8. MODEL APPLICATIONS

All experimental results reported herein as well as previously reported research results have been compiled into a database that is provided in the Appendix. Each entry in the database summarizes a particular experiment, including operating conditions, chemical stripping efficiencies, and, where applicable, estimated values of K_LA, k_lA, k_gA, and percent mass recovery. The database could serve as a tool for a user to find the most appropriate modeling parameters for a specific contamination event. At this time, the database includes 164 shower results (including 50 from this study), 44 dishwasher results (all from this study), 128 washing machine results (including 114 from this study), 85 bathtub results (all from this study), and 33 kitchen sink results. Using the available information, it is now possible to estimate chemical emissions from tap water sources for numerous scenarios, without having to assume 100% volatilization for all chemicals.

Based on experimental results, values of K_LA and, where appropriate, headspace ventilation rates can be used in conjunction with associated source mass balance models to determine chemical emissions during a specific source event. In this chapter, an example event for each of the four sources discussed herein is presented. The methodology for predicting emissions for other chemicals of interest is provided. For each source, toluene was used as the surrogate compound (chemical j in Equation 2-15). Dibromochloromethane (DBCM), a common disinfection by-product, and methyl ethyl ketone (MEK), a common solvent, were used as the chemicals of interest (chemical i in Equation 2-15). A comparison of these three chemicals is provided in Table 8-1. For all cases, chemicals were assumed to be present in the water supply at a concentration of 10 µg/L.

8.1. SHOWER MODEL APPLICATION

Mass balance Equations 2-28 and 2-30 may be used to predict chemical liquid- and gas-phase concentrations during a shower event of any duration. The associated mass emissions may be estimated during a shower event by applying the predicted liquid-phase concentrations to Equation 2-32. For this example, a shower duration of 10 minutes was chosen. Other operating

Table 8-1. Comparison of the three chemicals used in model applications

Chemical	H_c @ 25°C $(m^3_{liq}/m^3_{gas})^a$	D_l @ 24°C $(cm^2/sec)^b$	D_g @ 24°C $(cm^2/sec)^b$
Toluene	0.27	9.1×10^{-6}	0.085
Dibromochloromethane	0.048	1.0×10^{-5}	0.086
Methyl Ethyl Ketone	0.0060	9.8×10^{-6}	0.097

[a]From Ashworth et al., 1988.

[b]From Tucker and Nelken, 1990.

conditions for this example, based on experimental operating conditions, were a water temperature of 35°C, a liquid flowrate of 9.1 L/minute, and a ventilation rate of 379 L/minute (resulting in an air exchange rate of 13/hour). A coarse water spray was assumed. The value of K_LA for toluene (used in Equations 2-28 and 2-30 to predict toluene liquid- and gas-phase concentrations, respectively, associated with these operating conditions) was assumed to be 12 L/minute. This value is the average K_LA determined for shower Experiments 5, 6, and 6 replicate (see Section 4.4.2). It should be noted that several values of K_LA based on different shower operating conditions are available in the experimental database (Appendix).

Based on an inlet liquid-phase concentration of 0.010 mg/L and an initial gas-phase concentration of 0 mg/L, the predicted mass emission rate for toluene is presented in Figure 8-1.
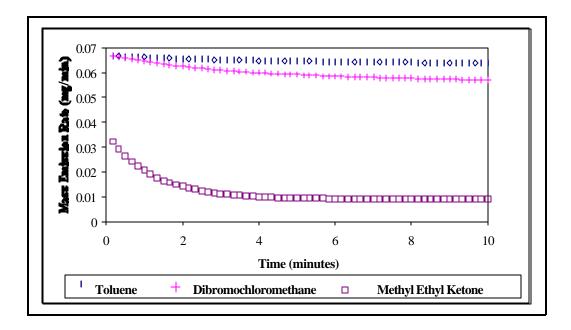

Figure 8-1. Mass emission rates for three chemicals for example shower event.

The total mass of emitted toluene was calculated by integrating under the mass emission rate curve shown in Figure 8-1. For this example, the total emitted mass of toluene was 650 μg. The total mass that entered the system was 910 μg. Thus, the overall stripping efficiency for toluene during the 10-minute shower event was 71%. The peak gas-phase concentration within the shower stall occurred at 10 minutes and was approximately 150 μg/m^3.

The mass emission rates for DBCM and MEK, two chemicals not used in this study, are also shown in Figure 8-1. For toluene and DBCM, the mass emission rate slowly decreased with time as each chemical accumulated within the shower stall. This effect was more dramatic for MEK, the chemical with the lower Henry's law constant. The overall stripping efficiencies for DBCM and MEK were 66% and 13%, respectively.

The procedure for predicting mass emissions for any chemical of interest based on the results of this study is illustrated by means of a step-by-step method for one chemical of interest, MEK. The shower conditions described earlier for toluene also apply for this example.

Step 1: Choose an experimental tracer to be the surrogate compound with an associated value of K_LA.

For this example, toluene was chosen as the surrogate compound (chemical j). As shown earlier, the value of K_LA for toluene and associated operating conditions was 12 L/minute.

Step 2: Choose appropriate experimentally determined k_g/k_l value for source operating conditions.

The value of k_g/k_l for any shower event was estimated to be 160 (see Section 4.4.3).

Step 3: Estimate Ψ_l for surrogate compound (chemical j) and chemical of interest (chemical i).

For toluene and MEK, the value of Ψ_l was calculated using Equation 2-12 as:

$$\Psi_l = \left(\frac{D_{l,\,MEK}}{D_{l,\,toluene}} \right)^{\frac{2}{3}} = 1.1$$

Step 4: **Estimate Ψ_g for surrogate compound (chemical j) and chemical of interest (chemical i).**

For toluene and MEK, the value of Ψ_g was calculated using Equation 2-13 as:

$$\Psi_g = \left(\frac{D_{g,\,MEK}}{D_{g,\,toluene}} \right)^{\frac{2}{3}} = 1.1$$

Step 5: **Estimate Ψ_m for surrogate compound (chemical j) and chemical of interest (chemical i).**

Ψ_m was calculated using Equation 2-15 with values from Steps 2 through 4 and Henry's law constants for each chemical listed in Table 8-1. The values of Henry's law constant for each chemical were adjusted for a temperature of 35°C using correlations developed by Ashworth et al. (1988).

$$\Psi_m = \Psi_l \Psi_g \left\{ \frac{H_{ci}}{H_{cj}} \right\} \left\{ \frac{1 + \left[\dfrac{k_{gj}}{k_{lj}} \right] H_{cj}}{\Psi_l + \Psi_g H_{ci} \left[\dfrac{k_{gj}}{k_{lj}} \right]} \right\}$$

$$\Psi_m = (1.1) \bullet (1.1) \bullet \left\{ \frac{0.0033}{0.37} \right\} \bullet \left\{ \frac{1 + 160 \bullet 0.37}{1.1 + 1.1 \bullet 0.0033 \bullet 160} \right\} = 0.38.$$

Step 6:   Calculate K_LA for chemical of interest.

The value of K_LA for MEK may be estimated using:

$$K_LA_{MEK} = \Psi_m \bullet K_LA_{toluene} = 0.38 \bullet 12 \text{ L/minute} = 4.5 \text{ L/minute.}$$

Step 7:   Predict liquid- and gas-phase concentrations as a function of time.

Applying a value of K_LA of 4.5 L/minute to Equations 2-28 and 2-30 enables prediction of liquid- and gas-phase concentrations, respectively, of MEK. At 10 minutes, the gas-phase concentration in the shower stall is the following:

$$C_{g,10min} = \frac{B}{D} + \left(C_{g,0} - \frac{B}{D}\right)\exp(-Dt)$$

$$C_{g,10 \text{ min}} = \frac{2.0\times10^{-5}\,\text{mg}/(\text{min}\bullet\text{L})}{0.83/\text{min}} + \left(0 - \frac{2.0\times10^{-5}\,\text{mg}/(\text{min}\bullet\text{L})}{0.83/\text{min}}\right)\exp(-0.83/\text{min}\bullet\ 10\,\text{min}) = 2.4\times10^{-5}\,\text{mg}/\text{L}$$

where

$$B = \frac{\left(Q_lC_{l,in}\left(1-\exp\left(-\frac{K_LA}{Q_l}\right)\right)+Q_gC_{g,in}\right)}{V_g}$$

$$B = \frac{9.1\,\text{L}/\text{min}\bullet\ 0.01\,\text{mg}/\text{L}\bullet\left(1-\exp\left(-\frac{4.5\ \text{L}/\text{min}}{9.1\ \text{L}/\text{min}}\right)\right)+379\,\text{L}/\text{min}\bullet\ 0\,\text{mg}/\text{L}}{1745\ \text{L}} = 2.0\times10^{-5}\,\text{mg}/(\text{min}\bullet\text{L})$$

8-5

$$D = \frac{\left(\left(\left(\dfrac{Q_l}{H_c}\right)\left(1-\exp\left(-\dfrac{K_LA}{Q_l}\right)\right)\right)+Q_g\right)}{V_g}$$

$$D = \frac{\left(\left(\left(\dfrac{9.1\ \text{L/min}}{0.0033}\right)\left(1-\exp\left(-\dfrac{4.5\ \text{L/min}}{9.1\ \text{L/min}}\right)\right)\right)+379\ \text{L/min}\right)}{1745\ \text{L}} = 0.83\,\text{min}^{-1}$$

The resulting liquid-phase concentration at the shower drain at 10 minutes is as follows:

$$C_{l,out} = C_{l,in}\,\exp\left(-\frac{K_LA}{Q_l}\right)+\left(\frac{C_g}{H_c}\right)\left(1-\exp\left(-\frac{K_LA}{Q_l}\right)\right)$$

$$C_{l,out} = 0.01\ \text{mg/L} \bullet \exp\left(-\frac{4.5\ \text{L/min}}{9.1\ \text{L/min}}\right)+\left(\frac{2.4\times10^{-5}\ \text{mg/L}}{0.0033}\right)\left(1-\exp\left(-\frac{4.5\ \text{L/min}}{9.1\ \text{L/min}}\right)\right) = 0.0090\ \text{mg/L}$$

Step 8:   Calculate mass emission rate as a function of time.

The mass emission rate for MEK at 10 minutes is calculated using Equation 2-32:

$$E_{10min} = Q_l(C_{l,in} \text{!} \ C_{l,out,10min}) = 9.1\ \text{L/minute} \bullet (0.01\ \text{mg/L} - 0.0090\ \text{mg/L}) = 0.0091\ \text{mg/min}.$$

The resulting mass emission rate as a function of time is shown in Figure 8-1. The lower value of K_LA for MEK resulted in a significantly lower mass emission rate. The same eight-step procedure was applied for toluene and DBCM, which resulted in a K_LA value of 12 L/minute for DBCM. The mass emission rate for DBCM is slightly lower than the rate for toluene in that DBCM has a lower Henry's law constant than toluene.

In previous modeling exercises, it has been assumed that the overall mass transfer coefficients between two chemicals may be solely related by $\Psi_1 = K_{Li}/K_{Lj}$. This relationship requires only knowledge of liquid molecular diffusion coefficients for each compound in accordance with Equation 2.12, and is valid when gas-phase resistance to mass transfer is negligible for each compound. As discussed previously, an assumption that gas-phase resistance is negligible is often reasonable only when both compounds are highly volatile (e.g., cyclohexane and radon). Equation 2.15, used to predict Ψ_m, incorporates a chemical's liquid- and gas-phase resistance to mass transfer and will converge to Ψ_1 as k_g/k_l and/or H_c for both i and j become relatively large. Thus, Ψ_m is a more appropriate value to predict values of K_LA for chemicals of wide-ranging volatility.

However, in the case of showers, the value of k_g/k_l is sufficiently large that the value of K_LA for even chemicals as low in volatility as MEK may be estimated using Ψ_1. As a result, the more important variable to predict is the chemical's Henry's law constant, which affects the concentration driving force for mass transfer (Equation 2.28) and hence mass emission rates. For this example, the emitted mass of DBCM was approximately 600 μg, and the emitted mass of MEK was approximately 120 μg.

8.2. DISHWASHER MODEL APPLICATION

Mass balance Equations 2-23 and 2-24 may be used to predict chemical emissions during a dishwasher event of single or multiple cycles, that is, number of separate fills during operation. For this example, the following dishwasher event was assumed: a prerinse cycle of 3.5 minutes, a wash cycle of 10 minutes, and two rinse cycles of 6 and 14 minutes, respectively. Each cycle was followed by a 2-minute drain period. The cycle order and times were based on those for the experiment dishwasher. Other specific operating conditions included a water temperature of 55°C and a liquid fill volume of 7.4 L resulting in a headspace volume of 181 L. Based on experiment results, the headspace ventilation rate was assumed to be 5.7 L/minute. The value of K_LA for toluene (used in Equations 2-23 and 2-24 to predict liquid and gas-phase concentrations associated with these operating conditions) was assumed to be 35 L/minute (average of K_LA values determined for Experiments 5 through 8 replicate in Table 5-5) for all cycles. Because of the relatively small difference in values of K_LA between experiments of

different operating conditions (wash versus rinse), the value of K_LA chosen for toluene represented the average of all dishwasher results for heated water experiments (see Section 5.4.3).

The mass emission rate for toluene was predicted using the following steps:

Step 1: Predict liquid- and gas-phase concentrations as a function of time.

The liquid-phase concentration in the dishwasher water after 3.5 minutes of operation for the first cycle (prerinse cycle) is predicted using Equation 2-23:

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

$$C_l = 0.01\,\text{mg/L}\left[\exp\left(-\frac{5.0/\text{min}}{2}\,3.5\text{min}\right)\cosh\left(\left(\sqrt{\frac{(5.0/\text{min})^2}{4}-0.15\,/\,\text{min}}\right)3.5\text{min}\right)\right]$$

$$+\left(\frac{7.5/\text{min}\bullet1.9\text{x}10^{-3}\,\text{mg/(L/min)}}{4.7/\text{min}} + \frac{0.15/\text{min}\bullet0.01\text{mg/L}}{4.7/\text{min}} - \frac{5.0/\text{min}\bullet0.01\text{mg/L}}{2}\right)$$

$$\bullet\left[\frac{1}{\sqrt{\frac{(5.0\,/\,\text{min})^2}{4}-0.15\,/\,\text{min}}}\exp\left(-\frac{5.0/\text{min}}{2}\,3.5\,\text{min}\right)\sinh\left(\left(\sqrt{\frac{(5.0/\text{min})^2}{4}-0.15\,/\,\text{min}}\right)3.5\text{min}\right)\right]$$

$$= 5.6\times10^{-4}\,\text{mg/L}.$$

where

$$D = Z + Y = 4.7\,/\text{min} + 0.34\,/\text{min} = 5.0\,/\text{min}$$

$$Z = \frac{K_L A}{V_l} = \frac{35\,L/min}{7.4L} = 4.7 \text{ /min}$$

$$Y = \frac{Q_g}{V_g} + \frac{K_L A}{V_g H_c} = \frac{5.7\,L/min}{181\,L} + \frac{35\,L/min}{181\,L \bullet 0.63} = 0.34 \text{ /min}$$

$$E = ZY - BX = 4.7/min \bullet 0.34/min - 7.5/min \bullet 0.19/min = 0.15 \text{ /min}$$

$$B = \frac{K_L A}{V_l H_c} = \frac{35L\,/min}{7.4\,L \bullet 0.63} = 7.5 \text{ /min}$$

$$X = \frac{K_L A}{V_g} = \frac{35\,L/min}{181\,L} = 0.19 \text{ /min}$$

$$F = ZC_{g,0} + XC_{l,0} = 4.7/min \bullet 0 + 0.19/min \bullet 0.01\,mg/L = 0.0019\,mg/(L \bullet min)$$

The gas-phase concentration at the end of the first cycle is calculated using Equation 2-24:

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

$$C_g = 0\,mg/L \exp\left(-\frac{5.1/min}{2} 3.5min\right) \cosh\left(\left(\sqrt{\frac{(5.1/min)^2}{4} - 0.15}\right)3.5min\right)$$

$$+ \left(1.9\times 10^{-3}\,mg/(L \bullet min) - \frac{5.1/min \bullet 0\,mg/L}{2}\right)\left[\frac{1}{\sqrt{\frac{(5.1/min)^2}{4} - 0.15}} \exp\left(-\frac{5.1}{2} 3.5min\right) \sinh\left(\left(\sqrt{\frac{(5.1/min)^2}{4} - 0.15/min}\right)3.5min\right)\right]$$

$$= 3.5 \times 10^{-4}\,mg/L.$$

Step 2: Calculate the mass emission rate as a function of time.

Using Equation 2-31, the mass emission rate at the end of the first cycle is

$$E = Q_g C_{g,3.5min} = 5.7 \text{ L/minute} \bullet 3.5 \times 10^{-4} \text{ mg/L} = 0.0020 \text{ mg/min.}$$

Step 3: Predict ventilation decay rate during drain period.

Between each cycle was a drain period, where water used during the cycle was pumped from the machine. During the drain period, the gas phase was modeled using the following equation with a ventilation rate of 5.7 L/minute:

$$C_g = C_{g,0} \exp\left(-\frac{Q_g}{V_g}t\right) \tag{8-1}$$

where

C_g =   headspace concentration (M/L^3)

$C_{g,0}$ =   headspace concentration at end of cycle (M/L^3)

Q_g =   machine ventilation rate (L^3/T)

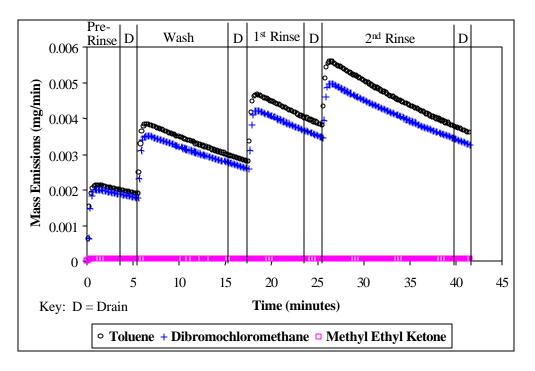V_g =   machine headspace volume (L^3)

t =   time (T).

The concentration of toluene in the dishwasher headspace at the end of the 2 minute drain period is:

$$Cg = 3.5 \times 10-4mg/L \bullet \exp\left(-\frac{5.7 \text{ L/min}}{181 \text{ L}} \bullet 2min\right) = 3.3 \times 10-4mg/L.$$

Step 4: Repeat Steps 1 to 3 for number of dishwasher cycles.

Each cycle was modeled separately with an inlet liquid-phase concentration of 10 μg/L. However, the gas-phase concentration of each cycle was dependent on that of the previous cycle; that is, the initial gas-phase concentration for each cycle ($C_{g,0}$) was equal to the final gas-phase concentration of the previous drain cycle.

The total mass of emitted toluene was calculated by integrating under the mass emission rate curve shown in Figure 8-2. For this example, the total mass of toluene emitted over the entire cycle was predicted to be 157 µg. It should be noted that an additional 117 µg of residual toluene was retained in the dishwasher headspace at the end of the final rinse cycle. This residual would be released as a "puff" if the dishwasher were opened soon after the final cycle. This more concentrated release might contribute a greater exposure route than corresponding emissions during the actual dishwasher operation. The stripping efficiency for toluene over all dishwasher cycles was 93%.
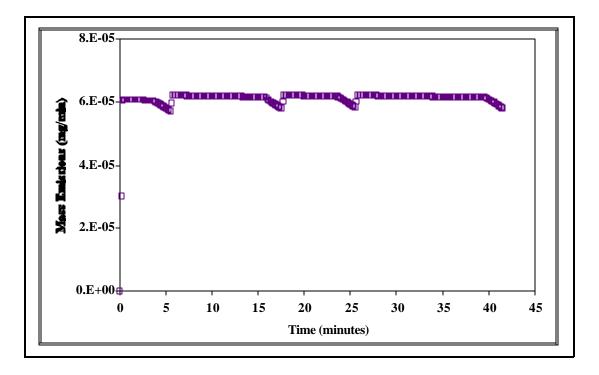
By means of the first six steps outlined in Section 8.1, values of K_LA for DBCM and MEK were estimated. Although values of K_LA were less important for this source because of equilibrium limitations, a value of K_LA for each chemical was needed to properly use the mass balance model. As discussed in Section 5.4.4, a value of k_g/k_l for dishwashers was not determined. Thus, to predict a value of K_LA for a chemical of interest, a k_g/k_l ratio had to be assumed. Given the hydrodynamic similarity between dishwashers and showers, the k_g/k_l value of 160 determined for showers was used. The value of K_LA estimated for DBCM was 37 L/minute, resulting in an **Figure 8-2. Mass emission rates for three**

chemicals for example dishwasher event.

overall emitted mass of 143 µg, and stripping efficiency of 84%. As for toluene, a potential puff release mass was calculated for DBCM to be 107 µg. The value of K_LA for MEK for this example was estimated to be 5.7 L/minute, resulting in a total mass emitted of 2.5 µg, a puff release of 1.9 µg, and a stripping efficiency of 1.5%. Using the identical operating conditions listed for toluene and an inlet concentration of 10 µg/L yielded mass emission rates for each chemical as presented in Figure 8-2. Again, the lower values of K_LA and Henry's law constant for MEK resulted in a significantly lower mass emission rate. To better see the shape of MEK emissions over time, the ordinate of Figure 8-2 was magnified as shown in Figure 8-3.

The general shape of the mass emission rate curve reflected the approach to a dynamic equilibrium condition for each chemical. Although DBCM had a slightly greater value of K_LA than toluene, the mass emission rate for DBCM was lower because of equilibrium limitations in the headspace. Thus, for equilibrium-limited cases, the value of K_LA for a given chemical merely indicates how rapidly equilibrium will be achieved within the headspace. As a result of the insignificance of K_LA, more emphasis is placed

on the accuracy of a chemical's Henry's law

Figure 8-3. Amplification of Figure 8-2 to show MEK mass emission rate.

constant. Currently, there is a lack of information regarding Henry's law constants for potential drinking water contaminants, especially at higher temperatures.

8.3. WASHING MACHINE MODEL APPLICATION

Different mass balance equations were used to predict emissions from each washing machine cycle. Mass balance Equations 3-8 and 3-9 were used to predict chemical concentrations during the fill cycle of a washing machine event. Mass balance Equations 2-23 and 2-24 were used to predict chemical concentrations during the wash and rinse cycles of a washing machine event. Similar to dishwashers, each cycle was modeled separately, with the initial conditions reflecting previous cycles. For example, the initial liquid- and gas-phase concentrations for the wash cycle were equal to the final liquid- and gas-phase concentrations, respectively, for the first fill cycle. Both fill cycles had an identical inlet chemical liquid-phase concentration of 10 µg/L. As for dishwashers, the headspace concentration during the drain/spin period for a washing machine was modeled using Equation 8-1 and the emission rate was calculated using Equation 2-31.

For this example, a washing machine event was assumed to consist of a 3.3-minute fill cycle at a flowrate of 13.8 L/minute ($\approx$ 46 L total liquid volume), a 10-minute wash cycle, a 4-minute drain and spin cycle, another 3.3-minute fill cycle also at a flowrate of 13.8 L/minute, a 4-minute rinse cycle, and finally a 6-minute drain and spin cycle. Other specific operating conditions for this example were a water temperature of 21°C, and ventilation rates of 55 L/minute for the fill cycle, and 53 L/minute for the remaining cycles. With a fill volume of 46 L and an approximate equivalent clothing volume of 11 L, the headspace volume was 92 L.

To predict mass emissions associated with the example operating conditions, a value of K_LA for toluene was chosen for each cycle. An "average" value of K_LA was not used for all cycles because of the significant effects of operating conditions on K_LA observed for washing machine experiments. Values

of K_LA for toluene were as follows: 2.9 L/minute for both fill cycles, 0.58 L/minute for the wash cycle, and 0.84 L/minute for the rinse cycle. On the basis of these values of K_LA and an inlet concentration of 10 µg/L, the mass emission rate was calculated using the following steps:

Step 1:   Predict liquid- and gas-phase concentrations as a function of time for fill cycle.

A second-order Runge-Kutta solution technique was used to determine the liquid- and gas-phase concentrations during filling. The applicable general second-order solution technique is:

$$x^{n+1} = x^n + \frac{\Delta t}{2}\left\{ f\left(t^n, x^n\right) + f\left[t^n + \Delta t, x^n + f\left(t^n, x^n\right)\right]\right\}$$

(8-2)

Applying this method to Equations 2-25 and 2-26 and using 1-second time steps enabled prediction of the liquid- and gas-phase concentrations at each time step, respectively. The liquid-phase concentration in the washing machine water after filling for 3.3 minutes follows:

Find first-order solution:

$$x^{n+1} = \left[\frac{Q_1 C_{1,in}}{V_1^{\ n}} - \frac{Q_1 C_1^{\ n}}{V_1^{\ n}} - \frac{K_L A C_1^{\ n}}{V_1^{\ n}} + \frac{K_L A C_g^{\ n}}{V_1^{\ n} H_c}\right] \bullet \Delta t + C_1^{\ n}$$

$$x^{n+1} = \left[\frac{13.8\,L/min \bullet 0.01\,mg/L}{45.8\,L} - \frac{13.8\,L/min \bullet 0.0084\,mg/L}{45.8\,L} - \frac{2.9\,L/min \bullet 0.0084\,mg/L}{45.8\,L} + \frac{2.9\,L/min \bullet 3.5 \times 10^{-4}\,mg/L}{45.8\,L \bullet 0.24}\right]$$
$$\bullet\,(1/60\,min + 0.0084\,mg/L$$

Find $f(t^n, x^n)$:

$$f\left(t^n, x^n\right) = \left[\frac{Q_1 C_{1,in}}{V_1^n} - \frac{Q_1 C_1^n}{V_1^n} - \frac{K_L A C_1^n}{V_1^n} + \frac{K_L A C_g^n}{V_1^n H_c}\right]$$

$$f\left(t^n, x^n\right) = \frac{13.8\,\text{L/min} \bullet 0.01\,\text{mg/L}}{45.8\,\text{L}} - \frac{13.8\,\text{L/min} \bullet 0.0084\,\text{mg/L}}{45.8\,\text{L}}$$

$$-\frac{2.9\,\text{L/min} \bullet 0.0084\,\text{mg/L}}{45.8\,\text{L}} + \frac{2.9\,\text{L/min} \bullet 3.4 \times 10^{-4}\,\text{mg/L}}{45.8\,\text{L} \bullet 0.24} = 3.0 \times 10^{-5}\,\text{mg/(L} \bullet \text{min)}$$

Find $f[t^n + \Delta t, x^n + \Delta t f(t^n, x^n)]$:

$$f\left(t^n + \Delta t, x^n + \Delta t f\left(t^n, x^n\right)\right) = \left[\frac{Q_1 C_{1,in}}{V_1^{n+1}} - \frac{Q_1 C_1^{n+1}}{V_1^{n+1}} - \frac{K_L A C_1^{n+1}}{V_1^{n+1}} + \frac{K_L A C_g^n}{V_1^{n+1} H_c}\right]$$

$$f\left(t^n + \Delta t, x^n + \Delta t f\left(t^n, x^n\right)\right) = \frac{13.8\,\text{L/min} \bullet 0.01\,\text{mg/L}}{46\,\text{L}} - \frac{13.8\,\text{L/min} \bullet 0.0084\,\text{mg/L}}{46\,\text{L}}$$

$$-\frac{2.9\,\text{L/min} \bullet 0.0084\,\text{mg/L}}{46\,\text{L}} + \frac{2.9\,\text{L/min} \bullet 3.4 \times 10^{-4}\,\text{mg/L}}{46\,\text{L} \bullet 0.24} = 3.0 \times 10^{-5}\,\text{mg/(L} \bullet \text{min)}$$

Insert appropriate values into Equation 8-2:

$$C_1^{n+1} = 0.0084\,\text{mg/L} + \frac{1/6.0\,\text{min}}{2} \bullet \left(3.1 \times 10^{-5}\,\text{mg/L} \bullet \text{min} + 3.0 \times 10^{-5}\,\text{mg/L} \bullet \text{min}\right) = 0.0084\,\text{mg/L}$$

Note: The second-order solution is virtually equivalent to the first-order solution; thus, a fourth-order solution technique was not deemed necessary. Also, values used in this example were rounded. More exact values were used in spreadsheet calculations.

Similarly, the gas-phase concentration in the washing machine headspace at the end of filling is calculated as follows:

Find first-order solution:

$$C_g^{n+1} = \left[\frac{-Q_g C_g^{n}}{\left(V_t - V_l^{n}\right)} + \frac{Q_l C_g^{n}}{\left(V_t - V_l^{n}\right)} + \frac{K_L A C_l^{n}}{\left(V_t - V_l^{n}\right)} - \frac{K_L A C_g^{n}}{\left(V_t - V_l^{n}\right) H_c} \right] \Delta t + C_g^{n}$$

$$C_g^{n+1} = \left[\frac{-55 L/\min \bullet 3.4 \times 10^{-4} mg/L}{\left(150 L - 45.8 L\right)} + \frac{13.8 L/\min \bullet 3.4 \times 10^{-4} mg/L}{\left(150 L - 45.8 L\right)} + \frac{2.9 L/\min \bullet 0.0084 mg/L}{\left(150 L - 45.8 L\right)} - \frac{2.9 L/\min \bullet 3.4 \times 10^{-4} mg/L}{\left(150 L - 45.8 L\right) \bullet 0.24} \right]$$

$$\bullet (1/60 \min) + 3.4 \times 10^{-4} mg/L = 3.5 \times 10^{-5} mg/L$$

Find $f(t^n, x^n)$:

$$f\left(t^n, x^n\right) = \left[\frac{-Q_g C_g^{n}}{\left(V_t - V_l^{n}\right)} + \frac{Q_l C_g^{n}}{\left(V_t - V_l^{n}\right)} + \frac{K_L A C_l^{n}}{\left(V_t - V_l^{n}\right)} - \frac{K_L A C_g^{n}}{\left(V_t - V_l^{n}\right) H_c} \right]$$

$$f\left(t^n, x^n\right) = \frac{-55 L/\min \bullet 3.4 \times 10^{-4} mg/L}{\left(150 L - 45.8 L\right)} + \frac{13.8 L/\min \bullet 3.4 \times 10^{-4} mg/L}{\left(150 L - 45.8 L\right)}$$

$$+ \frac{2.9 L/\min \bullet 0.0084 mg/L}{\left(150 L - 45.8 L\right)} - \frac{2.9 L/\min \bullet 3.4 \times 10^{-4} mg/L}{\left(150 L - 45.8 L\right) \bullet 0.24}$$

Find $f[t^n + \Delta t, x^n + \Delta t f(t^n, x^n)]$:

$$f\left(t^n + \Delta t, x^n + \Delta t f\left(t^n, x^n\right)\right) = \left[\frac{-Q_g C_g^{n+1}}{\left(V_t - V_l^{n+1}\right)} + \frac{Q_l C_g^{n+1}}{\left(V_t - V_l^{n+1}\right)} + \frac{K_L A C_l^{n}}{\left(V_t - V_l^{n+1}\right)} - \frac{K_L A C_g^{n+1}}{\left(V_t - V_l^{n+1}\right) H_c} \right]$$

$$f\left(t^n + \Delta t, x^n + \Delta t f\left(t^n, x^n\right)\right) = \frac{-55 \text{L/min} \bullet 3.5\text{x}10^{-4} \text{mg/L}}{(150\text{L} - 46\text{L})} + \frac{13.8\text{L/min} \bullet 3.5\text{x}10^{-4} \text{mg/L}}{(150\text{L} - 46\text{L})}$$

$$+ \frac{2.9 \text{ L/min} \bullet 0.0084 \text{ mg/L}}{(150 \text{ L} - 46 \text{ L})} - \frac{2.9 \text{ L/min} \bullet 3.5\text{x}10^{-4} \text{ mg/L}}{(150 \text{ L} - 46 \text{ L}) \bullet 0.24}$$

Insert appropriate values into Equation 8-2:

$$C_g^{n+1} = 3.5 \text{ x } 10^{-4} \text{ mg/L} + \left(\frac{1/60 \text{ min}}{2} \right) \left(5.6 \text{ x } 10^{-5} \text{ mg/L} \bullet \text{min} + 5.6 \text{ x } 10^{-5} \text{ mg/L} \bullet \text{min} \right)$$

Step 2: Calculate mass emission rate for each time step during fill cycle.

Through use of Equation 2-31, the mass emission rate at the end of the fill cycle is:

$$E = Q_g C_{g,3.4\text{min}} = 55 \text{ L/minute} \bullet 3.5 \times 10^{-4} \text{ mg/L} = 0.019 \text{ mg/min.}$$

Step 3: Predict liquid- and gas-phase concentrations as a function of time during wash cycle.

Equations 2-23 and 2-24 were used to predict liquid- and gas-phase concentrations as a function of time. Refer to dishwasher steps for use of equations. The initial liquid-phase concentration is equal to the final fill liquid-phase concentration, which in this example is 0.0084 mg/L. Likewise, the initial gas-phase concentration is equal to the final fill gas-phase concentration, which in this example is 3.5×10^{-4} mg/L. At the end of the 10-minute wash cycle, the estimated liquid-phase concentration is 0.0075 mg/L and the estimated gas-phase concentration is 8.1×10^{-5} mg/L.

Step 4: Calculate mass emission rate as a function of time for wash cycle.

Again, with the use of Equation 2-31, the mass emission rate may be calculated. For this example, the rate is:

$$E = 53 \text{ L/minute} \bullet 8.1 \times 10^{-5} \text{ mg/L} = 0.0043 \text{ mg/min.}$$
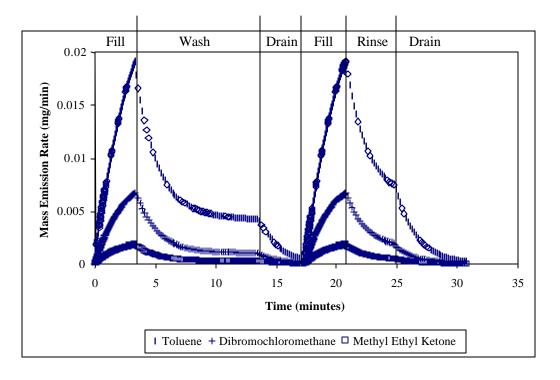
Step 5: Predict ventilation decay rate during drain period.

Between the end of the wash cycle and the next fill is a drain period, where water used during the wash cycle is pumped from the washing machine. This drain/spin cycle was modeled using Equation 8.1 with a ventilation rate of 53 L/minute. The concentration of toluene in the washing machine headspace at the end of the 4-minute drain period is nearly zero.

Step 6: Repeat Steps 1 through 5 for rinse fill, rinse, and final drain.

The wash and rinse cycles were modeled separately, both with an inlet liquid-phase concentration of 10 µg/L.

The total mass emitted for the entire washing machine event was 210 µg. The mass emission rate is shown in Figure 8-4. The mass of toluene remaining in the headspace after the final spin cycle was

0.41 µg, significantly lower than the residual mass observed in the dishwasher headspace. The low residual washing machine headspace mass may be attributed to its relatively high ventilation rate, which

effectively flushes the headspace of the machine. The stripping efficiency integrated over all cycles for toluene was 22%.

Figure 8-4. Mass emission rates for three chemicals for example washing machine event.

In addition to having different values of K_LA, each type of cycle was characterized by a different k_g/k_l ratio. The k_g/k_l values chosen for this example were 9.5 for the fill cycles and 2.2 for the wash and rinse cycles. The resulting values of K_LA for DBCM using the six-step procedure described in Section 8.1 were 1.1 L/minute for the fill cycles, 0.12 L/minute for the wash cycle, and 0.18 L/minute for the rinse cycle. The resulting values of K_LA for MEK following the same procedure were 0.31 L/minute for the fill cycle, 0.030 L/minute for the wash cycle, and 0.044 L/minute for the rinse cycle.

To illustrate the importance of gas-phase resistance to mass transfer, the total mass emissions for DBCM and MEK were calculated using values of K_LA based on Ψ_m and values of K_LA based only on Ψ_l. The total mass emitted for DBCM using Ψ_m to predict K_LA was 67 µg (stripping efficiency of 7.1%) compared with150 µg emitted when Ψ_l was used to predict K_LA. The total mass emitted for MEK using Ψ_m to predict K_LA was 18 µg (stripping efficiency of 1.9%) compared with 65 µg emitted when Ψ_l was used to predict K_LA.

8.4. BATHTUB MODEL APPLICATION

The same mass balance equations used for modeling emissions from washing machines were used for bathtubs (see washing machine steps). Equations 3.8 and 3.9 were used to predict chemical concentrations in the liquid and gas phases, respectively, during the fill portion of bathtub use. Equations 2.23 and 2.24 were used to predict liquid- and gas-phase concentrations during the bathing portion of bathtub use. Equation 2.33 was used to predict resulting mass emissions. The inlet chemical concentration was 10 µg/L. The initial concentrations for the bathing portion were equal to the final liquid- and gas-phase concentrations for the fill portion. For this example, a bathtub was assumed to be filled for 8 minutes using a water flowrate of 9.1 L/minute, resulting in a total liquid volume of approximately 73 L. There was a 20-minute bathing period after the filling experiment. It was also assumed that the bathing event occurred in a 13 m^3 bathroom with an air exchange rate of 1.0/hour (Q_g

= 217 L/minute). The temperature of the water was equivalent to the warmest experimental temperature of 36°C and remained constant for the entire bathing event.

The values of K_LA chosen for toluene were based on bathtub fill and surface volatilization experiments, respectively. Given the narrow range of bathtub fill results, an average value of 4.4 L/minute was chosen based on high flowrate average. Similarly, an average value of 1.2 L/minute was chosen to represent surface volatilization with a person present. The resulting mass emissions for the entire bathtub event are plotted in Figure 8-5. Integrating under the mass emission rate curve, the total mass of toluene emitted was 375 µg, with a corresponding integrated stripping efficiency of 51% .

As with the previous sources, values of K_LA were predicted for DBCM and MEK. For a bathtub event, the k_g/k_l ratio associated with filling was chosen to be 51 and the k_g/k_l ratio associated with bathing was chosen to be 70. The values of K_LA estimated for DBCM using Ψ_m were 4.0 L/minute for filling the tub and 1.1 L/minute for surface volatilization. The values of K_LA estimated for MEK using Ψ_m were 0.72 L/minute for filling the tub and 0.25 L/minute for surface volatilization. The mass emission rates for these two chemicals are presented in Figure 8-5.

The total mass emitted of DBCM using Ψ_m to predict K_LA was 350 µg (stripping efficiency of 48%) compared with 380 µg emitted using Ψ_l to predict K_LA. The total mass emitted of MEK using Ψ_m to predict K_LA was 89 µg (stripping efficiency of 12%) compared with 250 µg emitted using Ψ_l to predict K_LA.
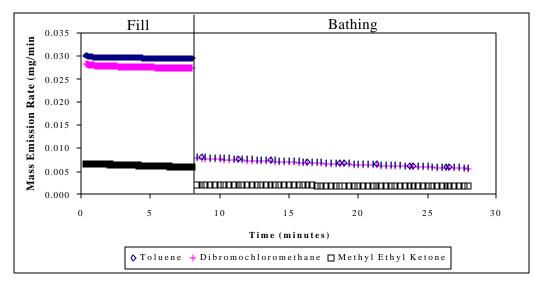

Figure 8-5. Mass emission rates for three chemicals for example bathtub event.