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 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

\[ \eta = 1 - \frac{C_{l,\text{end}}}{C_{l,0}} \]  

where \( \eta \) 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. Striping 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:

\[ \frac{1}{K_l} = \frac{1}{k_l} + \frac{1}{k_g H_c} \]  

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/M/L³).

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-
phase resistance to mass transfer. For \( k H_c \gg k_L \), 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

\[
\frac{dm}{dt} = \frac{dC_L V_l}{dt} = -K_l \left( C_i - \frac{C_g}{H_c} \right) A \tag{3}
\]

where \( m \) is the contaminant mass in water (M), \( C_i \) is the contaminant concentration in water (M/L^3), \( V_l \) is the volume of water (L^3), \( t \) is time (T), \( K_l \) is the overall mass transfer coefficient for the contaminant of interest (L^2/T), \( C_g \) is the contaminant concentration in air adjacent to water (M/L^3), \( H_c \) is the Henry’s law constant for contaminant of interest (L^3/L_ga), and \( A \) is the interfacial surface area between water and adjacent air (L^2).

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

\[
\frac{dC_g V_g}{dt} = Q_{g, in} C_g - Q_{g} C_g + K_l \left( C_i - \frac{C_g}{H_c} \right) A \tag{4}
\]

where \( V_g \) is the headspace volume (L^3), \( Q_g \) is the ventilation rate (L/second), and \( Q_{g, in} \) is the gas concentration entering system from outside air (M/L^3).

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

\[
\frac{dC_i}{dt} = -\frac{K_l A}{V_l} C_i + \frac{K_l A}{V_l H_c} C_g \tag{5}
\]

and

\[
\frac{dC_g}{dt} = \frac{K_l A}{V_g} C_i - \left( \frac{Q_g}{V_g} + \frac{K_l A}{V_g H_c} \right) C_g \tag{6}
\]

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

\[
C_i = C_{i,0} \left[ \exp \left( -\frac{D_l}{2} t \right) \cosh \left( \frac{\sqrt{D_l^2 - 4E}}{2} t \right) \right] +
\frac{BF}{Z} + \frac{EC_{i,0}}{Z} \left[ \frac{1}{\sqrt{D_l^2 - 4E}} \exp \left( -\frac{D_l}{2} t \right) \sinh \left( \frac{\sqrt{D_l^2 - 4E}}{2} t \right) \right] \tag{7}
\]

and

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

where \( C_{i,0} \) is the initial concentration in aqueous phase (M/L^3), \( C_{g,0} \) is the initial concentration in gas phase (M/L^3), \( Z \) is \( K_l A V_l / (1/T) \), \( B \) is \( K_l A V_l H_c / (1/T) \), \( X \) is \( K_l A V_g / (1/T) \), \( Z_g \) is \( Q_{g, in} V_g + K_l A V_g H_c / (1/T) \), \( D_l \) is \( Z + Y / (1/T) \), \( E \) is \( ZY - BX / (1/T^2) \), and \( F \) is \( ZC_{g,0} + XC_{i,0} / (M/L^3) \).

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

\[
E = Q_g C_g \tag{9}
\]

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

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:

\[
M_T = M_l + M_g = V_l C_i + V_g C_g \tag{10}
\]

and

\[
H_c = \frac{C_g}{C_i} = \frac{\left( \frac{M_g}{V_g} \right)}{\left( \frac{M_l}{V_l} \right)} \tag{11}
\]

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:

\[
C_{i,e} = \frac{M_T}{\left( 1 + \frac{V_g H_c}{V_l} \right) V_l} \tag{12}
\]

and
where $C_{le}$ is the liquid-phase concentration at equilibrium with gas phase (M/L$^3$) and $C_{ge}$ 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

$$E = Q_t C_{ge}$$

(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, $C_{ge}$ and $C_{le}$ 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 ($\sim 10$ 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*). For $t < t*$, it is more appropriate to use eqs 7–9 to estimate emissions, whereas eqs 12–14 could be used once $t > t*$. 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 189 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 ($\sim 42$ vs $\sim 54$ °C), dishwashing 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 were prepared by injecting known amounts ($\sim 0.60$ 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 Carbosieve III (Supelco) adsorbent tubes (0.64 cm i.d. ¥ 18 cm). Samples were collected using a gas sample pump (SKC PXR8) and bubble flowmeter (SKC Accublow) in series. Each sorbent tube was attached to a sample port located in the headspace of the dishwasher. A Teflon tube (2.5 cm i.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 was configured 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. Chemical Stripping Efficiencies for Experimental Dishwasher

<table>
<thead>
<tr>
<th>compd</th>
<th>Henry's law constant at 25 °C (m³/atom/m³ gas)</th>
<th>liquid diffusion coeff at 24 °C (cm²/s)</th>
<th>gas diffusion coeff at 24 °C (cm²/s)</th>
<th>boiling point (°C)</th>
<th>density (kg/L)</th>
<th>solubility (mg/L)</th>
<th>vapor pressure (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrile</td>
<td>0.0015</td>
<td>1.1E-05</td>
<td>0.11</td>
<td>56.5</td>
<td>0.79</td>
<td>miscible</td>
<td>270</td>
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<tr>
<td>toluene</td>
<td>0.27</td>
<td>9.1E-06</td>
<td>0.085</td>
<td>110.6</td>
<td>0.87</td>
<td>515</td>
<td>22.0</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>0.33</td>
<td>8.4E-06</td>
<td>0.077</td>
<td>136.2</td>
<td>0.87</td>
<td>152</td>
<td>7.0</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>7.2</td>
<td>9.0E-06</td>
<td>0.088</td>
<td>80.7</td>
<td>0.77</td>
<td>58</td>
<td>77</td>
</tr>
</tbody>
</table>

TABLE 2. Chemical Stripping Efficiencies for Experimental Dishwasher

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

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 runtime of 14.8 min. An HP-1 capillary column (30 m × 0.53 mm 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 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 Carbograp 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, washer was continuously monitored using a photoionization detector (Photovac Microtip, model HL-2000). The slope of a plot of $-\ln (C_t/C_{eq})$ versus $t/V_g$ provided an explicit determination of the ventilation rate ($Q_c$). Isobutylene gas was selected as a tracer due to its relatively high Henry's law constant ($H = 23 m³/atom/m³ gas$, 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%.
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, i.e., only one integrated gas sample was generally collected for toluene. As such, values of K_A were approximated by using only liquid concentrations based on samples collected during the first 45 s of each experiment and by assuming that C_L/H = C_L during that period. Equation 3 was then integrated to solve for C_L as a function of time and K_A. Values of K_A were based on a best-fit exponential curve through the experimental data.

As shown in Table 4, average values of K_A 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_A 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_A for this experiment was 31 L/min. The Henry’s law constant for toluene for experiment 8 (temperature = 55 °C) was 0.62 m^3/kg m/m. 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_L/C_G 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_A 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_A 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_A) were generally of the same order of magnitude as those previously reported for showers (27) and an order of magnitude higher than K_A 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 7–9 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

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

<table>
<thead>
<tr>
<th>Source</th>
<th>Water Temp (°C)</th>
<th>Toluene Overall Stripping Efficiency (%)</th>
<th>Water Consumption (L person⁻¹ day⁻¹)</th>
<th>Relative Source Strength a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dishwasher</td>
<td>55</td>
<td>93</td>
<td>10.4</td>
<td>9.7</td>
</tr>
<tr>
<td>Shower</td>
<td>35</td>
<td>74</td>
<td>61.2</td>
<td>45</td>
</tr>
<tr>
<td>Washing Machine (hot water cycle)</td>
<td>50</td>
<td>53</td>
<td>53</td>
<td>28</td>
</tr>
<tr>
<td>Washing Machine (cold water cycle)</td>
<td>21</td>
<td>22</td>
<td>53</td>
<td>19</td>
</tr>
<tr>
<td>Kitchen Sink</td>
<td>23</td>
<td>20</td>
<td>15.5</td>
<td>3.1</td>
</tr>
</tbody>
</table>

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

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**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_A.

Once a condition of dynamic equilibrium is achieved, subsequent data cannot be used to determine values of K_A. Thus, only data collected prior to 90 s were used to back-calculate K_A 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 toluene. As such, values of K_A were approximated by using only liquid concentrations based on samples collected during the first 45 s of each experiment and by assuming that C_L/H = C_L during that period. Equation 3 was then integrated to solve for C_L as a function of time and K_A. Values of K_A were based on a best-fit exponential curve through the experimental data.

As shown in Table 4, average values of K_A 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_A 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.
inflow of water (maximum liquid-phase toluene concentration, 10 \( \mu \)g/L) to the system. For both models, an additional 117 \( \mu \)g 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 \( \mu \)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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