

University of Montana

ScholarWorks at University of Montana

Graduate Student Theses, Dissertations, &
Professional Papers

Graduate School

2009

Indoor/Ambient Residential Air Toxics Results in Rural Western Montana

Heidi Lee Underberg
The University of Montana

Follow this and additional works at: <https://scholarworks.umt.edu/etd>

Let us know how access to this document benefits you.

Recommended Citation

Underberg, Heidi Lee, "Indoor/Ambient Residential Air Toxics Results in Rural Western Montana" (2009).
Graduate Student Theses, Dissertations, & Professional Papers. 571.
<https://scholarworks.umt.edu/etd/571>

This Professional Paper is brought to you for free and open access by the Graduate School at ScholarWorks at University of Montana. It has been accepted for inclusion in Graduate Student Theses, Dissertations, & Professional Papers by an authorized administrator of ScholarWorks at University of Montana. For more information, please contact scholarworks@mso.umt.edu.

**INDOOR/AMBIENT RESIDENTIAL AIR TOXES RESULTS IN RURAL
WESTERN MONTANA**

By

Heidi Lee Underberg

Bachelor's Degree (Biology and Chemistry),
Augustana College, Sioux Falls, SD, 2005

Professional Paper

presented in partial fulfillment of the requirements
for the degree of

Master of Science
in Chemistry, Environmental/Analytical

The University of Montana
Missoula, MT

Summer 2009

Approved by:

Perry Brown, Associate Provost for Graduate Education
Graduate School

Dr. Garon Smith, Chair
Chemistry and Biochemistry

Dr. Chris Palmer
Chemistry and Biochemistry

Dr. Tony Ward
Biomedical and Pharmaceutical Sciences

Indoor/ambient residential air toxics results in rural western Montana

Chairperson: Dr. Garon Smith

Indoor and ambient concentrations of 21 volatile organic compounds (including 14 hazardous air pollutants) were measured in the homes of nearly 80 western Montana (Missoula) high school students as part of the 'Air Toxics Under the Big Sky' program during the 2004/2005 and 2005/2006 school years. Target analytes were measured using low flow air sampling pumps and sorbent tubes, with analysis of the exposed samples by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS). The results reported here present the findings of the first indoor/ambient air toxics monitoring program conducted in a semi-rural valley location located in the Northern Rocky Mountain/Western Montana region. Of all of the air toxics quantified in this study, toluene was found to be the most abundant compound in both the indoor and ambient environments during each of the two school years. Indoor log-transformed mean concentrations were found to be higher when compared with ambient log-transformed mean concentrations at $P < 0.001$ for the majority of the compounds, supporting the results of previous studies conducted in urban areas. For the air toxics consistently measured throughout this program, concentrations were approximately six times higher inside the student's homes compared to those simultaneously measured directly outside their homes. For the majority of the compounds, there were no significant correlations between indoor and ambient concentrations.

ACKNOWLEDGEMENTS

The authors thank the teachers and students at Big Sky HS for participating in the program. Primary funding for this project was provided by Grant Number R25 RR020432 from the National Center for Research Resources (NCRR), a component of the National Institutes of Health (NIH). Additional support came from NIH COBRE grant P20 RR017670 from NCRR. The contents of this manuscript are solely the responsibility of the authors and do not necessarily represent the official views of NCRR or NIH.

TABLE OF CONTENTS

Title page.....	i
Abstract.....	ii
Acknowledgements.....	iii
Table of Contents.....	iv
List of Tables.....	v
Chapter 1 Introduction.....	1
Chapter 2 Experimental.....	3
Chapter 3 Results and Discussion.....	9
Chapter 4 Conclusion.....	17
References.....	19

LIST OF TABLES

Table 1: 2004/2005 Big Sky HS air toxics results ($\mu\text{g}/\text{m}^3$).....7

Table 2: 2005/2006 Big Sky HS air toxics results (ng/m^3).....8

Table 3: 2004/2005 and 2005/2006 indoor vs. ambient comparison.....13

Table 4: QA/QC data - blanks ($\mu\text{g}/\text{m}^3$) and spikes (% recovery).....15

CHAPTER 1

INTRODUCTION

Under Title III, Section 112.b.1 of the 1990 Clean Air Act, the United States Environmental Protection Agency (EPA) identified 189 hazardous air pollutants (HAPs), of which 97 are volatile organic compounds (VOCs). These include many toxic air pollutants that are known or suspected to cause adverse health effects. People exposed to toxic air pollutants at sufficient concentrations and durations may have an increased chance of getting cancer or experiencing other serious health effects, such as damage to the respiratory, neurological, developmental, immune, reproductive, and other systems.

Today, air toxics are routinely measured in urban ambient environments not only in the United States, but in other urban areas throughout the world. Sampling programs measuring indoor air toxics concentrations in nonoccupational environments (residences) are much less common. This is important, as most people spend the majority of their time indoors (Fishbein and Henry, 1991; Jenkins et al., 1992; Robinson and Nelson, 1995), as much as 95% in some areas. Several studies have been conducted that have simultaneously measured air toxics concentrations in the indoor, ambient, and personal breathing zone environments. Many of these studies report that a consistent pattern of Personal>Indoor>Ambient air toxics concentrations exists (Kim et al., 2002; Kinney et al., 2002; Weisel et al., 2002; Adgate et al., 2004; Payne-Sturges et al., 2004; Sexton et al., 2004b). Some of these studies also indicate that ambient air toxics measurements at central monitoring sites can seriously underestimate actual exposures for urban residents, suggesting that people typically encounter substantially higher air toxics concentrations

during their normal daily activities compared to ambient air toxics levels recorded at central monitoring sites.

Since air toxics are perceived to be an urban airshed pollution issue, much less research has been conducted on measuring the concentrations and health effects of these compounds in rural, less populated areas. This is especially true of residential indoor environments within these rural areas. A currently under-studied area of the country includes communities in valley locations throughout the northern Rocky Mountains. These communities and airsheds are impacted by temperature inversions formed during the winter months which trap pollutants in the valley for extended periods of times. Ambient concentrations of VOCs (including air toxics) have been shown to dramatically increase during periods of inversions formed in these mountainous communities throughout the winter months compared to the warmer summer months (Ward et al., 2005). Little is known about indoor concentrations of air toxics in these valley locations during these colder seasonal periods.

This research paper presents the results of a two-year air toxics monitoring program conducted in a semi-rural valley community in western Montana. More significantly, this paper presents the concentrations of air toxics measured simultaneously inside and outside the homes of nearly 80 high school students, providing the first information on indoor/ambient concentrations of air toxics in this region.

CHAPTER 2

EXPERIMENTAL

In this research project, air samples were collected using high school students as part of a program in western Montana called ‘Air Toxics Under the Big Sky’ (Adams et al., 2008). The existing program, which began in 2003 as a collaboration between researchers at The University of Montana (UM) and a chemistry teacher at Big Sky High School (Missoula, MT), involves junior and senior level (primarily upper-level chemistry) high school students that collect air samples inside and outside (simultaneously) their homes. This program not only incorporates real-world science into the high school chemistry course curriculum, but allows UM researchers to measure and evaluate concentrations of air toxics in the indoor and ambient environments of high school students throughout western Montana. This program is also unique in that it enables the collection of an expanded amount of samples at multiple locations throughout an airshed, compared to a single fixed central location.

The primary study area for this program was Missoula, Montana. Missoula (population ~70,000) is located in western Montana in a high mountain valley. During the 2004/2005 and 2005/2006 school years, over 80 students participated in the ‘Air Toxics Under the Big Sky’ program at Big Sky High School (HS). The goal was for each student to sample at least two times at their homes throughout the school year. During 2004/2005, 35 successful paired ambient and indoor samples were collected, while during the 2005/2006 school year, 51 successful paired ambient and indoor samples were taken. Samples were collected from October through February during both the 2004/2005 and 2005/2006 school years. For the 2004/2005 school year, the number of

successful paired (indoor/ambient) sampling events per month was as follows: Oct (2), Nov (11), Dec (11), Jan (0), and Feb (11). For the 2005/2006 school year, the amount of successful paired samples was: Oct (11), Nov (21), Dec (0), Jan (5), and Feb (14). The majority of the samples were collected in a 10-mile radius surrounding the high school, at elevations of approximately 3200 feet above sea level.

At the beginning of the 2004/2005 and 2005/2006 school years, respectively, students were initially trained within the classroom by UM researchers on how to collect air samples both within and outside of their homes. Prior to sampling, students were provided with two sampling kits (consisting of pump and sorbent tube) to take home, with one kit used to collect ambient samples and the other used for indoor sampling. VOCs were measured using low flow (Model Number 222-3) air sampling pumps (SKC, Eighty Four, PA) and Carbotrap 300 sorbent tubes (Sigma-Aldrich, St. Louis, MO). Before sampling, each sorbent tube was conditioned at UM for initial use by flushing the tube with approximately 200 ml/min of purified nitrogen gas and heating for 20 minutes at 350 °C to remove oxygen, moisture and organic contaminants. These pre-cleaned tubes were then delivered to the schools prior to sampling.

In an effort to minimize the variability in error associated with different students conducting flow measurements, the personal pumps were calibrated using a BIOS DryCal primary flow meter (Bios, Butler, NJ) within the classroom prior to each sampling event by a single point student in each class. During sampling, ambient air was drawn through sorbent tubes at a flow rate of 100 ml/min \pm 5 ml/min for 12 hours (7 AM to 7 PM) to collect a total volume of ~72 L. The optimum flow rate was chosen based on a series of preliminary field experiments (Woolfenden, 1997; Wrobel, 2000; Ward, 2001). This

flow rate was high enough to meet the minimum detection limits of the target analytes while low enough to not have breakthrough (when more than 5% of one or more of the target analytes is observed) through the sorbent tube. Separated by small plugs of silanized glass wool, each sorbent sample tube was composed of three different carbon sorbents: 20/40 mesh Carbotrap C, 20/40 Carbotrap B, and 60/80 Carbosieve S-III. For low level, low polarity, volatile contaminants, this combination of adsorbents/absorbents has been found to be extremely effective (Helmig and Greenburg, 1994).

Before sampling, the students were instructed to collect indoor samples in a common area of their home (living room), while samplers for the ambient location were to be placed in a secure location at least 10 feet away from their house. All samplers were to be placed three to five feet off the ground, and away from any obvious sources of air toxics that might bias the sample results.

Final flow rates were measured and recorded in the classroom by the point student after the students returned the pumps back to the classroom. The exposed sample tubes were kept refrigerated at Big Sky HS until they were returned to UM where they were analyzed using a Hewlett Packard 6890 series Gas Chromatograph (GC) with a 5973 Mass Spectrum Detector (MSD). A Dynatherm MTDU Model 910 thermal desorption unit and Model 900 ACEM sample concentrator were used in conjunction with the GC/MS during the VOC analyses, with analyte separations on a Restek RTX502.2 capillary column (60 m, 0.32 mm ID).

A standard suite of 10 VOCs were originally quantified during the 2004/2005 school year, with the list expanded to 21 compounds for the 2005/2006 school year. Before analysis, 1 μl of a 100 ng/ μl internal standard solution (fluorobenzene, 1,2-

dichlorobenzene-D4, and 4-bromofluorobenzene) was injected onto the sorbent tubes. Using a deactivated quartz “tee”, both the internal standard and standards solution (consisting of target analytes) were flash volatilized at 125 °C within the quartz tee (Wrobel, 2000). The compounds were then swept onto a sorbent tube at room temperature with purified nitrogen gas at a flow rate of 55 to 60 ml/min for 5 minutes.

Several measures were built into the sampling/analytical program to ensure that the data collected were of high quality. To address artifact contamination, field blanks were used throughout the VOC sampling program. System blanks (glass sorbent tubes without carbon sorbent) were also used to monitor for instrument artifact contamination during the VOC analyses. Quality control measures for the GC/MS included the analysis of bromofluorobenzene (25 ng/μl BFB) each day prior to sample analyses as a system check. Mid range standards (200 ng/μl spiked onto the sorbent tubes using the deactivated quartz “tee”) were periodically analyzed throughout the analysis to verify initial calibrations.

Minimum detection limits (MDL) were calculated for all of the reported parameters by the following formula: blank mean + (blank standard deviation x critical value of t), with these values presented in **Tables 1 and 2**. The critical value of t was the one-tailed probability at 0.01 with ($n - 1$) degrees of freedom. Any value in the data set that was below MDL was replaced with the 1/2 MDL value for that variable.

Table 1: 2004/2005 Big Sky HS air toxics results ($\mu\text{g}/\text{m}^3$).

	Indoor Median	Indoor Max Min	Ambient Median	Ambient Max Min	Indoor vs. Ambient	MDL
Benzene ^a	1.8	34.3 <0.1	0.5	6.2 <0.1	P < 0.001	0.2
1,4-dimethylbenzene (p xylene)	2.6	34.0 0.4	0.5	3.8 <0.02	P < 0.001	0.04
1,2-dimethylbenzene (o xylene)	2.0	22.0 0.4	0.5	2.7 0.1	P < 0.001	0.05
Ethylbenzene ^a	2.0	20.6 0.3	0.4	3.3 0.01	P < 0.001	0.003
Isopropylbenzene	0.1	1.7 <0.04	<0.04	0.1 <0.04	P < 0.001	0.1
Propylbenzene	0.2	10.7 <0.1	<0.1	0.7 <0.1	P < 0.001	0.2
Carbon tetrachloride ^a	0.8	1.6 N.D.	0.6	1.4 N.D.	P < 0.01	0.1 ^b
Toluene ^a	7.9	57.6 1.7	0.9	4.3 0.3	P < 0.001	0.04
1,3,5- trimethylbenzene	0.5	15.3 <0.1	<0.1	1.0 <0.1	P < 0.001	0.2
1,2,4- trimethylbenzene	1.6	23.9 0.6	0.6	4.6 <0.1	P < 0.001	0.2

^aClean Air Act Hazardous Air Pollutant. ^bNo measurable blanks for these compounds, values

estimated using method from Principles of Instrumental Analysis (Skoog, 1998). For the 2004/2005 program, sample size (n) was 35 paired observations.

Table 2: 2005/2006 Big Sky HS air toxics results (ng/m³).

Compound	Indoor Median	Indoor Max Min	Ambient Median	Ambient Max/Min	Indoor vs. Ambient	MDL
Benzene ^a	1.2	21.6 <0.1	0.3	8.7 <0.1	P < 0.001	0.2
Bromoform ^a	b	0.3 N.D.	b	0.3 N.D.	N/A	0.1 ^c
Chlorobenzene ^a	b	0.04 N.D.	b	<0.004 N.D.	P < 0.001	0.01 ^c
Chloroform ^a	0.1	3.1 <0.003	<0.003	1.0 <0.003	P < 0.001	0.01
Cis-1,3-dichloropropene	b	0.4 N.D.	b	N.D. N.D.	N/A	0.001 ^c
1,2-dibromo-3-chloropropane ^a	b	N.D. N.D.	b	0.05 N.D.	N/A	0.02 ^c
1,4-dichlorobenzene ^a	b	0.2 N.D.	b	<0.01 N.D.	N/A	0.02 ^c
1,4-dimethylbenzene (p xylene)	1.8	26.5 <0.02	0.3	6.3 <0.02	P < 0.001	0.04
1,2-dimethylbenzene (o xylene)	1.3	18.7 <0.02	0.2	4.2 <0.02	P < 0.001	0.1
1,3-dichloropropene ^a	b	0.05 N.D.	b	0.03 N.D.	N/A	0.02 ^c
Ethylbenzene ^a	1.1	19.2 0.03	0.2	3.8 <0.001	P < 0.001	0.003
Isopropylbenzene	<0.04	2.4 <0.04	<0.04	0.3 <0.04	P < 0.001	0.1
Naphthalene ^a	0.3	1.4 <0.01	0.1	0.4 <0.01	P < 0.001	0.03
n-propylbenzene	0.2	3.0 <0.1	<0.1	0.6 <0.1	P < 0.001	0.2
Trichloroethylene ^a	0.02	4.6 N.D.	<0.01	1.7 N.D.	P < 0.001	0.02 ^c
1,1,2,2-tetrachloroethane ^a	<0.06	2.0 N.D.	<0.06	0.3 N.D.	P < 0.001	0.1 ^c
Carbon tetrachloride ^a	0.3	0.8 0.1	0.2	0.4 0.1	P < 0.01	0.1 ^c
Toluene ^a	12.6	132.5 0.2	1.1	25.4 0.1	P < 0.001	0.04
1,2,4-trichlorobenzene ^a	<0.02	0.2 N.D.	<0.02	<0.02 N.D.	P < 0.001	0.04 ^c
1,3,5-trimethylbenzene	0.3	5.5 <0.1	<0.1	0.7 <0.1	P < 0.001	0.2
1,2,4-trimethylbenzene	1.2	12.7 <0.1	0.3	2.4 <0.1	P < 0.001	0.2

^aClean Air Act Hazardous Air Pollutant. ^bIndicates no statistical analyses possible because less than 3 nonzero values measured. ^cNo measurable blanks for these compounds, values estimated using method from Principles of Instrumental Analysis (Skoog, 1998). N.D. = not detected. For the 2005/2006 program, sample size (n) was 51 paired observations.

CHAPTER 3

RESULTS AND DISCUSSION

The statistical analysis conducted in this study compared the concentrations of indoor vs. ambient air toxics. Analysis of variance (ANOVA) was conducted on all of the measured compounds to determine differences in source. All of the raw data were lognormal in distribution, and therefore log-transformed prior to analysis for distribution normalization and equalization of variances. The indoor/ambient data were paired based on location and sampling time, resulting in a two-level random factor. The fixed factor in the model was the sample year, which also had two levels. A mixed model two-way ANOVA, with one within-subjects factor (indoor/ambient), and one between-subjects factor (year), was run for all compounds independently. Statistical significance was determined at a probability of less than 5% for type I error ($P < 0.001$ if adjusted for all multiple testing). Sample size was 35 paired observations for 2004/2005, and 51 paired observations for 2005/2006, establishing adequate statistical power on the log transformed data for all compounds analyzed. As stated earlier, the goal was for each student to sample at least two times at their homes throughout the school year. Although nearly 80 students participated during the 2-year program, we were not successful in collecting 160 complete indoor/ambient sample data sets. Most of the students were only able to collect one set of samples within their homes due to time constraints within the school semesters. Other samples were invalidated due to incomplete paired data sets (either a missing indoor or ambient sample), low final flow readings (below 90 ml/min),

pump failure, breaking the sample tube during transport, less than a 12-hour sample collection period, or TD/GC/MS malfunctions.

Tables 1 (2004/2005) **and 2** (2005/2006) present the air toxics raw data median concentrations, maximum/minimum concentrations per analyte, and minimum detection limits for the two-year sampling program. These values are not blank corrected. Of all of the air toxics quantified in this study, toluene was found to be the most abundant compound in both the indoor and ambient environments throughout each of the two school years. Other EPA HAPs (air toxics) consistently measured include benzene, chloroform, ethylbenzene, naphthalene, trichloroethylene, 1,1,2,2-tetrachloroethane, and 1,2,4-trichlorobenzene. Several other of the target HAPs were not detected in this sampling program.

Median concentrations of ambient air toxics measured in this program were two - eight times lower than those concentrations measured in urban areas such as Minneapolis-St. Paul (Pratt et al., 2004; Adgate et al., 2004) and Baltimore (Payne-Sturges, et al., 2004), 10-20 times lower than those measured in other urban areas such as Chicago, St. Louis (Sweet and Vermette, 1992), and New Jersey (Wallace, 1987), and ~20-50 times lower compared to ambient air toxics measured in Los Angeles (Wallace, 1987). Ambient concentrations of the BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) measured in this study were comparable or slightly more elevated when compared to median concentrations reported in a four Oklahoma city study (Phillips et al., 2005), and in Greensboro, NC (Wallace, 1987). Ambient concentrations measured in this program (Missoula, MT) were higher than those measured in rural Devils Lake, ND during the Total Exposure Assessment Methodology

(TEAM) Study conducted between 1979 and 1985 (Wallace, 1987). For the indoor measurements made in this study, concentrations for many of the compounds were comparable to the previous studies conducted in Baltimore (Payne-Sturges, et al., 2004), Minneapolis (Sexton et al., 2004b), and in Arizona (Gordon et al., 1999).

From the ANOVA results presented in the “Indoor vs. Ambient” column of **Tables 1 and 2**, indoor log-transformed mean concentrations were found to be higher when compared with ambient log-transformed mean concentrations at $P < 0.001$ for the majority of the compounds. For the air toxics consistently measured throughout this program, concentrations were approximately six times higher inside the student’s homes compared to measurements made directly outside their homes. The findings in this program are consistent with those in other studies, where there is a common pattern of indoor air toxics concentrations $>$ ambient concentrations (Wallace, 1987; Sexton et al., 1995; Kim et al., 2002; Kinney et al., 2002; Weisel et al., 2002; Adgate et al., 2004; Payne-Sturges et al., 2004; Sexton et al., 2004b; Phillips et al., 2005).

Table 3 presents the results of the ANOVA on the log-transformed data for all compounds measured during the 2004/2005 and 2005/2006 school years, respectively, including the indoor/ambient Pearson correlations, the coefficients of determination (r^2), and level of statistical significance for all compounds. For the majority of the compounds, there were no significant correlations between indoor and ambient concentrations. The exceptions to this include benzene ($P < 0.05$), toluene ($P < 0.001$), and carbon tetrachloride ($P < 0.001$) for 2004/2005, and 1,2,4-trichlorobenzene ($P < 0.05$) for 2005/2006. This lack of correlation is not surprising, as indoor exposures are typically dominated by indoor sources, a result of mostly localized, short-term emissions

(Phillips et al., 2005). Because of the proximity of the source to the receptor (people), these sources of air toxics within homes can greatly contribute to exposure even though they are small when compared with ambient emissions (Weisel, 2002).

Table 3: 2004/2005 and 2005/2006 indoor vs. ambient comparison.

Compound	2004/2005 I/O correlation	2004/2005 Proportion of variance explained (r^2) indoor vs. ambient	2004/2005 Correlation significance indoor vs. ambient	2005/2006 I/O correlation	2005/2006 Proportion of variance explained (r^2) indoor vs. ambient	2005/2006 Correlation significance indoor vs. ambient
Benzene ^a	0.37	0.137	$P < 0.05$	-0.15	0.023	n.s.
Bromoform ^a	N/A	N/A	N/A	^b	^b	N/A
Chlorobenzene ^a	N/A	N/A	N/A	0.04	0.002	n.s.
Chloroform ^a	N/A	N/A	N/A	0.151	0.022	n.s.
Cis-1,3-dichloropropene	N/A	N/A	N/A	^b	^b	N/A
1,2-dibromo-3- chloropropane ^a	N/A	N/A	N/A	^b	^b	N/A
1,4-dichlorobenzene ^a	N/A	N/A	N/A	^b	^b	N/A
1,4-dimethylbenzene (p xylene)	0.21	0.044	n.s.	-0.07	0.005	n.s.
1,2-dimethylbenzene (o xylene)	0.27	0.073	n.s.	-0.07	0.005	n.s.
1,3-dichloropropene ^a	N/A	N/A	N/A	^b	^b	N/A
Ethylbenzene ^a	0.23	0.053	n.s.	-0.10	0.010	n.s.
Isopropylbenzene	0.12	0.014	n.s.	-0.13	0.017	n.s.

Naphthalene ^a	N/A	N/A	N/A	0.032	0.001	n.s.
n-propylbenzene	0.17	0.029	n.s.	-0.03	0.009	n.s.
Trichloroethylene ^a	N/A	N/A	N/A	-0.05	0.003	n.s.
1,1,2,2-tetrachloroethane ^a	N/A	N/A	N/A	0.03	0.009	n.s.
Carbon tetrachloride ^a	0.49	0.240	$P < 0.001$	-0.07	0.005	n.s.
Toluene ^a	0.64	0.409	$P < 0.001$	-0.15	0.023	n.s.
1,2,4-trichlorobenzene ^a	N/A	N/A	N/A	-0.35	0.123	$P < 0.05$
1,3,5-trimethylbenzene	0.16	0.026	n.s.	0.19	0.036	n.s.
1,2,4-trimethylbenzene	0.15	0.023	n.s.	0.12	0.014	n.s.

Note: ^aClean Air Act Hazardous Air Pollutant. ^b Indicates no statistical analyses possible because less than 3 nonzero values measured. n.s.:

not significant.

Table 4 presents the results of the quality assurance / quality control (QA/QC) component conducted throughout the two-year sampling and analytical program. Blank concentrations (in $\mu\text{g}/\text{m}^3$) were calculated by dividing analyte concentrations measured

Table 4: QA/QC data - blanks ($\mu\text{g}/\text{m}^3$) and spikes (% recovery).

Compound	Blanks	Spikes
Benzene ^a	0.1 ^b	87 ± 28%
Bromoform ^a	N.D.	97 ± 14%
Chlorobenzene ^a	N.D.	107 ± 12%
Chloroform ^a	0.003 ^b	95 ± 32 %
Cis-1,3-dichloropropene	N.D.	125 ± 42%
1,2-dibromo-3-chloropropane ^a	N.D.	106 ± 18%
1,4-dichlorobenzene ^a	N.D.	105 ± 22%
1,4-dimethylbenzene (p xylene)	0.02 ^b	109 ± 14%
1,2-dimethylbenzene (o xylene)	0.03 ^b	109 ± 11%
1,3-dichloropropene ^a	N.D.	103 ± 18%
Ethylbenzene ^a	0.002 ^b	109 ± 9%
Isopropylbenzene	0.04 ^b	111 ± 12%
Naphthalene ^a	0.01 ± 0.001	91 ± 49%
n-propylbenzene	0.04 ± 0.1	109 ± 27%
Trichloroethylene ^a	N.D.	125 ± 40%
1,1,2,2-tetrachloroethane ^a	N.D.	106 ± 20%
Carbon tetrachloride ^a	N.D.	80 ± 20%
Toluene ^a	0.02 ± 0.01	117 ± 11%
1,2,4-trichlorobenzene ^a	N.D.	94 ± 46%
1,3,5-trimethylbenzene	0.1 ^b	103 ± 25%
1,2,4-trimethylbenzene	0.1 ± 0.1	104 ± 32%
N	4	7

Note: ^aClean Air Act Hazardous Air Pollutant. ^bOnly detected in one blank, so not able to calculate standard deviation.

from field blanks by the average measured flow rate (0.074 m³) for the actual sample episodes. Results from the air toxics field blank analyses showed that some of the measured analytes had low but consistent background levels in the blanks. Continuing calibration (spike) results were generally well within the desired range of $\pm 30\%$, indicating acceptable recovery of the desired analytes.

CHAPTER 4

CONCLUSION

This research paper presents the results of a two-year air toxics monitoring program conducted in a valley location in western Montana. More significantly, this paper presents the results of air toxics measured simultaneously inside and outside the homes of nearly 80 high school students, providing the first information on indoor/ambient concentrations of air toxics in the rural / semi-rural western Montana / northern US Rocky Mountain region.

Results of this study were consistent with those found in other studies, specifically in studies conducted within urban airsheds. Of all of the air toxics quantified in this study, toluene was found to be the most abundant compound in both the indoor and ambient environments during each of the two school years. Indoor log-transformed mean concentrations were found to be higher when compared with ambient log-transformed mean concentrations at $P < 0.001$ for the majority of the compounds. For the air toxics consistently measured throughout this program, concentrations were approximately six times higher inside the student's homes compared to those simultaneously measured directly outside their homes. Results from this study also showed that although ambient concentrations measured in this study were lower compared to many of the studies conducted in more urban areas, indoor concentrations of the air toxics measured in this study were comparable to the indoor urban measurements in the previous studies.

For the majority of the compounds, there were no significant correlations between indoor and ambient concentrations, suggesting that there were independent sources for both indoor and ambient air toxics. Future source apportionment activities using a receptor-oriented model (such as chemical mass balance, positive matrix factorization, or principal component analysis / absolute principal component scores, among others) could be utilized in this research program to determine the sources in the indoor and ambient environments, respectively. No significant interactions were found between source and year, indicating no change in indoor/ambient patterns between years.

It is essential to characterize the composition, magnitude, and the distribution of air toxics through air monitoring to assess the impact of these components on human health. Although personal exposure is the most relevant for human health impacts, indoor concentrations provide a substantially better estimate of measured personal concentrations when compared to an ambient measurement (Sexton et al., 2004). In the future, these measured data on HAPs (air toxics) in a northern Rocky Mountain airshed may provide information in establishing air quality standards for the indoor environment. In addition, these data can be used to improve the quality of health risk assessments, and to evaluate the efficacy of risk management decisions.

References

- Adams, E., Ward, T.J., Vanek, D., Marra, N., Smith, G., Jones, D., Henthorn, M., Striebel, J. (2008). Air toxics under the Big Sky – a high school science teaching tool, *Journal of Chemical Education*, 85, 2, 221-224
- Adgate, J.L., Church, T.R., Ryan, A.D., Ramachandran, G., Fredrickson, A.L., Stock, T.H., Morandi, M.T., Sexton, K. (2004). Outdoor, indoor, and personal exposure to VOCs in children. *Environmental Health Perspectives*, 112, 14, 1386-1392.
- Adgate, J.L., Ramachandran, G., Pratt, G.C., Waller, L.A., Sexton, K. (2002). Spatial and temporal variability in outdoor, indoor, and personal PM_{2.5} exposure. *Atmospheric Environment*, 36, 3255-3265.
- Akland, G.A., Schwab, M., Zenick, H., Pahl, D. (1997). An interagency partnership applied to the study of environmental health in the low Rio Grande Valley of Texas. *Environment International*, 23, 595-609.
- Buckley, T.J., Liddle, J., Ashley, D.L., Paschal, D.C., Burse V.W., Needham, L.L., et al. (1997). Environmental and biomarker measurements in nine homes in the Lower Rio Grande Valley: multimedia results for pesticides, metals, PAHs, and VOCs. *Environment International*, 23(5), 705-732.
- Clayton, C.A., Pellizzari, E.D., Whitmore, R.W., Perritt, R.L., Quackenboss, J.J. (1999). National Human Exposure Assessment Survey (NHEXAS): distributions and associations of lead, arsenic, and volatile organic compounds in EPA Region 5. *Journal of Exposure Analysis and Environmental Epidemiology*, 9(5), 381-392.
- Cohen, M., Ryan, B., Ozkaynak, H., Epstein, P. (1989). Indoor/outdoor measurements of volatile organic compounds in the Kanawha Valley of West Virginia. *Journal of the Air Pollution Control Association*, 39, 1086-1093.
- Fishbein, L., Henry, C.J. (1991). Introduction: workshop on the methodology for assessing health risks from complex mixtures in indoor air. *Environmental Health Perspectives*, 95, 3-5.
- Gordon, S.M., Callahan, P.J., Nishioka, M.G., Brinkman, M.C., O'Rourke, M.K., Lebowitz, M.D., Moschandreas, D.J. (1999). Residential environmental measurements in the National Human Exposure Assessment Survey (NHEXAS) pilot study in Arizona: preliminary results for pesticides and VOCs. *Journal of Exposure Analysis and Environmental Epidemiology*, 9(5), 456-470.
- Helmig, D., Greenburg, J.P. (1994). Automated in situ gas chromatographic-mass spectrometric analysis of ppt level volatile organic trace gases using multistage solid-adsorbent trapping. *Journal of Chromatography A*, 677, 123-132.

- Jenkins, P.L., Phillips, T.J., Mulberg, J.M., Hui, S.P. (1992). Activity patterns of Californians: use of and proximity to indoor pollutant sources. *Atmospheric Research*, 26A, 2141-2148.
- Kim, Y.M., Harrad, S., Harrison, R.M. (2002). Levels and sources of personal inhalation exposure to volatile organic compounds. *Environmental Science & Technology*, 36, 5405-5410.
- Kinney, P.L., Chillrud, S.N., Ramstrom, S., Ross, J., Spengler, J.D. (2002). Exposures to multiple air toxics in New York City. *Environmental Health Perspectives*, 110(suppl 4), 539-546.
- Leung, P.L., Harrison, R.M. (1998). Evaluation of personal exposure to monoaromatic hydrocarbons. *Occupational & Environmental Medicine*, 55(4), 249-257.
- Lioy, P. (1990). Assessing total human exposure to contaminants. *Environmental Science & Technology*, 24(7), 938-945.
- Otson, R., Fellin P., Tran Q. (1994). VOCs in representative Canadian residences, *Atmospheric Environment*, 28(22), 3563-3569.
- Ott, W. (1990). Total human exposure: basic concepts, EPA field studies and future research needs. *Journal of the Air & Waste Management Association*, 40(7), 966-975.
- Payne-Sturges, D.C., Burke, T.A., Breyse, P., Diener-West, M., Buckley, T.J. (2004). Personal exposure meets risk assessment: a comparison of measured and modeled exposures and risks in an urban community. *Environmental Health Perspectives*, 112(5), 589-598.
- Pellizzari, E., Perritt, R., Clayton, C. (1999). National human exposure assessment survey: exploratory survey of exposure among population subgroups in EPA Region V. *Journal of Exposure Analysis and Environmental Epidemiology*, 9(1), 49-55.
- Phillips, M.L., Esmen, N.A., Hall, T.A., Lynch, R. (2005). Determinants of exposure to volatile organic compounds in four Oklahoma cities. *Journal of Exposure Analysis and Environmental Epidemiology*, 15, 35-46.
- Pratt, G.C., Wu, C.Y., Bock, D., Adgate, J.L., Ramachandran, G., Stock, T.H., Morandi, M., Sexton, K. (2004). Comparing air dispersion model predictions with measured concentrations of VOCs in urban communities. *Environmental Science & Technology*, 38, 1949-1959.
- Robinson, J., Nelson, W.C. (1995). National human activity pattern survey data base. US Environmental Protection Agency, Research Triangle Park, NC.

- Seifert, B., Mailahn, W., Schulz, C., Ullrich, D. (1989). Seasonal variation of concentrations of volatile organic compounds in selected German homes. *Environment International*, 15, 397-408.
- Sexton, K., Kleffman, D.E., Callahan, M.A. (1995). An introduction to the National Human Exposure Assessment Survey (NHEXAS) and related Phase I field studies. *Journal of Exposure Analysis and Environmental Epidemiology*, 5(3), 229-232.
- Sexton, K., Adgate, J.L., Mongin, S.J., Pratt, G.C., Ramachandran, G., Stock, T.H., Morandi, M.T. (2004a). Evaluating differences between measured personal exposures to volatile organic compounds and concentrations in outdoor and indoor air. *Environmental Science & Technology*, 38, 2593-2602.
- Sexton, K., Adgate, J.L., Ramachandran, G., Pratt, G.C., Mongin, S.J., Stock, T.H., Morandi, M.T. (2004b). Comparison of personal, indoor, and outdoor exposures to hazardous air pollutants in three urban communities. *Environmental Science & Technology*, 38, 423-430.
- Skoog, D.A., Holler, J.F., Nieman, T.A. (1998). Principles of instrumental analysis. (Orlando: Harcourt Brace and Company).
- Sweet, C.W., Vermette, S.J., (1992). Toxic volatile organic compounds in urban air in Illinois. *Environmental Science & Technology*, 26, 165-173.
- Wallace, L.A., Pellizzari, E.D., Hartwell, T., Sparacino, C., Sheldon, L., Zelon, H. (1985). Personal exposures, indoor-outdoor relationships and breath levels of toxic air pollutants measured for 355 persons in New Jersey. *Atmospheric Environment*, 19, 1651-1661.
- Wallace, L. (1987). The Total Exposure Assessment methodology (TEAM) study: summary and analysis, vol 1. Washington, DC: U.S. Environmental Protection Agency.
- Ward, T.J. (2001). Chemical mass balance (CMB) source apportionment and organic speciation of PM_{2.5} in Missoula, Montana including the 2000 wildfire season. Ph.D. Thesis, The University of Montana.
- Ward, T.J., Hamilton, R.F., Smith, G.C. (2005). The Missoula Valley semivolatile and volatile organic compound study – seasonal average concentrations. *Journal of the Air & Waste Management Association*, 55, 1007-1013.
- Weisel, C.P. (2002). Assessing exposure to air toxics relative to asthma. *Environmental Health Perspectives*, 110(suppl 4), 527-537.

- Woolfenden, E. (1997). Monitoring VOCs in air using sorbent tubes followed by thermal desorption-capillary GC analysis: summary of data and practical guidelines. *Journal of the Air & Waste Management Association*, 47, 20-36.
- Wrobel, C.L. (2000). Investigating volatile organic compounds in an urban inter-mountain valley using a TD/GC/MS methodology and intrinsic tracer molecules; Ph.D. Thesis, The University of Montana.