4. SHOWER EXPERIMENTS

Shower operation consists of a single water activity, that is, no separate cycles. To study this activity, a wide range of operating conditions were applied to a consistent experimental design.

4.1. EXPERIMENTAL SYSTEM

A 140 cm × 70 cm × 178 cm (1.7 m^3 total volume) shower stall (with bathtub) was purchased to complete all shower experiments. The shower stall was installed in the stainless steel chamber on a 58 cm high cinder-block platform. The platform served two purposes: (1) it elevated the system to an appropriate height for draining and collecting liquid samples and (2) it elevated the shower stall such that it reached the stainless steel chamber's ceiling, which provided a system boundary. Other system boundaries included three walls and a floor made of fiberglass coated with an unknown plastic, and one wall (a curtain) made of Tedlar™.

Showering involves production of a spray of water that impacts on and cascades down surfaces to the bathtub floor. The floor slopes toward a drain where water is removed from the system. The experimental shower system required an auxiliary water supply (see Figure 4-1). To meet this need, the washing machine described in Section 6.1.1 effectively served as a tracer reservoir. The washing machine was directly plumbed to the building cold and hot water supply. Chemicals were added to the washing machine as it filled (~ 90 L). The reservoir's contents were further mixed by using wash cycle agitation. The washing machine contents were pumped with a rotary vane pump (PROCON™) through 1.3 cm OD Teflon™ tubing to the shower head. An adjustable low-flow (9.5 L/minute maximum) showerhead (Interbath™) was used for all experiments. The showerhead could be adjusted between fine and coarse spray. A 60 mm, 19 L/min maximum rotameter (King Instrument Co.) was installed in the Teflon™ tubing line to measure the liquid flowrate through the system. The experimental flowrates were based on typical values and the restrictions of the showerhead. The accuracy of the rotameter was verified by timing the collection of a known volume of liquid from the showerhead.
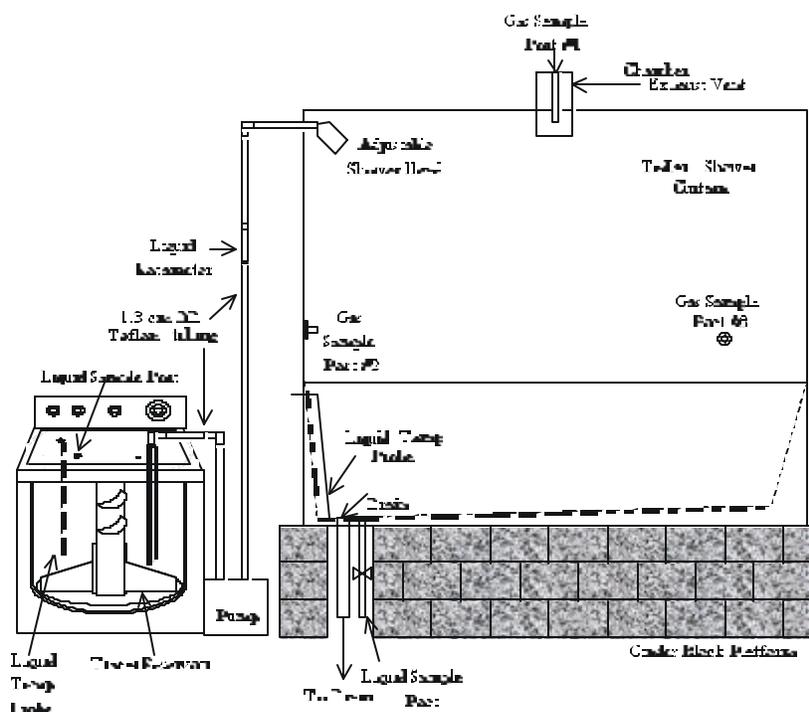
Figure 4-1. Shower experimental system.

Liquid samples were collected from the washing machine reservoir in a manner similar to the actual washing machine experiments (see Section 6.1.1). The shower stall was designed to collect the necessary samples to solve the shower mass balance equations (Equations 2-28 and 2-30). A liquid sample port was installed in the base of the bathtub near the drain. A 30 cm length of 0.64 cm OD Teflon™ tubing with a Teflon™ sample valve was connected to this port. Liquid samples were collected as described in Section 3.3.1.

Three gas sample ports were installed in the system to better understand the gas-phase chemical concentration distribution in the stall. Sample port #1 was located within the chamber exhaust vent and consisted of a 91-cm-long 0.64 cm OD Teflon™ tube attached to a stainless steel Swagelok™ union at which point a sorbent tube was connected. Port #2 was a bore-through Swagelok™ fitting located on the wall with the showerhead, 53 cm from the bathtub floor. Port #3 was located on the shower curtain, 61 cm from the floor of the bathtub. A Swagelok™ fitting was inserted in the curtain for sample collection. Because of time constraints, only gas samples collected from sample ports #1 and #3 were collected as described in Section 3.3.2. The sampling flowrates for sorbent tubes used for

sample collection at port #2 were measured and recorded before the start of each experiment with clean air. Thus, a bubble flowmeter was not used in the sampling train (see Figure 3-1) at this port.

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

4.2. EXPERIMENTAL DESIGN

The following operating variables were selected for shower experiments: water temperature, liquid flowrate, and shower spray type. The impact of these operating conditions on chemical volatilization rates was studied using a $2 \times 2 \times 2$ factorial array. As shown in Figure 4-2, variable ranges were cold ($T \approx 22°C$) versus warm ($T \approx 35°C$), low liquid flowrate (6.1 L/minute) versus high liquid flowrate (9.1 L/minute), and fine shower spray versus coarse shower spray. Eight experiments were completed, with two additional experiments serving as replicates.

Figure 4-2. Shower factorial experimental design.
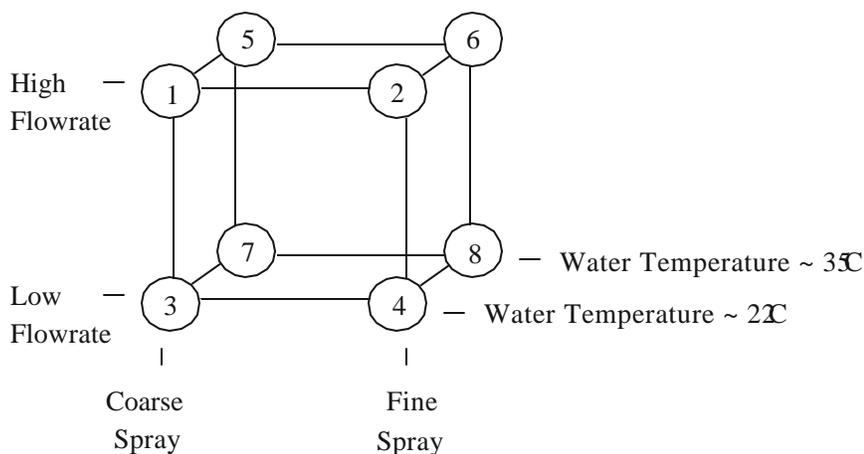
4.3. SOURCE-SPECIFIC METHODOLOGY

Prior to each shower experiment, the following tasks were completed:

- Flowrates for sorbent tubes used at port #2 were measured with clean air
- The desired experimental liquid flowrate was set using the rotameter
- The tracer reservoir (washing machine) was filled with either cold or warm tap water
- The chemical tracer solution was pumped into the washing machine as it filled
- The washing machine reservoir solution was mixed by allowing the washing machine to agitate for approximately 1 minute
- An initial gas-phase sample was collected from sample port #1 in the shower stall
- Two initial reservoir liquid-phase samples were collected.

4.3.1. Sample Schedule

Shower experiments lasted 8 minutes, during which time liquid-phase samples were collected from both the tracer reservoir and the shower stall. Five shower stall liquid samples were collected at experimental times of 0.5, 1.5, two at 3.75, and 7.75 minutes. Although the tracer reservoir chemical concentrations did not change significantly for most experiments, three tracer reservoir samples and one duplicate sample were collected and scheduled within 45 seconds of each shower stall sample so that several independent stripping efficiencies could be determined for a single experiment.

A total of 12 gas samples were collected for every shower experiment. Six gas samples were collected at port #1 for 30 seconds and were scheduled such that a shower stall liquid sample was collected at the midpoint of the gas sample time. Three gas samples were collected at each port #2 and port #3. The sampling times at these ports were scheduled to occur simultaneously, as well as at the same time as a gas sample collected at port #1. Thus, the gas-phase chemical concentration distribution was determined for three separate time periods in an experiment. Finally, a gas sample was collected after the experiment had ended and no water flowed through the system. The start time of this sample ranged from 5 to 20 minutes after the completion of an experiment. The gas collection time was 5 minutes.

4.3.2. Ventilation Rate

Through use of a smoke test, it was determined that gas primarily exited the chamber through the 10 cm exhaust port. Plastic dryer hose was sealed to the chamber exhaust port and was connected to a 76 cm length of straight PVC pipe. An anemometer was used to measure the velocity in this 8.3 cm ID pipe. The system ventilation rate (Q_g) was calculated using the cross-sectional area of the pipe (54 cm^2) and the measured velocity. The air exchange rate was determined by dividing the system's ventilation rate by the system volume. The shower system was well ventilated, with air exchange rates ranging from 12 to 13 air changes per hour (ACH). The specific air exchange rate for each experiment was measured during the actual experiment.

4.3.3. Parameter Estimation

Each shower experiment was divided into three periods: initial (0 to 1 minute), intermediate (3.5 to 4.5 minutes), and final (5.75 to 8 minutes). During each period, at least one tracer reservoir liquid sample, shower outlet sample, and shower gas sample were collected. Chemical stripping efficiencies and values of K_LA were determined for each time period and averaged, respectively, to obtain final values. Ratios of k_g/k_l, k_lA, and k_gA were estimated based on averaged values of K_LA for each chemical.

4.4. SHOWER RESULTS

Based on the experimental methodology presented in Sections 3.0 and 4.3, the overall chemical stripping efficiencies and mass transfer coefficients (K_LA, k_lA, and k_gA) for 10 shower experiments are presented in this chapter. In addition, the effects of liquid temperature, liquid flowrate, shower spray type, and chemical properties on each response are discussed. The determination of k_g/k_l values and associated implications are also presented.

The operating conditions for each experiment are listed in Table 4-1.

4.4.1. Chemical Stripping Efficiencies

Stripping efficiencies for each experimental chemical are presented in Tables 4-2 to 4-6, respectively. Stripping efficiencies were based on liquid-phase measurements collected from the tracer

reservoir and shower outlet drain. In addition to chemical stripping efficiencies, Tables 4-2 to 4-6 provide the results of the factorial main effect analysis (see Section 3.7 for

Table 4-1. Shower experiment operating conditions

Experiment #	Liquid temperature (°C)	Liquid flowrate (L/min)	Gas flowrate (L/min)	ACH (1/hr)	Spray type
1	21	9.1	370	13	Coarse
2	22	9.1	343	12	Fine
3	21	6.1	360	12	Coarse
4	22	6.1	358	12	Fine
5	35	9.1	379	13	Coarse
6	34	9.1	354	12	Fine
6 replicate	34	9.1	373	13	Fine
7	36	6.1	364	13	Coarse
8	35	6.1	371	13	Fine
8 replicate	34	6.1	367	13	Fine

 methodology). The three factors of the shower experimental two-level factorial arrays were shower spray type, liquid flowrate, and liquid temperature. As explained in Section 3.7, the main effect for a single variable was calculated as the average of the differences between responses at two levels of the factor of interest. For example, the shower spray effect on acetone's stripping efficiency may be calculated as:

Corresponding experiments:		Difference in stripping efficiencies
1 – 2	=	! 2.1 %
3 – 4	=	! 0.2 %
5 – Average (6 and 6 replicate)	=	1.0%
7 – Average (8 and 8 replicate)	=	! 1.0%
Average	=	! 0.075%

As shown in Table 4-2, the difference in experimental response was listed twice, once for each corresponding experiment. Duplicating the listing of each difference in response, however, does not

affect the average value for each variable. The experimental results for Experiments 6 and 6 replicate

and Experiments 8 and 8 replicate were averaged, respectively, before applying factorial analyses.

Tables 4-3 to 4-6 follow this same format.

Table 4-2. Acetone stripping efficiencies for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	Stripping efficiency (%)	Shower spray effect[a] (%)	Liquid flowrate effect[b] (%)	Liquid temperature effect[c] (%)
1	Cold	High	Coarse	6.3	! 2.1	! 2.8	6.7
2	Cold	High	Fine	8.4	! 2.1	! 0.90	3.6
3	Cold	Low	Coarse	9.1	! 0.20	! 2.8	6.9
4	Cold	Low	Fine	9.3	! 0.20	! 0.90	5.7
5	Warm	High	Coarse	13	1.0	! 3.0	6.7
6	Warm	High	Fine	11	1	! 3.0	3.6
6 rep.	Warm	High	Fine	12			
7	Warm	Low	Coarse	16	1.0	! 3.0	6.9
8	Warm	Low	Fine	14	1	! 3.0	5.7
8 rep.	Warm	Low	Fine	15			
				Average =	! 0.075	! 2.4	5.7

[a] Shower spray effect from fine to coarse.
[b] Liquid flowrate effect from low to high.
[c] Liquid temperature effect from cold to warm.

Table 4-3. Ethyl acetate stripping efficiencies for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	Stripping efficiency (%)	Shower spray effect[a] (%)	Liquid flowrate effect[b] (%)	Liquid temperature effect[c] (%)
1	Cold	High	Coarse	15	0	! 5.0	12
2	Cold	High	Fine	15	0	! 5.0	14
3	Cold	Low	Coarse	20	0	! 5.0	12
4	Cold	Low	Fine	20	0	! 5.0	15
5	Warm	High	Coarse	27	! 2.0	! 5.0	12
6	Warm	High	Fine	28	! 2.0	! 6.0	14
6 replicate	Warm	High	Fine	29			
7	Warm	Low	Coarse	32	! 3.0	! 5.0	12

8	Warm	Low	Fine	33	! 3.0	! 6.0	15
8 replicate	Warm	Low	Fine	36			
				Average =	**! 1.3**	**! 5.3**	**13**

[a] Shower spray effect from fine to coarse.

[b] Liquid flowrate effect from low to high.

[c] Liquid temperature effect from cold to warm.

Table 4-4. Toluene stripping efficiencies for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	Stripping efficiency (%)	Shower spray effect[a] (%)	Liquid flowrate effect[b] (%)	Liquid temperature effect[c] (%)
1	Cold	High	Coarse	61	! 7.0	! 2.0	7.0
2	Cold	High	Fine	68	! 7.0	4.0	7.0
3	Cold	Low	Coarse	63	! 1.0	! 2.0	11
4	Cold	Low	Fine	64	! 1.0	4.0	11
5	Warm	High	Coarse	68	! 7.0	! 6.0	7.0
6	Warm	High	Fine	75	! 7.0	0	7
6 replicate	Warm	High	Fine	74			
7	Warm	Low	Coarse	74	! 1.0	! 6.0	11
8	Warm	Low	Fine	73	! 1.0	0	11
8 replicate	Warm	Low	Fine	77			
				Average =	**! 4.0**	**! 1.0**	**9.0**

[a] Shower spray effect from fine to coarse.

[b] Liquid flowrate effect from low to high.

[c] Liquid temperature effect from cold to warm.

Table 4-5. Ethylbenzene stripping efficiencies for experimental shower

Expteriment #	Liquid temp.	Liquid flowrate	Shower spray	Stripping efficiency (%)	Shower spray effect[a] (%)	Liquid flowrate effect[b] (%)	Liquid temperature effect[c] (%)
1	Cold	High	Coarse	62	! 6.0	! 1.0	6.0
2	Cold	High	Fine	68	! 6.0	5.0	7.0
3	Cold	Low	Coarse	63	0	! 1.0	10
4	Cold	Low	Fine	63	0	5.0	11
5	Warm	High	Coarse	68	! 7.0	! 5.0	6.0
6	Warm	High	Fine	75	! 7.0	1	7
6 replicate	Warm	High	Fine	74			
7	Warm	Low	Coarse	73	! 1.0	! 5.0	10
8	Warm	Low	Fine	72	! 1.0	1	11
8 replicate	Warm	Low	Fine	75			
				Average =	**! 3.5**	**0**	**8.5**

[a] Shower spray effect from fine to coarse.

[b] Liquid flowrate effect from low to high.

[c] Liquid temperature effect from cold to warm.

Table 4-6. Cyclohexane stripping efficiencies for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	Stripping efficiency (%)	Shower spray effect[a] (%)	Liquid flowrate effect[b] (%)	Liquid temperature effect[c] (%)
1	Cold	High	Coarse	65	! 8.0	! 1.0	10
2	Cold	High	Fine	73	! 8.0	7.0	4.0
3	Cold	Low	Coarse	66	0	! 1.0	10
4	Cold	Low	Fine	66	0	7.0	12
5	Warm	High	Coarse	75	! 2.0	1.0	10
6	Warm	High	Fine	77	! 2.0	! 1.0	4
6 replicate	Warm	High	Fine	77			
7	Warm	Low	Coarse	76	! 2.0	1.0	10
8	Warm	Low	Fine	75	! 2.0	! 1.0	12
8 replicate	Warm	Low	Fine	80			
				Average =	! 3.0	1.0	9.0

[a] Shower spray effect from fine to coarse.
[b] Liquid flowrate effect from low to high.
[c] Liquid temperature effect from cold to warm.

Stripping efficiencies for acetone ranged from 6.3% to 16%, with the highest value for the conditions of warm water, low liquid flowrate, and coarse shower spray.   The single variable with the largest effect on acetone's stripping efficiency was liquid temperature, with a main effect of 5.7%. The main effect due to differences in liquid temperature, was calculated by subtracting cold water stripping efficiencies from corresponding warm water stripping efficiencies. Thus, 5.7% indicates an absolute increase in stripping efficiency with higher temperature water. The shower experiments were grouped according to similar liquid temperature, and the following stripping efficiencies resulted: 8.3% for cold water experiments (Experiments 1 to 4), and 14% for warm water experiments (Experiments 5 to 8 replicate). This result was expected, owing to the increase in Henry's law constant with increasing temperature. For the temperatures listed in Table 4-1, Henry's law constants for acetone ranged from 0.0010 m^3_{liq}/m^3_{gas} (21°C, Experiments 1 and 3) to 0.0023 m^3_{liq}/m^3_{gas} (36°C, Experiment 7).

The second highest main effect involved liquid flowrate with a value of –2.4%. The liquid flowrate effect was determined by the difference in high flowrate and low flowrate stripping efficiencies, so a negative effect indicates an increase in stripping efficiency at low flowrates. At lower shower flowrates, a

liquid droplet has a longer residence time in the shower stall, which may lead to higher chemical volatilization. The experiments were grouped according to liquid flowrate and temperature, and the following average stripping efficiencies were calculated: 7.4% for high flowrate and cold water (Experiments 1 and 2), 9.2% for low flowrate and cold water (Experiments 3 and 4), 12% for high flowrate and warm water (Experiments 5, 6, and 6 replicate), and 15% for low flowrate and warm water (Experiments 7, 8, and 8 replicate). Shower spray had a less significant impact on acetone stripping efficiencies.

Shower Experiments 6 and 8 were replicated. The acetone stripping efficiencies for these two experiments were compared and the following relative differences calculated: 8.7% for Experiments 6 and 6 replicate, and 6.9% for Experiments 8 and 8 replicate.

Ethyl acetate stripping efficiencies ranged from 15% to 36% (see Table 4-3). As with acetone, the highest value corresponded to the conditions of warm water and low flowrate. However, unlike acetone, the highest stripping efficiency for ethyl acetate occurred during fine spray conditions. The variable with the highest main effect on ethyl acetate's stripping efficiency was liquid temperature, with a value of 13%. Ethyl acetate stripping efficiencies were grouped according to liquid temperature, and the following average values calculated: 18% for cold water experiments and 31% for warm water experiments. Again, increasing the water temperature increased ethyl acetate's Henry's law constant, resulting in significantly higher stripping efficiencies. The Henry's law constant effect is also evident when comparing acetone and ethyl acetate stripping efficiencies for similar experimental conditions. In all cases, ethyl acetate, which has a higher Henry's law constant, had higher stripping efficiencies than acetone. For the temperatures listed in Table 4-1, Henry's law constants (H_c) for ethyl acetate ranged from 0.0041 m^3_{liq}/m^3_{gas} (21°C, Experiments 1 and 3) to 0.0080 m^3_{liq}/m^3_{gas} (36°C, Experiment 7), that is, approximately four times that of acetone.

With a main effect value of –5.3%, liquid flowrate had less than half the impact of water temperature on ethyl acetate stripping efficiency. When experiments were grouped according to liquid flowrate and water temperature, the following average values resulted: 15% for cold water and high flowrate experiments, 20% for cold water and low flowrate experiments, 28% for warm water and high flowrate

experiments, and 34% for warm water and low flowrate experiments. Again, shower spray had a less significant main effect on ethyl acetate's stripping efficiency.

For the two replicate experiments, Experiments 6 and 8, the following relative differences were determined: 3.5% for Experiment 6 and Experiment 6 replicate, and 8.7% for Experiment 8 and Experiment 8 replicate.

As shown in Table 4-4, toluene stripping efficiencies ranged from 61% to 77%. As expected, the highest toluene stripping efficiencies resulted when warm water was used. The main effect for liquid temperature was 9.0%. Experiments using cold water had an average stripping efficiency of 64%, and experiments using warm water had an average stripping efficiency of 74%. The gap between the cold water average stripping efficiency and warm water average stripping efficiency was much narrower than for acetone and ethyl acetate. For the temperatures listed in Table 4-1, Henry's law constants for toluene ranged from 0.24 m^3_{liq}/m^3_{gas} (21°C, Experiments 1 and 3) to 0.38 m^3_{liq}/m^3_{gas} (36°C, Experiment 7).

The second largest main effect for toluene stripping efficiencies, unlike those for acetone and ethyl acetate, was the type of shower spray, with a value of –4.0%. Interestingly, the magnitude of the shower spray, main effect was highly dependent on liquid flowrate. The difference in stripping efficiency between shower spray types at high flowrates was –7.0%, but at low flowrates the difference was only –1.0%. Interaction between these two variables is likely to influence the magnitude of a chemical's liquid-phase mass transfer coefficient (k_l). Thus, the associated effects of liquid flowrate and shower spray will have the greatest effect on chemicals dominated by liquid-phase resistance to mass transfer (toluene, ethylbenzene, and cyclohexane). Toluene stripping efficiencies were grouped according to the two largest main effects, water temperature and shower spray type, and the following average values were calculated: 62% for cold water and coarse spray (Experiments 1 and 3), 66% for cold water and fine spray (Experiments 2 and 4), 71% for warm water and coarse spray (Experiments 5 and 7), and 75% for warm water and fine spray (Experiments 6, 6 replicate, 8, and 8 replicate).

Replicate experimental results led to a 1.3% relative difference in toluene stripping efficiencies for Experiments 6 and 6 replicate, and 5.3% relative difference for Experiments 8 and 8 replicate.

Ethylbenzene stripping efficiencies ranged from 62% to 75% (see Table 4-5). This range was similar in magnitude to the range of stripping efficiencies reported for toluene. As discussed in Section 3.2.1, toluene and ethylbenzene have similar Henry's law constants (for the temperatures listed in Table 4-1, ethylbenzene has Henry's law constants between 0.26 m^3_{liq}/m^3_{gas} and 0.57 m^3_{liq}/m^3_{gas}), and thus should yield similar volatilization results. On an experiment-by-experiment basis, toluene and ethylbenzene stripping efficiencies were nearly identical. The largest relative deviation in stripping efficiencies for the two compounds was less than 3% (Experiment 8 replicate). It should also be noted that the stripping efficiencies for toluene and ethylbenzene were significantly higher than those observed for acetone and ethyl acetate. Again, an increase in Henry's law constant led to an increase in chemical stripping efficiencies.

As expected, ethylbenzene had main effects similar to those of toluene. Grouping stripping efficiencies based on water temperature yielded the following averages: 64% for cold water experiments and 73% for warm water experiments. Separating the liquid temperature groups to account for shower spray type resulted in the following average values: 63% for cold water and coarse spray, 66% for cold water and fine spray, 71% for warm water and coarse spray, and 74% for warm water and fine spray.

Relative differences in stripping efficiency for replicate experiments were 1.3% for Experiments 6 and 6 replicate, and 4.1% for Experiments 8 and 8 replicate.

Finally, cyclohexane stripping efficiencies ranged from 65% to 80% (see Table 4-6). For similar experimental conditions, cyclohexane consistently had the highest stripping efficiency of the five experimental tracers. The largest main effect was liquid temperature with a value of 9.0%. Following the format for previous tracers, the average cold water stripping efficiency was 68%, and the average warm water stripping efficiency was 77%. Similar to toluene and ethylbenzene, shower spray type had the second highest main effect with a value of –3.0%. Experimental results were regrouped according to shower spray type and water temperature, and the following averages were calculated: 66% for cold water and coarse spray, 70% for cold water and fine spray, 76% for warm water and coarse spray, and 77% for warm water and fine spray. This second regrouping did not yield results significantly different from the first set of averages for cold and warm water, and was thereby unnecessary. For the

temperatures listed in Table 4-1, Henry's law constants for cyclohexane ranged from 6.3 m^3_{liq}/m^3_{gas} (21°C, Experiments 1 and 3) to 10 m^3_{liq}/m^3_{gas} (36°C, Experiment 7).

Unlike the other chemical tracers, the liquid flowrate main effect on cyclohexane's stripping efficiencies was positive, indicating a decrease in stripping efficiency with decreasing flowrate. A specific reason for this trend could not be identified.

Replicate experimental stripping efficiencies had a relative difference of 0% for Experiments 6 and 6 replicate and 6.5% for Experiments 8 and 8 replicate.

An attempt was made to compare the chemical stripping efficiencies described above with those reported by other researchers who used similar operating conditions and chemical tracers. A summary of previous research related to volatilization in showers was presented in a Phase I report to EPA as part of this project (Corsi et al., 1996) and are also given in the database in the Appendix. Additional papers have been reviewed since the Phase I report was submitted *(e.g.,* Giardino and Andelman [1996]), and all of these have been added to the database.

Previous researchers have not studied chemicals with Henry's law constants as low as acetone. Thus, the results described herein are unique for this compound and extend the range of chemical volatilities to values much lower than those previously reported.

Overall, Giardino and Andelman (1996) used operating conditions most similar to those in this study and will serve as the primary basis of comparison. Giardino and Andelman studied emissions of trichloroethene (TCE), chloroform ($CHCl_3$), and 1,2-dibromo-3-chloropropane (DBCP) in a 1.5 m^3 experimental shower. As in the results of this study, they determined that water temperature had a dominant effect on the total release of each tracer chemical.

Giardino and Andelman's Experiment 17 included an air exchange rate of 12.3/hour, water flowrate of 5 L/minute, and water temperature of 30°C. For these conditions, the stripping efficiency of DBCP, which has the lowest Henry's law constant of any chemical tested to date for showers, was only 17%.

For this study, Experiment 8 replicate included operating conditions similar to those reported above (air exchange rate = 13/hour; water flowrate = 6.1 L/minute; water temperature = 34°C). The corresponding stripping efficiency for ethyl acetate, a chemical with a Henry's law constant at 34°C (slightly lower than that of DBCP at 30°C), was over twice (36%) the value reported by Giardino and Andelman for DBCP. Ethyl acetate's Henry's law constant is similar to that of DBCP, and thus differences in stripping efficiency between DBCP and ethyl acetate cannot be accounted for entirely by water temperature. Differences are likely due to differences in commercial showerheads that were used, as well as subsequent differences in droplet sizes and velocities.

Giardino and Andelman (1996) also studied TCE, which has a Henry's law constant approximately 25% greater than that for ethylbenzene, at 22°C. Thus, TCE would be expected to have slightly greater stripping efficiencies for similar operating conditions. Giardino and Andelman reported a TCE stripping efficiency of 60% for their Experiment 2 (air exchange rate = 10.8/hour; water flowrate = 5.1 L/minute; water temperature = 22°C). In this study, the stripping efficiency for ethylbenzene was slightly higher (63%) for similar conditions (Experiment 3; air exchange rate = 12/hour; water flowrate = 6.1 L/minute; water temperature = 21°C). For a second experiment involving a higher water flowrate (10 L/minute), Giardino and Andelman observed a TCE stripping efficiency of 57%. For similar experimental conditions (Experiments 1 and 2 of this study), the stripping efficiency for ethylbenzene was observed to be 62% (coarse spray) and 68% (fine spray). In an earlier study, Giardino et al. (1992) observed TCE stripping efficiencies of 59% to 67% for similar operating conditions.

McKone and Knezovich (1991) also studied stripping efficiencies for TCE in an experimental shower. One of their operating conditions (air exchange rate = 12/hour; liquid flowrate = 9.5 L/minute; water temperature = 22°C) was nearly identical to those used in Experiments 1 and 2 of this study. The stripping efficiency for TCE was reported to be 58%, consistent with Giardino and Andelman (1996) and Giardino *et al.* (1992), and slightly lower than those obtained for ethylbenzene in this study. The differences in stripping efficiencies between TCE and ethylbenzene could easily be caused by differences in hydrodynamic conditions associated with water flowrate and shower configurations, as well as experimental errors associated with each study.

Finally, several researchers used chemicals with relatively high Henry's law constants (> 2.0 m^3_{liq}/m^3_{gas}) in shower experiments. It was expected that these higher volatility chemicals would have similar stripping efficiencies because of the associated insignificance of gas-phase resistance to mass transfer. For example, Bernhardt and Hess (1995) studied stripping efficiencies for radon in household showers. Radon has a slightly lower Henry's law constant than cyclohexane, but both compounds should be dominated by liquid-phase resistance to mass transfer. For a water temperature of 23°C and liquid flowrate of 5.7 L/minute (gas exchange rate in the shower stall was not measured), the stripping efficiency for radon was reported to be 78%. For similar operating conditions (Experiments 3 and 4 of this study), the stripping efficiency for cyclohexane was determined to be 66%. The range of radon stripping efficiencies reported by Bernhardt and Hess was 57% to 88%. Cyclohexane stripping efficiencies for this study ranged from 65% to 80%.

At liquid flowrates of 2 to 4 L/minute, Giardino and Hageman (1996) measured radon stripping efficiencies ranging from 67% to 70%. Studies with unknown operating parameters led to observed radon stripping efficiencies of 63% to 71% (Gesell and Prichard, 1980; Hess et al., 1982; Hopke et al., 1995; Partridge, 1979).

Tancrede et al. (1992) measured the stripping efficiencies of five experimental chemicals including carbon tetrachloride (CCl_4), which has a Henry's law constant of 2.3 m^3_{liq}/m^3_{gas} at 42°C. The chemical stripping efficiency for CCl_4 was 59% at a liquid flowrate of 9.7 L/minute and 77% for a liquid flowrate of 13 L/minute. Again, these results are consistent with those observed for other chemicals with relatively high Henry's law constants.

It is clear from this study, as well as several others reported in the literature, that for the same operating conditions stripping efficiency increases with increasing Henry's law constant. It is also evident that chemicals of sufficiently high Henry's law constant have comparable stripping efficiencies for similar operating conditions. Because the conditions used in this study should represent a reasonable spectrum of those associated with residential showering, an average stripping efficiency was determined for each chemical tracer and is plotted in Figure 4-3 as a function of Henry's law constant at 25°C. This plot may be used as a screening tool for approximating chemical stripping efficiencies, given knowledge of that

chemical's Henry's law constant at 25°C, the temperature for which Henry's law constants are most widely reported. The best-fit line associated with the averaged data in Figure 4-3 stems from the following relationship:

$$h = 7.5 \cdot \ln\left(H_C\right) + 68.2 \qquad (4\text{-}1)$$

where

H_c =   Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas}).

Although Equation 4-1 provides a relationship for chemical stripping efficiencies averaged over a wide range of shower operating conditions, it does provide insight into differences in potential stripping efficiencies for various types of compounds. However, application of Equation 4-1 to chemicals with Henry's law constants beyond the range of those used to develop this relationship is not recommended.

Equation 4-1 can be rearranged to solve for the value of Henry's law constant that leads to specific stripping efficiencies. For example, the value of H_c that leads to $\eta = 55\%$ is $0.19 \ m^3_{liq}/m^3_{gas}$. This Henry's law constant is consistent with reported values for chloroform at 25°C

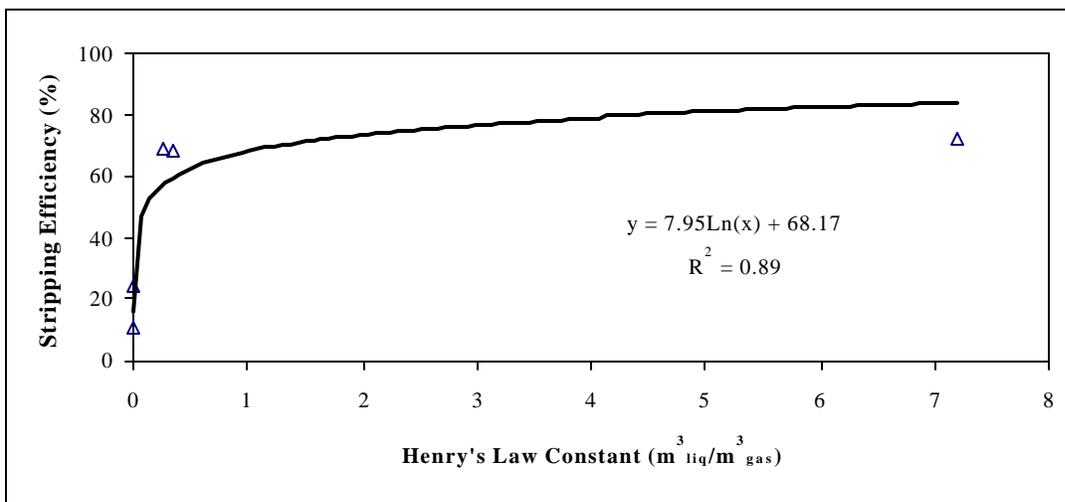**Figure 4-3. Relationship between Henry's law constant and average stripping efficiency.**

4-18

(Howard, 1990), a common disinfection by-product. Tancrede et al. (1992) reported chloroform stripping efficiencies ranging from 52% to 53%, Giardino and Andelman (1991) reported a value of 55%, and Giardino and Andelman (1996) reported chloroform stripping efficiencies ranging from 44% to 52%, all in good agreement with Equation 4-1.

4.4.2. $K_L A$ Values

Values of $K_L A$ for each chemical tracer are reported in Tables 4-7 to 4-11. The determination of values of $K_L A$ was based on liquid-phase data for all chemicals. Tables 4-7 through 4-11 have a format similar to that of Tables 4-2 to 4-6, except the main effects are based on values of $K_L A$.

Values of $K_L A$ for acetone ranged from 1.4 to 3.7 L/minute (see Table 4-7). The highest value corresponded to the experimental conditions of warm water, high flowrate, and fine shower spray. The largest main effect was liquid flowrate, with a value of 0.93 L/minute. In a manner similar to that for stripping efficiency results, $K_L A$ values can be grouped according to liquid flowrate, resulting in the following average values: 2.9 L/minute for high flowrate and 2.0 L/minute for low flowrate.

Liquid temperature had the second highest main effect on $K_L A$ values for acetone. The liquid temperature main effect was 0.83 L/minute, which indicated an increase in $K_L A$ with increased temperature. As expected from its greater surface to volume ratio, fine shower spray was determined to increase stripping efficiencies more than did coarse spray.

Values of $K_L A$ for the replicate experiments were also compared. For Experiments 6 and 6 replicate, the relative difference in values of $K_L A$ was 8.5%. For Experiments 8 and 8 replicate, the relative difference in values of $K_L A$ was 8.3%.

Measured and predicted liquid-phase and gas-phase concentrations of acetone for Experiment 7 are presented in Figure 4-4, and are representative of other experiments. The operating conditions used in Experiment 7 were warm water, low flowrate, and coarse shower spray. As described in Section 4.3.3, each shower experiment was divided into three separate

Table 4-7. Acetone K_LA values for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	K_LA (L/min)	Shower spray effect[a] (L/min)	Liquid flowrate effect[b] (L/min)	Liquid temperature effect[c] (L/min)
1	Cold	High	Coarse	1.8	!1.2	0.40	1.0
2	Cold	High	Fine	3.0	!1.2	1.5	0.60
3	Cold	Low	Coarse	1.4	!0.10	0.40	0.80
4	Cold	Low	Fine	1.5	!0.10	1.5	0.90
5	Warm	High	Coarse	2.8	!0.80	0.60	1.0
6	Warm	High	Fine	3.4	!0.80	1.2	0.6
6 replicate	Warm	High	Fine	3.7			
7	Warm	Low	Coarse	2.2	!0.20	0.60	0.80
8	Warm	Low	Fine	2.3	!0.20	1.2	0.9
8 replicate	Warm	Low	Fine	2.5			
				Average =	**!0.58**	**0.93**	**0.83**

[a] Shower spray effect from fine to coarse.
[b] Liquid flowrate effect from low to high.
[c] Liquid temperature effect from cold to warm.

Table 4-8. Ethyl acetate K_LA values for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	K_LA (L/min)	Shower spray effect[a] (L/min)	Liquid flowrate effect[b] (L/min)	Liquid temperature effect[c] (L/min)
1	Cold	High	Coarse	2.9	!1.1	0.60	2.6
2	Cold	High	Fine	4.0	!1.1	1.5	2.8
3	Cold	Low	Coarse	2.3	!0.20	0.60	1.5
4	Cold	Low	Fine	2.5	!0.20	1.5	2.5
5	Warm	High	Coarse	5.5	!1.3	1.7	2.6
6	Warm	High	Fine	6.9	!1.3	1.8	2.8
6 replicate	Warm	High	Fine	6.7			
7	Warm	Low	Coarse	3.8	!1.2	1.7	1.5
8	Warm	Low	Fine	4.7	!1.2	1.8	2.5
8 replicate	Warm	Low	Fine	5.3			
				Average =	**!0.95**	**1.4**	**2.4**

[a] Shower spray effect from fine to coarse.
[b] Liquid flowrate effect from low to high.

Table 4-9. Toluene K_LA values for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	K_LA (L/min)	Shower spray effect[a] (L/min)	Liquid flowrate effect[b] (L/min)	Liquid temperature effect[c] (L/min)
1	Cold	High	Coarse	8.8	! 2.2	2.6	2.2
2	Cold	High	Fine	11	! 2.2	4.6	2.0
3	Cold	Low	Coarse	6.2	! 0.20	2.6	2.2
4	Cold	Low	Fine	6.4	! 0.20	4.6	2.2
5	Warm	High	Coarse	11	! 2.0	2.6	2.2
6	Warm	High	Fine	13	! 2.0	4.3	2
6 replicate	Warm	High	Fine	12			
7	Warm	Low	Coarse	8.4	! 0.30	2.6	2.2
8	Warm	Low	Fine	8.1	! 0.30	4.3	2.2
8 replicate	Warm	Low	Fine	9.2			
				Average =	**! 1.2**	**3.5**	**2.2**

[a] Shower spray effect from fine to coarse.
[b] Liquid flowrate effect from low to high.
[c] Liquid temperature effect from cold to warm.

Table 4-10. Ethylbenzene K_LA values for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	K_LA (L/min)	Shower spray effect[a] (L/min)	Liquid flowrate effect[b] (L/min)	Liquid temperature effect[c] (L/min)
1	Cold	High	Coarse	8.9	! 2.1	2.9	1.1
2	Cold	High	Fine	11	! 2.1	4.8	2.0
3	Cold	Low	Coarse	6.0	! 0.20	2.9	2.2
4	Cold	Low	Fine	6.2	! 0.20	4.8	2.2
5	Warm	High	Coarse	11	! 2.0	2.8	1.1
6	Warm	High	Fine	13	! 2.0	4.6	2
6 replicate	Warm	High	Fine	12			
7	Warm	Low	Coarse	8.2	! 0.20	2.8	2.2
8	Warm	Low	Fine	7.9	! 0.20	4.6	2.2
8 replicate	Warm	Low	Fine	8.8			
				Average =	**! 1.1**	**3.8**	**2.1**

a Shower spray effect from fine to coarse.
b Liquid flowrate effect from low to high.
c Liquid temperature effect from cold to warm.

Table 4-11. Cyclohexane K_LA values for experimental shower

| Experiment #	Liquid temp.	Liquid flowrate	Shower spray	K_LA (L/min)	Shower spray effect[a] (L/min)	Liquid flowrate effect[b] (L/min)	Liquid temperature effect[c] (L/min)
1	Cold	High	Coarse	9.6	! 2.4	3.1	3.4
2	Cold	High	Fine	12	! 2.4	5.3	2.0
3	Cold	Low	Coarse	6.5	! 0.20	3.1	2.1
4	Cold	Low	Fine	6.7	! 0.20	5.3	2.5
5	Warm	High	Coarse	13	! 1.0	4.4	3.4
6	Warm	High	Fine	14	! 1.0	4.8	2.1
6 replicate	Warm	High	Fine	13			
7	Warm	Low	Coarse	8.6	! 0.60	4.4	2.0
8	Warm	Low	Fine	8.4	! 0.60	4.8	2.5
8 replicate	Warm	Low	Fine	9.9			
				Average =	**! 1.1**	**4.4**	**2.5**

a Shower spray effect from fine to coarse.

b Liquid flowrate effect from low to high.

c Liquid temperature effect from cold to warm.

Figure 4-4. Acetone experimental data for Experiment 7.

periods: initial, intermediate, and final. As shown in Figure 4-4, 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 shower outlet concentration in both the liquid and gas phases may be estimated using the shower mass balance models (Equations 2-28 and 2-30). To determine the best value of K_LA for the shower model, the residuals between the measured and predicted concentrations were minimized using the method described in Section 3.6.2. Two liquid samples were collected in the initial period for one gas sample. Thus, for this period the liquid-phase residual was based on the average of two measured liquid samples and a model-predicted value. For Experiment 7 shown in Figure 4-4, the best-fit value of K_LA for acetone was 2.2 L/minute.

During each experiment, the chemical concentration in the tracer reservoir was relatively constant
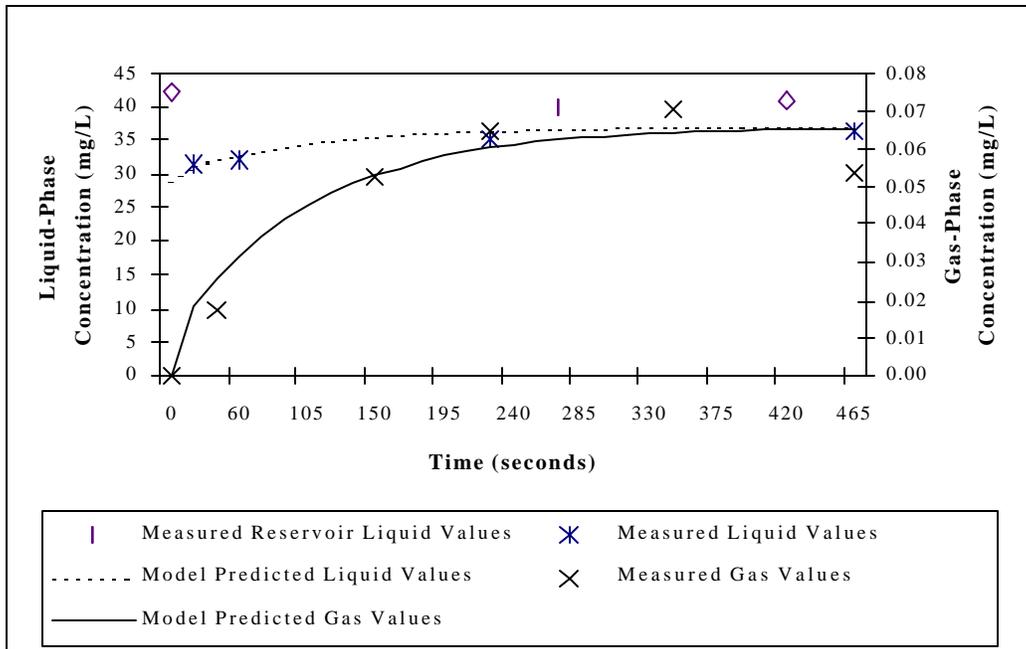
between each period. For acetone, the liquid-phase concentration measured in the shower drain tended to increase with experimental time, as mass accumulated in the shower atmosphere (gas phase). This

accumulation resulted in a decreased chemical concentration driving force. The acetone gas-phase concentration continually increased during each experiment.

Values of K_LA for ethyl acetate ranged from 2.3 to 6.9 L/minute, approximately 1.6 times greater than values reported for acetone. The highest value was for the experimental conditions of warm water, high flowrate, and fine spray. The largest main effect was liquid temperature, with a value of 2.4 L/minute. The average cold water value of K_LA for ethyl acetate was 2.9 L/minute, and the average warm water value of K_LA was 5.5 L/minute. Again, values of K_LA tended to increase with increasing flowrate and fine spray.

Replicate values of K_LA for ethyl acetate had a relative difference of 2.9% for Experiments 6 and 6 replicate, and 12% for Experiments 8 and 8 replicate.

Experimental results for ethyl acetate during shower Experiment 7 are presented in Figure 4-5. The value of K_LA of 3.8 L/minute for this experiment was determined by minimizing the residuals between the measured liquid concentration data points and predicted liquid concentrations. As shown in Figure 4-5, for relatively constant inlet liquid concentrations (measured tracer reservoir liquid values), the measured outlet liquid-phase concentrations increased with time. This increase in concentration reflected the decreasing chemical driving force as mass accumulated in the shower stall. As with acetone, ethyl acetate gas-phase concentrations increased with experimental time, rapidly within the first 150 seconds and more gradually thereafter. All gas-phase data in experimental plots represent measurements taken at gas sample port #1.

Values of K_LA for toluene ranged from 6.2 to 13 L/minute (see Table 4-9). Similar to acetone and ethyl acetate, the operating conditions of warm water, high liquid flowrate, and fine shower spray resulted in the highest value. However, for toluene the highest main effect was not for water temperature, but rather liquid flowrate. This trend is consistent with a shift from gas-phase resistance dominating volatilization of acetone and ethyl acetate to liquid-phase resistance dominating for toluene, ethylbenzene, and cyclohexane. Because water temperature has its greatest influence on Henry's law constant, for higher values of H_c the effect of temperature is significantly reduced as the C_g/H_c term on the right-hand side of Equation 2.27 is reduced. Consequently, hydrodynamic effects on k_l and A become more important.

A main effect value of 3.5 L/minute indicated that toluene K_LA values increased with

Figure 4-5. Ethyl acetate experimental data for Experiment 7.

increasing liquid flowrate.   Values of K_LA for toluene were grouped according to high and low flowrate, and the following average values were calculated: 11 L/minute for high flowrate experiments
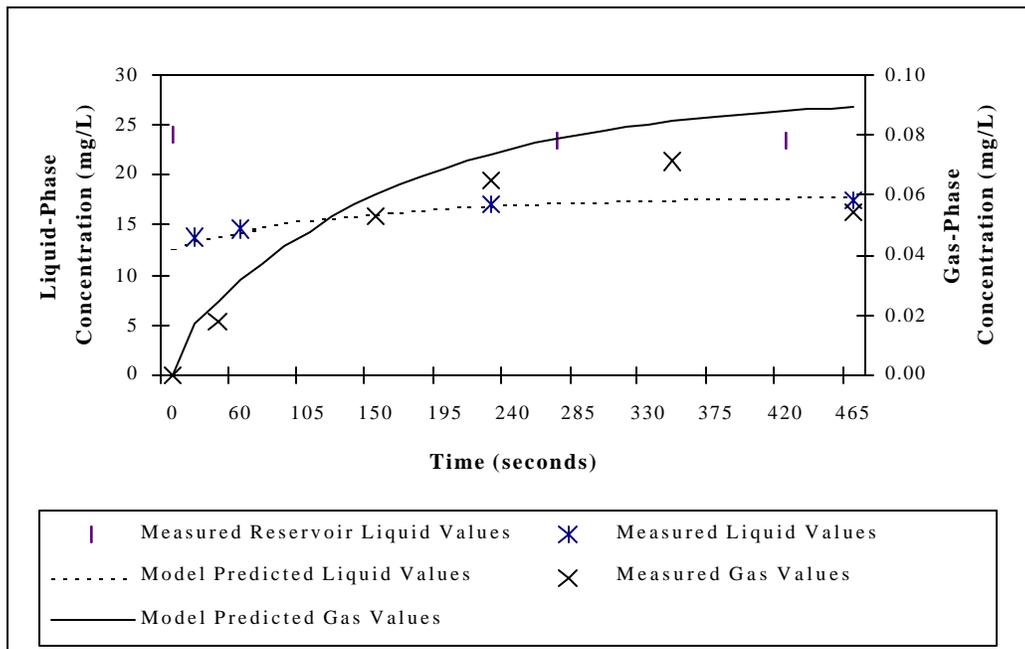

(Experiments 1, 2, 5, 6, and 6 replicate) and 7.7 L/minute for low flowrate experiments (Experiments 3, 4, 7, 8, and 8 replicate).

4-25

The second largest main effect was for liquid temperature, with a value of 2.2 L/minute. When the experiments were regrouped using liquid flowrate and liquid temperature, the following averages resulted: 9.9 L/minute for cold water and high flowrate (Experiments 1 and 2), 6.3 L/minute for cold water and low flowrate (Experiments 3 and 4), 12 L/minute for warm water and high flowrate (Experiments 5, 6, and 6 replicate), and 8.6 L/minute for warm water and low flowrate (Experiments 7, 8 , and 8 replicate). Fine shower spray resulted in higher values of K_LA for toluene than coarse spray as a result of the increased total surface area for the liquid phase.

Toluene results for Experiment 7 are presented in Figure 4-6. Differences between toluene concentrations in the tracer reservoir concentrations and shower outlet were significantly greater than differences shown in Figures 4-4 and 4-5 for acetone and ethyl acetate, respectively. This larger difference reflects the greater chemical volatilization rate for toluene, which is less affected

Figure 4-6. Toluene experimental data for Experiment 7.

by an approach to chemical equilibrium, that is, reduction in the concentration driving force between water and air, and gas-phase resistance to mass transfer. For toluene, the ratio of gas concentration to
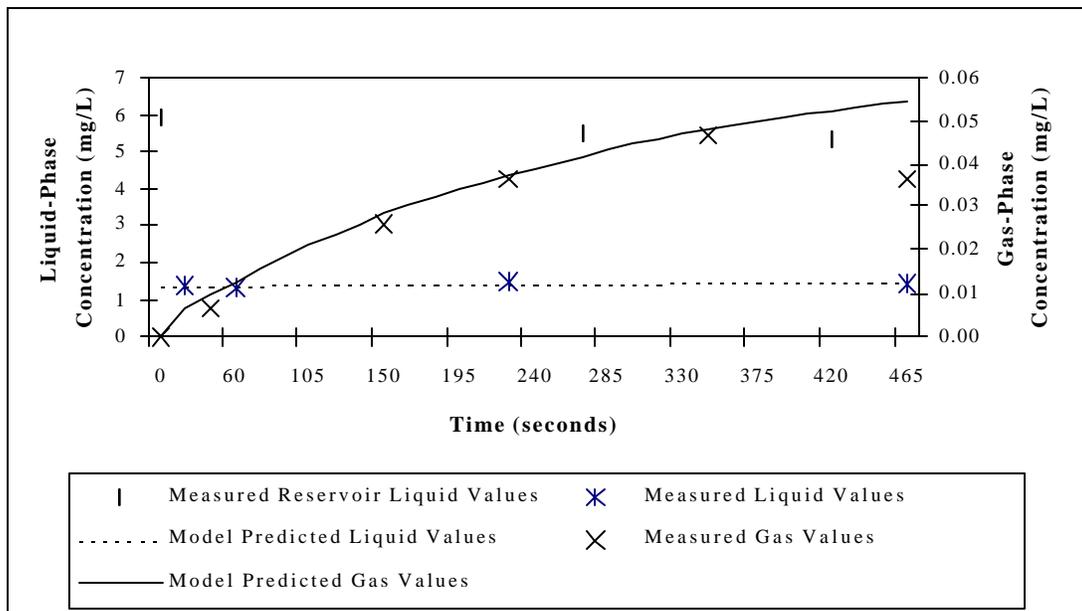
Henry's law constant was always small relative to inlet or outlet water concentration ($C_g/H_c << C_l$ in

Equation 2.27). This condition led to nearly constant values of toluene concentration in water draining from the shower and constant stripping efficiencies during the course of an experiment, trends that were also observed for ethylbenzene and cyclohexane.

Values of K_LA for ethylbenzene ranged from 6.0 to 13 L/minute (see Table 4-10). As expected, this range is similar in magnitude to that of toluene. Ethylbenzene also shared main effects similar to those calculated for toluene. Grouping ethylbenzene K_LA values by high and low flowrate resulted in the following average values: 11 L/minute and 7.4 L/minute, respectively.

Values of K_LA for ethylbenzene may also be grouped according to liquid flowrate and liquid temperature. Average values were 10 L/minute for high flowrate and cold water, 6.1 L/minute for low flowrate and cold water, 12 L/minute for high flowrate and warm water, and 8.3 L/minute for low flowrate and warm water.

Figure 4-7. Ethylbenzene experimental data for Experiment 7.

Ethylbenzene data for Experiment 7 are plotted in Figure 4-7. Chemical concentration values and
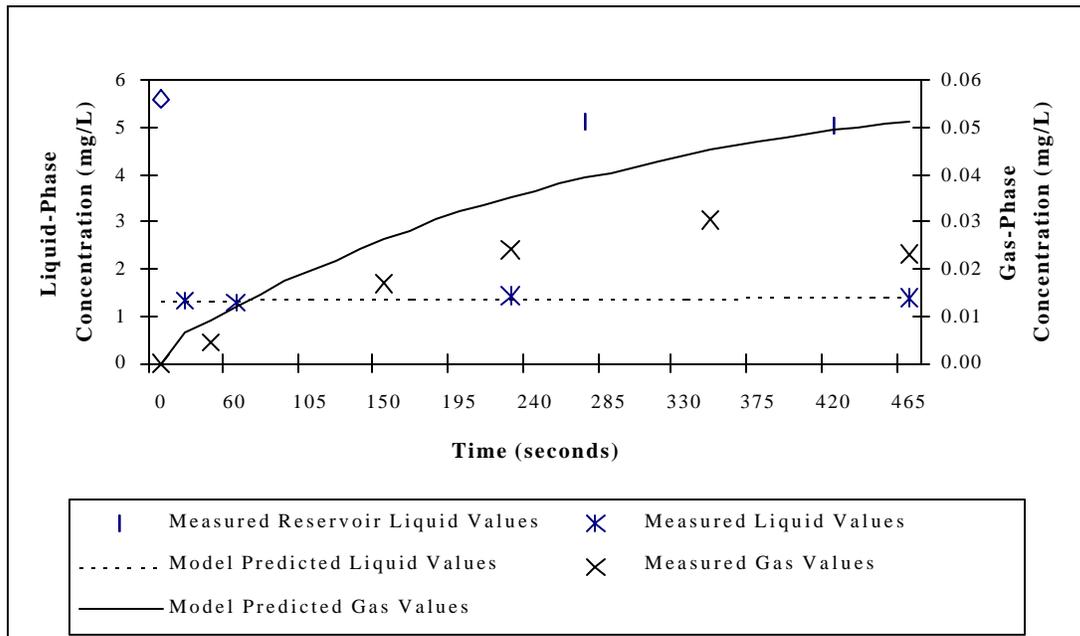
trends follow those discussed for toluene. Both chemicals had a value of K_LA of 13 L/minute for this experiment.

Finally, values of K_LA for cyclohexane ranged from 6.5 to 14 L/minute (see Table 4-11). The fact that cyclohexane has a significantly higher Henry's law constant than either toluene or ethylbenzene but its values of K_LA were only slightly higher suggests that gas-phase resistance to mass transfer was small for each of these three tracers. Following the trend of toluene and ethylbenzene, cyclohexane also had the highest main effect value associated with liquid flowrate, with a value of 4.4 L/minute. Average values of K_LA based on liquid flowrate were 12 L/minute for high flowrate and 8.0 L/minute for low flowrate.

Cyclohexane data are plotted in Figure 4-8 for Experiment 7. Again, for relatively constant inlet liquid concentrations, the outlet liquid-phase concentrations were consistent with one another. Cyclohexane gas-phase concentrations increased at a consistent rate throughout each experiment.

Figure 4-8. Cyclohexane experimental data for Experiment 7.

To calculate K_LA for each chemical tracer using the shower mass balance models (Equations 2-28
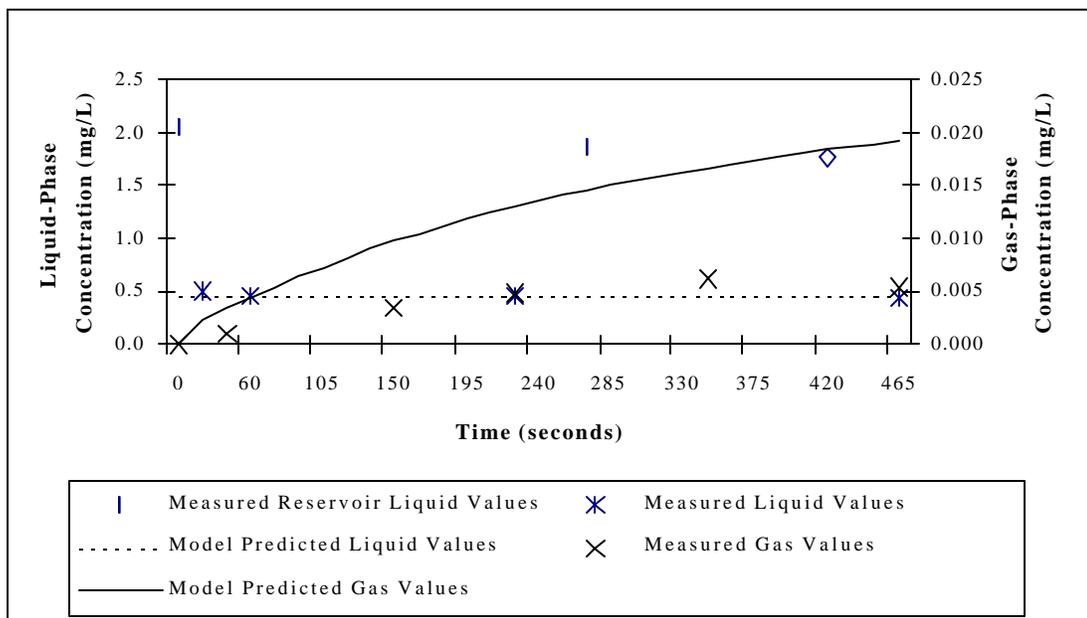
and 2-30), the gas phase was assumed to simulate a well-mixed reactor. To check the validity of this assumption, gas-phase samples were collected at three locations within the shower atmosphere as shown in Figure 4-1. Based on the percent difference between measured gas-phase concentrations at each

sample port, the shower stall appeared to be relatively well mixed. The average of percent differences (absolute values) between gas-phase samples for acetone were 18% when comparing sample port #1 and sample port #2, 16% when comparing sample port #2 and sample port #3, and 16% when comparing sample port #1 and sample port #3. The concentration differences between sample ports appeared to be random between experiments; that is, the relative differences were both positive and negative. In addition, 85% of compared samples were within 0.02 mg/L. The average percent differences for ethyl acetate were 20% when comparing sample ports #1 and #2, 17% when comparing sample ports #2 and #3, and 20% when comparing sample ports #1 and #3. The average percent differences for the remaining compounds ranged from 18% to 30%. Over 93% of the compared gas-phase samples for toluene and ethylbenzene were within 0.02 mg/L, and over 88% of the compared gas-phase samples for cyclohexane were within 0.002 mg/L. Small deviations from this well mixed assumption should have no effect on experimentally determined values of K_LA for toluene, ethylbenzene, and cyclohexane, in that $C_g/H_c << C_l$ for these chemicals.

4.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients

For future model applications, it is valuable to separate K_LA into liquid- and gas-phase components, that is, k_lA and k_gA, and to predict k_g/k_l values for different operating conditions. For a specific system, values of k_g/k_l should not vary significantly between volatile chemicals (Munz and Roberts, 1989). Values of k_lA and k_gA for each chemical tracer are listed in Table 4-12. A single value of k_g/k_l is presented based on all chemical tracer experimental K_LA values and physicochemical properties, as described in Section 3.6.3. The relative difference between replicate experiments was 15% for Experiments 6 and 6 replicate and 3.6% for Experiments 8 and 8 replicate.

With use of the factorial analysis described in Sections 3.7 and 4.4.1, the impact of shower operating conditions on k_lA and k_gA was investigated. As with K_LA, the most significant operating condition affecting k_lA was liquid flowrate, except for ethyl acetate, which was most affected by temperature. The most significant factor affecting k_gA was liquid flowrate, this time for all chemicals. As expected, temperature generally had a greater relative impact on k_lA than k_gA.

Table 4-12. Liquid- and gas-phase mass transfer coefficients for shower experiments (continued).

As shown in Table 4-12, the ratio of k_g/k_l for showers ranged from 110 to 223, with an average value of 156. This value is consistent with the typical value of 150 reported by Mackay et al. (1979). However, Little (1992) reported three values of k_g/k_l for showers based on other researchers' work (Giardino and Andelman, 1991; Tancrede et al., 1992). These values were 13 for a liquid temperature of approximately 44°C and liquid flowrate of 5 L/minute, 22 for a liquid temperature of 42°C and a liquid flowrate of 13 L/minute, and 17 for a liquid temperature of 33°C and liquid flowrate of 14 L/minute.

An important parameter that influences the back-calculation of k_g/k_l is the Henry's law constant for each chemical. As discussed in Section 4.2.1, there is uncertainty associated with Henry's law constants for chemicals, especially at elevated temperatures. Increasing the Henry's law constant for toluene in Experiment 7 by 40% results in a 1.1% decrease in K_LA. Thus, values of K_LA for chemicals of higher volatility are less sensitive to changes in Henry's law constant. However, this is not the case for chemicals such as acetone or ethyl acetate.

Table 4-12. Liquid- and gas-phase mass transfer coefficients for shower experiments

Experiment #	Chemical	k_lA (L/min)	k_gA (L/min)	k_g/k_l
1	A	13	1,986	153
	EA	7.3	1,111	
	T	9.0	1,380	
	EB	9.1	1,395	
	C	9.6	1,468	
2	A	16	3,519	223
	EA	8.1	1,807	
	T	11	2,434	
	EB	11	2,384	
	C	12	2,652	
3	A	8.6	1,723	200
	EA	5.1	1,030	
	T	6.4	1,274	
	EB	6.2	1,234	
	C	6.5	1,305	
4	A	8.8	1,720	195
	EA	5.3	1,031	

| Experiment #	Chemical	k_lA (L/min)	k_gA (L/min)	k_g/k_l
	T	6.5	1,275	
	EB	6.3	1,232	
	C	6.7	1,309	
5	A	14	1,548	111
	EA	12	1,322	
	T	11	1,223	
	EB	11	1,188	
	C	13	1,439	
6	A	16	2,095	131
	EA	14	1,852	
	T	14	1,776	
	EB	13	1,708	
	C	14	1,786	
6 replicate	A	15	2,316	153
	EA	13	1,945	
	T	13	1,930	
	EB	12	1,855	
	C	13	1,950	
7	A	11	1,169	110
	EA	8.2	901	
	T	8.6	949	
	EB	8.3	917	
	C	8.6	943	
8	A	9.6	1,380	143
	EA	9.0	1,292	
	T	8.3	1,189	
	EB	8.0	1,139	
	C	8.4	1,203	
8 replicate	A	11	1,507	138
	EA	10	1,443	
	T	9.3	1,291	
	EB	8.9	1,227	
	C	9.9	1,366	
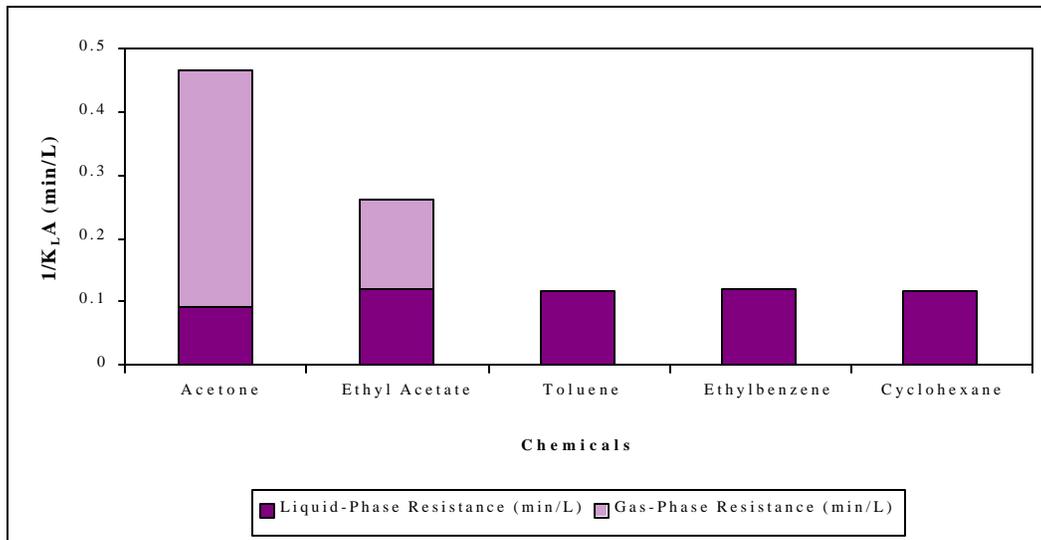
Figure 4-9. Resistances to mass transfer for each chemical in Experiment 7.

Increasing the Henry's law constants of these two chemicals by 40% results in a 17% decrease in K_LA for ethyl acetate and 23% decrease in K_LA for acetone. The decrease in K_LA for these two compounds then results in a best-fit k_g/k_l value of 46, 58% of the value reported in Table 4-12 for Experiment 7. Interestingly, the best-fit k_g/k_l value using only toluene, ethylbenzene, and cyclohexane data from Experiment 7 was 116.

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, the overall resistance to mass transfer ($1/K_LA$) may be written as the sum of liquid-phase resistance to mass transfer ($1/k_lA$) and gas-phase resistance to mass transfer ($1/k_gA \bullet H_c$). These resistances are shown graphically in Figure 4-9 for each chemical in Experiment 7. As shown in Figure 4-9, the overall resistance to mass transfer for acetone is dominated by resistance in the gas phase. The overall resistance to mass transfer for ethyl acetate is distributed relatively equally between liquid-phase resistance and gas-phase resistance. Finally, the gas-phase resistances to mass transfer for toluene, ethylbenzene, and cyclohexane are insignificant relative to their respective liquid-phase resistances to mass transfer.

4.4.4. Mass Closure

For shower experiments, mass closure values as defined by Equation 3.12 ranged from 96% to 103% for acetone, 98% to 108% for ethyl acetate, 71% to 90% for toluene, 54% to 73% for ethylbenzene, and 40% to 74% for cyclohexane. The more volatile chemicals (toluene, ethylbenzene, and cyclohexane) tended to achieve mass closure values less than 100%. This may have been due to the dissolution problems described in Section 3.4.2. A separate calibration curve was developed to assess this effect, based on a 4-day standard calibration period, that is, allowing chemicals to dissolve in the Tedlar™ bag for 4 days instead of 1 day. The resulting mass closures improved for toluene (77% to 106%), ethylbenzene (64% to 92%), and cyclohexane (66% to 85%).

Previous researchers (Keating and McKone, 1993; Keating et al., 1997; Tancrede et al., 1992) have also observed differences in predicted gas-phase concentrations and measured gas-phase concentrations for volatile chemicals. It has often been suggested that there exists a second compartment in the shower system that acts as a chemical sink. Keating and McKone discussed the possibility that the second-compartment effect could be accounted for by one to all of the following: incomplete mixing within the shower stall, sorption of chemicals onto surfaces, and/or scavenging of chemicals by aerosols. A number of tests were completed to investigate these possibilities. Cyclohexane is used as the example chemical, because it had the most problems meeting the mass closure requirements.

First, a shower experiment with clean (no chemicals) warm water was completed. At the end of the experiment, sponges were used to soak up the water collected in known areas on the different types of surfaces within the shower stall (plastic-coated fiberglass wall and floor, stainless steel ceiling, and Tedlar™ shower curtain). The sponges were weighed before and after water collection to estimate total volume of water collected on each surface type. Based on this experiment, the total water volume present on surfaces at the end of an experiment was approximately 0.2 L. Using the gas-phase concentration measured for each chemical and assuming that equilibrium conditions hold at the wetted surface, the expected chemical concentration of the wall surface water may be calculated. For example, the maximum concentration measured for cyclohexane was approximately 0.01 mg/L. For a Henry's law constant of 10 m^3_{liq}/m^3_{gas}, the expected liquid-phase concentration would be 0.001 mg/L. For a total wetted surface volume of 0.2 L, the total mass to be added to the mass closure assessment would be

0.0002 mg. The total mass of cyclohexane in the shower stall gas phase was 17 mg. Therefore, the wetted surfaces were not likely to cause the difference between predicted and measured gas-phase concentrations.

As discussed in Section 4.3.1, a gas-phase sample was collected at the end of an experiment with no water flowing through the system. This sample was collected to determine the extent of chemical desorption from shower stall surfaces resulting from chemical adsorption during an experiment. Measured chemical concentrations were consistently lower than predicted values based on decay due to ventilation.

As explained in Section 4.4.2, gas-phase samples were collected at different locations within the shower stall. In general, the shower stall was determined to be well mixed. For mass closure calculations, concentrations measured at the system's exhaust port were used, and for the most part appeared to be representative of gas-phase concentrations within the shower stall.

Liquid droplet sizes produced by the experimental showerhead were not measured, making it difficult to predict the aerosol scavenging effect. On the basis of other shower studies (Keating and McKone, 1993), it is expected that this phenomenon did not contribute significantly to the chemical "sink" effect.

When possible, mass closures were determined for previously reported studies. Results were reported in the Phase I report (Corsi et al., 1996) of this project and in the Appendix to this report. In general, the mass closures determined for this study compared favorably with previously reported shower experiments and in most cases improved upon mass closures for chemicals with similar Henry's law constants.