

Mass Transfer of Volatile Organic Compounds from Drinking Water to Indoor Air: The Role of Residential Dishwashers

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Contaminated tap water may be a source of volatile organic compounds (VOCs) in residential indoor air. To better understand the extent and impact of chemical emissions from this source, a two-phase mass balance model was developed based on mass transfer kinetics between each phase. Twenty-nine experiments were completed using a residential dishwasher to determine model parameters. During each experiment, inflow water was spiked with a cocktail of chemical tracers with a wide range of physicochemical properties. In each case, the effects of water temperature, detergent, and dish-loading pattern on chemical stripping efficiencies and mass transfer coefficients were determined. Dishwasher headspace ventilation rates were also measured using an isobutylene tracer gas. Chemical stripping efficiencies for a single cycle ranged from 18% to 55% for acetone, from 96% to 98% for toluene, and from 97% to 98% for ethylbenzene and were consistently 100% for cyclohexane. Experimental results indicate that dishwashers have a relatively low but continuous ventilation rate (~5.7 L/min) that results in significant chemical storage within the headspace of the dishwasher. In conjunction with relatively high mass transfer coefficients, low ventilation rates generally lead to emissions that are limited by equilibrium conditions after approximately 1–2 min of dishwasher operation.

Introduction

Current Federal drinking water (chemical) standards are primarily based on associated ingestion exposure. However, researchers are finding that other exposure routes, i.e., inhalation and dermal contact, may be as important or more important in terms of human health risk (1). Volatile chemicals in contaminated tap water can enter indoor air in a home through several sources, including bathtubs, dishwashers, showers, toilets, wash basins, and washing machines. Previous studies related to the volatilization of chemicals from drinking water to indoor air, however, have focused on just one household source, showers (2–13). As a result, current models used for estimating inhalation

exposures related to contaminated tap water (14–16) are often based on simplifying assumptions and/or extrapolation techniques that fail to capture the mechanistic behavior of the volatilization process for other sources.

To improve chemical emission estimates for contaminated tap water, the United States Environmental Protection Agency (U.S. EPA) commissioned a study that involved a series of experiments with the intention of filling existing knowledge “gaps” related to sources other than showers. Research findings related to chemical emissions from washing machines have been published elsewhere (17, 18). This paper focuses on emissions from residential dishwashers, a source that has received little attention in the published literature.

Two different models for estimating chemical emissions from dishwashers are presented herein. The first is a two-phase, dynamic mass balance model that requires the use of source- and chemical-specific mass transfer coefficients as well as air exchange (ventilation) rates. The second is a simplified model using air exchange rates and an assumption of instantaneous chemical equilibrium to predict emissions. Parameters for each model were estimated based on 11 mass transfer experiments involving four chemicals (acetone, toluene, ethylbenzene, and cyclohexane) and 18 ventilation experiments using isobutylene as a tracer gas. Chemical stripping efficiencies were also determined. Using experimentally determined parameters, a comparison of each model's prediction of chemical emissions from a dishwasher is provided for a typical water contamination scenario.

Model Development. The most common way to characterize the potential for chemical volatilization from tap water is in terms of a stripping efficiency. The chemical-specific stripping efficiency related to dishwashers is defined by

$$\eta = 1 - \frac{C_{l,\text{end}}}{C_{l,0}} \quad (1)$$

where η is the stripping efficiency per cycle (fractional), $C_{l,\text{end}}$ is the final contaminant concentration in water (M/L³), and $C_{l,0}$ is the initial contaminant concentration in water (M/L³).

Chemical stripping efficiency requires the measurement of initial liquid-phase concentration and measurement of the final liquid-phase concentration in a dishwasher. Stripping efficiencies are influenced by several factors, including chemical properties, e.g., Henry's law constant (H_c), temperature, droplet size, ventilation rate, detergent use, and loading pattern of dishes.

Another parameter used to characterize chemical volatilization from water is the overall mass transfer coefficient (K_L). This parameter is a function of contaminant physicochemical properties, fluid characteristics, and flow characteristics. Molecular diffusion is important as volatile compounds approach an air–liquid interface. In accordance with two-film theory (19), the overall mass transfer coefficient can be expressed in terms of resistances as shown:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g H_c} \quad (2)$$

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

The term $1/K_L$ is often referred to as an overall resistance to mass transfer. The term $1/k_l$ is referred to as liquid-phase resistance to mass transfer and $1/(k_g H_c)$ is referred to as gas-

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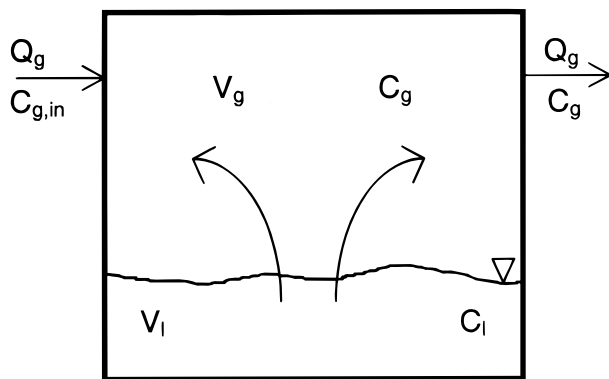


FIGURE 1. Mass balance model for dishwasher.

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 often true for highly volatile compounds such as radon. If gas-phase resistance is significant, K_L becomes a function of H_c as well as molecular diffusivities.

Mass Balance on Dishwasher. Figure 1 represents a dishwasher for which the liquid phase may be treated as a batch reactor. A mass balance on the liquid phase leads to

$$\frac{dm}{dt} = \frac{dC_l V_l}{dt} = -K_L \left(C_l - \frac{C_g}{H_c} \right) A \quad (3)$$

where m is the contaminant mass in water (M), C_l is the contaminant concentration in water (M/L³), V_l is the volume of water (L³), t is time (T), K_L is the overall mass transfer coefficient for the contaminant of interest (L/T), C_g is the contaminant concentration in air adjacent to water (M/L³), H_c is the Henry's law constant for contaminant of interest (L³_{liq}/L³_{gas}), and A is the interfacial surface area between water and adjacent air (L²).

The gas phase of the system shown in Figure 1 is assumed to approach a continuous-flow, well-mixed reactor. A corresponding mass balance leads to

$$\frac{dC_g V_g}{dt} = Q_g C_{g,in} - Q_g C_g + K_L \left(C_l - \frac{C_g}{H_c} \right) A \quad (4)$$

where V_g is the headspace volume (L³), Q_g is the ventilation rate (L³/T), and $C_{g,in}$ is the gas concentration entering system from outside air (M/L³).

In eqs 3 and 4, the term $(C_l - C_g/H_c)$ is often referred to as a "concentration driving force" between the liquid and gas phases. As the difference between C_l and C_g/H_c decreases, a dishwasher may approach a condition of dynamic equilibrium, i.e., C_l and C_g are related by Henry's law. The onset of such a condition should be enhanced for systems with low headspace ventilation rates and high products of mass transfer coefficients and surface area ($K_L A$).

Assuming that both the liquid and gas volumes are constant during operation and that the background room air is relatively clean ($C_{g,in} = 0$), the liquid- and gas-phase mass balances may be rewritten as

$$\frac{dC_l}{dt} = -\frac{K_L A}{V_l} C_l + \frac{K_L A}{V_l H_c} C_g \quad (5)$$

and

$$\frac{dC_g}{dt} = \frac{K_L A}{V_g} C_l - \left(\frac{Q_g}{V_g} + \frac{K_L A}{V_g H_c} \right) C_g \quad (6)$$

Equations 5 and 6 are interdependent and must be solved simultaneously. Analysis using Laplace transforms leads to

$$C_l = C_{l,0} \left[\exp\left(-\frac{D}{2}t\right) \cosh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) + \left(\frac{BF}{Z} + \frac{EC_{l,0}}{Z} - \frac{DC_{l,0}}{2}\right) \left[\frac{1}{\sqrt{\frac{D^2}{4} - E}} \exp\left(-\frac{D}{2}t\right) \sinh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) \right] \right] \quad (7)$$

and

$$C_g = C_{g,0} \exp\left(-\frac{D}{2}t\right) \cosh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) + \left(F - \frac{DC_{g,0}}{2}\right) \left[\frac{1}{\sqrt{\frac{D^2}{4} - E}} \exp\left(-\frac{D}{2}t\right) \sinh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) \right] \quad (8)$$

where $C_{l,0}$ is the initial concentration in aqueous phase (M/L³), $C_{g,0}$ is the initial concentration in gas phase (M/L³), Z is $K_L A/V_l$ (1/T), B is $K_L A/V_l H_c$ (1/T), X is $K_L A/V_g$ (1/T), Y is $Q_g/V_g + K_L A/V_g H_c$ (1/T), D is $Z + Y$ (1/T), E is $ZY - BX$ (1/T²), and F is $ZC_{g,0} + XC_{l,0}$ (M/L³·T).

Equations 7 and 8 can be used to determine chemical concentrations in the liquid and gas phases throughout an entire dishwashing event. The emission rate for a chemical of interest can then be determined as

$$E = Q_g C_g \quad (9)$$

where E is the emission rate for a specific chemical of interest (M/T).

Alternately, if a dynamic equilibrium is achieved within a dishwasher, the process outlined above to predict chemical emissions may be simplified by using a Henry's law analysis that accounts for total mass in the system and the volumes of the liquid and gas phases. Assuming that the dishwasher liquid and gas phases are instantaneously at equilibrium, the following relationships may be used to predict liquid- and gas-phase concentrations:

$$M_T = M_l + M_g = V_l C_l + V_g C_g \quad (10)$$

and

$$H_c = \frac{C_g}{C_l} = \frac{\left(\frac{M_g}{V_g}\right)}{\left(\frac{M_l}{V_l}\right)} \quad (11)$$

where M_T is the total mass in system (M), M_l is the mass in liquid phase of system (M), and M_g is the mass in gas phase of system (M).

Combining eqs 10 and 11 results in the following instantaneous equilibrium concentrations:

$$C_{l,e} = \frac{M_T}{\left(1 + \frac{V_g H_c}{V_l}\right) V_l} \quad (12)$$

and

$$C_{g,e} = H C_{l,e} \quad (13)$$

where $C_{l,e}$ is the liquid-phase concentration at equilibrium with gas phase (M/L^3) and $C_{g,e}$ is the gas-phase concentration at equilibrium with liquid phase (M/L^3).

To predict chemical emissions using the equilibrium analysis, eq 9 can be modified to

$$E = Q_g C_{g,e} \quad (14)$$

The equilibrium state within the dishwasher is dynamic due to the continual loss of mass from the system via ventilation of the headspace. As a result, $C_{l,e}$ and $C_{g,e}$ must be recalculated using eqs 12 and 13 as the total mass in the system changes with time. A numerical solution with relatively small time steps (<10 s) may be used to predict the mass emission rate over time.

Although simpler to use, the Henry's law analysis will lead to an overestimate of chemical emissions. The significance of this overestimate is dependent on the time to reach a condition of dynamic equilibrium (t_e). For $t < t_e$, it is more appropriate to use eqs 7–9 to estimate emissions, whereas eqs 12–14 could be used once $t > t_e$.

Whichever approach is selected provides a chemical mass emission rate curve for the duration of dishwasher operation. Integration under this curve results in total chemical mass emitted during a dishwashing event. The resulting chemical concentration to which human inhabitants are exposed can be predicted by incorporating the mass emission rate profile into a mass balance on the associated room air.

Experimental Methodology

Experimental System. A Kenmore dishwasher (model 17651) was purchased to complete all experiments. The experimental system is illustrated in Figure 2. The experimental dishwasher had an interior volume of 188 L. It had five different types of wash cycles (quick rinse, china light, water miser, normal, and pots and pans). These cycles differed only by the number of fills, i.e., total volume of water used and time of operation. Due to the similar operating characteristics of each cycle, only a single cycle was tested. Other dishwasher operation variables included water temperature (~ 42 vs ~ 54 °C), dish-loading patterns (full vs empty), and use of detergent (wash vs rinse). Experiments were designed to study the effects of the above parameters on chemical mass transfer rates.

The sequence of operation was as follows: the dishwasher was directly plumbed to a pressurized hot water line. At the start of each portion of a cycle, water entered the dishwasher from the hot water line at a flow rate of 4.0 L/min. Twenty seconds after starting the fill, water from the growing basin pool was pumped to the rotary arm, which began spinning and spraying water throughout the dishwasher headspace. Water continued to enter the dishwasher from the hot water line for a total of 99 s, such that a total of 6.6 L of water existed in the dishwasher. During the wash portion of a cycle, detergent was released from its compartment as the dishwasher filled. At the end of each portion of a cycle, the water was pumped from the basin to a drain. Once all wash and rinse events for a particular cycle were completed, there was an approximate 30-min drying time.

Experimental Tracers. The water used in the dishwasher was spiked with a multi-tracer stock solution. These tracers included acetone, toluene, ethylbenzene, and cyclohexane, four chemicals that represent a wide range of Henry's law constants. Physicochemical properties for each of these chemicals are given in Table 1. Dishwasher experiments were completed at significantly higher temperatures than 25 °C. As a result, Henry's law constants for the experimental chemicals were adjusted to reflect actual temperatures using existing correlations (23, 24). Chemical tracer stock solutions

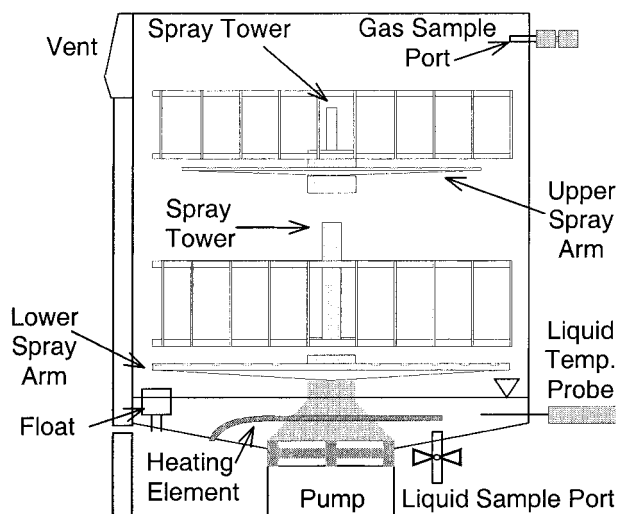


FIGURE 2. Experimental system.

were prepared by injecting known amounts (<0.60 mL) of pure chemical into 0.75 L of cold tap water. The stock solution was contained in a Tedlar bag that was manually agitated to enhance mixing and dissolution.

Sample Collection. The dishwasher was configured to allow for the required variable measurements to solve eqs 7–9. A liquid sample port was installed at the bottom of the dishwasher. A 15 cm length of 6 mm i.d. Teflon tubing and a Teflon sample valve were connected to this port. The port inlet was submerged at all sampling times, and the residence time of the sample tube was estimated to be approximately 2 s. Liquid samples were collected in 22-mL glass vials that were sealed with an aluminum cap fitted with a silicon rubber/Teflon-faced septum. A total of 10 liquid samples, including two duplicate samples, were collected during each experiment. Samples were stored at 4 °C in a laboratory refrigerator until analysis (for no more than 1 week).

For each experiment, a total of five gas samples were collected on Carbotrap 300 (Supelco) adsorbent tubes (0.64 cm o.d. \times 18 cm). Samples were collected using a gas sample pump (SKC-PCXR8) and bubble flowmeter (SKC Accuflo) in series. Each sorbent tube was attached to a sample port located in the headspace of the dishwasher. A Teflon tube (2.5 cm o.d.) was connected to the port on the inside of the dishwasher. This larger diameter tube prevented liquid droplets from being drawn onto the sorbent tube. The total volume of gas that was drawn through each sorbent tube was determined by timing the event. Sample flow rates were in the range of 0.2–0.4 L/min. Sampling times were approximately 30 s and scheduled such that a liquid sample was also collected during this time period. Stainless steel Swagelok fittings were used at all connection points in the sampling train. Gas sample tubes were sealed with stainless steel Swagelok caps after collection and stored at 4 °C in a hermetically sealed jar containing activated carbon.

Henry's law constants and mass transfer coefficients are dependent on temperature. Thus, temperature monitoring was necessary during each experiment. A thermocouple probe was submerged in the dishwasher pool and connected to a digital monitor to allow for constant temperature readings.

Ventilation Rate. A grated exhaust vent was located on the top face of the dishwasher door from which gas naturally exited the dishwasher. A total of 18 experiments were completed to characterize the headspace ventilation rate. Before starting the dishwasher for each ventilation experiment, isobutylene gas was introduced at 100 ppm to the dishwasher headspace. The concentration inside the dish-

TABLE 1. Summary of Physicochemical Properties for Experimental Tracers (20–22)

compd	Henry's law constant at 25 °C ($\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$)	liquid diffusion coeff at 24 °C (cm^2/s)	gas diffusion coeff at 24 °C (cm^2/s)	boiling point (°C)	density (kg/L)	solubility (mg/L)	vapor pressure (mmHg)
acetone	0.0015	$1.1\text{E}-05$	0.11	56.5	0.79	miscible	270
toluene	0.27	$9.1\text{E}-06$	0.085	110.6	0.87	515	22.0
ethylbenzene	0.33	$8.4\text{E}-06$	0.077	136.2	0.87	152	7.0
cyclohexane	7.2	$9.0\text{E}-06$	0.088	80.7	0.77	58	77

TABLE 2. Chemical Stripping Efficiencies for Experimental Dishwasher

exp	liquid temp (°C)	cycle type	dish-loading pattern	acetone η (%)	toluene η (%)	ethylbenzene η (%)	cyclohexane η (%)
1	43	rinse	empty	50	97	97	100
2	42	rinse	full	34	96	97	100
2 (replicate)	39	rinse	full	45	97	98	100
3	43	wash	empty	37	96	97	100
4	45	wash	full	47	97	98	100
4 (replicate)	38	wash	full	42	96	97	100
5	55	rinse	empty	55	98	98	100
6	55	rinse	full	18	96	97	100
7	54	wash	empty	51	98	98	100
8	55	wash	full	37	97	97	100
8 (replicate)	53	wash	full	40	97	98	100
			average	41	97	97	100

washer was continuously monitored using a photoionization detector (Photovac Microtip, model HL-2000). The slope of a plot of $-\ln(C_g/C_{g,0})$ versus t/V_g provided an explicit determination of the ventilation rate (Q_g). Isobutylene gas was selected as a tracer due to its relatively high Henry's law constant ($H_c = 23 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ at 25 °C). On the basis of isobutylene's high Henry's law constant and the dishwasher's large gas-to-liquid volume ratio, the maximum amount of isobutylene mass absorbed into the liquid phase was determined to be no more than 0.2%.

Analytical Methods

Liquid Samples. Liquid samples were analyzed using a headspace concentrator with autosampler (Tekmar 7000) and a gas chromatograph (Hewlett-Packard, 5890 series II plus) equipped with a flame ionization detector (GC/FID). Each liquid sample was heated at 70 °C for 60 min. A sample loop was then filled with headspace contents and injected into the GC/FID. The GC parameters included an inlet temperature of 200 °C and a detection temperature of 250 °C. For each sample, the initial oven temperature was 32 °C, which was held constant for 0.5 min before being ramped at 10 °C/min to a final oven temperature of 65 °C. This final temperature was held constant for 11 min giving a total run time of 14.8 min. An HP-1 capillary column (30 m \times 0.53 mm \times 2.65 μm film thickness) was used for all analyses.

Gas Samples. Gas samples were analyzed using a thermal desorber with autosampler (Tekmar 6016) and a purge-and-trap system (Tekmar 3000). This system was also plumbed to the GC/FID described above. Each tube was heated at 200 °C for 8 min. The desorbed contaminants were transported to an internal purge-and-trap column (packed with Tenax-TA) through a transfer line at a temperature of 200 °C. Once the desorption phase was complete, the Tenax column was heated to 250 °C for 2 min. During this time, contaminants were desorbed from the trap and injected into the inlet of the GC/FID. The GC/FID parameters for gas samples were identical to those given above for liquid samples.

Analytical Standards. Chemical standards were developed and analyzed to determine the concentrations associated with GC responses. Liquid- and gas-phase standards were prepared for all experimental analyses. For each phase, a six-point calibration curve was developed using known

amounts of each chemical tracer. The liquid-phase standard stock solution was prepared in a Tedlar bag and different volumes from the bag were injected into 10 mL of water contained in capped 22-mL vials. Standard solution vials were analyzed with experimental liquid samples.

A pressurized cylinder containing a known gas-phase concentration of each chemical tracer was purchased to prepare gas standards (calibrated by Scott Specialty Gases, NIST traceable to Project 0454764). Different volumes of gas standard were passed through several Carbotrap 300 sorbent tubes. These standard tubes were analyzed with experimental gas-phase samples.

Experimental Results. Eleven experiments were completed to determine chemical specific stripping efficiencies and mass transfer coefficients for a residential dishwasher. Eight experiments represented unique operating conditions, and the remaining three were replicates. Each experiment was completed with the same wash portion of a dishwasher cycle, the same volume of water, and nearly the same ventilation rate. Ventilation rates were determined in 18 separate experiments incorporating all operating condition combinations and ranged from 5 to 7 L/min, with an average of 5.7 L/min.

An important protocol for each dishwasher experiment was to obtain adequate mass closure. Over all experiments and individual tracers, percent mass recoveries (mass closure) ranged from 84 to 124%.

Chemical Stripping Efficiencies. Chemical stripping efficiencies were determined using eq 1 and are listed in Table 2. The average stripping efficiencies were 41% for acetone, 97% for toluene, 97% for ethylbenzene, and 100% (>99% based on liquid concentrations above detection limit) for cyclohexane. For all experiments, chemical stripping efficiencies increased with increasing Henry's law constant. Due to the consistently high stripping efficiencies for cyclohexane, ethylbenzene, and toluene, no trends related to dishwasher operating conditions could be identified for these compounds. With the exception of experiments 3 and 4, acetone stripping efficiencies tended to be lower for a fully loaded dishwasher. The differences in stripping efficiencies between empty and fully loaded dishwashers was particularly large for experiments 5 and 6. A specific reason for this difference could not be ascertained. However,

TABLE 3. Relative Source Strengths Based on Toluene Stripping Efficiencies (2, 17, 26) and Typical Water Consumption Rates (16)

source	water temp (°C)	toluene overall stripping efficiency (%)	water consumption (L person ⁻¹ day ⁻¹)	relative source strength ^a
dishwasher	55	93	10.4	9.7
shower	35	74	61.2	45
washing machine (hot water cycle)	50	53	53	28
washing machine (cold water cycle)	21	22	53	19
kitchen sink	23	20	15.5	3.1

^a Relative source strength = stripping efficiency/100 × water consumption.

the authors did observe some accumulation of water in the concave portions of dishware. Such removal of water to quiescent "pools" could effectively shield a fraction of chemical mass from enhanced mass transfer during droplet formation and transport and thus account for some reduction in stripping efficiency. Despite the presence of surfactants during wash cycles, there was no apparent trend in acetone stripping efficiencies between wash and rinse cycles. This is likely due to the fact that the overall resistance to mass transfer for acetone is dominated by the gas phase, which is less affected by the presence of surface active agents. Within the range of conditions studied, there were no apparent trends between temperature and acetone stripping efficiency.

For similar chemicals, experimentally determined stripping efficiencies for a residential dishwasher exceed those reported for any other tap water source to date (25). The combination of high water temperature and spray droplets (increased surface area-to-volume ratio) results in nearly 100% volatilization for chemicals with a Henry's law constant greater than that of toluene. Even chemicals as soluble as acetone are expected to have relatively high stripping efficiencies (average value of 41%) for a single cycle. However, due to the low headspace ventilation rate and subsequent accumulation of chemicals in the dishwasher headspace, dishwasher events consisting of multiple cycles (e.g., pre-rinse, wash, rinse, etc.) will typically have lower overall stripping efficiencies than those measured for a single cycle, i.e., as the concentration driving force in eq 3 is reduced. Overall chemical stripping efficiencies may be predicted using eqs 7 and 8 for multiple cycles.

Tap water sources may be compared on a mass basis by computing a relative source strength defined as the product of the overall stripping efficiency and typical water consumption rate. Assuming equal toluene concentrations in the inlet water, relative source strengths are provided for selected sources and operating conditions in Table 3. Although dishwashers exhibit a greater stripping efficiency than other sources, it is also characterized by the lowest water consumption rate. As a result, the source strength estimated for dishwashers is lower than the source strengths determined for showers and washing machines. However, mass emissions from a dishwasher still potentially provide a significant contribution to background levels of volatile organic compounds in residential indoor air. The authors recognize that this comparison does not account for "direct" human exposure while in close proximity to a source, i.e., during showering or use of a kitchen sink. Effects of water usage on inhalation exposure to chemicals released from household water have been published elsewhere (28, 29) and were not the focus of this study.

Mass Transfer Coefficients. With the exception of cyclohexane, the time to reach a condition of dynamic equilibrium (t_e) was rapid for each tracer, i.e., within approximately 90 s for every experiment. Thus, for these chemicals it may be appropriate to use eqs 12–14 to approximate emissions throughout a dishwashing event. Alternately, eqs 7–9 can be used to estimate emissions given appropriate values of K_LA .

Once a condition of dynamic equilibrium is achieved, subsequent data cannot be used to determine values of K_LA . Thus, only data collected prior to 90 s were used to back-calculate K_LA for each tracer. Furthermore, this short time period precluded a determination of a concentration profile in the gas phase, i.e., only one integrated gas sample was generally collected for $t < t_e$. As such, values of K_LA were approximated by using only liquid concentrations based on samples collected during the first 45 s of each experiment and by assuming that $C_g/H_c \ll C_l$ during that period. Equation 3 was then integrated to solve for C_l as a function of time and K_LA . Values of K_LA were based on a best-fit exponential curve through the experimental data.

As shown in Table 4, average values of K_LA were 6.0 L/min for acetone, 33 L/min for toluene, 36 L/min for ethylbenzene, and 53 L/min for cyclohexane. As with stripping efficiencies, values of K_LA were relatively similar in magnitude for the various operating conditions such that the only identifiable trend was the increase in value with increasing Henry's law constant.

As an example, toluene results for experiment 8 are presented in Figure 3. The best-fit value of K_LA for this experiment was 31 L/min. The Henry's law constant for toluene for experiment 8 (temperature = 55 °C) was 0.62 m³_{liq}/m³_{gas}. Figure 3 illustrates the initial drop in liquid-phase concentration followed by a dynamic equilibrium condition. In general, for all but cyclohexane, the ratio of C_g/C_l for measured data occurring after 90 s was approximately equal to the predicted Henry's law constant for that temperature.

On the basis of the assumption described above, the reader should consider the K_LA values provided herein as only approximate. For example, small errors in the liquid sampling time could have an effect on the shape of the liquid-phase concentration profile presented in Figure 3. Errors in liquid sampling time of ± 5 s for the second and third data points in Figure 3 would lead to K_LA values ranging from 28 to 36 L/min. However, even within this range, the system still reaches equilibrium rapidly.

For similar chemicals, the values of the product of the overall mass transfer coefficient and interfacial area (K_LA) were generally of the same order of magnitude as those previously reported for showers (27) and an order of magnitude higher than K_LA values reported for washing machines (17, 18) and kitchen sinks (26).

Predicted Dishwasher Cycle Emissions. Equations 7–9 may be used to predict chemical emissions during a dishwasher event of single or multiple cycles, i.e., number of separate fills during operation. For example, a dishwasher event may include a pre-rinse cycle of 3.5 min; a wash cycle of 10 min; and two rinse cycles of 6 and 14 min, respectively; a water temperature of 55 °C; and may contain toluene at 10 µg/L (1% of the maximum contaminant level (MCL) as mandated by the U.S. Environmental Protection Agency). At this concentration and a headspace ventilation rate of 5.7 L/min, the total mass emission of toluene over the entire cycle is predicted to be 157 µg. Alternately, application of eqs 12–14 throughout the entire dishwashing event leads to a predicted total mass emission of 158 µg. Figure 4 illustrates the predicted mass emission rate of toluene as a function of dishwasher cycle time for each emissions approach.

As shown in Figure 4, periodic increases in the toluene emission rate follow each drain cycle and correspond to the

TABLE 4. Values of K_LA for Experimental Dishwasher

exp	liquid temp (°C)	cycle type	dish-loading pattern	acetone K_LA (L/min)	toluene K_LA (L/min)	ethylbenzene K_LA (L/min)	cyclohexane K_LA (L/min)
1	43	rinse	empty	7.0	33	31	45
2	42	rinse	full	4.2	30	32	49
2 (replicate)	39	rinse	full	5.8	32	35	58
3	43	wash	empty	5.1	30	33	51
4	45	wash	full	6.8	33	35	50
4 (replicate)	38	wash	full	9.4	34	36	62
5	55	rinse	empty	8.2	39	42	57
6	55	rinse	full	1.7	33	36	56
7	54	wash	empty	7.6	38	41	50
8	55	wash	full	4.9	31	34	47
8 (replicate)	53	wash	full	5.2	35	37	55
			average	6.0	33	36	53

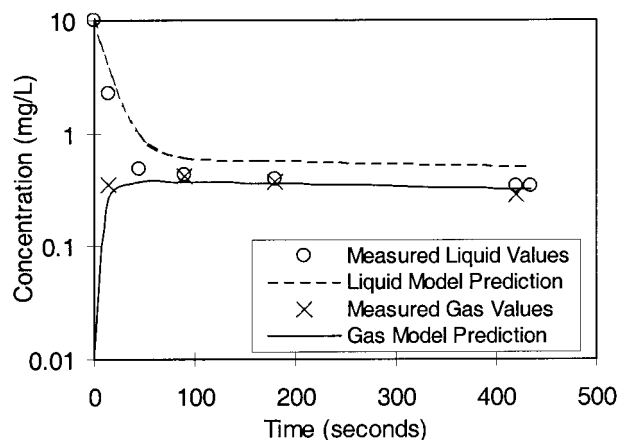


FIGURE 3. Toluene concentrations for experiment 8.

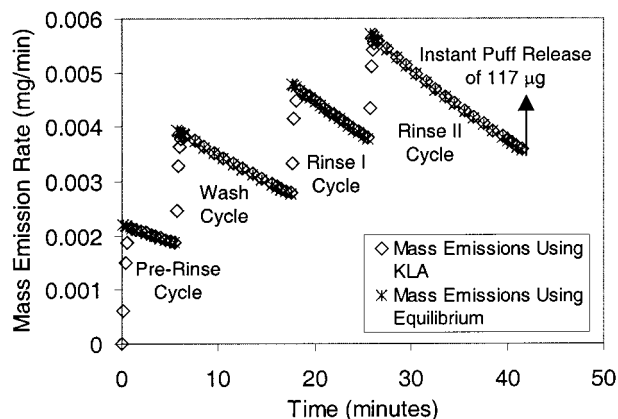


FIGURE 4. Mass emission rates for toluene for example dishwasher event.

inflow of water (maximum liquid-phase toluene concentration, 10 $\mu\text{g/L}$) to the system. For both models, an additional 117 μg of residual toluene is retained in the dishwasher headspace at the end of the final rinse cycle. This residual would be released as a "puff" if the dishwasher is opened soon after the final cycle. While this instantaneous "puff" release contains less mass than the total emissions associated with machine operation, it may actually be more important in terms of inhalation exposure, i.e., due to the elevated concentration of chemicals in the puff and close proximity of the human subject.

Interestingly, at elevated temperatures the Henry's law constant of a common disinfection byproduct (chloroform) is similar to that of toluene. Thus, applying the equilibrium

model (eqs 12–14) for chloroform at 10 $\mu\text{g/L}$ in water results in mass emissions similar to those predicted for toluene.

The dynamic mass balance models presented herein are an improvement over current methods used to predict chemical volatilization from a dishwasher. Experimental results indicate that most volatile chemicals are efficiently stripped from water in a dishwasher. However, emissions are limited by a low headspace ventilation rate that allows for chemical accumulation within the headspace of the dishwasher. Using experimentally determined operating parameters and specific chemical properties, total mass emission rates associated with dishwasher usage may be predicted for any contamination scenario.

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