6. WASHING MACHINE EXPERIMENTS

In washing machine operation, chemicals originating in a tap water supply can be emitted to indoor air during the fill and wash/rinse cycles. As previously discussed, the fill cycle is characterized by different mass transfer mechanisms from those of the wash and rinse cycles, which are similar in operation. Thus, washing machine volatilization experiments are divided into two separate groups. Fill cycle experiments are presented in Section 6.1, followed by wash/rinse cycle experiments in Section 6.2. It should be noted, however, that the results of these two experimental groups can be combined to determine an overall mass emission rate during typical washing machine operation.

6.1. FILL CYCLE EXPERIMENTS

6.1.1. Experimental System

A Kenmore™ washing machine (Model No. 25822) was purchased to complete all (both fill cycle and wash/rinse cycle) washing machine experiments. The experimental washing machine had a dual basket design with a total interior volume of 150 L (58 cm diameter and 56 cm height). Operation options included water volume setting (low, medium low, medium, medium high, high), water temperature setting (cold, warm, hot), agitation speed (slow, fast), and time of wash cycle (2 to 10 minutes).

The first action of a washing machine is to fill the tub with water. Typically, a washing machine is directly plumbed to the house water supply. However, for this project, it was necessary to add chemical tracers to the supply water upstream of the machine. To meet this need, an auxiliary water supply and pump system was added to provide inlet water to the machine (see Figure 6-1). A 120 L container served as a tracer reservoir and was filled with 60 to 90 L of tap water (depending on desired fill volume) prior to each experiment. This water was spiked with the tracer solution in a manner similar to that described in Section 3.2.2. To fill the washing machine, liquid was pumped at a prescribed flowrate from the tracer reservoir to the washing machine hose connection using a rotary vane pump (PROCON™) and 1.3 cm OD Teflon™ tubing. The liquid flowrate was confirmed by timing the collection of a known volume of liquid. An effort was made to replicate typical washing machine fill rates of 13.1 to 13.8

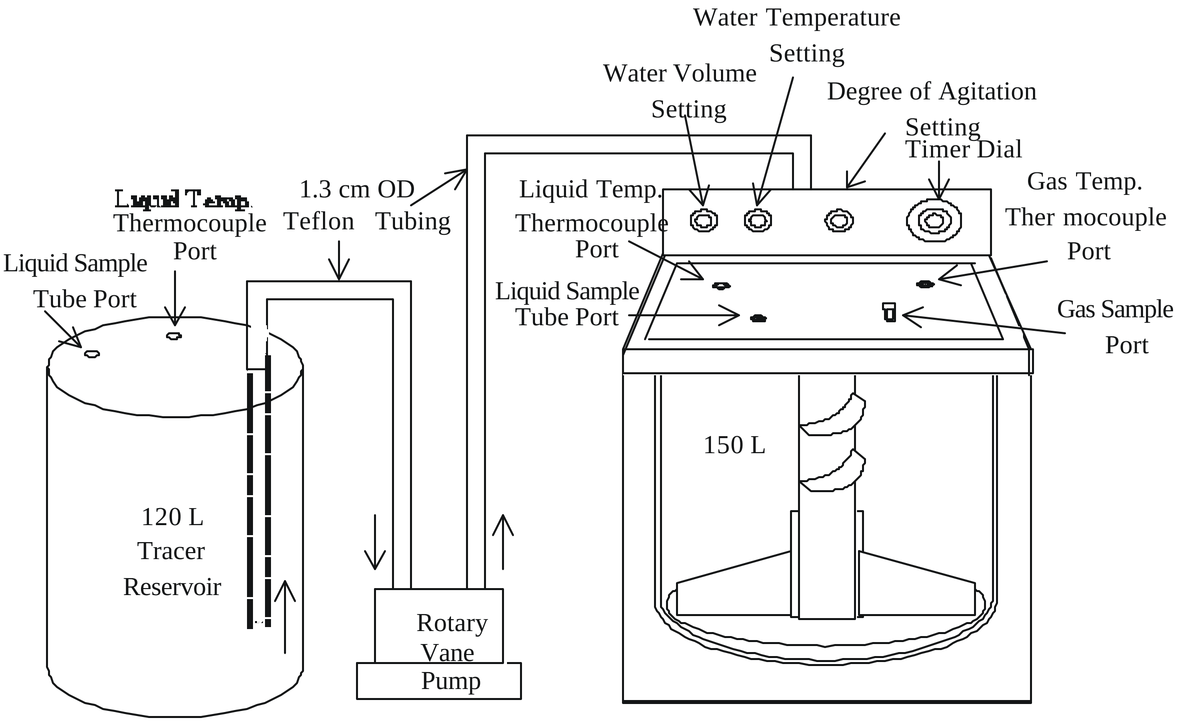


Figure 6-1. Washing machine fill cycle experimental system.

L/minute with the pump and reservoir system. In addition, typical fill times of 3 minutes and 20 seconds for low volume and 6 minutes and 25 seconds for high-volume fills were also used for appropriate experiments.

For both fill and wash/rinse cycle experiments, the washing machine was configured to allow for liquid- and gas-phase sampling. A hole 0.32 cm in diameter was drilled in the washing machine lid for liquid sampling. During an experiment, 0.32 cm OD Teflon™ tubing was inserted through the port, and liquid was pumped from the washing machine basin with a peristaltic pump (Masterflex™, L/S). After the line was flushed for 10 seconds, a liquid sample was collected in a 22 mL glass vial as described in Section 3.3.1. For fill cycle experiments, an additional liquid sample port was drilled in the tracer reservoir lid. Liquid samples from the tracer reservoir were collected in the same manner as described for the washing machine. Liquid samples collected from the tracer reservoir represented the initial liquid-phase concentration used to solve the fill cycle mass balance equations (Equations 3-8 and 3-9), and were observed to remain relatively constant during each experiment.

For gas samples, a 0.64 cm ID bore-through stainless steel Swagelok™ fitting was inserted in the washing machine lid. A 0.64 cm OD sorbent tube was inserted through the fitting into the washing machine headspace and locked into place with a Teflon™ ferrule located inside the fitting. A gas sample was pulled through the tube as described in Section 3.3.2, at a sample flowrate between 0.2 L/minute and 0.4 L/minute. Gas sampling times for wash/rinse cycle experiments were approximately 30 seconds, whereas a single gas sample was collected for the duration of a fill cycle experiment.

Liquid-phase temperature was continuously monitored in both the tracer reservoir and the washing machine. Thermocouple wires were submerged in each basin pool and were connected to a digital monitor to allow for continuous temperature measurements. There was no significant difference in temperature between the tracer reservoir liquid and washing machine liquid for the duration of an experiment.

6.1.2. Experimental Design

Fill cycle experiments were designed to compare the volatilization rate for a standard condition with the volatilization rate associated with changes in one variable. The fill cycle standard condition was defined as cold water (T ≈ 20°C), no detergent, no clothes in machine, approximately 13.8 L/minute liquid flowrate, low water volume (≈ 45 L), and a fill time of 3.33 minutes. The independently varied parameters included hot water (T ≈ 50°C), addition of detergent (≈ 40 g of Tide™ detergent), addition of clothes (equivalent liquid volume ≈ 11 L), 8.6 L/minute liquid flowrate (4.75 minute fill time), and high water volume (≈ 90 L, 6.5 minute fill time). Six experiments and three replicates were completed.

6.1.3. Source-Specific Methodology

A standard procedure for each fill cycle was developed. Prior to the start of each experiment the following tasks were completed:

- The tracer reservoir was filled with at least 60 L of tap water (hot or cold)
- The liquid flowrate was measured and set to the appropriate value
- The tracer cocktail was added to the reservoir water and was mixed manually
- The reservoir tracer solution was mixed for an additional minute
- Detergent and/or clothes were added to the empty washing machine basin when appropriate
- Two initial liquid samples were collected from the reservoir.

It should be noted that there is no standard protocol for filling a washing machine. Users commonly add clothes and/or detergent at different times during the filling process, which incidentally results in the lid being open at different times and for varying time periods. It was not practical to replicate all possible combinations of procedures associated with loading a washing machine. Thus, a consistent protocol was adopted for all experiments. The lid was always closed, and, where applicable, clothes and/or detergent were added to the machine before the experiment was started.

6.1.3.1. *Sample Schedule*

Liquid samples were collected from the tracer reservoir throughout the experiment to monitor any chemical losses, that is, changes in the initial chemical concentrations. Five liquid samples were collected from the tracer reservoir, and four liquid samples were collected from the washing machine basin. Liquid samples from the washing machine basin were collected at experimental times of 2.0 and 2.3 minutes. Two additional samples were collected at the end of filling (3.33 minutes). These liquid sample times were adjusted for longer experiments (low flowrate and high volume). A single gas sample was collected from the washing machine headspace for the duration of the experiment, during which time sample volumes were recorded using a bubble flowmeter downstream of the adsorbent tube. A final gas sample was also collected for 30 seconds after experiment completion. Liquid temperatures were monitored for both the tracer reservoir and the washing machine.

6.1.3.2. *Ventilation Rates*

The experimental methodology used to estimate ventilation rates during the fill cycle was similar to that given in Section 5.3.2. However, the mass balance equation describing the washing machine headspace during filling incorporated changing liquid and headspace volumes, as shown:

$$\frac{d\left(C_g V_g\right)}{dt} = Q_g C_{g,in} - Q_g C_g \qquad (6\text{-}1)$$

where

C_g = tracer gas-phase concentration in headspace (M/L^3)
V_g = headspace volume (L^3)
t = time (T)
Q_g = headspace ventilation rate (L^3/T)
$C_{g,in}$ = tracer gas-phase concentration entering headspace (M/L^3).

If one assumes the background air was relatively clean ($C_{g,in} = 0$), Equation 6-1 may be rewritten as:

$$C_g \frac{dV_g}{dt} + V_g \frac{dC_g}{dt} = -Q_g C_g \qquad (6\text{-}2)$$

where

C_g = tracer gas-phase concentration in headspace (M/L^3)
V_g = headspace volume (L^3)
t = time (T)
Q_g = headspace ventilation rate (L^3/T).

Further simplifications of Equation 6.2 include rewriting the change in gas volume (dV_g/dt) as – (dV_l)/dt, which is equivalent to – Q_l. Also, the liquid volume (V_l) equals $Q_l \bullet t$. Finally, the gas volume (V_g) may be expressed as the difference between the total washing machine volume and the liquid volume ($V_t - Q_l \bullet t$). The integrated form of Equation 6-2 is then:

$$C_g = \exp\left[\left(Q_l - Q_g\right)\left(-\frac{1}{Q_l}\ln\left(V_t - Q_l t\right) + \frac{1}{\left(Q_l - Q_g\right)}\ln\left(C_{g,0}\right) + \frac{1}{Q_l}\ln\left(V_t\right)\right)\right] \qquad (6\text{-}3)$$

where

C_g = tracer gas-phase concentration in headspace (M/L^3)

t = time (T)

Q_g = headspace ventilation rate (L^3/T).

Q_l = liquid flowrate (L^3/T)

V_t = total machine volume (L^3)

$C_{g,0}$ = initial tracer gas-phase concentration (M/L^3).

The ventilation rate (Q_g) was determined by fitting Equation 6-3 to the measured data, using the procedure outlined in Section 3.6.

6.1.3.3. *Parameter Estimation*

Ethyl acetate was affected by the presence of detergent. As explained in Section 5.3.3, a compound present in dishwasher detergent eluted from the GC column at the same residence time as ethyl acetate, thereby masking ethyl acetate results. Interestingly, a compound present in Tide™ detergent had an opposite effect on ethyl acetate, because no peak was detected for ethyl acetate in experiments involving detergent. This result was replicated with controlled laboratory experiments in which ethyl acetate was added to vials containing water and detergent. Apparently, a detergent compound reacted with the ethyl acetate in solution such that ethyl acetate was no longer measurable using the GC/FID. Thus, ethyl acetate results are not reported for this cycle.

The duplicate liquid-phase samples collected at the end of the fill cycle were averaged to determine the $C_{l,end}$ value used in Equation 2-2 to estimate chemical stripping efficiencies. If these duplicate liquid samples were not within 20% of each other, then the average of the previous liquid samples was used to predict chemical stripping efficiency. The value of $C_{l,init}$ in Equation 2-2 was taken to be the average of liquid-phase concentrations measured in the tracer reservoir over the course of an experiment.

As discussed in Section 3.6.2, mass balance models for the fill cycle could not be solved analytically, such that a Runge-Kutta second-order numerical solution method was adopted. This method involved prediction of the following time-dependent parameters: V_l, V_g, C_l, and C_g, at 1-second intervals. The value of K_LA for each chemical, except acetone, was based on minimization of the normalized residuals (Equation 3-7) between the liquid-phase concentrations measured at 2.0, 2.3, and 3.3 (experiment end time) in the washing machine basin and the model-predicted value at each of these time steps. Because the change in acetone chemical concentration in the liquid phase was relatively low, the value of K_LA for acetone should be based on gas-phase data. However, for fill cycle experiments, only a single measurement was collected in the gas phase. Thus, values of K_LA for acetone were based on minimizing the normalized residuals for data in both phases. The normalized residual between the final measured gas-phase concentration and the final predicted gas-phase concentration in the washing machine headspace was added to the normalized residuals between the measured liquid-phase concentrations and model predicted values.

6.1.4. Fill Cycle Results

Nine fill cycle experiments were completed to predict chemical mass emissions. Fourteen additional experiments were completed to characterize the ventilation rate during the fill cycle. Fill cycle results can be combined with wash/rinse cycle results presented in Section 6.2.4 to characterize total mass emissions during typical washing machine use. Based on the experimental methodology presented in Sections 3.0 and 6.1.3, the ventilation rates, overall chemical stripping efficiencies, and mass transfer coefficients (K_LA, k_lA, k_gA, and k_g/k_l) are presented in this chapter. In addition, the effects of liquid temperature, liquid volume, liquid fill rate, detergent use, presence of clothes, and chemical properties on each response are discussed.

Operating conditions for each mass transfer experiment are listed in Table 6-1. Fill cycle experiments were designed to compare a standard condition of cold water, liquid flowrate of ~13.8 L/minute, low liquid volume, no detergent or clothes in the machine, and fill time of 3.33 minutes. Experiments 1 and 1 replicate represented this standard condition. The remaining experiments have one variable that is different from the standard conditions. The differing variable is listed in the last column of Table 6-1.

Table 6-1. Washing machine fill cycle experimental conditions

Experiment #	Liquid temp. (°C)	Fill time (min:sec)	Liquid flowrate (L/min)	Liquid final volume (L)	Ventilation rate (L/min)	Headspace final volume (L)	Variable change
1	19	3:20	14.6	49	55	101	None
1 replicate	21	3:20	13.7	46	55	104	None
2	19	3:20	13.8	46	55	104	Detergent
3	21	3:20	13.7	46	55	93	Clothes
4	49	3:20	13.6	46	160	104	Hot water
4 replicate	47	3:20	13.8	46	160	104	Hot water
5	20	6:30	13.7	89	55	61	High volume
6	21	4:45	8.6	41	55	109	Low flowrate
6 replicate	19	4:45	8.5	40	55	110	Low flowrate

6.1.4.1. *Ventilation Rates*

Ventilation rates listed in Table 6-1 represent average values based on 14 fill cycle ventilation rates. The headspace ventilation results listed in Table 6-2 were determined as explained in Section 6.1.3.2. Several components compose the system ventilation rate. First, the process of filling involves an expanding liquid pool that naturally displaces air from the washing machine headspace. The ventilation rate is complicated because additional air is drawn into the machine by the falling film of water. Also, there are buoyancy effects at elevated temperatures.

As shown in Table 6-2, ventilation rates measured at cold temperatures were lower than at hot temperatures. Heated water had a significantly higher ventilation rate because of buoyancy (chimney) effects. Other operating variables (clothes, detergent, high volume, low flowrate) did not appear to have a significant impact on headspace ventilation. Thus, ventilation rates were averaged based on liquid temperature. The average cold water ventilation rate was 55 L/minute and the average hot water ventilation rate was 160 L/minute. These average values were applied to respective experiments using cold or hot water.

A representative plot for a ventilation experiment is shown in Figure 6-2. The experimental conditions for this plot were hot water and a liquid flowrate of 13.1 L/minute (Ventilation Experiment 13). The best-fit ventilation rate for this experiment was 157 L/minute.

Table 6-2. Washing machine fill cycle ventilation rates

Experiment #	Liquid temp. setting	Fill time (min)	Liquid flowrate (L/min)	Ventiliation rate (L/min)	Variable change
1	Cold	3.0	13.8	49	None
2	Cold	3.25	13.8	33	None
3	Cold	3.25	13.8	81	None
4	Cold	3.5	13.8	33	None
5	Cold	3.5	13.8	57	None
6	Cold	2.75	13.8	42	Clothes
7	Cold	3.0	13.8	47	Detergent
8	Cold	5.5	13.8	79	High volume
9	Cold	5.5	13.8	67	High volume
10	Cold	6.0	13.8	52	High volume
11	Cold	4.75	8.6	53	Low flowrate
12	Cold	4.75	8.5	52	Low flowrate
13	Hot	2.25	13.1	157	Hot water
14	Hot	2.0	13.1	161	Hot water

6.1.4.2. *Chemical Stripping Efficiencies*

Chemical stripping efficiencies (η) for fill cycle experiments are reported in Table 6-3. Stripping efficiencies for low-volume experiments (Experiments 1 to 4 replicate) were based on a fill time of 3.33 minutes. Stripping efficiencies for low fill rate experiments (Experiments 6 and 6 replicate) were based on a fill time of 4.75 minutes. Finally, chemical stripping

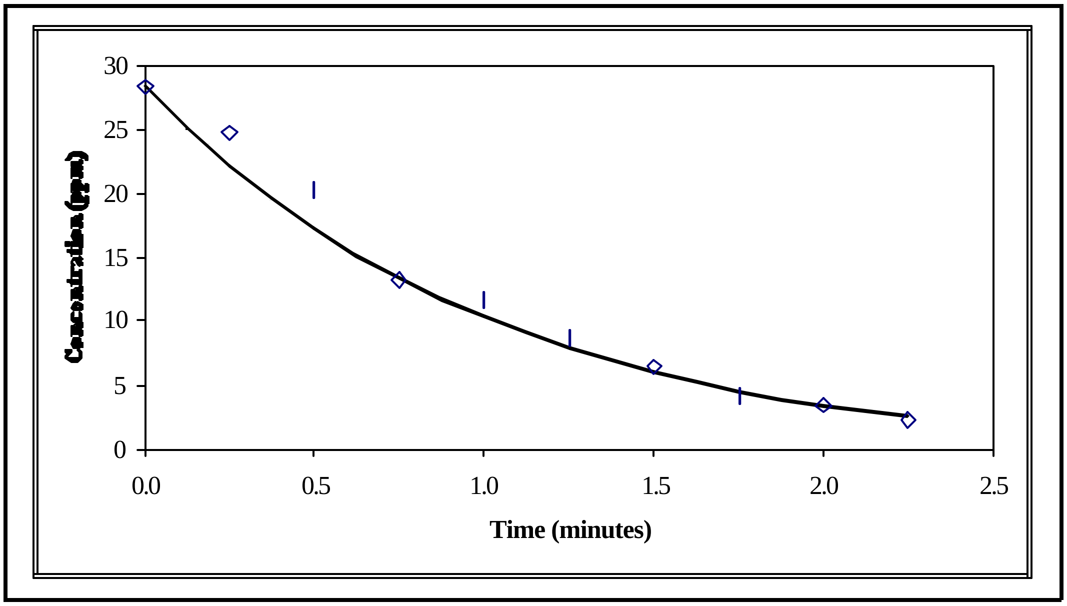


Figure 6-2. Isobutylene decay due to ventilation for Experiment 13.

Table 6-3. Chemical stripping efficiencies (η) for washing machine fill cycle

Experiment #	Variable change	Acetone h (%)	Toluene h (%)	Ethylbenzene h (%)	Cyclohexane h (%)
1	None	2.1	9.8	9.5	15
1 replicate	None	0.96	13	13	25
2	Detergent	0.74	13	16	26
3	Clothes	3.0	8.2	10	6.9
4	Hot water	1.2	22	20	28
4 replicate	Hot water	2.3	35	36	45
5	High volume	1.8	17	19	33
6	Low flowrate	1.2	23	24	37
6 replicate	Low flowrate	3.0	9.7	9.4	12

efficiencies for high-volume experiments (Experiment 5) were based on a fill time of 6.5 minutes.

The average stripping efficiencies for the standard condition (liquid flowrate ≈ 13.8 L/minute, low liquid volume, no detergent or clothes in the machine, and fill time of 3.33 minutes) were 1.5% for acetone, 11% for toluene, 11% for ethylbenzene, and 20% for cyclohexane. In general, stripping efficiencies tended to increase with increasing Henry's law constant, and toluene and ethylbenzene had similar values for the same experiment. The highest stripping efficiencies for chemicals (except acetone) were associated with hot water use (average of Experiments 4 and 4 replicate). The highest stripping efficiency for acetone was for the condition of clothes in the machine (Experiment 3).

Compared with the standard case, the following conditions led to an increase in chemical stripping: detergent in the machine for toluene, ethylbenzene, and cyclohexane; clothes in the machine for acetone; and hot water and low flowrate for all chemicals. In general, however, overall stripping efficiencies were similar in magnitude for acetone. An average stripping efficiency based on all experiments was calculated to be 1.8% for acetone. For the remaining chemicals, liquid temperature appeared to be a significant factor, resulting in the following averages: 13% for cold water and 29% for hot water for toluene, 14% for cold water and 28% for hot water for ethylbenzene, and 22% for cold water and 37% for hot water for cyclohexane.

Replicate experimental results for the washing machine fill cycles were less consistent than for other sources. The reasons for high relative differences in replicate experimental results could not be determined. However, with the exception of one cyclohexane value, the absolute differences in replicate stripping efficiencies were all within 17%.

6.1.4.3. *K_LA Values*

As a washing machine fills, a significant quantity of air is drawn into the underlying pool. The resulting entrained air influences the rate of chemical volatilization by increasing a chemical's gas-phase resistance to mass transfer and by decreasing a chemical's concentration driving force. These factors are reflected in values of K_LA predicted for the fill cycle.

Values of K_LA for all chemicals and operating conditions are reported in Table 6-4. Values of K_LA are based on the same fill times discussed for stripping efficiencies. The average values of K_LA for the standard case were 0.23 L/minute for acetone, 2.3 L/minute for toluene, 2.3 L/minute for ethylbenzene, and 4.1 L/minute for cyclohexane. Again, there were general trends of increasing values of K_LA with increasing Henry's law constant as well as similar values for toluene and ethylbenzene. The impact of entrained air is evident from the 44% difference between ethylbenzene's K_LA and that of cyclohexane for the standard case.

As shown in Table 6-4, there was a great deal of variability in values of K_LA for acetone. Some values could not be determined by the Excel™ solver. This inconsistency likely resulted from the calculation method of K_LA and limited gas-phase data. Thus, a greater emphasis was placed on the values of K_LA for toluene, ethylbenzene, and cyclohexane for fill cycle experiments. For this particular source, the importance of gas-phase resistance to mass transfer was evident for these higher volatility compounds.

The highest values of K_LA for toluene, ethylbenzene, and cyclohexane were associated with hot water. The presence of clothes led to a reduction in values of K_LA for all chemicals. The presence of clothes in the washing machine basin visibly reduced the splashing associated with the falling liquid film and its impact in the underlying pool. In general, experiments completed with cold water resulted in similar values of K_LA. Average values of K_LA for cold water experiments were 2.9 L/minute for toluene, 3.2 L/minute for ethylbenzene, and 4.6 L/minute for cyclohexane. For comparison, average values of K_LA associated with hot water experiments were 6.7 L/minute for toluene, 6.6 L/minute for ethylbenzene, and 8.2 L/minute for cyclohexane.

Table 6-4. Values of K_LA for washing machine fill cycles

Experiment #	Variable change	Acetone K_LA (L/min)	Toluene K_LA (L/min)	Ethylbenzene K_LA (L/min)	Cyclohexane K_LA (L/min)
1	None	0.23	1.8	1.7	2.8
1 replicate	None	n/s	2.8	2.9	5.3
2	Detergent	n/s	4.2	5.0	7.5
3	Clothes	0.086	1.5	1.9	1.2
4	Hot water	0.19	5.0	4.7	5.4
4 replicate	Hot water	0.22	8.4	8.4	11
5	High volume	0.038	2.5	2.8	4.8
6	Low flowrate	0.12	4.2	4.4	6.4
6 replicate	Low flowrate	1.2	3.5	3.7	4.5

Note: Excel solver was unable to find a feasible K_LA to fit the model to the measured data.

6.1.4.4. *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 was determined for each specific experiment. These values are reported in Table 6-5. For the fill cycle, values of k_g/k_l ranged from 4.5 to 20 with an average value of 9.5 for all experiments. A value of k_g/k_l was not determined for Experiment 3 because the Excel solver could not find a feasible solution for the available data.

Again, the variability associated with values of K_LA for acetone prevented them from being incorporated into the solution matrix. Thus, values reported in Table 6-5 are based solely on toluene, ethylbenzene, and cyclohexane data. However, the last column of Table 6-5 lists the predicted average value of K_LA for acetone using the reported k_g/k_l value, Equation 2-15, and experimental values of K_LA for toluene, ethylbenzene, and cyclohexane. By comparison, values of K_LA predicted for acetone in Table 6-5 tend to be lower than those reported for acetone in

Table 6-4. However, values of K_LA for acetone for Experiments 4 replicate and 5 are comparable between the predicted and measured values.

Table 6-5. Liquid and gas-phase mass transfer coefficients for washing machine fill cycle experiments

Experiment #	Chemical	k_lA (L/min)	k_gA (L/min)	k_g/k_l	Predicted acetone K_LA (L/min)[a]
1	T EB C	2.9 2.8 2.9	21 20 21	7.1	0.022
1 replicate	T EB C	5.4 5.3 5.5	25 24 25	4.5	0.031
2	T EB C	7.0 8.1 7.6	47 54 51	6.7	0.056
3	T EB C	n/s	n/s	n/s	n/s
4	T EB C	5.5 4.9 5.4	111 101 110	20	0.54
4 replicate	T EB C	12 10 11	58 50 57	5.0	0.27
5	T EB C	4.6 5.0 4.9	24 26 25	5.1	0.029
6	T EB C	6.3 6.4 6.5	54 54 55	8.5	0.066
6 replicate	T EB C	4.3 4.5 4.5	80 84 84	19	0.088

[a] Acetone value of K_LA based on k_g/k_l, Equation 2-15, and values of K_LA for toluene, ethylbenzene, and cyclohexane.

Note: Excel solver unable to find a feasible solution.

6.1.4.5. *Mass Closure*

Both liquid and gas samples were collected from the filling basin such that the percentage of mass recovered could be calculated. For fill cycles, 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 102% for acetone, 90% to 117% for toluene, 84% to 103% for ethylbenzene, and 69% to 102% for cyclohexane. Mass closure values for all experiments are reported in database in the Appendix.

6.2. WASH/RINSE CYCLE EXPERIMENTS

6.2.1. Experimental System

The experimental system for wash/rinse cycle experiments was similar to that shown in Figure 6-1. The same washing machine configured for liquid and gas samples described in Section 6.1.1 was used, but for wash/rinse cycle experiments it was directly plumbed to the building water supply. Chemicals were added to the washing machine basin after filling such that the auxiliary reservoir was not needed. Variable operating conditions for the wash/rinse cycle included water volume, water temperature, agitation speed, mass of clothing, and presence of detergent for a wash cycle versus none for the rinse cycle.

The wash/rinse cycle experimental system is shown in Figure 6-3. During the cycle, an impeller was used to agitate the water. The "normal" wash cycle was used for all experiments. This cycle can be varied in length. A typical value of 10 minutes was chosen for all experiments.

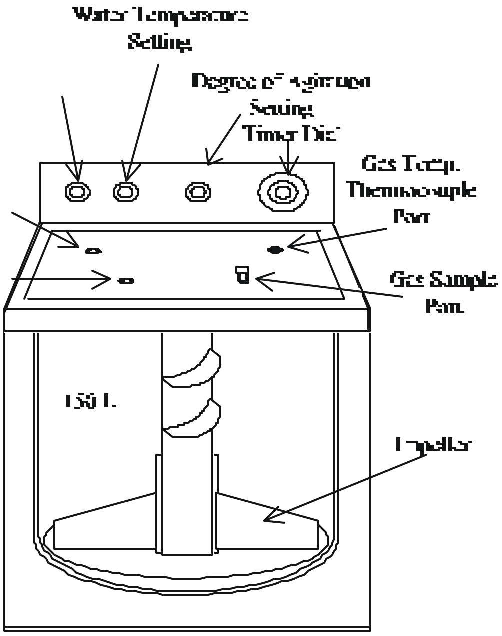


Figure 6-3. Wash/rinse cycle experimental system.

6.2.2. Experimental Design

To accommodate all of the variable operating conditions, wash and rinse cycles were studied using two (2 × 2 × 2) factorial arrays as shown in Figure 6-4. The first design consisted of a wash cycle (≈ 40 g Tide™ detergent) versus rinse cycle, hot water (T ≈ 50°C) versus cold water (T ≈ 20°C), and clothes (equivalent liquid volume ≈ 11 L) versus no clothes. The second array consisted of low water volume (≈ 45 L) versus high water volume (≈ 90 L), slow versus fast agitation speed, and cold water (T ≈ 20°C) versus hot water (T ≈ 50°C). A total of 14 experiments were completed to fulfill both factorial designs, and 3 additional experiments were completed as replicates.

6.2.3. Source-Specific Methodology

The following preexperimental tasks were completed for wash/rinse cycle experiments:

The necessary items were added to the washing machine basin (clothes and/or detergent)

The appropriate settings for a particular experiment (water volume, agitation speed, water temperature) were applied

The washing machine wash time was set to 10 minutes

The washing machine was filled with a known volume of water

The washing machine operation was stopped after the fill was complete (before agitation cycle began)

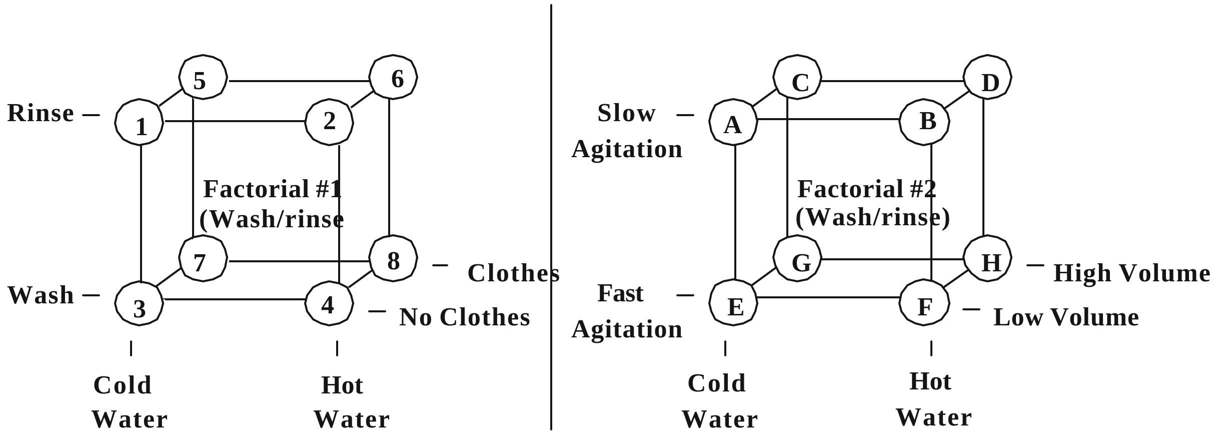
Figure 6-4. Wash/rinse cycle factorial experimental design.

- A background water sample was collected
- The chemical tracer solution was added to the washing machine basin and was mixed well (manually)
- The washing machine lid was closed
- An initial liquid sample was collected that corresponded to the initial liquid-phase concentration for an experiment
- An initial gas sample was collected that corresponded to the initial gas-phase concentration for an experiment.

6.2.3.1. *Sample Schedule*

A total of 12 liquid samples were collected for each wash/rinse cycle experiment. In addition to initial samples, liquid samples were collected at the experimental times of .5, 1.25, 1.75, 2.75, 3.25, 6.75, and 7.25 minutes. Two additional samples were collected at 10 minutes.

These sampling times corresponded to the start and end times of each respective gas sample. For example, a gas sample was collected from time 0 to 30 seconds, 1.25 to 1.75, and so on. Including the initial sample, six gas samples were collected for each experiment. Liquid and gas-phase temperatures were recorded for the duration of the experiment.



6.2.3.2. *Ventilation Rates*

Washing machines are characterized by a relatively high ventilation rate. This rate was determined for all wash/rinse cycle experimental conditions using the same methodology as described in Section 5.3.2. Ventilation rates determined using isobutylene decay were used in wash/rinse cycle mass balance models with data from mass transfer experiments.

6.2.3.3. *Parameter Estimation*

An important measurement used to determine chemical stripping efficiencies and mass transfer coefficients was the initial liquid-phase concentration. For several experiments, the liquid-phase concentration increased in magnitude for various lengths of time before decreasing as expected. This initial increase was likely caused by improved mixing of the chemical tracer solution in the washbasin. For consistency, each chemical's stripping efficiency was calculated based on the highest measured liquid-phase concentration during an experiment and the final measured liquid-phase concentration. This procedure resulted in experimental stripping efficiencies based on different time periods; for example, an experiment with the highest liquid-phase concentration at time zero had a total time of 10 minutes, and an experiment with the highest value occurring after 2 minutes into the experiment had a total time of only 8 minutes. To correct for this time difference, a plot was constructed based on measured liquid-phase concentration values versus time. For experiments with a late initial concentration peak, a curve was fitted to the data and extended to reach 10 minutes. On the basis of the graph's liquid-phase concentration value at 10 minutes and the measured initial concentration, a 10-minute stripping efficiency was reported for every experiment.

Values of K_LA for each chemical were calculated based on measurements collected from an experimental time of 180 seconds to the end of the experiment. This method ensured that the washing machine contents were well mixed. The difference in experimental time should not affect the reported K_LA values for each chemical, as long as equilibrium conditions did not exist in the machine's headspace. Values of K_LA for acetone and ethyl acetate were based on minimizing the residuals between the model and gas-phase data. Values of K_LA for toluene, ethylbenzene, and cyclohexane were based on minimizing the residuals between the model and liquid-phase data. For experiments with conditions leading to relatively high volatilization rates, the more volatile chemicals often had results below the predetermined method detection level (see Section 3.5.4). In these cases, the determination of K_LA was modified to include only measurements meeting this quality assurance requirement, that is, above method detection limit.

6.2.4. Wash/Rinse Cycle Results

A total of 17 wash/rinse cycle mass transfer experiments and 17 ventilation experiments were completed to characterize the emission rate from a residential washing machine during these cycles. Wash and rinse cycle results can be combined with fill cycle results presented in Section 6.1.4 to characterize total mass emissions during typical washing machine use. Based on the experimental methodology presented in Sections 3.0 and 6.2.3, the ventilation rates, overall chemical stripping efficiencies and mass transfer coefficients (K_LA, k_lA, k_gA, and k_g/k_l) are presented in this chapter. In addition, the effects of liquid temperature, liquid volume, detergent use, mass of clothes, agitation speed, and chemical properties on each response are discussed.

The operating conditions for each mass transfer experiment are given in Table 6-6.

6.2.4.1. *Ventilation Rates*

It was difficult to estimate ventilation rates and mass transfer coefficients during a single experiment. Therefore, ventilation rates were predicted separately, following the methodology given in Section 5.3.2, for similar operating conditions used during mass transfer experiments. A total of 17 ventilation rate experiments were completed including 9 replicate experiments. A summary of the ventilation experimental operating conditions and results is provided in Table 6-7.

As shown in Table 6-7, ventilation rates measured at cold temperatures were significantly lower than ventilation rates measured at hot temperatures. The heated water led to a buoyancy (chimney) effect, which acted to flush the headspace at a faster rate. Other factors such as agitation speed, mass of clothing, presence of detergent, and volume of water had less impact on

Table 6-6. Washing machine wash/rinse cycle experimental operating conditions

Experiment #	Liquid temp. (°C)	Liquid volume (L)	Headspace volume (L)	Ventilation rate (L/min)	Agitation speed	Detergent present?	Clothes present?
1, A	24	47	103	53	Slow	No	No
1, A replicate	22	49	101	53	Slow	No	No
2, B	49	48	102	200	Slow	No	No
3	23	49	101	53	Slow	Yes	No
3 replicate	22	47	103	53	Slow	Yes	No
4	51	49	101	200	Slow	Yes	No
5	21	50	88	53	Slow	No	Yes
6	50	47	92	200	Slow	No	Yes
7	18	49	90	53	Slow	Yes	Yes
8	49	49	90	200	Slow	Yes	Yes
C	21	82	58	53	Slow	No	No
C replicate	21	95	55	53	Slow	No	No
D	51	96	54	200	Slow	No	No
E	20	48	102	53	Fast	No	No
F	49	49	101	200	Fast	No	No
G	18	95	55	53	Fast	No	No

H	50	94	56	200	Fast	No	No

Table 6-7. Ventilation rate experiment results

Experiment #	Water temperature	Water volume	Agitation speed	Detergent present?	Clothes present?	Ventilation rate (L/min)
1	Cold	Low	Slow	No	No	50
2	Cold	Low	Slow	No	No	63
3	Cold	Low	Slow	No	No	43
4	Cold	High	Slow	No	No	35
5	Cold	High	Slow	No	No	38
6	Cold	Low	Fast	No	No	78
7	Cold	Low	Fast	No	No	41
8	Cold	Low	Fast	No	No	51
9	Cold	Low	Slow	Yes	No	41
10	Cold	Low	Slow	Yes	No	64
11	Cold	Low	Slow	No	Yes	77
12	Hot	Low	Slow	No	No	116
13	Hot	Low	Slow	No	No	254
14	Hot	Low	Slow	No	No	160
15	Hot	High	Slow	No	No	246
16	Hot	Low	Slow	No	Yes	184
17	Hot	Low	Slow	No	Yes	210

the wash/rinse cycle ventilation rate. To determine an appropriate ventilation rate to use in conjunction with mass transfer data, ventilation experimental values were grouped according to water temperature. The average cold water ventilation rate was assumed to be 53 L/minute and was applied to all mass transfer data analyses based on experiments using cold water. The average hot water ventilation rate was assumed to be 200 L/minute and was applied to all mass transfer data analyses based on hot water experiments.

A representative data plot for a ventilation experiment is shown in Figure 6-5. The experimental conditions for this plot were cold water, no clothes, no detergent, low water volume, and fast agitation. The slope for the exponential line was –0.492 with an R^2 value of 0.99. Values of R^2 ranged from 0.88 to 0.997 for all ventilation plots, with all but one value above 0.93. These high correlation values indicated a relatively constant ventilation rate for the duration of the wash/rinse cycle. For this experiment, the washing machine filled at 13.8 L/minute for 3.43 minutes, resulting in a total liquid volume of 47 L. Based on a total volume of 150 L, the remaining headspace volume was 103 L. The corresponding ventilation rate for this experiment was 103 L multiplied by the negative of the slope for a value of 51 L/minute.

6.2.4.2. *Chemical Stripping Efficiencies*

Chemical stripping efficiencies are reported in Tables 6-8 to 6-16 for each chemical, respectively. The results for each chemical are reported in two tables based on each factorial design. The three factors incorporated into the first group were liquid temperature, mass of

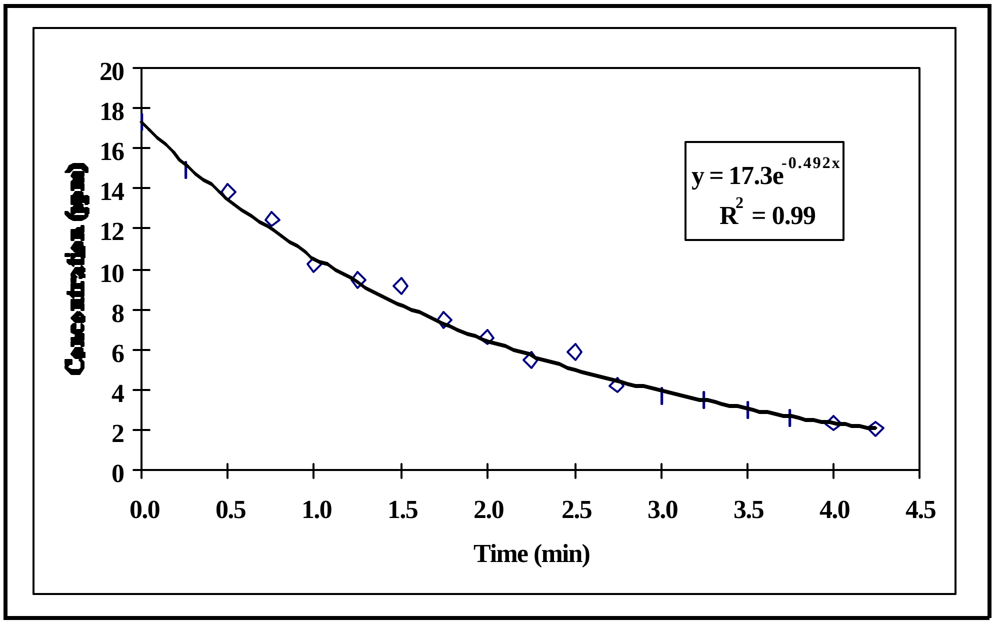


Figure 6-5. Isobutylene decay due to ventilation for Experiment 8.

Table 6-8. Acetone stripping efficiencies for washing machine wash/rinse cycle — Factorial #1

Experiment #	Liquid temp.	Detergent?	Clothes?	Stripping efficiency (%)	Clothes effect[a] (%)	Detergent effect[b] (%)	Liquid temperature effect[c] (%)
1	Cold	No	no	7.1	!8.0	!1.0	25
1 replicate	Cold	No	no	15			
2	Hot	No	no	36	27	6.0	25
3	Cold	Yes	no	7.0	!8.0	!1.0	18
3 replicate	Cold	Yes	no	5.1			
4	Hot	Yes	no	30	8.0	6.0	18
5	Cold	No	Yes	19	&8.0	&1.0	&9.6
6	Hot	No	Yes	9.4	27	!13	!9.6
7	Cold	Yes	Yes	20	&8.0	&1.0	2.0
8	Hot	Yes	Yes	22	8.0	&13	2.0

	Average =	**4.7**	**−2.2**	**8.9**

[a] Clothes effect from full to none.

[b] Detergent effect from 40 grams to none.

[c] Liquid temperature effect from cold to hot.

Table 6-9. Acetone stripping efficiencies for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	Stripping efficiency (%)	Agitation speed effect[a] (%)	Liquid volume effect[b] (%)	Liquid temperature effect[c] (%)
A	Cold	Low	Slow	7.1	!5.0	6.9	25
A replicate	Cold	Low	Slow	15			
B	Hot	Low	Slow	36	5.0	33	25
C	Cold	High	Slow	3.4	!5.9	6.9	1.0
C replicate	Cold	High	Slow	4.8			
D	Hot	High	Slow	3.1	-12	33	1.0
E	Cold	Low	Fast	16	-5.0	6.0	15
F	Hot	Low	Fast	31	5.0	16	15
G	Cold	High	Fast	10	-5.9	6.0	5.0
H	Hot	High	Fast	15	-12	16	5.0
				Average =	**!4.5**	**15**	**11**

[a]Agitation speed effect from fast to slow.
[b]Liquid volume effect from high to low.
[c]Liquid temperature effect from cold to hot.

Table 6-10. Ethyl acetate stripping efficiencies for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	Stripping efficiency (%)	Agitation speed effect[a] (%)	Liquid volume effect[b] (%)	Liquid temperature effect[c] (%)
A	Cold	Low	Slow	12	!6.0	4.8	38
A replicate	Cold	Low	Slow	8.1			
B	Hot	Low	Slow	48	14	43	38
C	Cold	High	Slow	5.2	!2.6	4.8	0.10
C replicate	Cold	High	Slow	5.2			
D	Hot	High	Slow	5.1	!17	43	0.10
E	Cold	Low	Fast	16	!6.0	8.2	18
F	Hot	Low	Fast	34	14	12	18
G	Cold	High	Fast	7.8	!2.6	8.2	14
H	Hot	High	Fast	22	!17	12	14
				Average =	**!2.9**	**17**	**18**

[a]Agitation speed effect from fast to slow.
[b]Liquid volume effect from high to low.

[c] Liquid temperature effect from cold to hot.

Table 6-11. Toluene stripping efficiencies for washing machine wash/rinse cycle— Factorial #1

Experiment #	Liquid temp.	Detergent?	Clothes?	Stripping efficiency (%)	Clothes effect[a] (%)	Detergent effect[b] (%)	Liquid temperature effect[c] (%)
1	Cold	No	no	72	24	35	26
1 replicate	Cold	No	no	65			
2	Hot	No	no	95	39	28	26
3	Cold	Yes	no	33	!8.0	35	33
3 replicate	Cold	Yes	no	34			
4	Hot	Yes	no	67	5.0	28	33
5	Cold	No	Yes	45	24	3.0	11
6	Hot	No	Yes	56	39	!6.0	11
7	Cold	Yes	Yes	42	!8.0	3.0	20
8	Hot	Yes	Yes	62	5.0	!6.0	20
				Average =	**15**	**15**	**23**

[a]Clothes effect from full to none.
[b]Detergent effect from 40 grams to none.
[c]Liquid temperature effect from cold to hot.

Table 6-12. Toluene stripping efficiencies for washing machine wash/rinse cycle— Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	Stripping efficiency (%)	Agitation speed effect[a] (%)	Liquid volume effect[b] (%)	Liquid temperature effect[c] (%)
A	Cold	Low	Slow	72	!1.0	42	26
A replicate	Cold	Low	Slow	65			
B	Hot	Low	Slow	95	!4.0	62	26
C	Cold	High	Slow	26	3.0	42	6.0
C replicate	Cold	High	Slow	28			
D	Hot	High	Slow	33	0.0	62	6.0
E	Cold	Low	Fast	70	!1.0	46	29
F	Hot	Low	Fast	99	!4.0	66	29
G	Cold	High	Fast	24	3.0	46	9.0
H	Hot	High	Fast	33	0.0	66	9.0
				Average =	**!0.50**	**54**	**18**

[a]Agitation speed effect from fast to slow.
[b]Liquid volume effect from high to low.
[c]Liquid temperature effect from cold to hot.

Table 6-13. Ethylbenzene stripping efficiencies for washing machine wash/rinse cycle—Factorial #1

Experient #	Liquid Temp.	Detergent?	Clothes?	Stripping efficiency (%)	Clothes effect[a] (%)	Detergent effect[b] (%)	Liquid temperature effect[c] (%)
1	Cold	No	No	76	16	36	24
1 replicate	Cold	No	No	69			
2	Hot	No	No	97	32	25	24
3	Cold	Yes	No	36	!17	36	35
3 replicate	Cold	Yes	no	37			
4	Hot	Yes	No	72	3.0	25	35
5	Cold	No	Yes	57	16	3.0	8.0
6	Hot	No	Yes	65	32	!4.0	8.0
7	Cold	Yes	Yes	54	!17	3.0	15
8	Hot	Yes	Yes	69	3.0	!4.0	15
				Average =	**8.5**	**15**	**21**

[a]Clothes effect from full to none.
[b]Detergent effect from 40 grams to none.
[c]Liquid temperature effect from cold to hot.

Table 6-14. Ethylbenzene stripping efficiencies for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	Stripping efficiency (%)	Agitation speed effect[a] (%)	Liquid volume effect[b] (%)	Liquid temperature effect[c] (%)
A	Cold	Low	Slow	76	!1.0	43	24
A replicate	Cold	Low	Slow	69			
B	Hot	Low	Slow	97	!2.0	65	24
C	Cold	High	Slow	28	6.0	43	2.0
C replicate	Cold	High	Slow	31			
D	Hot	High	Slow	32	!2.0	65	2.0
E	Cold	Low	Fast	74	!1.0	50	25
F	Hot	Low	Fast	99	!2.0	65	25
G	Cold	High	Fast	24	6.0	50	10
H	Hot	High	Fast	34	!2.0	65	10
				Average =	**0.25**	**56**	**15**

[a]Agitation speed effect from fast to slow.
[b]Liquid volume effect from high to low.
[c]Liquid temperature effect from cold to hot.

Table 6-15. Cyclohexane stripping efficiencies for washing machine wash/rinse cycle—Factorial #1

Experiment #	Liquid temp.	Detergent?	Clothes?	Stripping efficiency (%)	Clothes effect[a] (%)	Detergent effect[b] (%)	Liquid temperature effect[c] (%)
1	Cold	No	No	99	20	20	1.0
1 replicate	Cold	No	No	99			
2	Hot	No	No	100	16	2.0	1.0
3	Cold	Yes	No	82	0.0	20	19
3 replicate	Cold	Yes	No	76			
4	Hot	Yes	No	98	4.0	2.0	19
5	Cold	No	Yes	79	20	0.0	5.0
6	Hot	No	Yes	84	16	!10	5.0
7	Cold	Yes	Yes	79	0.0	0.0	15
8	Hot	Yes	Yes	94	4.0	!10	15
				Average =	**10**	**3.0**	**10**

[a] Clothes effect from full to none.
[b] Detergent effect from 40 grams to none.
[c] Liquid temperature effect from cold to hot.

Table 6-16. Cyclohexane stripping efficiencies for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	Stripping efficiency (%)	Agitation speed effect[a] (%)	Liquid volume effect[b] (%)	Liquid temperature effect[c] (%)
A	Cold	Low	Slow	99	!1.0	59	1.0
A replicate	Cold	Low	Slow	99			
B	Hot	Low	Slow	100	0.0	56	1.0
C	Cold	High	Slow	36	!8.0	59	4.0
C replicate	Cold	High	Slow	44			
D	Hot	High	Slow	44	!18	56	4.0
E	Cold	Low	Fast	100	!1.0	52	0.0
F	Hot	Low	Fast	100	0.0	38	0.0
G	Cold	High	Fast	48	!8.0	52	14
H	Hot	High	Fast	62	!18	38	14
				Average =	**!6.8**	**51**	**4.8**

[a] Agitation speed effect from fast to slow.
[b] Liquid volume effect from high to low.
[c] Liquid temperature effect from cold to hot.

detergent, and mass of clothes. The second group involved an investigation of other factors: liquid temperature, liquid volume, and agitation speed. In order to focus on single-variable effects, detergent and clothes were not used for this second group of experiments.

For each group, the results of the factorial main effect analysis (see Section 3.7 for methodology) are given. To illustrate this analysis, the calculation of the main effect of detergent on acetone's stripping efficiency in factorial #1 is shown below.

Corresponding Experiments:		**Difference in Stripping Efficiencies**
Average (1 and 1 rep) to Average (3 and 3 rep)	=	!1.0 %
2 to 4	=	6.0 %
5 to 7	=	!1.0 %
6 to 8	=	!13 %
Average	=	!2.2 %

As shown in Table 6-8, the difference in experimental response was listed twice, once for each corresponding experiment. Replicating the listing of each response, however, does not affect the average value for each variable. As shown in the example, the results for Experiments 1 and 1 replicate, and Experiments 3 and 3 replicate were averaged, respectively, before applying any factorial analyses. Tables 6-9 to 6-16 follow this same format.

Acetone stripping efficiencies are reported for each factorial group in Tables 6-8 and 6-9. For both groups of factorials, stripping efficiencies for acetone ranged from 3.1% to 36%. The highest stripping efficiency value was for the conditions of low water volume, no clothes or detergent, hot water, and slow agitation. The second highest value associated with the second factorial group was 31%, also associated with hot water, no clothes or detergent present, and low water volume. However, this value occurred during a fast agitation speed. It was expected that for similar operating conditions, experiments completed at a higher temperature would result in higher stripping efficiencies because of the corresponding increase in Henry's law constant. For the temperatures listed in Table 6-6, Henry's law constants for acetone ranged from 0.00085 m^3_{liq}/m^3_{gas} (Experiments 7 and G at 18°C) to 0.0051 m^3_{liq}/m^3_{gas} (Experiments 4 and D at 51°C).

The first factorial analysis for acetone stripping efficiencies was based on values calculated using Experiments 1 through 8. In keeping with these values, the highest main effect was 8.9% for the single variable factor of liquid temperature. The main effect from differences in liquid temperature was calculated by subtracting cold water stripping efficiencies from corresponding (similar amounts of clothing and detergent present) hot water stripping efficiencies. A positive effect indicated an absolute increase in stripping efficiency with increasing water temperature. This result was expected, based on the increasing Henry's law constant as described above. When the experiments were grouped according to liquid temperature and the respective stripping efficiencies averaged, the following values resulted: 12% for cold water experiments (Experiments 1, 1 replicate, 3, 3 replicate, 5, and 7) and 24% for hot water experiments (Experiments 2, 4, 6, and 8).

A more practical way to group the experimental results was to combine the liquid temperature effects with using clothes in a wash or rinse (no detergent present) cycle. The average stripping efficiencies were 20% and 19% for cold water use during wash and rinse cycles, respectively, and 22% and 9.4% for hot water use during wash and rinse cycles, respectively.

The second factorial group also included liquid temperature as a factor (11% main effect). However, liquid volume had a slightly greater main effect, with a value of 15%. The main effect from differences in liquid volume was calculated by subtracting high water volume stripping efficiencies from low water volume stripping efficiencies. Thus, a positive 14% indicated an absolute increase in stripping efficiency with decreasing water volume. At lower water volumes, the total kinetic energy (TKE) resulting from agitation of the water surface increases, thereby increasing the potential for chemical volatilization.

When the second factorial results were grouped according to liquid volume, the following average stripping efficiencies resulted: 21% for low volume experiments and 7.3% for high volume experiments. Liquid temperature also had a significant impact on acetone stripping efficiencies. Grouping experiments according to volume and liquid temperature resulted in the following average values: 13% for low volume and cold water experiments, 34% for low volume and hot water experiments, 6.1% for high volume and cold water experiments, and 9.1% for high volume and hot water experiments.

As for all chemicals, the reported acetone stripping efficiencies represent a range of possible transfer efficiencies for different operating conditions. A better estimation of chemical volatilization may be made using K_LA values reported in Section 6.2.4.3. These values were based on a well-mixed initial liquid-phase concentration, rather than the highest peak.

Washing machine wash/rinse cycle Experiments 1 (A), 3, and C were replicated. When the acetone stripping efficiencies for these three experiment were compared, the following relative differences were calculated: 71% for Experiments 1(A) and 1(A) replicate, 31% for Experiments 3 and 3 replicate, and 34% for Experiments C and C replicate.

Because of detergent interaction discussed in Section 6.2.3, only ethyl acetate results for the second factorial group are reported in this section. As shown in Table 6-10, *ethyl acetate stripping efficiencies* ranged from 5.1% to 48%. Again, the highest stripping efficiency corresponded to the conditions of low water volume, low agitation speed, and hot water. The highest main effect for ethyl acetate stripping efficiencies was liquid temperature, with a value of 18%. Grouping the stripping efficiencies according to liquid temperature, resulted in a cold water average of 9.1% and a hot water average of 27%. For the temperatures listed in Table 6-6, Henry's law constants for ethyl acetate ranged from 0.0037 m^3_{liq}/m^3_{gas} to 0.016 m^3_{liq}/m^3_{gas}.

The second highest factor on ethyl acetate stripping efficiencies was liquid volume, with a value of 17%. As with acetone, the stripping efficiencies for ethyl acetate may be grouped according to liquid volume and liquid temperature such that 12% is the average for cold water and low volume, 41% is the average for hot water and low volume, 6.1% is the average for cold water and high volume, and 14% is the average value for hot water and high volume.

Replicate experiments with ethyl acetate results included Experiments A and A replicate and C and C replicate. Stripping efficiencies were within 39% for Experiments A and A replicate and were identical for Experiments C and C replicate.

Toluene stripping efficiencies ranged from 24% to 99% for both factorial experimental groups (Tables 6-11 and 6-12). The highest stripping efficiency corresponded to conditions of hot water, low volume, no clothes or detergent present, and fast agitation. Again, hot water led

to higher stripping efficiencies. For temperatures listed in Table 6-6, Henry's law constants for toluene ranged from 0.22 m^3_{liq}/m^3_{gas} to 0.57 m^3_{liq}/m^3_{gas}.

Toluene stripping efficiencies exhibited a wide range of values depending on associated operating conditions. Thus, the factorial analysis was a useful tool in determining variable impacts. For the first factorial group, the variable with the single highest effect was liquid temperature at a value of 23%. Grouping stripping efficiencies according to liquid temperature resulted in an average value of 49% for cold water experiments and 70% for hot water experiments.

The clothes main effect was 15%, indicating that stripping efficiencies tended to decrease with clothes in the machine. This phenomenon was previously observed by Shepherd et al. (1996) for chloroform in washing machines, and is likely caused by suppression of turbulent kinetic energy by clothes in the washbasin. The cold water wash and rinse cycles with clothes had stripping efficiencies of 42% and 45%, respectively. The hot water wash and rinse cycles with clothes were characterized by higher stripping efficiencies of 62% and 56%, respectively.

Both the cold water and hot water wash and rinse cycles had lower stripping efficiencies than the averages calculated based on temperature. This difference may be attributed to the impact of detergent and clothes on stripping efficiencies. The detergent main effect was also 15%, indicating that stripping efficiencies tended to decrease for wash cycles. Surfactants present in detergent act to suppress chemical volatilization by increasing liquid-phase resistance to mass transfer. Thus, it is not coincidental that the presence of detergents has a greater effect on those tracers that were dominated by liquid-phase resistance to mass transfer (toluene, ethylbenzene, cyclohexane) than those dominated by gas-phase resistance to mass transfer (acetone).

The second factorial group was used to investigate the impacts of water temperature, water volume, and agitation speed. A wide range of values also characterizes this group of experiment results. For this group, the effects of liquid volume far exceeded the effects of temperature and agitation speed, with a value of 54%. Grouping experimental stripping efficiencies according to liquid volumes resulted in an 80% average for low-volume experiments, and 29% average for high-volume experiments. Accounting for the second highest factor of liquid temperature further separated these averages. The average stripping efficiency for low volume and cold water was 69%, the average for low volume and hot water was 97%, the average for high volume and cold water was 26%, and the average for high volume and hot water was 33%. As a worst case scenario, operating at conditions of hot water and low water volume, virtually all of the toluene mass initially present in the washing machine basin would be emitted to room air. However, operating with conditions of high water volume with cold water, only 25% of the toluene mass would be emitted. Thus, using a 100% volatilization estimate would dramatically overestimate chemical emissions for several operating conditions.

Replicate experiment results for toluene had relative differences of 10% for Experiments 1(A) and 1(A) replicate, 3.0% for Experiments 3 and 3 replicate, and 7.4% for Experiments C and C replicate.

As discussed in Section 3.2.1, toluene and ethylbenzene have similar Henry's law constants and thus should yield similar volatilization results. As shown in Tables 6-13 and 6-14, *ethylbenzene stripping efficiencies* ranged from 24% to 99%. This range was similar in magnitude to the range of stripping efficiencies reported for toluene. Over 17 experiments, the average relative difference between toluene and ethylbenzene stripping efficiencies was 8.3%.

Main effect values for ethylbenzene were only slightly different from those for toluene. Again, for the first factorial group, liquid temperature had the dominant main effect on stripping efficiency, with a value of 21%. Contrary to results obtained for toluene, there was a difference in the magnitude of the main effect associated with clothes and detergent. In fact, detergent had a main effect value almost twice as high as that observed for clothes. Thus, there was a greater difference between wash and rinse cycles for this compound. However, ethylbenzene stripping efficiencies were similar for wash and rinse cycles at similar temperatures.

For the second factorial group, ethylbenzene again shared common main effects with toluene. For example, the main effect for liquid volume was 56% and by far exceeded other main effect values. Grouping stripping efficiencies according to this one effect resulted in an average stripping efficiency of 83% for low liquid volume and 30% for high liquid volume, again a factor of three difference. Adding temperature effects to these averages resulted in values of 73% for low volume and cold water, 98% for low volume and hot water, 28% for high volume and cold water, and 33% for high volume and hot water.

Replicate experiment results for ethylbenzene stripping efficiencies were 10% for Experiments 1(A) and 1(A) replicate, 2.7% for Experiments 3 and 3 replicate, and 10% for Experiments C and C replicate.

Finally, *cyclohexane stripping efficiencies* ranged from 36% to 100% (see Tables 6-15 and 6-16). For similar experimental conditions, cyclohexane consistently had the highest stripping efficiency of the five experimental tracers. Experiments involving hot or cold water, fast or slow agitation, and low liquid volume resulted in stripping efficiencies of at least 99%. For the temperatures listed in Table 6-6, Henry's law constants for cyclohexane ranged from 5.8 m^3_{liq}/m^3_{gas} to 16 m^3_{liq}/m^3_{gas}.

Presence of clothes in the machine and water temperature had equal main effect magnitudes for cyclohexane in the first factorial group. Grouping cyclohexane stripping efficiencies according to these two factors resulted in the following averages: 89% for no clothes and cold water, 99% for no clothes and hot water, 79% for clothes and cold water, and 89% for clothes and hot water. Washing and rinsing clothes in cold water each led to a stripping efficiency of 79%. A stripping efficiency of 89% was observed for wash and rinse cycles involving clothes and hot water.

For factorial group #2, cyclohexane had a wider range of experimental results. This wider range derives primarily from the large main effect value for liquid volume. This effect was approximately seven times greater than the main effects for the other two variables. Grouping stripping efficiencies according to liquid volume resulted in an average value of 100% for low-volume experiments and 45% for high-volume experiments.

Replicate experiments had the following relative differences in results: 0% for Experiments 1(A) and 1(A) replicate, 7.6% for Experiments 3 and 3 replicate, and 20% for C and C replicate.

In general, the presence of clothes and/or detergent and using high water volumes resulted in reduced chemical stripping efficiencies. Accounting for these variable effects leads to significantly lower transfer efficiencies than the often assumed value of 100%.

6.2.4.3. K_LA *Values*

Values of K_LA for each chemical tracer are reported in Tables 6-17 to 6-25, using the same two factorial groups as for chemical stripping efficiencies. Again, the first factorial group was designed to investigate the effects of liquid temperature, use of detergent, and presence of clothes on K_LA. The second factorial group was designed to investigate the effects of liquid temperature, liquid volume, and agitation speed on K_LA. Values of K_LA for acetone and ethyl acetate were based on minimizing the residuals between the measured and predicted gas-phase data (see Section 3.6.2 for methodology). Values of K_LA for the remaining tracers were based on minimizing the residuals between the measured and predicted liquid-phase data. Tables 6-17 through 6-25 have a similar format to that of Tables 6-8 to 6-16, except that the main effects are based on values of K_LA.

Values of K_LA for acetone spanned nearly two orders of magnitude, ranging from 0.0075 to 0.31 L/minute (see Tables 6-17 and 6-18). The highest value corresponded to the experimental conditions of hot water, low water volume, no detergent or clothes present, and fast agitation. The highest value in the first factorial also corresponded to conditions of hot water, low water volume, no detergent or clothes present, but slow agitation.

The largest main effect for the first factorial group was liquid temperature, with a value of 0.10 L/minute. In a manner similar to that for stripping efficiency results, values of K_LA were grouped according to liquid temperature, resulting in the following average values: 0.024 L/minute for cold water experiments and 0.13 L/minute for hot water experiments.

Table 6-17. Acetone K_LA values for washing machine wash/rinse cycle—Factorial #1

Experiment #	Liquid temp.	Detergent?	Clothes?	K_LA (L/min)	Clothes effect[a] (L/min)	Detergent effect[b] (L/min)	Liq. temp. effect[c] (L/min)
1	Cold	No	no	0.069	0.023	0.037	0.25
1 replicate	Cold	No	no	0.024			
2	Hot	No	no	0.30	0.20	0.28	0.25
3	Cold	Yes	no	0.011	0.0022	0.037	0.012
3 replicate	Cold	Yes	no	0.0084			
4	Hot	Yes	no	0.022	!0.060	0.28	0.012
5	Cold	No	Yes	0.024	0.023	0.017	0.075
6	Hot	No	Yes	0.099	0.20	0.017	0.075
7	Cold	Yes	Yes	0.0075	0.0022	0.017	0.072
8	Hot	Yes	Yes	0.082	!0.060	0.017	0.072
				Average =	**0.042**	**0.087**	**0.10**

[a]Clothes effect from full to none.

[b]Detergent effect from 40 grams to none.

[c]Liquid temperature effect from cold to hot.

Table 6-18. Acetone K_LA values for washing machine wash/rinse cycle—Factorial #2

Experiment. #	Liquid Temp.	Liquid volume	Agitation speed	K_LA (L/min)	Agitation effect[a] (L/min)	Liq. volume effect[b] (L/min)	Liq. temp. effect[c] (L/min)
A	Cold	Low	Slow	0.069	!0.0010	0.025	0.25
A replicate	Cold	Low	Slow	0.024			
B	Hot	Low	Slow	0.30	!0.010	0.15	0.25
C	Cold	High	Slow	0.024	0.0010	0.025	0.13
C replicate	Cold	High	Slow	0.020			
D	Hot	High	Slow	0.15	0.064	0.15	0.13
E	Cold	Low	Fast	0.048	!0.0010	0.025	0.26
F	Hot	Low	Fast	0.31	!0.010	0.22	0.26
G	Cold	High	Fast	0.023	0.0010	0.025	0.063
H	Hot	High	Fast	0.086	0.064	0.22	0.063
				Average =	**0.013**	**0.11**	**0.18**

[a]Agitation speed effect from fast to slow.

[b]Liquid volume effect from high to low.

[c]Liquid temperature effect from cold to hot.

Table 6-19. Ethyl acetate K_LA values for washing machine wash/rinse cycle—Factorial #2

Experiment. #	Liquid temp.	Liquid volume	Agitation speed	K_LA (L/min)	Agitation effect[a] (L/min)	Liq. volume effect[b] (L/min)	Liq. temp. effect[c] (L/min)
A	Cold	Low	Slow	0.15	0.019	0.064	0.50
A replicate	Cold	Low	Slow	0.073			
B	Hot	Low	Slow	0.61	!0.21	0.36	0.50
C	Cold	High	Slow	0.053	!0.0090	0.064	0.20
C replicate	Cold	High	Slow	0.039			
D	Hot	High	Slow	0.25	0.12	0.36	0.20
E	Cold	Low	Fast	0.091	0.019	0.036	0.73
F	Hot	Low	Fast	0.82	!0.21	0.69	0.73
G	Cold	High	Fast	0.055	!0.0090	0.036	0.075
H	Hot	High	Fast	0.13	0.12	0.69	0.075
				Average =	**!0.020**	**0.29**	**0.38**

[a] Agitation speed effect from fast to slow.

[b] Liquid volume effect from high to low.

[c] Liquid temperature effect from cold to hot.

Table 6-20. Toluene K_LA values for washing machine wash/rinse cycle—Factorial #1

Experiment #	Liquid temp.	Detergent?	Clothes?	K_LA (L/min)	Clothes effect[a] (L/min)	Detergent effect[b] (L/min)	Liq. temp. effect[c] (L/min)
1	Cold	No	no	9.4	7.5	6.3	6.7
1 replicate	Cold	No	no	7.1			
2	Hot	No	no	15	11	12	6.7
3	Cold	Yes	no	1.5	1.4	6.3	1.5
3 replicate	Cold	Yes	no	2.5			
4	Hot	Yes	no	3.5	1.4	12	1.5
5	Cold	No	Yes	0.84	7.5	0.26	3.1
6	Hot	No	Yes	3.9	11	1.8	3.1
7	Cold	Yes	Yes	0.58	1.4	0.26	1.5
8	Hot	Yes	Yes	2.1	1.4	1.8	1.5
				Average =	**5.3**	**5.0**	**3.2**

[a] Clothes effect from full to none.

[b] Detergent effect from 40 grams to none.

[c] Liquid temperature effect from cold to hot.

Table 6-21. Toluene K_LA values for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	K_LA (L/min)	Agitation effect[a] (L/min)	Liq. volume effect[b] (L/min)	Liq. temp. effect[c] (L/min)
A	Cold	Low	Slow	9.4	!2.7	5.5	6.7
A replicate	Cold	Low	Slow	7.1			
B	Hot	Low	Slow	15	!23	12	6.7
C	Cold	High	Slow	2.7	1.3	5.5	0.50
C replicate	Cold	High	Slow	2.9			
D	Hot	High	Slow	3.3	1.8	12	0.50
E	Cold	Low	Fast	11	!2.7	9.5	27
F	Hot	Low	Fast	38	!23	37	27
G	Cold	High	Fast	1.5	1.3	9.5	0
H	Hot	High	Fast	1.5	1.8	37	0
				Average =	**!5.7**	**16**	**8.6**

[a] Agitation speed effect from fast to slow.
[b] Liquid volume effect from high to low.
[c] Liquid temperature effect from cold to hot.

Table 6-22. Ethylbenzene K_LA values for washing machine wash/rinse cycle—Factorial #1

Experiment #	Liquid temp.	Detergent?	Clothes?	K_LA (L/min)	Clothes effect[a] (L/min)	Detergent effect[b] (L/min)	Liq. temp. effect[c] (L/min)
1	Cold	No	no	10	8.0	6.7	7.9
1 replicate	Cold	No	no	8.1			
2	Hot	No	no	17	13	13	7.9
3	Cold	Yes	no	2.2	1.5	6.7	1.9
3 replicate	Cold	Yes	no	2.6			
4	Hot	Yes	no	4.3	2.1	13	1.9
5	Cold	No	Yes	1.1	8.0	0.17	2.9
6	Hot	No	Yes	4.0	13	1.8	2.9
7	Cold	Yes	Yes	0.93	1.5	0.17	1.3
8	Hot	Yes	Yes	2.2	2.1	1.8	1.3
				Average =	**6.1**	**5.3**	**3.5**

[a] Clothes effect from full to none.
[b] Detergent effect from 40 grams to none.
[c] Liquid temperature effect from cold to hot.

Table 6-23. Ethylbenzene K_LA values for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	K_LA (L/min)	Agitation effect[a] (L/min)	Liq. volume effect[b] (L/min)	Liq. temp. effect[c] (L/min)
A	Cold	Low	Slow	10	!2.9	6.0	7.9
A replicate	Cold	Low	Slow	8.1			
B	Hot	Low	Slow	17	!21	14	7.9
C	Cold	High	Slow	3.0	1.6	6.0	!0.20
C replicate	Cold	High	Slow	3.2			
D	Hot	High	Slow	2.9	1.2	14	!0.20
E	Cold	Low	Fast	12	!2.9	11	26
F	Hot	Low	Fast	38	!21	36	26
G	Cold	High	Fast	1.5	1.6	11	0.20
H	Hot	High	Fast	1.7	1.2	36	0.20
				Average =	**!5.3**	**17**	**8.5**

[a]Agitation speed effect from fast to slow.
[b]Liquid volume effect from high to low.
[c]Liquid temperature effect from cold to hot.

Table 6-24. Cyclohexane K_LA values for washing machine wash/rinse cycle—Factorial #1

Experiment #	Liquid Temp.	Detergent?	Clothes?	K_LA (L/min)	Clothes effect[a] (L/min)	Detergent effect[b] (L/min)	Liq. temp. effect[c] (L/min)
1	Cold	No	No	24	21	15	22
1 replicate	Cold	No	No	23			
2	Hot	No	No	46	39	22	22
3	Cold	Yes	No	9.4	5.7	15	15
3 replicate	Cold	Yes	No	9.2			
4	Hot	Yes	No	24	18	22	15
5	Cold	No	Yes	2.9	21	!0.7	3.9
6	Hot	No	Yes	6.8	39	0.8	3.9
7	Cold	Yes	Yes	3.6	5.7	!0.7	2.4
8	Hot	Yes	Yes	6.0	21	0.8	2.4
				Average =	**21**	**9.2**	**11**

[a]Clothes effect from full to none.
[b]Detergent effect from 40 grams to none.
[c]Liquid temperature effect from cold to hot.

Table 6-25. Cyclohexane K_LA values for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	K_LA (L/min)	Agitation effect[a] (L/min)	Liq. volume effect[b] (L/min)	Liq. temp. effect[c] (L/min)
A	Cold	Low	Slow	24	!28	20	22
A replicate	Cold	Low	Slow	23			
B	Hot	Low	Slow	46	!48	42	22
C	Cold	High	Slow	3.4	1.4	20	0.2
C replicate	Cold	High	Slow	5.2			
D	Hot	High	Slow	4.5	!1.4	42	0.2
E	Cold	Low	Fast	52	!28	49	42
F	Hot	Low	Fast	94	!48	88	42
G	Cold	High	Fast	2.9	1.4	49	3.0
H	Hot	High	Fast	5.9	!1.4	88	3.0
				Average =	**!19**	**50**	**17**

[a] Agitation speed effect from fast to slow.
[b] Liquid volume effect from high to low.
[c] Liquid temperature effect from cold to hot.

The second largest main effect on acetone K_LA values was use of detergent, with a value of 0.087 L/minute. Regrouping experiments according to water temperature and detergent use resulted in the following average K_LA values: 0.039 L/minute for cold water and no detergent, 0.20 L/minute for hot water and no detergent, 0.0090 L/minute for cold water and detergent, and 0.052 L/minute for hot water and detergent. As shown by these average values, operating conditions influence the appropriate selection of K_LA.

The highest main variable effect for the second factorial group was 0.18 L/minute, again for liquid temperature. Grouping acetone results according to this main effect resulted in an average value of K_LA of 0.035 L/minute for cold water experiments and 0.21 L/minute for hot water experiments. The dominance of liquid temperature effects on acetone K_LA values for both factorial groups illustrates the importance of this factor.

Values of K_LA for replicate experiments were also compared. For experiments 1(A) and 1(A) replicate, the relative difference in K_LA values was 97%. For Experiments 3 and 3 replicate, the relative difference in values of K_LA was 27%. Finally for Experiments C and C replicate, the relative difference in values of K_LA was 18%. For wash/rinse cycles, acetone had relatively low values of K_LA, which resulted in larger relative differences. For example, acetone's K_LA values for Experiments 1 (A) and 1 (A) replicate differed by only 0.0445 L/minute, which resulted in a 97% relative difference.

Measured and predicted liquid-phase and gas-phase concentrations for Experiment 6 are presented in Figure 6-6, and are representative of other experiments. The operating conditions used in Experiment 6 were hot water, low water volume, slow agitation speed, clothes, and rinse cycle (no detergent present). As described in Section 6.2.3.3, values of K_LA for acetone were determined by fitting the gas-phase predicted concentrations to the measured gas-phase data for points collected after 180 seconds into the experiment. As shown in Figure 6-6, the experimental time of 180 seconds was set to time 0, and the remaining data were also shifted by 180 seconds. The best-fit value of K_LA for acetone for this experiment was 0.099 L/minute. The corresponding hot water wash cycle K_LA was 0.082 L/minute. When cold water was used, the associated wash and rinse cycle values of K_LA were 0.0075 L/minute and 0.024 L/minute, Respectively.

At 180 seconds into each experiment (zero in Figure 6-6), the liquid-phase concentration of acetone was observed to slowly decrease because of the relatively low value of K_LA. Figure 6-7

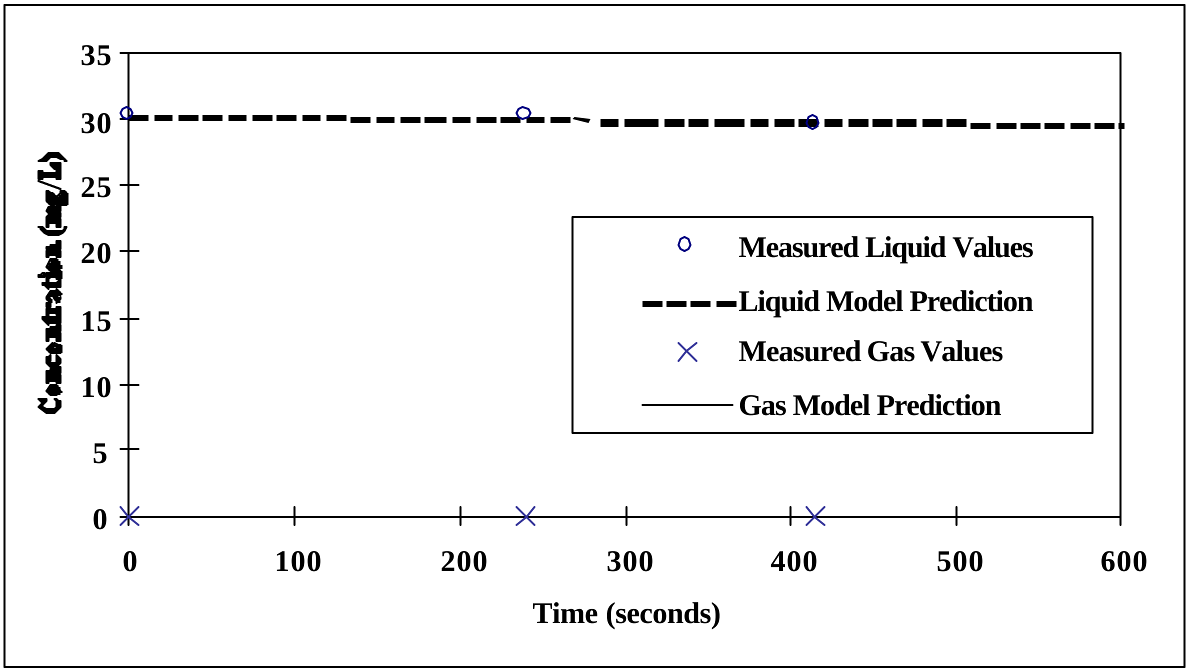


Figure 6-6. Acetone concentrations from experiment 6.

shows a magnification of the y-axis in Figure 6-6 to illustrate the general decrease in the gas-phase concentration of acetone during the experiment. The high ventilation rate for washing machines precluded an approach to chemical equilibrium for all tracers, including acetone.

Values of K_LA for ethyl acetate ranged from 0.039 to 0.82 L/minute for factorial group #2, as shown in Table 6-19. Again, the detergent effect on ethyl acetate's elution from the GC negated the use of factorial #1 experiments in the data analysis. The highest value of K_LA was for the experimental conditions of hot water, low water volume, no clothes or detergent present, and fast agitation. As with acetone, the largest main effect was liquid temperature with a value of 0.38 L/minute. The average cold water value of K_LA for ethyl acetate was 0.077 L/minute, and the average hot water value was 0.45 L/minute. Based on the factorial analysis, values of K_LA for ethyl acetate tended to increase with increasing temperature and agitation speed, and decrease with higher water volumes.

Replicate values of K_LA for ethyl acetate had a relative difference of 69% for Experiments A and A replicate, and 30% for Experiments C and C replicate. Again, the relatively small values of K_LA led to larger relative differences than generally observed for toluene, ethylbenzene, and cyclohexane.

As shown in Tables 6-20 and 6-21, *values of K_LA for toluene* ranged from 0.58 to 38 L/minute, a range covering two orders of magnitude. Similar to the acetone and ethyl acetate experiments, the

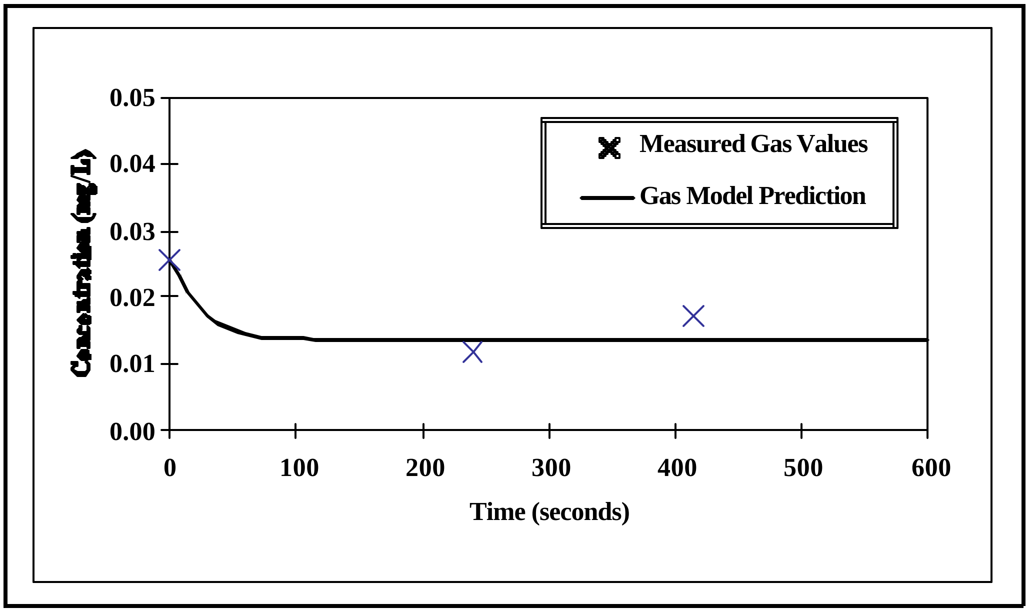


Figure 6-7. Amplification of Figure 6-6 for acetone gas-phase data.

operating conditions of hot water, low water volume, no detergent or clothes, and fast agitation resulted in the highest value of K_LA. Unlike acetone and ethyl acetate, the largest main effect for toluene associated with factorial #1 was presence of clothes, with a value of 5.3 L/minute. Detergent's main effect was similar to the clothes effect at 5.0 L/minute. As with stripping efficiency, both of these factors appeared to decrease values of K_LA for toluene.

Grouping values of K_LA for toluene according to use of detergent and clothes in the experiment resulted in the following averages: 11 L/minute for no clothes or detergent present, 2.5 L/minute for only detergent present, 2.4 L/minute for only clothes present, and 1.3 L/minute for both clothes and detergent present. Individually, detergent and clothes had a similar effect on values of K_LA for toluene. These effects appeared to be compounded when both were present in the machine to lower K_LA.

For factorial #2, the liquid volume main effect (16 L/minute) was approximately three times as high as the main effect associated with agitation speed (&5.7 L/minute), and approximately two times as high as the main effect associated with liquid temperature (8.6 L/minute). The average value of K_LA was 2.4 L/minute for a high water volume as opposed 16 L/minute for a low liquid volume.

Values of K_LA for replicate experiments were also compared. For experiments 1(A) and 1(A) replicate, the relative difference in values of K_LA was 28%. For Experiments 3 and 3 replicate, the relative difference in values of K_LA was 50%. Finally, for Experiments C and C replicate, the relative difference in values of K_LA was 7.1%.

Toluene results for Experiment 6 are presented in Figure 6-8. Toluene K_LA values were determined by fitting the predicted liquid concentrations to the measured liquid-phase concentrations. The best-fit K_LA value for this experiment was 3.9 L/minute. The y-axis in Figure 6-8 is magnified to illustrate the general decrease in toluene gas-phase concentration after

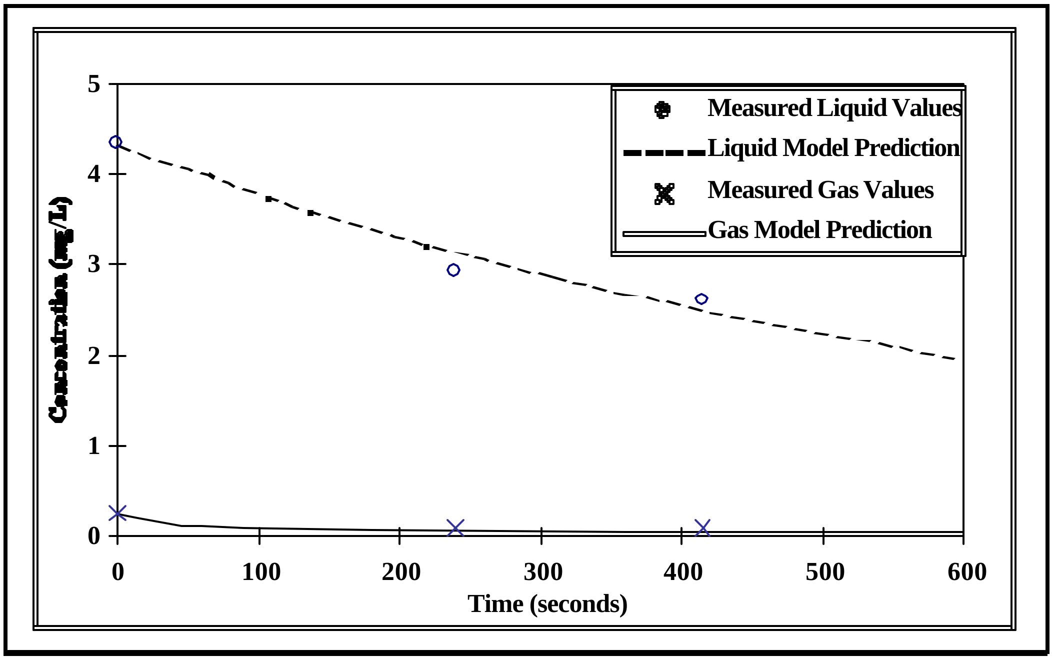


Figure 6-8. Toluene concentrations for Experiment 6.

the initial 180 seconds of the experiment. Like other chemicals, the general shape of the gas-phase curve for the entire experiment included an increase in gas-phase concentration to a peak, followed by a decrease in gas-phase concentration as shown in Figure 6-9.

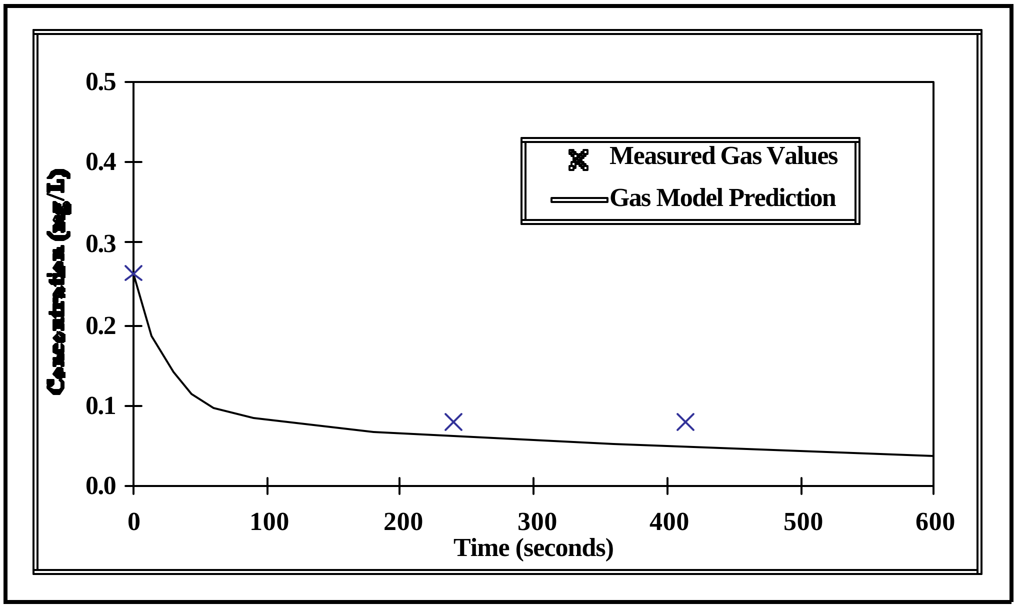


Figure 6-9. Magnification of Figure 6-8 to illustrate toluene's gas-phase concentration over time.

Values of $K_L A$ for ethylbenzene ranged from 0.93 to 38 L/minute for both factorial groups (see Tables 6-22 and 6-23). Again, this range is similar in magnitude to that of toluene, despite some difference in Henry's law constant at higher temperatures. Ethylbenzene also had main effects similar to those calculated for toluene. Based on these main effects, the average ethylbenzene K_LA value for experiments using no detergent or clothes was 12 L/minute. When detergent or clothes were added to the machine, the average values of K_LA were 3.0 L/minute and 2.6 L/minute, respectively. Finally, when both clothes and detergent were added to the machine together, the average value of K_LA was 1.6 L/minute.

Values of K_LA for ethylbenzene in the second factorial group were most dependent on liquid volume. An average K_LA for ethylbenzene during high water volume experiments was 2.5 L/minute, and an average low water volume K_LA for ethylbenzene was 17 L/minute, a difference of a factor of 7.

Comparing results for replicate experiments yielded the following relative differences in values of K_LA for ethylbenzene: 21% for Experiments 1(A) and 1(A) replicate, 17% for Experiments 3 and 3 replicate, and 6.5% for Experiments C and C replicate.

Ethylbenzene data for Experiment 6 are plotted in Figure 6-10. Liquid-phase and gas-phase curves have the same shape as those for toluene. The ethylbenzene K_LA value for this plot was 4.0 L/minute.

Finally, values of K_LA for cyclohexane ranged from 2.9 L/minute to 94 L/minute for both factorial groups listed in Tables 6-24 and 6-25. Cyclohexane has a relatively high Henry's law constant compared with other tracers, which led to consistently higher values of K_LA. For these experiments, there appeared to be significant gas-phase resistance to mass transfer evident by the wide range of results between tracers.

The greatest main effect for cyclohexane based on factorial #1 was the presence of clothes. The main effect value of 21 L/minute for clothes was twice as high as the main effect associated with

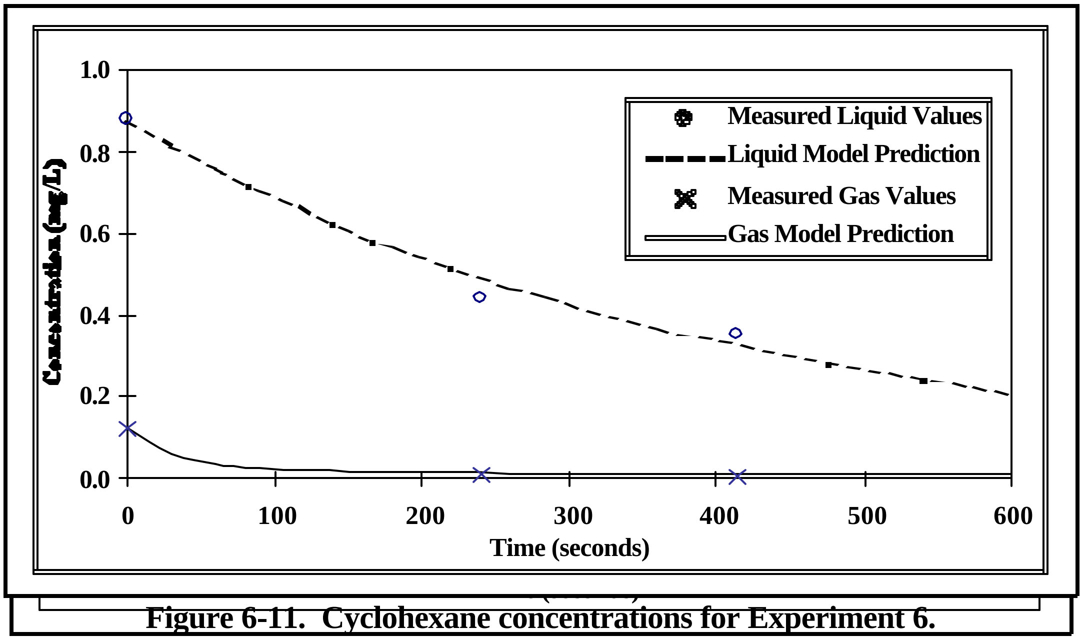


Figure 6-11. Cyclohexane concentrations for Experiment 6.

Figure 6-10. Ethylbenzene concentrations for Experiment 6.

detergent or water temperature. For the second factorial, the largest main effect was again water volume. Average values of K_LA for low water volume and high water volume were 48 L/minute and 4.4 L/minute, respectively, a difference of a factor of 10 between averages.

Comparing results for replicate experiments yielded the following relative differences in values of K_LA for cyclohexane: 4.3% for Experiments 1(A) and 1(A) replicate, 2.2% for Experiments 3 and 3 replicate, and 42% for Experiments C and C replicate.

Cyclohexane experimental data are plotted in Figure 6-11 for Experiment 6. The liquid-phase curve shown in Figure 6-11 has a steeper slope than observed for toluene and ethylbenzene. The value of K_LA for this experiment was 6.8 L/minute for cyclohexane. The gas-phase curve followed the same shape as for the other tracers.

6.2.4.4. *Liquid- and Gas-Phase Mass Transfer Coefficients*

To apply the reported values of K_LA to other chemicals, it is necessary to separate K_LA into liquid- and gas-phase values (i.e., k_lA, and k_gA), and to determine k_g/k_l for each experiment. For this system, values of k_g/k_l should not vary significantly between volatile chemicals. Values of k_lA and k_gA for each chemical tracer are listed in Tables 6-26 and 6-27. A single value of k_g/k_l is presented based on all chemical tracer experimental values of K_LA and physicochemical properties, as described in Section 3.6.3.

The impact of operating conditions on k_lA and k_gA was investigated for both factorial groups as outlined in Section 3.7. For factorial group #1, the most significant factor affecting k_lA for all chemicals was presence of clothes. This result is similar to that of K_LA, where the most significant factor was presence of clothes for all chemicals except acetone (most affected by temperature). The most significant factor affecting k_gA for all chemicals was use of detergent. For factorial group #2, the most significant factor affecting k_lA and k_gA for all chemicals was water volume. These results for toluene, ethylbenzene, and cyclohexane are similar to those for K_LA. The values of K_LA for acetone and ethyl acetate were more significantly affected by temperature. As seen with the shower factorial analysis, there was typically less dependence on temperature for k_gA than for k_lA.

As shown in Tables 6-26 and 6-27, the ratio of k_g/k_l for washing machine wash/rinse cycles ranged from 0.13 to 8.6, with an average value of 2.2 for factorial group #1 and 2.4 for factorial group #2. These are relatively low values of k_g/k_l and are similar in magnitude to values reported by Hsieh et al. (1994) for diffused bubble aeration.

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 6-12 for each chemical (except ethyl acetate) in Experiment 6. The operating conditions for Experiment 6 included hot water, low water volume, clothes, no detergent, and slow agitation. As shown in Figure 6-12, resistance to mass transfer is predominantly gas-phase resistance dominated for acetone. In fact, the y-axis was adjusted for this plot, because acetone's overall resistance to mass transfer was much higher (9.8 minutes/L) than the other three chemicals. Although toluene and ethylbenzene had similar overall resistances to mass transfer for this experiment, their respective liquid- and gas-phase resistances to mass transfer were distributed differently. Gas-phase resistance to mass transfer was slightly greater than liquid-phase resistance for toluene. With a higher Henry's law constant for this experiment, gas-phase resistance to mass transfer was smaller than liquid-phase resistance for ethylbenzene. Finally, gas-phase resistance to mass transfer was insignificant for cyclohexane.

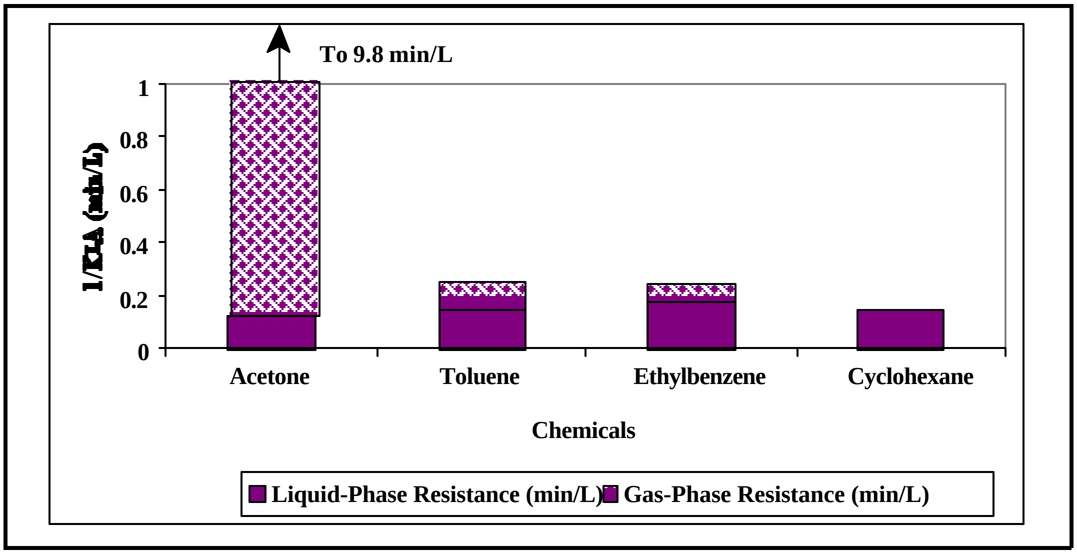


Figure 6-12. Liquid and gas-phase resistances to mass transfer for Experiment 6.

6.2.4.5. *Mass Closure*

For washing machine wash/rinse cycle experiments, mass closure for each chemical was calculated using Equation 3.10 and based on liquid- and gas-phase measurements collected during the same period in which values of K_LA were determined. Mass closure was reported in terms of the percentage of mass recovered based on initial total mass.

Values of mass closure for acetone ranged from 95% to 104%, with an average value of 99% for all 17 experiments. Percentages representing mass closure for ethyl acetate ranged from 98% to 114%, with an average value of 104% for applicable experiments (factorial #2 experiments). Mass closure values for toluene ranged from 65% to 135%, with an overall average of 89%. Ethylbenzene mass closure percentages ranged from 49% to 132%, with an overall average of 83%. Finally, cyclohexane had a mass closure range of 27% to 137%, with an average overall value of 72%.

As discussed in Section 4.4.4, mass closure for more volatile chemicals (toluene, ethylbenzene, and cyclohexane) may be affected by differences in liquid-phase calibration curves based on tracer bag ages. Again, the actual calibration slope does not affect determination of chemical stripping efficiencies or values of K_LA. It does, however, affect determination of mass closure for each chemical because of the relation between gas- and liquid-phase mass. As shown in Section 4.4.4 for showers, improving the liquid-phase calibration curve resulted in as much as a 15% improvement for toluene mass closure values, a 30% improvement for ethylbenzene values, and 39% improvement for cyclohexane values.

Table 6-26. Liquid- and gas-phase mass transfer coefficients for washing machine wash/rinse cycle experiments—Factorial #1

Experiment #	Chemical	k_lA (L/min)	k_gA (L/min)	k_g/k_l
1	A	29	57	1.9
	T	27	53	
	EB	28	54	
	C	26	50	
1 replicate	A	24	22	0.92
	T	38	35	
	EB	40	36	
	C	26	34	
2	A	56	67	1.2
	T	38	46	
	EB	31	37	
	C	49	58	
3	A	13	10	0.74
	T	9.6	7.1	
	EB	12	9.2	
	C	11	8.4	
3 replicate	A	9.3	7.5	0.81
	T	15	12	
	EB	15	12	
	C	11	8.8	
4	A	32	4.3	0.13
	T	49	6.6	
	EB	31	4.2	
	C	34	4.6	
5	A	2.9	24	8.6
	T	1.3	11	
	EB	1.6	13	
	C	3.0	25	
6	A	7.7	21	2.8
	T	6.5	18	
	EB	5.4	15	
	C	6.9	19	
7	A	5.6	9.0	1.6
	T	2.2	3.6	
	EB	3.6	5.7	
	C	4.0	6.4	
8	A	5.9	18	3.1
	T	3.4	11	
	EB	2.9	8.9	
	C	6.2	19	

Table 6-27. Liquid-and gas-phase mass transfer coefficients for washing machine wash/rinse cycle experiments—Factorial #2

Experiment #	Chemical	k_lA (L/min)	k_gA (L/min)	k_g/k_l
A	A	40	57	1.4
	EA	23	32	
	T	34	49	
	EB	34	49	
	C	26	37	
A replicate	A	30	22	0.74
	EA	23	17	
	T	46	34	
	EB	47	35	
	C	27	20	
B	A	62	67	1.1
	EA	41	45	
	T	41	44	
	EB	33	36	
	C	49	53	
C	A	6.4	24	3.7
	EA	3.4	12	
	T	5.6	21	
	EB	6.1	23	
	C	3.6	13	
C replicate	A	9.7	20	2.1
	EA	4.8	9.5	
	T	8.8	18	
	EB	9.1	19	
	C	5.6	12	
D	A	6.0	30	5.1
	EA	3.5	18	
	T	4.4	23	
	EB	3.4	17	
	C	4.5	23	
E	A	99	49	0.50
	EA	45	22	
	T	103	51	
	EB	110	55	
	C	68	34	
F	A	120	69	0.58
	EA	103	59	
	T	161	92	
	EB	101	58	
	C	105	61	
G	A	4.2	27	6.4
	EA	2.4	15	
	T	2.5	16	
	EB	2.6	17	
	C	3.0	19	
H	A	6.3	18	2.8
	EA	3.2	8.8	
	T	2.5	7.0	

	EB C	2.2 6.1	6.3 17	