a liquid sample port made of Teflon. Liquid samples were collected in 22 mL glass vials that were sealed with an aluminum cap fitted with a Teflon-faced septum.

A total of 12 gas samples were collected from the three ports to determine the gas-phase concentration. A gaseous sample was also collected after the experiment had ended and no water flowed through the system. Air flow rates were confirmed using a bubble flowmeter between the adsorbent tube and pump. Breakthrough tests were completed to ensure that each tracer was entirely collected on a single tube. (More details about the sample collection are provided in the Supporting Information.)

Mass closure for the shower experiments was assessed using

$$\% \text{ mass recovery} = \frac{Q_l \int_{t_1}^{t_2} C_{l,\text{out}} dt + V_g C_{g,2} + Q_g \int_{t_1}^{t_2} C_g dt}{Q_l \bar{C}_{l,\text{in}}(t_2 - t_1) + V_g C_{g,1}} \quad (10)$$

where Q_l = liquid flow rate in and out of the system (L^3/T), $C_{l,\text{out}}$ = chemical concentration in water at outlet (M/L^3), V_g = headspace volume (shower stall volume) (L^3), $C_{g,2}$ = chemical concentration in gas phase at time 2 (M/L^3), Q_g = ventilation rate of the system (L^3/T), C_g = chemical concentration in gas phase (M/L^3), $\bar{C}_{l,\text{in}}$ = average chemical concentration measured in tracer reservoir (M/L^3), t_1 = time 1 (T), t_2 = time 2 (T), and $C_{g,1}$ = chemical concentration in gas phase at time 1 (M/L^3).

Results and Discussion

Chemical stripping efficiencies and K_LA values were determined for each time period and averaged, respectively, to obtain final values. Values of k_g/k_l , k_lA , and k_gA were estimated on the basis of the averaged K_LA values for each chemical. Values of k_g/k_l were determined by minimization of residuals between predicted values of Ψ_m (from eq 4) and experimental values of Ψ_m , as determined by all possible ratios of K_LA among the five tracer chemicals. Values of k_lA , and k_gA were determined using eq 1 in conjunction with H_c , experimental values of K_LA , and the aforementioned values of k_g/k_l for each experiment. Values of K_LA and volatilization rates for each chemical and experiment are listed in Table 2. Ratios of k_g/k_l are also presented for each experiment and varied from 110 to 223 with an average of 156.

For all chemicals, the highest overall mass transfer coefficients were observed for experiments 6 and 6-replicate, each with conditions represented by a high water temperature, high water flow rate, and fine spray. In contrast, the lowest overall mass transfer coefficients were observed for experiments 3 and 4, that is, low water temperature and low water flow rate.

Temperature was the factor with the greatest influence on chemical stripping efficiencies, a finding that is consistent with those reported by Giardino and Andelman (13), Tancrede et al. (14), and McKone and Knezovich (15). For acetone, stripping efficiencies were <10% for all low-temperature experiments and between 10 and 16% for all high-temperature experiments. Stripping efficiencies for ethyl acetate ranged from 15 to 20% for low-temperature experiments and from 27 to 36% for high-temperature experiments. Both stripping efficiencies and overall mass transfer coefficients were nearly identical for toluene and ethylbenzene, an expected result given the similarity of their Henry's law constants and one that serves as an internal check of experimental quality. Stripping efficiencies for toluene and ethylbenzene ranged from 61 to 68% for low-temperature experiments and from 68 to 77% for high-temperature experiments. Both stripping efficiencies and overall mass transfer coefficients were consistently highest for cyclohexane, with stripping efficiencies ranging from 65 to 73% for low-temperature experiments and from 75 to 80% for high-temperature experiments.

In general, the effects of spray type (coarse versus fine) and water flow rate (6.1 versus 9.1 L/min) had little influence on chemical stripping efficiencies. Stripping efficiencies for both acetone and ethyl acetate did consistently decrease with increasing water flow rate, but generally by only a few percent (absolute). A similar trend was not observed for the other volatile tracers.

Mass closure was assessed using eq 10. Mass closure values ranged from 96 to 103% for acetone, from 98 to 108% for ethyl acetate, from 77 to 106% for toluene, from 64 to 92% for ethylbenzene, and from 66 to 85% for cyclohexane. The more volatile compounds (i.e., toluene, ethylbenzene, and cyclohexane) tended to achieve mass closure values of <100%. While the mass recoveries for ethylbenzene and cyclohexane were consistently below 100%, experimental stripping efficiencies and mass transfer coefficients for ethylbenzene were always similar to those for toluene, as expected on the basis of their similar chemical properties. These results should lend confidence in the experimental results. Although cyclohexane mass recoveries were lower than desired, the stripping efficiencies and mass transfer coefficients for cyclohexane were consistently high, and excellent agreement was observed between two sets of replicate experiments.

A series of tests were conducted to determine the effect of absorption of chemicals onto wetted surfaces such as shower walls. A shower experiment was run with clean (no chemicals) warm water. At the end of the experiment, preweighed sponges were used to soak up the water collected on the surfaces of the shower stall (i.e., plastic-coated fiberglass wall and floor, stainless steel ceiling, and shower curtain). Sponges were weighed after water collection to estimate the volume of water collected. On the basis of this experiment, the total volume of water collected was 0.2 L. Using the gas-phase concentration measured for each chemical and assuming that equilibrium conditions were achieved at the wetted surfaces, the chemical concentration at the wall surface can be predicted. For example, the maximum gas-phase concentration measured for cyclohexane was ~0.01 mg/L. Using the Henry's law constant for cyclohexane at 35 °C, $10 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$, the expected liquid-phase concentration would be 0.001 mg/L. For a total water

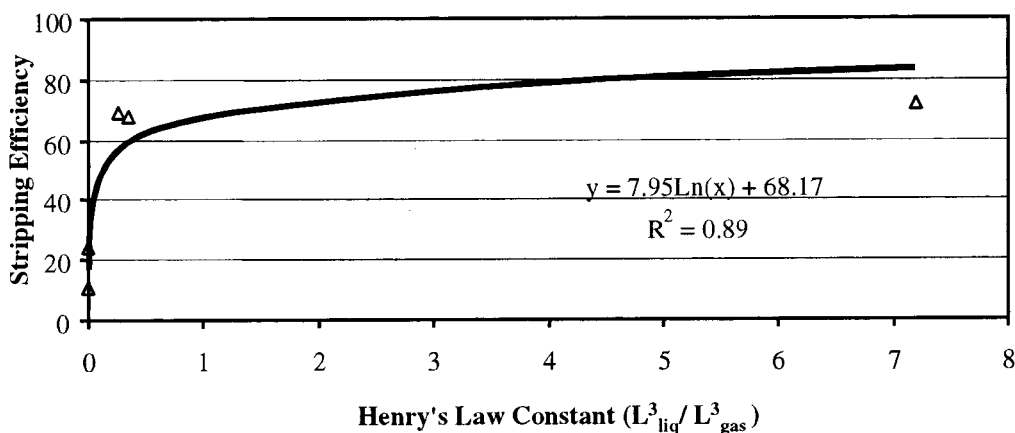


FIGURE 2. Relationship between Henry's law constant and average stripping efficiency.

volume at the surfaces of 0.2 L, the total mass of cyclohexane in the shower stall surfaces would be 0.0002 mg. The total mass of cyclohexane emitted from the shower stall was 17 mg. Therefore, the surfaces of the shower stall would not contribute significantly to the total mass of cyclohexane emitted. Water can also accumulate on the bottom of the bathtub during routine use of the shower. The shower experiments were designed to prevent this pool of water from forming on the bottom of the bathtub (i.e., the bathtub was tilted). Therefore, the effects that this pool of water may have on volatilization could not be studied.

The approach used to derive this methodology assumes that the shower system is well-mixed. To validate this assumption, the shower stall was divided into three zones and gas-phase concentrations were measured at each sampling port shown in Figure 1 (i.e., gas sampling ports 1–3). The average percentages for acetone in each zone were 32% for sample port 1, 34% for sample port 2, and 34% for sample port 3. The average concentrations for acetone were equal for ports 2 and 3. The gas-phase chemical distribution for other tracers followed the same trend as acetone. On the basis of these results, it appears that the shower stall was well-mixed, leading to reasonably uniform gas-phase concentrations.

To demonstrate the effects of chemical properties on volatilization, an average stripping efficiency was determined for each chemical and is plotted in Figure 2 as a logarithmic function of Henry's law constant at 25 °C. This plot may also be used to approximate the chemical stripping efficiency given a known Henry's law constant. The best-fit curve associated with the averaged data in Figure 2 is derived from the following empirical equation

$$\eta = 7.95 \ln(H_c) + 68.17 \quad (11)$$

where η = stripping efficiency (percent) and H_c = Henry's law constant (L^3_{liq}/L^3_{gas}).

Equation 11 is presented simply as an approximation and involves averaging over a set of experimental conditions that should provide reasonable bounds relative to actual in-home use of showers. It does not account for the time-dependent nature of stripping efficiencies during the showering event, that is, decreasing values of η as mass accumulates in shower air. This phenomenon is particularly important for VOCs with lower values of H_c , that is, for which equilibrium conditions may be rapidly approached between the aqueous and gaseous phases. Although caution should be used in the application of eq 11 to chemicals beyond the range of conditions for which it was developed, it provides some insight into differences in potential volatilization rates for various types of chemicals. Although values found in the

TABLE 3. Physicochemical Properties for Toluene and Methyl Ethyl Ketone (12, 17, 19)

chemical	H_c at 25 °C (m^3_{liq}/m^3_{gas})	D_i at 24 °C (cm^2/s)	D_g at 24 °C (cm^2/s)
toluene	0.27	9.1 E-06	0.085
methyl ethyl ketone	0.006	9.8 E-06	0.097

literature were developed under a variety of experimental conditions, they are in good agreement with eq 11. For example, Tancrede et al. (14) reported carbon tetrachloride ($H_c = 1.67 m^3_{liq}/m^3_{gas}$ at 33 °C and $2.34 m^3_{liq}/m^3_{gas}$ at 42 °C) stripping efficiencies ranging from 76 to 77%. Values obtained using eq 9 ranged from 72 to 75%. As another example, the value of H_c that leads to a stripping efficiency of 55% is $0.19 m^3_{liq}/m^3_{gas}$ at 25 °C. This value is consistent with chloroform, a common disinfection byproduct. Tancrede et al. (14) reported chloroform stripping efficiencies of 52–53%, and Giardino (13) reported stripping efficiencies ranging from 44 to 52%, both in reasonable agreement with eq 11.

Alternatively, on the basis of experimental results, values of K_LA can be used in conjunction with associated source mass balance models to determine chemical emissions. The procedure for predicting mass emissions for any chemical of interest is described below. For example, if the chemical of interest is methyl ethyl ketone (MEK), the mass emission rate can be calculated on the basis of the following steps.

Step 1: Choose a chemical for which the K_LA value is known. For this example, toluene was chosen as chemical j in eq 4. The mean K_LA value was calculated experimentally to be 9.4 L/min.

Step 2: Obtain physicochemical properties for both chemicals i and j . Table 3 presents Henry's law constants and diffusion coefficients for both toluene and MEK.

Step 3: Choose the appropriate k_g/k_i value for the source operating conditions. The mean value of k_g/k_i for any shower event was estimated to be 156.

Step 4: Estimate Ψ_1 for chemicals i and j . For toluene and MEK, using eq 2 and $n_1 = 2/3$, the value of Ψ_1 was calculated to be 1.1.

Step 5: Estimate Ψ_g for chemicals i and j . For toluene and MEK, using eq 3 and $n_2 = 2/3$, the value of Ψ_g was calculated to be 1.1.

Step 6: Estimate Ψ_m for chemical j and chemical of interest i . Ψ_m was calculated using eq 4, the values derived from steps 2–4, and the Henry's law constant for each chemical listed in Table 3. The values of Henry's law constant for each chemical were adjusted for a temperature of 36 °C using correlations developed by Ashworth (12), $\Psi_m = 0.38$

Step 7: Calculate K_LA for the chemical of interest (i).

$$K_L A_{\text{MEK}} = \Psi_m K_L A_{\text{toluene}} \quad (12)$$

$$= 3.6 \text{ L/min}$$

Step 8: Calculate the resulting chemical concentration using equations derived by Little (11) using eqs 5–8. Table 4 presents results obtained for various time periods during a 10 min shower and assuming a water concentration ($C_{i,\text{in}}$) of 10 $\mu\text{g/L}$, a water flow rate of 9.1 L/min, an air flow rate of 379 L/min, and a shower stall volume of 1745 L.

Step 9: Calculate the resulting emission rate of the chemical of interest using the following equation:

$$E = Q_i(C_{i,\text{in}} - C_{i,\text{out}}) \quad (13)$$

where E is the emission rate (M/T). Emission rates for MEK at various times during a 10 min shower are presented in Table 4. Using these results and eq 9, stripping efficiencies for MEK were calculated and also presented in Table 4. For example, the stripping efficiency for MEK is predicted to be 28% at $t = 20$ s and 9.7% at $t = 10$ min. In contrast, the stripping efficiency for toluene is predicted to be 64% at $t = 20$ s and 62% at $t = 10$ min. The overall stripping efficiencies were predicted to be 13% for MEK and 63% for toluene.

Predicted mass transfer coefficients obtained using this approach were compared with the experimental results for some of the tracers used in this study. Mass transfer coefficients for acetone and ethylbenzene were derived using eqs 4 using toluene as the known chemical and then compared with the values obtained experimentally. The predicted mass transfer coefficients for acetone and ethylbenzene were 2.9 and 8.9 L/min, respectively. The values obtained experimentally were 2.5 L/min for acetone and 9.3 L/min for ethylbenzene. These experimental results are in good agreement with predicted values.

Summary

On the basis of the results of this study, stripping efficiencies in showers for chemicals with H_c greater than or equal to that for toluene should range from 60 to 80%. It is worth noting, however, that the calculation of the overall mass transfer coefficient ($K_L A$) is very sensitive to the Henry's law constant. Therefore, a reasonably accurate estimation of Henry's law constant is important.

The basic assumption made in the derivation of this approach is that the shower stall atmosphere is well-mixed. During this study, gas-phase concentrations were relatively homogeneous throughout the shower stall, providing evidence for the validity of this assumption.

Previous research focused on high-volatility chemicals, for which liquid-phase resistance to mass transfer dominates. For lower volatility chemicals, such as ethyl acetate, both gas- and liquid-phase resistances are important. The approach presented above accounts for both gas- and liquid-phase resistances to mass transfer, making it applicable to a wider range of chemicals than previous research had allowed.

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TABLE 4. Model Results for Methyl Ethyl Ketone^a

time (s)	C_g ($\mu\text{g/L}$)	$C_{i,\text{out}}$ ($\mu\text{g/L}$)	E ($\mu\text{g/min}$)	η
20	0.005	7.23	25.2	0.28
40	0.009	7.62	21.7	0.24
60	0.012	7.93	18.9	0.21
80	0.014	8.17	16.7	0.18
100	0.016	8.36	15.0	0.16
120	0.018	8.50	13.6	0.15
140	0.019	8.62	12.6	0.14
160	0.020	8.71	11.8	0.13
180	0.021	8.78	11.1	0.12
200	0.021	8.83	10.6	0.12
220	0.022	8.88	10.2	0.11
240	0.022	8.91	9.9	0.11
260	0.022	8.94	9.7	0.11
280	0.022	8.96	9.5	0.10
300	0.023	8.97	9.3	0.10
320	0.023	8.99	9.2	0.10
340	0.023	9.00	9.1	0.10
360	0.023	9.00	9.1	0.10
380	0.023	9.01	9.0	0.099
400	0.023	9.02	9.0	0.098
420	0.023	9.02	8.9	0.098
440	0.023	9.02	8.9	0.098
460	0.023	9.02	8.9	0.098
480	0.023	9.03	8.9	0.097
500	0.023	9.03	8.9	0.097
520	0.023	9.03	8.8	0.097
540	0.023	9.03	8.8	0.097
560	0.023	9.03	8.8	0.097
580	0.023	9.03	8.8	0.097
600	0.023	9.03	8.8	0.097

^a C_g = chemical concentration in air adjacent to water; $C_{i,\text{out}}$ = outlet chemical concentration in water; E = chemical emission rate; η = fractional stripping efficiency.

views expressed in this paper are those of the author(s) and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

Supporting Information Available

Details regarding equation derivation, sampling techniques, and experimental operating conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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