

9. SUMMARY AND CONCLUSIONS

9.1. SUMMARY

The research described in this report consisted of 113 experiments involving 5 tracer chemicals (acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane) and 4 sources (showers, dishwashers, washing machines, and bathtubs). The source experiments completed for this study have significantly increased the existing knowledge base of published experiments involving chemical volatilization from drinking water to indoor air.

A determined attempt was made to follow a rigorous quality assurance project plan and to perform mass closure assessments on all sources. The latter are not often reported in the published literature and necessitate simultaneous collection of liquid and gas samples. The resulting database allowed determination of chemical stripping efficiencies (η), overall mass transfer coefficients ($K_L A$), and liquid- and gas-phase mass transfer coefficients ($k_l A$ and $k_g A$) for each chemical and source. In addition, headspace ventilation rates were measured for washing machines and dishwashers.

An important contribution from these experiments was the calculation of mass transfer parameters for acetone and ethyl acetate, two chemicals with Henry's law constants considerably lower than any used in previous experiments. Use of these lower volatility chemicals greatly improves the ability to estimate mass transfer coefficients for many disinfection by-products, pesticides, and other low-volatility compounds.

The ratio of gas- and liquid-phase mass transfer coefficients (k_g/k_l) was calculated for varying operating conditions for each source. As described in Chapter 2 and illustrated in Chapter 8 of this report, knowledge of the magnitude of k_g/k_l is critical for improved estimates of chemical volatilization from drinking water to indoor air. This is particularly true when an overall mass transfer coefficient for one chemical is to be extrapolated to a second chemical of interest. Experimentally predicted values of k_g/k_l should serve as a major contribution of this study.

A series of dynamic emission models were developed for each source and were based on fundamental reactor analyses, mass balances, and mass transfer kinetics. The experimental mass transfer coefficients, air exchange rates, and protocols described in this report can be used as direct input values or to estimate reasonable input values for the reported emission models. In addition to input parameters based on this research, values based on previous research are provided. All experimental results related to chemical volatilization from tap water are now available in a single database provided in the Appendix. The database contains 454 experimental results (including 293 results from this study) and is a valuable source of information for those interested in modeling human inhalation exposures related to specific contamination scenarios.

Values of $K_L A$, $k_g A$, $k_1 A$, k_g/k_1 , and headspace ventilation rates are presented in Chapters 4 through 7. A summary of chemical stripping efficiencies is provided in Table 9-1 for each source. The ranges of stripping efficiencies for each chemical and source reflect the fact that, for some sources, the rate of volatilization from drinking water to indoor air, and subsequent human exposure, is highly dependent on source operating conditions. In many cases, assuming 100% volatilization will significantly overestimate emissions and human inhalation exposure to chemicals originating in drinking water.

A set of general conclusions is provided in Section 9.2. Source-specific conclusions are provided in Sections 9.3 through 9.6. Finally, recommendations for future research are provided in Section 9.7.

Table 9-1. Summary of experimental stripping efficiencies and k_g/k_1

Chemical	Showers	Bathtubs^a	Dishwashers	Washing machines^b
Acetone	6.3 – 16	2.6 – 14	18 – 55	3.8 – 38
Ethyl Acetate	15 – 36	4.6 – 16	*	*
Toluene	61 – 77	35 – 53	96 – 98	30 – 99
Ethylbenzene	62 – 75	33 – 54	97 – 98	31 – 99
Cyclohexane	65 – 80	64 – 69	100	40 – 100
k_g/k_1	110 – 223	Flow-through: 37 – 96 Fill: 27 – 77 Bathing: 54 – 78	*	Fill: 4.5 – 20 Wash/Rinse: 0.13 – 8.6

^aStripping efficiency based on combined effects of filling and bathing (20 minutes) in series.

^bStripping efficiency based on combined effects of fill and wash (or rinse) in series.

*Unable to determine

9.2. CONCLUSIONS: GENERAL

The findings of this study lead to several general conclusions about all, or most, sources and chemicals:

1. System operating conditions can have a significant effect on chemical emissions. This is particularly true for lower volatility chemicals (e.g., ethyl acetate and acetone) and for all chemicals emitted from washing machines.
2. For higher volatility chemicals (e.g., with Henry's law constants greater than toluene), chemical stripping efficiencies should vary by approximately 30% or less (relative) over a wide range of system operating conditions for showers, bathtubs, and dishwashers.
3. Although many operating conditions can affect chemical volatilization rates from water to indoor air, water temperature appears to have the greatest effect over all sources and chemicals. This is generally caused by a combination of increases in Henry's law constants (H_c) and liquid-phase mass transfer coefficients, as well as by increases in headspace ventilation rates for washing machines and dishwashers.
4. Chemical stripping efficiencies increase as Henry's law constant increases from lower volatility chemicals, (e.g., acetone and ethyl acetate) to higher volatility chemicals (e.g., toluene, ethylbenzene, and cyclohexane). However, stripping efficiencies are relatively insensitive to Henry's law constant for H_c greater than that of toluene. The one exception is for the fill cycle of bathtubs.
5. Failure to properly account for gas-phase resistance to mass transfer can lead to significant overestimates of chemical volatilization to indoor air. This is particularly true for lower volatility

chemicals or those sources with low values of gas- to liquid-phase mass transfer coefficients (k_g/k_l)(e.g., washing machines).

6. Significant improvements in emissions estimates are possible by incorporating appropriate values of k_g/k_l into the estimation process. However, values of k_g/k_l are specific to individual systems and operating conditions and should therefore be chosen carefully.
7. The use of dual tracers with similar physicochemical properties (e.g., toluene and ethylbenzene) can be effective as internal checks of the quality of experimental results.

9.3. CONCLUSIONS: SHOWERS

Showers are the most extensively studied source of chemical volatilization from drinking water to indoor air. However, previous studies are limited in terms of the separation of gas- and liquid-phase mass transfer coefficients, and analyses of compounds with significant gas-phase resistance to mass transfer. Furthermore, previous researchers have speculated on the validity of the assumptions that shower stall atmospheres are well mixed. The following conclusions stem from this study and directly address the issues listed above:

1. The shower stall atmosphere is relatively well mixed; that is, gas-phase concentrations should be relatively homogenous throughout a shower stall.
2. Gas-phase resistance to mass transfer dominates the overall resistance to mass transfer for acetone and chemicals with Henry's law constants lower than H_c for acetone. Gas- and liquid-phase resistances are both important for compounds with H_c similar to ethyl acetate.
3. Liquid-phase resistance to mass transfer is dominant for chemicals with H_c greater than toluene. Thus, overall mass transfer coefficients for two or more of these compounds can be related using only liquid-phase molecular diffusion coefficients.

4. On the basis of the results of this study, stripping efficiencies for chemicals with H_c greater than or equal to toluene should range from 60% to 80%. Slight deviations between this range and those previously reported by other researchers are likely caused by differences in showerheads.
5. Mass emission rates from water to shower stall air decrease with time depending on the volatility of a chemical and its approach to equilibrium. Thus, knowing a chemical's Henry's law constant at typical shower temperatures is important.

9.4. CONCLUSIONS: DISHWASHERS

Previous to this study, dishwashers had received little attention as emission sources. The following conclusions are derived from 29 experiments involving a commercial dishwasher:

1. Dishwashers are characterized by a low, but continuous and constant, headspace ventilation rate during operation.
2. Dishwashers are extremely effective at stripping a wide range of chemicals from water.
3. High stripping efficiencies (approaching 100% for chemicals with $H_c \geq$ toluene) can be attributed to the high water temperatures used in dishwashers, relatively high liquid-phase mass transfer coefficients associated with airborne droplets, and large headspace volume relative to water volume within the dishwasher.
4. Chemicals are rapidly stripped from water to the interior headspace of dishwashers during the first minute of water spraying, that is, during rinse and wash cycles. Thereafter, chemicals with Henry's law constants less than or equal to those associated with ethylbenzene approach a state of chemical equilibrium.

5. The most significant release of chemicals to indoor air would occur if the dishwasher door is opened immediately after use.

9.5. CONCLUSIONS: WASHING MACHINES

Chemical emissions from washing machines have received some attention in the published literature. However, variations in machine operating conditions and chemical properties have been limited. Furthermore, previous researchers have not addressed the potential for emissions during fill cycles. The following conclusions come from 57 experiments using a commercial washing machine:

1. Washing machines are well ventilated, with air exchange rates exceeding those for dishwashers by one to two orders of magnitude.
2. The use of hot water leads to significant increases in washing machine ventilation rates caused by buoyancy-induced air flows.
3. Stripping efficiencies from washing machines, more than any other source, are extremely sensitive to system operating conditions.
4. Under appropriate conditions (hot water, rinse cycle with no detergent present, low clothes loading), stripping efficiencies for chemicals with Henry's law constants greater than toluene can approach 100%.
5. Chemical emissions during machine filling are generally lower than emissions during wash and rinse cycles.

6. During wash and rinse cycles, gas-phase resistance to mass transfer is important for all chemicals with Henry's law constants less than or equal to H_c for ethylbenzene.

9.6. CONCLUSIONS: BATHTUBS

Previous research has focused on volatilization of chemicals during shower events. The argument for such studies is that, unlike other sources, showers lead to potentially significant human exposure. However, this is also true for bathing, that is, volatilization from bathtubs to indoor air. For this study, 17 experiments were completed to assess chemical volatilization during the filling of bathtubs, during bathing events, and for applications in which water enters a tub and is allowed to flow directly into an open drain. Significant conclusions are listed below:

1. Chemical stripping efficiencies are similar during flow-through, filling, and bathing events. Here, bathing refers to volatilization from the water surface with mild agitation of the water over a 20-minute event.
2. Stripping efficiencies are more sensitive to chemical properties, particularly Henry's law constant (H_c), during tub filling than during flow-through or surface volatilization events. This is because of the significant degree of air entrainment that occurs as the water jet impacts the underlying bath pool. Diffused air bubbles promote gas-liquid mass transfer, that is, chemicals transferred from liquid to bubbles. This transfer mechanism is sensitive to H_c , as accumulation of chemical mass in bubbles can lead to an approach to chemical equilibrium for compounds with low H_c . Furthermore, gas-phase resistance to mass transfer tends to be more significant when air bubbles are present. This fact is consistent with the relatively low value of k_g/k_l for fill events.
3. Combined stripping efficiencies for fill and bathing events are slightly lower, but comparable, to those associated with shower events. Not included in the bathtub estimate are emissions from

water flowing through the tub when attempting to attain a water temperature appropriate for bathing.

4. Because of the longer exposure times, chemical emissions during the use of bathtubs may be as, or more, significant than during showers, in terms of human inhalation. This is particularly important given that small children are typically washed in bathtubs rather than showers and are generally more sensitive to chemical exposure than are healthy adults.

9.7. RECOMMENDATIONS FOR FUTURE RESEARCH

The research described herein has increased the existing knowledge base associated with chemical volatilization from water to indoor air. A natural progression would be to use the results of this study to complete an integrated exposure assessment for various water contaminants and water usage scenarios. The assessment should include bounds that account for uncertainties in mass transfer parameters and other relevant exposure factors. However, based solely on the findings of the study described in this report, recommendations for future research are as follows:

1. The database that now exists for volatilization during showers is large. Additional research related to chemical volatilization during showers is not recommended. However, information regarding aerosol formation and the associated impact on chemical volatilization for showers and other relevant sources is warranted.
2. Currently, there is a lack of information on Henry's law constants at elevated temperatures for most potential drinking water contaminants. As shown by this work, the total mass emissions from several sources are highly dependent on this parameter and could be significantly over- or underestimated for these chemicals. Additional research is needed to determine Henry's law constants at water temperatures ranging from 30°C to 60°C.

3. The results of this study suggest that volatilization during the use of bathtubs may be as, or more, significant than during showers in terms of human exposure, particularly for small children. Additional research may be warranted to improve estimates of chemical volatilization from bathtubs, including an assessment of the effects of soap films on retardation of mass transfer. Furthermore, additional studies should be completed to better simulate the kinetic energy imparted on bath water by human bathing activities.
4. The database that has been generated for dishwashers is novel and suggests that chemical equilibrium is achieved rapidly between the water and the dishwasher headspace. As such, the rate of air exchange between dishwasher and room atmospheres is a critical parameter. In this study, that rate was quantified for a commonly purchased commercial dishwasher. It would be beneficial to repeat a series of air exchange experiments on several commercially available dishwashers. These experiments could be used to quantify a range or distribution of air exchange rates.
5. Washing machines may need the greatest amount of additional research based on the range of experimental results achieved for a single washing machine, and the potential for nearly complete volatilization of many chemicals. Specific research should focus on improved estimates of headspace air exchange rates, particularly during the use of hot water, and the formation of chlorination by-products during the use of sodium-hypochlorite containing bleaches. The latter was not studied as part of this research effort, but was previously documented by the principal investigator of this project. Additional washing machine designs should be considered, including upright machines (vertical door) such as are often used in laundromats.
6. Several additional sources of chemical volatilization from water to indoor air were not studied during this research effort and are deserving of future experimental work. These include toilets,

indoor saunas and tubs, aquariums, and humidifiers. The latter should include centralized humidification systems, which are now common in many parts of the United States.

7. It would be beneficial to incorporate the source models developed herein into an indoor air quality model.
8. The model described in Recommendation 7 should be used in conjunction with information related to water usage and human activity patterns to assess the significance of human inhalation exposure to chemicals that originate in drinking water. An important example involves lower volatility disinfection by-products, which should be characterized by significant gas-phase resistance to mass transfer.
9. The database and models developed during this research effort should be supported with field data. In addition to water and air sampling in a home with a contaminated water supply, other potential sources include laundromats, gymnasium shower facilities, and restaurant kitchens.