The Dissertation Committee for David Alan Olson
Certifies that this is the approved version of the following dissertation:

IN-HOME FORMATION OF HALOGENATED VOLATILE ORGANIC COMPOUNDS (VOCS): IMPLICATIONS FOR HUMAN EXPOSURE AND INDOOR AIR QUALITY

Committee:

Richard L. Corsi, Supervisor

Robert B. Gilbert, Supervisor

Desmond F. Lawler

Sheldon Landsberger

Howard M. Liljestrand

IN-HOME FORMATION OF HALOGENATED VOLATILE ORGANIC COMPOUNDS (VOCS): IMPLICATIONS FOR HUMAN EXPOSURE AND INDOOR AIR QUALITY

by

David Alan Olson, B.S., M.S.

Dissertation

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Doctor of Philosophy

The University of Texas

May 2002

ACKNOWLEDGMENTS

I would like to express my appreciation to the College of Engineering and the Gulf Coast Hazardous Substance Research Center for providing financial support during my doctoral education. Funding for my dissertation research was provided by a United States Environmental Protection Agency (USEPA) STAR graduate fellowship.

It has been a privilege working with my graduate advisor, Dr. Richard L. Corsi, for the past eight years. I thank Rich for his passion for research and teaching, his encouragement and support through the years, his advice, his humor and (of course) his cynicism. Rich has been an inspiration throughout my graduate studies, and I hope to someday evoke at least a fraction of that enthusiasm and passion for future students.

I would also like to thank my co-supervisor, Dr. Robert Gilbert, as well as the other members of my dissertation committee, Drs. Sheldon Landsberger, Desmond Lawler, and Howard Liljestrand. I appreciate their input to my dissertation research, and feel that their insight strengthened the quality of this work.

I would like to thank present and past members of Team Corsi. I would particularly like to thank Mike Rynes for his laboratory expertise.

I have been lucky to develop many wonderful friendships during my years in Austin. I would especially like to thank Matt, Dustin, and Marlo, for being true friends.

I wish to thank my family, Richard and Nancy, Julie and Phil, Bob and Sheryl, Matthew, Mike, and Peter, for all their support throughout my education. Your love and encouragement will always be an inspiration for me.

IN-HOME FORMATION OF HALOGENATED VOLATILE ORGANIC COMPOUNDS (VOCS): IMPLICATIONS FOR HUMAN EXPOSURE AND INDOOR AIR QUALITY

Publication No. _____

David Alan Olson, Ph.D.
The University of Texas at Austin, 2002

Supervisors: Richard L. Corsi and Robert B. Gilbert

Recent studies have shown that drinking water can be an important source of indoor air pollution. For many chemicals a much greater risk is posed when these chemicals are emitted from residential water sources and then inhaled, compared to risks by ingestion. The overall goal of this research was to better characterize emissions and subsequent exposures of building occupants to chlorinated organic compounds. A series of 14 preliminary flask experiments and 16 laboratory experiments were completed to quantify formation and emission of disinfection by-products (DBPs) from the use of chlorine-containing detergents in residential dishwashers.

Flask experiments involved mixing food and dishwasher detergent in water and were intended to identify chemicals that may form from dishwasher usage. Liquid concentrations of chloroform ranged from 1-41 mg/L. Laboratory experiments involved collection of liquid and gas samples over the course of a dishwasher operating cycle. Background concentrations of chloroform in the water supply were generally between 0 and 10 μg/L; liquid chloroform levels in the wash cycle were

typically at least 50 μg/L. The other trihalomethanes (THMs) were detected less frequently, though this result was likely a result of low bromide ion levels in the water supply. Gas chloroform concentrations were generally between 0 and 5 μg/L in the dishwasher headspace. Concentrations of the other THMs were lower than chloroform but consistent with corresponding liquid samples.

A computational model was used to complete a detailed assessment of the contribution of dishwashers to chloroform inhalation exposure. Overall exposure to chloroform was found to be highly dependent on activity patterns. Inhalation was predicted to be a more important exposure pathway than ingestion for chloroform exposure.

A series of field experiments was completed in three homes to measure chloroform concentrations during periods of residential water usage. Field experiments involved operating a shower and dishwasher at each test house and a washing machine in one home, then measuring gas chloroform concentrations in two different rooms. Room chloroform concentrations were typically between 0 and 5 $\mu g/m^3$. The highest concentrations were generally measured immediately after dishwashing and showering events.

TABLE OF CONTENTS

1. INTRODUCTION 1
   - 1.1. Problem statement 1
   - 1.2. Research objectives 2
   - 1.3. Scope of research 2
   - 1.4. Organization of dissertation 3
2. BACKGROUND 4
   - 2.1. Human exposure assessment 4
     - 2.1.1. Development as a science 4
     - 2.1.2. Indoor air quality 6
     - 2.1.3. TEAM studies 11
   - 2.2. Disinfection by-products (DBPs) 12
     - 2.2.1. Health effects 13
     - 2.2.2. Formation principles 14
     - 2.2.3. Factors affecting DBP formation 15
     - 2.2.4. Detection in drinking water 16
     - 2.2.5. Empirical correlations of DBP formation 17
   - 2.3. Existing studies of DBP exposure 18
     - 2.3.1. Large-scale surveys at drinking water treatment plants 18
     - 2.3.2. TEAM studies 21
     - 2.3.3. Food and beverages 23
     - 2.3.4. Volatilization from residential water devices 24
     - 2.3.5. Swimming pools 26
     - 2.3.6. In-home formation of DBPs 28
     - 2.3.7. Outdoor air 29
     - 2.3.8. Body burden measurements 29
3. SCREENING ASSESSMENT 33
   - 3.1. Selection of typical DBP levels 33

3.2. Mixing assumptions 34
3.3. Activity scenario 35
3.4. Dermal Uptake 35
3.5. Exposure calculations for specific activities 37
3.5.1. Ingestion exposure from drinking water 37
3.5.2. Ingestion exposure from carbonated beverages 37
3.5.3. Inhalation exposure from showering 38
3.5.4. Dermal exposure from showering 40
3.5.5. Inhalation exposure from bath tubs 41
3.5.6. Dermal exposure from bath tubs 42
3.5.7. Inhalation exposure from washing machines (from-plant) 43
3.5.8. Inhalation exposure from washing machines (in-home formation) 45
3.5.9. Inhalation exposure from dishwashers (from-plant) 47
3.5.10. Inhalation exposure from wash basins 48
3.5.11. Dermal exposure from hand washing 49
3.5.12. Inhalation exposure from cooking 50
3.5.13. Inhalation exposure from toilets 51
3.5.14. Inhalation exposure from swimming pools 52
3.5.15. Dermal exposure from swimming pools 52
3.5.16. Exposure from hot tubs 53
3.5.17. Inhalation exposure from residential cleaning 53
3.6. Hypothesis for proposed research 55
3.6.1. Rationale 55
3.6.2. Screening assessment 55
3.6.3. Gaps in current understanding/research needs 59
4. GENERAL EXPERIMENTAL METHODOLOGY 61
4.1. Preliminary flask experiments 61

4.2. Dishwasher experiments 62
4.3. Experimental design 63
4.4. Target chemicals 67
4.5. Sample collection 68
4.5.1. Liquid-phase sampling 68
4.5.2. Gas-phase sampling 69
4.5.3. Water quality parameters 71
4.6. Sample storage 71
4.7. Sample preparation and analysis 72
4.7.1. Liquid sample analysis 72
4.7.2. Liquid standards 73
4.7.3. Gas sample analysis 74
4.7.4. Gas standards 75
4.7.5. Water quality parameters 76
4.7.6. Preventative maintenance 76
4.7.7. Conditioning and cleaning of sample devices 76
4.8. Quality assurance objectives and measures 77
4.8.1. Duplicate samples 77
4.8.2. Replicate experiments 77
4.8.3. Data quality assessment 77
4.8.4. Breakthrough sorbent tube samples 78
4.8.5. Experimental blanks 78
4.8.6. Method detection limit 78
4.9. Data analysis 80
4.9.1. Gas sample data 80
4.9.2. DBP formation rates 80
5. LABORATORY RESULTS 82
5.1. Chlorine analysis of detergents 82

5.2. Flask experiments....82
5.3. Dishwasher experiments....84
5.3.1. Typical dishwasher experiment....85
5.3.2. Trends between dishwasher experiments....90
5.4. Water quality parameters....100
5.5. Emission rates....110
5.6. Formation rates....112
5.7. Summary....115
6. FIELD EXPERIMENTS AND MODEL CALIBRATION....117
6.1. Experimental methodology....117
6.1.1. Site description....117
6.1.2. Experimental design....117
6.1.3. Sample collection, storage, and analysis....120
6.2. Description of model....120
6.2.1. Overview....120
6.2.2. Specific emission sources....121
6.2.3. Model calibration....123
6.2.4. Inputs to exposure model....125
6.3. Chloroform concentrations in room air....127
6.4. Updated statistics....134
6.5. Experimental design....137
7. EXPOSURE ASSESSMENT....139
7.1. Model inputs....139
7.1.1. House characteristics....139
7.1.2. Ventilation characteristics....140
7.1.3. Chemical characteristics....140
7.1.4. Water device characteristics....141
7.1.5. Activity patterns....141

7.2. Results 143
7.3. Sensitivity analysis 145
7.4. Comparison to field experiments 150
7.5. Exposure assessment 151
8. CONCLUSIONS AND RECOMMENDATIONS 154
8.1. Summary 154
8.2. Conclusions 155
8.3. Recommendations for future research 156
APPENDIX 157
A.1 Example GC-MS calibration data 158
A.2 Summary of gas and liquid concentrations 163
A.3 Description of uncertainty analysis using a second-moment Bayesian method 169
REFERENCES 179
VITA 196

LIST OF TABLES

Table 2–1. Comparison of national TTHM surveys. 20
Table 2–2. Concentrations in tap water for all major TEAM study locations. 21
Table 2–3 Chloroform concentrations in personal air for all major TEAM study locations. 23
Table 2–4. Summary of Heikes (1987) study of chloroform concentrations in food. 24
Table 2–5. Summary of THM data from Armstrong and Golden (1986). 27
Table 2–6. Chloroform concentrations in exhaled breath for all major TEAM study locations. 30
Table 2–7. THM concentrations (µg/L) in blood from NHANES 32
Table 3–1. Typical values used for exposure calculations 34
Table 3–2. Values of P_m used in dermal exposure calculations. 36
Table 3–3. Summary of exposure calculations. 57
Table 4–1. Approximate cycle timings. 63
Table 4–2. Experimental operating conditions. 64
Table 4–3. Food intake from USDA (1997). 65
Table 4–4. Summary of physicochemical properties for target chemicals. 67
Table 4–5. Liquid sampling schedule. 69
Table 4–6. Gas sampling schedule. 70
Table 4–7. Liquid sampling MDLs. 79
Table 4–8. Gas sampling MDLs. 79
Table 5–1. Summary of TOC concentration data. 100
Table 5–2. Summary of UV-254 absorbance data. 103
Table 5–3. Summary of free and total chlorine data. 104
Table 5–4. Summary of pH data. 105
Table 5–5. Estimated average gas concentrations and total mass emitted for chloroform. 111
Table 5–6. Estimated chloroform formation rates. 112

Table 6–1. Room volumes for test houses. 117
Table 6–2. Emission rate characteristics used for all test houses..... 126
Table 6–3. Measured values for test houses..... 127
Table 6–4. Prior means and standard deviations for model parameters..... 134
Table 6–5. Updated mean values for all test houses. 135
Table 6–6. Updated standard deviations for all test houses. 136
Table 6–7. Correlation coefficients for selected model parameters. 137
Table 6–8. Variance reductions for three sampling plans (using updated values from House A). 138
Table 7–1. Room volumes. 139
Table 7–2. Volatilization from water sources data for base case. 141
Table 7–3. Summary of water usage characteristics (USEPA, 1996)..... 142
Table 7–4. Activity pattern for base case. 143

LIST OF FIGURES

Figure 2-1. Conceptual framework for exposure analysis (adapted from Lioy, 1999). 4
Figure 3-1. Summary of daily chloroform exposure for various activities..... 59
Figure 4-1. Dishwasher experimental system. 62
Figure 4-2. Gas sampling train..... 70
Figure 4-3. Liquid calibration curve for chloroform..... 74
Figure 4-4. Gas calibration curve for chloroform. 75
Figure 5-1. Summary of flask experiments..... 83
Figure 5-2. Chloroform concentrations as a function of time for Experiment 7 (standard food mix, Sunlight™ detergent) (Gas samples taken over four-minute intervals shown). 87
Figure 5-3. Ratio of gas concentration to liquid concentration as a function of time for Experiment 7 (standard food mix, Sunlight™ detergent)..... 89
Figure 5-4. Chloroform and BDCM concentrations as a function of time for Experiment 1 (actual plates, Sunlight™ detergent) (Gas samples taken over four-minute intervals shown). 91
Figure 5-5. Chloroform and BDCM concentrations as a function of time for Experiment 5 (standard food mix, Electrasol™ detergent) (Gas samples taken over four-minute intervals shown). 94
Figure 5-6. Chloroform and BDCM concentrations as a function of time for Experiment 10 (standard food mix, Sunlight™ detergent, water heat option) (Gas samples taken over four-minute intervals shown). 97
Figure 5-7. Chloroform and BDCM concentrations as a function of time for Experiment 11 (standard food mix, Sunlight™ detergent, rinsed plates) (Gas samples taken over four-minute intervals shown)..... 99
Figure 5-8. Liquid concentration versus free chlorine and versus total chlorine..... 106
Figure 5-9. Liquid concentration versus total organic carbon concentration. 107
Figure 5-10. Liquid concentration versus UV-254 absorbance. 108

Figure 5-11. Liquid chloroform concentration versus hydrogen ion concentration. 109
Figure 5-12. Liquid chloroform concentration versus (UV-254 absorbance) x (free chlorine). 110
Figure 6-1. Schematic of sample locations for test houses. 119
Figure 6-2. Measured and predicted chloroform concentrations in room air (House A) (Gas samples taken over 30-minute intervals shown)..... 128
Figure 6-3. Measured and predicted chloroform concentrations in room air (House A replicate) (Gas samples taken over 30-minute intervals shown)..... 130
Figure 6-4. Measured and predicted chloroform concentrations in room air (House B) (Gas samples taken over 30-minute intervals shown)..... 132
Figure 6-5. Measured and predicted chloroform concentrations in room air (House C) (Gas samples taken over 30-minute intervals shown)..... 133
Figure 7-1. Predicted chloroform concentrations as a function of time for base case activity scenario..... 144
Figure 7-2. Predicted chloroform concentrations for base case (except shower). 145
Figure 7-3. Predicted chloroform concentrations at different water flow rates. 146
Figure 7-4. Predicted chloroform concentration at different indoor-outdoor air exchange rates. 147
Figure 7-5. Predicted chloroform concentration at different return air exchange rates. 149
Figure 7-6. Predicted chloroform concentration at different dishwasher emission rates. 150
Figure 7-7. Summary of chloroform inhalation exposure from hypothetical water usage pattern. 152

1. INTRODUCTION

1.1. Problem statement

On average, Americans spend nearly 90% of their time indoors, and a mounting base of scientific evidence suggests that many hazardous pollutants that are regulated outdoors are found at higher concentrations inside of homes, schools, and offices (Cohen *et al.*, 1989; Michael *et al.*, 1990; Chuang *et al.*, 1991; Namiesnik *et al.*, 1992; Brown *et al.*, 1994; Daisey *et al.*, 1994; Zhang *et al.*, 1994). The health implications associated with poor indoor air quality in the United States are staggering. These include a sharp rise in childhood asthma, hundreds of thousands of annual respiratory infections in infants, cancer risks that the USEPA ranks amongst the highest of all environmental issues, and symptoms of "sick building syndrome" that result in a nearly quarter *trillion* dollar annual loss in national productivity (Fisk and Rosenfeld, 1997; and Chen and Vine, 1998).

Studies have shown that drinking water can be an important source of indoor air pollution (McKone, 1987; Jo *et al.*, 1990a; and Giardino *et al.*, 1992). Growing scientific evidence suggests that for many chemicals a greater risk may be posed when those chemicals are emitted from residential water sources and then inhaled, i.e., relative to risks by ingestion. Although some contaminants originate in the water supply before purification at a water treatment plant, chemicals also can form as a result of water treatment processes. Though added to drinking water to protect against the spread of infectious diseases, chlorine (or other disinfectants) forms chemicals collectively known as disinfection by-products (DBPs). In addition to chlorinated compounds formed from water treatment, it is likely that many halogenated organic chemicals form when chlorinated bleaches and dishwasher detergents are used in the home. This "in-home" formation may be a significant source of human exposure to these chemicals, as research has shown that a significant percentage of volatile organic chemicals may be emitted from water to indoor air during the use of common

household appliances (Howard and Corsi, 1996; Howard and Corsi, 1998; Moya *et al*., 1999).

1.2. Research objectives

The overall objective of this research was to improve existing knowledge related to in-home formation of halogenated by-products. In particular, the work focused on the importance of dishwasher usage on overall exposure to these contaminants.

The research consisted of three major tasks:

1) Characterize chemical emissions from dishwashers experimentally. This task determined what chemicals form from typical dishwasher usage, what quantity of these chemicals was formed and then released to indoor air, and how chemical emissions varied with environmental and operating conditions.
2) Complete exposure estimates comparing dishwashers with other sources of chlorinated organics.
3) Complete a series of field experiments and evaluate the resulting data within a probabilistic framework. This task involved the integration of an indoor exposure model into a probabilistic framework referred to as the Second Moment Bayesian Method (SMBM).

1.3. Scope of research

This research was completed in five major phases. The first phase was an extensive review of literature on DBP occurrence in drinking water supplies. The second phase was a screening assessment to determine what DBP sources most affect exposure and to identify gaps in the current base of knowledge. The third phase was a series of 16 laboratory experiments aimed at quantifying emissions of DBPs from residential dishwashers. The fourth phase was to complete a series of field experiments and to calibrate the results within a probabilistic framework. The final

phase involved using the emissions data to determine the importance of dishwashers on human exposure to DBPs by simulating a series of hypothetical water usage and activity scenarios.

1.4. Organization of dissertation

Chapter 2 includes background information on exposure and indoor air quality. A review of important sources of indoor pollution as well as a description of major indoor air and exposure studies is presented. It also includes background on the formation and occurrence of disinfection by-products in drinking water supplies with a review of the relevant experimental data. A source assessment that was completed to determine important sources of DBP occurrence and exposure and to identify gaps in current understanding is presented in Chapter 3. Chapter 4 includes a description of the experimental methodology for laboratory experiments. The chapter includes descriptions of the experimental system, experimental design, sample collection, sample analysis, and quality assurance measures. Laboratory experiments completed for this research are described in Chapter 5. Field experiments and model calibration within a probabilistic framework are described in Chapter 6. Estimated exposure from several different activity patterns that were simulated using a computational model are presented in Chapter 7. Conclusions and recommendations based on this research are given in Chapter 8. Experimental data are listed in the Appendix.

2. BACKGROUND

2.1. Human exposure assessment

2.1.1. Development as a science

Human exposure assessment is the science of determining how pollutants enter the human body. Lioy (1999) noted that exposure bridges the gap between source emission and health effect. Traditional environmental sciences focus on quantification and control of chemical emissions, and characterization of the fate and transport of a chemical once it has been emitted (Figure 2-1). Toxicology and epidemiology are concerned with health effects from a chemical once it has reached a biologically available form, e.g., incorporation into the blood system. Exposure analysis is the connection between chemical concentration in the environment and bioavailable concentration in the body. Issues central to exposure analysis include how many people are affected by a given chemical or activity, what is the level of an individual or population exposure, how was the exposure caused, and what preventative measures can lessen or eliminate further exposure.

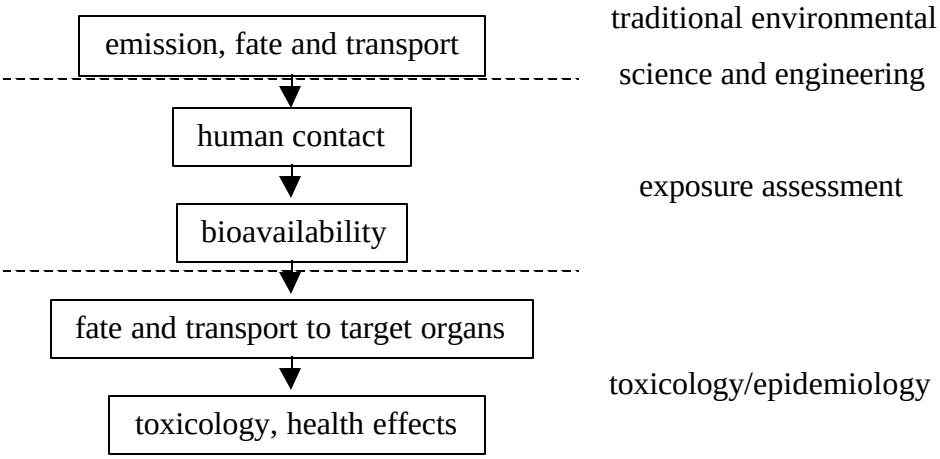


Figure 2-1. Conceptual framework for exposure analysis (adapted from Lioy, 1999).

Though several definitions of exposure have been developed in the literature (Ott, 1982; and Georgopoulos and Lioy, 1994), one general statistical definition is given by Ott (1995):

$$E(t) = \left\{ \begin{array}{l} \text{person is present at} \\ \text{location } (x, y, z) \text{ at time } t \end{array} \right\} \cap \left\{ \begin{array}{l} \text{concentration C is present} \\ \text{at location } (x, y, z) \text{ at time } t \end{array} \right\} \qquad (2\text{-}1)$$

where

E(t) = person's exposure to a given concentration

Numerous formulations describing exposure have been developed from this basic concept to represent variations of concentration with time, e.g., instantaneous exposure, average exposure, running average exposure, peak exposure, maximum exposure, and minimum exposure (Ott, 1982; and Georgopoulos and Lioy, 1994). However, the underlying premise remains the same for all definitions of exposure; namely, that exposure depends on both chemical concentration and chemical contact with the target population. In this context, contact can refer to any carrier medium, i.e., air, food, drinking water, and dermal contact. General formulations of exposure assessment have been discussed in several summary papers (Duan, 1982; Ott, 1982; Ott, 1985; Lioy, 1990; Ott, 1990; Georgopoulos and Lioy, 1994; and Ott, 1995).

The science of human exposure assessment is founded in industrial and occupational hygiene. These disciplines make extensive use of tools also common to the exposure field, such as personal monitoring, biological monitoring, and occupational histories (questionnaires). Early exposure studies, e.g., Ott (1985), illustrated a distinct difference between exposure assessment and traditional environmental sciences: exposure assessment uses a "receptor-oriented" approach, whereas environmental sciences have generally used a source-oriented approach. Typical exposure monitoring studies involve measurement of chemical body burden, e.g., blood or breath analysis, thereby giving a direct measure of the amount of

chemical entering the body. Traditional environmental sciences, as well as most environmental regulations, have focused on emission sources.

Another example of the receptor-based approach can be found in the public health profession. When a harmful virus or disease has been newly identified, public health officials make the following determinations (in chronological order): whether a person has been exposed, the number of people exposed, the cause of the exposure, and steps that can be taken to reduce or eliminate the exposure. In other words, a virus is traced "backwards" from receptor to point of origin. The reason for this approach is clear, since a person cannot get sick unless an exposure has occurred. Similarly, a person cannot experience adverse health effects from an environmental pollutant unless that person also is exposed to that pollutant. In this respect, a receptor-based approach can have a greater influence on public health and the environment, since effort can focus on reducing or eliminating sources that have the largest overall contribution to exposure.

2.1.2. Indoor air quality

A major development in the field of human exposure assessment was the recognition of the importance of indoor air quality. Indoor air quality is important for two main reasons: (1) people spend most of their time indoors and (2) numerous field studies have indicated that concentrations of pollutants are typically much higher indoors than outdoors. Recent studies on human activity patterns, i.e., studies quantifying how people spend their time, have indicated that people spend the vast majority of their time indoors. For instance, a survey of 1579 California adults found an average of 87% of time was spent indoors, 7% in enclosed transit, and 6% outdoors (Jenkins *et al*., 1992). The most extensive data on activity patterns comes from the National Human Activity Pattern Survey (NHAPS), which involved the compilation of minute-by-minute surveys of 9,386 randomly selected individuals between 1992 and 1994. Weighted over all respondents, 87% of time was spent

indoors, 7.5% in enclosed transit, and 5.5% outdoors (Klepeis and Tsang, 1996). The dominant activity location involved time spent inside residences (69%).

Numerous monitoring studies have indicated that concentrations of pollutants are typically much higher indoors than outdoors. Recent studies involving simultaneous measurement of indoor and outdoor air indicate that concentrations in indoor air are typically between 2 and 5 times outdoor air concentrations for most organic compounds (Shah and Singh, 1988; Cohen *et al*., 1989; Chuang *et al*., 1991; Namiesnik *et al*., 1992; Zhang *et al*., 1994; Baek *et al*., 1997; and Brickus *et al*., 1998), and can be over 100 times outdoor concentrations in extreme cases (Namiesnik *et al*., 1992). For example, Dietert and Hedge (1996) measured indoor air concentrations generally 2-3 times outdoor concentrations in older buildings, but up to 400 times outdoor concentrations in new buildings. A review of pollutant levels in indoor air indicated ratios of indoor to outdoor concentrations ranging from 10 to 50 for volatile halogenated hydrocarbons (Namiesnik *et al*., 1992).

Pollutant concentrations are typically much higher indoors than outdoors for two main reasons. First, newer homes have been designed to be much more energy efficient due largely as a response to the energy crisis of the 1970s. Measured air exchange rates of 0.2 to 0.3 air changes per hour (ACH) are common in newer homes, in comparison to exchange rates greater than 1.0 ACH typical of older homes (Platts-Mills *et al*., 1996). Thus, pollutant levels can accumulate to higher levels as a result of tightening house envelopes. Second, numerous sources of pollutants originate indoors. Examples include insulation (asbestos), gas stoves (carbon monoxide, nitrogen oxides, and particulate matter), building materials (VOCs and formaldehyde), soil and concrete (radon), and tobacco smoke (VOCs, polycyclic aromatic hydrocarbons, carbon monoxide, nitrogen oxides, particulate matter, and radionuclides). Volatile organic compounds also can originate from consumer products, paints, adhesives, and volatilization from potable water.

Typical concentrations of individual VOCs are on the order of 0-20 $\mu g/m^3$. For example, Ott and Roberts (1998) listed typical concentrations in indoor air of 15 $\mu g/m^3$ for *m,p*-xylene, 12 $\mu g/m^3$ for benzene, 5 $\mu g/m^3$ for *m,p*-dichlorobenzene, 3 $\mu g/m^3$ for chloroform, and 150 $\mu g/m^3$ for total organic compounds (daytime). Of the more than 900 chemical and biological substances detected in the indoor environment, more than 350 of these are VOCs that have been reported to exceed 1 ppb (Brooks *et al*., 1991). Shah and Singh (1988) reported measurements of 66 VOCs in indoor air, most of which ranged from 0.4 to 4 $\mu g/m^3$. Brown *et al*. (1994) reviewed 50 studies of VOCs in indoor air completed between 1978 and 1990; most VOC concentrations were between 0 and 5 $\mu g/m^3$. Daisey *et al*. (1994) measured 39 VOCs in 12 California office buildings. Indoor total volatile organic compound (TVOC) concentrations ranged from 230 to 7,000 $\mu g/m^3$ with a geometric mean of 510 $\mu g/m^3$. Most individual VOCs were less than 5 $\mu g/m^3$. Otson *et al*. (1994) reported a monitoring survey involving passive sampling of 757 randomly selected residences in Canada. Forty VOCs were detected out of 52 target chemicals, with concentrations of individual VOCs ranging from 1 to 104 $\mu g/m^3$. Kosianinen (1995) measured indoor concentrations in 50 “normal” and 38 “sick” homes; TVOC concentrations ranged from 40 to 235 $\mu g/m^3$.

Building materials and construction products have been noted to be important contributors to indoor pollution, most notably from emission of formaldehyde and other VOCs. Building materials include floorings, e.g., textile and vinyl, gypsum board, particleboard, foams, wallpaper, and plywoods. Construction materials include adhesives, glues, sealants, wood stains, laquers, varnishes, and paints. Brown *et al*. (1994) provided a summary of total VOC emissions from building materials and construction products. Wide variations in VOC emissions were observed, even for particular product types (Brown *et al*., 1994).

Carpets have received considerable attention as a source of VOCs, both because of their widespread usage and the large number of potential chemicals that

are emitted. New carpets have been reported to emit between 3 and 40 VOCs (Dietert and Hedge, 1996). The most frequently detected chemicals include styrene, 4-phenylcyclohexene, undecane, propylbenzene, decane, ethylbenzene, 2-butoxyethanol, isoproyl benzene, 1-ethyl-3-methylbenzene, toluene, and *p*-xylene.

Environmental tobacco smoke (ETS) is one of the most widespread and significant contributors to indoor air pollution, and has been estimated to cause approximately 3,000 lung cancer deaths to non-smokers in the United States annually (U.S. EPA, 1993). It is believed to contain more than 4,700 chemical species (Namiesink *et al*., 1992). Ligocki *et al*. (1995) listed 40 chemicals associated with ETS that are classified as hazardous air pollutants (HAPs) as defined by Title III of the Clean Air Act Amendments of 1990. Chemicals and average emission factors (μg per cigarette) for several VOCs are as follows: benzene (435), cresol (150), ethylbenzene (130), methyl ethyl ketone (290), naphthalene (108), toluene (830), and total xylenes (520).

Organic compounds also can be emitted from household appliances due to incomplete combustion. These compounds include methane, ethane, propane, and hexane (Hines *et al*., 1993). In a study by Namiesnik *et al*. (1992), resulting concentrations of formaldehyde and acetaldehyde from a bag sample connected to a gas oven vent were 0.14 and 0.01 μg/L, respectively. Chamber studies related to emissions from kerosene heaters have been reported by several authors, e.g., Tichenor *et al*. (1990) and Sparks *et al*. (1991).

Virtually all household products contain VOCs that are emitted during their use (Hines *et al*., 1993). Though emissions from consumer products are generally higher than those from building materials and carpets, consumer products are typically much more dynamic or intermittent in nature. Various studies have been completed to quantify emission rates from particular product groups, e.g., Girman *et al*. (1986) and Tichenor and Mason (1988). However, the most extensive experimental research to date was completed by the U.S. National Aeronautics and

Space Agency (NASA) for materials used in space missions (Nuchia, 1986). Data from this study includes about 5,000 different materials and products, of which as many as 3,000 were in general commercial use at the time the study was completed (Ozkaynak *et al*., 1987). The chemicals emitted in the largest number of materials from this database were toluene, methyl ethyl ketone, and xylenes.

Soil gas transport is another potential pathway contributing to increased chemical concentrations in the indoor environment. Contaminated soil can derive from a variety of sources, including naturally-occurring radon, leaking underground storage tanks, landfill gases, and contaminated groundwater. The driving force for soil gas entry into buildings is the negative pressure difference that typically exists between indoor and outdoor environments.

Transport of radon into the indoor environment has been the most studied source related to soil gas intrusion to indoor air. The U.S. Environmental Protection Agency estimates that between 5,000 and 20,000 cancer deaths can be attributed to exposure to environmental radon annually (USEPA, 1986). Research indicates that the soil to indoor air pathway is the dominant source of radon exposure in residential dwellings in the U.S. (Nero and Nazaroff, 1984). Radon originates in rocks and soil that contain radium, a radioactive decay product of both uranium and thorium.

Several case studies also have quantified soil gas intrusion for organic chemicals. For example, Wood and Porter (1987) detected methane concentrations of nearly 1% in enclosed spaces in homes nearby a landfill. Moseley and Meyer (1992) sampled near several underground petroleum storage tanks that were suspected of contributing to sub-surface contamination near a school. Hydrocarbon concentrations in the school were as high as 40% of the lower explosion limit (LEL). Further studies indicated total hydrocarbon concentrations of 8,400 $\mu g/m^3$ in classrooms and 390,000 $\mu g/m^3$ in the crawl space below the floor. Fisher *et al*. (1996) conducted experiments at a building located near a site characterized by gasoline contamination. Indoor air concentrations of several gasoline-range VOCs were between 1.9 and 37 $\mu g/m^3$.

While many of the indoor emission sources listed above are often sporadic or site-specific in nature, a more persistent source involves volatilization from potable water. Volatilization from drinking water can lead to increased chemical concentrations in indoor air. Two possible sources of contamination from this pathway are: (1) contaminated drinking water from either groundwater or municipal water supplies, and (2) disinfection byproducts (DBPs) formed as a result of water treatment processes. Contaminated water may enter the indoor environment from a variety of sources, including showers, dishwashers, washing machines, wash basins, and bathtubs. Low concentrations in indoor air (relative to the liquid phase) creates a concentration driving force whereby chemical mass is transferred to the gas phase.

2.1.3. TEAM studies

Perhaps the single most important set of monitoring studies to date has been the Total Exposure Assessment Methodology (TEAM) studies conducted by the Environmental Protection Agency (EPA). The TEAM studies were a series of four major human exposure studies completed between 1980 and 1990. The studies involved about 800 individuals representing 800,000 residents and eight different locations. Study participants were selected from a probability-based sample of residents in a given area. The studies dealt with the following classes of pollutants: carbon monoxide (Akland *et al*., 1985), volatile organic compounds (Wallace *et al*., 1984a and 1984b, 1985, 1986, 1987a, 1988, 1989; Wallace, 1986), particles (Clayton *et al*., 1993; Thomas *et al*., 1993), and pesticides (Whitmore *et al*., 1994).

For the VOC studies, 25 target pollutants (included the four THMs) were selected for analysis, based on exposure level and toxicity. Pilot studies were carried out in Beaumont, Texas (Wallace *et al*., 1982) and Bayonne-Elizabeth, New Jersey (Wallace *et al*., 1984a). These were followed by full-scale studies involving 350 persons in Bayonne-Elizabeth (Wallace *et al*., 1987a) and 200 persons each in Los Angeles, Antioch, and Pittsburgh, California (Wallace *et al*., 1988). Smaller studies

were completed in Greensboro, North Carolina and Devils Lake, North Dakota (Wallace *et al*., 1988). Drinking water samples at the tap, personal air samples (using personal monitors), and outdoor air samples were collected for each individual. Personal air samples were collected using a pump and sorbent tube that were worn during the day and placed near the bed at night. In addition, exhaled breath measurements were collected at the end of each 24-hour monitoring period.

Results were similar for all studies: median personal air concentrations were generally 2 to 5 times outdoor air concentrations, and the highest personal air concentrations were generally 5 to 70 times the highest outdoor air concentrations (Wallace, 1993).

A final series of studies was carried out in 1987 in Los Angeles (Wallace *et al*., 1991), Bayonne (Lioy *et al*., 1991), and Baltimore. For these studies, a fixed indoor monitor was used in addition to the samples used previously. It was found that in most cases personal air concentrations were greater than indoor air concentrations. This implies that human activities can greatly affect personal air concentrations, since many activities are in close proximity to personal air, e.g., showering and hand washing. Furthermore, it illustrates that measuring or estimating indoor air concentrations at a fixed location is not necessarily indicative of personal exposure. This phenomenon has commonly been referred to as the "personal cloud" effect (Rodes *et al.*, 1991; Wallace, 1993).

2.2. Disinfection by-products (DBPs)

Disinfection of drinking water is intended to eliminate pathogenic organisms that are responsible for numerous waterborne diseases. The most widely used disinfectant has been chlorine (Cl_2). Though effective at protecting microbial drinking water quality, chlorination of natural water results in the formation of disinfection by-products (DBPs). Some of these chemicals are a public health concern. Several alternative disinfectants have been developed, such as ozone (O_3), chlorine dioxide

(ClO_2), and chloramines (NH_2Cl, monochloramine). However, each alternative disinfectant produces its own set of DBPs.

2.2.1. Health effects

Several toxicological studies have concluded that chloroform and other trihalomethanes (THMs) cause cancer in rats and mice (NCI, 1976; NTP, 1985, 1987, 1989a and b). Later epidemiological studies have suggested that chlorinating drinking water could be associated with a range of health effects including colon, breast, rectal, and brain cancer (Cantor *et al*., 1978; Young *et al*., 1981; Bean *et al*., 1982; Gottlieb *et al*., 1982; Cantor *et al*., 1987; Morris *et al*., 1992; Vena *et al*., 1993). Both Cantor *et al*. (1987) and Vena *et al*. (1993) determined qualitatively a dose-response relationship, where it was found that risks of developing bladder cancer increased with increased fluid intake. More recent studies have suggested an association between DBPs and reproductive outcomes. These include low birth weight, spontaneous abortion, and birth defects such as neural tube defects, oral clefts, and cardiac defects (Aschengrau *et al*., 1989; Kramer *et al*., 1992; Bove *et al*., 1995; Savitz *et al*., 1995; and Gallagher *et al*., 1998).

Though much attention has been placed on THMs, it is believed that haloacids (especially the brominated compounds) are more significant in terms of toxicity (Wallace, 1997). It also is suggested that brominated compounds are more likely to contribute to adverse pregnancy outcomes. In particular, brominated compounds are suspected to affect fetus viability, as studies have indicated that exposure to both bromoform and bromodichloromethane resulted in full-litter pregnancy loss in rats (Narotsky, 1992).

2.2.2. Formation principles

Chlorine can be used as a disinfectant in liquid form as Cl_2 or sodium hypochlorite (NaOCl), or in powdered form as calcium hypochlorite ($Ca(OCl)_2$). Chlorine (as Cl_2) hydrolyzes in water to form hypochlorous acid (HOCl):

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2\text{-}2)$$

Hypochlorous acid is a weak acid with a pK_a of 7.5, and reversibly dissociates into hydrogen ions (H^+) and hypochlorite ions (OCl^-)

$$HOCl \leftrightarrow H^+ + OCl^- \quad (2\text{-}3)$$

The formation of DBPs in drinking water occurs when hypochlorous acid reacts with natural organic matter (NOM), generally humic and fulvic acids. A generalized equation of DBP formation can be written as:

$$HOCl + Br^- + NOM \rightarrow \text{Halogenated by-products} \quad (2\text{-}4)$$

When no bromide ion (Br^-) is present, only chlorinated by-products are formed. When bromide is present, free chlorine (in the form of hypochlorous acid, HOCl) quickly oxidizes the bromide to hypobromous acid (HOBr). The hypobromous acid and the remaining hypochlorous acid then react with the NOM to form mixed bromo-chloro species.

The major DBPs that have been identified in drinking water are trihalomethanes (THMs), haloacetic acids (HAA), haloacetonitriles (HAN), haloketones, chloropicrin, and chloral hydrate. THMs are typically the most abundant group of chemicals. Studies also have indicated that HAAs constitute a large fraction of non-THM halogenated organic chemicals (Miller and Uden, 1983; and Oliver, 1983). HAA formation is favorable under slightly acidic conditions with low bromide concentrations (World Health Organization, 2000). Under such conditions, total HAA concentrations can be more than 50% total THM concentrations (World Health Organization, 2000). Dichloroacetonitrile (DCAN) is the most abundant of the HAN species, particularly for bromide levels less than 20 µg/L. At higher bromide

concentrations (50-80 μg/L), bromochloroacetonitrile (BCAN) is the second most common HAN (World Health Organization, 2000).

2.2.3. Factors affecting DBP formation

The wide variety and levels of chemicals formed after disinfection of natural waters suggest that several factors may influence DBP formation. Though mechanistic models of DBP formation have not been developed, field studies indicate that chlorine concentration, bromide concentration, pH, temperature, reaction time, concentration of total organic carbon, and degree of aromaticity can influence the formation of DBPs (Krasner *et al*. 1989; Stevens *et al*. 1989; Pourmoghaddas *et al*. 1993; Nieminski *et al*. 1993; Singer, 1994; and Summer *et al*. 1996).

Several factors related to source water characteristics can influence the variety and amount of DBPs that form. The amount and nature of NOM can affect DBP levels, as increasing NOM concentrations should lead to increasing DBP levels. Both total organic carbon (TOC) concentration and ultraviolet absorbance at 254 nm wavelength (UV-254) have been noted to be useful indicators of NOM levels (Singer, 1994). Since humic and fulvic acids are suggested as important components of NOM that facilitate DBP formation, the nature of the NOM (as indicated by UV-254) also may be important.

The effect of pH on DBP formation has been noted, with several authors reporting increased THM levels with increasing pH, e.g., Stevens *et al*. (1976), Miller and Uden (1983), and Nieminski *et al*. (1993). Increasing pH has generally been associated with increasing concentrations of THMs and decreasing concentrations of HAAs (especially TCA) (World Health Organization, 2000). Stevens *et al*. (1976) reported significantly lower TCA concentrations at pH 9.4 versus pH of 5 and 7. Past studies indicate no strong relationship between pH and HAN formation, though it is suspected that both HANs and haloketones may decrease somewhat with increasing pH (World Health Organization, 2000).

Studies have indicated that levels of THMs, HAA, and HANs increase with increasing temperature (Siddiqui and Amy, 1993). This effect is more pronounced as the reaction time increases (Carlson and Hardy, 1998)

The variety and concentrations of DBPs also can be affected by design variables of the water treatment plant. These include the addition of ammonia, the amount of disinfectant dose, and lowering of NOM levels through enhanced coagulation and softening. These effects are described in more detail elsewhere, e.g., Siddiqui and Amy (1993), Kavanaugh *et al*. (1980), and Crozes *et al*. (1995).

2.2.4. Detection in drinking water

Prior to 1970, there were limited accounts of the presence of trihalomethanes (THMs), e.g., chloroform, in drinking water. In the early 1970s, advances in gas chromatography and mass spectrometry led to improvements in the detection of THMs in drinking water. Following these advances, Rook (1974), Bellar *et al.* (1974) and Symons *et al.* (1975) discovered that THMs result from the disinfection process. Evidence that chloroform is a carcinogen in mice and rats raised significant concerns about the presence of THMs in drinking water. In 1979, the USEPA issued the National Interim Primary Drinking Water Regulations which established a maximum contaminant level (MCL) of 100 μg/L for total trihalomethanes (TTHM).

Several other DBPs have been observed in chlorinated drinking water. For example, median concentrations of dichloroacetic acid in United States drinking water were reported to range from 6.4 to 17 μg/L (USEPA, 1992). A similar range (5.5 to 15 μg/L) was reported for trichloroacetic acid. Furthermore, in areas where naturally occurring bromide ion is present in surface water, significant amounts of bromo- and chlorobromo acetic acids can form (Ireland *et al.*, 1998). Collectively, these compounds are referred to as haloacetic acids (HAA).

An increasing awareness of potential health effects from exposure to DBPs prompted Congress to pass amendments to the Safe Drinking Water Act (SDWA) in

1986, an action that required the USEPA to establish regulations for a wide range of drinking water contaminants. The USEPA published the Drinking Water Priority List (DWPL) in 1988, and revised it in 1991. The DWPL includes THMs, as well as several of the other DBPs described above.

The significant attention given to DBPs has led to concerns regarding the effects of DBP control on microbiological risks. To address this "risk-risk" trade-off, in May of 1996 the USEPA issued an Information Collection Rule (ICR) (Federal Register, 1996) which required approximately 300 water utilities to perform extensive monitoring for microbial contaminants and DBPs. A wide range of DBPs and surrogate parameters were quantified on a quarterly basis over an 18 month period beginning in 1997, and included the following: THM, HAA, haloacetonitriles (HAN), haloketones (HK), chloropicrin (CP), chloral hydrate (CH), ammonia, bromide, and total organic halides (TOX).

The USEPA recently developed the Stage I Disinfectants/Disinfection By-products Rule (D/DBPR) (Federal Register, 1998). This rule sets lower limits for total organic carbon (TOC), establishes maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) for disinfection by-products (the MCL for TTHMs was lowered from 100 to 80 mg/L), and sets maximum residual disinfectant levels (MRDLs) for disinfectants.

2.2.5. Empirical correlations of DBP formation

Research efforts also have focused on attempts to mathematically describe the rate of DBP formation from chlorination of drinking water. Such models are generally empirical in nature and generally do not address mechanistic or kinetic considerations. Though DPB formation can be highly subject to water source characteristics and treatment plant design, most empirical correlations that have been developed are based on a similar set of factors. Thus, the concentration of total THM or a single THM species are typically as a function of TOC, bromide ion

concentration, chlorine dose, pH, water temperature, and reaction time. For example, correlations for total THM, chloroform, and bromodichloromethane were developed for the EPA's Water Treatment Plant Simulation Program as reported by Singer (1994):

$$[TTHM] = 0.00309\,[(TOC)\,(UV\text{-}254)]^{0.440}\,(Cl_2)^{0.409}\,(t)^{0.265}\,(T)^{1.06}\,(pH\text{-}2.6)^{7.15}\,(Br+1)^{0.715} \quad (2\text{-}5)$$

$$[CHCl_3] = 0.278\,[(TOC)\,(UV\text{-}254)]^{0.616}\,(Cl_2)^{0.391}\,(t)^{0.265}\,(T)^{1.15}\,(pH\text{-}2.6)^{0.80}\,(Br+1)^{-2.23} \quad (2\text{-}6)$$

$$[BDCM] = 0.863\,[(TOC)\,(UV\text{-}254)]^{0.177}\,(Cl_2)^{0.309}\,(t)^{0.271}\,(T)^{0.72}\,(pH\text{-}2.6)^{0.925}\,(Br+1)^{-0.722} \quad (2\text{-}7)$$

where

[TTHM] = total trihalomethane concentration (μmol/L)

TOC = total organic carbon (mg/L)

UV-254 = ultraviolet absorbance at 254 nm (cm^{-1})

Cl_2 = free chlorine concentration (mg/L)

t = time (hr)

T = temperature (°C)

Br = bromide ion concentration (mg/L)

$[CHCl_3]$ = chloroform concentration (μmol/L)

[BDCM] = bromodichloromethane concentration (μmol/L)

2.3. Existing studies of DBP exposure

2.3.1. Large-scale surveys at drinking water treatment plants

Several different sampling methods have been used to measure DBP levels in drinking water. Since these methods can lead to different results, they are described briefly here. One method is to add a reducing agent such as sodium thiosulfate when

the sample is collected. This method will quench subsequent formation of DBPs and thus represents the DBP levels at the time of collection. For another method, the sample is refrigerated until analysis. This will slow the formation but not quench formation entirely, and thus may be representative of DBP levels at the tap. The third method is to not use any quenching procedure and allow formation reactions to occur to completion. This will give the maximum potential to form DBPs. The formation potential test also usually has a higher chlorine dose than is used in practice. Each method was used in at least one of the monitoring studies described below.

Three major surveys have been completed to examine THM levels in finished drinking water at the treatment plant. The National Organic Reconnaissance Survey (NORS) was completed from 1974 to 1975 in a total of 80 cities serving 36 million people (Symons *et al*., 1975). Water supplies originated from rivers (47%), lakes (33%), and groundwater (20%). One treatment plant used ozonation for disinfection of drinking water; all remaining plants used chlorination. This survey employed the method where samples were refrigerated before analysis.

The National Organic Monitoring Survey (NOMS) was conducted from 1976 to 1977 for 113 community water supplies (Wallace, 1997). Ninety-two of the water supplies originated from surface water and the remainder from groundwater. All three sampling methods were used in this survey. In phase 1, samples were refrigerated before analysis. In phases 2 and 3T, samples were stored at 20 ºC to 25 ºC for 2 to 3 weeks. In phase 3Q, a quenching agent was added. Across all methods median THM levels ranged from 37 to 74 µg/L (Wallace, 1997).

The American Water Works Association Research Foundation (AWWARF) Survey included quarterly measurements at 727 utilities (serving more than 105 million people) collected between 1984 and 1986 (McGuire and Meadow, 1988). Median THM concentrations ranged from 30 µg/L in the winter quarter to 44 µg/L in the summer. This survey employed a quenching agent. In comparing the AWWARF survey to the NORS and NOMS surveys, the authors noted that frequency

distributions were similar except at the upper percentiles, where the AWWARF survey had significantly lower THM levels relative to the previous surveys. It was suggested that plants with higher THM levels altered treatment processes to meet 1974 Safe Drinking Water Acts limitations of 100 µg/L total THMs, as 543 of the 727 systems surveyed employed some type of treatment change.

A summary of these surveys is given in Table 2-1. As expected, the maximum potential sampling method gives the highest TTHM concentrations and the quench sampling method gives the lowest.

Table 2–1. Comparison of national TTHM surveys.

Survey	Sampling method	Number of cities	TTHM concentration (µg/L)		
			Mean	Median	Range
NORS	Refrigeration	80	68	41	ND-482
NOMS-phase 1	Refrigeration	111	68	45	ND-457
NOMS-phase 2	Maximum potential	113	117	87	ND-784
NOMS-phase 3Q	Quench	106	53	37	ND-295
NOMS-phase 3T	Maximum potential	105	100	74	ND-695
NOMS-all phases		105-113	84	55	ND-784
AWWARF	Quench	727	42	39	ND-360

ND = not detected

Several other studies have been completed on DBP occurrence in water treatment plants. Nieminski *et al*. (1993) reported DBP occurrences for Utah water treatment plants. Chlorine was used for primary and secondary disinfection at all plants. THMs and HAAs constituted 64 and 30% of the total DBPs by weight, respectively. Krasner *et al*. (1989) measured DBP concentrations at 35 water treatment plants across the U.S. Total THM concentrations ranged from 30 to 44 µg/L; concentration ranges were 9.6-15 µg/L for chloroform, 4.1-10 µg/L for

bromodichloromethane, 2.6-4.5 µg/L for dichlorodibromomethane, and 0.33-0.88 µg/L for bromoform. Median total HAA concentrations ranged from 13 to 21 µg/L.

2.3.2. TEAM studies

One drawback to the DBP surveys described in Section 2.3.1 is that samples were collected at the treatment plant. Since human exposure from drinking water occurs at the tap, and DBPs will continue to form throughout the distribution system, it is likely that these measurements underestimate exposure. The main body of knowledge related to DBP tap water measurements was completed as part of the TEAM studies. All tap water measurements collected as part of the TEAM study used sodium thiosulfate as a quenching agent. Samples were collected at each participant's main source of drinking water. A summary of concentrations in tap water for chloroform ($CHCl_3$), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform ($CHBr_3$) is given in Table 2-2. Multiple values for a given location indicate different years or seasons when the monitoring took place.

Table 2–2. Concentrations in tap water for all major TEAM study locations.

Location	Median concentration (µg/L)			
	$CHCl_3$	BDCM	DBCM	$CHBr_3$
Bayonne-Elizabeth, NJ	67, 55, 16	13, 12, 5.8	2.4, 1.9, 1.6	*
Devils Lake, ND	0.38	0.18	0.06	*
Greensboro, NC	44	7.8	1.2	*
Los Angeles, CA (1984)	14, 33	12, 24	11, 32	0.54, 3.0
Antioch-Pittsburgh, CA	49	17	6.4	0.58
Los Angeles, CA (1987)	7.5, 9.6	24, 27	12, 18	3.2, 9.6
Baltimore, MD	24	10	2.6	*

*More than 90% of samples were below detection limits for these locations

Median concentrations of chloroform were consistently higher than the other THMs. Chloroform was measured above detection limits for all samples collected in

New Jersey, Maryland, and North Dakota (Wallace, 1997). For the California site, the percentage of measurable samples ranged from 84 to 100%. Bromodichloromethane and dibromochloroform also were frequently detected, with the percentage of measurable samples ranging from 73 to 100% for all sites. Occurrence of bromoform was less common, with less than 10% samples detectable from New Jersey, North Dakota, North Carolina, and Maryland samples. In California, the number of detectable samples ranged from 69 to 100%. Wallace (1997) noted that the California sites used mixed surface and groundwater supplies, and that levels of brominated organics were a function of the amount of groundwater used (which was seasonally dependent). Relatively low median THM concentrations were measured in North Dakota, where water supplies originated from private wells that were not chlorinated.

Exposure to DBPs is not limited to ingestion of drinking water. The TEAM studies indicated that chloroform levels in indoor air were typically four to five times those found in outdoor air (Wallace *et al*., 1984a). It was suspected that ratios were even higher in showers.

Consecutive 12-hour (day and night) samples were collected in personal air for each of the TEAM study sites. The percentage of detectable samples ranged from 22-24% in Devils Lake, ND to 92-99% in both Baltimore and Los Angeles. Typical personal air concentrations ranged from between 4 to 9 $\mu g/m^3$ in New Jersey to between 0.5 to 4 $\mu g/m^3$ in California. Day and night samples were similar in magnitude. A summary of chloroform personal air measurements is given in Table 2-3.

One limitation to the TEAM studies is that (for analytical reasons) personal monitors were placed in the bedroom while each participant was showering. Thus, it is likely that concentrations in personal air were underestimated. A further limitation is that only 12-hour samples (or longer) were collected, so that an assessment of the relative importance of personal activities is not possible.

Table 2–3 Chloroform concentrations in personal air for all major TEAM study locations.

Location	Season	Year	Median chloroform concentration ($\mu g/m^3$) Day	Night
Bayonne-Elizabeth, NJ	Sept.-Nov.	1981	3.1	3.3
	July-August	1982	0.75	0.88
	Feb.	1983	2.2	2.2
Devils Lake, ND	Oct.	1982	0.19	0.56
Greensboro, NC	May	1982	0.81	2.6
Los Angeles, CA	Feb.	1984	1.0	1.5
	May	1984	0.59	0.37
	Feb.	1987	0.03	0.03
	June	1987	0.44	0.98
Antioch-Pittsburgh, CA	June	1984	0.59	0.37
Baltimore, MD	April	1987	3.1	3.0

2.3.3. Food and beverages

A few studies have measured chloroform concentrations in carbonated beverages. For a pilot study completed in 1980 as part of the TEAM studies, food was sampled for VOCs from representative groceries in New Jersey, North Carolina, and Washington, D.C. (Entz *et al.*, 1982). Chloroform concentrations averaged 49 µg/L in cola soft drinks and 11 µg/L in non-cola soft drinks. Chloroform was detected in five different types of dairy products. Average chloroform concentrations were 4 ng/g for milk and cheese, 12 ng/g for butter, 23 ng/g for ice cream, and 34 ng/g for mayonnaise.

In unpublished data reported to the Food and Drug Administration (FDA), an average chloroform concentration of 23 µg/L was measured from 75 cola soft drinks and other beverages (Wallace, 1997). Abdel-Rahman (1982) reported chloroform concentrations ranging from 9 to 61 µg/L for cola soft drinks and from 2.7 to 10.9

µg/L for non-cola soft drinks. Concentrations of bromodichlorobenzene ranged from 0.2 to 6.6 µg/L for cola soft drinks and from 0.1 to 0.2 µg/L for non-cola soft drinks.

Daft (1987, 1988, and 1989) analyzed foods selected from the FDA's Market Basket Survey. Foods were cooked or prepared so that they were ready to eat and then analyzed for chloroform levels. The largest study included 549 food items; 302 of these items contained chloroform. Chloroform concentrations ranged from 2 to 830 ng/g, with a mean of 71 ng/g.

Heikes (1987) analyzed 18 food items, 10 of which contained chloroform. A follow-up study took additional samples from the food items which contained chloroform. The number of samples and mean chloroform concentrations are summarized in Table 2-4. Over ten cities, concentrations of chloroform in tap water ranged from 0 to 58 µg/L with an average concentration of 15.4 µg/L.

Table 2–4. Summary of Heikes (1987) study of chloroform concentrations in food.

Food item	Number of samples	Mean chloroform concentration (ppb)
Butter/magarine	14	364
Cheese	8	182
Cereal	11	60
Peanut butter	7	51.3
Processed foods	12	122

2.3.4. Volatilization from residential water devices

Several researchers have examined the effects of showering on exposure to contaminants that originate in drinking water. Andelman (1985a and b) estimated that inhalation exposure to chloroform while showering is comparable to drinking between 1 and 6 L of water a day. These estimates assumed steady-state conditions and treated a house as one well-mixed reactor. Subsequent studies have indicated that inhalation exposure to VOCs (including DBPs) in drinking water supplies can be

substantially higher than from ingestion alone (McKone, 1987; Jo *et al.* 1990a and 1990b; and Giardino *et al.*, 1992).

Several studies have been completed to determine chemical stripping efficiency from showers for various chemicals (Moya *et al*.,1999; Keating *et al*., 1997; Giardino and Andelman, 1996; Giardino and Hageman, 1996; Hopke *et al*., 1994; Keating and McKone, 1993; Tancrede *et al*., 1992; Giardino *et al*., 1992; McKone and Knezovich, 1991; Jo *et al*., 1990a and b; Giardino *et al*., 1988; Hodgson *et al*., 1988; Hess *et al*., 1982; and Gesell and Prichard, 1980). Several operational factors have been noted to affect the extent of chemical stripping from showers to indoor air, including liquid flow rate, liquid temperature, nozzle design, and physicochemical properties of the chemical of interest.

Efforts to quantify DBP inhalation exposure have focused mainly on exposure to chloroform in showers; others studies have been completed using chemicals with properties similar to chloroform. Moya *et al*. (1999) measured shower stripping efficiencies ranging from 61 to 77% for toluene and from 62 to 75% for ethylbenzene. Keating *et al*. (1997) completed 19 experiments and measured stripping efficiencies for 10 minutes. Stripping ranged from 65 to 91% for chloroform, with liquid temperatures varied from 35 ºC to 45 ºC and two different droplet sizes used ("coarse" and "fine" sprays). The highest stripping efficiency occurred for a liquid temperature of 45 ºC and "coarse" spray. Giardino and Andelman (1996) measured stripping efficiencies ranging from 44 to 62% for chloroform. Additional experiments involving trichloroethene (TCE) revealed that air exchange rate and inlet chemical concentration had no effect on chemical stripping. The stripping efficiency of TCE increased with increasing liquid temperature and decreasing liquid flowrate. Tancrede *et al*. (1992) completed four experiments using five VOCs (including chloroform and TCE). Chemical stripping generally increased with increasing liquid temperature, increasing chemical volatility, and decreasing liquid flowrate. Measured stripping efficiencies ranging from 42 to 63% for chloroform and from 55 to 67% for TCE.

McKone and Knezovich (1991) measured stripping efficiency of TCE from the shower of a vacant house, where efficiencies ranged from 58 to 63% for trichloroethene.

Recent evidence suggests that a significant fraction of a chemical present in drinking water can volatilize to indoor air from water devices other than showers (Howard and Corsi, 1996; Howard and Corsi, 1998; Moya *et al*., 1999). Stripping efficiencies and mass transfer coefficients for dishwashers, washing machines, showers, and bathtubs were determined for five volatile chemicals representing a wide range of chemical properties. For example, dishwasher stripping efficiencies were 100% for cyclohexane, between 97% and 98% for ethylbenzene, and between 95% and 98% for toluene (Howard-Reed *et al*., 1999). Stripping efficiencies for acetone were highly sensitive to dishwasher operating conditions, but still ranged from a low of 18% to a high of 55%.

These results indicate that stripping efficiencies for dishwashers are higher than those reported for similar compounds in showers (Moya *et al*., 1999). Results for acetone also suggest that low-volatility DBPs, many of which have higher Henry's law constants than acetone, may exhibit significant stripping efficiencies from previously neglected sources. These results are plausible since dishwashers are characterized by turbulent water conditions (high mass transfer coefficients) and high liquid temperatures (high Henry's law constant) relative to showers.

2.3.5. Swimming pools

Several studies have indicated that swimming pools can be an important source of chloroform exposure (Beech *et al*., 1980; Lahl *et al*., 1981; and Wester and Maibach, 1989). Exposure can occur through the skin while swimming and via inhalation. Indoor pools may have higher THMs concentrations (in the gas phase) relative to outdoor pools due to lower ventilation rates.

Armstrong and Golden (1986) measured THM levels in swimming pools and adjacent air (2 m above surface) at four indoor swimming pools, five outdoor swimming pools, and four hot tubs. Mean THM concentrations are summarized in Table 2-5. All sampling locations used the same tap water supply. Concentrations of individual THMs in tap water were 1.7 µg/L for chloroform, 1.0 µg/L for BDCM, 0.43 µg/L for DBCM, and below 0.1 µg/L for bromoform.

Table 2–5. Summary of THM data from Armstrong and Golden (1986).

Location	Phase	Mean concentration (µg/L)			
		$CHCl_3$	BDCM	DBCM	$CHBr_3$
Indoor pool	Liquid	133	16	9.5	6
Outdoor pool	Liquid	128	33	4.2	<0.1
Hot tub	Liquid	115	17	14.4	13
Indoor pool	Gas	90	1.7	0.9	9
Outdoor pool	Gas	1*	<0.1	<0.1	<0.1
Hot tub	Gas	12	1.4	0.7	8

* represents maximum value

Jo (1994) measured liquid and gas concentrations of chloroform at three indoor pools in Korea. All pools were disinfected with chlorine and ozone. Mean indoor air concentrations were from 28 and 33.6 µg/m^3 and liquid concentrations were from 19.5 to 31.1 µg/L. The author suggested that use of ozone as a disinfectant leads to lower THM levels relative to other swimming pool studies. This approach would also leave no residual disinfectant.

2.3.6. In-home formation of DBPs

Preliminary evidence suggests that in-home formation of DBPs may be a significant exposure pathway. As part of the TEAM study, the USEPA conducted a pilot study to determine the significance of hot water usage on chloroform exposure. Study participants were asked to take long showers, boil water, and wash clothes and dishes as indoor air samples were collected. Results indicated that chloroform concentrations increased significantly (from <4.5 to 44 $\mu g/m^3$) from washing clothes or dishes, but that no increase in chloroform concentrations occurred from either showering or boiling water (Wallace, 1989). These experiments were completed as the result of an earlier study in which chlorine bleach was used as a cleanser in a well-ventilated, room-sized chamber (Wallace *et al*., 1987b). Calculated chloroform emission rates were 15 $\mu g/min/m^2$ with concentrations as high as 283 $\mu g/m^3$.

Shepherd *et al*. (1996) completed a series of 22 experiments on a residential washing machine to determine the extent of chloroform formation and mass transfer after bleach addition to the wash water. Three different types of experiments were completed: (1) with clothes, (2) with clothes removed from the machine after a pre-rinse cycle, and (3) with no clothes added to the machine. The highest amount of chloroform formation occurred for experiments using clothes. Yield coefficients (in μg chloroform per mg Cl_2) ranged from 0.16 to 5.2 $\mu g/mg$ for clothes removed experiments and from 2.7 to 5.2 $\mu g/mg$ when clothes were included in the wash cycle. Rates of residual chlorine removal were highest for experiments where clothes were included in the wash cycle, suggesting that both organic matter in the wash water and the clothes themselves compete for residual chlorine. Headspace ventilation rates, measured from pulse injections of sulfur hexafluoride (SF_6), ranged from 51 to 98 L/min. Stripping efficiencies resulting from eight mass transfer experiments ranged from 10 to 18%. One limitation to this research is that only chloroform concentrations were measured during the formation experiments.

2.3.7. Outdoor air

As part of the TEAM study, consecutive 12-hour (day and night) samples were collected in personal air for each study site. Outdoor concentrations were generally lower than either indoor air or personal air concentrations at all locations. Median outdoor air concentrations ranged from 0.2 to 0.6 $\mu g/m^3$ in California and from 0.1 to 1.5 $\mu g/m^3$ in New Jersey (Wallace, 1997).

The California Air Resources Board (CAARB) collects 24-hour samples every 12 days at several locations throughout the state. These are analyzed for several VOCs, including chloroform. A total of 3,142 samples were collected from 1986 to 1991, 2,251 of which were analyzed for chloroform. Of those analyzed for chloroform, 675 samples (30%) were below the detection limit of 0.02 ppb (about 0.1 $\mu g/m^3$). Only six samples exceeded 1 $\mu g/m^3$, and none were greater than 2 $\mu g/m^3$. Assigning a value of one half the detection limit for the 675 samples below 0.02 ppb, the following summary statistics were reported (Wallace, 1997): mean of 0.033 ppb (0.16 $\mu g/m^3$), 25^{th} percentile of 0.01 ppb (0.05 $\mu g/m^3$), 50^{th} percentile of 0.03 ppb (0.15 $\mu g/m^3$), and 75^{th} percentile of 0.04 ppb (0.2 $\mu g/m^3$).

2.3.8. Body burden measurements

Though mathematical modeling of chemical distribution in the human body can give an indication of dose to target organs, these methods are subject to significant uncertainty. Thus, body burden measurements provide a direct measure of chemical uptake into the body. These include exhaled breath and blood measurements.

The largest set of exhaled breath measurements comes from the TEAM study. More than 1,250 breath samples were collected from approximately 800 individuals (Wallace, 1997). A summary of chloroform exhaled breath measurements is given in Table 2-6.

Table 2–6. Chloroform concentrations in exhaled breath for all major TEAM study locations.

Location	Season	Year	Time	Median chloroform concentration ($\mu g/m^3$)
Bayonne-Elizabeth, NJ	Sept.-Nov.	1981	Evening	1.8
	Feb.	1983	Evening	0.07
Devils Lake, ND	Oct.	1982	Evening	2.9
Greensboro, NC	May	1982	Evening	0.67
Los Angeles, CA	Feb.	1984	Evening	0.10
	May	1984	Evening	0.03
	Feb.	1987	Evening	0.37
	Feb.	1987	Morning	0.56
	Feb.	1987	Evening	0.11
	June	1987	Evening	0.34
	June	1987	Morning	0.34
	June	1987	Evening	0.37
Antioch-Pittsburgh, CA	June	1984	Evening	0.04
Baltimore, MD	April	1987	Evening	0.11
	April	1987	Morning	0.35
	April	1987	Evening	0.37

Several researchers have measured exhaled breath from swimmers. Aggazzotti *et al*. (1993) measured exhaled breath from 163 persons at an indoor swimming pool. Mean aveolar air concentrations of chloroform were 83 $\mu g/m^3$. Weisel and Shepard (1994) collected chloroform measurements five different times at an indoor swimming pool with one subject. Liquid concentrations of chloroform ranged from 30 to 150 $\mu g/L$ and gas concentrations from 23 to 120 $\mu g/m^3$. Preexposure breath concentrations were always less than 2 $\mu g/m^3$, and increased to between 15 and 25 $\mu g/m^3$ after 30 minutes of swimming. Levesque *et al*. (1994) measured chloroform levels at an indoor pool for 11 swimmers over a weeklong period. Indoor air, liquid, and exhaled breath samples were collected. Liquid concentrations were increased daily, from 158 to more than 550 $\mu g/L$. Over that same

time, indoor air concentrations increased from 507 to 1,630 ppb and mean breath concentrations increased from 100 to approximately 1,000 ppb. Lindstrom *et al*. (1997) measured exhaled breath from two Olympic-level swimmers. After swimming in a pool for two hours at a liquid concentration of chloroform of 70 µg/L, exhaled breath measurements of the swimmers were 340 and 370 $\mu g/m^3$.

Several researchers have measured THM levels in blood. The first involved measurements of drinking water and human blood in New Orleans (Dowty *et al*., 1975). Though only approximate quantification of chloroform levels in blood were made ("low ppb range"), the work was nonetheless an important catalyst for the Safe Drinking Water Act of 1974 (Wallace, 1997). Pfaffenberger and Peoples (1982) measured the chloroform levels of 25 adult females over a six-month period. Most measurements were between 0 and 25 ppb, though some samples were noted to exceed 1,000 ppb. Antoine *et al*. (1986) analyzed the blood of 250 hospital patients. Mean chloroform levels were 1.5 ppb with a maximum of 7 ppb. Bromoform was detected with a mean of 0.6 ppb and a maximum of 3.4 ppb. Aggazzotti *et al*. (1990) measured chloroform in the plasma of 127 swimmers using indoor pools in Italy. Chloroform levels ranged from 0.1 to 3.1 µg/L.

The largest study to date in which THM levels were measured in blood was completed by Ashley *et al*. (1994). Blood from about 1,000 individuals was analyzed for 28 VOCs (including the four THMs) as part of the National Health and Nutrition Examination Survey (NHANES) completed between 1988 and 1992. Results from the study are summarized in Table 2-7. Tap water concentrations of THMs were not reported.

In a more recent study, Backer *et al*. (2000) measured THM levels in blood from 31 individuals. Participant groups completed one of the following activities: showering for 10 minutes, bathing for 10 minutes, or drinking 1 L of tap water over a 10-minute time period. Mean concentrations of chloroform in tap water were 31.0 µg/L for showering, 31.8 µg/L for bathing, and 20.4 µg/L for drinking activities.

Mean concentrations of BDCM in tap water were 6.27 µg/L for showering, 6.22 µg/L for bathing, and 5.52 µg/L for drinking activities. Mean concentrations of DBCM in tap water were 1.2 µg/L for showering, 1.2 µg/L for bathing, and 1.0 µg/L for drinking activities. Blood samples were taken before exposure, 10 minutes after exposure, and either 30 minutes or 1 hour after exposure.

Table 2–7. THM concentrations (µg/L) in blood from NHANES.

	$CHCl_3$	BDCM	DBCM	$CHBr_3$
Number of samples	979	1,072	1,035	Not given
Detection limit	0.021	0.009	0.013	0.027
Percent detected	54	14	12	<10
Mean	0.0444	0.0077	0.00886	
Standard deviation	0.162	0.0178	0.00856	

The highest THM levels in blood were found from showering and bathing, and lowest were found from drinking tap water. The highest concentrations were measured for the sample taken 10 minutes after exposure. Approximate concentrations of chloroform, BDCM, and DBCM after either 10 minutes of showering or bathing were 125, 20, and 5 ng/L, respectively.

3. SCREENING ASSESSMENT

A screening assessment was completed to estimate the relative exposure to DBPs from a variety of personal activities. A series of deterministic calculations involving a variety of personal activities that contribute to DBP exposure was completed. Sources included: drinking water, carbonated beverages, showers, bathtubs, washing machines, dishwashers, kitchen sinks, cooking, toilets, swimming pools, hot tubs, and residential cleaning. Calculations involving residential water devices were generally limited to volatilization of DBPs originally in the drinking water and did not consider in-home formation due to a lack of experimental data. Emphasis was placed on non-occupational exposure to DBPs, including dermal uptake, ingestion and inhalation exposure. The screening assessment was also limited to THMs since little experimental data are available on exposure to other DBPs.

3.1. Selection of typical DBP levels

The sampling method most representative for assessing exposure would occur at the tap. Although the most extensive database of DBP measurements at the tap comes from the TEAM studies, these results are somewhat dated. The most recent DBP measurements at treatment plants come from the Information Collection Rule (ICR). Median TTHM levels for this survey were generally around 40 µg/L. This value is consistent with TTHM levels obtained from earlier studies (Table 2-1). Thus, it is unlikely that DBP levels in drinking water have changed significantly over the past two decades. Based on values collected at the tap from the TEAM studies (Table 2-2), the concentrations listed in Table 3-1 were chosen as typical and were used for subsequent exposure calculations in Section 3.5.

Table 3–1. Typical values used for exposure calculations.

Chemical	Typical concentration (μg/L)
Chloroform	30
Dichlorobromomethane	15
Dibromochloromethane	5
Bromoform	1

3.2. Mixing assumptions

For purposes of this screening assessment, it is assumed that well-mixed conditions exist for both the house and room where the exposure occurs. In addition, emissions of DBPs are assumed to occur either in the form of a pulse (instantaneous) release or a time-averaged (step) release. Equations describing concentration as a function of time for a pulse and step release are as follows:

$$C(t) = C_0\, e^{-t/\theta}, \text{ pulse} \qquad (3\text{-}1)$$

$$C(t) = C_0\,(1 - e^{-t/\theta}) = E/Q_g\,(1 - e^{-t/\theta}), \text{ step} \qquad (3\text{-}2)$$

where

$C(t)$ = concentration at time t (μg/L)

C_0 = initial concentration (μg/L)

t = time (hr)

$1/\theta$ = air exchange rate (/hr)

Another parameter of interest is the average concentration over a given time. The average concentration (C_{avg}) over time t from a pulse input can be determined by integrating Equation 3-1 from 0 to t:

$$C_{avg} = \frac{\int_0^t C(t)\,dt}{t} = \frac{\int_0^t C_0\, e^{-t/\theta}\,dt}{t} = \frac{C_0}{t}\left[-\theta\, e^{-t/\theta}\right]_0^t = \frac{C_0\,\theta}{t}\left[1 - e^{-t/\theta}\right] \qquad (3\text{-}3)$$

Similarly, the average concentration over time t from a step input can be determined by integrating Equation 3-2 from 0 to t:

$$C_{avg} = \frac{\int_0^t C(t)}{t} = \frac{\int_0^t \frac{E}{Q_g}\left(1 - e^{-t/\theta}\right)dt}{t} = \frac{E}{Q_g} - \frac{E}{Q_g t}\int_0^t e^{-t/\theta}\,dt = \frac{E}{Q_g} + \frac{E}{Q_g t}\left[\theta\, e^{-t/\theta}\right]_0^t$$

$$= \frac{E}{Q_g} + \frac{E\,\theta}{Q_g t}\left[e^{-t/\theta} - 1\right] \qquad (3\text{-}4)$$

3.3. Activity scenario

The calculations that follow were developed assuming a family of four persons. Other assumptions used throughout this section include:

- Average adult inhalation rate = 15.2 m^3/day (10.6 L/min); recommended value, USEPA (1996)
- House volume = 2000 ft^2 x 8 ft = 16,000 ft^3 = 453.3 m^3
- Air exchange rate = 0.3 hr^{-1}
- Ventilation rate = (0.3/hr)(453,300 L)(hr/60 min) = 2,267 L/min

3.4. Dermal Uptake

The outer layer of human skin consists of a dense, protein-lipid region referred to as the stratum corneum. From the stratum corneum, chemicals pass through a more permeable layer called the viable epidermis and are then incorporated directly into the bloodstream. Chemical concentrations increase in the stratum corneum until a steady-state condition is reached where the rate of mass entering the skin is equivalent to the mass entering the bloodstream. The time for this condition to be reached is called the lag time. Cleek and Bunge (1993) developed empirical equations describing the total mass entering the body due to dermal uptake, based on diffusion through the stratum corneum:

$$M_{in} = AC_l\sqrt{\frac{4\,R_{sc}\,L_{sc}P_{sc}\,t_{exp}}{\pi}} \qquad \text{for } t_{exp} < 2.4\,t_{lag} \qquad (3\text{-}5)$$

$$M_{in} = AC_1\left[P_{sc}\, t_{exp} + \frac{(R_{sc}\, L_{sc})}{3}\right] \quad \text{for } t_{exp} > 2.4\, t_{lag} \tag{3-6}$$

where

M_{in} = mass that leaves the skin to enter systemic circulation (μg)

A = skin surface area (m^2)

C_1 = liquid concentration of the chemical ($\mu g/m^3$)

R_{sc} = partition coefficient between water and the stratum corneum (-)

L_{sc} = diffusion path length of the stratum corneum (m)

P_{sc} = permeability coefficient across the stratum corneum (m/hr)

t_{exp} = exposure time (hr)

t_{lag} = lag time (hr)

Assuming diffusion is dominated by resistance through the stratum corneum, P_{sc} can be approximated as the overall skin permeability (P_m). A widely-used correlation of skin permeability was developed by Potts and Guy (1992):

$$\log_{10} P_m \text{ (cm/hr)} = -2.72 + 0.71 \log_{10} K_{ow} - 0.0061\, MW \tag{3-7}$$

where

P_m = permeability coefficient across the entire skin (cm/hr)

K_{ow} = octanol-water partition coefficient for chemical of interest (-)

MW = molecular weight of the chemical (g/mol)

Values of P_m for the four THMs based on the above equation and on measured data are listed in Table 3-2.

Table 3–2. Values of P_m used in dermal exposure calculations.

Chemical	P_m (cm/hr)	Source
Chloroform	0.13	Bogen *et al*. (1992)
Bromoform	2.6×10^{-3}	Estimated
Bromodichloromethane	5.8×10^{-3}	Estimated
Chlorodibromomethane	3.9×10^{-3}	Estimated

Bunge *et al*. (1994) developed the following correlation for R_{sc}, based on a review of data on steroids, phenolic compounds, aromatic alcohols, normal alcohols, and undissociated acids:

$$\log_{10} R_{sc} = 0.71 \log_{10} K_{ow} \quad (3\text{-}8)$$

Bunge and Cleek (1995) used a value of 16 μm for L_{sc}, which is consistent with experimental data reported by Kalia *et al*. (1996).

A few attempts have been made to estimate the lag time. McKone (1993) developed a shower exposure model and estimated the lag time from existing data. The USEPA (1992) developed a dermal exposure model based on correlations of skin permeability. Predicted lag times from the two models were 12 and 29 minutes, respectively. Recent research by Corley *et al*. (2000) was aimed at quantifying temperature dependency of chloroform uptake during bathing. Lag times based on exhaled breath samples ranged from 0 to 9 minutes, with the lower lag times occurring during experiments completed at higher bath water temperatures.

3.5. Exposure calculations for specific activities

3.5.1. Ingestion exposure from drinking water

Assumptions:

- Adult drinking water intake = 1.4 L/day; recommended value, USEPA (1996)

Exposure = (1.4 L/day)(30 μg chloroform/L water) = 42.0 μg chloroform/day

3.5.2. Ingestion exposure from carbonated beverages

Assumptions:

- Adult carbonated beverage intake = 0.355 L (one can)

- Chloroform concentration in beverage = 40 µg/L; typical value from studies discussed in Section 2.3.3.
- Other THMs are proportional to drinking water concentrations

Exposure = (0.355 L/day)(40 µg chloroform/L)

= 14.2 µg chloroform/day

3.5.3. Inhalation exposure from showering

Assumptions:

- Chloroform stripping efficiency = 60%; typical value from studies discussed in Section 2.3.4.
- Stripping for other THMs = 15%; typical value using chemicals with similar properties from Moya *et al*. (1999)
- Shower flow rate = 3.4 gal/min (12.85 L/min); non-conserving head, USEPA (1996)
- Time spent showering = 8 minutes; recommended value, USEPA (1996)
- Time spent in bathroom after shower = 5 minutes; median value, USEPA (1996)
- Concentration used for after shower direct exposure is equal to concentration in bath room at end of shower
- One shower/day
- Shower ventilation rate = (0.3/hr)(3 ft x 8 ft x 8 ft)(28.3 L/ft^3)(hr/60 min) = 27.2 L/min
- Bath room ventilation rate = (0.3/hr)(6 ft x 10 ft x 8 ft)(28.3 L/ft^3)(hr/60 min) = 67.9 L/min

Estimation of direct exposure

Shower emission rate = (30 µg chloroform/L)(12.85 L/min)(0.6) = 231.3 µg/min

Average concentration during shower (step injection, Equation 3-4, with E = 231.3 μg chloroform/min, t = 8 minutes, Q_g = 27.2 L/min):

C_g = 0.168 μg/L

Concentration in shower at end of shower (step injection, Equation 3-2, with E = 231.3 μg chloroform/min, t = 8 minutes, Q_g = 27.2 L/min):

C_g = 0.333 μg/L

This value is consistent with data reported by Jo *et al*. (1990a) in an actual shower with a person showering, where air concentrations in the shower ranged from 0.13 to 0.31 μg chloroform/L. Chloroform concentrations in tap water ranged from 22.0 to 35.6 μg chloroform/L for these experiments.

Concentration in bath room at end of shower (step injection, Equation 3-2, with E = 231.3 μg chloroform/min, t = 8 minutes, Q_g = 67.9 L/min):

C_g = 0.134 μg/L

Exposure = (10.6 L/min)(0.168 μg/L)(8 min/shower)(1 shower/day) + (10.6 L/min)(0.134 μg/L)(5 min/shower)(1 shower/day)

= 21.4 μg chloroform/day

Contribution to background concentration

This is likely an upper-bound case where at least two persons shower in the evening and exposure occurs throughout the night. An exposure duration of 10 hours is assumed for this case. The initial concentration in the house is estimated using a pulse injection of two showers.

Initial concentration in the house = (2)(30 μg chloroform/L)(12.85 L/min)(8 minutes)(0.6)/453,300 L

= 0.00816 μg/L

Average concentration in house (pulse injection, Equation 3-3, with C_o = 0.00816 μg/L, t = 10 hours):

C_g = 0.00258 μg/L

Exposure = (10.6 L/min)(0.00258 μg/L)(60 min/hr)(10 hr/day)

= 16.4 μg chloroform/day

3.5.4. Dermal exposure from showering

Assumptions:

- Mean shower time = 8 minutes; recommended value, USEPA (1996)
- One shower per day
- Mean adult surface area = 1.94 m^2; recommended value, USEPA (1996)
- 50% of surface area covered with water during shower at any given time
- L_{sc} = 16 μm; Bunge and Cleek (1995)
- Negligible resistance from viable epidermis ($P_{sc} = P_m$)
- Lag time = 5.0 minutes; typical value from Corley *et al*. (2000)

$R_{sc} = 10^{(0.71 \log 10 Kow)} = 10^{(0.71 \times 1.97)} = 25.04$

$2.4\ t_{lag}$ = 2.4 (5 minutes) = 12 minutes > t_{exp} ⇒ non steady-state conditions

Exposure:

$$M_{in} = AC_l\sqrt{\frac{4 R_{sc} L_{sc} P_{sc} t_{exp}}{\pi}}$$

$$= \left(0.5 \times 1.94\ m^2\right)\left(30{,}000\ \mu g/m^3\right)\sqrt{\frac{4(25.04)16 \times 10^{-6}\ m(0.0013\ m/hr)(8/60\ hr)}{\pi}}$$

= 8.65 μg chloroform/day

3.5.5. Inhalation exposure from bath tubs

Assumptions:

- Mean bath time = 20 minutes; recommended value, USEPA (1996)
- One bath per day
- Time spent in bathroom after bath = 5 minutes; median value, USEPA (1996)
- Emission rate averaged over time of bath
- Liquid volume in bath tub = 100 L
- Stripping efficiency = 25% for chloroform, 5% for other THMs; typical values using chemicals with similar properties from Corsi and Howard (1998)
- Bath room ventilation rate = (0.3/hr)(6 ft x 10 ft x 8 ft)(28.3 L/ft^3)(hr/60 min) = 67.9 L/min

Estimation of direct exposure

Bath emission rate = (30 μg chloroform/L)(100 L)(0.25)/20 min = 37.5 μg chloroform/min

Average concentration during bath (step injection, Equation 3-4, with E = 37.5 μg/min, t = 20 minutes, Q_g = 67.9 L/min):

C_g = 0.0267 μg/L

Concentration at end of bath (step injection, Equation 3-2, with E = 37.5 μg chloroform/min, t = 20 minutes, Q_g = 67.9 L/min):

C_g = 0.0526 μg/L

Exposure = (10.6 L/min)(0.0267 μg/L)(20 min/bath)(1 bath/day) + (10.6 L/min)(0.0526 μg/L) (5 min/bath)(1 bath/day)

= 8.5 μg chloroform/day

Contribution to background concentration

This is likely an upper-bound case where at least two persons take a bath in the evening and exposure occurs throughout the night. An exposure duration of 10 hours is assumed for this case. The house concentrations are estimated using a step injection of two consecutive baths.

Average concentration in house during baths (two consecutive baths using step injection, Equation 3-4, with E = 37.5 μg/min, t = 40 minutes, Q_g = 2267 L/min):

C_g = 0.00155 μg/L

Concentration in house at end of baths (two consecutive baths using step injection, Equation 3-2, with E = 37.5 μg/min, t = 80 minutes, Q_g = 2267 L/min):

C_g = 0.00300 μg/L

Average concentration in house after baths (pulse injection, Equation 3-3, with C_o = 0.00300 μg/L, t = 9.33 hours):

C_g = 0.00101 μg/L

Exposure = (10.6 L/min)(0.00155 μg/L)(40 min/day) + (10.6 L/min)(0.00101 μg/L)
(60 min/hr)(9.33 hr/day)
= 6.7 μg chloroform/day

3.5.6. Dermal exposure from bath tubs

Assumptions:

- Mean bath time = 20 minutes; recommended value, USEPA (1996)
- One bath per day

- Mean adult surface area = 2.0 m^2; recommended value for bathing, USEPA (1996)
- L_{sc} = 16 μm; Bunge and Cleek (1995)
- Negligible resistance from viable epidermis ($P_{sc} = P_m$)
- Lag time = 5.0 minutes; typical value from Corley *et al*. (2000)

$R_{sc} = 10^{(0.71 \log 10 Kow)} = 10^{(0.71 \times 1.97)} = 25.04$

2.4 t_{lag} = 2.4 (5 minutes) = 12 minutes < $t_{exp} \Rightarrow$ steady-state conditions

Exposure:

$$M_{in} = AC_l\left[P_{sc}\, t_{exp} + \frac{(R_{sc}\, L_{sc})}{3}\right]$$

$$= \left(2.0\ m^2\right)\left(30{,}000\ \mu g/m^3\right)\left[\left(0.0013\ m/hr\right)\left(20/60\ hr\right) + \frac{(25.04)\left(16 \times 10^{-6}\right)}{3}\right]$$

= 34.1 μg chloroform/day

3.5.7. Inhalation exposure from washing machines (from-plant)

Assumptions:

- 2 washing machine loads/week/person; median value, USEPA (1996)
- Liquid volume used per event = 50 gal (189 L); typical value, USEPA (1996)
- Stripping efficiency = 50% chloroform, 20% for other THM; typical value using chemicals with similar properties from Howard and Corsi (1998)
- Duration of washing event = 45 minutes
- Washing events are successive; 4 washing events on two separate days for each week
- Emission rate averaged over time of event
- Room volume = 10 ft x 8 ft x 8 ft = 640 ft^3 = 18.1 m^3 (direct exposure calculation)

- Ventilation rate = (0.3/hr)(18,100 L)(hr/60 min) = 90.7 L/min (direct exposure calculation)

Emission rate = (189 L water/event)(30 μg chloroform/L water)(0.5)(event/45 min)
= 63.0 μg/min

Estimation of direct exposure

It is unlikely that a person is in the room during the entire washing event. It is assumed that a person is in the laundry room for 5 minutes for every washing machine event.

Average concentration in laundry room during washing (step injection, Equation 3-4, with E = 63.0 μg/min, t = 45 minutes, Q_g = 90.7 L/min):

C_g = 0.0726 μg/L

Exposure = (10.6 L/min)(0.0726 μg/L)(5 min/event)(8 events/week)(week/7 days)
= 4.40 μg chloroform/day

Contribution to background concentration

An exposure duration of 10 hours is assumed for this case. The house concentrations are estimated using a step injection of four consecutive washing events.

Average concentration in house during washing (four consecutive washing events using step injection, Equation 3-4, with E = 63 μg/min, t = 180 minutes, Q_g = 2267 L/min):

C_g = 0.00947 μg/L

Concentration in house at end of washing (four consecutive washing events using step injection, Equation 3-2, with E = 63 μg/min, t = 180 minutes, Q_g = 2267 L/min):

C_g = 0.0165 μg/L

Average concentration in house after washing (decay, Equation 3-3, with C_o = 0.0165 μg/L, t = 7 hours):

C_g = 0.00689 μg/L

Exposure = (10.6 L/min)(0.00947 μg/L)(45 min/event)(8 event/week)(week/7 day)
+ (10.6 L/min)(0.00689 μg/L)(60 min/hr)(7 hr)(2/week)(week/7 day)
= 13.9 μg chloroform/day

3.5.8. Inhalation exposure from washing machines (in-home formation)

Assumptions:

- 1 washing machine load/week using bleach
- Mass emitted = 10 mg chloroform/event; typical value, Shepherd *et al*. (1996)
- Duration of washing event = 45 minutes
- Emission rate averaged over time of event
- Room volume = 10 ft x 8 ft x 8 ft = 640 ft^3 = 18.1 m^3 (direct exposure calculation)
- Ventilation rate = (0.3/hr)(18,100 L)(hr/60 min) = 90.7 L/min (direct exposure calculation)

Emission rate = (10 mg chloroform/event)(event/45 min)(1000 μg/mg)
= 222.2 μg/min

Estimation of direct exposure

It is unlikely that a person is in the room during the entire washing event. It is assumed that a person is in the washing machine room for 5 minutes for every washing machine event.

Average concentration in laundry room during washing (step injection, Equation 3-4, with E = 222.2 μg/min, t = 45 minutes, Q_g = 90.7 L/min):

C_g = 0.256 μg/L

Exposure = (10.6 L air inhaled/min)(0.256 μg/L)(5 min/week)(week/7 days)

= 1.94 μg chloroform/day

Contribution to background concentration

An exposure duration of 10 hours is assumed for this case. The house concentrations are estimated using a step injection.

Average concentration in house during washing (step injection, Equation 3-4, with E = 222.2 μg/min, t = 45 minutes, Q_g = 2267 L/min):

C_g = 0.0102 μg/L

Concentration in house at end of washing (step injection, Equation 3-4, with E = 222.2 μg/min, t = 45 minutes, Q_g = 2267 L/min):

C_g = 0.0197 μg/L

Average concentration in house after washing (decay, Equation 3-3, with C_o = 0.0197 μg/L, t = 9.25 hours):

C_g = 0.00666 μg/L

Exposure = (10.6 L air inhaled/min)(0.0102 μg/L air)(45 min/week)(week/7 day) +
(10.6 L air inhaled/min)(0.00666 μg/L air)(60 min/hr)(9.25 hrs/week)(week/7 day)
= 6.29 μg chloroform/day

3.5.9. Inhalation exposure from dishwashers (from-plant)

Assumptions:

- 3 dishwasher events/week/person; median value, USEPA (1996)
- Liquid volume in dishwasher = 7.4 L; Howard-Reed *et al*. (1999)
- Stripping efficiency = 100% chloroform, 50% for other THM; using chemicals with similar properties from Howard-Reed *et al*. (1999)
- 4 dishwasher cycles/event
- Duration of washing event = 45 minutes
- Emission rate averaged over time of event
- Room volume = 10 ft x 8 ft x 8 ft = 640 ft^3 = 18.1 m^3 (direct exposure calculation)
- Ventilation rate = (0.3/hr)(18,100 L)(hr/60 min) = 90.7 L/min (direct exposure calculation)

Emission rate = (7.4 L water/cycle)(4 cycles/event)(30 μg chloroform/L water)(1 event/45 min)
= 19.7 μg/min

Estimation of direct exposure

It is unlikely that a person is in the room during the entire washing event. It is assumed that a person is in the room for 5 minutes for every dishwashing event.

Average concentration in room during washing (step injection, Equation 3-4, with E = 19.7 μg/min, t = 45 minutes, Q_g = 90.7 L/min):

C_g = 0.0227 μg/L

Exposure = (10.6 L/min)(0.0227 μg/L)(5 min/event)(12 events/week)(week/7 days)

= 2.06 μg chloroform/day

Contribution to background concentration

Average concentration in house during washing (step injection, Equation 3-4, with E = 19.7 μg/min, t = 45 minutes, Q_g = 2267 L/min):

C_g = = 0.000908 μg/L

Concentration in house at end of washing (step injection, Equation 3-2, with E = 19.7 μg/min, t = 45 minutes, Q_g = 2267 L/min):

C_g = 0.00175 μg/L

Average concentration in house after washing (decay, Equation 3-3, with C_o = 0.00175 μg/L, t = 9.25 hours):

C_g = 0.000591 μg/L

Exposure = (10.6 L/min)(0.000908 μg/L air)(45 min/day) + (10.6 L/min)(0.000591 μg/L air)(60 min/hr)(9.25 hr/day)

= 3.91 μg chloroform/day

3.5.10. Inhalation exposure from wash basins

Assumptions:

- 6 hand washings per day/person; median value, USEPA (1996)
- Washing events are equally spaced throughout day
- Time between washings = 10 hr/(6/person)/(4 persons) = 0.417 hr

- Stripping efficiency = 25% for chloroform, 5% for other THMs; using chemicals with similar properties from Howard and Corsi (1996)
- Water used per washing event = 1 L/event

Contribution to background concentration

Initial house concentration = (30 μg chloroform/L)(1 L)(0.25)/453,300 L

$= 1.65 \times 10^{-5}$ μg/L

Average concentration in house (pulse injection, Equation 3-3, with $C_o = 1.65 \times 10^{-5}$ μg/L, t = 0.417 hours):

$C_g = 1.55 \times 10^{-5}$ μg/L

Exposure = (10.6 L/min)(1.55 x 10^{-5} μg/L air)(10 hr/day)(60 min/hr)

= 0.099 μg chloroform/day

3.5.11. Dermal exposure from hand washing

Assumptions:

- Mean washing time = 0.5 minute
- 6 hand washings per day; median value, USEPA (1996)
- Mean adult surface area of hands = 0.084 m^2; recommended value, USEPA (1996)
- L_{sc} = 16 μm; Bunge and Cleek (1995)
- Negligible resistance from viable epidermis ($P_{sc} = P_m$)
- Lag time = 5.0 minutes; typical value from Corley *et al*. (2000)

$R_{sc} = 10^{(0.71 \log_{10} Kow)} = 10^{(0.71 \times 1.97)} = 25.04$

$2.4\ t_{lag} = 2.4$ (5 minutes) = 12 minutes > $t_{exp} \Rightarrow$ non steady-state conditions

$$M_{in} = AC_l\sqrt{\frac{4\,R_{sc}\,L_{sc}P_{sc}\,t_{exp}}{\pi}}$$

$$= \left(0.084\,m^2\right)\left(30{,}000\,\mu g/m^3\right)\sqrt{\frac{4\,(25.04)16\,x\,10^{-6}\,m\,(0.0013\,m/hr\,)(0.5/60\,hr)}{\pi}}$$

$$= 0.19\ \mu g/event$$

Exposure = (6 events/day)(0.33 μg chloroform/events)

= 1.12 μg chloroform/day

3.5.12. Inhalation exposure from cooking

Assumptions:

- Average volume water boiled per day = 2 cups
- All THMs completely volatilize to room during boiling
- One cooking event per day
- Person is in room during entire cooking activity
- 1 hour exposure period
- Room volume = 10 ft x 15 ft x 8 ft = 2250 ft^3 = 63.8 m^3
- Ventilation rate = (0.3/hr)(34,000 L)(hr/60 min) = 319 L/min

Mass emitted = (2 cups/event)(1 gal/16 cups)(3.78 L/gal)(30 μg chloroform/L)

= 14.2 μg chloroform

Estimation of direct exposure

Initial room concentration = (14.2 μg chloroform)/63,800 L

= 2.23 x 10^{-4} μg/L

Average concentration in room (pulse injection, Equation 3-3, with $C_o = 2.23 \times 10^{-4}$ µg/L, t = 1 hour):

$C_g = 1.93 \times 10^{-4}$ µg/L

Exposure = (10.6 L/min)(1.93 x 10^{-4} µg/L air)(1 hr/day)(60 min/hr)

= 0.123 µg chloroform/day

Contribution to background concentration

Initial room concentration = (14.2 µg chloroform)/453,300 L

$= 3.13 \times 10^{-5}$ µg/L

Average concentration in room (pulse injection, Equation 3-3, with $C_o = 3.13 \times 10^{-5}$ µg/L, t = 10 hour):

$C_g = 9.19 \times 10^{-6}$ µg/L

Exposure = (10.6 L/min)(9.19 x 10^{-6} µg/L air)(10 hr/day)(60 min/hr)

= 0.058 µg chloroform/day

3.5.13. Inhalation exposure from toilets

Assumptions:

- Steady-state conditions
- Well-mixed house
- $K_L A = 0.07$ L/min (continuous); assumed value, Little (1996)

Writing a mass balance on the house:

$$\frac{d}{dt}(CV) = 0 = Q_g(C_{in} - C_g) + K_L A\left(C_l - \frac{C_g}{H_c}\right) = -Q_g C_g + K_L A\left(C_l - \frac{C_g}{H_c}\right)$$

$$C_g = \frac{C_l}{\frac{Q_g}{K_L A} + \frac{1}{H_c}} = \frac{30\,\mu g\ chloroform\ /L}{\frac{2267\ L/min}{0.07\ L/min}\left(\frac{hr}{60\ min}\right) + 0.17\ L/L} =$$

$= 9.26 \times 10^{-5}$ µg chloroform/L

Exposure = (10.6 L/min)(9.26×10^{-5} µg chloroform/L)(60 min/hr)(10 hr/day)

= 5.89 µg chloroform/day

3.5.14. Inhalation exposure from swimming pools

Assumptions:

- Adult inhalation rate = 1.9 m^3/hr (31.7 L/min); recommended for heavy activity, USEPA (1996)
- Average air concentrations for indoor pools for chloroform, bromodichloromethane, and dibromochloromethane, and bromoform are 90, 1.7, 0.9, and 9.0 µg/m^3, respectively (Armstrong and Golden, 1986)
- Time spent in pool = 60 minutes; mean value, USEPA (1996)
- Three swimming events/week

Exposure = (1.9 m^3/hr)(90 µg chloroform/m^3)(1 hr)(3/week)(week/7 days)

= 73.3 µg chloroform/day

3.5.15. Dermal exposure from swimming pools

Assumptions:

- Average liquid concentrations for indoor pools for chloroform, bromodichloromethane, and dibromochloromethane, and bromoform are 133, 33, 4.2, and <0.1 µg/L, respectively (Armstrong and Golden, 1986).
- Time spent in pool = 60 minutes; mean value, USEPA (1996)
- Three swimming events/week

- Mean adult surface area = 2.0 m^2; recommended value for bathing, USEPA (1996)
- L_{sc} = 16 μm; Bunge and Cleek (1995)
- Negligible resistance from viable epidermis ($P_{sc} = P_m$)
- Lag time = 5.0 minutes; typical value from Corley *et al*. (2000)

$R_{sc} = 10^{(0.71 \log 10 Kow)} = 10^{(0.71 \times 1.97)} = 25.04$

2.4 t_{lag} = 2.4 (5 minutes) = 12 minutes < $t_{exp} \Rightarrow$ steady-state conditions

$$M_{in} = AC_l\left[P_{sc}\, t_{exp} + \frac{(R_{sc}\, L_{sc})}{3}\right]$$

$$= \left(2.0\ m^2\right)\left(133{,}000\ \mu g/m^3\right)\left[(0.0013\ m/hr)(1\ hr) + \frac{(25.04)\left(16 \times 10^{-6}\right)}{3}\right]$$

= 381.3 μg/event

Exposure = (381.3 μg chloroform/event)(3 events/week)(week/7 days)

= 163.4 μg chloroform/day

3.5.16. Exposure from hot tubs

A recent industry survey estimated that 3.3 million residences own hot tubs (National Spa and Pool Institute, 1998). As this represents a relatively small percentage of the U.S. population, it will not be considered further for this research. It is possible, however, that elevated exposure may occur to this sub-population in cases of frequent hot tub usage.

3.5.17. Inhalation exposure from residential cleaning

Assumptions:

- Concentration in room during cleaning = 283 μg/m^3 (Wallace *et al*., 1987b)
- One cleaning event/month which uses bleach
- 30 minutes/event
- Room volume = 10 ft x 15 ft x 8 ft = 2250 ft^3 = 63.8 m^3
- Ventilation rate = (0.3/hr)(34,000 L)(hr/60 min) = 319 L/min

Estimation of direct exposure

Exposure = (10.6 L/min)(283 μg chloroform/m^3)(m^3/10^3 L)(30 min/event)(1 event/month) (month/31 days)

= 2.9 μg chloroform/day

Contribution to background concentration

An effective mass emission rate can be calculated. Using a step injection, Equation 3-2, with t = 30 minutes, Q_g = 319 L/min, the resulting emission rate for a final concentration of 283 μg/m^3 is:

Emission rate = 648 μg/min

Concentration in house at end of cleaning (step injection, Equation 3-2, with E = 648 μg/min, t = 30 minutes, Q_g = 2267 L/min):

C_g = 0.0398 μg/L

Average concentration in house after cleaning (decay, Equation 3-4, with C_o = 0.0398 μg/L, t = 10 hours):

C_g = 0.0126 μg/L

Exposure = (10.6 L/min)(0.0126 μg/L)(60 min/hr)(10 hr/month)(month/31 days)

= 2.6 μg chloroform/day

3.6. Hypothesis for proposed research

3.6.1. Rationale

Considerable attention has been given to balancing the risks between microbial infection and long-term health effects associated with DBPs. The costs associated with implementing more stringent DBP levels in drinking water are also significant. For example, the USEPA estimated that the cost of implementing the recently developed Stage I Disinfectants/Disinfection By-products Rule (in 1998 dollars) would be $701 million (Federal Register, 1998).

Despite such regulatory scrutiny, overall exposure to DBPs is still poorly characterized. The maximum contaminant levels described above are based entirely on traditional notions that ingestion of drinking water is the dominant exposure pathway. As described in Section 1.2.3, previous research has indicated that inhalation and dermal uptake are also significant. Incomplete characterization of DBP exposure has important consequences. First, it means that risks associated with DBP exposure are underestimated. Second, it points to a misallocation of resources. For example, common ways to lower DBP levels in drinking water include reducing DBP precursor levels (such as enhanced coagulation to reduce organic matter levels) or using alternative disinfectants (such as ozone). As noted above, these methods are marked by considerable financial burden. If the majority of one's DBP exposure comes from in-home sources, then it is unlikely that these control strategies will have a major impact on reducing overall exposure.

3.6.2. Screening assessment

The first major task of this research involved a screening assessment to determine DBP exposure from a variety of personal activities. A series of deterministic calculations of personal activities that contribute to DBP exposure was

completed. The intent of this screening assessment was to eliminate activities having negligible contribution to exposure and to identify gaps in knowledge.

A summary of exposure calculations is shown in Table 3-3. Results are given in terms of micrograms entering the body per day (µg/day) for each of the four THMs (chloroform, BDCM, DBCM, and bromoform). For THMs other than chloroform, daily exposure was estimated using the methodology described in Section 3.5. For some sources, the stripping efficiencies of BDCM, DBCM, and bromoform were different than those used for chloroform. For example, a stripping efficiency of 60% from showers was used for chloroform while a stripping efficiency of 15% was used for the other THMs. For sources with identical stripping efficiencies, daily exposure for the other THMs was equivalent to the ratio of liquid concentrations. Calculations include major non-occupational exposures to DBPs. It should be noted that the results from Table 3-3 on body burden via ingestion, inhalation, and dermal uptake were not reported using a common metric, e.g., bioavailable concentration.

For some of the activities listed in Table 3-3, the terms “from-plant” and “in-home” are used to denote where DBP formation occurs. The term “from-plant” refers to DBPs formed at the treatment plant or in the distribution system. Thus, “from-plant” inhalation exposure refers to DBPs formed from disinfection of drinking water and later emitted to indoor air. The term “in-home” refers to DBPs both formed and released indoors, e.g., DBPs resulting from dishwasher and washing machine usage with addition of chlorine-containing detergents. In addition, two types of inhalation exposures were considered: (1) “direct” exposure, where a person inhales chemicals in the same room as the given activity; and (2) “background” exposure, where a person inhales chemicals in the house from the contribution of a given activity to background concentration.

Table 3–3. Summary of exposure calculations.

Activity	Daily exposure (µg/day)			
	$CHCl_3$	DCBM	DBCM	$CHBr_3$
Drinking water (ingestion)	42	21	7.0	1.4
Carbonated beverages (ingestion)	14	7.1	2.4	0.47
Total ingestion	56	28	9.4	1.9
Showering (inhalation)				
Direct exposure	21	2.7	0.89	0.18
Background	16	2.1	0.68	0.14
Showering (dermal)	8.7	0.72	0.25	0.06
Total showering	46	5.5	1.8	0.38
Bath tubs (inhalation)				
Direct exposure	8.5	0.84	0.28	0.06
Background	6.7	0.67	0.22	0.04
Bath tubs (dermal)	34	3.9	1.7	0.54
Total bath tubs	49	5.4	2.2	0.64
Washing machines, from-plant (inhalation)				
Direct exposure	4.4	0.88	0.29	0.06
Background	14	2.8	0.93	0.19
Washing machines, in-home (inhalation)				
Direct exposure	1.9	n/d	n/d	n/d
Background	6.3	n/d	n/d	n/d
Total washing machines	27	3.7	1.2	0.25
Dishwashers, from-plant (inhalation)				
Direct exposure	2.1	0.52	0.17	0.03
Background	3.9	0.98	0.33	0.07
Dishwashers, in-home (inhalation)	n/d	n/d	n/d	n/d
Total dishwashers	6.0	1.5	0.50	0.10
Wash basins (inhalation)	0.1	0.01	>0.01	>0.01
Wash basins (dermal)	1.1	0.09	0.03	0.01
Total wash basins	1.2	0.1	0.03	0.01
Cooking (inhalation)				
Direct exposure	0.1	0.06	0.02	>0.01
Background	0.1	0.03	0.01	>0.01
Total cooking	0.2	0.09	0.03	0
Toilets, from-plant (inhalation)	5.9	3.0	0.98	0.20
Toilets, in-home (inhalation)	n/d	n/d	n/d	n/d
Total toilets	5.9	3.0	0.98	0.2
Indoor swimming pools (inhalation)	73	1.4	0.73	7.3
Indoor swimming pools (dermal)	163	4.4	0.70	0.02
Total swimming	236	5.8	1.43	7.3
Residential cleaning (inhalation)				
Direct exposure	2.9	n/d	n/d	n/d
Background	2.6	n/d	n/d	n/d
Total residential cleaning	5.5	n/d	n/d	n/d

n/d = no available data

Perhaps the most important result in Table 3-3 is that no one activity dominates DBP exposure. One notable exception to this finding is swimming in indoor pools, which is likely to be the most important activity for persons with high swimming frequency. Other sub-populations not considered for this research but that have potential for extreme DBP exposures include hot tub users, restaurant and hotel workers, and custodial workers. Another important general conclusion is that the number of times a given activity is completed per week is an important factor. For example, significant exposure per event can occur when bleach is added to laundry (approximately 40 μg chloroform/event, Section 3.5.8). However, only a small fraction of laundry loads use bleach for a typical household. In contrast, activities such as showering generally occur daily and thus constitute a greater fraction of overall exposure on a cumulative basis.

Ingestion of drinking water has traditionally been viewed as the major pathway for exposure to DBPs (Figure 3-1). Though significant contributions to body burden occur from this pathway (approximately 55 μg chloroform/day), it is clear that activities contributing to inhalation and dermal exposure are also significant. The most important of these appears to be either showering or bathing (approximately 50 μg/day for each), though it is unlikely that both of these activities occur on a daily basis. The next most important activities are from-plant inhalation from washing machines (16 μg/day), in-home inhalation from washing machines (7 μg/day), from-plant inhalation from toilets (6 μg/day), from-plant inhalation from dishwashers (5 μg/day), and inhalation from residential cleaning (5 μg/day). Similar trends are also evident for the other THMs. It is unlikely that either wash basins or cooking make significant contributions to overall DBP exposure and thus can be eliminated from further analysis. In addition, the calculations for residential cleaning probably represent an extreme case and will not be considered further in this research.

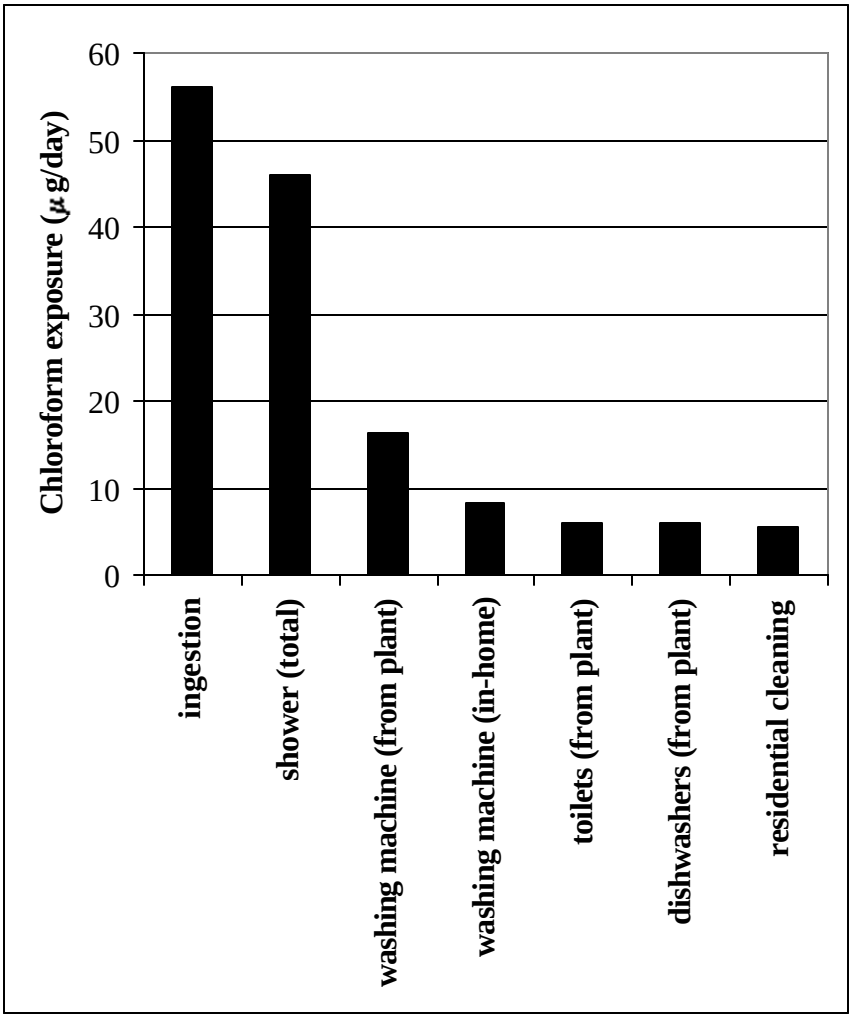


Figure 3-1. Summary of daily chloroform exposure for various activities. (Unless otherwise noted values refer to inhalation exposure)

3.6.3. Gaps in current understanding/research needs

It was hypothesized that dishwashers constitute a significant fraction of overall exposure to DBPs, based on data from similar processes as described below. A major component of this research included experiments to determine DBP formation in, and emissions from, dishwashers. The resulting data were then used to

challenge the hypothesis that these activities constitute a significant fraction of overall DBP exposure.

For several of the activities listed in Table 3-3, no experimental data are available to estimate DBP exposure. These include inhalation of in-home formation from dishwashers, inhalation of in-home formation from toilets, inhalation of in-home formation from washing machines (for THMs other than chloroform), and inhalation from residential cleaning (for THMs other than chloroform).

Since chloroform uptake from washing machines and residential cleaning are low relative to inhalation from showering (approximately 5 μg/day for each compared with 40 μg/day for showering), it is unlikely that significant exposure occurs from these activities for the other THMs.

It is tempting to reach a similar conclusion for in-home formation from dishwashers since from-plant exposure from this activity are also low relative to inhalation from showering (approximately 5 μg/day for each compared with 40 μg/day for showering). However, it is possible that significantly higher concentrations of DBPs in water result from dishwashers as compared with from-plant exposures. For instance, inhalation from showering (40 μg/day) is roughly eight times from-plant inhalation from dishwashing (5 μg/day). For an equivalent exposure, this means that the liquid concentration in the dishwasher resulting from in-home formation must be approximately eight times the concentration ordinarily found in tap water. For a typical chloroform concentration of 30 μg/L (see Appendix A), this would imply a chloroform concentration resulting from in-home formation that is on the order of 250 μg/L. Shepherd *et al*. (1996) measured chloroform concentrations in washing machines after 10 minutes in the wash water ranging from 800 to 1,500 μg/L. It is reasonable to argue that DBPs are at least as likely to form in a dishwasher as in a washing machine. Residence times for these devices are roughly equivalent on a per cycle basis. Temperatures are typically much higher in a dishwasher than in a washing machine.

4. GENERAL EXPERIMENTAL METHODOLOGY

The overall objective of these experiments was to identify and quantify DBPs that are formed and then emitted to indoor air as a result as dishwasher usage. Two types of experiments were completed. The first was a series of 14 preliminary flask experiments. These experiments involved mixing food and dishwasher detergent in water and were intended to identify chemicals that may form from dishwasher usage. The second type of experiment was a series of 16 laboratory experiments. These experiments were completed to quantify formation and emission of THMs from the use of chlorine-containing detergents in residential dishwashers.

4.1. Preliminary flask experiments

A series of preliminary experiments was completed to isolate possible effects of food type on DBP formation. A variety of different foods was successively placed in a 250-mL flask with 200 mL of water and 5 mL of Sunlight™ detergent. These volumes were selected since they were approximately proportional to volumes of wash water and detergent expected during the wash cycle. The flask was then heated at 40 °C for 12 minutes. One gram of each of the following foods were used: beans, beef, bread, cereal, eggs, fish, lima beans, oil, pasta, potatoes, poultry, rice, sugar, and tomatoes.

At the end of the 12-minute cycle, liquid samples were collected in 40-mL amber glass vials with Teflon™-lined screwcaps. Before collection of each liquid sample, approximately 0.5 g of sodium sulfite was added to each vial to quench additional formation of chlorinated by-products before analysis. Immediately after collection, samples were stored at 4 °C in a laboratory refrigerator until analysis. The time from sample collection to analysis was generally less than one week and in all cases less than two weeks. All liquid samples were analyzed as described in Section 4.7.

4.2. Dishwasher experiments

A Kenmore^{TM} dishwasher (Model No. 17651) was used for all experiments (Figure 4-1). The interior volume of the dishwasher was 188 L. It had five different cycles types: Quick Rinse, China Light, Water Miser, Normal, and Pots and Pans. The only difference between these options was the number of fill cycles, which would affect the total water volume used and length of operation. Normal operation consisted of four cycles: pre-rinse (6 minutes), wash (12 minutes), 1st rinse (8 minutes), and 2nd rinse (22 minutes).

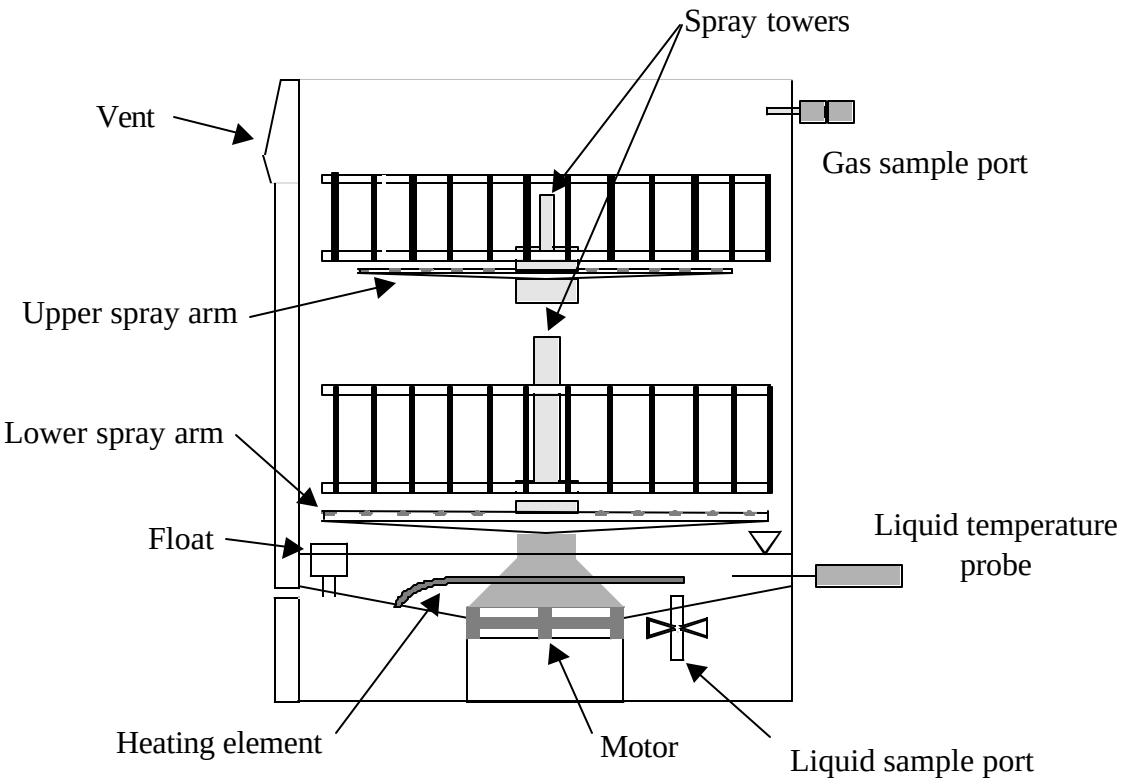


Figure 4-1. Dishwasher experimental system.

The dishwasher was connected to a municipal water supply; water entered the dishwasher at the start of each cycle. This process lasted approximately 100 seconds

such that 6.8 L of water filled the bottom of the dishwasher. Twenty seconds after the beginning of each fill cycle, water in the underlying pool was pumped to the rotary arm. The rotary arm sprayed water throughout the dishwasher headspace. During the wash cycle, detergent was released into the underlying pool. At the end of each cycle, the water in the underlying channel was pumped to a drain. After completion of all wash and rinse cycles, the dishwasher began a drying cycle of approximately 30 minutes. Approximate cycle timings are listed in Table 4-1.

Table 4–1. Approximate cycle timings.

Cycle	Cycle time (min)	Total elapsed time (min)
Pre-rinse	6:00	6:00
Wash	12:00	18:00
1st rinse	8:00	26:00
2nd rinse	22:00	48:00

The dishwasher was retrofitted for collection of liquid and gas samples. A liquid sample port was connected to the bottom of the dishwasher. The port consisted of a 15-cm length of 0.635-cm o.d. Teflon^{TM} tubing. The port inlet was observed to be submerged at all times. A gas sampling line was installed by connecting 0.635-cm o.d. Teflon^{TM} tubing to the inside of the dishwasher headspace. All gas sampling connections were held in place by 0.635-cm i.d. Swagelok^{TM} fittings. In addition to liquid and gas sampling ports, a thermocouple probe was submerged in the dishwasher to allow for measurement of liquid temperature. A thermocouple probe was also placed in the dishwasher headspace.

4.3. Experimental design

A series of twelve experiments (and four replicate experiments) was completed; these experiments represented a range of environmental and operating

conditions (Table 4-2). It was anticipated that the following parameters would be important factors in DBP formation: water temperature, food type, dish soap amount, and detergent type. Two different water temperatures were possible for this dishwasher model: normal dish cycle (approximately 41 ºC) and water heat option (approximately 54 ºC). Experiments were completed using either a "standard" food mix or an actual food mix. The actual food mix refers to dirty dishes obtained from an actual house. The purpose of using actual dishes was to verify whether the "synthetic" mix was representative of a typical household.

Table 4–2. Experimental operating conditions.

Expt.	Water temp. (ºC)	Food type	Food amount	Dish soap amount	Detergent
1	41	Actual	Std.	Normal	Sunlight™
1 (Rep)					
2	54	Actual	Std.	Normal	Sunlight™
3	41	Actual	Rinsed	Normal	Sunlight™
4	41	Std.	Std.	Normal	Sunlight™
4 (Rep)					
4 (Rep)					
5	41	Std.	Std.	Normal	Electrasol™
6	41	Std.	Std.	Normal	Cascade™
7*	41	Std.	Std.	Normal	Sunlight™
8**	41	Std.	Std.	Normal	Sunlight™
9	41	Std.	Std.	Max.	Sunlight™
10	54	Std.	Std.	Normal	Sunlight™
10 (Rep)					
11	41	Std.	Rinsed	Normal	Sunlight™
12	41	None	None	Normal	Sunlight™

*Additional liquid and gas samples collected
**Only three cycles used

A "standard" food mix was used for most experiments based on a USDA survey of food intake by U.S. consumers (USDA, 1997). The 1994-96 Continuing

Survey of Food Intakes by Individuals contains survey data from 16,103 individuals on 1-day dietary intake and from 15,303 individuals on 2-day dietary intake (USDA, 1997). The survey reported food intake from the following broad categories: grain products, vegetables, fruits, milk and milk products, meat, poultry, and fish, eggs, legumes, nuts and seeds, fats and oils, sugars and sweets, and beverages. Many of these categories, e.g., vegetables, were further subdivided into more specific foods. A summary of food intakes from the USDA (1997) that was used for this research is given in Table 4-3.

Table 4–3. Food intake from USDA (1997).

Food	Mean consumption (g/day)*
Yeast, breads and rolls	50
Cereal	16
Rice	23
Pasta	18
Mixtures (mainly grains)	109
White potatoes	61
Tomatoes	28
Corn, green peas, and lima beans	13
Beef	24
Poultry	25
Fish and shellfish	10
Mixtures (mainly beef, poultry, fish)	99
Eggs	18
Legumes	25
Fats and oils	14
Sugars	25
Total	558

*Based on data from all individuals

For several foods it is expected that only a small fraction would be left on dishware. These included fruits, milk and milk products, and beverages, each of which was omitted from the standard food mix. In addition, foods with comparatively small mean consumption rates, i.e., less than 10 g/day, were omitted from the standard food mix. Mixtures of grains were divided equally between rice and pasta. Mixtures of meats were divided equally between beef, poultry, and fish. It was assumed that 5% of the food amounts listed in Table 4-3 was left on dishware. By visual inspection, these amounts appeared to be reasonably representative of a household that did not rinse plates before operating the dishwasher. Since typical dishwasher usage has been to reported as 3 events/week/person (USEPA, 1996), this corresponds to approximately one dishwasher event every two days. The mass of food for each experiment using the standard mix can be calculated. Using two days food consumption and 5% of food remaining on the dishware, this corresponded to (558 g/day)(2 days)(0.05) = 56 g food.

Two different dishwasher soap amounts were used: normal and maximum. A normal dish amount refers to the recommended level of dish soap for the dishwasher. A maximum dish amount was approximately twice the recommended level and was characterized by overflow to the outside soap compartment.

There are numerous dishwashing detergents on the market, many of which contain chlorine as a disinfectant. Three different detergent brands were used for this study: Cascade™, Electrasol™, and Sunlight™. These three brands were the highest selling dishwasher detergents based on a recent survey (Brandweek, 1998). It is important to note that, of the three brands tested, only Sunlight™ contained chlorine; Cascade™ also has a formulation containing chlorine, but the non-chlorine containing formula was used here. All detergent brands were used under normal operating conditions with the standard food mix for comparative purposes (Experiments 4-6). The remaining experiments were completed using Sunlight™ detergent.

In addition, one experiment was completed using clean dishes and detergent to quantify chemicals formed from organic matter in the drinking water and not originating from organic matter on the dishes (Experiment 15). Two experiments were completed using rinsed dishes, one with the standard food mix (Experiment 16) and one with actual dishes (Experiment 17). The purpose of these experiments was to determine the extent to which plate rinsing can lower the organic content in the wash water and thereby lower emissions.

Three experiments were replicates (Experiments 1, 5, and 11); this corresponded to approximately 15% of the experiments.

4.4. Target chemicals

The four THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) were selected to be the focus of the laboratory study. These chemicals were chosen because they are more volatile than other commonly-analyzed DBPs, e.g., HAAs and HANs, and thus more likely to contribute to higher inhalation exposures. Table 4-4 lists a few relevant physicochemical properties.

Table 4–4. Summary of physicochemical properties for target chemicals.

Compound	H_c at 25°C (m^3_{liq}/m^3_{gas})	vapor pressure (atm)	T_b (°C)
Chloroform[1]	0.16	0.26	61.7
Bromodichloromethane[2]	0.12	0.078	90
Dibromochloromethane[2]	0.032	0.020	120.2
Bromoform[1]	0.025	0.0074	149.5

(1) Schwarzenbach *et al*. (1993)
(2) USEPA (1994)

4.5. Sample collection

4.5.1. Liquid-phase sampling

Liquid samples were collected using 6-mm i.d. Teflon™ tubing and a Masterflex™ peristaltic pump (Cole-Parmer model 7553-70) connected to the liquid sampling port. Samples were collected in 40-mL amber glass vials with Teflon™-lined screwcaps. Prior to collection of each sample the sample lines were flushed for approximately 30 seconds to remove any residual from previous samples. Before collection of each liquid sample approximately 0.5 g of sodium sulfite was added to each vial to quench additional formation of chlorinated by-products before analysis. Immediately after collection, samples were placed in a cooler containing ice packs. Immediately after each experiment was completed, samples were stored at 4 °C in a laboratory refrigerator until analysis. The time from sample collection to analysis was generally less than one week and in all cases less than two weeks.

A total of six liquid samples (and two duplicates) was collected during experiments (Table 4-5). The first sample was a tap water sample (before dishwasher usage) and the remaining samples were collected during dishwasher operation. One sample was collected during each cycle, and an additional sample was collected at the end of the 2nd rinse cycle. Samples were collected at the middle of each cycle.

Table 4–5. Liquid sampling schedule.

Sample	Cycle	Time (min)
1*	n/a	n/a
2	Pre-rinse	3:00
3	Wash	12:00
3D (duplicate)		
4	1st rinse	22:00
5	2nd rinse	36:00
5D (duplicate)		
6	2nd rinse	48:00

*tap water sample

4.5.2. Gas-phase sampling

Gas samples were collected by drawing dishwasher headspace air through adsorbent tubes using a gas sampling pump (Figure 4-2). The sample pump was activated for approximately 30 seconds before each sample was collected in order to remove residual chemical mass from the sampling line. Air was drawn from the headspace via 6-mm i.d. Teflon™ tubing into a Tenax® TA sorbent tube (6 mm o.d. x 178 mm). The air then passed through a bubble flowmeter (SKC UltraFlo™ Model No. 709). Finally, the air was drawn through a personal sampling pump with manifold for flow calibration (SKC PCXR8) and was discharged into ambient air. Stainless steel Swagelok™ fittings with Teflon™ ferrules were used at all connection points in the sampling train.

The volume of air drawn through the sorbent tube was determined from the sampling flow rate (using the bubble flowmeter) and sampling time. Sample flowrates were typically between 0.06 L/min and 0.10 L/min. Immediately after collection, samples were sealed with Swagelok™ end caps and placed in a cooler containing ice packs. Immediately after each experiment was completed samples were stored at 4 °C

in a laboratory refrigerator until analysis. The time from sample collection to analysis was generally less than two days and in all cases less than one week.

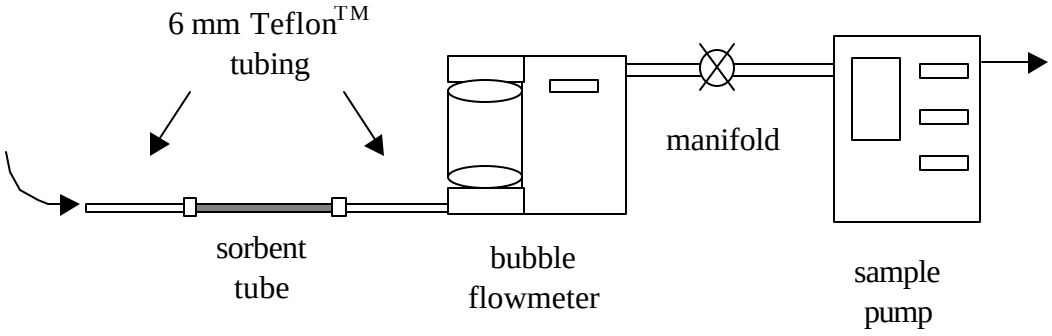


Figure 4-2. Gas sampling train.

A total of six gas samples was collected during experiments (Table 4-6). One background sample was collected before each experiment. Breakthrough sample tubes (two sample tubes connected in succession) were used for the third sample of each experiment. Sample collection lasted 4 minutes and was scheduled such that a liquid sample was collected at the midpoint of the gas sampling time.

Table 4–6. Gas sampling schedule.

Sample	Cycle	Time (min)
1*	n/a	n/a
2	Pre-rinse	1:00-5:00
3	Wash	10:00-14:00
3B (breakthrough)		
4	1st rinse	20:00-24:00
5	2nd rinse	34:00-38:00
6	2nd rinse	46:00-50:00

*Background sample

4.5.3. Water quality parameters

In addition to gas and liquid sampling, the following water quality parameters were measured: pH, liquid temperature, air headspace temperature, total organic carbon (TOC), free and total chlorine, and ultraviolet absorbance at 254 nm wavelength (UV-254). Liquid samples for pH, TOC, free and total chlorine, and UV-254 were collected with no headspace in 40-mL amber glass vials with Teflon^{TM}-lined screwcaps. Liquid samples were filtered for subsequent analysis using a filtering apparatus with P5 medium porosity filter paper (Fisher Scientific No. 09-801J).

Three samples were collected for pH, TOC, free and total chlorine, and UV-254. Samples were collected during the pre-rinse cycle (3:00 total elapsed time), wash cycle (12:00 total elapsed time), and 1st rinse cycle (36:00 total elapsed time). Liquid and air headspace temperature were measured during the wash cycle (12:00 total elapsed time) and 1st rinse cycle (36:00 total elapsed time). Analyses for pH and UV-254 were completed immediately after completion of an experiment. TOC samples were stored in a refrigerator maintained at approximately 4 ºC until analysis. Free and total chlorine samples were analyzed immediately after collection.

4.6. Sample storage

During the period between collection and analysis, vials were stored in a laboratory refrigerator maintained at 4 °C. Previous research had shown that vials stored in such a manner experienced minimal tracer losses after several days of storage (Shepherd, 1996). Sorbent tubes were stored in a laboratory refrigerator maintained at 4 °C. Previous research indicated that minimal sample deterioration occurs after one week of storage at 4 °C (Fitzgerald, 1996).

4.7. Sample preparation and analysis

4.7.1. Liquid sample analysis

All liquid samples were analyzed using a purge and trap autosampler (Tekmar ALS 2016) plumbed to a gas chromatograph (Hewlett Packard, 5890 Series II Plus) equipped with a mass selective detector (MSD, HP 5971A). A 50-m capillary column was installed in the GC (Osge model 054950 BP1 PONA, 0.15-mm i.d.). The purge and trap autosampler was equipped to analyze up to 16 samples successively. For each sample, a 10-mL liquid volume was purged with high-purity helium for a period of 12 minutes. Chemicals purged from this step were collected onto an internal concentrating trap. This trap with then desorbed for 4 minutes at a temperature of 250 °C. Helium gas was used to transfer chemicals from the concentrating trap to the GC capillary column. The GC oven temperature was initially maintained at 35 °C, ramped at a rate of 7 °C/min until reaching a temperature of 70 °C, and then ramped at a rate of 20 °C/min until a final temperature of 170 °C was reached. The total GC run time was 16.0 minutes. MSD parameters included a solvent delay of 6 minutes, scans from masses 35.0 to 350.0 amu, and 1.45 scans/second. Chromatographic analysis was completed using Hewlett-Packard ChemStation Version B.02.05 and EnviroQuant ChemStation G1701BA Version B.01.00.

For all liquid sample batches, the first two vessels in the purge and trap autosampler were used for quality assurance purposes. Vessel 1 was a blank consisting of distilled water and was used to verify that no contamination was present in any of the purge and trap lines or the GC/MS lines. Vessel 2 consisted of the internal standards at a concentration of 10 µg/L in distilled water. This was to check whether any of the target compounds were in the distilled water (since distilled water was used to clean the purge and trap vessels). The remaining vessels consisted of the actual samples. In all cases, a 10-mL liquid sample was analyzed.

4.7.2. Liquid standards

A volatile standard mix (NSI Solutions) at an initial concentration of 2,000 μg/mL was used for liquid standards. This solution was diluted by mixing 40 μL of the original standard mix with 0.960 mL of purge and trap grade methanol (Sigma-Aldrich) in 2-mL vials with Teflon™-lined screwcaps. Internal standards containing chlorobenzene, flourobenzene, and 1,4-dichlorobenzene at a concentration of 2,500 μg/mL (NSI Solutions) also were used for liquid standards. An internal standard solution with a concentration of 10 μg/mL was prepared by mixing 4 μL of the original solution with 0.996 mL of purge and trap grade methanol in 2-mL vials with Teflon™-lined screwcaps. A 10-μL volume of the 10-μg/mL internal standard solution was injected into every sample and calibration standard for quantification purposes. Sample quantitation was based on GC response for target chemical and internal standard from both the sample and the calibration standard.

Concentrations of target chemicals of 1, 5, 10, 20, 50 and 100 μg/L were used for calibration curves. Calibration standards were prepared by injecting the appropriate volume of VOC mix solution and 10 μL of the 10-μg/mL internal standard mix into 10 mL of distilled water. Calibration standards were analyzed by purge and trap and GC/MSD using the same methodology as for liquid samples (Section 4.7.1). Calibration curves were linear for all compounds, with R^2 values ranging from 0.999 for chloroform and bromoform to 1.000 for bromodichloromethane and dichlorobromomethane. Liquid calibration curves are presented in the Appendix. An example liquid calibration curve is shown in Figure 4-3 for chloroform.

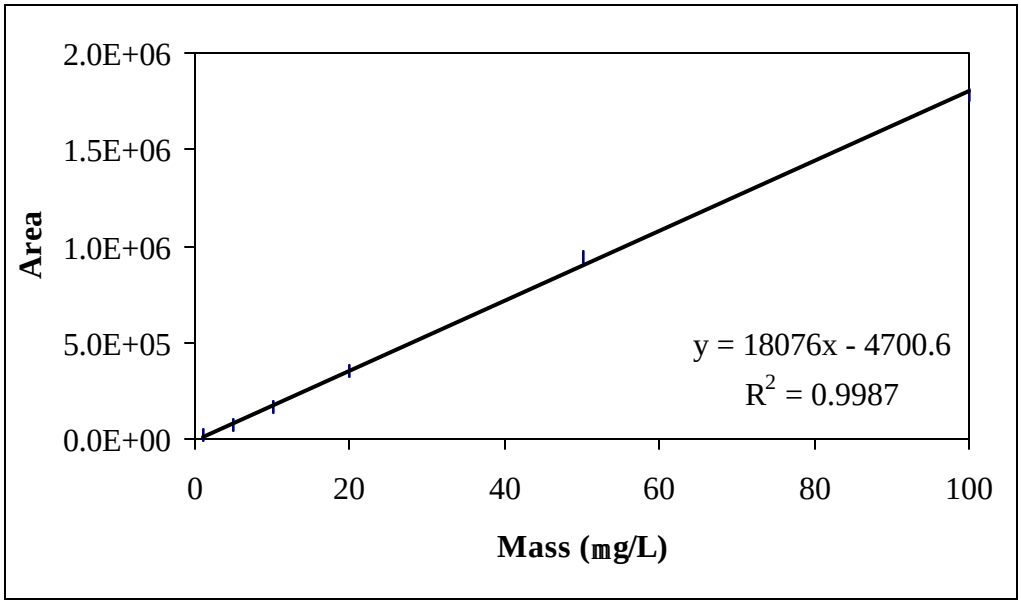


Figure 4-3. Liquid calibration curve for chloroform.

4.7.3. Gas sample analysis

Gas samples were analyzed using a thermal desorber (Tekmar 1600 Aerotrap) and purge and trap controller (Tekmar 3000). This system was plumbed to the GC/MSD described above. The thermal desorber autosampler allowed for up to 16 samples to be analyzed for a given set. Two blanks were used to check for internal system contamination. These blanks were placed in the first and ninth positions of the autosampler.

To analyze gas samples, sorbent tubes were first placed in the thermal desorber (Tekmar 1600 Aerotrap). Each tube was then heated at 225 °C for a period of 8 minutes as chromatographic grade helium was swept through the heated tube. Chemicals removed from the tube were concentrated onto an internal concentrating trap located in a purge and trap controller (Tekmar 3000) via a transfer line maintained at a temperature of 200 °C. The internal trap was then desorbed for two minutes at 225 °C and chemicals were carried by helium gas to the GC/MSD

injection port. GC/MSD methods parameters were identical to those used for liquid samples (Section 4.7.1).

4.7.4. Gas standards

Gas standards were made from the same VOC standards described in Section 4.6.2. The appropriate volume of diluted standard was injected into five different sorbent tubes that had previously been tested to be clean. Concentrations of target chemicals of 50, 100, 200, 400 and 800 nanograms (ng) were used for calibration curves. Calibration standards were analyzed by thermal desorption and GC/MSD using the same methodology as for gas samples (Section 4.6.3). Calibration curves were linear for all compounds, with R^2 values ranging from 0.994 for bromoform and limonene to 1.000 for dichlorobromomethane. Gas calibration curves are presented in the Appendix. An example gas calibration curve is shown in Figure 4-4 for chloroform.

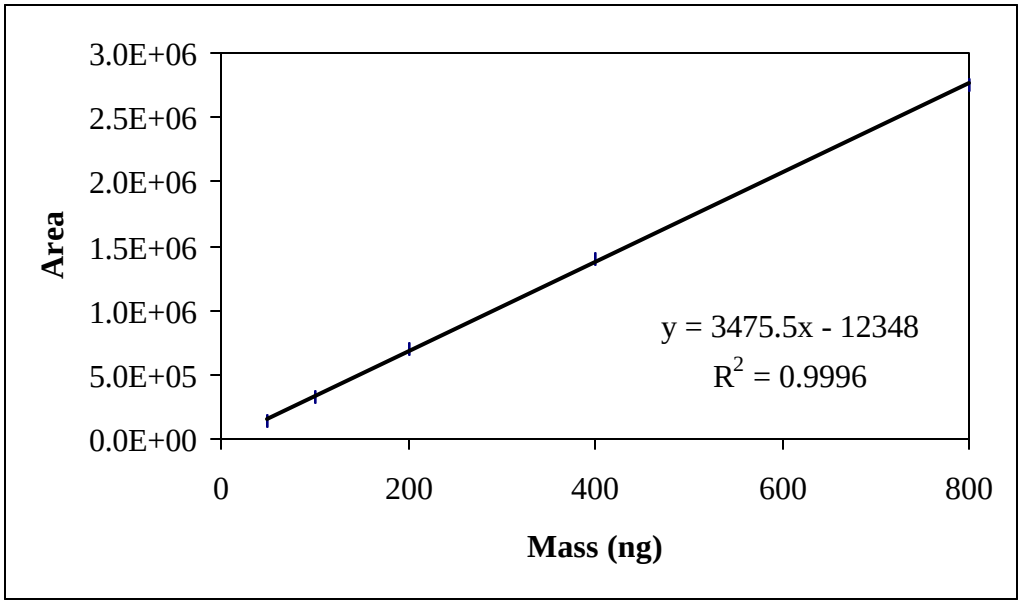


Figure 4-4. Gas calibration curve for chloroform.

4.7.5. Water quality parameters

The pH was measured using an Accumet Model 50 pH/ion/conductivity meter. Liquid and air temperatures were measured using thermocouples. TOC samples were analyzed using a Tekmar Dohrmann Apollo 9000 using Standard Method 5310B (Standard Methods, 1989); calibration standards were developed using potassium hydrogen phthalate. Calibration curves were linear for all experiments, with R^2 values ranging from 0.997 to 0.999. Free and total chlorine analysis was completed using Standard Method 4500-Cl F and G (Standard Methods, 1989). UV-254 was measured using a Turner Model 690 Spectrophotometer with a Model 69F02-01 UV-vis source.

4.7.6. Preventative maintenance

Changes in column temperature, carrier gas flows, injection techniques, injection leaks, and contamination of the column can lead to shifts in GC retention times. Since these occurrences could lead to confounding experimental results, several preventative procedures were completed. The GC column was routinely conditioned to remove residual volatile compounds. The plumbing system was monitored for leaks. Fittings, column connections, and septum were all monitoring as part of this check. Gas cylinder pressures were kept above 500 psi since lower pressures could damage the gas chromatograph system.

4.7.7. Conditioning and cleaning of sample devices

Sampling devices that required cleaning included glassware, sorbent tubes, and syringes. For glassware, each item was washed with hot soapy water and a brush. Glassware was then rinsed with clean hot water where the final rinse consisted of deionized water.

Following analysis, each sorbent tube was cleaned in a thermal conditioner (Tekmar Thermotrap). For a period of two hours, 250 °C chromatographic grade

nitrogen was allowed to flow through each tube, removing residual tracers from the adsorbent. The tubes were then capped by stainless steel Swagelok^{TM} end caps to prevent contamination prior to their next use. For each set of sorbent tubes cleaned, at least one tube was randomly selected and analyzed using the GC/MSD to check that no chemicals were present.

Before each set of injections, syringes were flushed three times with methanol and three times with deionized water. In each case a full sample of solvent or water was drawn into the syringe. All syringes were cleaned in this manner before use of a new chemical.

4.8. Quality assurance objectives and measures

4.8.1. Duplicate samples

Duplicate liquid samples were collected for every experiment. For this research, duplicate samples refer to samples that were collected sequentially and differed in time by less than 20 seconds. Any sample where duplicates were not within 20% of one another was discarded from further analysis.

4.8.2. Replicate experiments

For this research, replicate experiments refer to experiments that were completed under approximately identical conditions, but not at sequential times. For this study, 20% of dishwasher experiments were repeated.

4.8.3. Data quality assessment

Relative percent difference (RPD) was used to quantify differences in concentrations for duplicate samples and replicate experiments:

$$\text{RPD} = \frac{(C_1 - C_2)}{(C_1 + C_2)/2} \text{x}\, 100\% \qquad (4\text{-}1)$$

where,

RPD = relative percent difference (%)

C_1 = larger of two observed values

C_2 = smaller of two observed values

4.8.4. Breakthrough sorbent tube samples

At least one breakthrough sorbent tube sample (two sample tubes connected in succession) was collected for each experiment. Breakthrough tubes were collected to insure that the chemical mass collected during sampling did not exceed the capacity of the tube.

4.8.5. Experimental blanks

At least two blanks were analyzed for each set of experimental samples. These blanks were prepared and analyzed in a manner similar to experimental samples. The concentration of target chemicals in the analytical blanks were in all cases below the detection limit.

4.8.6. Method detection limit

The method detection limit was defined as:

$$MDL = t_{(n-1,1-\alpha=0.99)} \bullet s_r \qquad (4\text{-}2)$$

where,

MDL = method detection limit

s = sample standard deviation of replicate analyses

$t_{(n-1,1-\alpha=0.99)}$ = student's t value for a one-sided 99% confidence level and a standard deviation estimate (s_r) with n-1 degrees of freedom. This estimate assumes that concentration is normally distributed and samples are statistically independent.

The USEPA method for determining MDLs involves preparation of seven aliquots of a prepared solution. The resulting value of t for 7 samples (6 degrees of

freedom) with 99% confidence is 3.143. Method detection limits were completed for both liquid and gas sampling methods using spiked amounts of target chemicals and were analyzed using the procedures described in Section 4.6. MDLs for liquid sampling are listed in Table 4-7.

Table 4–7. Liquid sampling MDLs.

Target chemical	MDL (μg/L)
Chloroform	0.06
BDCM	0.05
DCBM	0.16
Bromoform	0.28

The MDLs for gas sampling are listed in Table 4-8. The detection limit on a concentration basis is sample specific and depends on sampling time and flow rate. For a typical sampling time of 4 minutes and sample flow rate of 75 mL/min, an MDL of 2.00 ng would correspond to 6.67 $\mu g/m^3$. These detection limits on a concentration basis may be relatively high, especially compared with background concentrations of VOCs typically on the order on 1-10 $\mu g/m^3$ (Chapter 2). However, the detection limits are a result of the relatively short sample time (compared with typical 8-hour samples). Furthermore, chemicals were much more concentrated in the dishwasher headspace during experiments relative to background.

Table 4–8. Gas sampling MDLs.

Target chemical	MDL (ng)
Chloroform	2.18
BDCM	3.50
DCBM	2.50
Bromoform	2.00
Limonene	1.15

4.9. Data analysis

4.9.1. Gas sample data

As described in Section 4.6, gas samples were analyzed in terms of mass collected on a particular sorbent tube. The concentration in the dishwasher headspace was calculated by dividing the mass by the sample flow rate and time:

$$\overline{C} = \frac{m}{Q\,t} \tag{4-3}$$

where,

$\overline{C}$ = average concentration in dishwasher headspace for sample time (ng/L)

m = mass collected on sorbent (ng)

Q = sample flow rate (L/min)

t = sample time (min)

4.9.2. DBP formation rates

Howard-Reed *et al*. (1999) presented a mass balance model to predict liquid and gas concentrations in a dishwasher as a function of time. Assuming liquid and gas phases are each well-mixed and that background air concentrations are negligible, the following mass balances resulted:

$$\frac{dC_l}{dt} = -\frac{K_L A}{V_l} C_l + \frac{K_L A}{V_l H_c} C_g \tag{4-4}$$

$$\frac{dC_g}{dt} = \frac{K_L A}{V_g} C_l - \left(\frac{Q_g}{V_g} + \frac{K_L A}{V_l H_c} \right) C_g \tag{4-5}$$

where

C_l = chemical concentration in the liquid phase (µg/L)

t = time (min)

$K_L A$ = overall mass transfer coefficient (L/min)

V_l = liquid volume of dishwasher (L)

H_c = Henry's law constant for a chemical of interest (L_{liq}/L_{gas})

C_g = chemical concentration in the gas phase (µg/L)

V_g = volume of dishwasher headspace (L)

Q_g = headspace ventilation rate (L/min)

Experiments completed by Howard-Reed *et al*. (1999) involved liquid tracer chemicals and were aimed at quantifying transfer to the gas phase of chemicals that were originally in the liquid phase. The focus of the present research is on formation (and subsequent release) from the liquid phase of DBPs. Equation 4-4 can be modified as follows:

$$\frac{dC_l}{dt} = -\frac{K_L A}{V_l} C_l + \frac{K_L A}{V_l H_c} C_g + R_{form} \qquad (4\text{-}6)$$

where

R_{form} = rate of chemical formation in the liquid phase (µg/L-min)

5. LABORATORY RESULTS

5.1. Chlorine analysis of detergents

Three detergent brands were used for this research: Cascade™, Electrasol™, and Sunlight™. Five milliliters of each detergent were successively combined with 500 mL of distilled water. Free and total chlorine analyses were then completed on each detergent using Standard Method 4500-Cl F. Triplicate samples were analyzed for each detergent. Resulting free chlorine concentrations (based on average of triplicate samples) were 0.0 mg/L for Cascade™, 0.0 mg/L for Electrasol™, and 4.2 mg/L for Sunlight™. Resulting total chlorine concentrations (based on average of triplicate samples) were also 0.0 mg/L for Cascade™, 0.0 mg/L for Electrasol™, and 4.2 mg/L for Sunlight™. Most experiments were completed using Sunlight™ detergent, though two dishwasher experiments were completed using Cascade™ and Electrasol™ as verification of the above results.

5.2. Flask experiments

A summary of the flask experiments is given in Figure 5-1. Liquid-phase concentrations of chloroform at the end of a 12-minute cycle are given for each of the 14 foods tested. All the foods shown in Figure 5-1 were also used in the standard mix (described in Section 4.3). Chloroform concentrations were approximately three orders of magnitude greater than typical tap water concentrations measured during this research (which were generally from 0 to 5 µg/L). Across all food types, the average concentration of chloroform was 7.8 mg/L; the median value was 2.7 mg/L.

Dibromochloromethane and bromoform were not detected in any of the flask samples. Bromodichloromethane was only detected in 4 of the 14 flasks, where each of those samples were less than 0.5 mg/L. The trend that only chloroform was detected may have been caused by high chloroform concentrations masking the

presence of other THMs. Sample dilution needed to quantitate chloroform levels likely led to lowering other THM levels to below instrument detection.

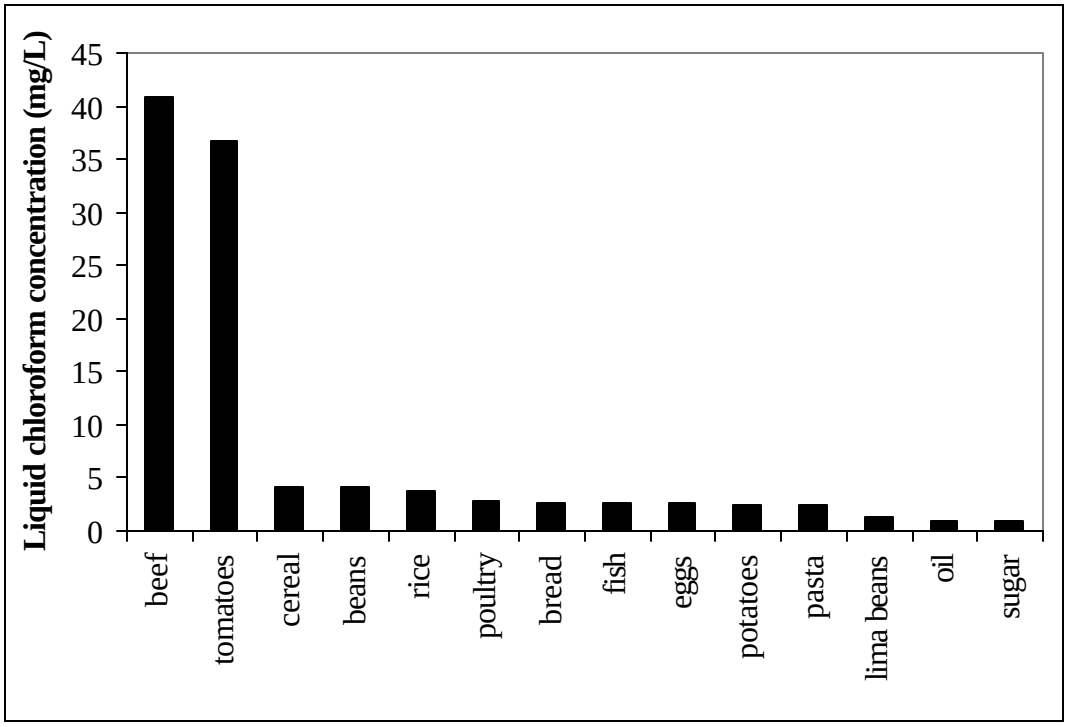


Figure 5-1. Summary of flask experiments.

Food type clearly has an effect on resulting chloroform concentrations in the liquid phase. The amount of protein in a particular food was expected to affect resulting concentrations, since DBPs are thought to form mainly from this type of organic matter. However, these foods had a relatively narrow range of protein contents, ranging from 0.05 g protein/g food for beans to 0.16 g protein/g food for fish (based on manufacturer's nutrition labels).

The other factor most likely to influence DBP formation was protein solubility, i.e., the amount of protein in a sample that dissolves in solution. Li-Chen *et al*. (1985) reported protein solubilities near 100% for beef, results that are consistent with those in Figure 5-1. Although protein solubilities for other meats are also

relatively high, the actual solubility is affected by the number of days that the meat was stored frozen (Zayas, 1997). Both the fish and poultry used for these experiments were frozen before use, so this may explain why resulting concentrations were lower than those for beef.

Relatively high chloroform concentrations were also observed for tomatoes, although this food has relatively little protein. Protein solubility has been noted to increase under acidic conditions (Zayas, 1997). It is possible that the tomatoes lowered the pH such that the organic matter was much more soluble, though data on pH and TOC were not collected for flask experiments and would be needed to confirm this hypothesis.

Values of protein solubilities have not been reported for the type of beans used in the flask experiments (pinto beans). Values have been reported for other beans, ranging from 14% for tepary beans (Idouraine *et al*., 1991) to as high as 86% for faba beans (Sosulski and McCurdy, 1987). It is possible that protein solubility accounted for most of the difference between chloroform formed from beef and from beans, though this would suggest that the beans used for flask experiments were near minimum values from the literature.

Data are less available for vegetables and grains, though Bera and Mukherjee (1989) reported rice protein solubilities ranging from 13 to 75% and Jackman and Yada (1998) reported potato protein solubilities ranging from 80 to 99%. These data do not entirely account for differences with the beef results, though in the case of grains it is possible that food processing had an effect on protein solubility (Zayas, 1997).

5.3. Dishwasher experiments

A total of 16 experiments were completed over a range of environmental and operating conditions to examine THM formation and subsequent release from dishwashers. Across all experiments, 137 liquid samples and 81 gas samples were

collected (excluding background samples). For the liquid samples, chloroform was detected and above the MDL in all 137 samples. Bromodichloromethane and dibromochloromethane were detected and above the MDL in 74 (54%) and 26 (19%) samples, respectively. In no liquid sample was either of these THMs detected but below the MDL. For the gas samples, chloroform, bromodichloromethane and dibromochloromethane were detected and above the MDL in 78 (96%), 48 (59%) and 12 (15%) samples, respectively. Chloroform, bromodichloromethane and dibromochloromethane were detected but below the MDL in an additional 1, 6, and 1 samples, respectively. Bromoform was not detected in any liquid or gas samples. The lack of bromoform in liquid or gas samples was likely due to high TOC levels in the wash water, since chloroform outcompetes other species under these conditions and less bromo-species are formed.

A total of 31 duplicate liquid samples was collected for all experiments. Nineteen duplicate samples had relative percent differences (RPDs) of less than 5%. An additional four duplicates had RPDs between 5 and 10%. Of the remaining eight duplicates, six of those samples had low chloroform concentrations (less than 5 μg/L) and RPDs were thus sensitive to division by small numbers. Thus, the duplicate samples reflected a reasonable degree of compatibility.

5.3.1. Typical dishwasher experiment

Chloroform concentrations for Experiment 7 are shown in Figure 5-2, where liquid concentrations (left vertical axis) and gas concentrations (right vertical axis) are given as a function of time. Horizontal bars are used to represent gas samples collected over a 4-minute sampling interval. Liquid and gas samples shown at time = 0 minutes were background samples collected before the experiment.

Experiment 7 was one of four experiments completed using the standard food mix, recommended detergent amount, and Sunlight^{TM} detergent. For liquid samples, chloroform concentrations during the pre-wash cycle were relatively small (<5 μg/L).

Chloroform concentrations in the liquid phase increased as detergent was released during the wash cycle, reaching a maximum of approximately 50 μg/L at the end of the cycle. The concentration decreased throughout the two rinse cycles. This result is expected since the dish water was drained at the end of a cycle and then replaced with clean water as a new cycle began. It was likely that not all of the detergent, residual chlorine, and organic compounds were removed from the system at the end of the wash cycle, which explains why liquid chloroform levels did not immediately approach background levels at the start of the 1st rinse cycle. By the end of the 2nd rinse cycle, chloroform concentrations in the liquid phase approached background levels.

For gas samples, chloroform concentrations during the pre-wash cycle were also relatively small (below detection limit of 0.008 μg/L). Chloroform concentrations in the gas phase increased during the wash cycle as chloroform formed in the liquid was transferred to the dishwasher headspace. Chloroform concentrations continued to increase throughout the entire wash cycle, reaching a maximum of approximately 3 μg/L at the end of the cycle. The concentration decreased throughout the two rinse cycles. By the end of the 2nd rinse cycle, chloroform concentrations in the gas phase approached a concentration of approximately 1 μg/L.

Liquid data from the wash cycle were highly linear; the linear r^2 value for the regression of chloroform concentration with time was 0.97. The linear trend also suggests that time (not the concentration of reactants) limited the formation of THMs in the dishwasher. It is likely that the rate of THM formation depends on the concentration of chlorine and the concentration of organic matter, i.e.:

$$\frac{dC_{THM}}{dt} = k\, C_{Cl}(t)\, C_{OM}(t) \qquad (5\text{-}1)$$

where

C_{THM} = concentration of THM in the liquid phase (μg/L).

k = rate constant (L/μg/t).

C_{Cl} = concentration of chlorine in the liquid phase (μg/L).

C_{OM} = concentration of organic matter in the liquid phase (μg/L).

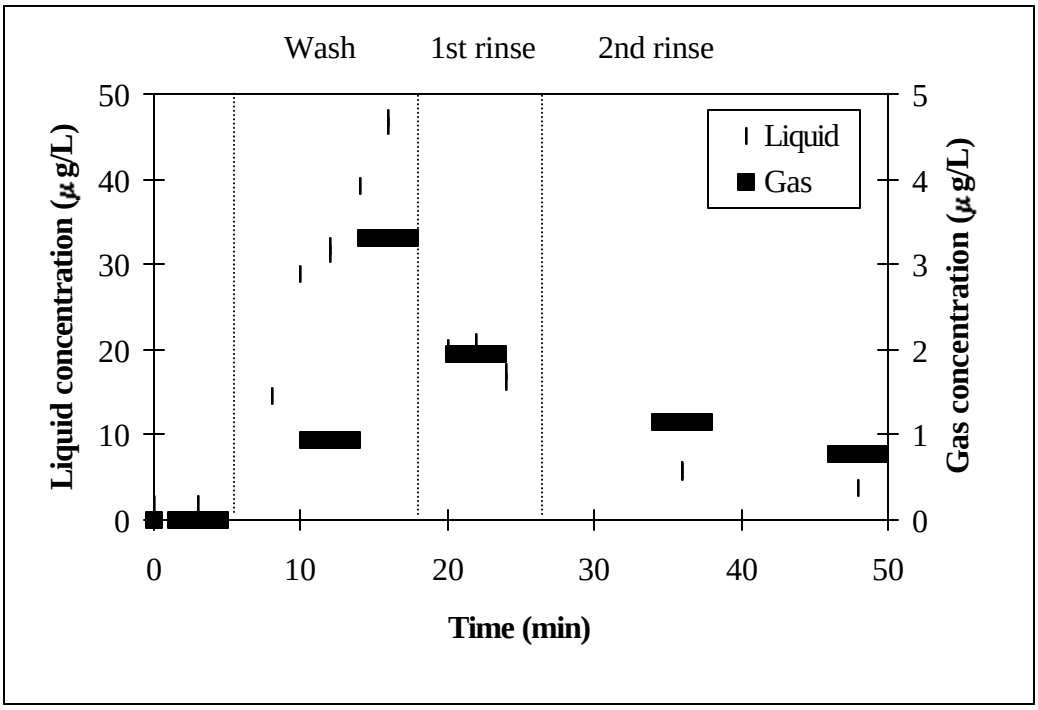


Figure 5-2. Chloroform concentrations as a function of time for Experiment 7 (standard food mix, Sunlight™ detergent) (Gas samples taken over four-minute intervals shown).

The fact that chloroform in the liquid phase increased approximately linearly with time implies that the right-hand side of Equation 5-1 was approximately constant with time (otherwise the slope of the line would change with time), and the chloroform generation rate is reasonably modeled as a zero-order reaction for short cycles. Neither chlorine nor organic matter was in limited supply in the dishwasher pool, i.e., neither of these factors was limiting in the formation of THMs.

Concentrations of chloroform in the liquid phase decreased by the start of the 1st rinse cycle, though the decrease was not as large as expected. It was expected that

the concentration of chloroform in the liquid phase at t = 18 minutes would approach background levels; instead, the concentration of chloroform from the end of the wash cycle to the 1st rinse cycle decreased from approximately 50 to 20 μg/L. It was possible that chloroform in the gas headspace was transferred back into the liquid phase. At 40 °C, the Henry's law constant for chloroform is 0.37 L_{air}/L_{liquid} using a temperature correlation developed by Ashworth *et al*. (1998). Using a chloroform concentration in the gas phase of 3.31 μg/L and assuming equilibrium conditions existed between liquid and gas phases, this would imply a chloroform concentration in the liquid phase of 8.94 μg/L. This estimated value is lower than the measured value of 20.3 μg/L (collected at t = 20 minutes), indicating a net flux from water to air.

Residual liquid that remained in the dish wash water from the previous (wash) cycle also may have contributed to this discrepancy. However, a concentration of chloroform in the liquid phase of 20 μg/L in the rinse cycle would imply that a large fraction of the water from the wash cycle (at concentration of 50 μg/L) would have remained in the dishwasher. Experiments were completed where the water discharged at the end of a cycle was measured. The measured volume of discharged water was generally within 10% of the volume measured during the cycle. Thus, it was unlikely that residual liquid from the previous cycle entirely accounted for this discrepancy. Water droplets resided on plates and the dishwasher tray during cycle drainage, though this was likely not a large enough volume to influence subsequent cycles. Residual detergent and organic matter were also likely present after the wash cycle, such that some THM formation continued during the rinse cycles.

In the gas phase, measured concentrations displayed similar trends to the liquid samples discussed above. Since liquid and gas levels closely parallel one another, it was possible that the system reached a condition of chemical equilibrium. Figure 5-3 shows the ratio of gas concentration to liquid concentration as a function of time for Experiment 7. Values in Figure 5-3 represent times where liquid samples

were collected at the midpoint of a gas sampling interval. The average chloroform concentration in the liquid phase was used when duplicate samples were collected. The ratio of gas-to-liquid concentrations increased from 0.01 (at t = 12 minutes) to 0.21 (at t = 48 minutes). Under normal operating conditions, measured dishwasher temperatures were approximately 40 °C during the wash cycle (t = 12 minutes) and approximately 55 °C during the rinse cycle (t = 36 minutes) (see Appendix). Using the temperature correlation developed by Ashworth *et al*. (1998), this would correspond to a Henry's law constant of 0.37 L_{air}/L_{liquid} in the wash cycle and 0.73 L_{air}/L_{liquid} in the rinse cycle.

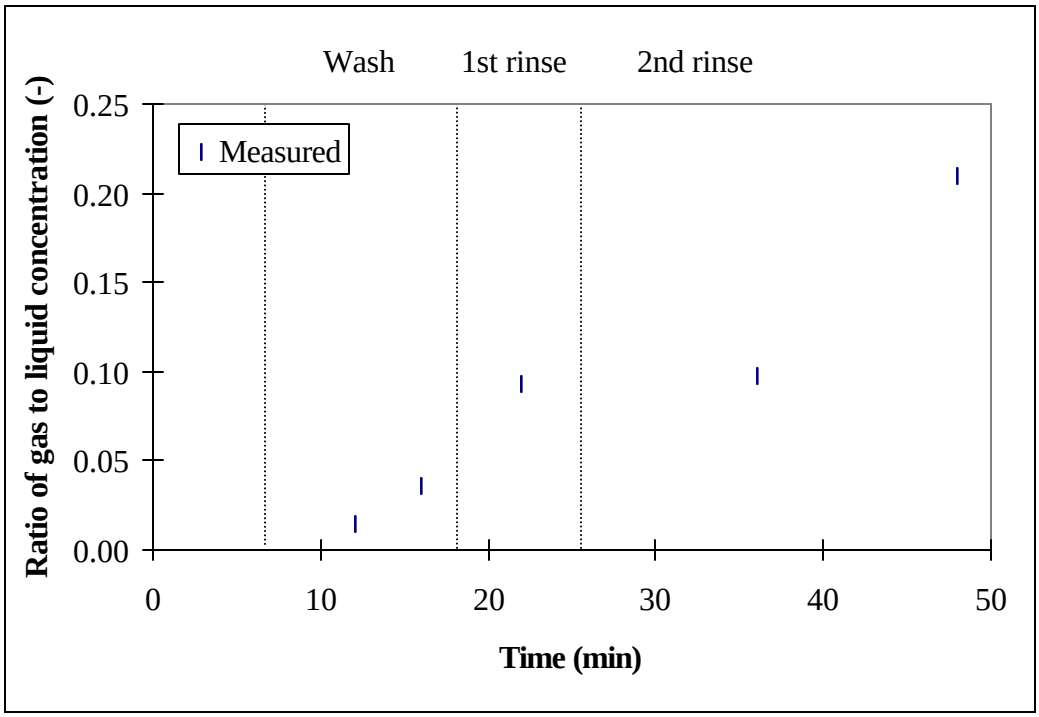


Figure 5-3. Ratio of gas concentration to liquid concentration as a function of time for Experiment 7 (standard food mix, Sunlight™ detergent).

The values in Figure 5-3 were consistently lower than the predicted Henry's law constant. This indicates that a condition of chemical equilibrium was not attained.

Howard and Corsi (1998) reported equilibrium conditions within one minute of dishwasher operation. It is possible that surfactants in the detergent may have influenced mass transfer processes, leading to low values of C_g/H_c for these experiments, particularly during the wash cycle.

5.3.2. Trends between dishwasher experiments

Concentrations of chloroform and bromodichloromethane from Experiment 1 are shown in Figure 5-4, where liquid concentrations (left vertical axis) and gas concentrations (right vertical axis) are given as a function of time. Experiment 1 was one of four experiments involving actual plates. Dibromochloromethane and bromoform concentrations were not plotted since these chemicals were generally not detected in the liquid or gas samples.

Experiment 1 (actual plates) displayed similar trends as compared to Experiment 7 (standard mix). Tap water and pre-rinse levels of chloroform in the liquid phase were relatively low (<5 µg/L). Peak concentrations of chloroform in the liquid phase occurred during the wash cycle. Chloroform levels in both liquid and gas phases decreased in subsequent samples.

One noticeable difference was that chloroform concentrations from Experiment 1 (actual plates) were higher, in both liquid and gas samples, than those from Experiment 7 (standard mix). For Experiment 1, concentrations of chloroform in the liquid phase reached a maximum of approximately 110 µg/L (t = 12 minutes), compared with a value of approximately 30 µg/L for Experiment 7 (t = 12 minutes). Concentrations of chloroform in the liquid phase for Experiment 1 were generally between a factor of 2 and 4 times those from Experiment 7.

It is unclear why chloroform concentrations were significantly different between actual plate and standard food mix experiments. However, many of the actual plate experiments involved heavy use of tomatoes, which was noted in Figure 5-1 to be significant contributors to chloroform formation.

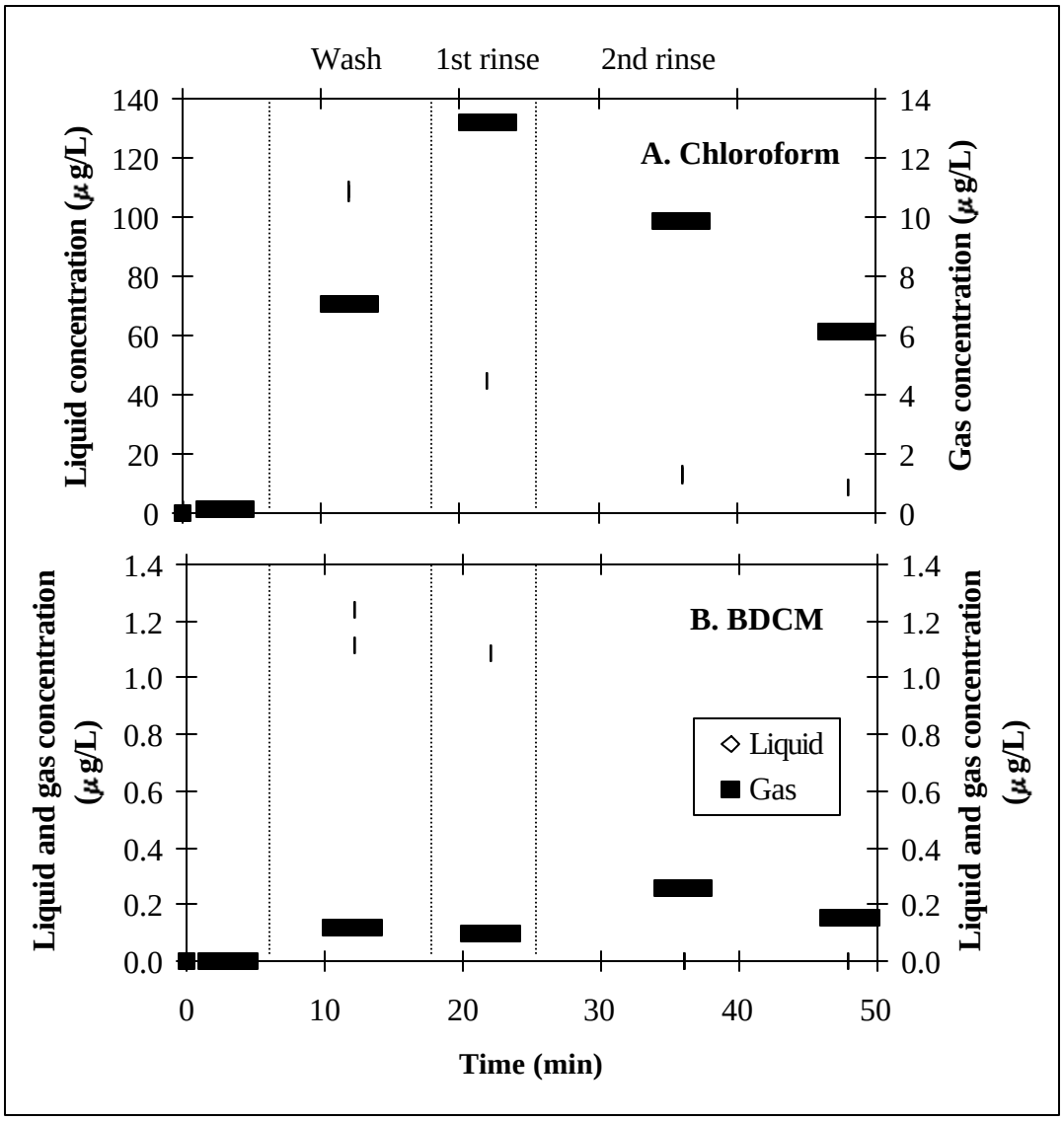


Figure 5-4. Chloroform and BDCM concentrations as a function of time for Experiment 1 (actual plates, Sunlight™ detergent) (Gas samples taken over four-minute intervals shown).

As described in Section 4.3, a standard mix was developed based on a USDA (1997) survey of food consumption patterns. Tomatoes constituted 5 wt% and beef 10 wt% of the standard mix. Assuming that values from flask experiments represented

linear rates of chloroform formation, i.e., the rate of chloroform formation was constant over the 10-minute flask experiment, a preliminary indication of the effect of tomatoes on chloroform formation can be made. An average value of 2.6 mg/L was used to represent food other than beef and tomatoes; concentrations for beef (40.9 mg/L) and tomatoes (36.8 mg/L) were obtained directly from Figure 5-1. For the mass percentages listed above, the relative formation potential of the standard mix is then:

$$CHCl_3 \text{ formed} = (40.9 \text{ mg/L})(10\%) + (36.8 \text{ mg/L})(5\%) + (2.6 \text{ mg/L})(85\%)$$
$$= 8.1 \text{ mg/L} \qquad (5\text{-}2)$$

Assuming that the concentrations of chloroform in the liquid phase from Experiment 1 (actual plates) were typically 2.5 times those from Experiment 7 (standard mix) would result in a relative formation potential of 20.4 mg/L for actual plates. Solving for the wt% tomatoes, i.e., Equation 5-2 where $CHCl_3$ formed was 20.4 mg/L, resulted in a mixture in the actual plate experiment that was 40% tomatoes by weight. This result seems plausible for plates involving heavy tomato usage (as noted above). This assessment should be viewed as preliminary, since results from the flask experiments do not necessarily imply reaction rates of chloroform formation.

Chloroform concentrations in the gas phase reached a maximum of 13 µg/L during the 1st rinse and then decreased in subsequent cycles. The maximum was not reached during the wash cycle, possibly indicating that mass transfer of chloroform in the liquid phase continued to occur at the end of the wash cycle. Differences in chloroform concentrations in the gas phase between Experiments 1 and 7 were even more noticeable than for liquid samples, where concentrations in the gas phase from Experiment 1 were between a factor of 6 and 8 times those from Experiment 1. For the 2nd rinse gas sample (collected from t = 46 minutes to t = 50 minutes), the ratio of gas-to-liquid concentration of chloroform was 0.73; this value corresponds to the estimated Henry's law constant at 55 °C (0.73 L_{liq}/L_{gas}). Under such a condition, the net flux across the air-water interface would be zero.

Similar trends also can be seen for bromodichloromethane (BDCM). Liquid BDCM concentrations were approximately one tenth chloroform concentrations in the wash cycle, and decreased to negligible concentrations by the 2nd rinse cycle. The concentration of BDCM for the tap water sample was below the detection limit, so it was not possible to attribute differences between chloroform and BDCM entirely to source water characteristics. These results were similar, however, to the relative formation of chloroform and BDCM from the flask experiments. For example, chloroform levels were typically between 10 and 30 times BDCM levels for the flask experiments (for foods where BDCM was detected). The lower concentrations of bromonated species in liquid or gas samples was likely due to high TOC levels in the wash water, since chloroform outcompetes other species in this case and less bromo-species are formed.

Similar to the chloroform gas samples, BDCM gas samples reached a maximum after the wash cycle. The ratio of gas-to-liquid concentrations for BDCM was less than that for chloroform, indicating that less BDCM was emitted to the headspace. This result was expected since BDCM is less volatile (lower Henry's law constant) than chloroform. The ratio of gas-to-liquid BDCM concentration was approximately 0.1 for the wash and 1st rinse samples; for other samples concentrations were below detection. These values were similar to the Henry's law constant reported in Table 4-4 (0.12 L_{liq}/L_{gas}).

Concentrations of chloroform and bromodichloromethane from Experiment 5 are shown in Figure 5-5, where liquid concentrations (left vertical axis) and gas concentrations (right vertical axis) are given as a function of time. Experiment 5 involved the standard food mix with normal food amount, normal dish soap amount, and Electrasol™ detergent. It was one of two experiments completed with a detergent other than Sunlight™.

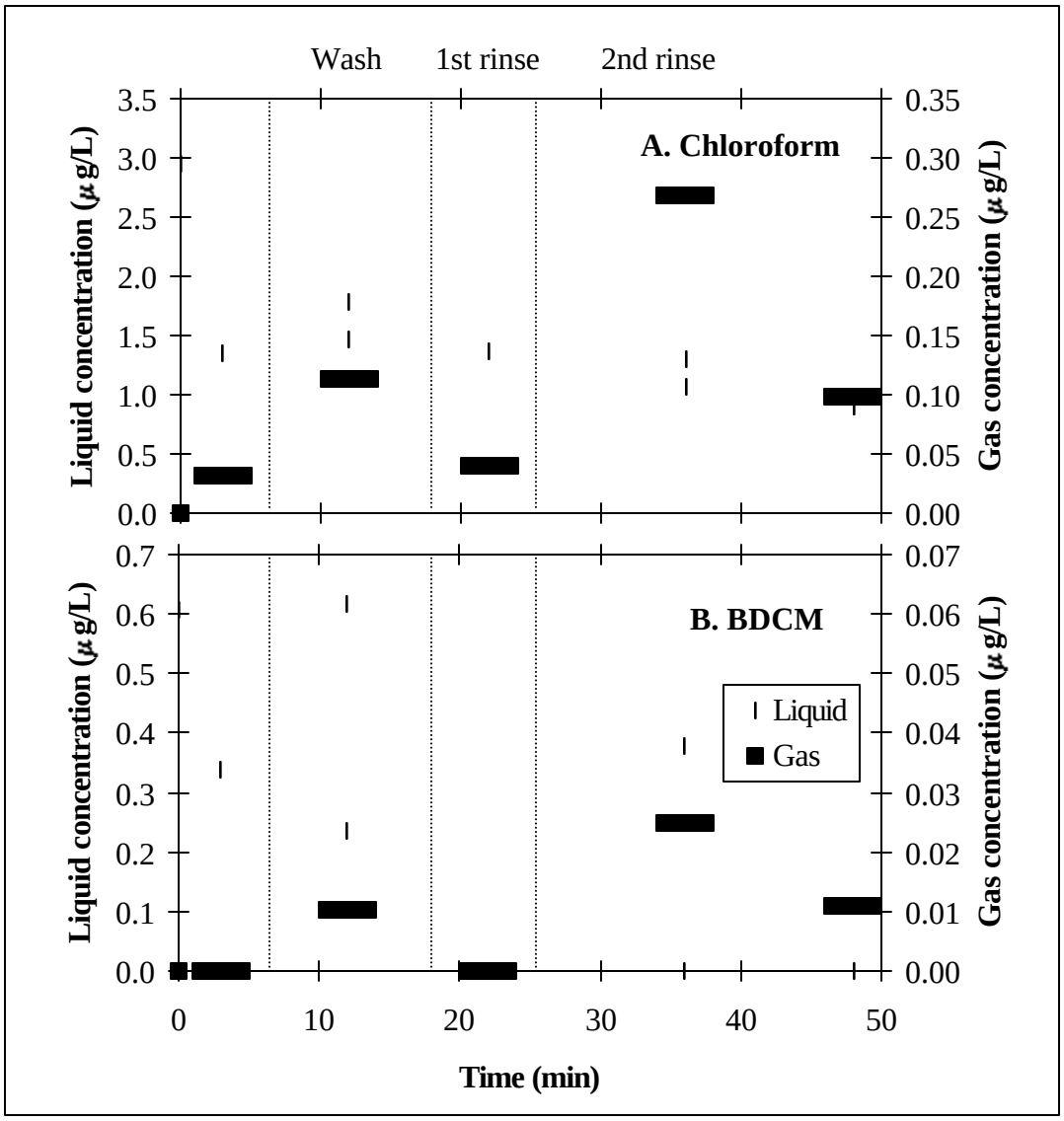


Figure 5-5. Chloroform and BDCM concentrations as a function of time for Experiment 5 (standard food mix, Electrasol™ detergent) (Gas samples taken over four-minute intervals shown).

Only trace amounts of chloroform were present during Experiment 5. Less than 5 µg/L of chloroform was present in the tap water sample. Since results in Section 5.1 indicated that no free or total chlorine was present in either Electrasol™

or Cascade™ detergent, and chloroform concentrations in both liquid and gas samples were below 5 µg/L throughout the experiment, most (if not all) of the chloroform present likely came from what was originally in the tap water and did not form from the detergent itself.

This result can also be verified by examining liquid and gas concentrations during Experiment 5. The concentration of chloroform in tap water was 3.0 µg/L; the average concentration of chloroform in the liquid phase for samples collected during dishwasher operation was 1.3 µg/L. For four cycles, a liquid volume of 6.8 L/cycle, and assuming a concentration of 1.3 µg/L exits the dishwasher in the liquid phase, an approximate mass of chloroform released to the headspace is then:

$$\text{Mass of } CHCl_3 = (3.0\ \mu g/L - 1.3\ \mu g/L)(6.8\ L/cycle)(4\ cycles)$$
$$= 45\ \mu g \text{ chloroform} \quad (5\text{-}3)$$

The average concentration of chloroform in the gas phase for samples collected during dishwasher operation was 0.13 µg/L. Assuming a gas flow rate of 5.7 L/min (Howard and Corsi, 1998), emissions of chloroform during operation can be estimated as:

$$\text{Mass of } CHCl_3 \text{ (during operation)} = (0.13\ \mu g/L)(5.7\ L/min)(40\ min)$$
$$= 30\ \mu g \text{ chloroform} \quad (5\text{-}4)$$

The concentration of chloroform in the gas phase at the end of dishwasher operation was 0.10 µg/L. For a gas volume of 181 L and assuming all mass at the end of dishwasher operation is emitted, the mass in the headspace is:

$$\text{Mass of } CHCl_3 \text{ (after operation)} = (0.10\ \mu g/L)(181\ L)$$
$$= 18\ \mu g \text{ chloroform} \quad (5\text{-}5)$$

The total mass leaving the dishwasher based on gas samples was 38 µg chloroform (from Equations 5-4 and 5-5), which compares favorably to the total mass based on liquid samples (45 µg). Thus, it was likely that chloroform emissions from Experiment 5 were due to gas-liquid mass transfer from chloroform originally in the

tap water and not chloroform formation from the detergent. Experiment 6 (using Cascade^{TM} detergent) also displayed similar results.

A similar analysis was not completed for BDCM, since several gas samples were near detection limits. BDCM concentrations were similar to background levels in both liquid and gas samples throughout the experiment.

Figure 5-6 shows liquid and gas concentrations for Experiment 10 (standard mix, water heat option). This experiment was similar to Experiment 7 (standard mix), except that the water heat option was used. This option increased the water temperature during the rinse cycles. Liquid temperatures during the wash cycle of Experiments 7 and 10 were similar (approximately 40 °C). Liquid temperatures during the 2nd rinse with the water heat option (approximately 60 °C) were higher than without the water heat option (approximately 50 °C).

Liquid chloroform concentrations in the wash cycle of Experiment 7 (standard mix) and Experiment 10 (standard mix, water heat option) were both between 30 and 40 µg/L. This result is expected since liquid temperatures during the wash cycle of these experiments were both approximately 40 °C. Some differences were evident between the liquid chloroform concentration in the 1st rinse (approximately 40 µg/L in Experiment 10 versus 20 µg/L in Experiment 7). This difference became more pronounced in the first sample of the 2nd rinse (approximately 40 µg/L in Experiment 10 versus 5 µg/L Experiment 7).

It was likely that temperature had an effect on the emission of chloroform. This trend also was reflected in the gas samples in the rinse cycle, where chloroform concentrations in the gas phase of the 2nd rinse cycle of Experiment 10 were approximately twice that of Experiment 4.

One effect of temperature is that the chemical Henry's law constant was higher and this resulted in a greater tendency for chemicals to be transferred to the gas phase. For liquid temperatures during 2nd rinse of approximately 60 °C (water

heat option) and 50 °C (normal operation), this corresponded to Henry's law constants of 0.91 L_{liq}/L_{gas} and 0.58 L_{liq}/L_{gas}, respectively.

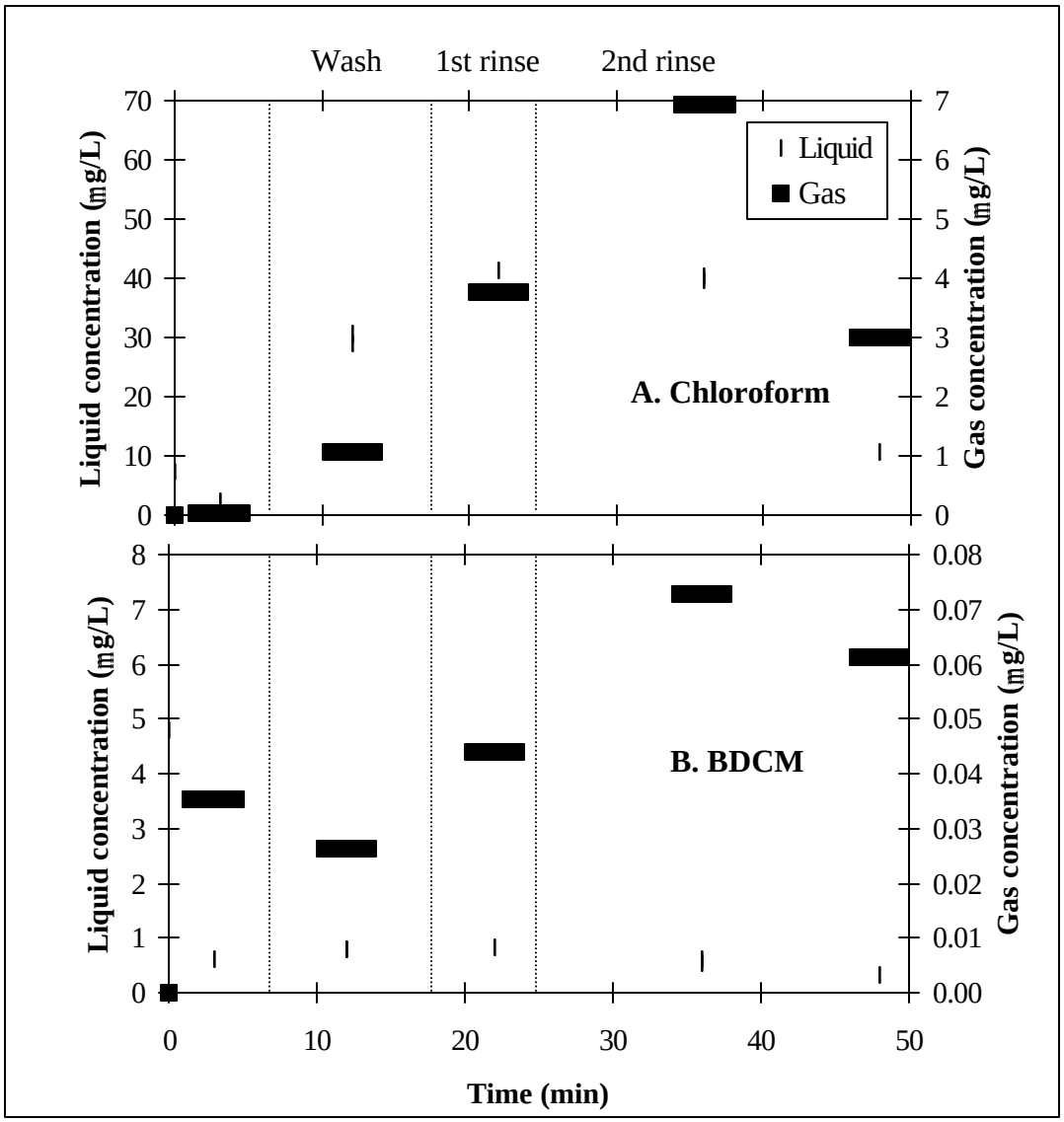


Figure 5-6. Chloroform and BDCM concentrations as a function of time for Experiment 10 (standard food mix, Sunlight™ detergent, water heat option) (Gas samples taken over four-minute intervals shown).

The estimated H_c from Experiment 10 (water heat) was only 1.5 times that from Experiment 7. The increased H_c does not entirely account for differences in concentrations, since chloroform concentrations in the liquid phase from Experiment 10 (water heat) were at least twice those from Experiment 7. In addition, the increased Henry's law constant would have not have led to additional THM formation during rinse cycles, only a greater tendency to be transferred from liquid to gas phases.

The second effect of temperature is that it could have led to more rapid THM formation. From the correlation describing chloroform formation from treatment plants (Singer, 1994), the rate of chloroform formation varies with temperature (in °C) raised to the 1.15 power, i.e., $T^{1.15}$. The difference in rate constants from 60 °C to 50 °C is then $(60\ °C / 50\ °C)^{1.15} = 1.2$. This effect also does entirely explain differences between experiments. Further, this effect would imply that a source of chlorine was present in the rinse cycles, a trend that was not displayed consistently in free chlorine samples.

Some similar trends were also observed in the formation and emission of BDCM between Experiments 7 and 10. However, several of the liquid and gas samples were below detection limit for these experiments and so direct comparisons are less clear. Some differences in BDCM concentrations also may have been attributable to differences in tap water samples. Nonetheless, BDCM was more likely to be detected in the gas samples of Experiment 10 (water heat).

Figure 5-7 shows liquid and gas concentrations for Experiment 11. This experiment was similar to Experiment 4 except that the plates were rinsed prior to placing them in the dishwasher. Liquid chloroform concentrations reached a maximum of approximately 18 µg/L in the wash cycle and decreased steadily after the wash cycle. Though some chloroform formed in the wash cycle, it was clearly less significant than in Experiment 4. This decreased formation of chloroform was also reflected in the gas samples, where most of the gas concentrations for chloroform

were below 1 µg/L (compared with gas concentrations generally between 1 and 2 µg/L for chloroform during Experiment 4). BDCM was generally not detected in liquid or gas samples in Experiment 11 (rinsed plates).

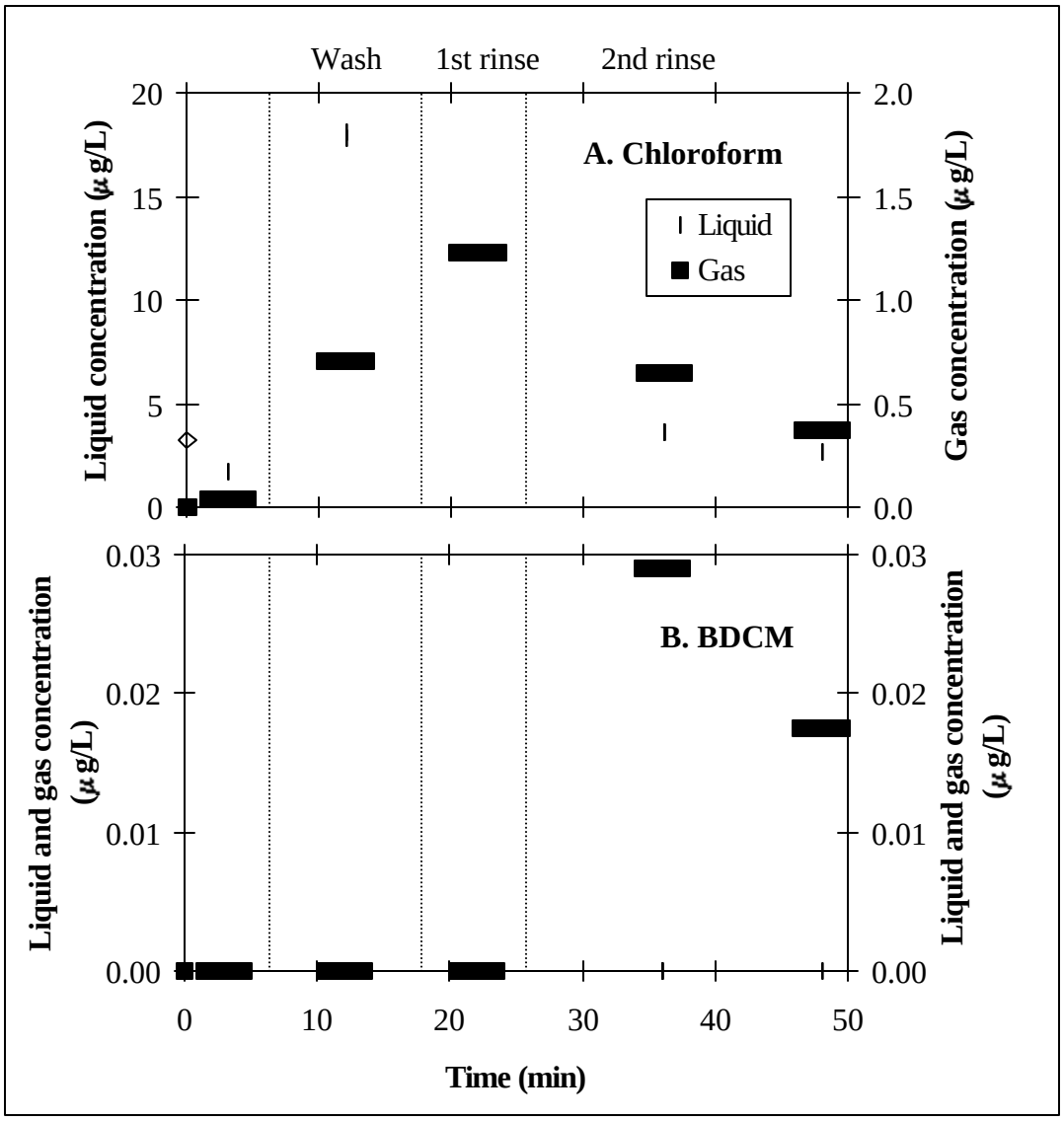


Figure 5-7. Chloroform and BDCM concentrations as a function of time for Experiment 11 (standard food mix, Sunlight™ detergent, rinsed plates) (Gas samples taken over four-minute intervals shown).

5.4. Water quality parameters

A summary of all total organic carbon samples collected for this research is shown in Table 5-1. TOC concentrations varied considerably, both between experiments and between samples in a given experiment. Even for experiments that involved the standard food mix (Experiments 4-12), TOC concentrations for the pre-rinse samples ranged from 34 to 1,242 mg/L. Similarly, TOC concentrations for the wash samples ranged from 128 to 1,071 mg/L. Significant variations also existed between experiments involving actual plates. As described in Section 4.3, 56 g of food were used for all experiments using the standard mix (Experiments 4-12). It was anticipated that this method would have led to more consistent TOC concentrations between similar experiments, though several reasons may explain these discrepancies.

Table 5–1. Summary of TOC concentration data.

Expt.	Conditions*	Total organic carbon concentration (mg/L)		
		Pre-rinse	Wash	2nd rinse
1	Actual plates	1,463	509	40
1 (Rep)		951	497	37
2	Actual plates, water heat	233	1,050	923
3	Actual plates, rinsed	68	129	28
4 (Rep1)	Standard mix	171	172	17
4 (Rep2)		34	126	14
5	Standard mix, Electrasol™	451	290	22
6	Standard mix, Cascade™	308	141	2
8	Standard mix, three cycles	1,242	1,071	
9	Standard mix, maximum detergent	486	187	15
10	Standard mix, water heat	486	182	435
10 (Rep)		394	182	424
11	Standard mix, rinsed	39	128	28
12	No food	45	435	37

*unless otherwise noted, experiments involved Sunlight™ detergent and normal detergent amount.

One possible explanation for these variations could have been the condition of the food on the plates. Namely, food that was dried onto a plate may have taken longer to remove. Though effort was made to apply food onto the plates consistently, this may have been a source of variation.

Another possible explanation could have been that TOC concentration was not a reliable method for characterizing organic content in dishwasher. It was expected that organic matter in the dishwasher was largely particulate. However, it was likely that available chlorine reacted more readily with dissolved organic matter, particularly dissolved proteins. Dissolved organic carbon (DOC) may have been a better metric for characterizing organic matter in the dishwasher.

In general, the pre-rinse samples had the highest TOC concentrations, and TOC concentrations decreased for each successive sample. In almost all cases, the lowest TOC concentration for each experiment occurred for the 2nd rinse samples. This result was expected since most organic matter originating from food was removed by the 2nd rinse cycle.

One interesting trend was that the highest TOC concentrations tended to occur for the pre-rinse sample. This would indicate that most of the food was removed from the plates during the pre-wash cycle and not during the wash cycle. This result also may suggest that liquid THM concentrations (and subsequent emissions to indoor air) would have been higher had the pre-wash cycle been less effective at removing food. For this case, more organic matter would have been available to react with chlorine released during the wash cycle.

Several of the 2nd rinse samples were higher than other samples. In particular, TOC concentrations from the 2nd rinse samples of Experiment 2 (922 mg/L), Experiment 10 (435 mg/L), and Experiment 10 replicate (424 mg/L) were significantly higher than average of 2nd rinse samples from all other experiments (24 mg/L). Experiments 2, 10, and 10 (replicate) were the three experiments completed

using the water heat option, suggesting that temperature had an effect on these samples. One possible explanation is that the last remaining food dried onto plates was only removed from the higher temperatures attained using the water heat option.

The concentration of TOC from the wash cycle of Experiment 12 (435 mg/L) was much higher than other samples for that experiment (41 mg/L). Since Experiment 12 was completed without the presence of food, it is unclear why the TOC concentration in wash sample was much higher than the other samples.

A summary of all UV-254 absorbance samples collected for this research is shown in Table 5-2. In general, UV-254 measurements decreased with each successive sample for a given experiment. The 2nd rinse sample consistently had the lowest UV-254 levels, indicating that much of the proteins had been removed from the system by that time.

The trends in Table 5-2 are similar to those shown for TOC concentrations. UV-254 levels varied considerably, both between experiments and between samples in a given experiment. The highest UV-254 absorbances tended to occur during experiments with the highest THM levels, e.g., Experiments 1 and 2. As expected, experiments involving little or no food (Experiments 3, 11, and 12) had the lowest UV-254 levels.

As with the TOC concentrations, UV-254 levels from the 2nd rinse samples of Experiment 2 (0.258 cm^{-1}), Experiment 10 (0.220 cm^{-1}), and Experiment 10 replicate (0.246 cm^{-1}) were significantly higher than average of 2nd rinse samples from all other experiments (0.012 cm^{-1}). Experiments 2, 10, and 10 (replicate) were the three experiments completed using the water heat option. Since TOC and UV-254 samples displayed similar trends, these data further confirm that the higher temperature had an effect on water quality characteristics.

Table 5–2. Summary of UV-254 absorbance data.

Expt.	Conditions	UV-254 (cm^{-1})		
		Pre-rinse	Wash	2nd rinse
1	Actual plates	0.632	0.283	0.027
1 (Rep)		0.397	0.271	0.013
2	Actual plates, water heat	0.128	0.298	0.258
3	Actual plates, rinsed	0.008	0.064	0.004
4	Standard mix	0.143	0.172	0.024
4 (Rep1)		0.452	0.246	0.014
4 (Rep2)		0.160	0.196	0.011
5	Standard mix, Electrasol™	0.286	0.095	0.009
6	Standard mix, Cascade™	0.265	0.113	0.005
8	Standard mix, three cycles	n/a	0.429	0.009
9	Standard mix, maximum detergent	0.438	0.179	0.012
10	Standard mix, water heat	0.338	0.174	0.220
10 (Rep)		0.431	0.218	0.246
11	Standard mix, rinsed	0.005	0.055	0.006
12	No food	0.013	0.087	0.008

*unless otherwise noted, experiments involved Sunlight™ detergent and normal detergent amount.

A summary of all free and total chlorine samples collected for this research is shown in Table 5-3. For chlorine samples equal to zero, no color change occurred in completing Standard Methods 4500-Cl F and G. It is unclear why free and total chlorine were approximately equal for some samples and not for others. A higher total chlorine concentration would imply a source of ammonia, though the free and chlorine test described in Section 5.1 indicated that ammonia was not present in any of the detergents. It was possible that constituents in the detergents contributed to interferences while completing the free and chlorine analysis, though the most common interferences are manganese, copper, chromate (Standard Methods, 1989). Given the inconsistent trends evident in Table 5-3, conclusions regarding general trends can not be accurately characterized. However, chlorine levels appear higher

when little or no food was present (Experiment 3, 11, and 12), indicating that less carbon was available to form THMs.

Table 5–3. Summary of free and total chlorine data.

Expt.	Conditions*	free chlorine (mg/L) Pre-rinse	Wash	2nd rinse	total chlorine (mg/L) Pre-rinse	Wash	2nd rinse
1	Actual plates	0.0	4.8	1.5	0.0	4.8	1.5
1 (Rep)		0.0	3.5	1.4	0.0	8.3	1.7
2	Actual plates, water heat	0.0	4.0	3.9	0.0	4.0	4.1
3	Actual plates, rinsed	0.1	0.7	0.0	0.5	12.4	0.0
4 (Rep2)	Standard mix	0.0	0.0	0.0	1.2	0.0	1.6
5	Standard mix, Electrasol™	0.0	0.0	0.0	0.0	0.0	0.0
6	Standard mix, Cascade™	0.0	0.0	0.0	0.0	0.0	0.0
9	Standard mix, maximum detergent	0.0	0.0	0.0	4.4	0.0	1.2
11	Standard mix, rinsed	0.0	0.6	0.0	0.0	10.9	0.1
12	No food	0.1	1.0	0.1	0.1	9.5	0.2

*unless otherwise noted, experiments involved Sunlight™ detergent and normal detergent amount.

A summary of pH measurements for all experiments is shown in Table 5-4. The pH was typically between 9 and 11 for most samples. The pH generally increased during the wash cycle, likely the result of adding detergent to the dishwasher pool. One noteworthy result was that the dishwasher operated under basic conditions. This suggests little chlorine gas (Cl_2) would have been emitted during dishwasher usage, since liquid chlorine will volatilize when it is in the form of HOCl (and not its more basic component, OCl^-).

Table 5–4. Summary of pH data.

Expt.	Conditions*	pH		
		Pre-rinse	Wash	2nd rinse
1	Actual plates	9.63	10.57	9.54
1 (Rep)		9.68	10.69	9.52
2	Actual plates, water heat	7.93	10.59	10.49
3	Actual plates, rinsed	11.47	12.14	11.07
4 (Rep1)	Standard mix	10.25	12.09	11.70
4 (Rep2)		8.80	10.90	9.75
5	Standard mix, Electrasol™	10.20	12.04	11.42
6	Standard mix, Cascade™	9.41	10.80	9.80
8	Standard mix, three cycles	n/a	10.62	9.43
9	Standard mix, maximum detergent	10.54	10.69	9.75
10	Standard mix, water heat	9.77	10.71	10.64
10 (Rep)		8.88	10.69	10.66
11	Standard mix, rinsed	10.28	12.15	11.03
12	No food	8.89	10.87	9.86

*unless otherwise noted, experiments involved Sunlight™ detergent and normal detergent amount.

Figure 5-8 shows liquid chloroform concentration as a function of free chlorine (Figure 5-8A) and total chlorine (Figure 5-8B). Samples collected during the wash cycle of all experiments were used for this figure. Chloroform data from Experiments 5 (Electrasol™) and 6 (Cascade™) were not included in this figure since little or no chloroform formed from these detergents. Though the linear r^2 value for the regressions of both free chlorine with chloroform concentration and total chlorine with chloroform concentration were above 0.4, there does not appear to be a strong linear relationship. Since few data were available from these samples, prescribing a relationship between chlorine level and chloroform concentration would be inappropriate.

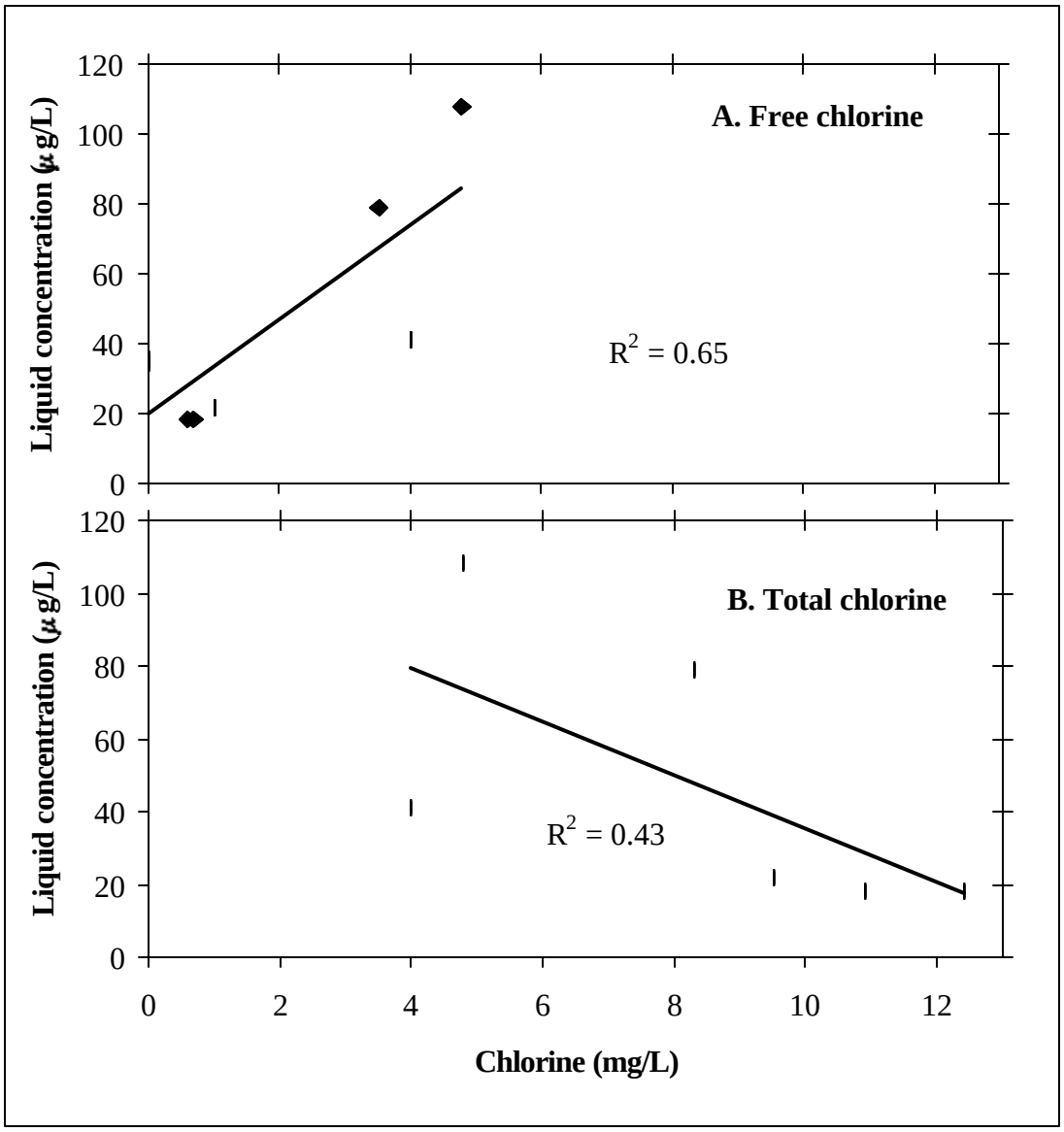


Figure 5-8. Liquid concentration versus free chlorine and versus total chlorine.

Chloroform concentration as a function of total organic carbon concentration is presented in Figure 5-9. As before, chloroform data from Experiments 5 (Electrasol^{TM}) and 6 (Cascade^{TM}) were not included in this figure. Data from Experiment 8 (three cycles) were also not included. TOC concentrations in the wash cycle of Experiment 8 were likely to be higher than for other experiments since there was no pre-rinse cycle to initially remove food from dishware. As with the free and

total chlorine regressions, the linear r^2 value for the regressions of TOC with chloroform concentration and total chlorine with chloroform concentration were low. As described earlier, Experiments 1-3 (actual plate) and Experiment 8 (three cycles) had TOC concentrations in the wash cycle greater than 400 mg/L; all other experiments (except Experiment 12) had concentrations between 120 and 190 mg/L. With much of the data of Figure 5-9 between 120 and 190 mg/L and more variability for other experiments, prescribing a relationship between TOC and chloroform concentration would be inappropriate.

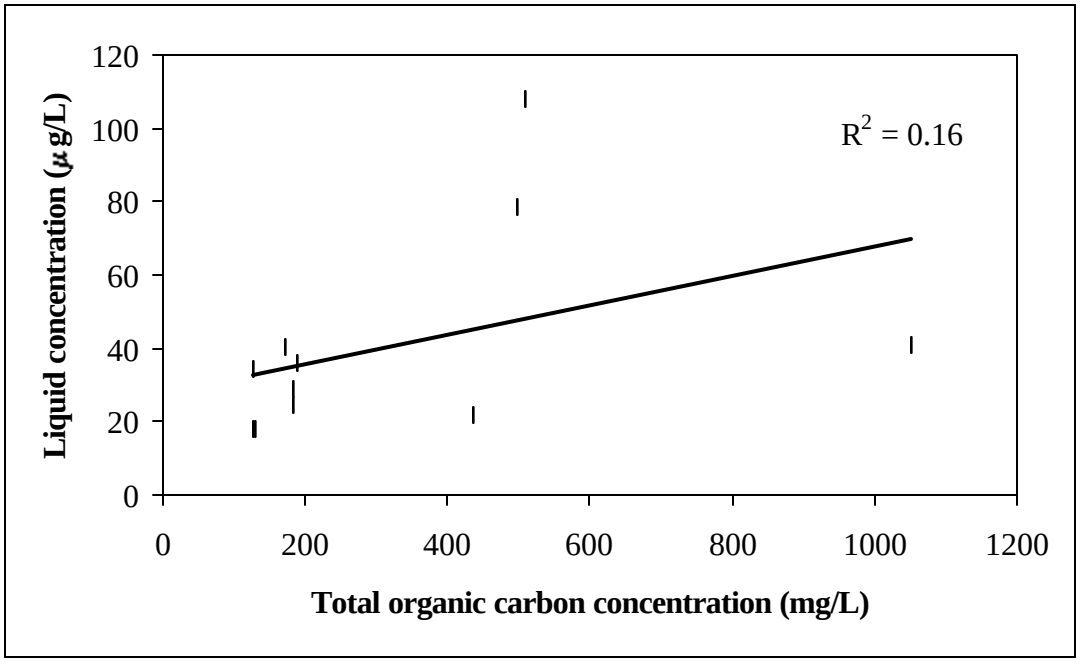


Figure 5-9. Liquid concentration versus total organic carbon concentration.

Chloroform concentration as a function of UV-254 absorbance is presented in Figure 5-10. As before, chloroform data from Experiments 5 (Electrasol^{TM}) and 6 (Cascade^{TM}) were not included in this figure. Similar to previous results, chloroform concentrations in the liquid phase and UV-254 appear to be weakly correlated.

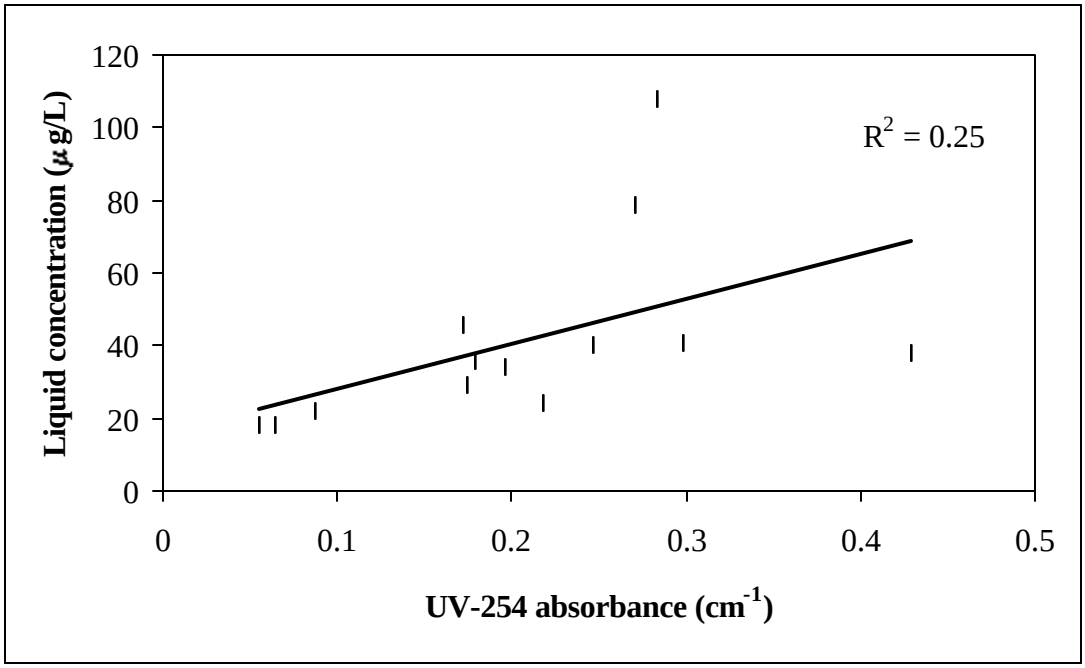


Figure 5-10. Liquid concentration versus UV-254 absorbance.

Chloroform concentration as a function of hydrogen ion concentration is given in Figure 5-11. Hydrogen ion concentration was used instead of pH in Figure 5-11 so that both concentrations could be displayed on a linear scale. As before, chloroform data from Experiments 5 (Electrasol^{TM}) and 6 (Cascade^{TM}) were not included in this figure. Similar to previous results, chloroform concentrations in the liquid phase and hydrogen ion concentration appear to be weakly correlated.

Several possible reasons may explain why these water quality parameters were poor indicators of chloroform formation. Probably the most important of these was the linear nature of the chloroform increase in the liquid phase (see Figure 5-2), indicating that the chloroform rate of formation was constant with time. These parameters were likely not limiting factors in the production of THMs, and the actual nature of organic precursors was the dominant factor affecting chloroform formation.

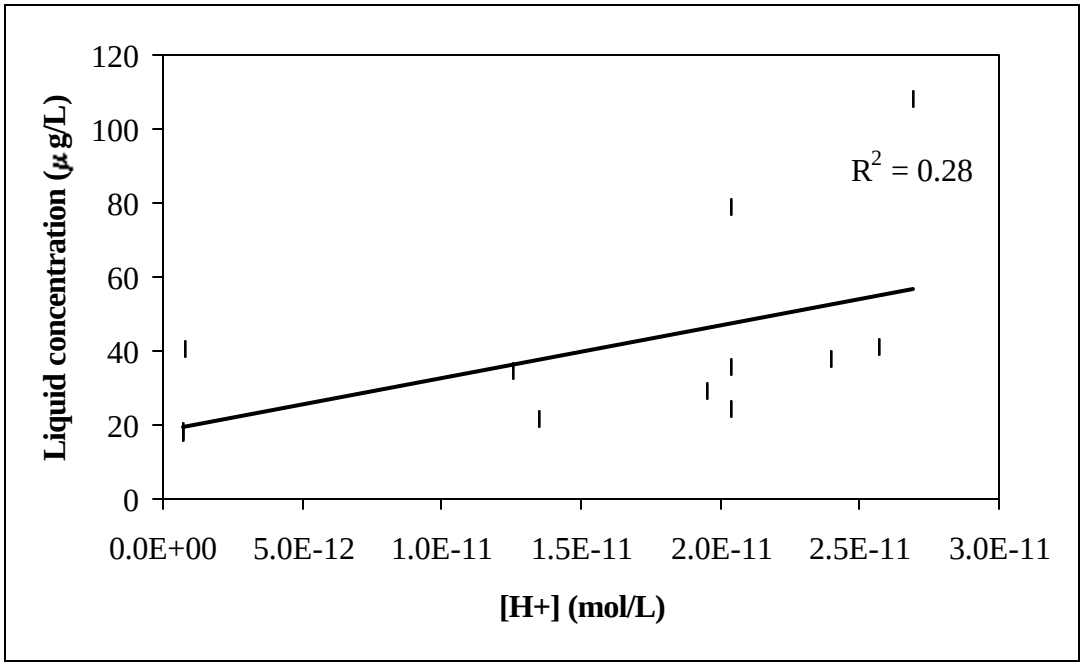


Figure 5-11. Liquid chloroform concentration versus hydrogen ion concentration.

Several other factors were also likely contributors to the poor correlation between water quality parameters and chloroform concentration in the liquid phase. It was possible that TOC was not the best indicator of THM formation. Dissolved organic carbon (DOC) may have been more indicative of THM formation since chlorine will react more readily with dissolved-phase organics. Another complication for using either TOC or DOC is that these measures do not distinguish between organics (or proteins) that have faster reaction kinetics when mixed with chlorine. For UV-254 absorbance measurements, it was possible that dissolved food (other than proteins) absorbed UV light.

Chloroform concentration as a function of UV-254 absorbance multiplied by free chlorine is given in Figure 5-12. Though only a few data points were available for this regression, there appears to be a linear trend with these parameters. Such a relationship is consistent with the notion that chloroform formation is a function of reactive organic carbon and free chlorine. UV-254 was expected to be more reflective

of the actual nature of organic precursors (opposed to TOC alone), so a linear relationship between chloroform concentration and UV-254 absorbance multiplied by free chlorine is plausible, although counter to the previous observation of constant formation rate.

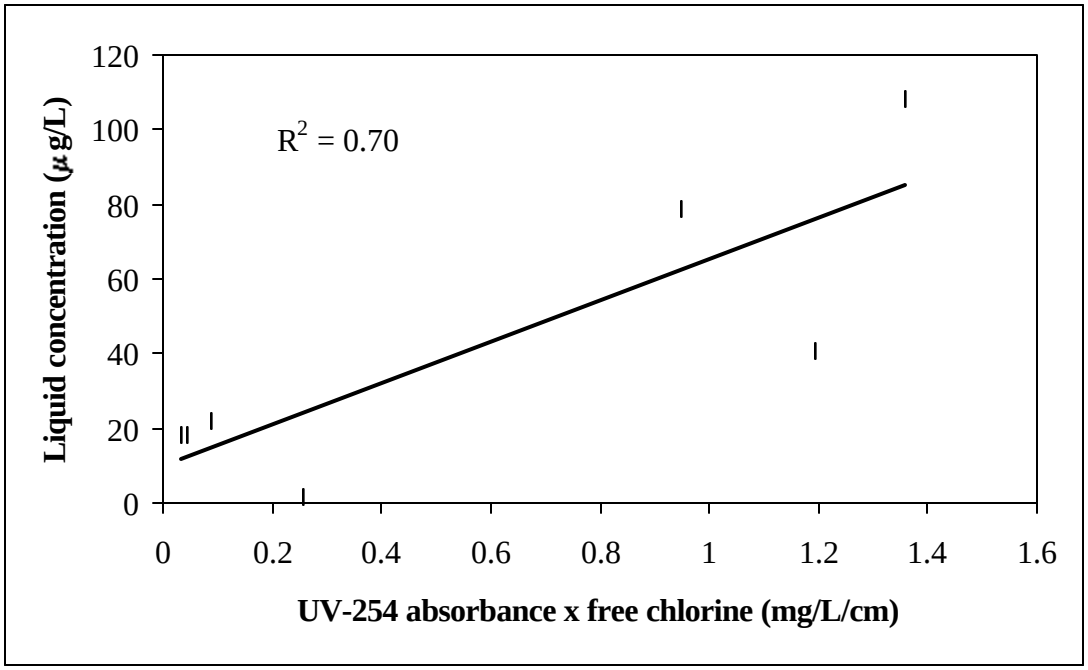


Figure 5-12. Liquid chloroform concentration versus (UV-254 absorbance) x (free chlorine).

5.5. Emission rates

The average concentration of chloroform in the gas phase of each experiment is summarized in Table 5-5. These values refer to the average concentration in the headspace while the dishwasher was operating (excluding the drying cycle). These values were estimated since gas samples were typically collected over a four-minute interval and not during the entire dishwasher event. Headspace concentrations between samples were estimated by interpolating between adjacent samples.

Table 5–5. Estimated average gas concentrations and total mass emitted for chloroform.

Expt.	Conditions*	Average gas concentration (μg/L)
1	Actual plates	8.07
1 (Rep)		7.85
2	Actual plates, water heat	19.9
3	Actual plates, rinsed	0.73
4	Standard mix	4.16
4 (Rep1)		1.05
4 (Rep2)		1.31
5	Standard mix, Electrasol™	0.12
6	Standard mix, Cascade™	0.05
7	Standard mix	1.06
9	Standard mix, maximum detergent	1.25
10	Standard mix, water heat	3.45
10 (Rep)		1.53
11	Standard mix, rinsed	0.66
12	No food	0.90

*unless otherwise noted, experiments involved Sunlight™ detergent and normal detergent amount.

The highest concentrations came from the experiments using actual plates, and the highest of these occurred when the water heat option was used. Little chloroform was emitted when either Electrasol™ or Cascade™ was used (Experiments 5 and 6). There appeared to be some effect of environmental conditions as well, such as increased total mass emitted for the higher water temperature (Experiment 10). However, replicate experiments showed some variation and so it would be inappropriate to attribute these differences entirely to environmental conditions. The average concentration decreased somewhat when rinsed or clean plates were used (Experiments 11 and 12).

5.6. Formation rates

Table 5-6 summarizes estimated chloroform formation rates during the wash cycle of each experiment. Experiments 5 (Electrasol™) and 6 (Cascade™) were not included in this analysis since no free chlorine was present during these experiments. Experiment 7 (three cycles) and 8 (standard mix) were not included since fewer water quality samples were collected.

Table 5–6. Estimated chloroform formation rates.

Expt.	Conditions*	Formation rate (µg/L/min)	
		Equations 5-6 and 5-7	Equation 5-9
1	Actual plates	236	346
1 (Rep)		166	300
2	Actual plates, water heat	201	566
3	Actual plates, rinsed	41	35
4	Standard mix	101	69
4 (Rep1)		88	109
4 (Rep2)		74	75
9	Standard mix, maximum detergent	78	73
10	Standard mix, water heat	65	77
10 (Rep)		53	95
11	Standard mix, rinsed	39	31
12	No food	47	87

*unless otherwise noted, experiments involved Sunlight™ detergent and normal detergent amount.

Two different methods were used to estimate formation rates. In the first method, formation rates were estimated using Equations 4-5 and 4-6. Those equations are repeated here:

$$\frac{dC_l}{dt} = -\frac{K_L A}{V_l} C_l + \frac{K_L A}{V_l H_c} C_g + R_{form} \qquad (5\text{-}6)$$

$$\frac{dC_g}{dt} = \frac{K_L A}{V_g} C_l - \left(\frac{Q_g}{V_g} + \frac{K_L A}{V_l H_c} \right) C_g \qquad (5\text{-}7)$$

where

C_l = chemical concentration in the liquid phase (µg/L)

t = time (min)

$K_L A$ = overall mass transfer coefficient (L/min)

V_l = liquid volume of dishwasher (L)

H_c = Henry's law constant for a chemical of interest (L_{liq}/L_{gas})

R_{form} = rate of chemical formation in the liquid phase (µg/L-min)

C_g = chemical concentration in the gas phase (µg/L)

V_g = volume of dishwasher headspace (L)

Q_g = headspace ventilation rate (L/min)

The following values were used based on previous work by Howard-Reed *et al*. (1999): V_g = 181, V_l = 7.4 L, Q_g = 5.7 L/min, and $K_L A$ = 35 L/min. A Henry's law constant of 0.37 L_{liquid}/L_{gas} was used for chloroform, based on correlations developed by Ashworth *et al*. (1988) at a liquid temperature of 40 °C. The estimated formation rate was chosen as the constant value that minimized the residual between predicted and measured values. The assumption of a constant formation rate is reasonable given the highly linear results from the wash cycle shown in Figure 5-2. In many cases measured values were based on only one set of duplicate samples, however, so these results should be viewed as approximate.

The resulting formation rate from Experiment 1 (236 µg/L/min) is used here to describe the above solution method. Neglecting background liquid or gas levels, using the values listed above, and using numerical approximation to solve Equation 5-6 results in the following expression (for dt = 0.1 minutes):

$$C_{l,\,t+1} = C_l + \left(-\frac{K_L A}{V_l} C_l + \frac{K_L A}{V_l H_c} C_g + R_{form} \right) dt$$

$$= \left(-\frac{35\ \text{L/min}}{7.4\ \text{L}}(0\ \mu\text{g/L}) + \frac{35\ \text{L/min}}{(7.4\ \text{L})(0.37\ \text{L/L})}(0\ \mu\text{g/L}) + 236\ \mu\text{g/L/min} \right)(0.1\ \text{min})$$

= 23.6 µg/L $CHCl_3$ (at t = 0.1 minutes) (5-8)

The updated liquid concentration is now used for C_l and the process is repeated. Similar methods were also used for gas-phase concentrations. The formation rate was chosen such that it minimized the residual between measured and calculated levels in the liquid phase. Gas samples were not used for this procedure as a few samples were near detection limits. For the example described in Equation 5-8, the predicted concentration of chloroform in the liquid phase was 109 µg/L at t = 3 minutes. Measured concentrations were 108 and 109 µg/L at this sampling time.

In the second method, formation rates were estimated using Equation 2-6, an empirical formation equation developed from treatment plant data (Singer, 1994). These formation rates were then based on source water characteristics, e.g., TOC and pH. Median values were used in cases where data were unavailable. A bromide ion concentration of 0.15 mg/L was assumed. Equation 2-6 is repeated here:

$$[CHCl_3] = 0.278\ [(TOC)\ (UV\text{-}254)]^{0.616}\ (Cl_2)^{0.391}\ (t)^{0.265}\ (T)^{1.15}\ (pH\text{-}2.6)^{0.80}\ (Br+1)^{-2.23} \quad (5\text{-}9)$$

where

$[CHCl_3]$ = chloroform concentration (µmol/L)

TOC = total organic carbon (mg/L)

UV-254 = ultraviolet absorbance at 254 nm (cm^{-1})

Cl_2 = free chlorine concentration (mg/L)

t = time (hr)

T = temperature (°C)

Br = bromide ion concentration (mg/L)

Estimated formation rates displayed trends similar to those for the total mass emitted (Table 5-5). The highest formation rates occurred for the experiments

involving actual food on plates. One difference from earlier trends was the relatively narrow range of values for experiments using the standard food mix (from approximately 50 to 100 μg/L/min) using Equations 4-6 and 4-7.

The two estimation methods were reasonably consistent, though the empirical estimate from treatment plant data consistently predicted higher formation rates. One possible explanation for this discrepancy is that the TOC concentrations (Table 5-1) reported in this research were generally much higher than values reported for drinking water immediately prior to chlorination. For example, Arora *et al*. (1997) reported TOC concentrations ranging from 2.4 to 8.5 mg/L for 35 water treatment plants. Thus, estimated formation rates using water quality parameters from the dish water were extrapolated well outside the correlations developed from treatment plant data.

5.7. Summary

Flask experiments involved mixing food and dishwasher detergent in water, and were intended to identify chemicals that may form from dishwasher usage. The following foods were used: beans, beef, bread, cereal, eggs, fish, lima beans, oil, pasta, potatoes, poultry, rice, sugar, and tomatoes. Liquid concentrations of chloroform ranged from 1-41 mg/L.

Laboratory experiments involved collection of liquid and gas samples over the course of a dishwasher operating cycle. Experiments were completed using plates from an actual residence and using food from a standard mix developed from food consumption data. Food amount, dish soap amount, and detergent type were also varied for these experiments. Background concentrations of chloroform in the water supply were generally between 0 and 10 μg/L; liquid chloroform levels in the wash cycle were typically at least 50 μg/L. The other trihalomethanes (THMs) were detected less frequently, though this result was likely a result of low bromide ion levels in the water supply. Gas chloroform concentrations were generally between 0

and 5 μg/L in the dishwasher headspace. Concentrations of the other THMs were lower than chloroform but consistent with corresponding liquid samples.

6. FIELD EXPERIMENTS AND MODEL CALIBRATION

6.1. Experimental methodology

6.1.1. Site description

A series of field experiments was completed to better characterize chloroform emissions and subsequent transport from water devices at actual houses. Three houses were used for this study; all were located in Austin, Texas. Test house A consisted of one story, three bedrooms and two full bathrooms, with an area of approximately 1260 ft^2. Test house B consisted of one story with a basement, three bedrooms and two full bathrooms, with an area of approximately 2,300 ft^2. Test house C consisted of one story, three bedrooms and one full bathroom, with an area of approximately 1220 ft^2. Room volumes for the three houses are listed in Table 6-1.

Table 6–1. Room volumes for test houses.

Room	Volume (m^3) Test house A	Test house B	Test house C
Kitchen	90.8	88.5	65.2
Living Room	104.4	174.7	187.7
Dining Room	93.1	88.5	21.8
Bedroom #1	75.0	122.6	80.3
Bath #1	21.1	29.1	51.2
Bedroom #2	68.9	69.6	84.9
Bath #2	22.4	23.3	n/a
Bedroom #3	92.4	55.9	59.7
Hall	19.7	111.4	19.6
Other rooms	n/a	309.0	n/a

6.1.2. Experimental design

Field experiments involved operating the dishwasher and shower, then measuring gaseous chloroform concentrations in the house as a function of time.

First, a background gas sample was collected for one hour. At the same time, sulfur hexaflouride (SF_6) was injected into the HVAC system in order to estimate air exchange between the house and the outdoors. The fan for the HVAC system was also activated at this time. At the end of the background sample, the dishwasher and shower were activated. For test house B, the shower was activated one hour after the dishwasher was activated. Sunlight™ detergent was used for all experiments. The showers operated for 15 minutes and the dishwasher for the length of its normal operating cycle (typically about 45 minutes). For test house B, a washing machine (using liquid bleach) was activated at the same time as the dishwasher. A schematic showing all three test houses (not to scale) is shown in Figure 6-1. Sampling locations and dishwasher locations are also noted for each test house.

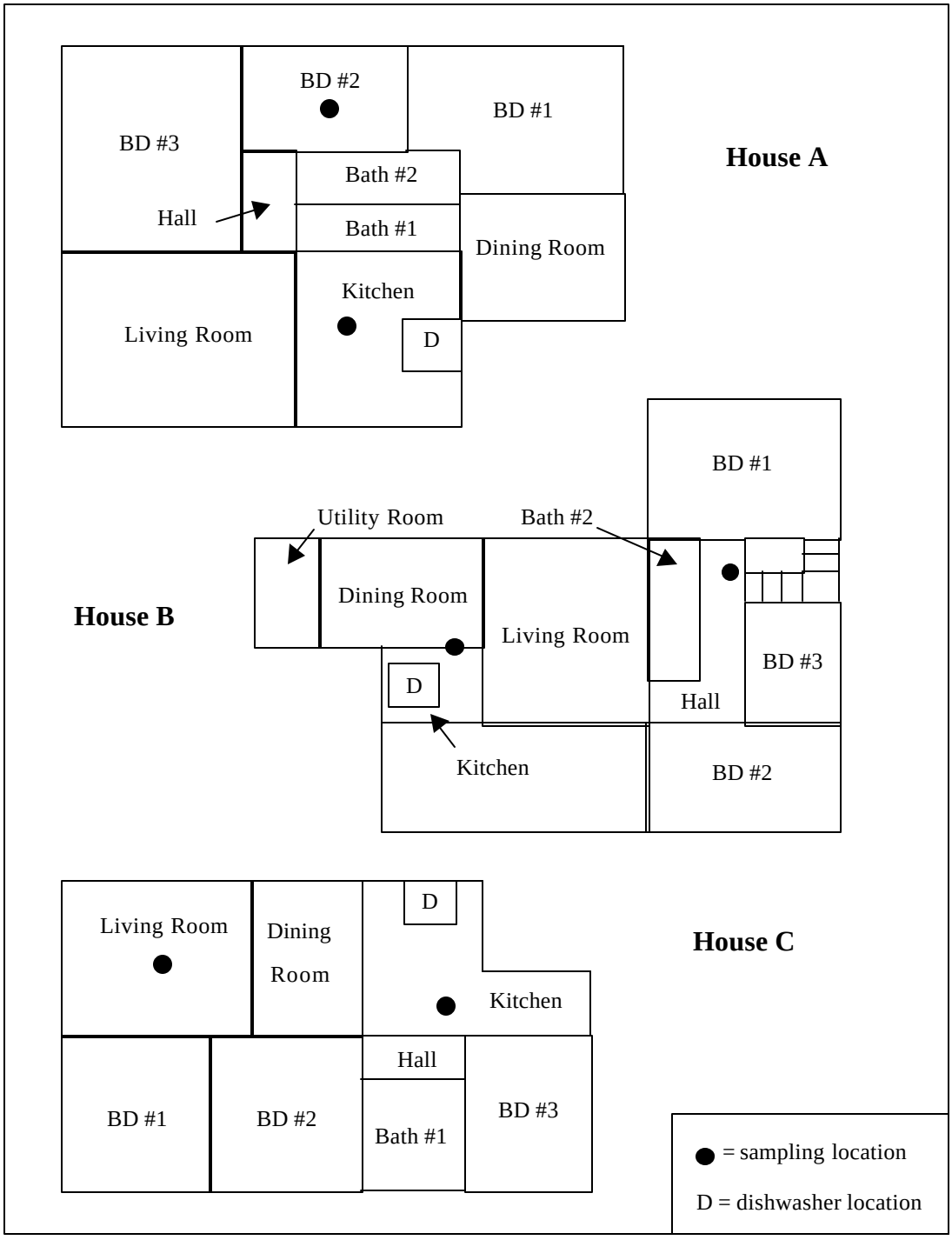


Figure 6-1. Schematic of sample locations for test houses.

6.1.3. Sample collection, storage, and analysis

After the initial injection of SF_6, samples were collected every 30 minutes for a period of four hours. Air from an HVAC supply vent was pumped to a 3-L Tedlar™ bag using 6-mm i.d. Teflon™ tubing and a personal sampling pump (SKC PCXR8). All samples were collected from the same vent. Tracer gas measurements were analyzed using a Lagus Applied Technology, Inc. Model 101 AUTOTRAC Automatic Tracer Gas Monitor. The device consisted of a gas chromatograph equipped with an electron capture detector (GC/ECD), an eight-port sampling manifold and a manual injection port.

Liquid and gas samples were collected, stored, and analyzed in a manner similar to the laboratory experiments (Chapter 4). Two liquid samples (one each from two different tap water sources) were collected before the start of each experiment. Gas samples were collected using the sampling train described in Section 4.4.2. Gas sampling began ten minutes after the start of the dishwasher drying cycle. Five consecutive thirty-minute samples were collected in both the kitchen and one other room. For both rooms, one duplicate sample (sorbent tubes in close proximity to one another) was collected. For test house B, three 30-minutes samples were collected (beginning at t = 1 hour) in the laundry room.

Air velocities exiting return vents were measured using hot wire anemometry (Alnor model 8563). Liquid and air temperatures were measured using a standard mercury thermometer.

6.2. Description of model

6.2.1. Overview

A model developed for related research (Won *et al*., 1998) was used to complete a detailed assessment of the contribution of dishwashers to chloroform inhalation exposure. The model estimates dynamic concentrations of chemicals in

building environments through numerical solution of simultaneous ordinary differential equations associated with each building zone. The model can treat any number of building compartments (rooms or zones), and incorporates source terms such as volatilization of chemicals from contaminated water.

The model considers a house to consist of well-mixed zones (rooms) with prescribed air flow connectivity. A mass balance for the chemical of interest is applied to the indoor air and material phases of each zone. Air exchange between zones includes natural ventilation and mechanical ventilation by a heating, ventilation, and air conditioning (HVAC) system.

A generalized mass balance for a particular zone is given by:

$$V_i \frac{dC_{g,i}}{dt} = \sum_j C_{g,j} Q_{ji} + \frac{\sum_j Q_{r,j} C_{g,j}}{\sum Q_{r,j}} Q_{r,i} - C_{g,i} \sum_j Q_{ij} - C_{g,i} Q_{r,i} + \sum_k E_{ik} \quad (6\text{-}1)$$

where

i = zone i

j = zone j

V_i = volume of zone i (m^3)

$C_{g,i}$ = gas-phase chemical concentration in zone i (mg/m^3)

Q_{ji} = air flow rate from zone j to zone i (m^3/hr)

$Q_{r,j}$ = recirculated air flow rate from zone j (m^3/hr)

E_{ik} = emission rate from source k in room i (mg/h)

6.2.2. Specific emission sources

Example mass balances for showers and dishwashers are described briefly here. A more detailed description of all sources is given by Won *et al*. (1998). The emission rate from a shower can be written as:

$$E = Q_l (C_{l,\,in} - C_l) \quad (6\text{-}2)$$

where

E = emission rate (mg/min)

Q_l = water flow rate (m^3/min)

$C_{l,\,in}$ = influent chemical concentration in the liquid phase (mg/m^3)

C_l = effluent chemical concentration in the liquid phase (mg/m^3)

By completing a mass balance on the descending liquid film as a function of travel time (distance) as described by Little (1992), the liquid concentration in the shower film can be written as:

$$C_l = C_{l,\,in}\ \exp\left(-\frac{K_L A}{Q_l}\right)+\left(\frac{C_g}{H_c}\right)\left(1-\exp\left(-\frac{K_L A}{Q_l}\right)\right) \qquad (6\text{-}3)$$

$K_L A$ = overall mass transfer coefficient (m^3/min)

C_g = chemical concentration in the gas phase (mg/m^3)

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

The emission rate from a dishwasher can be written as:

$$E = Q_g\,(C_g - C_{g,\,in}) \qquad (6\text{-}4)$$

where

E = emission rate (mg/min)

Q_g = gas flow rate (m^3/min)

C_g = headspace chemical concentration in the gas phase (mg/m^3)

The gas phase chemical concentration can be found from simultaneous solution of liquid- and gas-phase mass balances:

$$V_g\,\frac{dC_g}{dt} = \left(C_g - C_{g,\,in}\right)Q_l + K_L A\left(C_l - \frac{C_g}{H_c}\right) \qquad (6\text{-}5)$$

$$V_l\,\frac{dC_l}{dt} = -K_L A\left(C_l - \frac{C_g}{H_c}\right) \qquad (6\text{-}6)$$

Equations 6-4 through 6-6 characterize volatilization of chemicals originally in the water (from-plant emissions).

For chloroform formed and released as a result of dishwasher usage (in-home emissions), a mean (constant) emission source was used to simulate chemical

emissions during dishwasher operation. This assumption was reasonable since headspace concentrations in the dishwasher did not vary significantly during operation. After completion of the dishwasher event, emissions were estimated using an emission source that decayed exponentially with time. An emission rate of 1.36 mg/hr was used, based on an average value of 4.0 μg/L from Table 5-5 (except Experiments 5 and 6) and a gas flow rate of 5.7 L/min (Howard and Corsi, 1998). This average concentration was higher than the average concentration from the standard mix experiments (2.2 μg/L for Experiment 4 and replicates), but included data from all experiments (including actual plate experiments which were noted to have higher concentrations).

6.2.3. Model calibration

The exposure model described in Section 6.2.2 was used to predict room concentrations. Mean values predicted from this model were adjusted as follows:

$$\mu_{\bar{\phi}}\,(\text{room, t}) = C_g\,(\text{room, t}) + \phi_1 \qquad (6\text{-}7)$$

where

$\mu_{\bar{\phi}}$ (room, t) = adjusted room concentration averaged over 30-minutes ($\mu g/m^3$).

C_g (room, t) = predicted room concentration averaged over 30-minutes ($\mu g/m^3$).

ϕ_1 = fitting parameter.

Mean values in Equation 6-7 were originally adjusted by a multiplicative factor as well, i.e., a parameter ϕ_0 multiplied by C_g. Preliminary calibrations with field data indicated that ϕ_0 would approach a value of zero, indicating that the model would have no effect on predicted room concentrations.

Inputs to the exposure model, e.g., shower flow rates and mass transfer coefficients, were treated as constants. Overall accuracy in predicted mean values was

reflected in the fitting parameter ϕ_1, which represented systematic bias in model predictions. For accurate model predictions, ϕ_1 would approach a value of zero.

The standard deviation of a particular data point was described as follows:

$$\sigma(Y_i) = \phi_2 + \phi_3 \mu_{\bar{\phi}} \quad (6\text{-}8)$$

where

$\sigma(Y_i)$ = standard deviation of data point Y_i.

ϕ_2, ϕ_3 = fitting parameters.

Covariance between data points were described as follows (Ang and Tang, 1975):

$$COV(Y_i, Y_j) = \rho_{i,j} \sqrt{Var(Y_i) Var(Y_j)} \quad (6\text{-}9)$$

where

$COV(Y_i, Y_j)$ = covariance between data points Y_i and Y_j.

$\rho_{i,j}$ = correlation coefficient between data points Y_i and Y_j; it describes the extent to which data points Y_i and Y_j are linearly related.

$Var(Y_j)$ = variance of data point Y_j.

For this case the correlation coefficient $\rho_{i,j}$ represented the relationship between data points with respect to both time and space; it was described as follows:

$$\rho_{i,j} = \rho_{location}\ \rho_{noise}\ \rho_{time} \quad (6\text{-}10)$$

where

$\rho_{location}$ = correlation between samples collected at the same time and different locations.

$$= \begin{cases} 1, & \text{if samples were collected in the same room} \\ \phi_4, & \text{otherwise} \end{cases}$$

$\rho_{noise} = \phi_5$ = correlation between samples collected at the same time and location. The parameter ϕ_5 would be 1.0 if there is no random error ("noise") in the samples.

$$\rho_{time} = \exp\left(- \frac{\left| t_i - t_j \right|}{\phi_6} \right).$$

t_i = time that sample Y_i was collected.

t_j = time that sample Y_j was collected.

The parameter ϕ_4 represented the correlation between rooms for two data points. The parameter ϕ_5 represented the correlation between duplicate samples. The parameter ϕ_6 represented the time over which samples were correlated (assuming a normal distribution).

The model parameters ϕ_1-ϕ_6 were optimized using a statistical procedure called a second-moment Bayesian method (SMBM). The measured data and model parameters were described by a probability distribution called the likelihood function. It describes the likelihood that a given set of model parameters would predict the measured data. The model parameters ϕ_1-ϕ_6 were optimized such that the likelihood function was maximized. Additional details regarding the SMBM are given in the Appendix.

6.2.4. Inputs to exposure model

Two water devices were used during field experiments (shower and dishwasher). Emission rate characteristics that were used for all test houses are given in Table 6-2.

Table 6–2. Emission rate characteristics used for all test houses.

Variable	Mean value
Shower $K_L A$, L/min	9.95[(1)]
Dishwasher $K_L A$, L/min	33.5[(2)]
Dishwasher liquid flow rate, L/min	1.0[(2)]
Dishwasher gas flow rate, L/min	5.7[(2)]
Dishwasher emission rate, mg/hr	1.36[(3)]
Dishwasher liquid temperature, °C	40[(2)]

(1) Corsi and Howard (1998), toluene, fine spray
(2) Howard-Reed *et al.* (1999)
(3) average value from Table 5-5 multiplied by a gas flow rate of 5.7 L/min

Howard-Reed *et al.* (1999) completed a total of 18 experiments to characterize ventilation rates from dishwashers. All experiments were completed on the same dishwasher model used for this research. Experiments were completed by injecting isobutylene gas (at 100 ppm) in the dishwasher headspace and measuring concentration using a photoionization detector (Photovac Microtip model HL-2000). All experiments were completed during the wash cycle, though Howard (1998) noted that ventilation experiments were also completed for the entire dishwasher cycle and that there was little variation between cycles. Ventilation rates were calculated assuming a pulse injection followed by an exponential decay in concentration. This assumption is not likely to describe dishwasher ventilation dynamics since there is no air intake and ventilation occurs by volumetric expansion in the headspace. However, calculated decay in logarithmic concentration was noted to be higher linear (r^2 values generally greater than 0.98), suggesting that the approximation was a reasonable assumption. Calculated ventilation rates were generally between 5 and 7 L/min, with an average value of 5.7 L/min (Howard-Reed *et al.*, 1999). For this reason, an average value of 5.7 L/min was used for this research.

A summary of measured data collected during field experiments is given in Table 6-3. These data were also inputs to the exposure model.

Table 6–3. Measured values for test houses.

Variable	Test house A	A (replicate)	B	C
Liquid chloroform concentration (μg/L)	5.97	5.99	7.42	6.73
Shower #1 liquid temperature, °C	32	32	30	28
Shower #1 liquid flow rate, L/min	3.8	8.5	3.0	8.2
Shower #2 liquid temperature, °C	32	n/a	n/a	n/a
Shower #2 liquid flow rate, L/min	7.1	n/a	n/a	n/a
Dishwasher gas volume, L	180	180	160	175
Dishwasher liquid volume, L	5.2	5.2	5.0	5.1
Indoor-outdoor air exchange rate (hr^{-1})	1.06	1.21	1.2(1)	1.47
Return air flow (hr^{-1})	4.4	4.4	4.0(1)	3.8

(1) estimated

6.3. Chloroform concentrations in room air

Concentrations of chloroform in room air as a function of time from both the kitchen and bedroom #1 of house A are shown in Figure 6-2. Measured values refer to gas samples taken over the 30-minute intervals shown. Predicted values were estimated using the mass balance model described in Section 6.2. Estimated ranges of predicted values were developed by using maximum and minimum values from two input parameters: the return air flow rate and the dishwasher emission rate. These parameters were selected as they were subject to the most uncertainty. Maximum values that were twice mean values and minimum values that were half mean values were assumed to estimate approximate ranges. For example, a maximum of 8.8 hr^{-1}, an average of 4.4 hr^{-1}, a minimum of 2.2 hr^{-1} was used for the return air flow rate for house A.

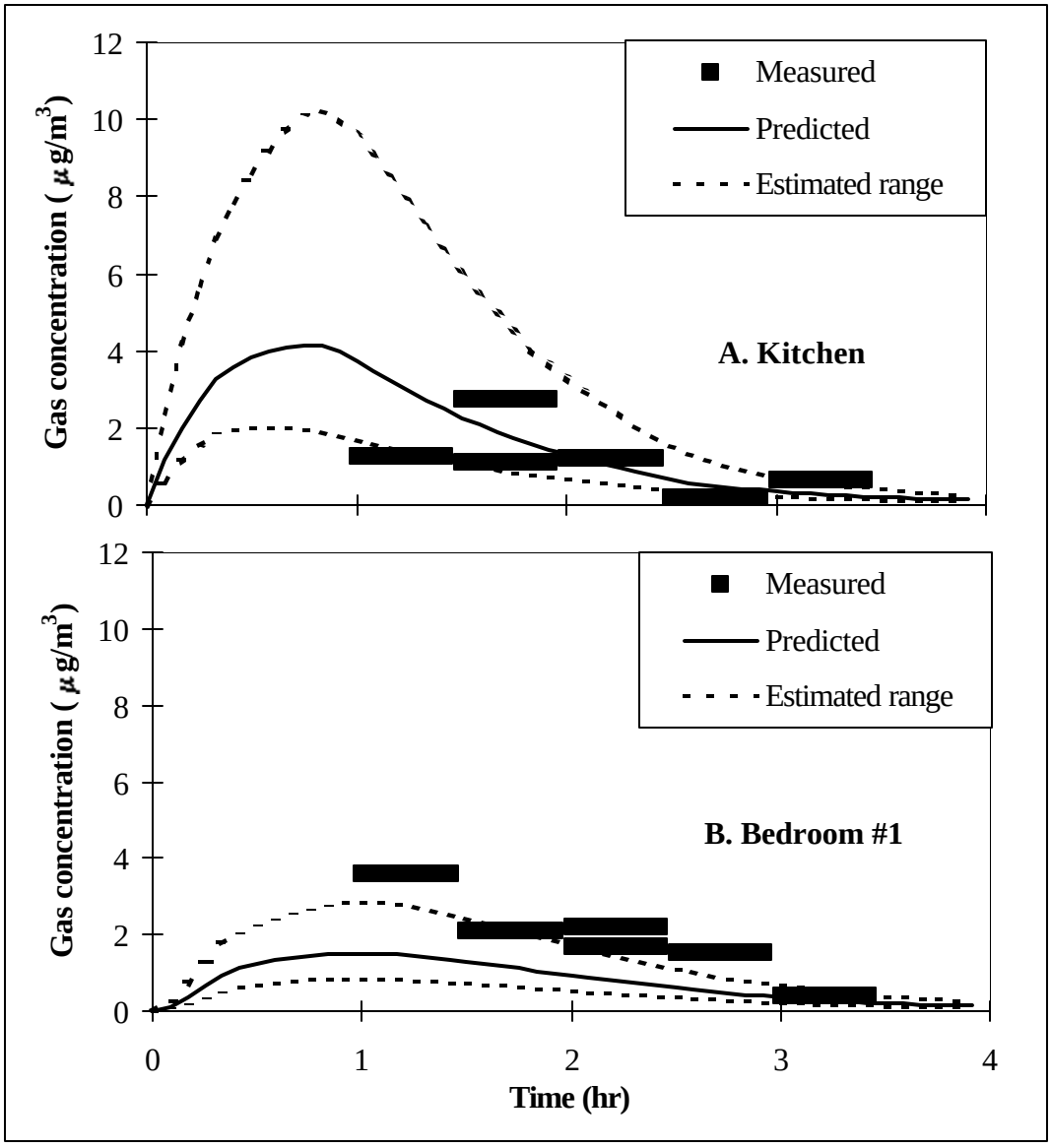


Figure 6-2. Measured and predicted chloroform concentrations in room air (House A) (Gas samples taken over 30-minute intervals shown).

Measured values were consistent with background chloroform levels reported in indoor air from previous monitoring studies, e.g., median values between 0 and 5 $\mu g/m^3$ from TEAM study sites (Wallace, 1997). For both sampling locations, chloroform concentrations generally decreased as a function of time. Measured

concentrations were generally between 1 and 3 $\mu g/m^3$ for both rooms, i.e., little difference existed between the two rooms. It was expected the concentrations in the kitchen would be higher than in the other rooms, a result not evident in Figure 6-2. It was possible that the assumption of homogeneous room concentrations contributed to this discrepancy, particularly given the comparatively short sampling interval for these experiments. In other words, gas samples collected in the kitchen were more representative of return air concentrations than from near-source concentrations.

Duplicate samples were only within a factor of two of one another for kitchen samples (from t = 1.5 to t = 2.0 hours). Differences of greater than a factor of two were measured for some samples in other test houses. Differences of greater than a factor of two were higher than those measured during laboratory experiments (generally within 20% of one another for liquid samples). Since estimated ranges were generally within a factor of two of mean values, duplication errors may have accounted for much of the difference between measured and predicted values.

Measured concentrations were generally within the estimated range of predicted values. Several of the bedroom samples were outside the estimated range, however, possibly due to the assumption of homogeneous mixing of room air. As expected, the estimated ranges were wider for the kitchen because an emission source was present in that room, i.e., a maximum condition for the dishwasher emission rate most affected concentrations in the kitchen.

Concentrations of chloroform in room air as a function of time from both the kitchen and bedroom #1 of house A (replicate) are shown in Figure 6-3. Measured values refer to gas samples taken over the 30-minutes intervals shown. Predicted values and estimated ranges were developed as discussed above.

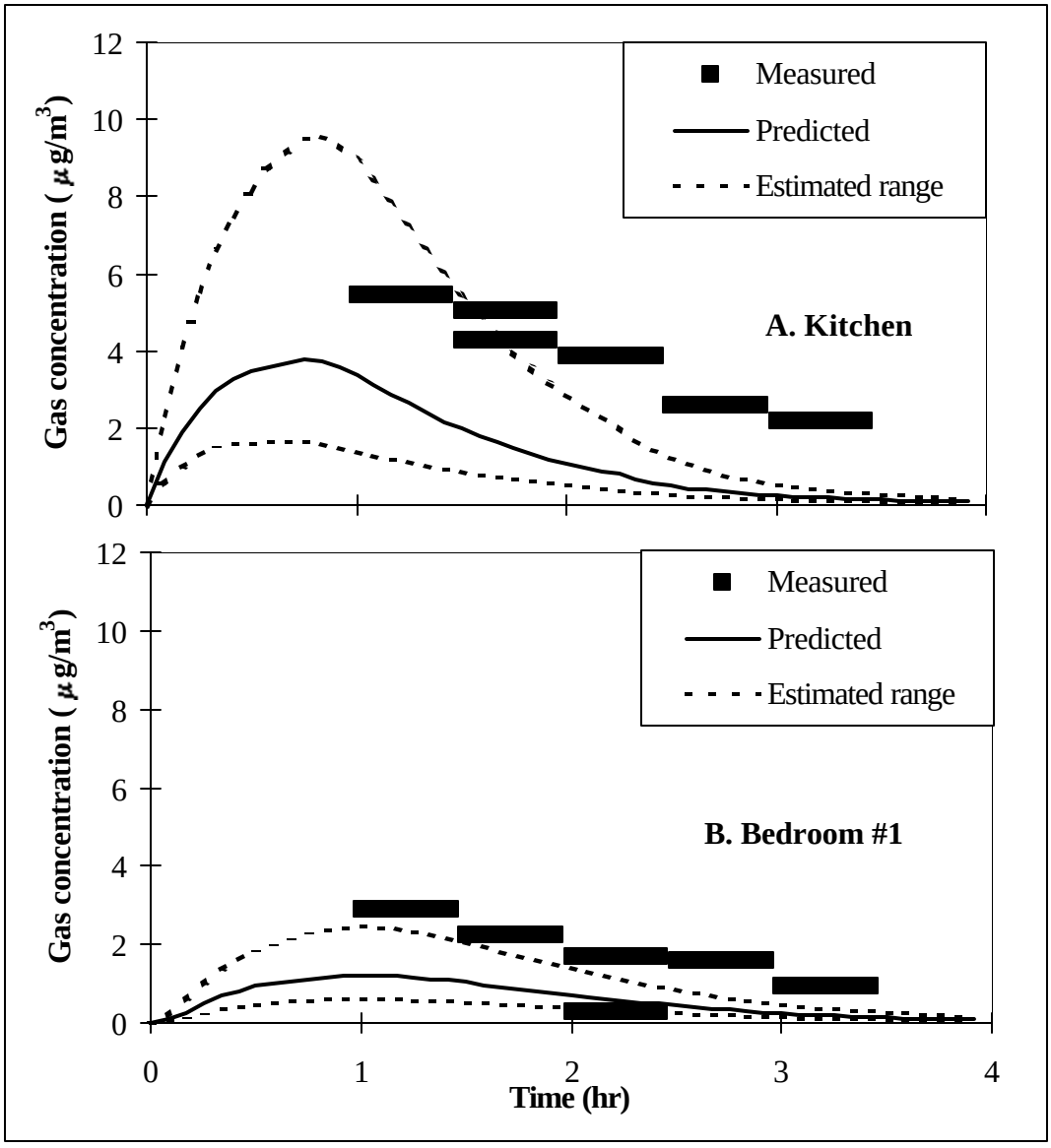


Figure 6-3. Measured and predicted chloroform concentrations in room air (House A replicate) (Gas samples taken over 30-minute intervals shown).

As before, measured concentrations of chloroform decreased with time. Measured concentrations were generally outside of the estimated range of predicted values. Similar to the bedroom sample from house A, samples from both the kitchen and bedroom of house A (replicate) were higher than predicted values. Since

measured values from the bedroom of these two experiments were similar, the assumption of homogeneous room concentrations may also explain discrepancies between measured and predicted values in the bedroom of house A (replicate). Samples from the kitchen of house A (replicate) were consistently more than twice those from house A. Though an average concentration of 4 μg/L in the dishwasher was used for predicted values, values from dishwasher experiments ranged from 0 to 20 μg/L (Table 5-5). It was possible that the dishwasher emission rate accounted for much of this difference, though this would imply that the emission rate was near the maximum of measured dishwasher emission rates reported in Table 5-5.

Concentrations of chloroform in room air as a function of time from both the kitchen and bedroom #1 of house B are shown in Figure 6-4. Measured values refer to gas samples taken over the 30-minute intervals shown. Predicted values and estimated ranges were developed as discussed above. Measured concentrations were generally within the estimated range of predicted values. Both predicted values and the estimated range bounding those values from house B were larger as compared with house A since an additional source was present (the washing machine).

Measured concentrations from house B were similar to previous results even though an additional source was present. This may either indicate that the washing machine had little effect on background levels or that there were discrepancies between measured data based on sampling location. Since concentrations were generally within the estimated range, the washing machine can not be discounted as a possible source of emissions. As with previous discussions, room heterogeneities may account for differences in measured concentrations between experiments.

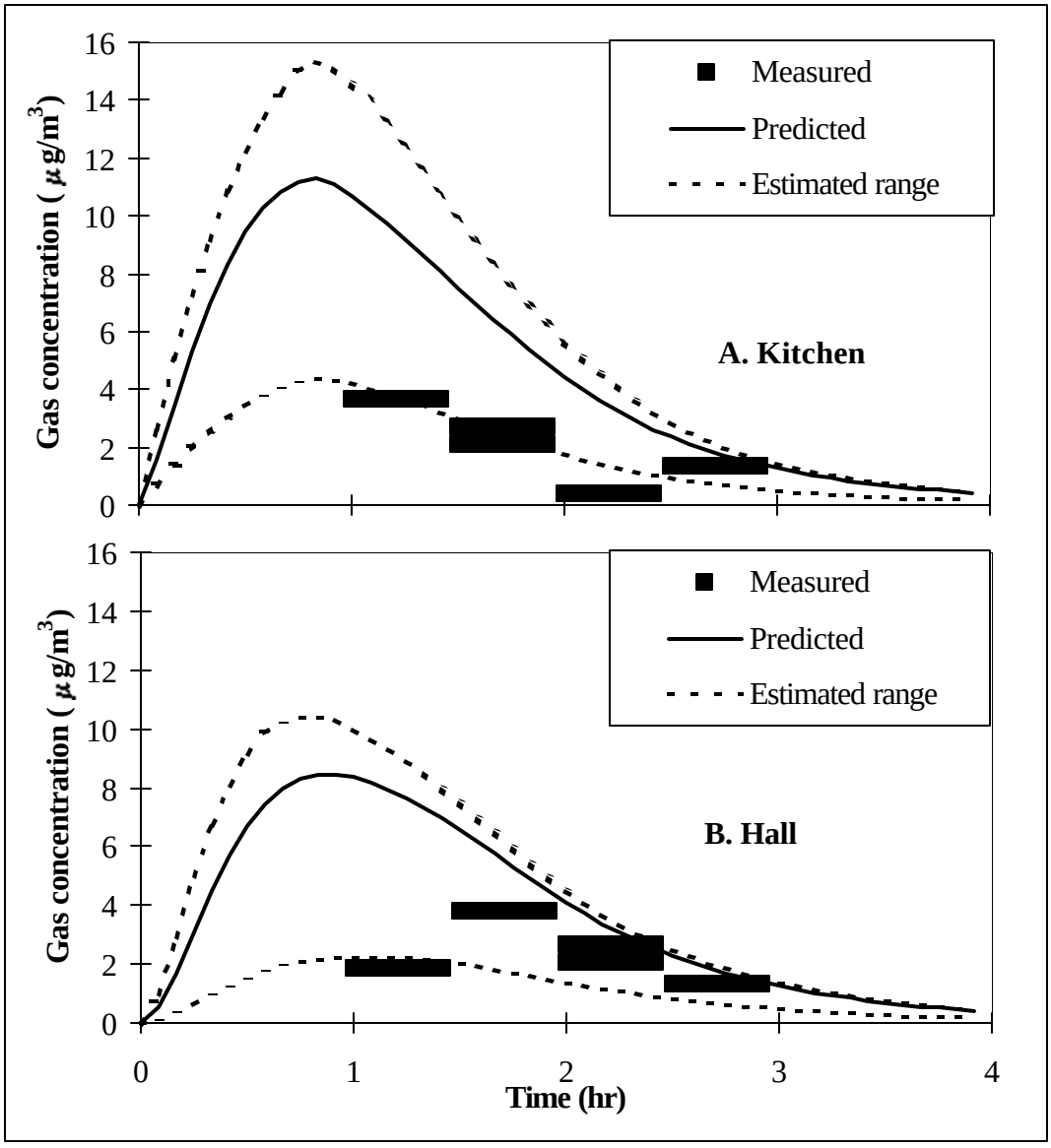


Figure 6-4. Measured and predicted chloroform concentrations in room air (House B) (Gas samples taken over 30-minute intervals shown).

Concentrations of chloroform in room air as a function of time from both the kitchen and bedroom #1 of house C are shown in Figure 6-5. Measured values refer to gas samples taken over the 30-minutes intervals shown. Predicted values and estimated ranges were developed as discussed above.

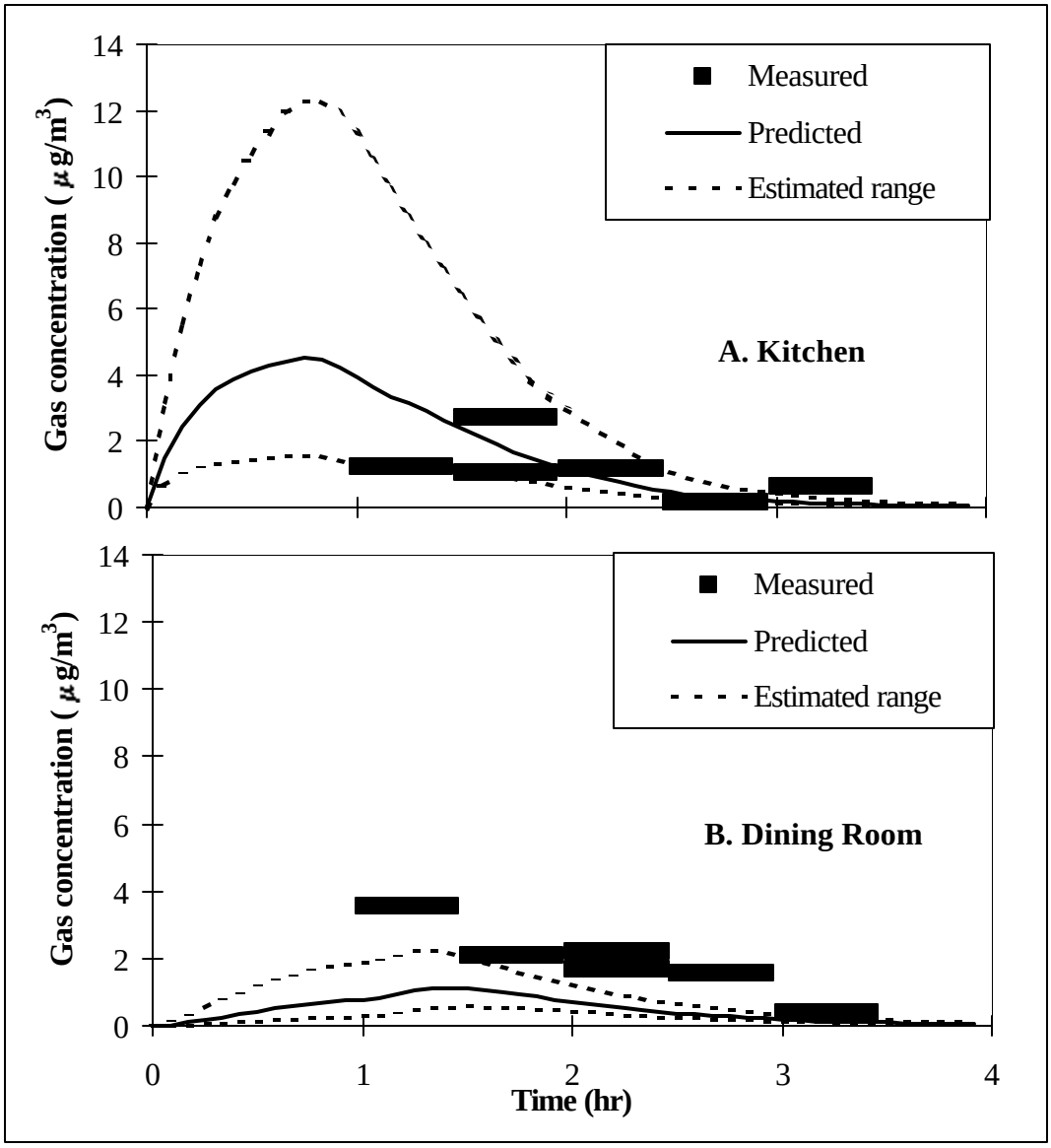


Figure 6-5. Measured and predicted chloroform concentrations in room air (House C) (Gas samples taken over 30-minute intervals shown).

Measured concentrations in the kitchen were generally within the estimated range of predicted values, though measured concentrations in the dining room were generally outside the estimated range. These results were similar to those from house

A and house B, where there was little difference between measured concentrations in the two rooms sampled.

6.4. Updated statistics

A summary of prior means and standard deviations for all model parameters is given in Table 6-4. These estimates were based on the assumption that the model would accurately predict the measured data. For this reason, ϕ_1 and ϕ_2 were assumed to have a value of zero. Standard deviations were estimated based on assumed accuracy of duplicate samples.

Table 6–4. Prior means and standard deviations for model parameters.

Variable	Mean	Standard deviation
ϕ_1	0 $\mu g/m^3$	2 $\mu g/m^3$
ϕ_2	0 $\mu g^2/m^6$	2 $\mu g^2/m^6$
ϕ_3	0.4 $\mu g/m^3$	1 $\mu g/m^3$
ϕ_4	0.5	0.03
ϕ_5	0.9	0.03
ϕ_6	1.0 hr	1.0 hr

A summary of updated mean values for all model parameters and for all test houses is given in Table 6-5. For a given model parameter ϕ_i, updated mean values were reasonably consistent between test houses. Updated mean values for ϕ_1 were between 1 and 3 $\mu g/m^3$, indicating that the model consistently underpredicted measured data. This may have been caused in part by the estimated value for the dishwasher emission rate, since it had more variability relative to other emission parameters. Updated mean values for ϕ_2 and ϕ_3 were typically between 0.3 and 0.5 $\mu g^2/m^6$ and between 0.33 and 0.44 $\mu g/m^3$, respectively. Since model predictions of room concentrations were typically between 0 and 3 $\mu g/m^3$, this would correspond to

predicted data variances of between 0.3 and 1.8 $\mu g^2/m^6$. A preliminary estimate of data variance also can be made from duplicate samples, which were generally between 1.0 and 1.4 $\mu g^2/m^6$. Thus, the model predictions of data variances were consistent with estimates from the measured data.

Table 6–5. Updated mean values for all test houses.

Variable	Updated mean values			
	A	A (replicate)	B	C
ϕ_1 ($\mu g/m^3$)	1.29	2.31	1.64	1.81
ϕ_2 ($\mu g^2/m^6$)	0.44	0.36	-0.43	0.40
ϕ_3 ($\mu g/m^3$)	0.44	0.37	0.33	0.42
ϕ_4 (-)	0.46	0.45	0.47	0.47
ϕ_5 (-)	0.96	0.98	0.94	0.91
ϕ_6 (hr)	1.40	1.36	1.07	1.26

Measured data were more strongly correlated between duplicates (ϕ_5 of between 0.91 and 0.98) than between rooms (ϕ_4 of between 0.45 and 0.47). The higher values of ϕ_5 confirmed similarity between duplicate samples and suggest that the likelihood function was relatively insensitive to changes in either ϕ_4 or ϕ_5. Updated variances of ϕ_6 were between 1 and 1.4 hr. This implies that correlations between samples should decrease by 63% every 1-1.4 hr, a trend that was only somewhat reflected in the experimental results. Since several data points deviated from a general trend of decreasing concentration as a function of time, this likely contributed to the relatively high values for ϕ_5 and ϕ_6. This is particularly true if model results predict a trend different from measured data, e.g., exponentially decaying model predictions versus constant measured data. One artifact of that example is that maximizing the likelihood could result in an assumption of highly correlated data points that were adjusted by a constant in order to more closely

resemble the measured data. Other updated mean values for model parameters were consistent with expected values, suggesting that this effect was relatively minor.

A summary of updated variance values for all model parameters and for all test houses is given in Table 6-6. There was a considerable reduction in variance between prior and updated values for ϕ_1 - ϕ_3 (variance reductions between 68 and 97% for ϕ_1-ϕ_2 and typically between 10 and 31% for ϕ_3). This result was expected since ϕ_1 - ϕ_3 involved estimates of model parameter mean values and data variance values and these estimates were likely to improve with additional information. Variance reductions were considerably smaller for ϕ_4 - ϕ_6 (typically about 10%). This result was expected since these parameters have a more restricted set of possible values. Values of ϕ_4 and ϕ_5 are always between –1 and 1 and values of ϕ_6 were likely to be on the same scale as the indoor-outdoor ventilation rate.

Table 6–6. Updated standard deviations for all test houses.

Variable	Updated standard deviations			
	A	A (replicate)	B	C
ϕ_1 ($\mu g/m^3$)	0.27	0.53	1.27	0.30
ϕ_2 ($\mu g^2/m^6$)	0.19	0.13	0.17	0.16
ϕ_3 ($\mu g/m^3$)	0.69	0.90	0.96	0.79
ϕ_4 (-)	0.09	0.09	0.09	0.09
ϕ_5 (-)	0.10	0.09	0.09	0.10
ϕ_6 (hr)	0.91	0.93	0.99	0.88

A summary of updated correlation coefficients for selected model parameters is given in Table 6-7. Table 6-7 lists all correlation coefficients greater than 0.1 for all model parameters. Only three parameters (ϕ_1, ϕ_2, and ϕ_3) showed a possible relationship. The highest of these were between ϕ_1 and ϕ_3 and between ϕ_2 and ϕ_3. The negative correlation between ϕ_1 and ϕ_3 implied that increased values of ϕ_1 were

associated with decreased values of ϕ_3. This result was not surprising since higher initial concentrations could have been associated with improved characterization of concentration trends (reflected in decreased ϕ_3). This also may explain the positive correlation between ϕ_2 and ϕ_3. If lower room concentrations led to comparatively increased variances between data points, then this would either imply increases in ϕ_2, ϕ_3, or both ϕ_2 and ϕ_3.

Table 6–7. Correlation coefficients for selected model parameters.

Variable	Value of correlation coefficient			
	A	A (replicate)	B	C
ρ (ϕ_1, ϕ_2)	<0.1	0.36	0.48	<0.1
ρ (ϕ_1, ϕ_3)	-0.50	-0.22	-0.13	-0.37
ρ (ϕ_2, ϕ_3)	0.76	0.70	0.54	0.82

6.5. Experimental design

The results in Section 6.4 can also be used for purposes of experimental design, i.e., selection of sampling times and locations that has the largest effect on reducing uncertainty. Three different sampling schemes were considered; in all cases a total of 12 samples was selected. For sampling scheme #1, samples were collected in two rooms, one location within each room, from t = 1 hour to t = 3 hours. For sampling scheme #2, samples were collected in one room, one location within that room, from t = 1 hour to t = 5.5 hours. For sampling scheme #3, samples were collected in two rooms, two locations within each room, from t = 1 hour to t = 2 hours. Updated means, standard deviations, and correlation coefficients from House A were used for this illustration, though similar results were also found from the other test houses. A summary of percent reduction in model parameter ϕ_1 - ϕ_6 for each of the sampling scheme described above is given in Table 6-8.

Table 6–8. Variance reductions for three sampling plans (using updated values from House A).

Variable	Updated standard deviations Plan #1(1)	Plan #2(2)	Plan #2(2)
ϕ_1	33.5%	41.7%	25.7%
ϕ_2	38.3%	42.1%	37.4%
ϕ_3	60.9%	68.7%	50.8%
ϕ_4	69.4%	69.4%	68.8%
ϕ_5	8.2%	6.3%	7.0%
ϕ_6	7.5%	9.3%	5.5%

(1) Plan #1: samples were collected in two rooms, one location within each room, from t = 1 hour to t = 3 hours.
(2) Plan #2, samples were collected in one room, one location within that room, from t = 1 hour to t = 5.5 hours.
(3) Plan #3, samples were collected in two rooms, two locations within each room, from t = 1 hour to t = 2 hours.

As shown in Table 6-8, all three sampling plans displayed similar results. The largest reduction in variances from model parameters ϕ_1 - ϕ_6 were generally seen for sampling plan #2 (one room, one location). This result was plausible since samples were noted to be more correlated in the same room than between different room (see Table 6-5.

7. EXPOSURE ASSESSMENT

An exposure assessment was completed to examine chloroform concentrations and resulting inhalation from typical water usage patterns. The model described in Section 6.2 was used for this assessment.

7.1. Model inputs

The computational model was evaluated using inputs and activity patterns that were expected to represent a typical family. Several of the inputs were similar to those used for the screening assessment (Chapter 3).

7.1.1. House characteristics

As with the screening assessment, all scenarios were developed with a house area of 2,000 ft^2 occupied by a family of four. Six different zones (rooms) were used: kitchen, utility (washer/dryer) room, shower, bath room, bedrooms, and living rooms. Individual room volumes were estimated using reasonable floor areas with an 8-ft ceiling. Volumes for the six rooms are listed in Table 7-1.

Table 7–1. Room volumes.

Room	Volume (m^3)
Kitchen	18.1
Utility Room	18.1
Shower	5.4
Bath	10.8
Bedrooms	200.5
Living Rooms	200.5
Total	453.4

It was assumed that an HVAC system was operated throughout; for this reason, individual bedrooms and living rooms were not separated. This simplification was reasonable since rooms without sources would have similar concentrations when an HVAC system operates (as indicated by Equation 6-1).

7.1.2. Ventilation characteristics

For this assessment, ventilation was assumed to occur through infiltration and mechanical ventilation. Transient air exchange between rooms was considered negligible. Any filtering capacity for the HVAC system was neglected.

Numerous studies have been completed on overall air exchange between indoor and outdoor air, the largest being a data set compiled by Brookhaven National Laboratory. Murray and Burmaster (1995) used these data to develop univariate lognormal distributions of air exchange rates. Over all regions and seasons, the arithmetic mean and standard deviation were 0.76 and 0.88 hr^{-1}, respectively. Based on the field experiments completed and the distribution described above, an air exchange rate of 1.0 hr^{-1} was assumed for air exchange between indoor and outdoor air.

For mechanical ventilation, a total return air flow of 1.0 hr^{-1} was used. Sherman (1999) reported a range of between 60 and 100 ft^3/min, which corresponds to between 0.22 hr^{-1} and 0.37 hr^{-1} from the total volume listed in Table 6-1 (453.4 m^3). Since return air flows from field experiments completed for this research were significantly higher (approximately 4.0 hr^{-1}), an intermediate value of 1.0 hr^{-1} was used.

7.1.3. Chemical characteristics

Chloroform was chosen as the chemical of interest. As with the screening assessment (Chapter 3), a chloroform concentration of 30 µg/L originally in the tap water was used. Henry's law constants at various temperatures were estimated using

data from Ashworth *et al*. (1988). Preliminary model estimates indicated that sorptive interactions with material surfaces only had a minor effect on predicted concentrations, so this effect was neglected.

7.1.4. Water device characteristics

It was assumed that four water devices were used: shower, dishwasher, washing machine, and toilet. Mass transfer data and flow rates for each water source are listed below in Table 7-2. Liquid temperatures were estimated based on typical operating conditions.

Table 7–2. Volatilization from water sources data for base case.

Variable	Device			
	Shower[1]	Dishwasher[2]	Washing machine[3]	Toilet[4]
K_LA, L/min	9.4	33.5	1.8	0.07
Liquid flow rate, L/min	9.3	1.0	13.9	0.2
Gas flow rate, L/min	n/a	5.7	55.0	n/a
H_c (m^3_{liq}/m^3_{gas})	0.27	0.52	0.34	0.27
Gas Volume, L	n/a	181	104.0	n/a
Liquid Volume, L	n/a	7.5	46.0	n/a
Liquid Temperature, °C	30	35	30	20

(1) Corsi and Howard (1998)
(2) Howard-Reed *et al.* (1999)
(3) Howard and Corsi (1998)
(4) Little (1996)

7.1.5. Activity patterns

Water usage rates were based on available data from the Exposure Factors Handbook (USEPA, 1996). Table 7-3 lists frequency and duration of water devices used in this assessment. Event frequency was based on a family of four occupying the house. This resulted in 12 dishwashing and 8 washing machine events in one week.

Since it was unlikely that the usage rates in Table 7-3 could have been linearly extrapolated to four persons, a typical day of two shower events, one dishwasher event and one washing machine events was selected. One water usage pattern was considered: two consecutive showers began at 7:00 a.m., one dishwasher event began at 8:00 p.m., and one washing machine event began at 8:00 p.m.

Table 7–3. Summary of water usage characteristics (USEPA, 1996).

Event	Duration	Basis
Shower	8 min	0.74 events/day/person; median value
Dishwasher	45 min(1)	3 dishwasher events/week/person; median value
Washing machine	45 min	2 washing machine loads/week/person; median value

(1) estimated

Since information was only available regarding total time spent in various locations and activities, specific activity patterns were prescribed. Activity patterns for this assessment were chosen such that they were consistent with available data. The USEPA (1996) listed the following median times spent for activities relevant to this assessment: 35 minutes in food preparation, 30 minutes in food cleanup, 30 minutes doing dishes/laundry, 540 minutes in the bedroom, 60 minutes in the utility room or laundry room, 60 minutes in the kitchen, and 25 minutes in the bath room. Table 7-4 lists times and locations for the base case activity pattern used for this assessment.

Table 7–4. Activity pattern for base case.

Room	Start time	End time
Bedroom	12:00 a.m.	7:00 a.m.
Shower	7:00 a.m.	7:10 a.m.
Bath Room	7:10 a.m.	7:20 a.m.
Dining Room	7:20 a.m.	8:00 a.m.
Living Room	8:00 a.m.	12:00 p.m.
Kitchen	12:00 p.m.	12:10 p.m.
Dining Room	12:10 p.m.	12:50 p.m.
Bath Room	12:50 p.m.	1:00 p.m.
out of house	1:00 p.m.	6:00 p.m.
Kitchen	6:00 p.m.	6:30 p.m.
Dining Room	6:30 p.m.	7:30 p.m.
Kitchen	7:30 p.m.	8:00 p.m.
Washer	8:00 p.m.	8:20 p.m.
Kitchen	8:20 p.m.	8:40 p.m.
Bath Room	8:40 p.m.	8:50 p.m.
Living Room	8:50 p.m.	11:00 p.m.
Bath Room	11:00 p.m.	11:10 p.m.
Bedroom	11:10 p.m.	12:00 a.m.

7.2. Results

Figure 7-1 shows predicted chloroform concentrations as a function of time using the water usage patterns described in Section 7.2. As shown as Figure 7-1, the showering events were the dominant source of chloroform emissions. After ten minutes of showering (at 7:10), the chloroform concentration in the shower was approximately 240 $\mu g/m^3$. Jo *et al*. (1990) measured concentrations of chloroform during a 10-minute shower ranging from 125 to 313 $\mu g/m^3$, where tap water concentrations ranged from 12 to 40 $\mu g/L$. This result is also comparable to the concentration after an 8-minute shower that was estimated from the screening assessment (333 $\mu g/m^3$), suggesting that the screening assessment was a reasonable first estimate of chloroform exposure. The chloroform concentration continued to increase after the second shower, reaching a maximum of approximately 450 $\mu g/m^3$.

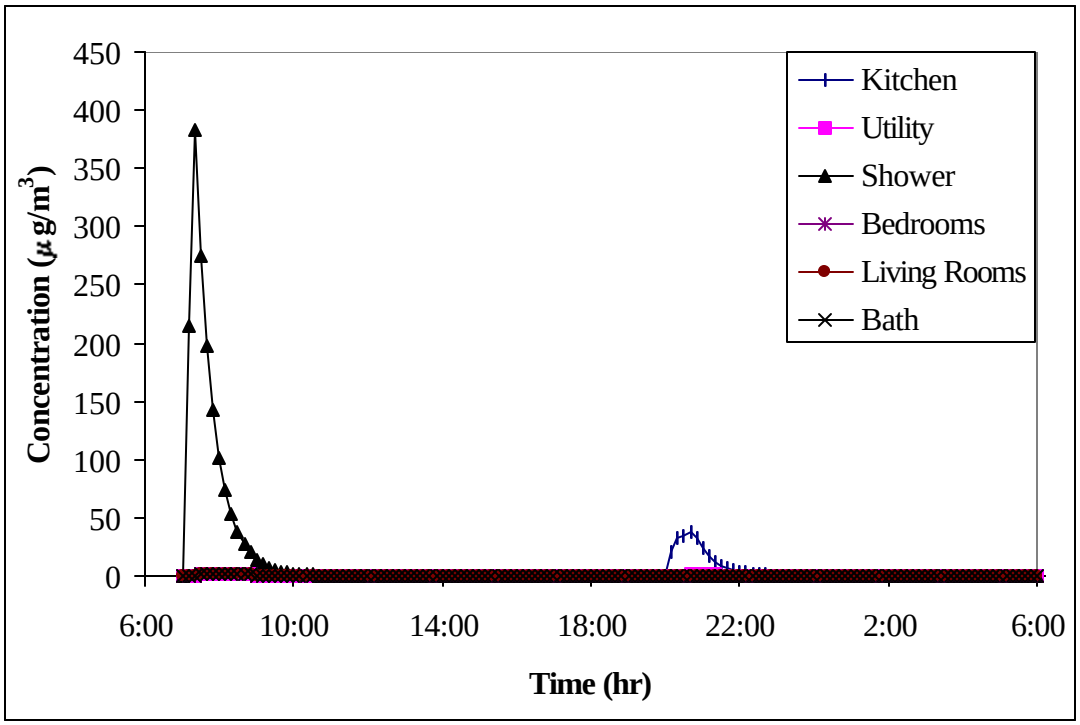


Figure 7-1. Predicted chloroform concentrations as a function of time for base case activity scenario.

The next largest chloroform concentration occurred in the kitchen. Figure 7-2 shows chloroform concentrations for all rooms except the shower to better examine chloroform concentrations in other rooms. Chloroform concentrations increased steadily at the beginning of the dishwasher and washing machine events and reached a maximum of approximately 40 µg/m^3.

Figures 7-1 and 7-2 indicate that the showering and kitchen events had only a minor effect on predicted chloroform levels in other parts of the house. Chloroform concentrations in the other rooms were generally between 0 and 5 µg/m^3, which are typical background concentrations for chloroform in indoor air.

Although predicted background concentrations of chloroform were consistent with typical values, predicted peak concentrations from the hypothetical house were much higher than those measured during field experiments. Measured chloroform

concentrations in rooms were typically between 0 and 5 g/m^3, and the highest measured concentration was 8.38 g/m^3 (House B, laundry room). A sensitivity analysis was completed to better understand differences between predicted concentrations from the hypothetical house and measured concentrations from the test houses.

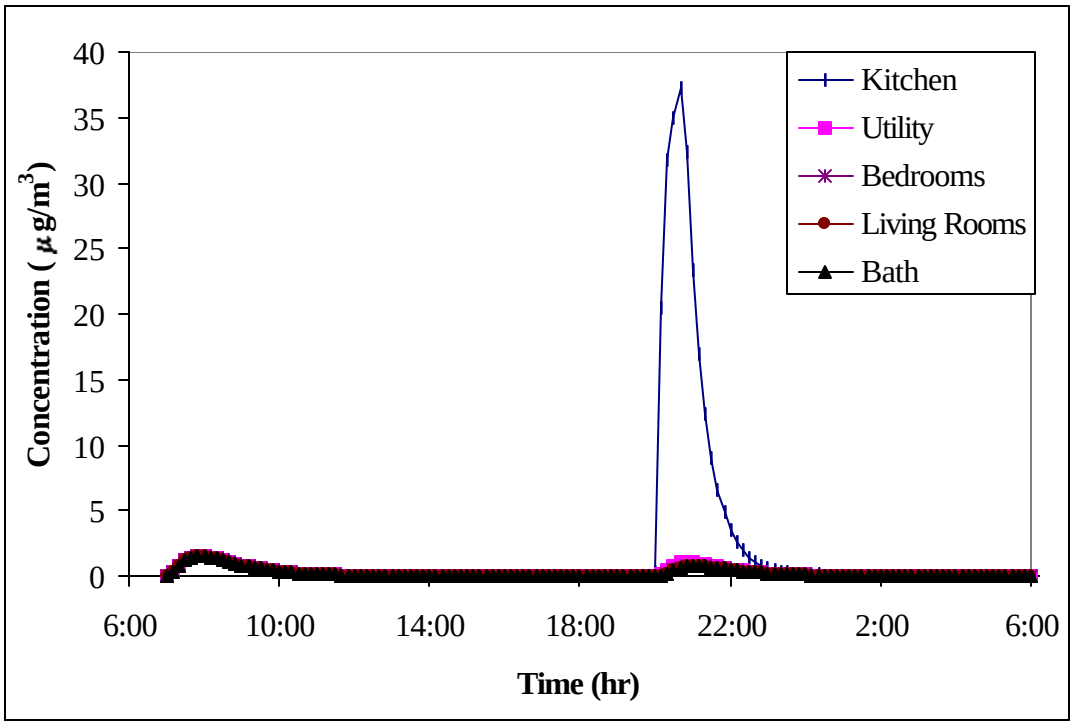


Figure 7-2. Predicted chloroform concentrations for base case (except shower).

7.3. Sensitivity analysis

Figure 7-3 illustrates the effect of shower flow rate on chloroform concentration in the shower. Two different flow rates were used: (1) a typical water flow rate of 3.4 gpm and (2) a lower water flow rate of 2.0 gpm. The lower flow rate represents the average flow rate from water conserving or "low-flow" shower heads (USEPA, 1996). A K_LA value of 8.0 L/min was used for the low-flow shower head, based on experimental work by Moya *et al*. (1999).

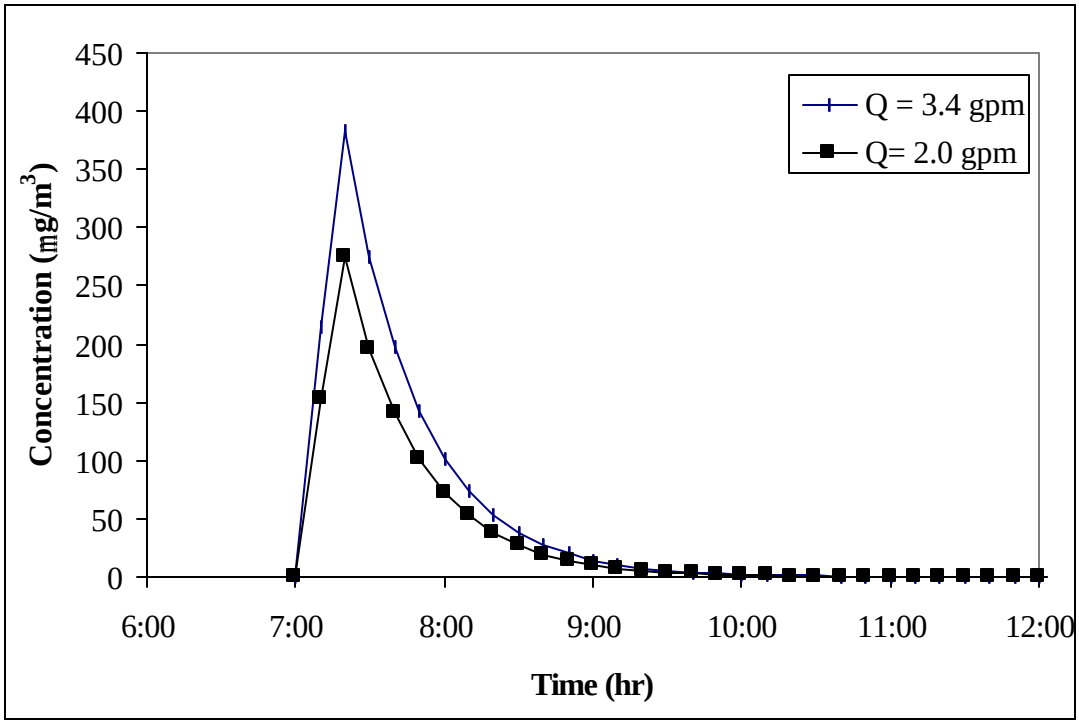


Figure 7-3. Predicted chloroform concentrations at different water flow rates.

As shown in Figure 7-3, installation of a low-flow shower head had only a minor effect on chloroform concentrations in the shower. The maximum concentration in the shower decreased from approximately 400 $\mu g/m^3$ at the normal water flow rate to approximately 275 $\mu g/m^3$ at the lower flow rate. Several reasons may explain why installation of a water-conserving shower head did not have a stronger effect on chloroform concentrations. The average $K_L A$ decreased from 9.4 to 8.0 L/min when using a low-flow shower, meaning that mass transfer characteristics changed little. As shown by the first term in Equation 6-3, chloroform emissions actually increase with a decrease in water flow rate. This occurs because a decrease in flow rate leads to an increase in travel time and thus an increase in the time for mass transfer to occur. Also, chloroform emissions are a function of the exponential of

water flow rate and K_LA, meaning that changes in either of these variables would not result in a linear change in effluent liquid concentration.

Figure 7-4 shows predicted chloroform concentrations as a function of three different indoor-outdoor air exchange rates: 0.5 air changes per hour (ACH), 1.0 ACH, and 2.0 ACH. Predicted chloroform concentrations in the gas phase of the kitchen are shown in Figure 7-4 (from time 18:00 to 0:00), and similar conclusions were also found for concentrations in all other rooms and times. Peak predicted chloroform concentrations decreased by 15% when the air exchange was increased from 0.5 to 1.0 hr^{-1}, and by 37% when the air exchange was increased from 0.5 to 2.0 hr^{-1}.

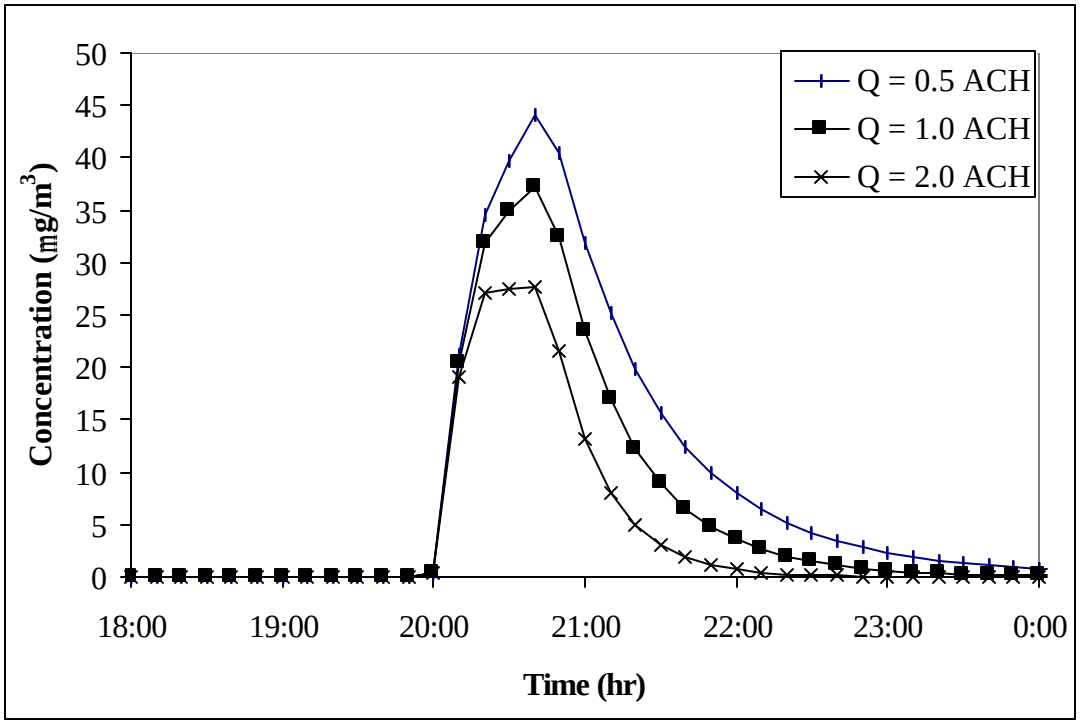


Figure 7-4. Predicted chloroform concentration at different indoor-outdoor air exchange rates.

This result was expected since the dishwasher was the only significant source of emissions at this time. The concentration of a chemical resulting from a time-averaged (step) release can be written as:

$$C(t) = \theta\, E/V\, (1 - e^{-t/\theta}) \qquad (6\text{-}7)$$

where

C(t) = concentration at time t (μg/L)

1/θ = air exchange rate (/hr)

E = emission rate (μg/hr)

V = volume (L)

t = time (hr)

In Figure 7-4, the step release occurred at 20:00 hours and the maximum at approximately 21:30 hours (a difference of 1.5 hours). For a time of 1.5 hours, the following concentrations were determined from Equation 6-7: 1.06 E/V for an air exchange rate of 0.5 hr^{-1}, 0.77 E/V for an air exchange rate of 1.0 hr^{-1}, and 0.48 E/V for an air exchange rate of 2.0 hr^{-1}. As expected, these concentrations were similar to the decreases described above. Resulting concentrations from the two methods were not identical since other emission sources were present at lower levels, e.g., showers.

Figure 7-5 shows predicted chloroform concentrations as a function of three different return air exchange rates: 1.0 ACH, 2.0 ACH, and 4.0 ACH. Predicted chloroform concentrations in the gas phase of the kitchen are shown in Figure 7-5, and similar conclusions were also found for concentrations in all other rooms and times. Peak predicted chloroform concentrations decreased by 24% when the air exchange was increased from 1.0 to 2.0 hr^{-1}, and by 45% when the air exchange was increased from 1.0 to 4.0 hr^{-1}. As before, these decreases were expected since only one source (the dishwasher) was dominant at this time and Equation 6-7 approximated the concentration as a function of time.

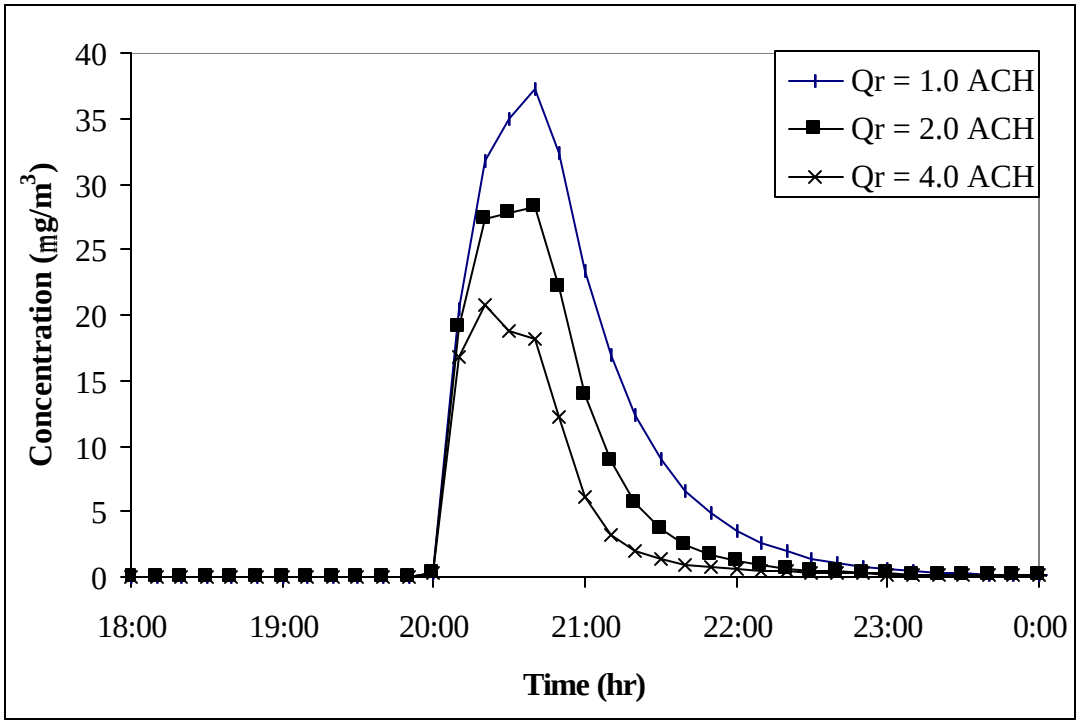


Figure 7-5. Predicted chloroform concentration at different return air exchange rates.

Figure 7-6 shows predicted chloroform concentrations as a function of three different dishwasher emission rates: 1.36 mg/hr, 0.68 mg/hr, and 0.34 mg/hr. Peak predicted chloroform concentrations decrease by 40% when emission rate was decreased from 1.36 to 0.68 mg/hr, and by 54% when emission rate was decreased from 1.36 to 0.34 mg/hr. As before, this result was expected since only one source (the dishwasher) was dominant at this time.

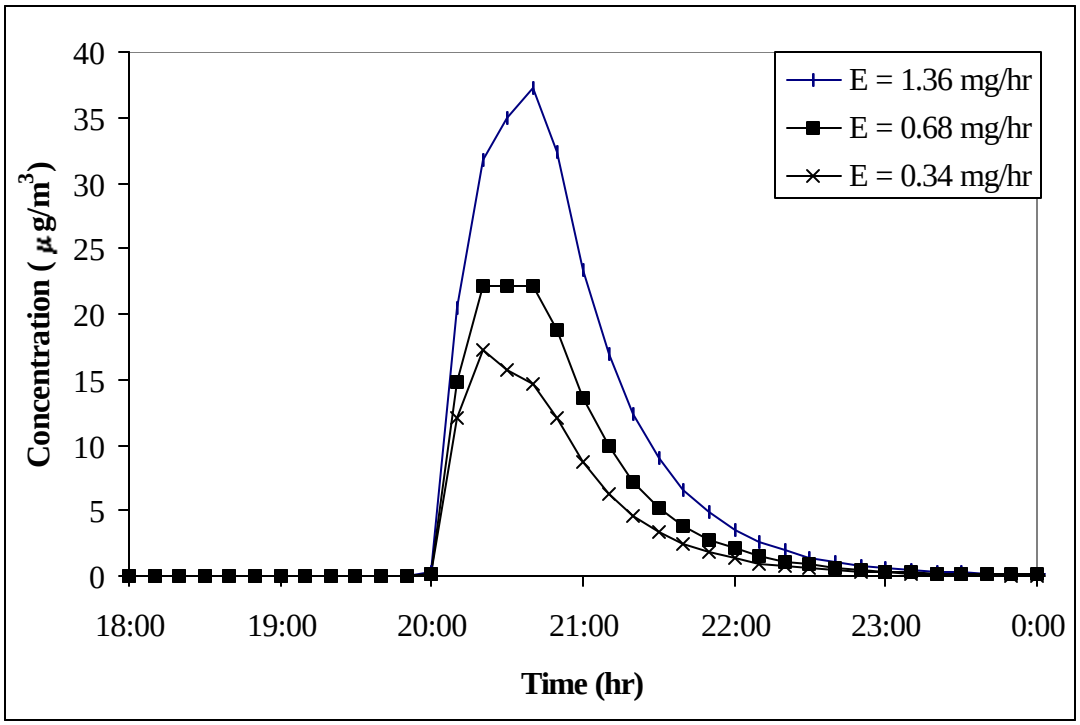


Figure 7-6. Predicted chloroform concentration at different dishwasher emission rates.

7.4. Comparison to field experiments

As noted earlier, predicted peak concentrations from the hypothetical house were much higher (factor of eight in the kitchen) than those measured during field experiments. One difference was that tap water concentrations from experiments were generally below 5 µg/L, whereas for the hypothetical house a concentration of 30 µg/L was used. The sensitivity analysis also pointed to key variables that contributed to differences between predicted concentrations from the hypothetical house and measured concentrations from the test houses.

For the hypothetical house a return air flow rate of 1.0 hr^{-1} was used whereas measured values were typically around 4.0 hr^{-1}. As shown in Figure 7-5, this factor alone led to a factor of two difference between predicted concentrations. Predicted

concentrations were also sensitive to the indoor-outdoor air exchange rate and the dishwasher emission rate. Thus, it was plausible that peak predicted concentrations in the kitchen (approximately 40 $\mu g/m^3$) could have been considerably higher than measured values (typically 5 $\mu g/m^3$).

Another factor that likely led to discrepancies between model house predictions involved the degree of mixing in rooms. The model described in Section 6.1 assumed that all rooms were homogeneously mixed, an ideal condition that is likely never achieved in actual houses (particularly involving transient concentration levels over comparatively short sampling intervals). Thus, concentration variations existed within a given room and likely contributed to the differences between predicted and measured concentrations.

7.5. Exposure assessment

The contribution to chloroform inhalation exposure from the water usage pattern described earlier is summarized in Figure 7-7. For this water usage pattern, two consecutive showers began at 7:00 a.m., one washing machine event began at 8:00 p.m., and one dishwasher event began at 8:00 p.m. As with the screening assessment, inhalation exposure was estimated based on average room concentration and an average inhalation rate of 10.6 L/min for adults (USEPA, 1996). Inhalation exposure associated with chloroform emissions from toilets was not included in Figure 7-7 as the mass inhaled was much lower than for other water sources. For dishwashing activities, both “in-home” and “from-plant” exposures were considered. The “from-plant” exposure involves chloroform that is formed at the treatment plant and later released to indoor air during residential water usage.

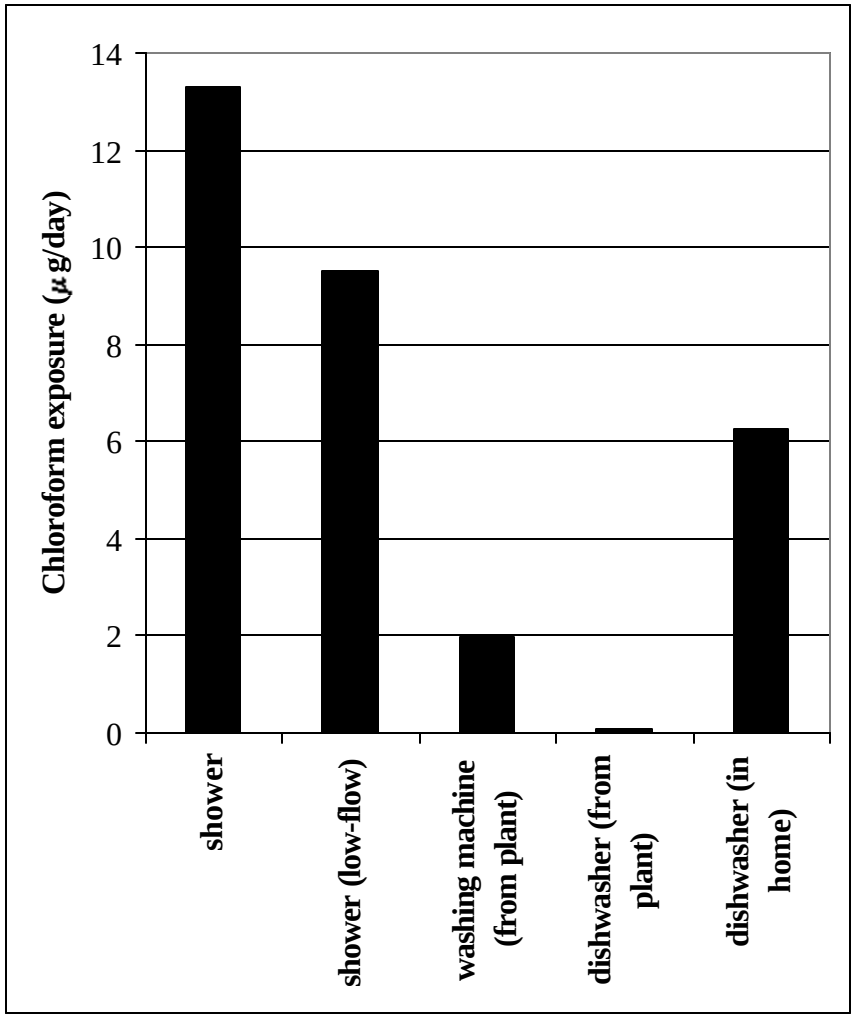


Figure 7-7. Summary of chloroform inhalation exposure from hypothetical water usage pattern.

Showering represented the largest percentage of total exposure at approximately 62%, with in-home dishwashing 29%, washing clothes 9.1%, and from-plant dishwashing less than 1%. A low-flow shower had only a minor effect on overall exposure. For this case, inhalation exposure from showering decreased from 13.3 to 9.5 μg of chloroform (44% of total). Dishwashing was also a significant activity. Though from-plant exposure for dishwashers was relatively insignificant (a

finding similar to the screening assessment), in-home dishwasher exposure was important relative to sources other than showers.

The above results were for one example water usage and activity pattern, so actual inhalation exposures are case-specific. For example, inhalation exposure from in-home dishwashing will increase if the occupant were in the kitchen while the dishwasher was operating. In addition, estimated concentrations of chloroform in room air were noted in Section 7.3 to be sensitive to recirculation and indoor-outdoor air exchange rates. Heterogeneities in concentration within a given room are also likely to be a source of error. Predicted chloroform concentrations were also noted to be considerably higher than measured concentrations from the test houses. Personal monitoring is likely to give a more accurate estimation of inhalation exposure to chloroform.

8. CONCLUSIONS AND RECOMMENDATIONS

8.1. Summary

The research described in this dissertation involved laboratory experiments, field experiments, exposure modeling predictions, and statistical evaluation of model predictions. The overall goal of this work was to better characterize emissions and subsequent exposure to chloroform in homes. A series of 14 preliminary flask experiments and 16 laboratory experiments were completed to quantify formation and emissions of THMs from the use of chlorine-containing detergents in residential dishwashers. A source/exposure model was used to predict chloroform exposure for a variety of activity scenarios. A series of field experiments were completed in three occupied homes to measure chloroform concentrations during periods of residential water usage. These data were then used to evaluate the exposure model within a statistical framework.

Flask experiments involved mixing food and dishwasher detergent in water, and were intended to identify chemicals that may form from dishwasher usage. The following foods were used: beans, beef, bread, cereal, eggs, fish, lima beans, oil, pasta, potatoes, poultry, rice, sugar, and tomatoes. Laboratory experiments involved collection of liquid and gas samples over the course of a dishwasher operating cycle. Experiments were completed using plates from an actual residence and using food from a standard mix developed from food consumption data. Food amount, dish soap amount, and detergent type were also varied for these experiments.

Field experiments involved operating a shower and dishwasher at each test house, then measuring gas chloroform concentrations in two different rooms. House and ventilation characteristics also were quantified. These data were then used to evaluate the exposure model using a second-moment Bayesian method.

A computational model developed for related research was used to complete a detailed assessment of the contribution of dishwashers to chloroform inhalation exposure. House characteristics and water usage patterns were constructed based on

existing literature. Activity patterns were developed from existing literature to estimate time spent in various locations in the house. Overall inhalation exposure to chloroform was estimated based on predicted room concentrations from the model and time spent in each location in the house.

8.2. Conclusions

1) *Food type is a significant factor in the formation of chloroform.*
   Flask experiments indicated that the highest chloroform concentrations formed from beef and tomatoes.
2) *Chloroform is the only THM consistently detected at elevated levels in liquid and gas samples.*
   DBCM and bromoform were generally not detected in dishwasher samples. BDCM was detected in most dishwasher samples, but typically one-tenth chloroform levels.
3) *There is significant potential for chloroform formation when chlorine-containing dishwasher detergents are used.*
   For flask experiments, chloroform was detected in all samples and liquid concentrations ranged from 1-41 mg/L. For dishwasher experiments, background samples of chloroform were generally between 0 and 10 μg/L; liquid chloroform levels in the wash cycle were typically at least 50 μg/L. Chloroform concentrations in the gas phase were generally between 0 and 5 μg/L in the headspace.
4) *Detergent brand has a major effect on the potential for chloroform formation.*
   Of the three detergents tested (Cascade™, Electrosol™, and Sunlight™), only Sunlight™, the one containing chlorine, produced elevated THM levels in the dishwasher.
5) *Shower and dishwasher usage are the dominant activities leading to elevated chloroform levels in indoor air.*

Chloroform concentrations in the rooms tested were typically between 0 and 5 $\mu g/m^3$. The highest concentrations were generally measured immediately after dishwashing and showering events.

8.3. Recommendations for future research

Recommendations for future research include:

1) A better understanding of reaction kinetics in the liquid phase of the dishwasher is needed. This would lead to improved identification of factors contributing to DBP formation.
2) Emission rates from the dishwasher are directly proportional to the dishwasher headspace air exchange rate. Additional experimental work from a wider range of commercial dishwashers would lead to better estimates of emission rates.
3) Other possible sources of chlorinated organic chemicals were not studied. These include toilet disinfectants, indoor saunas and hot tubs, and cleaning with chlorinated bleaches. Experimental work from these sources would identify additional routes of THM exposure for sub-populations involved with these sources.
4) Field experiments involving personal monitoring should be completed. Such monitoring would be of particular value in environments likely to have elevated DBP levels, e.g., hospitals, day care centers, restaurants, and laundromats.
5) Water devices can emit chlorine gas (as Cl_2) from either free chlorine residual or from in-home sources. Chlorine gas is a reactive chemical and likely influences chemical reactions in indoor air. An assessment of the relative contribution of residential water devices on chlorine gas emissions is needed.

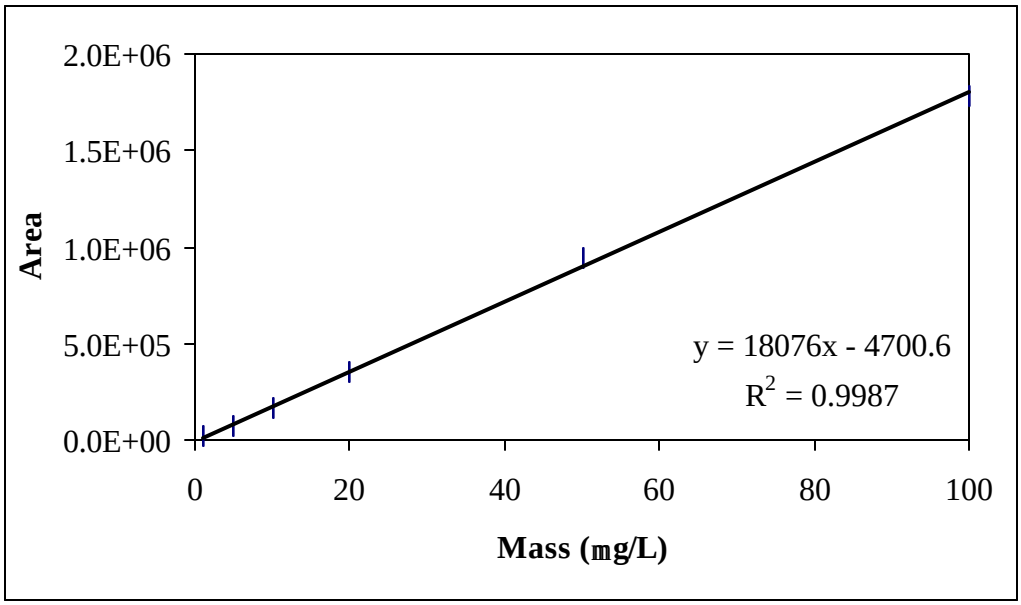
APPENDIX

A.1 Example GC-MS calibration data

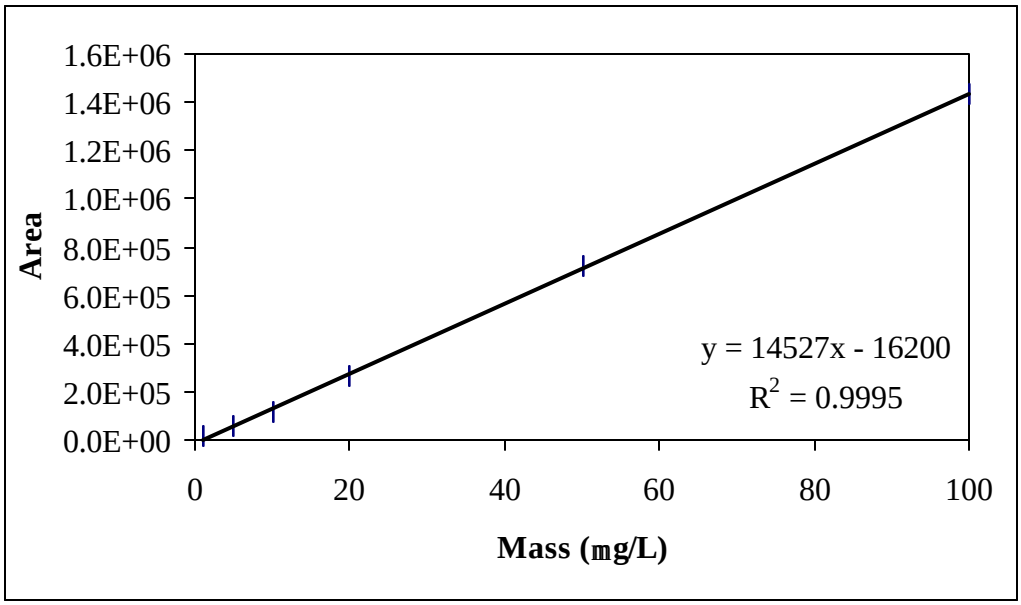
Liquid conc.	Area			
(µg/L)	$CHCl_3$	BDCM	DBCM	$CHBr_3$
1	15738	13828	8762	4946
5	74071	56660	30605	16118
10	163371	114238	63580	34305
20	351350	264356	151531	74981
50	948025	721686	390246	224281
100	1781306	1434029	793236	442771

Gas mass	Area			
(ng)	$CHCl_3$	BDCM	DBCM	$CHBr_3$
50	139909	109692	71437	53934
100	324602	256364	165914	116105
200	707059	544261	335381	228068
400	1400276	1080894	673353	486046
800	2753420	2057423	1360059	1157667

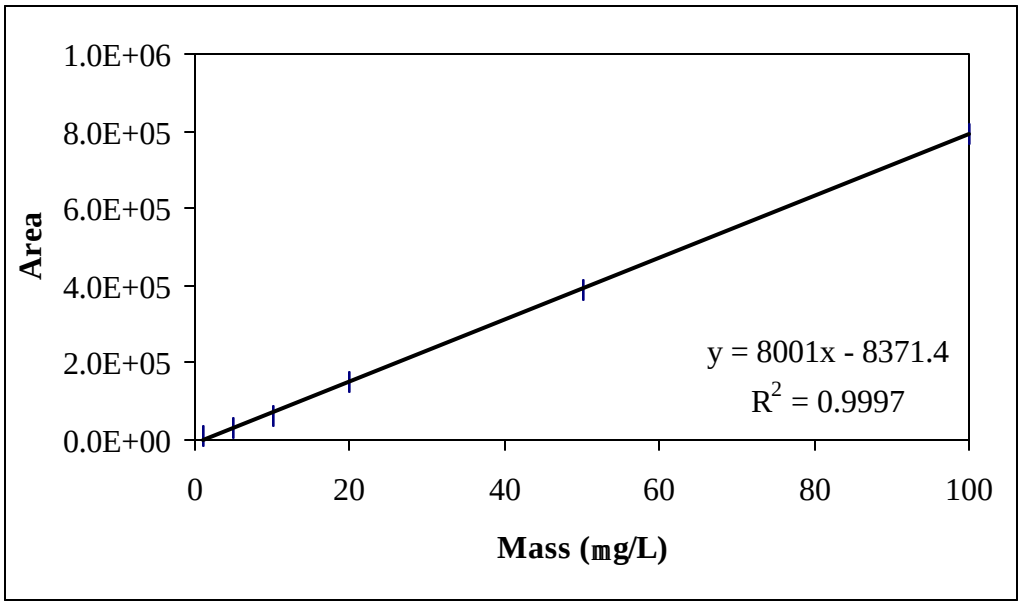
Chloroform (liquid)



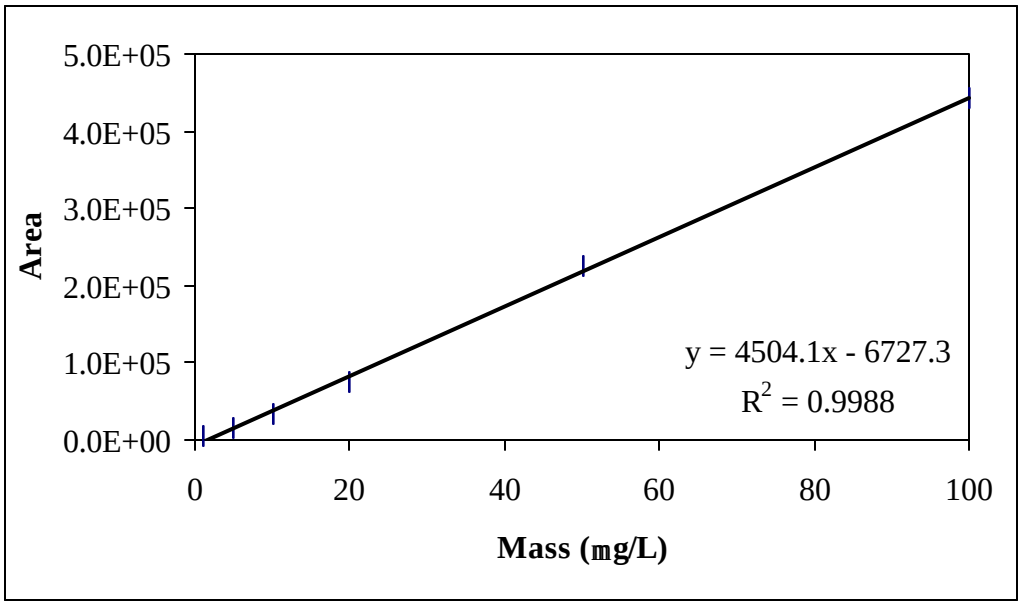
Bromodichloromethane (liquid)



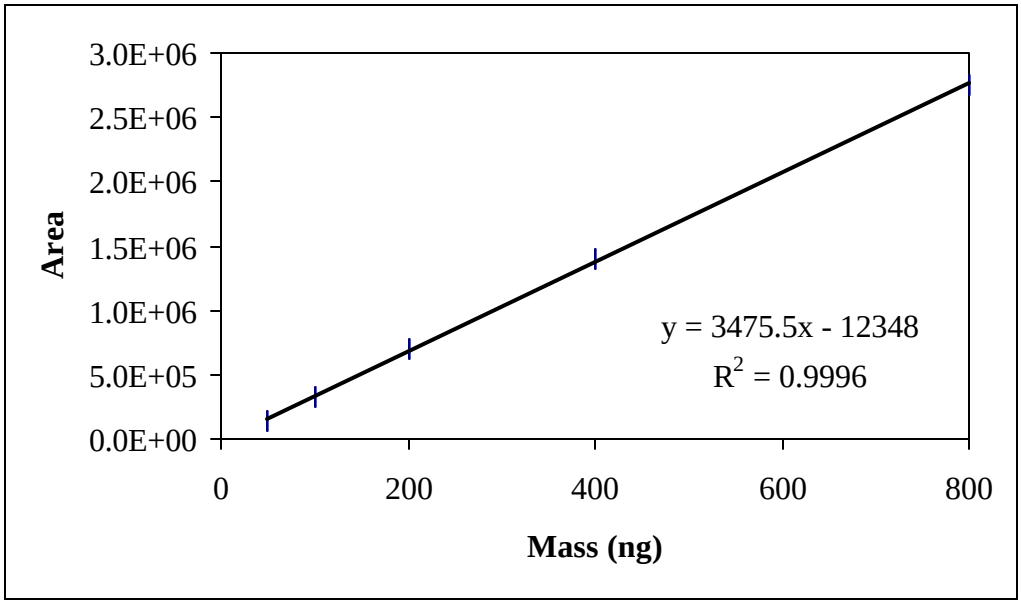
Dibromochloromethane (liquid)



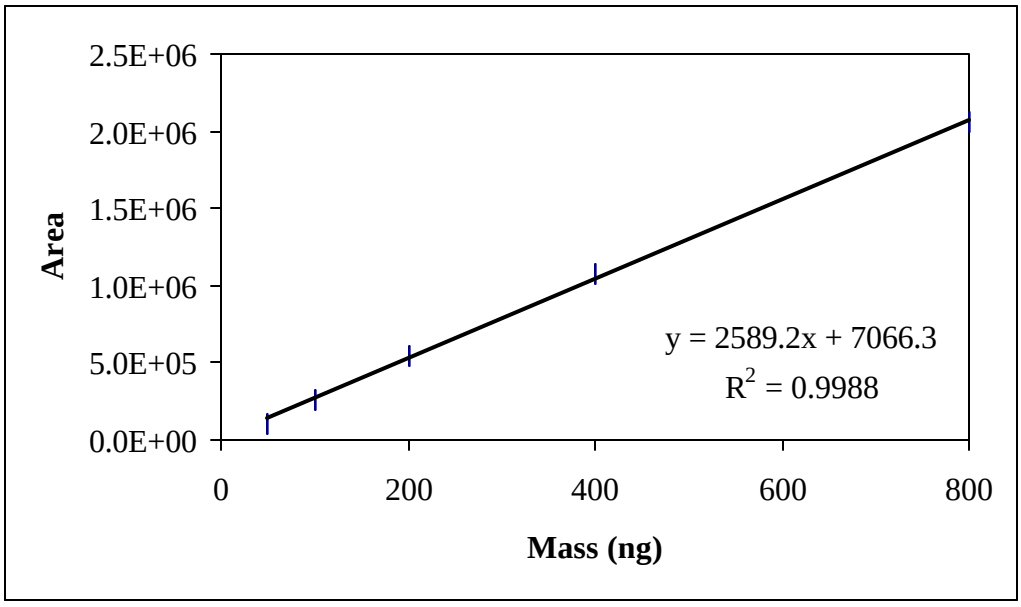
Bromoform (liquid)



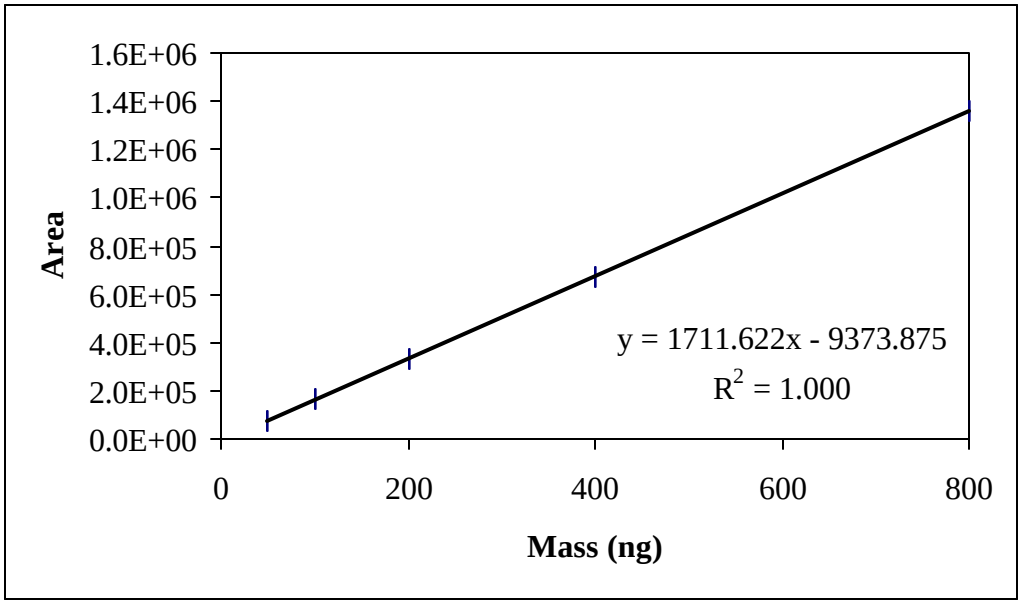
Chloroform (gas)



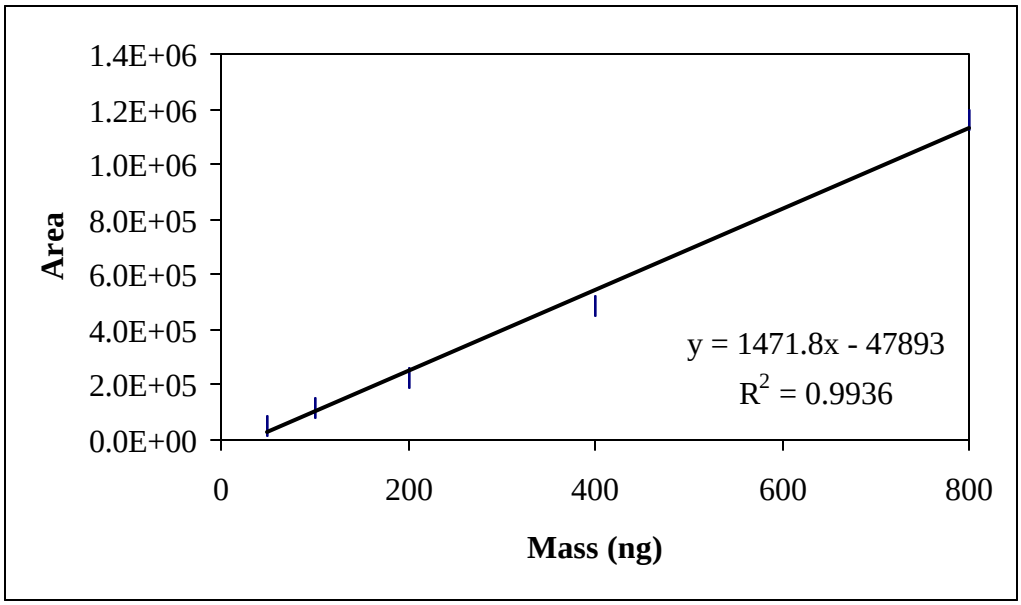
Bromodichloromethane (gas)



Dibromochloromethane (gas)



Bromoform (gas)



A.2 Summary of gas and liquid concentrations

Flask experiments

	Liquid concentration (mg/L)			Liquid concentration (mg/L)	
Food	$CHCl_3$	BDCM	Food	$CHCl_3$	BDCM
beef	40.9	0.3	eggs	2.6	0.0
tomatoes	6.8	0.0	fish	2.6	0.0
cereal	4.2	0.0	potatoes	2.5	0.0
beans	4.1	0.0	pasta	2.4	0.0
rice	3.7	0.1	lima beans	1.3	0.0
poultry	2.8	0.0	oil	1.0	0.1
bread	2.7	0.0	sugar	1.0	0.1

Dishwasher experiments

	Liquid chloroform concentration (µg/L)							
Experiment	tap	t=3 min		t=12 min	t=22 min	t=36 min		t=48 min
1	1.51	1.63	108.04	109.38	44.55	12.93	13.53	8.48
1 rep	2.83	2.02	78.82	73.68	36.83	11.91	12.05	4.41
2	1.79	2.14	40.97	92.56	122.34	50.16	64.03	21.92
3	2.21	3.83	18.23	19.62	10.99	4.10	3.36	2.59
4	9.33	1.54	45.80	47.59	66.00	31.38	8.51	9.10
4 rep1	1.24	1.15	40.45	41.01	21.47	6.45	6.32	4.38
4 rep2	6.97	1.87	34.39	33.94	22.36	2.58	6.00	3.98
5	2.96	1.35	1.46	1.79	1.36	1.30	1.06	0.90
6	3.82	1.07	1.07	1.09	1.07	0.83	0.86	0.47
8	8.87	30.91	37.98	39.09	11.92	5.36	4.28	3.49
9	0.40	10.84	35.82	36.43	19.42	7.48	6.10	3.69
10	7.31	2.33	29.08	30.76	41.43	39.77	40.34	10.55
10 rep	4.89	1.27	24.41	24.41	40.55	29.24	29.69	5.57
11	3.20	1.70	18.06	17.84	12.32	3.66	3.58	2.65
12	3.77	2.19	21.82	21.84	13.31	4.64	4.67	2.83

Experiment	Liquid bromodichloromethane concentration (µg/L)							
	tap	t=3 min		t=12 min	t=22 min	t=36 min		t=48 min
1	0.00	0.00	1.12	1.24	1.08	0.00	0.00	0.00
1 rep	0.00	0.00	0.00	1.04	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	1.05	1.62	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	1.38	0.00	0.00	0.00
4	1.49	0.00	0.96	1.10	1.26	1.03	0.62	0.00
4 rep1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4 rep2	1.44	0.52	0.84	0.92	0.00	0.16	0.42	0.18
5	0.61	0.34	0.23	0.62	0.00	0.38	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	2.00	1.26	1.38	1.45	1.46	1.35	0.70	0.91
9	0.00	0.76	1.56	1.47	1.44	0.98	0.68	0.41
10	4.78	0.61	0.80	0.79	0.84	0.53	0.62	0.32
10 rep	1.61	0.48	0.78	0.78	0.90	0.51	0.54	0.46
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	1.13	0.00	0.00	1.21	0.00	0.00	0.00	0.00

Experiment	Liquid bromodichloromethane concentration (µg/L)							
	tap	t=3 min		t=12 min	t=22 min	t=36 min		t=48 min
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1 rep	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	1.22	0.00	0.00	0.00
4	1.49	0.00	0.96	1.10	1.26	1.03	0.62	0.00
4 rep1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4 rep2	1.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	1.98	0.00	1.47	1.79	1.58	1.48	1.22	0.00
9	0.00	0.00	1.70	1.48	1.35	0.00	0.00	0.00
10	4.65	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10 rep	2.36	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Experiment	Gas chloroform concentration (µg/L)					
	bkgrd	t=1-5 min	t=10-14 min	t=20-24 min	t=34-38 min	t=46-50 min
1	0	0.13	7.05	13.21	9.85	6.16
1 rep	0	0.35	9.46	13.11	7.79	5.48
2	0	0.40	5.40	27.64	36.07	15.78
3	0	0.04	0.76	1.31	0.80	0.39
4	10.76	6.28	5.09	3.58	3.00	4.34
4 rep1	0	0.04	1.39	1.45	1.23	0.72
4 rep2	0	0.05	0.97	2.83	1.29	0.73
5	0	0.03	0.11	0.04	0.27	0.10
6	0	0.03	0.09	0.08	n/a	0.08
8	0	0.78	0.38	0.45	0.54	0.36
9	0	0.23	1.35	1.76	1.47	0.95
10	0	0.04	1.05	3.77	6.92	3.01
10 rep	0	0.05	1.04	4.46	0.01	1.74
11	0	0.04	0.71	1.23	0.64	0.37
12	0	0	1.13	1.50	0.89	0.62

Experiment	Gas bromodichloromethane concentration (µg/L)					
	bkgrd	t=1-5 min	t=10-14 min	t=20-24 min	t=34-38 min	t=46-50 min
1	0	0	0.12	0.09	0.26	0.15
1 rep	0	0.04	0.16	0.20	0.20	0.15
2	0	0	0	0.22	0.29	0.21
3	0	0	0	0.04	0.04	0.03
4	0	0	0	0	0	0
4 rep1	0	0	0.01	0	0.03	0.02
4 rep2	0	0	0.02	0.03	0.03	0.02
5	0	0	0.01	0	0.02	0.01
6	0	0	0.01	0	n/a	0.01
8	0	0.01	0.01	0	0.04	0.03
9	0	0	0.03	0.04	0.07	0.05
10	0	0.04	0.03	0.04	0.07	0.06
10 rep	0	0	0.03	0.07	1.56	0.05
11	0	0	0	0	0.03	0.02
12	0	0	0.04	0	0.06	0

Experiment	Gas dibromochloromethane concentration (µg/L) bkgrd	t=1-5 min	t=10-14 min	t=20-24 min	t=34-38 min	t=46-50 min
1	0	0	0.05	0	0.16	0.10
1 rep	0	0	0.04	0	0.07	0.06
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	0	0	0	0	0	0
4 rep1	0	0	0	0	0	0
4 rep2	0	0	0	0	0	0
5	0	0	0	0	n/a	0.01
6	0	0	0	0	0	0
8	0	0	0	0	0	0
9	0	0	0	0	0	0
10	0	0	0	0	0	0
10 rep	0	0	0	0	0	0
11	0	0	0	0	0	0.02
12						

Experiment 7

Time (min)	Liquid concentration (µg/L) $CHCl_3$	BDCM	DBCM
tap	1.83	1.59	1.65
3	1.79	0.57	1.00
8	14.64	0.60	0.87
10	28.93	0.93	1.13
12	31.26	0.77	1.05
12	32.24	0.79	0.95
14	39.18	0.93	0.00
16	46.31	1.02	0.00
16	47.20	1.03	0.00
20	20.27	0.81	0.89
22	20.85	0.85	0.00
24	16.21	0.65	0.00
24	17.40	0.59	0.00
36	5.94	0.44	0.00
36	5.72	0.44	0.00
48	3.71	0.31	0.00

Time (min)	Gas concentration (µg/L) $CHCl_3$	BDCM	DBCM
bkgrd	0.00	0.00	0.00
t=1-5 min	0.00	0.00	0.00
t=10-14 min	0.94	0.01	0.00
t=15-19 min	1.95	0.00	0.00
t=20-24 min	1.14	0.04	0.02
t=34-38 min	0.78	0.03	0.02
t=46-50 min	3.31	0.04	0.01

Summary of gas and liquid MDLs

#	Liquid concentration (µg/L) $CHCl_3$	BDCM	DBCM	$CHBr_3$
1	1.22	1.11	1.71	1.89
2	1.33	1.19	1.92	2.07
3	1.38	1.16	1.55	1.62
4	1.50	1.28	2.02	2.35
5	1.09	0.87	1.36	1.45
6	1.32	1.15	1.76	1.69
7	1.21	1.09	1.89	1.82
Variance	0.02	0.02	0.05	0.09
MDL	0.06	0.05	0.16	0.28

#	Gas mass (ng) $CHCl_3$	BDCM	DBCM	$CHBr_3$
1	9.90	11.39	13.51	12.88
2	9.18	11.32	11.71	12.22
3	10.97	11.12	11.33	11.36
4	11.30	9.50	13.16	11.39
5	11.51	11.50	12.64	13.38
6	10.71	11.60	11.25	12.63
7	10.09	9.02	12.56	13.04
Variance	0.70	1.11	0.79	0.63
MDL	2.18	3.50	2.50	2.00

Summary of gas and liquid temperatures (dishwasher experiments)

Experiment	Headspace temp. (°C) t=12 min	Headspace temp. (°C) t=36 min	Liquid temp. (°C) t=12 min	Liquid temp. (°C) t=36 min
1	39.3	49.9	39.3	49.9
1 rep	39.6	53.7	39.6	53.7
2	42.2	59.1	42.0	59.1
3	42.5	54.3	42.6	54.2
4	38.8	49.9	38.8	49.7
4 rep1	44.2	55.7	44.2	55.7
4 rep2	46.9	54.2	46.9	54.3
5	43.1	55.5	43.1	55.3
6	40.2	54.7	40.2	54.7
8	32.1	49.8	32.1	49.8
9	39.7	51.0	39.7	51.0
10	42.7	59.8	42.7	59.8
10 rep	45.6	61.6	45.5	61.8
11	43.3	55.4	43.3	55.4
12	40.2	51.0	40.3	51.0

Summary of gas chloroform concentrations from all test houses

Room	Time (hr)	Chloroform concentration ($\mu g/m^3$) A	A (replicate)	B	C
Kitchen	1.0	1.27	5.46	3.68	1.93
Kitchen	1.5	2.74	4.30	2.73	1.09
Kitchen	1.5	1.10	5.06	2.17	2.77
Kitchen	2.0	1.11	3.90	0.43	0.79
Kitchen	2.5	0.00	2.59	1.38	0.37
Kitchen	3.0	0.67	2.22	n/a(1)	0.34
Other	1.0	3.60	2.93	1.86	4.00
Other	1.5	2.11	2.24	3.80	2.34
Other	2.0	2.08	1.73	2.57	0.00
Other	2.0	2.23	0.29	2.10	1.35
Other	2.5	1.56	1.62	1.32	1.07
Other	3.0	0.43	0.97	n/a(1)	0.97

(1) Gas samples were collected in the laundry room at t = 1, 1.5 and 2 hours for this experiment; resulting chloroform concentrations were 8.38, 6.5, and 3.68 $\mu g/ m^3$, respectively.

A.3 Description of uncertainty analysis using a second-moment Bayesian method

Views of probability

Frequentist View of Probability

The frequentist or classical view of probability defines the probability of an event as the number of times an event occurs in a long sequence of similar trials. This approach is sometimes referred to as an empirical method, since probability of occurrence is based on observation.

One common application of this approach in probabilistic exposure assessment is Monte Carlo simulation. Monte Carlo simulation is a numerical method in which inputs are propagated through a model to determine the mean and variance of an output variable. A particular realization of each input variable is randomly selected from its probability density function. The model is then executed to generate a value of the output variable. This process is then repeated for a (typically large) number of iterations, thereby generating a simulated probability density function of the output variable.

One limitation to this approach is its limited reliability when data are scarce. This is because an observed probability only approaches the true probability as the number of trials approaches infinity. Such conditions can be realized in games of chance, e.g., flipping a coin or rolling dice, but occur less frequently for real-world data sets.

Bayesian View of Probability

The Bayesian or subjective view of probability defines probability relative to the knowledge of an event and the state of information. The Bayesian approach is a

systematic way to combine subjective information such as experience, inferred data, or data from similar events with any available observed information of the event.

The remainder of this chapter will focus on random variables and more specifically the relationship between existing and additional information (data). For discrete variables, Bayes' theorem can be expressed as:

$$P(\Theta = \theta_i \mid \varepsilon) = \frac{P(\varepsilon \mid \Theta = \theta_i)\, P(\Theta = \theta_i)}{\sum_{i=1}^{n} P(\varepsilon \mid \Theta = \theta_i)\, P(\Theta = \theta_i)} \qquad \text{(A-1)}$$

where

$P(\Theta = \theta_i|\varepsilon)$ = the probability that the random variable Θ has a value of θ_i given that the experimental data ε has occurred. This is the value of the parameter Θ after it is updated with the experiment data ε.

$P(\varepsilon|\Theta = \theta_i)$ = the likelihood that experimental data ε is observed when the random variable Θ has a value of θ_i.

$P(\Theta = \theta_i)$ = the probability that the random variable Θ has a value of θ_i. This is the value of the model parameter Θ before it is updated with the experimental data ε is observed.

The probability conditioned on existing information, $P(\Theta = \theta_i)$, is referred to as the *prior* information. It is based on existing on inferred data. The probability conditioned on additional information, $P(\varepsilon|\Theta = \theta_i)$, is referred to as the *posterior* information.

For the continuous variables, Bayes' theorem can be expressed as:

$$f_{\Theta}''(\theta) = \frac{P(\varepsilon \mid \theta)\, f_{\grave{E}}'(\theta)}{\int_{-\infty}^{\infty} P(\varepsilon \mid \theta)\, f_{\Theta}'(\theta)\, d\theta} \qquad \text{(A-2)}$$

where $f_{\Theta}'(\theta)$ and $f_{\Theta}''(\theta)$ are the prior and posterior probability distribution functions (PDFs), respectively. The term $P(\varepsilon|\theta)$ is called the *likelihood function* and hereafter will be denoted $L(\varepsilon|\theta)$. Since the prior distribution does not change with additional

data, the denominator in Equation A-2 is constant. Equation A-2 can then be rewritten as:

$$f_{\Theta}''(\theta) = k\, L(\varepsilon|\theta)\, f_{\Theta}'(\theta) \qquad \text{(A-3)}$$

where k is a normalizing constant. It can seen from Equation A-3 that the updated distribution depends on both the prior distribution (from k and $f_{\Theta}'(\theta)$) and the additional information (from $L(\varepsilon|\theta)$).

One drawback to Bayesian methods is that there are few instances where Equation A-2 can be solved analytically. Analytical solutions are restricted to discrete distributions and linear models. This limitation is addressed in this research through the use of a second-moment Bayesian method (SMBM). The method uses Taylor series approximations to characterize model nonlinearities.

Major functional elements to SMBM

The SMBM consists four major elements: (1) the model parameters, (2) the model, (3) the likelihood function, and (4) the measured data. The model parameters, hereafter denoted by the vector $\vec{\phi}$, represent the vector of model parameters needed to execute the model. These variables may be based on either measured or inferred data. The likelihood function, hereafter referred to as $L(\bar{y}\,|\,\vec{\phi})$, represents the link between the model and the measured data. It gives the likelihood that measured data would occur if the model parameters $\vec{\phi}$ were used to simulate conditions in nature. The measured data, hereafter denoted by the symbol vector $\bar{y}$, represents the state of nature at a given time and location and is not conditioned on the model parameters.

The SMBM is used in this research for inverse analysis. Inverse analysis (or model calibration) determines what set of realizations for the parameters has the greatest likelihood for predicting the observed data.

General SMBM equations

General expressions for the updated parameter mean vector and covariance matrix within the SMBM framework can be derived using Bayes' Theorem (Equation A-3). In vector notation, Equation A-3 can be rewritten as:

$$f_{\vec{\Phi}}(\vec{\Phi} \mid \bar{y}) = k \cdot L(\bar{y} \mid \vec{\phi}) \cdot f_{\vec{\Phi}}(\vec{\Phi}) \qquad \text{(A-4)}$$

(1) (2) (3)

where

$\vec{\Phi}$ = a vector representing the set of model parameters

$\bar{y}$ = a vector representing the set of measured data

$\vec{\phi}$ = a vector representing a particular realization of the model parameters

$f_{\vec{\Phi}}(\vec{\Phi} \mid \bar{y})$ = updated PDF of the model parameters

$f_{\vec{\Phi}}(\vec{\Phi})$ = prior PDF of the model parameters

$L(\bar{y} \mid \vec{\phi})$ = the likelihood function

The distributions $f_{\vec{\Phi}}(\vec{\Phi})$ and $f_{\vec{\Phi}}(\vec{\Phi} \mid \bar{y})$ are multivariate distributions representing the probability that the model parameters will duplicate the conditions measured in nature.

Three major steps are involved in developing general SMBM expressions from Equation A-4. In step 1, the likelihood function (term 2 in Equation A-4) is approximated using Taylor series expansion. The likelihood function incorporates information from both the measured data $\bar{y}$ and the model parameters $\vec{\phi}$. It is approximated using a second-order Taylor series expanded about the vector $\vec{\phi}_i^*$. This expansion point vector is determined by maximizing the likelihood function with respect to all model parameters. In step 2, the prior PDF of the model parameters (term 3 in Equation A-4) is defined as a multivariate normal distribution. Means and variances are determined based on available information. In step 3, the updated distribution (term 1 in Equation A-4) is defined in terms of the likelihood function

and prior distribution. Step 3 is executed once the approximated form of the likelihood function has been determined.

Step 1. Approximate the likelihood function

The term $g(\vec{\phi})$ is defined as the natural logarithm of the likelihood function as follows:

$$g(\vec{\phi}) = \ln\left(L(\vec{y} \mid \vec{\phi})\right) \tag{A-5}$$

This expression is then approximated as a second-order Taylor series expanded about the vector $\vec{\phi}^*$:

$$\ln\left(L(\vec{y} \mid \vec{\phi})\right) = g(\vec{\phi}) \cong g(\vec{\phi}^*) + \left\{\vec{\phi} - \vec{\phi}^*\right\}^T \left\{\frac{\partial g}{\partial \phi_i}\right\} + \frac{1}{2}\left\{\vec{\phi} - \vec{\phi}^*\right\}^T \left[\frac{\partial^2 g}{\partial \phi_i \partial \phi_j}\right] \left\{\vec{\phi} - \vec{\phi}^*\right\} \tag{A-6}$$

$\left\{\frac{\partial g}{\partial \phi_i}\right\}$ = the first derivative of the natural logarithm of the likelihood function for each model parameter; it is a vector where the number of elements is equal to the number of parameters.

$\left[\frac{\partial^2 g}{\partial \phi_i \partial \phi_j}\right]$ = the second derivative of the natural logarithm of the likelihood function for each model parameter; it is a square matrix with dimensions equal to the number of parameters.

Step 2. Express the prior distribution as multivariate normal

Using the form of a multivariate normal distribution, the prior distribution of model parameters can be expressed as:

$$f_{\vec{\Phi}}(\vec{\Phi}) = \frac{1}{(2\pi)^{n/2}\left|C_{\vec{\Phi}}\right|^{1/2}} \exp\left\{\vec{\phi} - \vec{\mu}_{\vec{\phi}}\right\}^T C_{\vec{\Phi}}^{-1} \left\{\vec{\phi} - \vec{\mu}_{\vec{\phi}}\right\} \tag{A-7}$$

where

$\vec{\mu}_{\vec{\phi}}$ = vector containing prior values of the model parameters

$C_{\vec{\Phi}}$ = matrix containing prior covariances between model parameters

n = number of parameters

All vectors and matrices used in Equation A-7 are not dependent on the measured data since they only contain prior information. This property will be used to simply expressions developed in Step 3. Taking the natural logarithm of Equation A-7 results in the following:

$$\ln\left(f_{\vec{\Phi}}(\vec{\Phi})\right) = \ln\left(\frac{1}{(2\pi)^{n/2}\left|C_{\vec{\Phi}}\right|^{1/2}}\right) - \left\{\vec{\phi} - \vec{\mu}_{\vec{\phi}}\right\}^{T} C_{\Phi}^{-1} \left\{\vec{\phi} - \vec{\mu}_{\vec{\phi}}\right\} \quad \text{(A-8)}$$

Step 3. Solve for the updated distribution

Using the expressions developed in Steps 1-2, the updated distribution can be determined using Bayes' theorem. Taking the natural logarithm of Bayes' theorem (Equation A-4) results in the following:

$$\ln\left(f_{\vec{\Phi}}(\vec{\phi} \mid \vec{y})\right) = \ln(k) + \ln\left(L(\vec{y} \mid \vec{\phi})\right) + \ln\left(f_{\vec{\Phi}}(\vec{\phi})\right) \quad \text{(A-9)}$$

Substituting the second-order approximation for the likelihood function (Equation A-5) and using the notation $G' = \left\{\frac{\partial g}{\partial \phi_i}\right\}$ and $G'' = \left[\frac{\partial^2 g}{\partial \phi_i \partial \phi_j}\right]$ results in:

$$\ln\left(f_{\vec{\Phi}}(\vec{\phi} \mid \vec{y})\right) \cong \ln(k) + g(\vec{\phi}^{*}) + \left\{\vec{\phi} - \vec{\phi}^{*}\right\}^{T} G' + \frac{1}{2}\left\{\vec{\phi} - \vec{\phi}^{*}\right\}^{T} G''\left\{\vec{\phi} - \vec{\phi}^{*}\right\} + \ln\left(f_{\vec{\Phi}}(\vec{\phi})\right) \quad \text{(A-10)}$$

Equation A-10 can be manipulated algebraically by expanding the product terms, collecting terms that do not contain terms in $\vec{\phi}$ (and are therefore constant), and using identity $a^T[B]c = c^T[B]a$. A complete derivation is given by Muchard (1997). The resulting equation includes a new constant k_2 and is given by:

$$\ln\left(f_{\vec{\Phi}}(\vec{\phi}\mid\vec{y})\right)\cong-\frac{1}{2}\left(\left\{\vec{\phi}-\left[-G''+C_{\vec{\Phi}}^{-1}\right]^{-1}\left\{\left[-G'\right]\left\{\vec{\phi}^{*}-G''^{-1}G'\right\}C_{\vec{\Phi}}^{-1}\vec{\mu}_{\vec{\Phi}}\right\}\right\}^{T}\left[-G''+C_{\vec{\Phi}}^{-1}\right]\right.$$

$$\left.+\left\{\vec{\phi}-\left[-G''+C_{\vec{\Phi}}^{-1}\right]^{-1}\left\{\left[-G'\right]\left\{\vec{\phi}^{*}-G''^{-1}G'\right\}+C_{\vec{\Phi}}^{-1}\vec{\mu}_{\vec{\Phi}}\right\}\right\}\right)+\ln(k_2)\qquad\text{(A-11)}$$

The above equation has the form of a multivariate normal distribution. The updated mean vector and covariance matrix are then given by:

$$\mu_{\vec{\Phi}|\vec{y}}\cong\left[-G''+C_{\vec{\Phi}}^{-1}\right]^{-1}\left\{\left[-G'\right]\vec{\phi}^{*}+G'-C_{\vec{\Phi}}^{-1}\vec{\mu}_{\vec{\Phi}}\right\}\qquad\text{(A-12)}$$

$$C_{\vec{\Phi}|\vec{y}}\cong\left[-G''+C_{\vec{\Phi}}^{-1}\right]^{-1}\qquad\text{(A-13)}$$

Using SMBM with a multivariate normal likelihood function

The previous section described general SMBM expressions for updating parameter means and covariances. The general SMBM equations can be applied to any form of the likelihood function. The multivariate normal distribution is used as the form of the likelihood function throughout this analysis.

The multivariate normal likelihood function is expressed as:

$$L(\vec{y}\mid\vec{\phi})=\frac{1}{(2\pi)^{n/2}\left|C_{\vec{Y}}\right|^{1/2}}\exp\left\{\vec{y}-\vec{\mu}_{\vec{Y}}\right\}^{T}C_{\vec{Y}}^{-1}\left\{\vec{y}-\vec{\mu}_{\vec{Y}}\right\}\qquad\text{(A-14)}$$

where

$\vec{\mu}_{\vec{Y}}$ = vector containing mean values of the measured data

$C_{\vec{Y}}$ = matrix containing covariances between measured data

The natural logarithm of the likelihood function is:

$$\ln\left(L(\vec{y}\mid\vec{\phi})\right)=g(\vec{\phi})=-\ln\left((2\pi)^{n/2}\right)-\frac{1}{2}\ln\left(\left|C_{\vec{Y}}\right|\right)-\frac{1}{2}\left\{\vec{y}-\vec{\mu}_{\vec{Y}}\right\}^{T}C_{\vec{Y}}^{-1}\left\{\vec{y}-\vec{\mu}_{\vec{Y}}\right\}\qquad\text{(A-15)}$$

The terms in Equation A-15 can be expanded to yield the following expression:

$$g(\vec{\phi}) = -\ln\left((2\pi)^{n/2}\right) - \frac{1}{2}\left(\ln\left(\left|C_{\vec{Y}}\right|\right) + \vec{y}^{T}C_{\vec{Y}}^{-1}\vec{y} - \vec{y}^{T}C_{\vec{Y}}^{-1}\vec{\mu}_{\vec{Y}} - \vec{\mu}_{\vec{Y}}^{T}C_{\vec{Y}}^{-1}\vec{y} + \vec{\mu}_{\vec{Y}}^{T}C_{\vec{Y}}^{-1}\vec{\mu}_{\vec{Y}}\right)$$

$$= -\ln\left((2\pi)^{n/2}\right) - \frac{1}{2}\left(\ln\left(\left|C_{\vec{Y}}\right|\right) + \vec{y}^{T}C_{\vec{Y}}^{-1}\vec{y} - 2\vec{y}^{T}C_{\vec{Y}}^{-1}\vec{\mu}_{\vec{Y}} + \vec{\mu}_{\vec{Y}}^{T}C_{\vec{Y}}^{-1}\vec{\mu}_{\vec{Y}}\right) \quad \text{(A-16)}$$

The derivative of Equation A-16 with respect to model parameter ϕ_i is:

$$\frac{\partial g}{\partial \phi_i} = -\frac{1}{2}\mathrm{tr}\left(C_{\vec{Y}}^{-1}\left[\frac{\partial C_{\vec{Y}}}{\partial \phi_i}\right]\right) - \frac{1}{2}\left(\left\{\frac{\partial \vec{y}^{T}}{\partial \phi_i}\right\}C_{\vec{Y}}^{-1}\vec{y} + \vec{y}^{T}\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial \phi_i}\right]\vec{y} + \vec{y}^{T}C_{\vec{Y}}^{-1}\left\{\frac{\partial \vec{y}}{\partial \phi_i}\right\}\right)$$

$$+\left(\left\{\frac{\partial \vec{y}^{T}}{\partial \phi_i}\right\}C_{\vec{Y}}^{-1}\vec{\mu}_{\vec{Y}} + \vec{y}^{T}\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial \phi_i}\right]\vec{\mu}_{\vec{Y}} + \vec{y}^{T}C_{\vec{Y}}^{-1}\left\{\frac{\partial \vec{\mu}_{\vec{Y}}}{\partial \phi_i}\right\}\right)$$

$$-\frac{1}{2}\left(\left\{\frac{\partial \vec{\mu}_{\vec{Y}}^{T}}{\partial \phi_i}\right\}C_{\vec{Y}}^{-1}\vec{\mu}_{\vec{Y}} + \vec{\mu}_{\vec{Y}}^{T}\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial \phi_i}\right]\vec{\mu}_{\vec{Y}} + \vec{\mu}_{\vec{Y}}^{T}C_{\vec{Y}}^{-1}\left\{\frac{\partial \vec{\mu}_{\vec{Y}}}{\partial \phi_i}\right\}\right) \quad \text{(A-17)}$$

where tr() denotes matrix trace. Since the actual measurements are independent of the model parameters, derivatives involving $\vec{y}$ and $\vec{y}^{T}$ are zero and Equation A-17 simplifies to:

$$\frac{\partial g}{\partial \phi_i} = -\frac{1}{2}\mathrm{tr}\left(C_{\vec{Y}}^{-1}\left[\frac{\partial C_{\vec{Y}}}{\partial \phi_i}\right]\right) - \frac{1}{2}\vec{y}^{T}\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial \phi_i}\right]\vec{y} + \vec{y}^{T}\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial \phi_i}\right]\vec{\mu}_{\vec{Y}} + \vec{y}^{T}C_{\vec{Y}}^{-1}\left\{\frac{\partial \vec{\mu}_{\vec{Y}}}{\partial \phi_i}\right\}$$

$$-\left\{\frac{\partial \vec{\mu}_{\vec{Y}}^{T}}{\partial \phi_i}\right\}C_{\vec{Y}}^{-1}\vec{\mu}_{\vec{Y}} - \frac{1}{2}\vec{\mu}_{\vec{Y}}^{T}\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial \phi_i}\right]\vec{\mu}_{\vec{Y}} \quad \text{(A-18)}$$

The derivative of the likelihood function with respect to ϕ_j can be obtained by taking the derivative of Equation A-18. The algebraic manipulations are similar to

those used for deriving Equation A-18 and will be omitted. The second derivative of the likelihood function is:

$$\frac{\partial^2 g}{\partial\phi_i\phi_j} = -\frac{1}{2}\mathrm{tr}\left(C_{\vec{Y}}^{-1}\left[\frac{\partial^2 C_{\vec{Y}}}{\partial\phi_i\phi_j}\right] + \left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial\phi_i}\right]\left[\frac{\partial C_{\vec{Y}}}{\partial\phi_j}\right]\right) - \frac{1}{2}\vec{y}^{\,T}\left[\frac{\partial^2 C_{\vec{Y}}^{-1}}{\partial\phi_i\phi_j}\right]\vec{y}$$

$$+ \vec{y}^{\,T}\left[\frac{\partial^2 C_{\vec{Y}}^{-1}}{\partial\phi_i\phi_j}\right]\vec{\mu}_{\vec{Y}} + \vec{y}^{\,T}\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial\phi_i}\right]\left\{\frac{\partial\vec{\mu}_{\vec{Y}}}{\partial\phi_i}\right\}$$

$$+ \vec{y}^{\,T}\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial\phi_i}\right]\left\{\frac{\partial\vec{\mu}_{\vec{Y}}}{\partial\phi_j}\right\} + \vec{y}^{\,T} C_{\overline{Y}}^{-1}\left\{\frac{\partial\vec{\mu}_{\vec{Y}}}{\partial\phi_i\partial\phi_j}\right\}$$

$$- \left\{\frac{\partial^2\vec{\mu}_{\vec{Y}}^{\,T}}{\partial\phi_i\phi_j}\right\}C_{\vec{Y}}^{-1}\vec{\mu}_{\vec{Y}} - \left\{\frac{\partial\vec{\mu}_{\vec{Y}}^{\,T}}{\partial\phi_j}\right\}\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial\phi_i}\right]\vec{\mu}_{\overline{Y}} - \left\{\frac{\partial\vec{\mu}_{\vec{Y}}^{\,T}}{\partial\phi_j}\right\}C_{\vec{Y}}^{-1}\left\{\frac{\partial\vec{\mu}_{\vec{Y}}}{\partial\phi_i}\right\}$$

$$- \left\{\frac{\partial\vec{\mu}_{\vec{Y}}^{\,T}}{\partial\phi_i}\right\}\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial\phi_j}\right]\vec{\mu}_{\vec{Y}} - \frac{1}{2}\vec{\mu}_{\vec{Y}}^{\,T}\left[\frac{\partial^2 C_{\vec{Y}}^{-1}}{\partial\phi_i\partial\phi_j}\right]\vec{\mu}_{\vec{Y}} \qquad \text{(A-19)}$$

The following identities are useful in evaluating terms in Equations A-18 and A-19.

$$\left[\frac{\partial C_{\vec{Y}}^{-1}}{\partial\phi_i}\right] = -C_{\vec{Y}}^{-1}\left[\frac{\partial C_{\vec{Y}}}{\partial\phi_i}\right]C_{\vec{Y}}^{-1} \qquad \text{(A-20)}$$

$$\left[\frac{\partial^2 C_{\vec{Y}}^{-1}}{\partial\phi_i\phi_j}\right] = C_{\vec{Y}}^{-1}\left[\frac{\partial C_{\vec{Y}}}{\partial\phi_i}\right]C_{\vec{Y}}^{-1}\left[\frac{\partial C_{\vec{Y}}}{\partial\phi_j}\right]C_{\vec{Y}}^{-1} + C_{\vec{Y}}^{-1}\left[\frac{\partial C_{\vec{Y}}}{\partial\phi_j}\right]C_{\vec{Y}}^{-1}\left[\frac{\partial C_{\vec{Y}}}{\partial\phi_i}\right]C_{\vec{Y}}^{-1}$$

$$- C_{\vec{Y}}^{-1}\left[\frac{\partial^2 C_{\vec{Y}}}{\partial\phi_i\phi_j}\right]C_{\vec{Y}}^{-1} \qquad \text{(A-21)}$$

Model calibration using SMBM

The second-moment Bayesian method was used in this research for purposes of model validation. Parameters describing model accuracy were calibrated by maximizing the natural logarithm of the likelihood function. In other words, the derivative of the likelihood function with respect to the model parameters (Equation A-17) was set to zero. The expansion points in the Taylor series, $\vec{\phi}_i^*$, were optimized such that Equation A-17 approached zero. Once the expansion point vector $\vec{\phi}_i^*$ was optimized, the updated mean vector and covariance matrix were determined from Equations A-12 and A-13.

REFERENCES

Aggazzotti, G., Fantuzzi, G., Righi, E., Tartoni, P.L., Cassinadri, T., and Predieri, G. (1993) "Chloroform in alveolar air of individuals attending indoor swimming pools," *Archives of Environmental Health*, **48**(4), 250-254.

Aggazzotti, G., Fantuzzi, G., Tartoni, P.L., and Predieri, G. (1990) "Plasma chloroform concentrations in swimmers using indoor swimming pools," *Archives of Environmental Health*, **45**(3), 175-179.

Akland, G.G., Hartwell, T.D., Johnson, T.R., and Whitmore, R.W. (1985) "Measuring human exposure to carbon monoxide in Washington, D.C., and Denver, Colorado, during the winter of 1982-1983," *Environmental Science & Technology*, **19**(10), 911-918.

Andelman, J.B. (1985a) "Human exposure to volatile halogenated organic chemicals in indoor and outdoor air," *Environmental Health Perspectives*, **62**, 313-318.

Andelman, J.B. (1985b) "Inhalation exposure in the home to volatile organic contaminants of drinking water," *Science of the Total Environment*, **47**, 443-460.

Ang, A.H-S., and Tang, W.H. (1975) *Probability concepts in engineering planning and design, Vol. 1 – Basic principles*, John Wiley & Sons, New York.

Ang, A.H-S., and Tang, W.H. (1984) *Probability concepts in engineering planning and design, Vol. 2 – Decision, risk and reliability*, John Wiley & Sons, New York.

Antoine, S.R., DeLeon, I.R., and O'Dell-Smith, R.M. (1986) "Environmentally significant volatile organic pollutants in human blood," *Bulletin of Environmental Contamination and Toxicology*, **36**, 364-371.

Armstrong, D.W., and Golden, T. (1986) "Determination of distribution and concentration of trihalomethanes in aquatic recreational and therapeutic facilities by electron-capture GC," *LC-GC Mag. Liquid Gas Chromatography*, **4**(7):652-655.

Arora, H., LeChevallier, M.W., and Dixon, K.L. (1997) "DBP occurrence survey," *Journal. American Water Works Association*, **89**(6), 60-68.

Aschengrau, A., Zierler, S., and Cohen, A. (1989) "Quality of community drinking water and the occurrence of spontaneous abortions," *Archives of Environmental Health*, **44**(5), 283-290.

Ashley, D.L., Bonin, M.A., Carkinali, L., McCraw, J.M., and Wooten, J.V. (1994) "Blood concentrations of volatile organic compounds in nonoccupationally exposed U.S. population and in groups with suspected exposure," *Clinical Chemistry*, **40**, 1401-1404.

Ashworth, R.A., Howe, G.B., Mullins, M.E., and Rogers, T.N. (1998) "Air-water partitioning coefficients of organics in dilute aqueous solutions," Journal of Hazardous Materials, **18**, 25-36.

Backer, L.C., Ashley, D.L., Bonin, M.A., Cardinali, F.L., Kieszak, S.M., and Wooten, J.V. (2000) "Household exposures to drinking water disinfection by-products: Whole blood trihalomethane levels," *Journal of Exposure Analysis and Environmental Epidemiology*, **10**(4), 321-326.

Baek, S.O., and Kim, Y.S. (1997) "Indoor air quality in homes, offices and restaurants in Korean urban areas—indoor/outdoor relationships," *Atmospheric Environment*, **31**(4), 529-544.

Bean, J.A., Isacson, P., Hausler, W.J., and Kohler, J. (1982) "Drinking water and cancer incidence in Iowa. I. Trends and incidence by source of drinking water and size of municipality," *American Journal of Epidemiology*, **116**, 912-923.

Beech, J.A., Diaz, R., Ordaz, C., and Palomeque, B. (1980) "Nitrates, chlorates and trihalomethanes in swimming pool water," *American Journal of Public Health*, **70**, 79-82.

Bellar, T., Lichtenberg, J., and Kroner, R. (1974) "The occurrence of organohalides in chlorinated drinking water," *Journal of the American Water Works Association*, **66**(12), 703-706.

Bera, M.B., and Mukherjee, R.K. (1989) "Solubility, emulsifying, and foaming properties of rice bran protein concentrates," *Journal of Food Science*, **54**, 143.

Bogen, K.T., Colston, B.W., and Machicao, L.K. (1992) "Dermal absorption of dilute aqueous chloroform, trichloroethylene, and tetrachloroethylene in hairless guinea pigs," *Fundamental and Applied Toxicology* **18**, 30-39.

Bove, F.J., Fulcomer, M.C., Klotz, J.B., Esmart, J., Dufficy, E.M., and Savrin, J.E. (1995) "Public drinking water contamination and birth outcomes," *American Journal of Epidemiology*, **141**(9), 850-862.

Box, G.E.P., and Tiao, G.C. (1974) *Bayesian inference in statistical analysis*, Addison Wesley Publishing Co., Reading, Massachusetts.

Brandweek (1998) "P&G brands top rankings," R. Tucker, The Cinncinnati Enquirer, www.enquirer.com, Wednesday, November 25, 1998.

Brickus, L.S.R., Cardoso, J.N., and De Aquino Neto, F.R. (1998) "Distributions of indoor and outdoor air pollutants in Rio de Janeiro, Brazil: Implications to indoor air quality in bayside offices," *Environmental Science & Technology*, **32**(22), 3485-3490.

Brooks, B.O., Utter, G.M., DeBroy, J.A., and Schimke, R.D. (1991) "Indoor air pollution: An edifice complex," *Clinical Toxicology*, **29**(3), 315-374.

Brown, S.K., Sim, M.R., Abramson, N.J., and Gray, C.N. (1994) "Concentrations of volatile organic compounds in indoor air—a review," *Indoor Air*, **4**(1), 123-134.

Bunge, A.L., and Cleek, R.L. (1995) "A new method for estimating dermal absorption from chemical exposure. 2. Effect of molecular weight and octanol-water partitioning," *Pharmaceutical Research*, **12**, 88-95.

Burge, A.L., Flynn, G.L., and Guy, R.H. (1994) "Predictive model for dermal exposure assessment," in *Drinking water contamination and health: Integration of exposure assessment, toxicology, and risk assessment*, R. Wang, ed., Marcel Dekkar, New York, 347-373.

Cantor, K.P., Hoover, R, Hartge, P. et al. (1987) "Bladder cancer drinking water sources, and tap water consumption: A case-control study," *Journal of the National Cancer Institute*, **79**(6), 1269-1279.

Cantor, K.P., Hoover, R, Mason, T.J., and McCabe, L.J. (1978) "Associations of cancer mortality with trihalomethanes in drinking water," *Journal of the National Cancer Institute*, **61**, 979-985.

Carlson, M., and Hardy, D. (1998) "Controlling DBPs with monochloramine. Effect of water quality conditions on controlling disinfection by-products with chloramines," *Journal. American Water Works Association*, **90**(2), 95-106.

Chen, A., and Vine, E.L. (1998) "A scoping study on the costs of indoor air quality illnesses: An insurance reduction perspective," Environmental Energy Technologies Division, Ernest Orlando Lawrence Berkeley National Laboratory, Report LBNL 41919.

Chuang, J.C., Mack, G.A., Kuhlman, M.R., and Wilson, N.K. (1991) "Polycyclic aromatic hydrocarbons and their derivatives in indoor and outdoor air in an eight-home study," *Atmospheric Environment*, **25B**(3), 369-380.

Clayton, C.A., Perritt, R.L., Pellizzari, E.D., Thomas, K.W., and Whitmore, R.W. (1993) "Particle Total Exposure Assessment Methodology (PTEAM) study: Distributions of aerosol and elemental concentrations in personal, indoor, and outdoor air samples in a Southern California community," *Journal of Exposure Analysis and Environmental Epidemiology*, **3**(2), 227-250.

Cleek, R.L., and Bunge, A.L. (1993) "A new method for estimating dermal absorption from chemical exposure. 1. General approach," *Pharmaceutical Research*, **10**, 497-506.

Clemen, R.T. (1991) *Making hard decisions – an introduction to decision analysis*, Cusbury Press, Belmont, California.

Cohen, M.A., Ryan, P.B., Yanagisawa, Y., Spengler, J.D., Ozkaynak, H., and Epstein, P.S. (1989) "Indoor/outdoor measurements of volatile organic compounds in the Kanawha Valley of West Virginia," *Journal of the Air Pollution Control Association*, **39**(8), 1086-1093.

Corley, R.A., Gordon, S.M., and Wallace, L.A. (2000) "Physiologically based pharmacokinetic modeling of the temperature-dependent dermal absorption of chloroform by humans following bath water exposures," *Toxicological Sciences*, **53**,13-23.

Corsi, R.L. and Howard, C. (1998) Volatilization rates from water to indoor air, Grant Number CR 824228-01, The National Center for Environmental Assessment, USEPA, Washington, D.C.

Crozes, G., White, P., and Marshall, M. (1995) "Enhanced coagulation: Its effects on NOM removal and chemical costs," *Journal. American Water Works Association*, **87**(1), 78-89.

Currado, G.M., and Harrad, S. (1998) "Comparison of polychlorinated biphenyl concentrations in indoor and outdoor air and the potential significance of inhalation as a human exposure pathway," *Environmental Science & Technology*, **32**(20), 3043-3047.

Daft, J.L. (1987) "Determining multifumigants in whole grains and legumes, milled and low-fat-grain products, spices, citrus fruits, and beverages," *Journal of the Association of Official Analytical Chemistry*, **70**, 734-739.

Daft, J.L. (1988) "Rapid determination of fumigant and industrial chemical residues in food," *Journal of the Association of Official Analytical Chemistry*, **71**, 748-60.

Daft, J.L. (1989) "Determination of fumigants in fatty and nonfatty foods," *Journal of Agricultural and Food Chemistry*, **70**, 734-739.

Daisey, J.M., Hodgson, A.T., Fisk, W.J., Mendell, M.J., and Brinke, J.T. (1994) "Volatile organic compounds in twelve California office buildings: Classes, concentrations and sources," *Atmospheric Environment*, **28**(22), 3557-3562.

Dietert, R.R., and Hedge, A. (1996) "Toxicological considerations in evaluating indoor air quality and human health: Impacts of new carpet emissions," *Critical Reviews in Toxicology*, **26**(6), 633-707.

Duan, N. (1982) "Models for human exposure to air pollution," *Environment International*, **8**, 305-309.

Entz, R., Thomas, K., and Diachenko, G. (1982) "Residues of volatile halocarbons in food using headspace gas chromatography," *Journal of Agricultural and Food Chemistry*, **30**, 846-849.

Envirofacts (1999) "Envirofacts Overview – ICR Overview," http://www.epa.gov/enviro/html/icr/index.html.

Federal Register (1996) "National Primary Drinking Water Regulations: Monitoring Requirements for Public Drinking Water Supplies; Final Rule," May 14, 1996, volume 61, no. 94, p.24353-24388.

Federal Register (1998) "National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts; Final Rule," December 16, 1998, volume 63, no. 241, p. 69389-69476.

Fisher, M.L., Bentley, A.J., Dunkin, K.A., Hodgson, A.T., Nazaroff, W.W., Sextro, R.G., Daisey, J. (1996) "Factors affecting indoor air concentrations of volatile organic compounds at a site of subsurface gasoline contamination," *Environmental Science & Technology*, **30**(10), 2948-2957.

Fisk, W.J., and Rosenfeld, A.H. (1997) "Estimates of improved productivity and health from better indoor environments," *Indoor Air*, **7**(3), 158-172.

Fitzgerald, B.M. (1996) "Evaluation of adsorbents for the collection and analysis of vapors during radio frequency heating of fuel contaminated soil," Master's Report, The University of Texas at Austin.

Gallagher, M.D., Nuckols, J.R., Stallones, L., and Savitz, D.A. (1998) "Exposure to trihalomethanes and adverse pregnancy outcomes," Epidemiology, **9**(5), 484-489.

Garbesi, K., and Sextro, R.G. (1989) "Modeling and field evidence of pressure-driven entry of soil gas into house through permeable below-grade walls," *Environmental Science & Technology*, **23**(12), 1481-1487.

Georgopoulos, P.G., and Lioy, P.J. (1994) "Conceptual and theoretical aspects of human exposure and dose assessment," *Journal of Exposure Analysis and Environmental Epidemiology*, **4**(3), 253-285.

Giardino N., Gummerman, E., Esmen, N, Andelman, J., Wilkes, C., Davidson, C., and Small, M. (1992) "Shower volatilization exposures in homes using tap water contaminated with disinfection byproducts," *Journal of Exposure Analysis and Environmental Epidemiology*, Suppl. 1, p. 147-158.

Giardino, N. J., Andelman, J. B., Borrazzo, J. E., and Davidson, C. I. (1988) "Sulfur hexafluoride as a surrogate for volatilization of organics from indoor water uses," *Journal of the Air Pollution Control Association*, **38**(3), 278-280.

Giardino, N.J., and Andelman, J.B. (1996) "Characterization of the emissions of trichloroethylene, chloroform, and 1,2-dibromo-3-chloropropane in a full-size, experimental shower," *Journal of Exposure Analysis and Environmental Epidemiology*, **6**(4), 413-423.

Giardino, N.J., and Hageman, J.P. (1996) "Pilot study of radon volatilization from showers with implications for dose," *Environmental Science & Technology*, **30**(4), 1242-1244.

Gilbert, R.B., and McGrath, T.C. (1997) "Design of site investigation programs for geotechincal engineering," book chapter in Uncertainty Modeling and Analysis in Civil Engineering, CRC Press.

Girman, J. R., Hodgson, A. T., Newton, A. S., and Winkes, A. W. (1986) 'Volatile organic emissions from adhesives with indoor applications." *Environment International*, **12**, 317-321.

Gottlieb, M.S., Carr, J.K., and Clarkson, J.R. (1982) "Drinking water and cancer in Louisiana. A retrospective mortality study," *American Journal of Epidemiology*, **116**, 652-667.

Heikes, D.L. (1987) "Purge and trap method for determination of volatile halocarbons and carbon disulfide in table-ready foods," *Journal of the Association of Official Analytical Chemists*, **70**, 215-226.

Hess, C. T., Weiffenbach, C. V., and Norton, S. A. (1982) "Variations of airborne and waterborne Rn-222 in houses in Maine," *Environment International*, **8**, 59-66.

Hines, A.L., Ghosh, T.K., Loyalka, S.K., and Warder, Jr., R.C. (1993) *Indoor air: Quality and Control*. PTR Prentice-Hall, Inc., Englewood Cliffs, NJ.

Hodgson, A. T., Garbesi, K., Sextro, R. G., and Daisey, J. M. (1988). Evaluation of Soil-Gas Transport of Organic Chemicals into Residential Buildings: Final Report. Lawrence Berkeley Laboratory Report, Contract No. DE-AC03-76SF00098.

Howard, C.L. (1998) "Volatilization rates of chemicals from drinking water to indoor air," Ph.D. dissertation, The University of Texas at Austin.

Howard, C., and Corsi, R.L. (1998) "Volatilization of hazardous contaminants from drinking water: the role of residential washing machines," *Journal of the Air & Waste Management Association*, **48**(10), 907-914.

Howard, C.H., and Corsi, R.L. (1996) "Volatilization of chemicals from drinking water to indoor air: Role of the kitchen sink," *Journal of the Air & Waste Management Association*, **46**(9):830-837.

Howard-Reed, C., Corsi, R.L., and Moya, J. (1999) "Mass transfer of volatile organic compounds from drinking water to indoor air: the role of residential dishwashers," *Environmental Science & Technology*, **33**(13), 2266-2277.

Idouraine, A., Jensen, S.B., and Weber, C.W. (1991) "Tepary bean flour albumin and globulin fractions functional properties compare with soy protein isolate," Journal of Food Science, **56**, 1316.

Ireland, J., Moore, L., Pourmoghaddas, H., and Stevens, A. (1998) "Gas chromatography/mass spectrometry study of mixed haloacetic acids found in chlorinated drinking water," *Biomedical and Environmental Mass Spectrometry*, **17**, 483-486.

Jackman, R.L., and Yada, R.Y. (1988) "Function properties of whey-potato protein composite blends in a model system," *Journal of Food Science*, **53**, 1427.

Jenkins, P.L., Phillips, T.J., Mulberg, E.J., and Hui, S.P. (1992) "Activity patterns of Californians: Use of and proximity to indoor pollutant sources," *Atmospheric Environment*, **26A**(12), 2141-2148.

Jo, W. (1994) "Chloroform in the water and air of Korean indoor swimming pools using both sodium hypochlorite and ozone for water disinfection," *Journal of Exposure Analysis and Environmental Epidemiology*, **4**, 491-502.

Jo, W., Weisel, C., and Lioy, P. (1990a) "Routes of chloroform exposure and body burden from showering with chlorinated tap water," *Risk Analysis*, **10**(4), 575-580.

Jo, W., Weisel, C., and Lioy, P. (1990b) "Chloroform exposure and the health risk associated with the multiple uses of chlorinated tap water," *Risk Analysis*, **10**(4), 581-585.

Kalia, Y.N., Pirot, F., and Guy, R.H. (1996) "Homogeneous transport in a heterogeneous membrane: Water diffusion across human stratum corneum in vivo," *Biophysical Journal*, **71**, 2692-2700.

Kavanaugh, M.C., Trussell, A.R., Cromer, J., and Trussell, R.R. (1980) "An empirical kinetic model of THM formation: Application to meet proposed THM standards," *Journal. American Water Works Association*, **72**(10), 578-582.

Keating, G. A., and McKone, T. E. (1993) "Measurements and evaluation of the water-to-air transfer and air concentration for trichloroethylene in a shower chamber." In Niren L. Nagda (Ed.), Modeling of Indoor Air Quality and Exposure, ASTM STP 1205 (pp. 14-24). Philadelphia: American Society for Testing Materials.

Keating, G.A., McKone, T.E., and Gillett, J.W. (1997) "Measured and estimated air concentrations of chloroform in showers: Effects of water temperature and aerosols," *Atmospheric Environment*, **31**(2), 123-130.

Klepeis, N.E., and Tsang, A.M. (1996) Analysis of the National Human Activity Pattern Survey (NHAPS) Respondents from a Standpoint of Exposure Assessment, Office of Research and Development, U.S. Environmental Protection Agency, EPA/600/R-96/074.

Kosianinen, R. (1995) "Volatile organic compounds in the indoor air of normal and sick houses," *Atmospheric Environment*, **29**(6), 693-702.

Kramer, M.D., Lynch, C.F., Isacson, P., and Hanson, J.W. (1992) "The association of waterborne chloroform and intrauterine growth retardation," *Epidemiology*, **3**, 407-413.

Krasner, S.W., McGuire, M.J., Jacangelo, J.G., Patania, N.L., Reagan, K.M., and Aieta, E.M. (1989) "The occurrence of disinfection by-products in US drinking water," *Journal. American Water Works Association*, **81**(8), 41-54.

Lahl, U., Batjer, K., van Duszelin, J., Gabel, B., and Thiemann, W. (1981) "Distribution and balance of volatile halogenated hydrocarbons in the water and air of covered swimming pools using chlorine for water disinfection, *Water Research*, **15**, 803-814.

Levesque, B., Ayotte, P., Leblanc, A., Dewailly, E., Prud'Homme, D., Lavoie, R., Sylvain, A., and Levallois, P. (1994) "Evaluation of dermal and respiratory

chloroform exposure in humans," *Environmental Health Perspectives*, **102**, 1082-1087.

Li-Chen, E., Nakai, S., and Wood, D.F. (1985) "Relationship between functional (fat, binding, emulsifying) and physicochemical properties of muscle proteins. Effects of heating, freezing, pH and species," *Journal of Food Science*, **50**, 1034.

Ligocki, M.P., Stiefer, P.S., and Rosenbaum, A.S. (1995) "Cumulative exposures to air toxics: Indoor source," *Proceedings of the 88th Annual Meeting & Exhibition of the Air & Waste Management Association*, San Antonio.

Lindstrom, A.B., Pleil, J.D., and Berkoff, D.C. (1997) "Alveolar breath sampling and analysis to assess trihalomethane exposures during competitive swimming training," *Environmental Health Perspectives*, **105**(6): 636-642.

Lioy, P.J. (1990) "Exposure analysis: Reflections on its growth and aspirations for its future," *Journal of Exposure Analysis and Environmental Epidemiology*, **9**(4), 273-281.

Lioy, P.J. (1999) "Assessing human exposure to contaminants," *Environmental Science & Technology*, **24**(7), 938-945.

Lioy, P.J., Wallace, L.A., and Pellizzari, E. (1991) "Indoor, outdoor and personal monitor and breath analysis relationships for selected volatile organic compounds measured at three home during New Jersey TEAM—1987," *Journal of Exposure Analysis and Environmental Epidemiology*, **1**, 45-61.

Little, J.C. (1992) "Applying the two-resistance theory to contaminant volatilization in showers," *Environmental Science & Technology*, **26**(7), 1341-1349.

Little, J.C. (1996) "Transfer of volatile organic compounds from drinking water to indoor air," Section 4.2 from "Exposure to contaminants in drinking water: Estimating uptake through the skin and by inhalation," final draft to ILSI Risk Institute Working Group, Washington, D.C.

McGuire, M.J., and Meadow, R.G. (1988) "AWWARF trihalomethane survey," *Journal. American Water Work Association*, **80**(1), 61-68.

McKone, T. (1987) "Human exposure to volatile organic compounds in household tap water: the indoor inhalation pathway," *Environmental Science & Technology*, **21**(12), 1194-1201.

McKone, T., and Knezovich, J. (1991) “The transfer of trichloroethyene (TCE) from a shower to indoor air: Experimental measurements and their implications,” *Journal of the Air & Waste Management Association*, **41**(6), 832-837.

McKone, T.E. (1993) “Linking a PBPK model for chloroform with measured breath concentrations in showers: Implications for dermal exposure models,” *Journal of Exposure Analysis and Environmental Epidemiology*, **3**(3):339-365.

Michael, L.C., Pellizzari, E.D., Perritt, R.L., Hartwell, T.D., Westerdahl, D., and Nelson, W.C. (1990) “Comparison of indoor, backyard, and centralized air monitoring strategies for assessing personal exposure to volatile organic compounds,” *Environmental Science & Technology*, **24**(7), 996-1003.

Miller, W.J., and Uden, P.C. (1983) “Characterization of nonvolatile aqueous chlorination products of humic substances,” *Environmental Science & Technology*, **17**(3), 150-152.

Morris, R.D., Audet, A.M., Angelillo, I.F., Chalmers, T.C., and Mosteller, F. (1992) “Chlorination byproducts and cancer: A meta-analysis,” *American Journal of Public Health*, **82**, 955-963.

Moseley, C.L., and Meyer, M.R. (1992) “Petroleum contamination of an elementary school: a case history involving air, soil-gas, and groundwater monitoring,” *Environmental Science & Technology*, **26**(1), 185-192.

Moya, J., Howard-Reed, C., and Corsi, R.L. (1999) “Volatilization of chemicals from tap water to indoor air from contaminated water used for showering,” *Environmental Science & Technology*, **33**(14), 2321-2327.

Muchard, S.M. (1997) “Estimating groundwater contaminant transport parameters with a second-moment Bayesian method,” M.S. thesis, the University of Texas at Austin.

Murray, D.M., and Burmaster, D.E. (1995) “Residential air exchange rates in the United States: Empirical and estimated parametric distributions by season and climatic region,” *Risk Analysis*, **15**(4), 459-465.

Namiesnik, J., Gorecki, T., Kozdron-Zabiegala, B., Lukasiak, J. (1992) “Indoor air quality (IAQ), pollutants, their sources and concentration levels,” *Building and Environment*, **27**(3), 339-356.

Narotsky, M.G., Hamby, B.T., Mitchell, D.S., and Kavlock, R.J. (1992) “Full-litter resorptions caused by low-molecular weight halocarbons in F-344 rats,” *Teratology*, **45**, 472-473.

National Spa and Pool Institute (1998) 1998 pool and spa market, report from the National Spa and Pool Institute, Alexandria, VA.

NCI (1976) National Cancer Institute, report carcinogenesis bioassay of chloroform, NTIS PB-264018, Springfield, VA.

Nero, A.V., and Nazaroff, W.W. (1984) 'Characterizing the source of radon indoors," *Radiation Protection Dosimetry*, **7**, 23-39.

Nieminski, E.C., Chaudhuri, S., and Lamoreaux, T. (1993) "The occurrence of DBPs in Utah drinking waters," *Journal. American Water Works Association*, **85**(9), 98-105.

NTP (1985) National Toxicology Program, Toxicology and carcinogenesis studies of chlorodibromomethane in F344/N rats and B6C3F1 mice (gavage studies). U.S. Department of Health and Human Services, Research Triangle Park, N.C., Technical Report Series No. 282.

NTP (1987) National Toxicology Program, Toxicology and carcinogenesis studies of bromodichloromethane (CAS No. 75-27-4) in F344/N rats and B6C3F1 mice (gavage studies). U.S. Department of Health and Human Services, Research Triangle Park, N.C., Technical Report Series No. 321.

NTP (1989a) National Toxicology Program, Toxicology and carcinogenesis studies of tribromomethane (bromoform) in F344/N rats and B6C3F1 mice (gavage studies). U.S. Department of Health and Human Services, Research Triangle Park, N.C., Technical Report Series No. 350.

NTP (1989b) National Toxicology Program, Bromoform: Reproduction and fertility assessment in Swiss CD-1 mice when administered by gavage. National Institute of Environmental Health Sciences, Research Triangle Park, N.C., NTP-89-068.

Nuchia, E. 1986. MDAC: Houston materials testing database user's guide. Houston, TX, NASA.

Oliver, B.G. (1983) "Dihaloacetonitriles in drinking water: Algae and fulvic acids as precursors," *Environmental Science & Technology*, **15**, 1075-1080.

Otson, R., Fellin, P., and Tran, Q. (1994) "VOCs in representative Canadian residences," *Atmospheric Environment*, **28**(22), 3563-3569.

Ott, W. (1982) "Concepts of human exposure to air pollution," *Environment International*, **7**, 179-196.

Ott, W. (1985) "Total human exposure: An emerging science focuses on humans as receptors of environmental pollution," *Environmental Science & Technology*, **19**(10), 880-886.

Ott, W.R. (1990) "Total human exposure: Basic concepts, EPA field studies, and future research needs," *Journal of the Air & Waste Management Association*, **40**(7), 966-975.

Ott, W.R. (1995) "Human exposure assessment: The birth of a new science," *Journal of Exposure Analysis and Environmental Epidemiology*, **5**(4), 449-471.

Ott, W.R., and Roberts, P.V. (1998) "Everyday exposure to toxic pollutants," *Scientific American*, **279**, 86-91.

Ozkaynak, H., Jensen, P.B., Wallace, L.A., Nelson, W.C., and Behar, J.V. (1987) Sources and emission rates of organic chemical vapors in homes and buildings, *Proceeding of the 4th International Conference on Indoor Air Quality and Climate*, West Berlin, West Germany, 1(3).

Pfaffenberger, C.D., and Peoples, A.J. (1982) "Long-term variation study of blood plasma levels of chloroform and related purgeable compounds," *Journal of Chromatography*, **239**, 217-226.

Platt-Mills, T.A.E., Woodfolk, J.A., Chapman, M.D., Heymann, P.W. (1996) "Changing concepts of allergic disease: The attempt to keep up with real changes in lifestyles," *Journal of Allergy and Clinical Immunology*, **98**(Suppl.), S297-S306.

Potts, R.O., and Guy, R.H. (1992) "Predicting skin permeability," *Pharmaceutical Research*, **9**, 663-669.

Pourmoghaddas, H., Stevens, A.A., Kinman, R.N., Dressman, R.C., Moore, L.A., and Ireland, J.C. (1993) "Effect of bromide ion on formation of HAAs during chlorination," *Journal. American Water Works Association*, **85**(1), 82-87.

Raifaa, H. (1968) *Decision analysis: introductory lectures on choices under uncertainty*, Addison-Wesley, Reading, Massachusetts.

Rodes, C.E., Kamens, R.M., and Wiener, R.W. (1991) "The significance and characteristics of the personal activity cloud on exposure assessment measurements for indoor contaminants," *Indoor Air*, **2**, 123-145.

Rook, J. (1974) "Formation of haloforms during chloronation of natural water," *Water Treatment and Examination*, **23**, 234-243.

Savitz, D.A., Andrews, K.W., and Pastore, L.M. (1995) "Drinking water and pregnancy outcome in central North Carolina: Source, amount, and trihalomethane levels," *Environmental Health Perspectives*, **103**, 592-596.

Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M. (1993) *Environmental Organic Chemistry*, John Wiley & Sons, Inc., New York.

Shah, J.J., and Singh, H.B. (1988) "Distribution of volatile organic chemicals in outdoor and indoor air: A national VOCs data base," *Environmental Science & Technology*, **22**(12), 1381-1388.

Shepherd, J., Kemp, J., and Corsi, R.L. (1996) "Chloroform in indoor air and wastewater: the role of residential washing machines," *Journal of the Air & Waste Management Association*, **46**(7), 631-642.

Shepherd, J.L. (1994) "Mass transfer of volatile organic compounds at industrial process drains," M.S. Thesis, The University of Texas at Austin.

Sherman, M.H. (1999) "Indoor air quality for residential buildings," *ASHRAE Journal*, **41**(5), 26-30.

Siddiqui, M.S., and Amy, G.L. (1993) "Factors affecting DBP formation during ozone-bromide reactions," *Journal. American Water Works Association*, **85**(1), 63-72.

Singer, P.C. (1994) "Control of disinfection by-products in drinking water," *Journal of Environmental Engineering, ASCE*, **120**(4), 727-744.

Sosulski, F.W., and McCurdy, A.R. (1987) "Functionality of flours, protein fractions and isolates from field peas and faba bean," *Journal of Food Science*, **52**, 1010.

Sparks, L.E., Tichenor, B.A., White, J.B., and Jackson, M.D. (1991) "Comparison of data from the IAQ test house with predictions of an IAQ computer model," *Indoor Air*, **4**, 577-592.

Standard Methods for the Examination of Water and Wastewater (1989) Seventeenth edition, L.S. Clesceri, A.E. Greenberg, and R.R. Trussell, eds., American Public Health Association, American Water Works Association, and Water Pollution Control Federation, pp. 4-58 – 4-64, 5-18 – 5-22.

Stevens, A.A., Moore, L.A., and Miltner, R.J. (1989) "Formation and control of non-trihalomethane disinfection by-products," *Journal. American Water Works Association*, **81**(8), 54-61.

Stevens, A.A., Slocum, C.J., Seeger, D.R., and Robeck, G.G. (1976) "Chlorination of organics in drinking water," *Journal. American Water Works Association*, **68**(11), 615-620.

Summer, R.S., Hooper, S.M., Shukairy, H.M., Solarik, G., and Owen, D. (1996) "Assessing DBP yield: Uniform formation conditions," *Journal. American Water Works Association*, **88**(6), 80-93.

Symons, J.M., Bellar, T.A., Carsell, J.K., DeMarco, J., Kropp, K.L., Robeck, G.G., Seeger, D.R., Slocum, C.J., Smith, B.L., and Stevens, A.A. (1975) "National Organics Reconnaissance Survey for halogenated organics," *Journal. American Water Works Association*, **67**(11), 634-647.

Tancrede, M., Yanagisawa, Y., and Wilson (1992) "Volatilization of volatile organic compounds from showers – I. Analytical method and quantitative assessment," *Atmospheric Environment*, **26A**(6), 1103-1111.

Thomas, K.W., Pellizzair, E.D., Clayton, C.A., Whitaker, D.A., and Shores, R.C. (1993) "Particule total exposure assessment methodology (PTEAM) 1990 study: Method performance and data quality for personal, indoor, and outdoor monitoring," *Journal of Exposure Analysis and Environmental Epidemiology*, **3**(2), 203-226.

Tichenor, B.A., and Mason, M.A. (1988) "Organic emissions from consumer products and building materials to the indoor environment," *Journal of the Air Pollution Control Association*, **38**(3), 264-268.

Tichenor, B.A., Guo, Z., Dunn, J.E., Sparks, L.E., and Mason, M.A. (1991) "The interaction of vapor phase organic compounds with indoor sinks" *Indoor Air*, **1**, 23-35.

Tribus, M. (1969) *Rational descriptions, decisions and designs*, Pergamon, New York.

USDA (1997) Agricultural Research Service. Results from USDA's 1994-96 Continuing Survey of Food Intakes by Individuals and 1994-96 Diet and Health Knowledge Survey. NTIS Accession Number PB98-500457.

USEPA (1986) A Citizen's Guide to Radon—What it is and what to do about it, EPA-86-004.

USEPA (1992) Dermal exposure assessment: Principles and applications, EPA/600/8-91/011b, Washington, D.C.

USEPA (1992) Occurrence Assessment for Disinfectants and Disinfection By-Products (Phase 6a) in Public Drinking Water.

USEPA (1993) Catalog of materials as potential sources of indoor air emissions: Volume 1. Insulation, wallcoverings, resilient, floor coverings, carpets, adhesives, sealants and caulks, and pesticide, EPA-600/R-93-108a.

USEPA (1994) Air emissions models for waste and wastewater, EPA-453/R-94-080A.

USEPA (1996) Exposure Factors Handbook, EPA/600/8-89/043, draft report, Washington, D.C.

Vena, J.E., Graham, S., Freudenheim, J., Marshall, J., Zielezny, M., Swanson, M., Sufrin, G. (1993) "Drinking water fluid intake and bladder cancer in western New York State," *Archives of Environmental Health*," **48**(3), 191-198.

Wallace, L.A. (1986) "Personal exposures, indoor and outdoor air concentrations, and exhaled breath concentrations of selected volatile organic compounds measured for 600 residents of New Jersey, North Dakota, North Carolina, and California," *Toxicology and Environmental Chemistry*, **12**, 215-236.

Wallace, L.A. (1989) "The Total Exposure Assessment Methodology (TEAM) study: An analysis of exposures, sources, and risks associated with four chemicals," *Journal of the American College of Toxicology*, **8**, 883-895.

Wallace, L.A. (1993) "A decade of studies of human exposure: What have we learned?" *Risk Analysis*, **13**(2), 135-139.

Wallace, L.A. (1997) "Human exposure and body burden for chloroform and other trihalomethanes," *Critical Reviews in Environmental Science and Technology*, **27**(2), 113-194.

Wallace, L.A., Nelson, W.C., Ziegenfus, R., and Pellizzari, E. (1991) "The Los Angeles TEAM study: Personal exposures, indoor-outdoor air concentrations, and breath concentrations of 25 volatile organic compounds," *Journal of Exposure Analysis and Environmental Epidemiology*, **1**, 37-72.

Wallace, L.A., Pellizzari, E., Hartwell, T., Rosenzweig, M., Erickson, M., Sparacino, C., and Zelon, H. (1984a) "Personal exposure to volatile organic compounds I. Direct measurements in breathing-zone air, drinking water, food, and exhaled breath," *Environmental Research*, **35**, 293-319.

Wallace, L.A., Pellizzari, E., Hartwell, T., Sparacino, C., and Zelon, H. (1984b) "Personal exposures, indoor-outdoor relationships and breath levels of toxic air pollutants measured for 355 persons in New Jersey," *Atmospheric Environment*, **19**(10), 1651-1655.

Wallace, L.A., Pellizzari, E., Hartwell, T.D., Whitmore, R., Sparacino, C., and Zelon, H. (1986) "Total exposure assessment methodology (TEAM) study: Personal exposures, indoor-outdoor relationships, and breath levels of volatile organic compounds in New Jersey," *Environment International*, **12**, 369-387.

Wallace, L.A., Pellizzari, E., Leaderer, B., Zelon, H., and Sheldon, L. (1987b) "Emissions of volatile organic compounds from building materials and consumer products," *Atmospheric Environment*, **21**(2), 385-393.

Wallace, L.A., Pellizzari, E.D., Hartwell, T.D., Davis, V., Michael, L.C., and Whitmore, R.W. (1989) "The influence of personal activities on exposure to volatile organic compounds," *Environmental Research*, **50**, 37-55.

Wallace, L.A., Pellizzari, E.D., Hartwell, T.D., Sparacino, C., Whitmore, R., Sheldon, L., Zelon, H., and Perritt, R. (1987a) "The TEAM study: Personal exposures to toxic substances in air, drinking water, and breath of 400 residents of New Jersey, North Carolina, and North Dakota," *Environmental Research*, **43**(2), 290-307.

Wallace, L.A., Pellizzari, E.D., Hartwell, T.D., Whitmore, R., Zelon, H., Perritt, R., and Sheldon, L. (1988) "The California TEAM study: Breath concentrations and personal exposures to 26 volatile organic compounds in air and drinking water of 188 residents of Los Angeles, Antioch, and Pittsburg, CA," *Atmospheric Environment*, **22**(10), 2141-2163.

Wallace, L.A., Zweidinger, R., Erickson, M., Cooper, S., Whitaker, D., and Pellizzari, E. (1982) "Monitoring individual exposure: Measurement of volatile organic compounds in breathing-zone air, drinking water, and exhaled breath," *Environment International*, **8**, 269-282.

Weisel, C.P., and Shepard, T.A. (1994) "Chloroform exposure and the body burden associated with swimming in chlorinated pools." In: Water Contamination and Health: Integration of Exposure Assessment, Toxicology, and Risk Assessment, pp. 135-147, Wang, R.G.M., ed., Marcel Dekker, New York.

Wester, R.C., and Maibach, H.I. (1989) "Human skin binding and absorption of contaminants from ground and surface water during swimming and bathing," *Journal of the American College of Toxicology*, **8**, 853-860.

Whitmore, R.W., Immerman, F.W., Camann, D.E., Bond, A.E., Lewis, R.G., and Schuam, J.L. (1994) "Non-occupational exposures to pesticides for residents of two U.S. cities," *Archives of Environmental Contamination and Toxicology*, **26**, 47-59.

Won, D., Corsi, R.L., and Rynes, M. (2001) "Sorptive interactions between VOCs and indoor materials," *Indoor Air*, **11**(4), 246-256.

Won, D., Howard, C., and Corsi, R.L. (1998) "Human exposure to VOCs in indoor air: combined effects of source and sink kinetics," *Proceedings of the 91st Annual Meeting & Exhibition of the Air and Waste Management Association*, St. Louis.

Wood, J.A., and Porter, M.L. (1987) "Hazardous pollutants in Class II landfills," *Journal of the Air Pollution Control Association*, **37**(5), 609-615.

World Health Organization (2000) Disinfection and Disinfection By-Products, Environmental Health Criteria 216, Geneva.

Young, T.B., Kanarek, M.S., and Tsiatis, A.A. (1981) "Epidemiologic study of drinking water chlorination and Wisconsin female cancer mortality," *Journal of the National Cancer Institute*, **67**, 1191-1198.

Zayas, J.F. (1997) *Functionality of protein in foods*, Springer-Verlag, Berlin.

Zhang, J., He, Q., and Lioy, P.J. (1994) "Characteristics of aldehydes: Concentrations, sources, and exposures for indoor and outdoor residential microenvironments," *Environmental Science & Technology*, **28**(1), 146-152.

VITA

David Alan Olson was born in Tuscaloosa, Alabama on January 11, 1971, the son of Nancy Norling Olson and Richard Edward Olson. After graduating from Washburn Rural High School in Topeka, Kansas, he entered the University of Kansas in Lawrence, Kansas. He received the degree of Bachelor of Science in Mechanical Engineering from the University of Kansas in May 1994. In August 1994 he entered the University of Texas and received the degree of Master of Science in Civil Engineering in May 1996. Upon graduation he worked as an environmental engineer for Waid and Associates in Austin, TX. In August 1998 he entered the University of Texas and received the degree of Doctor of Philosophy in Civil Engineering in May 2002.

Permanent Address: 2231 Brookfield, Topeka, Kansas 66614

This dissertation was typed by the author.