3. GENERAL METHODOLOGY

There is currently no standardized protocol for measuring volatilization rates from indoor sources. Thus, a general protocol was developed for this project and was applied to all sources. Common features of this protocol follow:

1. A stainless steel source chamber
2. Chemical tracers
3. Chemical sampling
4. Sample analysis
5. Quality assurance measures
6. Data analysis
7. Mass closure assessments

The experimental methodology and associated quality assurance measures applicable to all sources are presented in this section. Methodologies specific to individual sources are discussed in the respective source chapters (Chapters 4 to 7).

3.1. SOURCE CHAMBER

Previous experimental studies vary in their isolation of household tap water sources of volatilization, which range from abandoned houses to laboratories and exposure chambers. All experiments for this project were completed within a stainless steel exposure chamber. The chamber was 2.4 m × 1.8 m × 2.4 m (11 m^3 in volume). It was ventilated under negative pressure; that is, air was drawn into the chamber and exhausted through a ceiling port connected to a fume hood. The enclosed chamber had the advantages of allowing for a mass closure assessment through the measurement of both liquid- and gas-phase concentrations and volumetric flowrates. Although washing machines and dishwashers effectively served as their own exposure chambers, the experiments involving these sources were also completed in the stainless steel chamber.

3.2. CHEMICAL TRACERS

3.2.1. Physicochemical Properties

All experiments were completed using a chemical cocktail containing five volatile tracers: acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane. These five chemicals represent a wide range of Henry's law constants. Physicochemical properties for each chemical are given in Table 3-1. The five chemicals were chosen to meet the following requirements:

8. At least one chemical had an $H_c > 1.0$ m^3_{liq}/m^3_{gas} at 25°C.
9. At least one chemical had an $H_c < 0.005$ m^3_{liq}/m^3_{gas} at 25°C.
10. Two chemicals had similar physicochemical properties, that is, similar H_c and molecular diffusion coefficients.
11. All chemicals had the capability of being analyzed with the same gas chromatography (GC) system and flame ionization detector (FID), with adequate separation of peaks.
12. Chemicals were easily identified and quantified by GC/FID at low aqueous-phase concentrations (< 500mg/L) to minimize chemical usage and discharge during experiments.
13. Chemicals had a solubility > 10 mg/L in water.
14. At desired concentrations, chemicals posed minimum risks to researchers during experiments.

Henry's law constants for chemicals used in experiments completed at temperatures other than 25°C were adjusted to reflect the temperature change. To determine the change in Henry's law constant with increasing or decreasing temperature, existing equations developed by Ashworth et al. (1988) were used for toluene, ethylbenzene, and cyclohexane.

Table 3-1. Summary of physicochemical properties for selected chemical tracers

Compound	H_c @ 25°C (m^3_{liq}/m^3_{gas})	D_l @ 24°C (cm^2/s)	D_g @ 24°C (cm^2/s)	T_b (°C)	r (kg/L)	Solubility (mg/L)	Pv° (mm Hg)
Acetone	0.0015	1.1E-05	0.11	56.5	0.79	miscible	270
Ethyl Acetate	0.0050	9.5E-06	0.092	77.0	0.89	64000	115
Toluene	0.27	9.1E-06	0.085	110.6	0.87	515	22.0
Ethylbenzene	0.33	8.4E-06	0.077	136.2	0.87	152	7.0
Cyclohexane	7.2	9.0E-06	0.088	80.7	0.77	58	77

Sources: Ashworth (1988), CRC Handbook (1995), Howard (1990) and Tucker and Nelken (1990).
These equations have been validated for a temperature range of 10°C to 30°C.

$$\text{Toluene: } H_{c,T} = \exp[5.133 - 3024/(T + 273.15)]/(0.000082*(T + 273.15)) \quad (3.1)$$

$$\text{Ethylbenzene: } H_{c,T} = \exp[11.92 - 4994/(T + 273.15)]/(0.000082*(T + 273.15)) \quad (3.2)$$

$$\text{Cyclohexane: } H_{c,T} = \exp[9.141 - 3238/(T + 273.15)]/(0.000082*(T + 273.15)) \quad (3.3)$$

where

$H_{c,T}$ = Henry's law constant at experimental temperature (L^3_{liq}/L^3_{gas})

T = experimental temperature (°C).

Schoene and Steinhanses (1985) developed the following relationship between Henry's law constant and temperature for acetone.

$$\text{Acetone: } \log(H_{c,T}) = - 2218/(T + 273.15) + 4.545 \quad (3.4)$$

where

$H_{c,T}$ = Henry's law constant at experimental temperature (L^3_{liq}/L^3_{gas})

T = experimental temperature (°C).

There is a lack of published information related to temperature effects on Henry's law constant for ethyl acetate. The following relationship was used to predict the change in ethyl acetate's Henry's law constant at different experimental temperatures (Enviromega, 1993).

$$\text{Ethyl Acetate: } H_{c,T} = H_{c,25°C} \cdot 1.044^{(T-25°C)} \quad (3.5)$$

where

$H_{c,T}$ = Henry's law constant at experimental temperature (L^3_{liq}/L^3_{gas})

$H_{c,25°C}$ = Henry's law constant at 25°C (L^3_{liq}/L^3_{gas})

T = Experimental temperature (°C).

3.2.2. Chemical Tracer Addition

The water used in each experimental system was spiked with a multitracer stock solution. Tracer solutions were prepared in 3 L Tedlarä bags fitted with a stainless steel hose/valve with locking screw and a replaceable Teflonä-lined septum with a stainless steel cap. Tedlarä bags were ideal for preparing and transferring volatile tracer solutions because of the minimal headspace associated with filling and emptying the bag with liquid. A bag had the capability to expand or collapse without forming a headspace. Each bag was filled with cold tap water using a variable-speed peristaltic pump (Masterflexä Laboratory Standard Variable Speed Drive System). Teflonä tubing (0.635 cm OD) dedicated to clean water usage provided the means of water transfer through the inlet valve of each bag. Any air added during this procedure was removed by collecting it in a large bubble near the bag's valve opening and reversing the pump, thereby emptying the excess air. Syringes adequately cleaned with methanol and water were used for chemical injections. Known amounts of each chemical were injected into a known volume of tap water contained in the Tedlarä bag. In addition to resulting system concentrations, chemical solubilities were considered when determining the volume of chemical to be added. To facilitate dissolution, bags were manually agitated and allowed to sit for periods over 24 hours prior to use in any experiments.

The predissolved solution had to be added to the water supply of each experimental system. To add the chemical solution, the Masterflexä peristaltic pump described above with Teflonä tubing dedicated to chemical addition was used. As the bags were emptied, the chemical solution was manually mixed into the system's water supply. Additional experimental procedures are presented in each respective source chapter (Chapters 4 to 7).

3.3. CHEMICAL SAMPLING

3.3.1. Liquid-Phase Sampling

Each experimental system was retrofitted with a liquid sample port made of Teflonä. This port was designed to minimize chemical losses during sampling, for example, preventing air in the sample line. In addition, Teflonä tubing was connected to the end of the sample port such that when

a liquid sample was collected the water entered near the bottom of the sample vial, thereby minimizing splashing. Liquid samples were collected in 22 mL glass vials and sealed with an aluminum cap fitted with a Teflonä-faced silicon septum. Approximately 11 mL of water were collected in each vial, leaving a significant headspace in the vial.

Samples were stored at 4°C in a laboratory refrigerator until analysis. Preexperimental tests determined that samples could be stored up to 1 week at 4°C without significant losses. Samples moved to another location for analysis were transported in an ice chest at a temperature at or below 4°C. A data log book contained a record of each liquid sample including information regarding date of collection, date of transport (if necessary), length of storage, and date of analysis.

3.3.2. Gas-Phase Sampling

Each experimental system was also retrofitted with a stainless steel Swagelokä gas sample port. Gas samples were collected on Carbotrapä 300 (Supelcoä) adsorbent tubes (0.635 cm OD × 17.8 cm). Carbotrapä adsorbent tubes were packed with graphitized carbon black and were determined to be suitable for trapping and thermally desorbing the target organic compounds. Samples were collected using a gas sample pump and bubble flowmeter in series as shown in Figure 3-1. The sorbent tube was attached to the Swagelokä port open to the experimental system's headspace from which gas was drawn. The flowrate at which gas was drawn through the sorbent tube was measured by the bubble flowmeter. The volume of air drawn through the sorbent tube was determined by timing the event. Sample flowrates were in the range of 0.15 to 0.55 L/minute. For batch and flowthrough experiments, sampling times ranged from 30 to 60 seconds and were scheduled such that a liquid sample was collected during the gas sampling period. For fill cycle experiments, a single gas sample was collected for the duration of the 3- to 6-minute experiments. Preliminary tests were completed to ensure that experimental sample tubes were not achieving breakthrough at these sampling conditions.

Once the gas sample had been collected, the ends of the sorbent tube were sealed with stainless steel Swagelokä caps and stored at 4°C in a hermetically sealed jar containing activated carbon. Again, it was determined through preexperimental testing that gas samples could be stored up to 1 week without sample loss at these conditions.

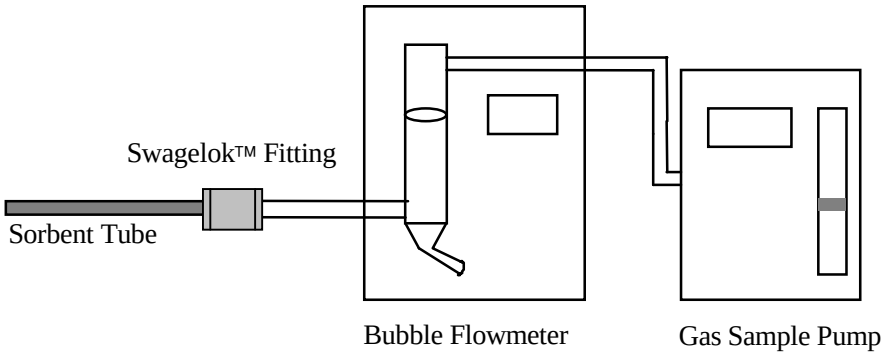

Figure 3-1. Gas sampling experimental setup.

3.4. SAMPLE ANALYSES

3.4.1. Liquid Sample Analysis

Liquid samples were analyzed using a headspace concentrator equipped with an autosampler (Tekmar 7000) and a gas chromatograph (Hewlett Packard, 5890 Series II Plus) with a flame ionization detector (GC/FID). Method parameters for the headspace concentrator were based on previous experimental work and were as follows: sealed vials containing liquid samples were lowered into a platen chamber where they were heated at 70°C for 60 minutes, allowing the volatile organic compounds to be transferred into the vial headspace and to reach equilibrium. Equilibrium concentration is highly dependent on temperature, and a platen temperature of 70°C was determined to be an optimum value for this study. Each liquid sample was heated for identical periods of time and temperatures, thus enhancing reproducibility. Following the platen equilibration time, the vial was pressurized with helium for 1 minute. The sample loop was then filled for 1 minute and allowed to stabilize for 0.2 minutes. To prevent condensation, the sample loop temperature was set at 100°C. The headspace sample was then injected for one minute into the gas chromatograph at a temperature of 100°C.

The GC/FID parameters included an inlet temperature of 200°C and a detector temperature of 250°C, once again preventing condensation. For each sample, the initial oven temperature was 32°C, which was held constant for 0.5 minutes before being ramped at 20°C/minute to a final oven temperature of 55°C. This final temperature was held constant for 1 minute, leading to a total run time of 2.65 minutes. Over the course of the experimental period, different GC/FID columns were

used. Analytical columns included a Restekä capillary column (30 m × 0.53 mm × 3.0 mm film thickness) and an HP-1 capillary column (5 m × 0.53 mm × 2.65 mm film thickness). Chromatographic peaks were drawn and integrated using HP 3365 Series II ChemStation (Version A.03.34) software. A sample chromatogram is shown in Figure 3-2, where the abscissa is time and the ordinate is the GC/FID response.

Liquid samples were analyzed within 1 week of collection, typically on the same day of collection. To limit column contamination, the vials were placed on the headspace autosampler tray in the order of increasing concentration. Vials containing clean water (blanks) were placed intermittently between sample vials, and served as indicators of system contamination, which was always minimal.

3.4.2. Liquid Standards

For each experiment, an additional stock solution was prepared as described in Section 3.2.2 for the preparation of liquid standards. Ten milliliters of cold tap water were added to a 22 mL glass vial using a volumetric glass pipette. The vial was sealed with a Teflonä-faced silicon septum and aluminum cap using a hand-held crimper. A small volume of stock solution with a known concentration of each chemical was injected into a solution with a known volume of clean water.

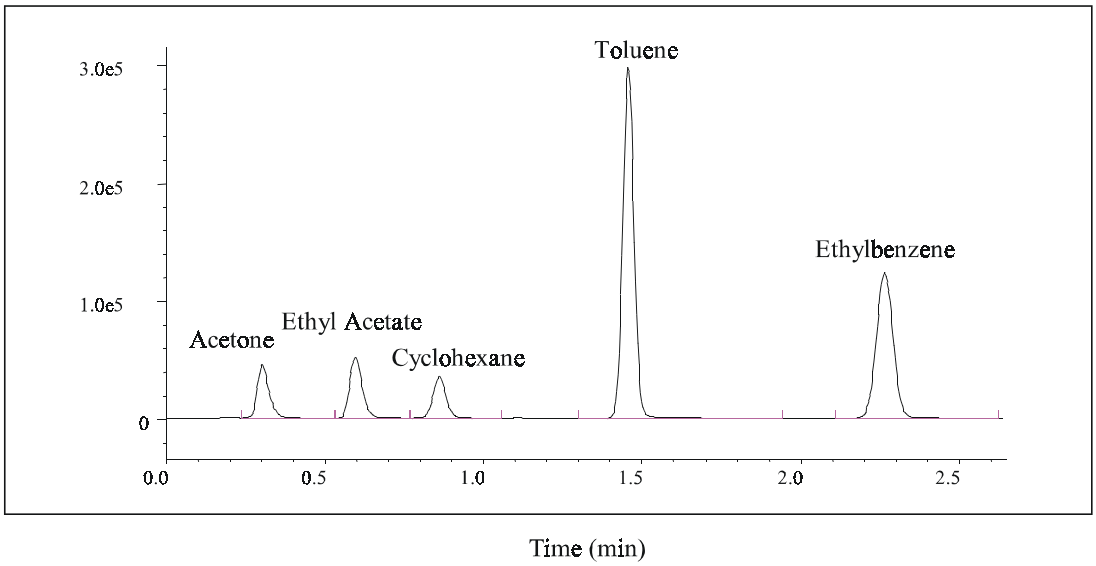

Figure 3-2. Liquid-phase sample chromatogram.

The resulting concentrations of each chemical in the vial were calculated. By varying the amount of stock solution extracted from the bag, six vials with different concentrations were prepared. These standards were used to develop a six-point linear calibration curve, for example, gas chromatograph area response versus chemical concentration. The six calibration points were chosen based on experimental data, such that liquid sample measurements were within the range of standards. A sample liquid calibration curve is shown in Figure 3-3. External calibration curves for each tracer had a coefficient of determination (R^2) of at least 0.95 and were nearly always greater than 0.98.

Since several experiments incorporated the use of detergent, a separate test was completed to determine the effects of detergent on chemical calibration curves. Using a single stock solution, two calibration curves were developed: one using clean (no detergent present) water as the matrix and a second using "soapy" water as the matrix. In a comparison of the two curves, only ethyl acetate was significantly affected by the presence of detergent in the water. This impact is further discussed in appropriate source-specific chapters.

As described in Section 3.2.2, it is conceivable that complete dissolution of some tracers, particularly cyclohexane, did not occur prior to the development of calibration curves. In such cases, liquid-phase concentrations may have been overestimated. This is likely the reason for relatively poor mass closures for cyclohexane during many experiments. However, stripping efficiencies and mass transfer coefficients for cyclohexane should not have been affected by this phenomenon. This

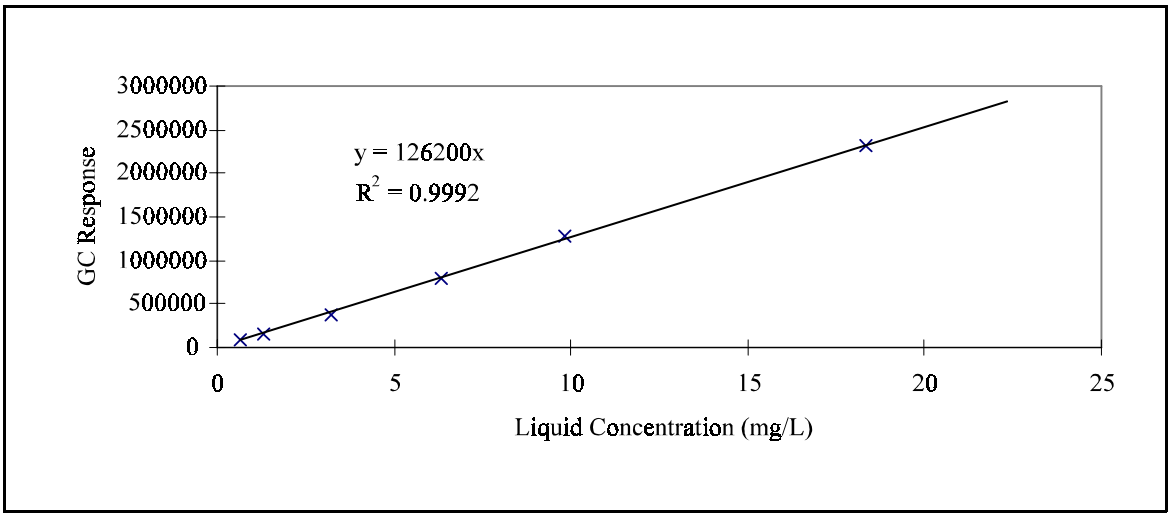

Figure 3-3. Liquid-phase calibration curve for ethylbenzene.

is true because all stripping efficiencies and mass transfer coefficients for cyclohexane were based on relative changes in liquid concentrations.

3.4.3. Gas Sample Analysis

Gas samples were analyzed using a thermal desorber with an autosampler (Tekmar 6016) and a purge and trap concentrator (Tekmar 3000). Over the course of the experimental period, this system was plumbed to different gas chromatographs. First, it was plumbed to the GC/FID described in Section 3.4.1. Most recently, the system was plumbed to a gas chromatograph (Hewlett Packard, 6890 Series) with a flame ionization detector (GC/FID#2). Method parameters for the thermal desorber and purge and trap system were based on recommended values for Carbotrapä 300 sorbent tubes. Each tube was heated at 200°C for 8 minutes. The desorbed contaminants were transported to the purge and trap column through a transfer line with a temperature of 200°C. Once the desorption phase was complete, the trap was heated to 250°C for 2 minutes. During this time, contaminants were desorbed from the trap and immediately injected into the GC/FID#2.

The GC/FID#2 method for gas samples included an inlet temperature of 225°C and a detection temperature of 250°C, once again preventing condensation. For each sample, the initial oven temperature was 34°C, which was held constant for 0.5 minutes before being ramped at 10°C/minute to a final oven temperature of 65°C. This final temperature was held constant for 11 minutes, yielding a total run time of 14.6 minutes. The primary analytical column for GC/FID#2 was a Restekä capillary column (30 m × 0.53 mm × 3.0 mm film thickness). Chromatographic peaks were drawn and integrated using HP GC ChemStation (Version Rev. A.04.02) software. A sample chromatogram for GC/FID#2 is shown in Figure 3-4, where the abscissa is time and the ordinate is the GC/FID response.

3.4.4. Gas Standards

A pressurized gas cylinder of known concentration of each chemical tracer was purchased (calibrated by Scott Specialty Gases, NIST traceable to Project 0454764). The cylinder contained a balance gas of air and was certified to contain: 40.0 ppm acetone, 50.6 ppm ethyl acetate, 40.5 ppm

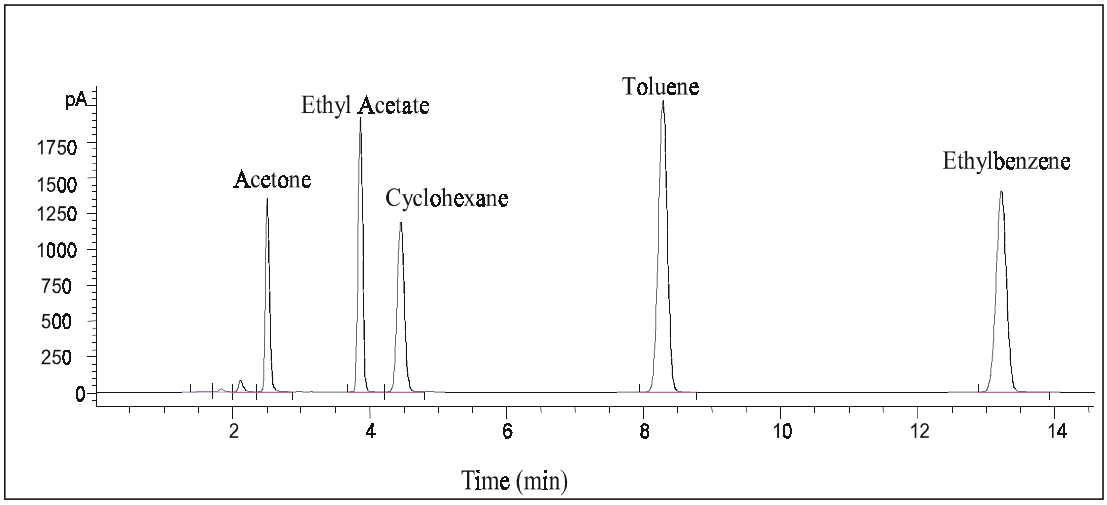

Figure 3-4. Gas sample chromatogram.

toluene, 27.7 ppm ethylbenzene, and 19.9 ppm cyclohexane. A 3 L Tedlarä sample bag dedicated to gas standards was filled with the gas stock solution from the tank. A sampling configuration similar to the one shown in Figure 3-1 was used to draw the standard gas from the Tedlarä bag through a clean sorbent tube. The volume of gas drawn through the tube was measured using a bubble flowmeter and a stopwatch. Different gas volumes were drawn through five sorbent tubes resulting in a five-point external calibration curve as shown in Figure 3-5. As with liquid standards, gas standards were prepared for each experiment in accordance with expected gas-phase measurements. External calibration curves for each tracer had a coefficient of determination (R^2) of at least 0.999.

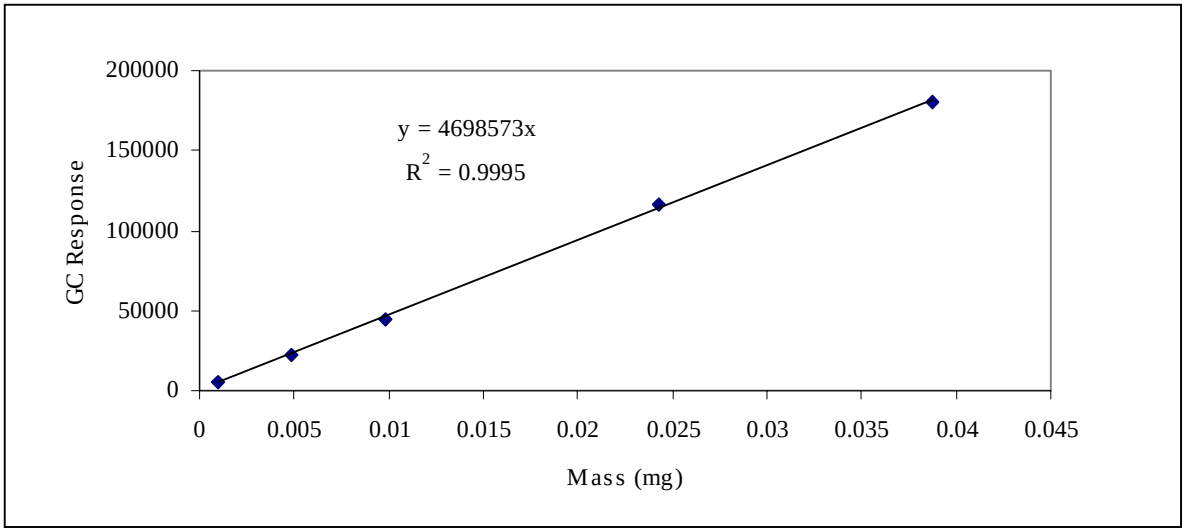

Figure 3-5. Gas-phase calibration curve for acetone.

3.5. QUALITY ASSURANCE MEASURES

A quality assurance plan was developed specifically for this project and was submitted to the US Environmental Protection Agency at an earlier date (September 1996). This plan was implemented throughout the entire study. A summary of quality assurance measures is given in this section.

3.5.1. Duplicate Samples

Because of the high volatility associated with several of the chemical tracers, duplicate liquid-phase samples were collected for every experiment. For the purposes of this study, duplicate samples refer to samples that were collected sequentially and that differed in time by fewer than 20 seconds. A summary of results associated with duplicate samples is presented in Table 3-2. The average difference reported in Table 3-2 includes all duplicates, even those that were removed for violating the quality assurance project plan.

The best duplication for liquid samples was achieved for ethyl acetate, with an average relative difference of 2.5%. Only 7.9% of all liquid sample duplicates had differences of greater than 20%. Twenty-six of the 38 liquid samples with poor duplication (>20% difference) were not included in the data analysis used to predict volatilization parameters. The remaining 12 duplicates had a relative difference between 22% and 36%, and were collected during the initial seconds of dishwasher experiments. As is explained in Chapter 5, chemicals rapidly volatilized from water used in a dishwasher within the first 45 seconds of operation. To characterize this drop in liquid-phase

Table 3-2. Duplicate sample results

Liquid Samples		
Compound	**Number of Duplicates**	**Average Difference[a] (%)**
Acetone	113	3.1
Ethyl Acetate	67	2.5
Toluene	111	7.7
Ethylbenzene	101	8.2
Cyclohexane	96	13

[a]Defined as $\frac{1}{n}\sum_{i=1}^{n}\frac{C_i - C_j}{\frac{C_i + C_j}{2}} \bullet 100.$

concentration, an initial value was needed. Dishwasher experiments using the average of these duplicates as initial concentrations are flagged in Chapter 5.

3.5.2. Replicate Experiments

Replicate experiments refer to experiments completed under approximately identical conditions, but not sequentially on the same day. For this study, 25% to 38% of experiments for each system were repeated. A summary of replicate experimental results is provided in Table 3-3.

Table 3-3 includes replicate experimental results for all sources. In fact, some replicate experiments for bathtubs and washing machine fill cycles were particularly poor for reasons that are explained later in this report. If those experiments are excluded from the analysis, the replicate sample results are improved significantly as presented in Table 3-4. The best replicate sample results were achieved for toluene, as shown in Table 3-4.

Table 3-3. Replicate sample results

Volatilization Parameters				
Compound	**Average Difference[a] for h (%)**	**Median Difference[a] for h (%)**	**Average Difference[b] for $K_L A$ (%)**	**Median Difference[b] for $K_L A$ (%)**
Acetone	38	30	26	19
Ethyl Acetate	23	26	26	27
Toluene	16	6.4	23	19
Ethylbenzene	18	6.9	22	17
Cyclohexane	20	5.0	28	19

[a]Defined as $\frac{1}{n}\sum_{i=1}^{n}\frac{\eta_i-\eta_j}{\frac{\eta_i+\eta_j}{2}}\bullet 100.$

[b]Defined as $\frac{1}{n}\sum_{i=1}^{n}\frac{K_L A_i - K_L A_j}{\frac{K_L A_i + K_L A_j}{2}}\bullet 100.$

Table 3-4. Replicate sample results excluding replicate experiments associated with filling

Volatilization Parameters				
Compound	**Average Difference[a] for h (%)**	**Median Difference[a] for h (%)**	**Average Difference[b] for K_LA (%)**	**Median Difference[b] for K_LA (%)**
Acetone	22	16	27	22
Ethyl Acetate	18	17	29	28
Toluene	6.1	4.2	17	12
Ethylbenzene	7.0	3.4	13	9.9
Cyclohexane	7.9	1.8	18	16

[a]Defined as $\frac{1}{n}\sum_{i=1}^{n}\frac{\eta_i-\eta_j}{\frac{\eta_i+\eta_j}{2}}\bullet 100.$

[b]Defined as $\frac{1}{n}\sum_{i=1}^{n}\frac{K_LA_i-K_LA_j}{\frac{K_LA_i+K_LA_j}{2}}\bullet 100.$

3.5.3. Experimental Blanks

A minimum of four analysis blanks were analyzed for every batch of experimental samples. These blanks were prepared in the laboratory and treated as an experimental sample through the analysis phase. The concentration of each volatile tracer in each blank was always below detection limit.

3.5.4. Method Detection Limit

The method detection limit was defined as:

$$MDL = t_{(n-1,1-\alpha=0.95)} \bullet s_r \qquad (3.6)$$

where

MDL = method detection limit

s_r = standard deviation of replicate analyses (M or M/L^3)

$t_{(n-1,1-a = 0.95)}$ = student's t value for a one-sided 95% confidence level and a standard deviation estimate (s_r) with n ! 1 degrees of freedom.

The MDLs were determined separately for liquid and gas samples. Results are listed in Table 3-5. It should be noted that the MDL test was completed for each GC/FID and column combination used in liquid and gas sample analyses. A majority of the liquid samples was analyzed using the 5 m column in GC/FID #1, and a majority of the gas samples was analyzed using the 30 m column in GC/FID #2. Less mass was used for each respective chemical to determine the MDLs for the 5 m column and GC/FID #2 than was used to determine the MDLs for the 30 m column and GC/FID #1. Subsequently, the standard deviation was lower for each chemical (s_r), resulting in a significantly lower associated MDL. If a lower mass had been used for the test with the 30 m column and GC/FID #2, the resulting MDLs would have been lower.

3.6. DATA ANALYSIS

Experimental systems with similar liquid flow patterns shared the same data analysis methods. The sources were grouped as follows:

1. Batch systems: dishwasher, washing machine (wash/rinse cycles), and bathtub (surface volatilization)
2. Plug-flow systems: shower and bathtub (flow-through)
3. Fill systems: washing machine (fill cycle) and bathtub (fill process)

The methods used to predict chemical stripping efficiencies, K_LA, k_g/k_l , and k_l and k_g for each type of experimental system are described below. The procedures in this section were applied independently for each chemical tracer. Thus, unless otherwise stated, five separate values were

Table 3-5. Method detection limits (MDLs) for liquid and gas samples

Chemical	Liquid MDL for 30 m column[a] (mg/L)	Liquid MDL for 5 m column[a] (mg/L)	Gas MDL for GC/FID #1[b] (mg)	Gas MDL For GC/FID #2[b] (mg)
Acetone	0.80	0.12	1.9	0.42
Ethyl Acetate	0.46	0.13	6.1	1.3
Toluene	0.23	0.09	4.0	1.2
Ethylbenzene	0.33	0.09	6.8	1.2
Cyclohexane	0.16	0.07	0.22	0.30

[a]Both 30 m and 5 m columns were used in GC/FID #1 for all liquid samples.
[b]The same 30 m column was used in both GC/FID #1 and GC/FID #2 for all gas samples.

reported for each volatilization parameter. Deviations from the solution techniques in this section are discussed in Chapters 4 to 7.

3.6.1. Chemical Stripping Efficiencies

Equations 2.1 and 2.2 were used to determine chemical stripping efficiencies for all experiments. For batch and fill systems, Equation 2.2 was used with $C_{l,end}$ equal to the final liquid-phase chemical concentration measurement, and $C_{l,init}$ equal to the measured liquid-phase chemical concentration before starting the experiment.

Equation 2.1 was used for the plug-flow systems, where $C_{l,in}$ was equal to the liquid-phase chemical concentration in the tracer reservoir and $C_{l,out}$ was equal to the liquid-phase chemical concentration in the specific system at the drain. When chemical volatilization in the tracer reservoir was a concern, that is, the inlet chemical concentration was changing, chemical stripping efficiencies were determined for several periods of the experiment. Each period consisted of at least one reservoir liquid-phase measurement and at least one system liquid-phase and gas-phase measurement. The stripping efficiency reported for the experiment was an average value based on each period.

3.6.2. Overall Mass Transfer Coefficients (K_LA)

In Section 2.3, mass balance models were developed for each experimental system. These models served as a way to determine K_LA for each chemical tracer and source operating condition. Most of the models could not be solved analytically to determine K_LA. Thus, an iterative solution technique was adopted.

For batch systems, liquid-phase and gas-phase concentrations were predicted using Equations 2.23 and 2.24, respectively, for a given K_LA value. For each experiment, liquid- and gas-phase chemical concentrations were measured at a given time. To determine the best K_LA associated with these measurements, the mathematical models represented by Equations 2.23 and 2.24 were "fitted" with the best K_LA value by minimizing the sum of squared normalized residuals between modeled and measured concentrations:

$$\text{Sum of square of residuals} = \sum \left(\frac{C_{expt} - C_m}{C_{expt}} \right)^2 \quad (3.7)$$

where

C_{expt} = experimentally measured liquid and gas concentrations (M/L^3)

C_m = mathematically predicted liquid and gas concentrations (M/L^3).

Equation 3.7 was minimized using two different approaches: (1) based on liquid-phase measurements only and (2) based on gas-phase measurements only.

An Excelä Spreadsheet solver was used to complete the iterations. Ideally, the two best-fit values of $K_L A$ should be the same. However, as is explained in a later section, this often was not the case. Gas samples were collected for a longer sampling time than liquid samples. Because liquid samples were more representative of actual conditions at specific experimental times, they were used to predict values of $K_L A$. However, in some cases, the change in liquid-phase concentration for acetone and ethyl acetate was relatively small for the duration of an experiment. Thus, a general protocol was developed such that when overall stripping efficiencies for a given chemical approached the value of error associated with duplicate samples (see Table 3-2), associated values of $K_L A$ were based solely on gas-phase data. The solution techniques for each chemical are described in Chapters 4 to 7.

For fill systems, the differential mass balance equations (Equations 2.25 and 2.26) could not be solved analytically. Thus, a second-order Runge-Kutta numerical solution technique was used with 1-second time steps to determine the liquid- and gas-phase concentrations for a given value of $K_L A$. The second-order approximations of Equations 2.25 and 2.26 are predicted with the following equations:

$$C_l^{n+1} = C_l^n + \frac{\Delta t}{2}\left\{ f\left(t^n, C_l^n\right) + f\left[t^n + \Delta t, C_l^n + \Delta t f\left(t^n, C_l^n\right)\right]\right\} \quad (3.8)$$

$$C_g^{n+1} = C_g^n + \frac{\Delta t}{2}\left\{ f\left(t^n, C_g^n\right) + f\left[t^n + \Delta t, C_g^n + \Delta t f\left(t^n, C_g^n\right)\right]\right\} \quad (3.9)$$

where

C_l^{n+1} = chemical liquid-phase concentration at time step n + 1 (M/L^3)

C_l^n = chemical liquid-phase concentration at time step n (M/L^3)

Dt = differential time step (T)

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

$C_{l,in}$ = inlet liquid-phase chemical concentration (M/L^3)

Q_l = liquid fill flowrate (L^3/T)

V_l^n = liquid volume at time step n (L^3) = $Q_l \cdot t$

t = time (T)

K_L = overall mass transfer coefficient (L/T)

A = interfacial surface area between water and adjacent air (L^2)

H_c = Henry's law constant (L^3_{liq}/L^3_{gas})

C_g^{n+1} = chemical gas-phase concentration at time step n + 1 (M/L^3)

C_g^n = chemical gas-phase concentration at time step n (M/L^3)

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

For plug-flow systems, $K_L A$ was determined by using Equation 3.7 with measured data and concentrations predicted by Equation 2.28 or Equation 2.30. Values of $K_L A$ were determined for different experimental periods and then averaged.

3.6.3. Ratio of Gas-to-Liquid Phase Mass Transfer Coefficients

An important component of this study involved the determination of k_g/k_l ratios for each experiment. Previous research has shown this ratio not to change significantly between chemicals for a given experimental system and operating conditions (Munz and Roberts, 1989). Thus, a single k_g/k_l value was estimated for each experiment, which was assumed to be constant for all chemicals. To determine this k_g/k_l value, the following steps were followed:

- For a given experiment, the value of K_LA for each chemical was determined as outlined in Section 3.6.2.
- Using the experimentally determined values of K_LA, the ratio of K_LA_i/K_LA_j for all combinations of chemicals ($K_LA_{acetone}/K_LA_{ethyl\ acetate}$, $K_LA_{acetone}/K_LA_{toluene}$, etc.) was calculated and organized in a 5 × 5 matrix (Matrix 1) as shown in Figure 3-6.
- The ratio of K_LA_i/K_LA_j for each chemical combination was also predicted using Equation 2.15 (Y_m) and a single assumed value of k_g/k_l. These predicted ratios were organized in a second 5 × 5 matrix (Matrix 2) also following the format of Figure 3-6.
- Equation 3.7 was used to calculate the normalized residuals between the measured ratios of Matrix 1 and the predicted ratios of Matrix 2. These residuals were placed in the associated column and row position in a third 5 × 5 matrix (Matrix 3).
- All of the entries in Matrix 3 were summed to find the total residual between Matrix 1 and Matrix 2. The total residual was minimized by choosing different values of k_g/k_l used to predict K_LA values in Matrix 2. The value of k_g/k_l which led to a minimum total residual between measured and predicted values was recorded and used for a given experiment.

K_LA_i / K_LA_j	Acetone	Ethyl Acetate	Toluene	Ethylbenzene	Cyclohexane
Acetone	$\frac{K_LA_{ace}}{K_LA_{ace}} = 1$	$\frac{K_LA_{ace}}{K_LA_{ea}}$	$\frac{K_LA_{ace}}{K_LA_{tol}}$	$\frac{K_LA_{ace}}{K_LA_{eb}}$	$\frac{K_LA_{ace}}{K_LA_{cyclo}}$
Ethyl Acetate	$\frac{K_LA_{ea}}{K_LA_{ace}}$	$\frac{K_LA_{ea}}{K_LA_{ea}} = 1$	$\frac{K_LA_{ea}}{K_LA_{tol}}$	$\frac{K_LA_{ea}}{K_LA_{eb}}$	$\frac{K_LA_{ea}}{K_LA_{cyclo}}$
Toluene	$\frac{K_LA_{tol}}{K_LA_{ace}}$	$\frac{K_LA_{tol}}{K_LA_{ea}}$	$\frac{K_LA_{tol}}{K_LA_{tol}} = 1$	$\frac{K_LA_{tol}}{K_LA_{eb}}$	$\frac{K_LA_{tol}}{K_LA_{cyclo}}$
Ethylbenzene	$\frac{K_LA_{eb}}{K_LA_{ace}}$	$\frac{K_LA_{eb}}{K_LA_{ea}}$	$\frac{K_LA_{eb}}{K_LA_{tol}}$	$\frac{K_LA_{eb}}{K_LA_{eb}} = 1$	$\frac{K_LA_{eb}}{K_LA_{cyclo}}$
Cyclohexane	$\frac{K_LA_{cyclo}}{K_LA_{ace}}$	$\frac{K_LA_{cyclo}}{K_LA_{ea}}$	$\frac{K_LA_{cyclo}}{K_LA_{tol}}$	$\frac{K_LA_{cyclo}}{K_LA_{eb}}$	$\frac{K_LA_{cyclo}}{K_LA_{cyclo}} = 1$

Figure 3-6. Matrix format used to determine k_g/k_l.

3.6.4. Liquid- and Gas-Phase Mass Transfer Coefficients

Once the $K_L A$ values for each chemical and a single k_g/k_l value were determined for an experiment, liquid- and gas-phase mass transfer coefficients were calculated for each chemical. The overall resistance equation (Equation 2.5) was used to solve for $k_l A$, where $k_g A$ was written in terms of $k_l A$ using the k_g/k_l value. Once $k_l A$ was determined, the value for $k_g A$ was predicted. Although, k_g/k_l was constant for all chemical tracers, $k_l A$ and $k_g A$ were compound dependent.

3.7. FACTORIAL ANALYSIS

A factorial analysis was used to determine the main effects associated with the primary experimental variables (Box and Bisgaard, 1988). For dishwasher, washing machine wash/rinse cycle, and shower experiments, 2 × 2 × 2 factorial arrays were designed. For these arrays, the main effect for a single variable was calculated as the average of the difference between responses at two levels of the factor of interest. Variable responses were in terms of stripping efficiencies and $K_L A$ values. This procedure was completed for all three factorial variables. The largest positive or negative value corresponded to the largest main effect.

3.8. MASS CLOSURE ASSESSMENT

Previous research related to the volatilization of chemicals from drinking water, in particular showers, has suffered from poor mass closure and, in some cases, lack of adequate experimental measurements to assess mass closure. Therefore, an important protocol for each source experiment was to obtain adequate mass closure. Mass closure for batch systems was determined using:

$$\% \text{ mass recovered} = \frac{V_l C_{l,2} + V_g C_{g,2} + Q_g \int_{t_1}^{t_2} C_g \, dt}{V_l C_{l,1} + V_g C_{g,1}} \qquad (3.10)$$

where

V_l = liquid volume (L^3)

V_g = headspace volume (L^3)

$C_{l,1}$ = chemical concentration in liquid phase at time 1 (M/L^3)

$C_{l,2}$ = chemical concentration in liquid phase at time 2 (M/L^3)

$C_{g,1}$ = chemical concentration in gas phase at time 1 (M/L^3)

$C_{g,2}$ = chemical concentration in gas phase at time 2 (M/L^3)

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

t_1 = time 1 (T)

t_2 = time 2 (T).

For fill systems, mass closure was determined by:

$$\% \text{ mass recovered} = \frac{V_l C_{l,2} + V_g C_{g,2} + Q_g \int_{t_1}^{t_2} C_g dt}{Q_l C_{l,in} (t_2 - t_1) + V_g C_{g,1}} \qquad (3.11)$$

where

V_l = liquid volume (L^3)

V_g = headspace volume (L^3)

$C_{l,in}$ = inlet chemical concentration (M/L^3)

$C_{l,2}$ = chemical concentration in liquid phase at time 2 (M/L^3)

$C_{g,1}$ = chemical concentration in gas phase at time 1 (M/L^3)

$C_{g,2}$ = chemical concentration in gas phase at time 2 (M/L^3)

Q_l = liquid flowrate in and out of system (L^3/T)

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

t_1 = time 1 (T)

t_2 = time 2 (T).

Finally, for plug-flow systems, the following mass closure equation was used:

$$\% \text{ mass recovered} = \frac{Q_l \int_{t_1}^{t_2} C_{l,out} dt + V_g C_{g,2} + Q_g \int_{t_1}^{t_2} C_g dt}{Q_l \overline{C}_{l,in} (t_2 - t_1) + V_g C_{g,1}} \qquad (3.12)$$

where

V_g = headspace volume (L^3)

$\overline{C}_{l,in}$ = average chemical concentration measured in tracer reservoir (M/L^3).

$C_{l,out}$ = chemical concentration in liquid phase at outlet (M/L^3)

C_g = chemical concentration in gas phase (M/L^3)

$C_{g,1}$ = chemical concentration in gas phase at time 1 (M/L^3)

$C_{g,2}$ = chemical concentration in gas phase at time 2 (M/L^3)

Q_l = liquid flowrate in and out of system (L^3/T)

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

t_1 = time 1 (T)

t_2 = time 2 (T).

For most experimental systems, C_g was measured at several times during an experiment. In these cases, there were periods where the exact gas concentration in the system's headspace was not known. To account for these unknown values in Equations 3.10 to 3.12, the concentrations of samples collected on either side of this period were averaged.

Mass closure results for all chemicals are reported in each respective source section. Adequate mass closure was defined as 75% to 125%.