

**VOLATILIZATION RATES FROM WATER TO INDOOR AIR
PHASE II**

**National Center for Environmental Assessment–Washington Office
Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460**

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EXECUTIVE SUMMARY

Contaminated water can lead to volatilization of chemicals to residential indoor air. Previous research has focused on only one source (shower stalls) and has been limited to chemicals in which gas-phase resistance to mass transfer is of marginal significance. As a result, attempts to extrapolate chemical emissions from high-volatility chemicals to lower volatility chemicals, or to sources other than showers, have been difficult or impossible.

In this study two-phase dynamic mass balance models were developed for estimating chemical emissions from washing machines, dishwashers, and bathtubs. An existing model was adopted for showers only. The mass transfer theory and derivations of these models are further described in chapter 2 of this report. Source- and chemical-specific mass transfer coefficients, as well as air exchange (ventilation) rates were estimated based on a series of experiments. These experiments were conducted using 5 tracer chemicals (acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane) and 4 sources (showers, bathtubs, washing machines, and dishwashers). Each set of experiments led to the determination of chemical stripping efficiencies and mass transfer coefficients (overall, liquid-phase, gas-phase), and to an assessment of the importance of gas-phase resistance to mass transfer.

A set of protocols for estimating emission rates for chemicals other than those used in this study was defined for each of the four sources. Example applications are provided and illustrate the dynamic behavior of emissions and importance of chemical properties on such emissions. 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.

Stripping efficiencies ranged from 6.3% to 80% for showers, 2.6% to 69% for bathtubs, 18% to 100% for dishwashers, and 3.8% to 100% for washing machines. Acetone and cyclohexane always defined the lower and upper bounds, respectively, of these ranges.

The findings of this study lead to several conclusions. A detailed discussion of conclusions is presented in chapter 9. Some of the most significant conclusions are summarized below.

- System operating conditions can have a significant effect on chemical emissions. In particular, chemical stripping efficiencies for washing machines were observed to be highly sensitive to system operating conditions.
- Water temperature was an important variable that affected stripping efficiencies and mass transfer coefficients for all sources.

- Chemical stripping efficiencies increase as Henry's law constant increases for lower-volatility chemicals. However, with the exception of the fill-cycle of bathtubs, chemical stripping efficiencies are relatively insensitive to Henry's law constant for chemicals with constants greater than that of toluene.
- Failure to 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.
- Results for shower experiments were reasonably consistent with those reported by other researchers with stripping efficiencies ranging from 60% to 80% for chemicals with Henry's law constant equal or greater than that of toluene.
- Gas-phase concentrations were homogeneous throughout the shower stall demonstrating that the frequent assumption of a well-mixed system is reasonably accurate.
- Dishwashers were determined to be very effective at removing chemicals from water to air, with low but continuous emissions during operation and significant storage within the dishwasher headspace. The most significant release of chemicals to indoor air would occur if the dishwasher door is opened immediately after use.
- Washing machines during the rinse cycle with hot water and low clothes loading resulted in stripping efficiencies that approached 100% for chemicals with Henry's law constant greater than toluene.
- Bathtubs may be more significant than showers with respect to human exposure to chemicals dissolved in water because of longer exposure times.

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NOMENCLATURE AND ABBREVIATIONS¹

A	interfacial surface area between water and adjacent air (L^2)
ACH	air changes per hour
ΔA	differential ¹ area (L^2)
C	chemical concentration (M/L^3)
C_{expt}	experimentally measured liquid- and gas-phase concentrations (M/L^3)
C_g	chemical concentration in air adjacent to water (M/L^3)
$C_{g,\text{in}}$	inlet concentration of contaminant in air (M/L^3)
$C_{g,0}$	initial chemical concentration in gas volume (M/L^3)
$C_{g,t}$	chemical concentration in air at any time t (M/L^3)
C_{in}	inlet chemical concentration (M/L^3)
C_l	chemical concentration in water (M/L^3)
$C_{l,\text{end}}$	final chemical concentration in water (M/L^3)
$C_{l,\text{in}}$	inlet chemical concentration in water (M/L^3)
$C_{l,\text{out}}$	outlet concentration of contaminant in water (M/L^3)
$C_{l,0}$	initial chemical concentration in water (M/L^3)
C_m	mathematically predicted liquid- and gas-phase concentrations (M/L^3)
CFSTR	continuous flow stirred tank reactor
cosh	hyperbolic cosine
coth	hyperbolic cotangent
D_g	molecular diffusion coefficient for a chemical in air (L^2/T)
D_{gi}	molecular diffusion coefficient for chemical i in air (L^2/T)
D_{gj}	molecular diffusion coefficient for chemical j in air (L^2/T)
D_l	molecular diffusion coefficient for a contaminant in water (L^2/T)
D_{li}	molecular diffusion coefficient for chemical i in water (L^2/T)
D_{lj}	molecular diffusion coefficient for chemical j in water (L^2/T)
DBCM	dibromochloromethane
DBCP	1,2-dibromo-3-chloropropane
E_{chem}	chemical mass emission rate (M/T)
FID	flame ionization detector
GC	gas chromatography

¹ Note: Terms in parentheses denote units; M corresponds to mass; L corresponds to length; T corresponds to time; (°) corresponds to temperature; dimensionless values are denoted as (-).

NOMENCLATURE AND ABBREVIATIONS (continued)

H_c	Henry's law constant ($L^3_{\text{gas}}/L^3_{\text{liq}}$)
$H_{c,i}$	Henry's law constant for chemical i ($L^3_{\text{gas}}/L^3_{\text{liq}}$)
$H_{c,j}$	Henry's law constant for chemical j ($L^3_{\text{gas}}/L^3_{\text{liq}}$)
$H_{c,T}$	Henry's law constant at experimental temperature ($L^3_{\text{gas}}/L^3_{\text{liq}}$)
ID	inside diameter (L)
k_g	gas-phase mass transfer coefficient (L/T)
k_{gi}	gas-phase mass transfer coefficient for chemical i (L/T)
k_{gj}	gas-phase mass transfer coefficient for chemical j (L/T)
K_L	overall mass transfer coefficient for contaminant of interest (L/T)
k_l	liquid-phase mass transfer coefficient (L/T)
K_{Li}	overall mass transfer coefficient for chemical i (L/T)
k_{li}	liquid-phase mass transfer coefficient for chemical i (L/T)
K_{Lj}	overall mass transfer coefficient for chemical j (L/T)
k_{lj}	liquid-phase mass transfer coefficient for chemical j (L/T)
m_c	degree of mass closure (-)
MDL	method detection limit
MEK	methyl ethyl ketone
n_1	power constant for ratio of liquid-phase diffusion coefficients (-)
n_2	power constant for ratio of gas-phase diffusion coefficients (-)
OD	outside diameter (L)
P	perimeter (L)
pFR	plug flow reactor
Pv	vapor pressure (L Hg)
Q	volumetric flowrate (L^3/T)
Q_g	gas flowrate (L^3/T)
Q_{in}	inlet volumetric flowrate (L^3/T)
Q_l	liquid flowrate (L^3/T)
Q_{out}	outlet volumetric flowrate (L^3/T)
r_A	area reaction rate ($M/L^2 \cdot T$)
r_g	rate of surface renewal for the gas side of the interface (1/T)
r_l	rate of surface renewal for the liquid side of the interface (1/T)
r_V	volume reaction rate ($M/L^3 \cdot T$)
sinh	hyperbolic sine
s_r	standard deviation of replicate analyses

NOMENCLATURE AND ABBREVIATIONS (continued)

t	time (T)
T	temperature ($^{\circ}\text{C}$)
T_b	boiling point ($^{\circ}\text{C}$)
TCE	trichloroethene
TKE	total kinetic energy
V	volume (L^3)
ΔV	differential volume (L^3)
V_g	local volume of air (L^3)
V_l	local volume of water (L^3)
z	direction of flow
δ_g	thickness of a hypothetical gas film adjacent to the interface and through which contaminant transport is solely by molecular diffusion (L)
δ_l	thickness of a hypothetical liquid film adjacent to the interface and through which contaminant transport is solely by molecular diffusion (L)
η	chemical stripping efficiency (-)
ρ	density (M/L^3)
Ψ_g	gas-phase mass transfer relational coefficient (-)
Ψ_l	liquid-phase mass transfer relational coefficient (-)
Ψ_m	overall mass transfer relational coefficient (-)

PREFACE

This report was prepared under the direction of the National Center for Environmental Assessment (NCEA) of EPA's Office of Research and Development (ORD). The purpose of this report is to provide a methodology for estimating chemical emissions from washing machines, dishwashers, showers, and bathtubs. The methodology presented in this report was derived from volatilization experiments conducted by The University of Texas at Austin under a Cooperative Agreement with NCEA. Results of these experiments are included in the report.

AUTHORS, CONTRIBUTORS, AND REVIEWERS

This report was prepared under Cooperative Agreement #CR 824228-01 between The University of Texas at Austin and the National Center for Environmental Assessment (NCEA), Office of Research and Development. It covers a period from June 1, 1995 to August 31, 1997, and work was completed as of August 31, 1997. Jackie Moya was responsible for the overall coordination, direction, and technical assistance.

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ACKNOWLEDGMENTS

The authors wish to thank EPA Project Officer Jacqueline Moya for her general guidance and enthusiasm regarding this project. The authors also wish to acknowledge Albert Chung, Jennifer Pettibon, Javier Ramirez, Tony Smith, and Ross Strader, undergraduate students at The University of Texas at Austin, for their assistance during experiments.