

## **7. BATHTUB EXPERIMENTS**

Three primary activities associated with bathtub operation can cause chemicals originating in tap water to volatilize: (1) when water flows through a tub spout with an open drain (flow-through), (2) when water fills the tub with the drain closed (fill), and (3) when the tub is filled with water (surface volatilization). Bathtub experiments were divided into these three groups. Bathtub flow-through experiments are described in Section 7.1, fill experiments are discussed in Section 7.2, and surface volatilization experiments are presented in Section 7.3.

### **7.1. BATHTUB FLOW-THROUGH EXPERIMENTS**

#### **7.1.1. Experimental System**

The same shower/bathtub unit described in Section 4.1 was used for all bathtub experiments. For flow-through experiments, the system had the same modifications and sample locations as the shower system. As shown in Figure 7-1, the only difference was that the washing machine contents were pumped through the bathtub spout rather than the showerhead.

#### **7.1.2. Experimental Design**

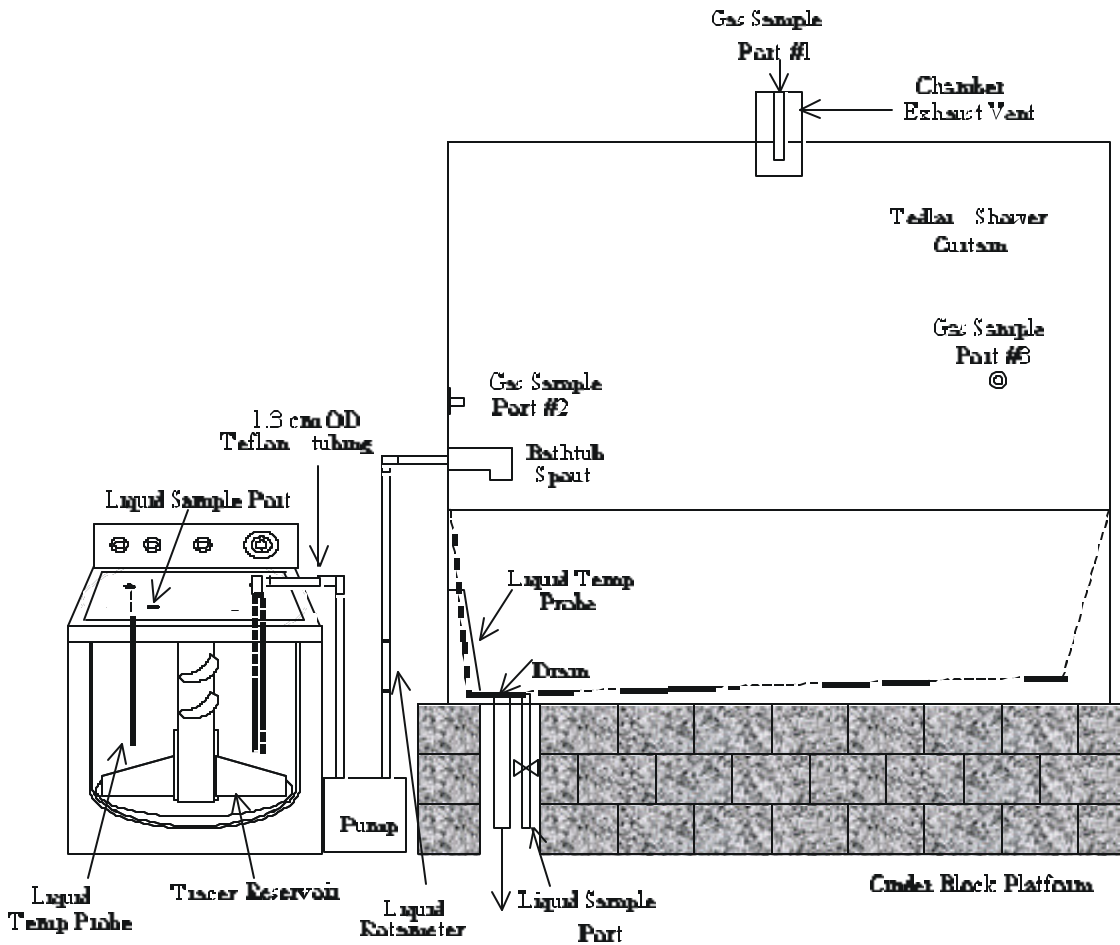
Similar to shower experiments, bathtub flow-through experiments were designed to last 8 minutes. Experimental variables were limited to water temperature and liquid flowrate. To test all combinations of these conditions, four experiments and one replicate experiment were completed.

#### **7.1.3. Source-Specific Methodology**

Bathtub flow-through experiments followed the same experimental methodology as for shower experiments (see Section 4.3).

##### **7.1.3.1. *Sample Schedule***

It was expected that flow-through experiments would have less chemical volatilization than shower experiments. Therefore, 11 gas samples were collected for 1 minute instead of 30 seconds. In order



to collect liquid samples at the mid point of gas sample collection times, the **Figure 7-1. Bathtub flow-through experimental system.**

liquid sample schedule was adjusted to 0.5, 1.5, two samples at 4.25 and 7.5 minutes. A nine liquid samples were collected for each experiment.

### 7.1.3.2. Ventilation Rate

Prediction of bathtub flow-through ventilation rates followed the same procedure developed for showers (see Section 4.3.2).

### 7.1.3.3. Parameter Estimation

The only difference between the parameter estimation for bathtub flow-through experiments and that for shower experiments (see Section 4.3.3) was the method to predict values of  $K_L A$  for

acetone. For showers, values of  $K_L A$  for acetone were predicted based on minimizing the square of the normalized residual between measured and predicted liquid concentrations. For bathtubs, volatilization of acetone was near the average duplicate liquid sample error (see Section 3.5.1), such that the value of  $K_L A$  was determined using gas-phase data. As for showers, values of  $K_L A$  for the remaining tracers were based on liquid-phase data.

#### 7.1.4. Bathtub Flow-Through Results

Six flow-through experiments were completed for which chemical stripping efficiencies and mass transfer coefficients ( $K_L A$ ,  $k_l A$ ,  $k_g A$ , and  $k_g/k_l$ ) were determined. In addition to these results, the effects of liquid temperature and liquid flowrate on chemical volatilization are described in this section.

The operating conditions for each flow-through experiment are listed in Table 7-1.

##### 7.1.4.1. Chemical Stripping Efficiencies

Chemical stripping efficiencies ( $\eta$ ) are reported in Table 7-2. Stripping efficiencies for each chemical were based on liquid-phase measurements.

Acetone stripping efficiencies ranged from 1.7% to 5.3%. The highest value corresponded to the conditions of high flowrate and warm water. In fact, the two experiments completed with warm water led to the highest stripping efficiencies for acetone. Grouping stripping efficiencies according to water temperature and averaging them resulted in a cold water average of 2.9% and a warm water average of 4.9%.

**Table 7-1. Bathtub flow-through operating conditions**

Experiment #	Liquid temperature (°C)	Liquid flowrate (L/min)	Gas flowrate (L/min)	ACH (1/hr)
1	22	9.1	355	12
1 replicate	23	9.1	345	12
2	36	9.1	359	12
3	25	6.1	350	12
4	36	6.1	361	12

4 replicate	37	6.1	365	13
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**Table 7-2. Chemical stripping efficiencies ( $\eta$ ) for experimental bathtub flow-through experiments**

Experiment #	Liquid temp.	Liquid flowrate	Acetone h (%)	Ethyl acetate h (%)	Toluene h (%)	Ethylbenzene h (%)	Cyclohexane h (%)
1	Cold	High	3.8	6.1	26	27	28
1 rep	Cold	High	3.1	4.7	24	24	29
2	Warm	High	5.3	11	38	39	38
3	Cold	Low	1.7	4.5	22	22	22
4	Warm	Low	4.6	14	30	29	27
4 rep	Warm	Low	4.8	10	38	38	41

Ethyl acetate stripping efficiencies ranged from 4.5% to 14% and followed the same trends as acetone. A cold water average stripping efficiency for ethyl acetate was 5.1% and a warm water average stripping efficiency was 12%. The trend of increasing stripping efficiency with increasing temperature is primarily caused by the resulting increase in Henry's law constant for each chemical.

The stripping efficiencies for toluene, ethylbenzene, and cyclohexane were of similar magnitude. The ranges of stripping efficiencies for each chemical were 22% to 38% for toluene, 22% to 39% for ethylbenzene, and 22% to 41% for cyclohexane. The fact that toluene and ethylbenzene results were similar was not surprising given their similar Henry's law constants. For the range of temperatures listed in Table 7-1, toluene had Henry's law constants of  $0.25 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$  (Experiment 1) to  $0.39 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$  (Experiment 4), and ethylbenzene had Henry's law constants of  $0.28 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$  (Experiment 1) to  $0.60 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$  (Experiment 4). The fact that cyclohexane also had results similar to toluene and ethylbenzene indicated that there was not significant gas-phase resistance to mass transfer for the more volatile chemicals for this system. For the temperatures listed in Table 7-1, cyclohexane had significantly higher Henry's law constants ( $6.6 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$  [Experiment 1] to  $11 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$  [Experiment 4]) than did either toluene or ethylbenzene.

The temperature-dependent average stripping efficiencies for toluene, ethylbenzene, and cyclohexane were as follows: cold water averages were 24%, 24%, and 26%, respectively; and warm water averages were 35% for all three chemicals.

Bathtub flow-through Experiment 1 and Experiment 4 were repeated and reported as Experiment 1 replicate and Experiment 4 replicate, respectively. The relative difference between stripping efficiencies determined for Experiment 1 and Experiment 1 replicate for each chemical was 20% for acetone, 26% for ethyl acetate, 8.0 % for toluene, 12% for ethylbenzene, and 3.5% for cyclohexane. The relative difference between stripping efficiencies determined for Experiment 4 and Experiment 4 replicate for each chemical was 4.3% for acetone, 33% for ethyl acetate, 24% for toluene, 27% for ethylbenzene, and 41% for cyclohexane.

#### 7.1.4.2. $K_LA$ Values

Values of  $K_LA$  for all chemicals are reported in Table 7-3. Values of  $K_LA$  for acetone were based on gas-phase data. Values of  $K_LA$  for ethyl acetate, toluene, ethylbenzene, and cyclohexane were based on liquid-phase data.

The highest values of  $K_LA$  for acetone and ethyl acetate were associated with warm water experiments. Values of  $K_LA$  for acetone ranged from 0.11 to 0.54 L/minute. The cold water average value of  $K_LA$  was 0.15 L/min and the warm water average was 0.48 L/min. Values of  $K_LA$  for ethyl acetate ranged from 0.32 to 1.2 L/minute. The temperature dependent averages of  $K_LA$  for ethyl acetate were 0.48 L/min for cold water and 1.0 L/min for warm water.

The highest values of  $K_LA$  for toluene, ethylbenzene, and cyclohexane were for the conditions of high flowrate and warm water. However, experiments using cold water and a high flowrate also resulted in higher values of  $K_LA$ . Because the range of values of  $K_LA$  was so

**Table 7-3. Values of  $K_LA$  for bathtub flow-through experiments**

Experiment #	Liquid temp.	Liquid flowrate	Acetone $K_LA$ (L/min)	Ethyl acetate $K_LA$ (L/min)	Toluene $K_LA$ (L/min)	Ethylbenzene $K_LA$ (L/min)	Cyclohexane $K_LA$ (L/min)
1	Cold	High	0.11	0.64	2.9	2.9	3.1
1 rep	Cold	High	0.15	0.49	2.4	2.4	2.9
2	Warm	High	0.54	1.2	4.5	4.5	5.1
3	Cold	Low	0.18	0.32	1.6	1.5	1.7
4	Warm	Low	0.43	1.1	2.2	2.1	1.9

4 rep	Warm	Low	0.46	0.79	2.9	2.9	3.2
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narrow for these compounds, an overall average is reported here. Values of  $K_LA$  for toluene ranged from 1.6 to 4.5 L/minute, with an overall average of 2.8 L/minute. Values of  $K_LA$  for ethylbenzene ranged from 1.5 to 4.5 L/minute, with an overall average of 2.7 L/minute. Finally, values of  $K_LA$  for cyclohexane ranged from 1.7 L to 5.1 L/minute, with an overall average of 3.0 L/minute.

Mass transfer data for bathtub flow-through experiments may be presented in the same format as shower experimental data (see Section 4.4.2). A representative plot is shown in Figure 7-2 for toluene and Experiment 4 replicate. The operating conditions used in Experiment 4 replicate were warm water and low flowrate. As shown in Figure 7-2, each experimental period consisted of a liquid sample collected from the tracer reservoir, an outlet liquid sample, and a gas sample. For each period, the bathtub outlet concentration in both the liquid and gas phases may be estimated using the mass balance models (Equations 2.28 and 2.30). To determine the best  $K_LA$  value for the model, the residuals between the measured and predicted concentrations were minimized using the method described in Section 3.6.2. For toluene, the residual between liquid-phase values was minimized, resulting in a value of 2.9 L/minute for Experiment 4 replicate.

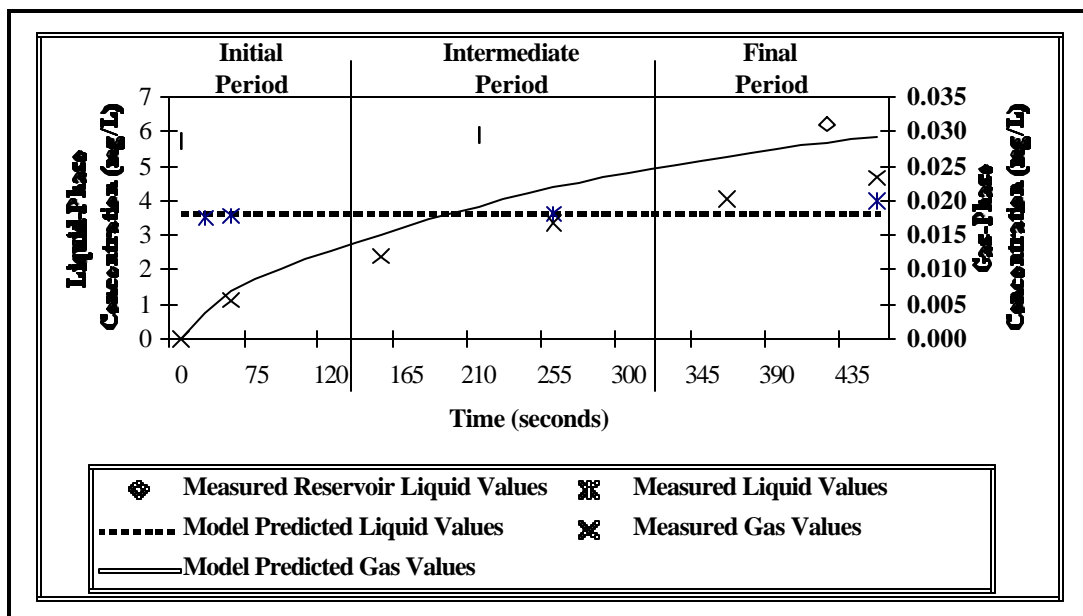


Figure 7-2. Toluene experimental data for Experiment 4 replicate.

### 7.1.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients

Values of  $K_L A$  for each chemical were separated into the components of  $k_1 A$  and  $k_g A$  using Equation 2-5 and a value of  $k_g/k_1$  determined for each specific experiment (see Sections 3.6.3 and 3.6.4 for methodology). Values of  $k_1 A$  and  $k_g A$  are reported in Table 7-4 for each chemical in addition to values of  $k_g/k_1$  for each experiment.

For bathtub flow-through experiments, values of  $k_g/k_1$  ranged from 37 to 96. In general, values of  $k_1 A$  and  $k_g A$  for each chemical were similar in magnitude. The ratio of  $k_g/k_1$  was higher at low flowrates (average  $k_g/k_1 = 71$ ) than at high flowrates (average  $k_g/k_1 = 41$ ).

**Table 7-4. Liquid- and gas-phase mass transfer coefficients for bathtub flow-through experiments**

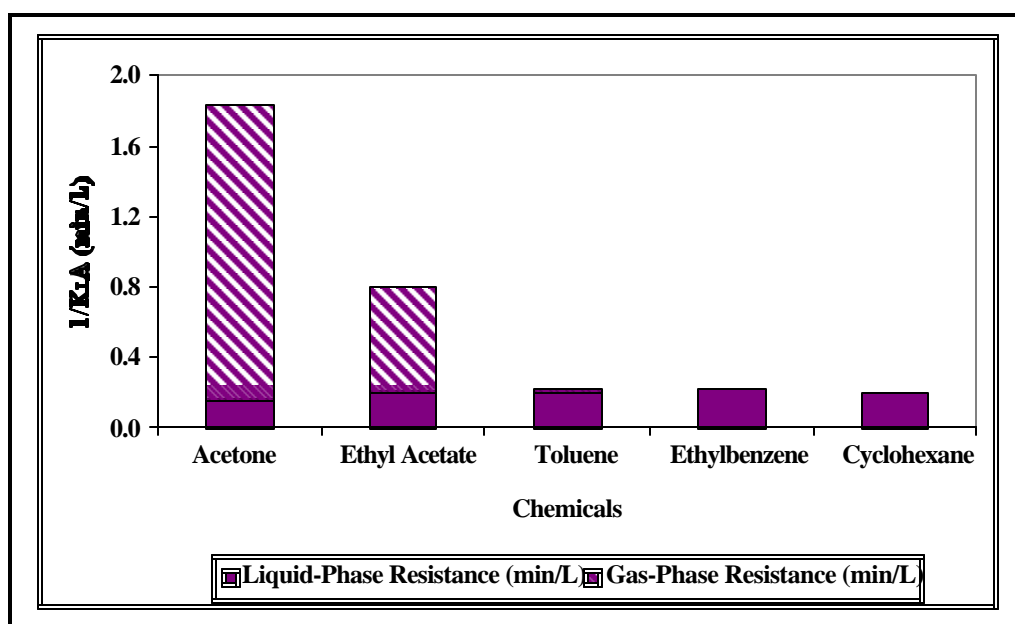
Experiment #	Chemical	$k_1 A$ (L/min)	$k_g A$ (L/min)	$k_g/k_1$
1	A	2.9	108	37
	EA	4.5	168	
	T	3.2	117	
	EB	3.1	117	
	C	3.1	115	
1 replicate	A	3.2	136	43
	EA	3.0	126	
	T	2.6	111	
	EB	2.6	109	
	C	2.9	126	
2	A	6.0	249	42
	EA	4.9	205	
	T	4.8	198	
	EB	4.7	196	
	C	5.1	211	
3	A	2.4	159	66
	EA	1.3	86	
	T	1.7	110	
	EB	1.6	106	
	C	1.7	110	
4	A	2.4	227	96
	EA	2.4	234	
	T	2.2	214	
	EB	2.2	207	
	C	1.9	182	
4 replicate	A	4.2	211	50
	EA	2.7	135	
	T	3.1	152	

	EB	3.0	151
	C	3.2	161

Liquid- and gas-phase mass transfer coefficients may also be used to determine the relative importance of liquid and gas-phase resistances to mass transfer for specific chemicals and operating conditions. As shown in Equation 2-5, overall resistance to mass transfer ( $1/K_L A$ ) may be written as the sum of liquid-phase resistance to mass transfer ( $1/k_l A$ ) and gas-phase resistance to mass transfer ( $1/k_g A \cdot H_c$ ). These resistances are shown graphically in Figure 7-3 for each chemical in Experiment 2. As shown in Figure 7-3, overall resistance to mass transfer for acetone and ethyl acetate is dominated by resistance in the gas phase. On the other hand, overall resistance to mass transfer for toluene, ethylbenzene, and cyclohexane is insignificant compared with their respective liquid-phase resistances to mass transfer.

#### 7.1.4.4. Mass Closure

The ranges of mass closure for each chemical were 98% to 102% for acetone, 98% to 105% for ethyl acetate, 89% to 107% for toluene, 86% to 100% for ethylbenzene, and 82% to 103% for cyclohexane. All mass closure values are given in the Appendix.





**Figure 7-3. Resistances to mass transfer for each chemical in Experiment 2.**

## **7.2. BATHTUB FILL EXPERIMENTS**

### **7.2.1. Experimental System**

As before, the same experimental system constructed for shower/bathtub flow-through experiments was used for bathtub fill experiments. However, the drain was plugged with a rubber stopper so the bathtub would fill. An additional modification shown in Figure 7-4 was a different liquid sample port location. Samples were collected from this port by pumping water from the bathtub using a 102 cm perforated 0.635 cm OD Teflon™ tube. The perforated Teflon™ tube was angled in the bathtub pool such that water was drawn through the holes at different depths, resulting in a more distributed liquid sample. Tracer reservoir samples were collected in the same manner as for shower and bathtub flow-through experiments. For bathtub fill experiments, only gas sample ports #1 and #2 were used. A more evenly distributed gas concentration was expected for these experiments.

### **7.2.2. Experimental Design**

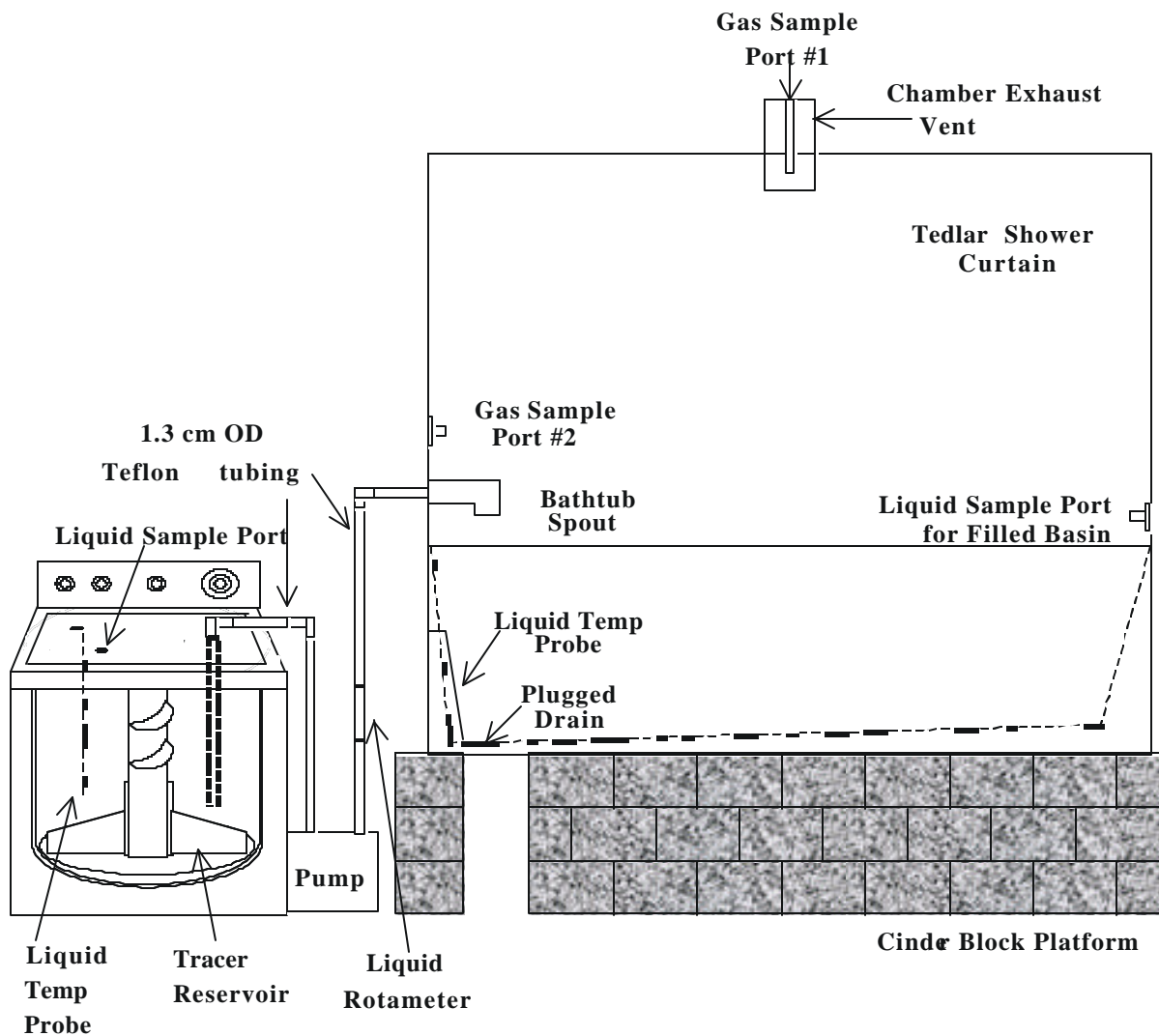
As with flow-through experiments, bathtub fill experimental variables were liquid temperature and liquid flowrate. Four experiments were completed with two replicates.

### **7.2.3. Source-Specific Methodology**

No different preexperimental tasks were completed for fill experiments, except for the introduction of a drain plug.

#### **7.2.3.1. Sample Schedule**

Bathtub fill experiments varied in length depending on experimental flowrate. For experiments completed at 9.1 L/min, the bathtub was filled for 8 minutes. For experiments completed at 6.1 L/min, the bathtub was filled for 12 minutes. A total of 10 liquid-phase samples were collected for each fill experiment. Liquid-phase samples were collected every 2 minutes for the high flowrate experiments, and every 3 minutes for the low flowrate experiments. Tracer reservoir samples were collected within 90 seconds of every bathtub sample.



**Figure 7-4. Bathtub fill experimental system.**

An initial gas sample was collected from sample port #1 before starting the experiment. Once an experiment began, a single gas sample was collected at this port for the duration of the experiment, followed by a 1-minute sample collected immediately after the experiment. One-minute gas samples were also collected at sample port #2. These samples were scheduled such that a bathtub liquid sample was collected at the midpoint of the gas sample time. Six gas-phase samples were collected for each experiment.

### **7.2.3.2. Ventilation Rates**

Prediction of bathtub (fill) ventilation rates followed the same procedure developed for showers (see Section 4.3.2).

### **7.2.3.3. Parameter Estimation**

The same parameter estimation techniques outlined in Section 6.1.3.3 for washing machine fill cycle experiments applied to bathtub fill experiments. Stripping efficiencies and values of  $K_LA$  were based on liquid-phase data for all chemicals. Values of  $K_LA$  were based on gas-phase data for acetone and ethyl acetate and were based on liquid-phase data for toluene, ethylbenzene, and cyclohexane.

### **7.2.4. Bathtub Fill Results**

Five bathtub fill experiments were completed to predict chemical mass emissions. Bathtub fill results can be combined with bathtub surface volatilization results presented in Section 7.3 to characterize total mass emissions during a typical bathing event. Ventilation rates, stripping efficiencies, and mass transfer coefficients ( $K_LA$ ,  $k_lA$ ,  $k_gA$ , and  $k_g/k_l$ ) are presented in this chapter and are based on the experimental methodology presented in Sections 3.0 and 7.2.3. In addition, the effects of liquid temperature, liquid fill rate, and chemical properties are discussed. The operating conditions for each mass transfer experiment are listed in Table 7-5.

#### **7.2.4.1. Chemical Stripping Efficiencies**

Chemical stripping efficiencies ( $\eta$ ) are reported in Table 7-6. Stripping efficiencies for high flowrate (9.1 L/min) experiments were based on a fill time of 8 minutes whereas stripping efficiencies for low flowrate (6.1 L/min) experiments were based on a fill time of 12 minutes.

Liquid-phase concentrations did not change significantly in the bathtub after approximately 1 minute of fill time, thereby allowing comparison of stripping efficiencies based on different experimental times.

**Table 7-5. Bathtub (fill) operating conditions**

Experiment #	Liquid temperature (°C)	Fill time (min)	Liquid flowrate (L/min)	Liquid volume (L)	Gas flowrate (L/min)
1	24	8:00	9.1	73	373
2	35	8:00	9.1	73	379
2 replicate	36	8:00	9.1	73	373
3	23	12:00	6.1	73	370
4	35	11:23	6.1	69	377

**Table 7-6. Chemical stripping efficiencies ( $\eta$ ) for bathtub (fill) experiments**

Expt. #	Liquid Temp.	Liquid Flowrate	Acetone $\eta$ (%)	Ethyl Acetate $\eta$ (%)	Toluene $\eta$ (%)	Ethylbenzene $\eta$ (%)	Cyclohexane $\eta$ (%)
1	Cold	High	4.9	3.0	31	33	46
2	Warm	High	5.2	5.3	30	32	47
2 rep	Warm	High	2.0	3.1	31	32	46
3	Cold	Low	5.8	3.1	29	31	43
4	Warm	Low	7.7	7.0	30	29	46

Stripping efficiencies for acetone ranged from 2.0% to 7.7%, with the highest value for low flowrate and warm water. The average stripping efficiency for acetone was 5.1%. Stripping efficiencies for ethyl acetate ranged from 3.0% to 7.0%, with an overall average of 4.3%.

There was little deviation between stripping efficiencies for toluene, ethylbenzene, and cyclohexane. Average stripping efficiencies were 30% for toluene, 31% for ethylbenzene, and 46% for cyclohexane. As expected, toluene and ethylbenzene had similar results. Cyclohexane stripping efficiencies were somewhat higher for this set of bathtub experiments, indicating more influence of gas-phase resistance to mass transfer for more volatile chemicals, possibly from formation of bubbles in the underlying pool as the bathtub filled.

Experiment 2 was repeated. The relative difference between stripping efficiencies determined for Experiments 2 and 2 replicate were 88% for acetone, 52% for ethyl acetate, 3.3% for toluene, 0% for ethylbenzene, and 2.2% for cyclohexane.

#### 7.2.4.2. $K_LA$ Values

Values of  $K_LA$  for all chemicals and operating conditions are reported in Table 7-7, and were based on the same fill times discussed for stripping efficiencies. In general, for all chemical tracers, values of  $K_LA$  were higher at higher liquid flowrates. The average values of  $K_LA$  at a liquid flowrate of 6.1 L/min were 0.39 L/min for acetone, 0.86 L/min for ethyl acetate, 2.7 L/min for toluene, 2.6 L/min for ethylbenzene, and 4.9 L/min for cyclohexane. At a liquid flowrate of 9.1 L/min, the average values of  $K_LA$  were 0.54 L/min for acetone, 1.3 L/min for ethyl acetate, 4.4 L/min for toluene, 4.4 L/min for ethylbenzene, and 8.5 L/min for cyclohexane.

#### 7.2.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients

Values of  $K_LA$  for each chemical were separated into the components of  $k_lA$  and  $k_gA$  using Equation 2.5 and a value of  $k_g/k_l$  determined for each specific experiment. These values are reported in Table 7-8. For the bathtub filling events, values of  $k_g/k_l$  ranged from 27 to 77, with an average value of 51. Bathtub water during a filling event is characterized by splashing at the surface and entrainment of air creating visible bubbles in the pool. As such, the average  $k_g/k_l$  value for high flowrate experiments was somewhat lower (45) than the average value associated with low flowrate experiments (62). These values were similar in magnitude to values of  $k_g/k_l$  predicted for surface aerator systems (38 to 110) (Hsieh et al., 1991).

#### 7.2.4.4. Mass Closure

For bathtub fill experiments, the percentage of mass recovered was based on Equation 3.11 applied for the entire time of fill. The range of mass closure for each chemical was 96% to 101% for acetone, 103% to 108% for ethyl acetate, 89% to 106% for toluene, 87% to 96% for ethylbenzene, and 68% to 87% for cyclohexane.

**Table 7-7. Values of  $K_LA$  for bathtub (fill) experiments**

Experiment #	Liquid temp.	Liquid flowrate	Acetone $K_LA$ (L/min)	Ethyl acetate $K_LA$ (L/min)	Toluene $K_LA$ (L/min)	Ethylbenzene $K_LA$ (L/min)	Cyclohexane $K_LA$ (L/min)
1	Cold	High	0.45	1.0	4.1	4.4	7.1

2	Warm	High	0.53	1.4	5.3	5.9	11
2 rep	Warm	High	0.64	1.5	3.7	3.8	7.4
3	Cold	Low	0.39	0.71	2.6	2.7	4.4
4	Warm	Low	0.39	1.0	2.7	2.5	5.4

**Table 7-8. Liquid- and gas-phase mass transfer coefficients for bathtub (fill) experiments**

Experiment #	Chemical	$k_lA$ (L/min)	$k_gA$ (L/min)	$k_g/k_l$
1	A	7.1	395	56
	EA	4.9	274	
	T	4.4	244	
	EB	4.6	257	
	C	7.1	396	
2	A	9.3	253	27
	EA	8.3	228	
	T	5.8	159	
	EB	6.3	172	
	C	11	311	
2 replicate	A	5.9	303	51
	EA	5.3	269	
	T	3.8	193	
	EB	4.0	202	
	C	7.4	376	
3	A	4.7	365	77
	EA	2.7	208	
	T	2.7	208	
	EB	2.8	220	
	C	4.4	344	
4	A	4.2	191	46
	EA	3.8	175	
	T	2.8	129	
	EB	2.6	121	
	C	5.4	245	

### 7.3. SURFACE VOLATILIZATION EXPERIMENTS

#### 7.3.1. Experimental System

The same experimental system presented in Section 7.2.1 was used for surface volatilization experiments. The only addition to the system was a simulated person. A model of a person was designed using empty 3 L Tedlar™ bags. Four bags were connected with string to create joints

between each bag. Additional strings were attached to the “head” bag and “foot” bag that allowed them to be moved from outside the system. Moving the strings resulted in bag motions that created waves and moderate splashing in the bathtub pool.

### **7.3.2. Experimental Design**

Four combinations of conditions were studied for surface volatilization experiments. Experimental variables were liquid temperature and the presence of a person.

### **7.3.3. Source-Specific Methodology**

Surface volatilization experiments followed bathtub fill experiments, so the bathtub contained a well-mixed solution of chemical tracers. The following tasks were completed before starting the surface volatilization portion of an experiment:

- For appropriate experiments, the Tedlar™ person was placed in the bathtub pool
- An initial liquid sample was collected
- An initial gas sample was collected from port #1.

#### **7.3.3.1. Sample Schedule**

Based on typical bathing times, surface volatilization experiments lasted 20 minutes. Liquid samples were collected from the bathtub every 4 minutes. Eight liquid-phase samples were collected for each experiment. Gas samples were collected from port #2 for 2 minutes each, starting at 3, 7, 11, and 15. minutes. A single gas sample was collected for the 20-minute experiment from port #1. A final gas sample was also collected from this port. Six gas samples were collected for each experiment.

#### **7.3.3.2. Ventilation Rates**

Prediction of ventilation rates associated with bathtub surface volatilization experiments followed the same procedure developed for showers (see Section 4.3.2).

#### **7.3.3.3. Parameter Estimation**

Chemical volatilization rates for bathtub experiments with standing water (no additional motion) were nearly zero. Therefore, for surface volatilization experiments, chemical stripping efficiencies were calculated using the following equation, which included gas-phase data:

$$h = \frac{Q_g \int_{t_1}^{t_2} C_g \Delta t + V_g (C_{g, \text{end}} - C_{g, \text{in}})}{V_l C_{l, \text{in}}} \quad (7-1)$$

where

$Q_g$  = system ventilation rate ( $L^3/T$ )

$C_g$  = integrated gas sample average concentration ( $M/L^3$ )

$\Delta t$  = time of experiment (T)

$V_g$  = headspace volume ( $L^3$ )

$V_l$  = bathtub fill volume ( $L^3$ )

$C_{g, \text{end}}$  = final gas-phase concentration in headspace ( $M/L^3$ )

$C_{g, \text{in}}$  = initial gas-phase concentration in headspace ( $M/L^3$ )

$C_{l, \text{in}}$  = average liquid-phase concentration in tracer reservoir ( $M/L^3$ ).

Bathtub surface volatilization experiments with a simulated person were characterized by significantly higher chemical stripping efficiencies than were quiescent bathtub experiments, such that liquid-phase values were used.

Because of the limited chemical volatilization for quiescent conditions (no “person” present), values of  $K_L A$  were not determined for this source. Values of  $K_L A$  for bathtub experiments with a simulated person were determined using the methodology outlined in Section 3.6.2. Gas-phase data were used to find the best-fit value of  $K_L A$  for acetone and ethyl acetate, and liquid-phase data were used to find the best-fit value of  $K_L A$  for toluene, ethylbenzene, and cyclohexane.

#### 7.3.4. Bathtub Surface Volatilization Results



Six bathtub surface volatilization mass transfer experiments were completed. Surface volatilization results may be combined with bathtub fill results presented in Section 7.2.4 to characterize total mass emissions during typical bathing events. Based on the experimental methodology presented in Sections 3.0 and 7.3.3, the ventilation rates, overall chemical stripping efficiencies, and mass transfer coefficients ( $K_LA$ ,  $k_1A$ ,  $k_gA$ , and  $k_g/k_1$ ) are presented in this chapter. In addition, effects of liquid temperature, presence of a person, and chemical properties on each response are discussed.

Operating conditions for each mass transfer experiment are given in Table 7-9.

#### 7.3.4.1. Chemical Stripping Efficiencies

Stripping efficiencies for each chemical are reported in Table 7-10. As mentioned in Section 7.3.3.3, chemical stripping efficiencies for experiments not using a simulated person (Experiments 1, 1 replicate, and 2) were based on gas-phase data. Values reported in Table 7-10 for these experiments ranged from 0.57% to 15% for all chemicals.

There were significant reductions in liquid-phase chemical concentrations for Experiments 3 through 4 replicate, allowing stripping efficiencies to be determined based on differences in liquid concentration. Stripping efficiencies ranged from 1.6% to 7.3% for acetone, 3.4% to 9.8% for ethyl acetate, 27% to 32% for toluene, 26% to 32% for ethylbenzene, and 30% to 41% for cyclohexane. The degree of splashing associated with surface volatilization experiments with a simulated person could not be reasonably quantified and was not consistent. As a result, it is difficult to report more than just stripping efficiency values for these experiments; that is, neither a trend analysis nor a determination of relative difference in values was completed.

**Table 7-9. Bathtub surface volatilization operating conditions**

Experiment #	Liquid temperature (°C)	Person present?	Liquid volume (L)	Gas flowrate (L/min)
1	23	No	73	370
1 replicate	24	No	73	377
2	34	No	69	377

3	24	Yes	73	373
4	33	Yes	73	379
4 replicate	35	Yes	73	373

**Table 7-10. Chemical stripping efficiencies (n) for bathtub surface volatilization experiments**

Experiment. #	Liquid temp.	Person present ?	Acetone h (%)	Ethyl acetate h (%)	Toluene h (%)	Ethylbenzene h (%)	Cyclohexane h (%)
1	Cold	No	0.57	1.6	7.9	5.1	4.7
1 rep	Cold	No	2.5	5.9	13	7.6	13
2	Warm	No	2.7	6.4	14	8.3	15
3	Cold	Yes	1.6	3.4	32	32	39
4	Warm	Yes	4.5	9.8	27	26	41
4 rep	Warm	Yes	7.3	8.9	30	29	30

#### 7.3.4.2 $K_LA$ Values

Values of  $K_LA$  were not determined for experiments using still water (no person present) given the near zero rate of chemical volatilization. Values of  $K_LA$  were determined, however, for Experiments 3, 4, and 4 replicate and are reported in Table 7-11.

Values of  $K_LA$  for each chemical were 0.11 to 0.25 L/minute for acetone, 0.24 to 0.49 L/minute for ethyl acetate, 1.2 L/minute for toluene, 1.1 to 1.2 L/minute for ethylbenzene, and 1.2 to 2.0 L/minute for cyclohexane. Again, because of the inconsistent nature of these experiments, values of  $K_LA$  are merely indicators of the order of magnitude of chemical volatilization during bathing events.

A representative experimental plot for surface volatilization experiments with a simulated person is presented in Figure 7-5. The plot shows toluene data. Experimental conditions were warm water and presence of the simulated person. The resulting value of  $K_LA$  for toluene for this example was 1.2 L/min.

**Table 7-11. Values of  $K_LA$  for bathtub surface volatilization experiments**

Experiment #	Liquid temp.	Person present?	Acetone $K_LA$ (L/min)	Ethyl acetate $K_LA$ (L/min)	Toluene $K_LA$ (L/min)	Ethylbenzene $K_LA$ (L/min)	Cyclohexane $K_LA$ (L/min)
3	Cold	Yes	0.11	0.24	1.2	1.2	1.4
4	Warm	Yes	0.25	0.49	1.2	1.1	2.0
4 rep	Warm	Yes	0.23	0.40	1.2	1.1	1.2

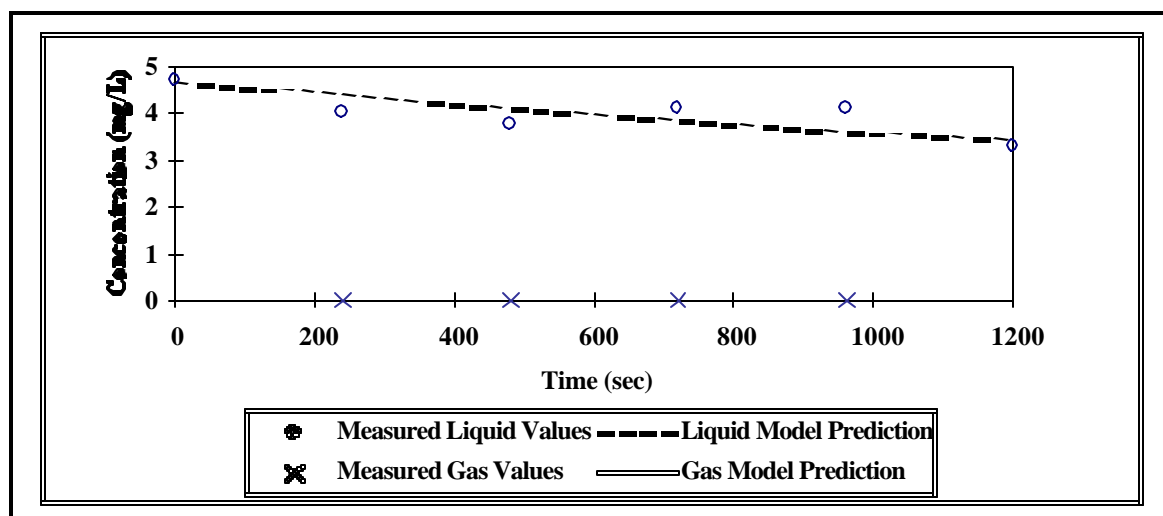


Figure 7-5. Toluene experimental data for Experiment 4 replicate.

### 7.3.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients

Values of  $K_LA$  for each chemical were separated into the components of  $k_lA$  and  $k_gA$  using Equation 2.5 and a value of  $k_g/k_l$  determined for each specific experiment (see Sections 3.6.3 and 3.6.4 for methodology). Values of  $k_lA$  and  $k_gA$  are reported in Table 7-12 for each chemical in addition to values of  $k_g/k_l$  for Experiments 3, 4, and 4 replicate.

For bathtub surface volatilization experiments with a simulated person present, values of  $k_g/k_l$  ranged from 54 to 78. Despite the randomness associated with these experiments, values of  $k_g/k_l$  were relatively similar in magnitude.

### 7.3.4.4. Mass Closure

For bathtub surface volatilization experiments, the percentage of mass recovered was based on Equation 3.10. The range of mass closure for surface volatilization experiments with no person present was 99% to 104% for acetone, 100% to 105% for ethyl acetate, 96% to 110% for toluene, 86% to 100% for ethylbenzene, and 93% to 117% for cyclohexane. For surface volatilization experiments involving a simulated person, the range of mass closure was 98% to 103% for acetone, 104% to 109% for ethyl acetate, 90% to 100% for toluene, 83% to 92% for ethylbenzene, and 80% to 91% for cyclohexane.

**Table 7-12. Liquid- and gas-phase mass transfer coefficients for bathtub surface volatilization experiments**

Experiment #	Chemical	$k_l A$ (L/min)	$k_g A$ (L/min)	$k_g/k_l$
3	A	1.8	97	54
	EA	1.2	63	
	T	1.3	69	
	EB	1.3	68	
	C	1.4	76	
4	A	1.8	143	78
	EA	1.4	107	
	T	1.2	97	
	EB	1.1	88	
	C	2.0	156	
4 replicate	A	1.6	122	78
	EA	1.1	84	
	T	1.2	97	
	EB	1.1	88	
	C	1.2	94	