ABSTRACT

Title of Document: CROSS SECTIONAL EVALUATION OF POTENTIAL VOLATILE ORGANIC COMPOUND EXPOSURES AROUND U.S. SCHOOLS

Advisor: Dr. Amir Sapkota,
Maryland Institute for Applied Environmental Health

Volatile Organic Compounds (VOCs), characterized by high vapor pressure and low water solubility, exist in gaseous phase at room temperature. Previous studies have suggested exposure to VOCs may be associated with adverse health effects such as asthma exacerbation and in some cases cancer. The major sources of outdoor VOCs include traffic and industrial emissions. Ambient VOCs can react with Nitrogen Oxides (NO_x) in the presence of sunlight to form ground level ozone, one of the U.S. Environmental Protection Agency (EPA) Criteria Air Pollutants. This thesis was designed to investigate the potential VOCs exposure among U.S. schoolchildren. Moreover, the influence of various neighborhood factors (urban vs. rural areas, distance from highways, presence/absence of industries) on VOCs concentrations around U.S. Schools was investigated. The findings of this thesis suggest that schools in urban areas, near industries and traffic activity have higher concentrations of VOCs compared to those not possessing such characteristics.

CROSS SECTIONAL EVALUATION OF POTENTIAL VOLATILE ORGANIC COMPOUND EXPOSURES AROUND U.S. SCHOOLS

By

Joanne Pérodin

Thesis submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
of the requirements for the degree of
Master of Public Health
2009

Advisory Committee:

Professor Amir Sapkota, Chair
Professor Betty Dabney
Professor Sam Joseph
Professor Amy Sapkota

Table of Contents

List of Figures

List of Tables

Acknowledgements

I owe my deepest gratitude to Dr. Amir Sapkota, my advisor. The completion of this thesis would not have been possible without his continuous support, guidance, and persistent help. Dr. Sapkota both encouraged and challenged me throughout my academic program. “Keep chugging along”, is a supportive saying of Dr. Sapkota that I will never forget.

I would like to thank my thesis committee members, Drs Betty Dabney, Sam Joseph, and Amy Sapkota for their valuable suggestions throughout my academic journey and thesis completion. The cooperation I received from each faculty member of the Maryland Institute for Applied Environmental Health is truly acknowledged. I also wish to acknowledge my colleagues at the institute for their assistance and support, with special thanks going to Nicole Favaro, Erinna Kinney, Shirley Micallef, Rachel Rosenberg, and Kristie Trousdale.

I am grateful to my strongest and most valuable supporters, my family. I want to especially thank my parents, Daniel P. and Marie José B. Pérodin, who taught me the value of hard work and have always been there to support me and encourage me in an endeavor.

Words fail me to express my gratitude to those who have seen me in my most stressful moments, provided me with endless support accompanied by the late-night

editing of my thesis. I want to thank my friends Alecia Anderson, Samanmalee Hewawasam, Negar Jahanbin, Soncia Shako and Aseem Sharma.

Lastly, I would like to thank all who have supported me both directly and indirectly in completing my thesis.

CHAPTER 1: INTRODUCTION

Over the past decades, there have been increasing concerns about the effects of air quality on human health. Despite environmental regulations, reduction in traffic and industrial emissions, ongoing changes in infrastructure such as modern buildings for better energy efficiency, and ventilation (Jones, 1999), high concentrations of toxic agents in the air still remain across the United States.

The reported increase in asthma prevalence as well as the high cancer rates are significant public health problems in the U.S. (CDC, 2006; American Cancer Society, 2009). Previous studies have shown that exposure to volatile organic compounds (VOCs) may contribute to respiratory health deterioration as well as cancer risk (Delfino, R.J, Gong, H., Linn, W. S., Hu, Y. & Pellizzari, E. D., 2003; Boeglin, M. L., Wessels, D. & Henshel, D., 2006). Exposure to concentrations even below standard recommendations can lead to an increase in asthma outcome by about 2 folds among children (Rumchev, K., Spickett, J., Bulsara, M., Phillips, M. & Stick, S., 2004). Others have suggested that air pollution from mobile sources, which include VOCs, may be related to the worldwide increase in asthma (D'Amato, G., Liccardi, G., D'Amato, M., & Cazzola, M., 2001). Likewise, chronic VOC exposure has also been linked with cancer (Guo, H., Lee, S. C., Chan, L. Y. & Li, W., 2004), many of which also originate from mobile sources. Studies have also shown elevated risks for cancer among populations exposed to VOCs (Woodruff, T. J., Caldwell, J., Cogliano, V. J. & Axelrad, D. A., 2000). The degree of adverse health effect from exposure to VOCs may depend primarily upon the frequency, duration of exposures (UNEP, 1994).

There are several sources of VOCs in indoor environments, including cleaning products, solvents, off-gassing from furniture/carpets as well as cigarette smoking. In addition to these indoor sources, outdoor sources also contribute to indoor levels of VOCs as they readily penetrate indoors. Even though indoor concentrations of VOCs have been shown to be much higher than outdoor concentrations, outdoor exposures also remain a concern to the public health. The levels of outdoor VOCs depend upon several factors including residential location (urban, semi-urban, rural), traffic density, and industrial activities (Fischer et al., 2000; Lee, S.C., Chiu, M. Y., Ho, K. F., Zou, S. C. & Wang, X., 2002). Despite this, very little is known about outdoor VOCs exposures among vulnerable populations such as children. Therefore, characterizing VOC exposures to such populations is important, as this information may be helpful in designing proper intervention strategies. Within this context, the potential exposures taking place within the school environment are important, as children spend a significant part of their day at schools.

Hypothesis:

To estimate potential exposure to VOCs at schools, a cross sectional study was carried out with the following hypotheses-

1) Schools in urban areas have higher VOCs concentration than schools in rural areas,

2) Schools near major industries have higher VOCs concentration then those without industries.

The variables used to test these hypotheses included presence and distance to mobile sources (major traffic roads) and stationary sources (industry), type of location (urban, rural), and region (Midwest, Northeast, South, and West).

The goal of this investigation was to find out whether some schoolchildren from specific areas are potentially exposed to high levels of VOCs, thus putting them at greater risk for potential acute and/or chronic health outcomes.

CHAPTER 2: BACKGROUND

2.1 Volatile Organic Compounds

Volatile organic compounds (VOCs) are carbon-based chemicals that exist in gaseous forms at room temperature. They are characterized by high vapor pressure and low water solubility. They are significant components of indoor as well as outdoor air pollution. The list of VOCs contains hundreds of compounds, including known human carcinogens such as benzene and 1,3-butadiene. The sources of these VOCs can be anthropogenic as well as natural.

Previous studies have shown that VOCs can react with oxides of nitrogen (NO_x) that are released from combustion products such as vehicle exhausts and power plants, in the presence of sunlight, to form ozone (Carter, 1994). Thus VOCs are considered important from a regulatory standpoint, as they serve as a precursor to ozone formation, an important Criteria Air Pollutant. Ground level ozone is made of three oxygen atoms, and not directly released into the air, but formed through a reaction of NO_x and VOCs in the presence of sunlight. Ground level ozone, also referred to as “bad” ozone is different from stratospheric ozone, referred to as the “good” ozone naturally formed in the stratosphere, which protects earth from harmful ultraviolet rays from the sun (US-Environmental Protection Agency). Therefore, one of the strategies of reducing ground level ozone is to reduce its precursors, NO_x and VOCs.

The Clean Air Act, which describes the EPA’s task in protecting public health, has classified areas throughout the U.S. according to their compliance with national standards for ground-level ozone as attaining or not-attaining the federal standards. An attainment area is one with air quality similar to or better than that of the national ambient air quality standards (NAAQS) per the Clean Air Act. It should be noted that an area is designated an attainment area for one pollutant basis. For example, an area may be considered an attainment area for one pollutant and not for another. Non-attainment areas are required to improve air quality by reducing VOC emissions within their territory by 3% each year until the national standard for ozone is met (American Chemistry Council, 2009).

Several factors associated with exposure to VOCs may affect health outcomes. These factors include concentration of the agent, duration as well as frequency of exposure, and the chemical agent involved (Paustenbach, 2000). Exposure to some VOCs may have acute (asthma exacerbation) or chronic (cancer) adverse health effects. The Environmental Protection Agency (EPA) developed an Integrated Risk Information System (IRIS), which is a collection of electronic reports on specific toxic substances found in the environment and presenting risk to human health. In this collection many VOCs have been identified as: a) known human carcinogens (class A), b) probable human carcinogen (class B), c) possible human carcinogen (class C), and d) not human carcinogen (class D). However, carcinogenicity has not been determined for many more VOCs due to inadequate data for carcinogenicity classification, or lack of assessment by the IRIS.

2.2 Sources of VOCs

The sources of VOCs can be divided into two major categories: point or fixed sources (stationary) and non-point or non-fixed sources (mobile). The major point sources include man-made sources such as industries and small dry cleaning business as well as natural sources such as forest fires and volcanoes. The non-point sources included mobile sources such as on-road and off-road sources, as well as consumer products (fragrances), and household cleaning products. The diverse nature of VOC sources suggest that the compounds can be detected in the indoor as well as the outdoor environment. A wide range of measures has been taken to regulate VOC emissions from motor vehicles, power plants, industrial and commercial processes. Some examples of regulatory measures are controlling VOC content in printing inks, floor wax strippers, and reducing emission from devices on certain printing machines.

2.2.1 *Indoor Sources*

To provide comprehensive measures of indoor and outdoor sources of VOCs among the U.S. population, the US-EPA conducted a Total Exposure Assessment Methodology (TEAM) study, which began in 1980 (Wallace, 1987). This study, broken down into three phases, provided a first quantitative measure of time activity pattern and VOC exposures for the U.S. population. Phase I tested the methodology for five months in Bayonne and Elizabeth, New Jersey, and Research Triangle Park, North Carolina. Phase II, which last seventeen months, observed the differences between the distribution of exposure to selected substances for selected populations living in industrial/chemical manufacturing areas (Bayonne and Elizabeth, New

Jersey) to that in non-industrialized manufacturing areas (Greensboro, North Carolina, and Devils Lake, North Dakota). Phase III consisted of applying the refined version of the assessment from Phase II to California over a period of four months. Further investigations were conducted in other cities throughout the U.S. under separate VOC TEAM studies. Overall, results showed much higher VOC concentrations in indoor than outdoor air. A later report showed about 99% of personal exposure to benzene was from air, and highest concentrations were observed for personal exposure, followed by indoor, then outdoor air (Wallace, 1991). The study further showed that majority of Americans spend over 90% of their time indoors (Edwards, R. D., Iurvelin, J., Saarela, K. & Jantunen, M., 2001). This result, combined with earlier findings of higher indoor concentration (Wallace, 1987) suggests that individuals may be exposed to high concentrations of VOCs throughout their life. These findings brought the issue of indoor pollutants to the forefront and highlighted that indoor concentrations of pollutants inside homes are very important from an exposure perspective.

Among the compounds assessed in the TEAM study, 1,1,1-trichoroethane, tetrachloroethylene, benzene, two xylene isomers, and ethyl benzene were present in 60-98% of all breath measurements and air samples (Wallace 1986). It was also reported that indoor VOC concentrations were higher than outdoor concentrations. Furthermore, the benzene levels inside homes of smokers were 30-50% higher than that of non-smokers (Wallace, 1986). The authors later reported that benzene concentrations were higher among smokers than non-smokers by 90% (Wallace, 1991). The TEAM study further showed that personal exposure to benzene was two times higher than that of outdoor levels. The researchers attributed this elevation in concentration level to “non-traditional sources of VOCs” including smoking, passive smoking, attached garages, and use/storage of cleaning products inside homes (Wallace, 1989). Subsequently, several studies have confirmed these findings (Lee et al., 2002; Son, B., Breysse, P. & Yang, W., 2003; Sexton et al., 2004).

These studies have unequivocally documented the diverse sources of VOCs, which can be highly heterogeneous from one home to the next. Besides these sources, additional factors may play a role in indoor concentrations, including frequency of the product usage, ventilation rates, and neighborhood-level outdoor sources (presence of industries, traffic density).

2.2.2 *Outdoor Sources*

The most common VOCs reported in outdoor ambient air are benzene, toluene, ethyl benzene, and xylenes (BTEX) (Fischer et al., 2000; Edwards et al., 2001). Other VOCs include naphthalene, styrene, chloroform, etc. Two major outdoor sources contributing to elevated levels of VOCs in ambient air are those originating from: a) mobile sources, and b) stationary sources. Mobile sources include on-road sources (motorcycles, light-duty vehicles, bus, trucks), and off-road sources (farm equipments, construction equipments), all of which release toxic substances in the air through combustion and fuel evaporation. VOC levels in ambient air have been shown to increase with increased traffic flow (Sapkota, A. & Buckley, T., 2003). This increase in VOC levels vary based on type and age of vehicle, speed of traffic, fuel used, and environmental conditions of roads (Muezzinoglu, A., Odabasi, M. & Onat, L., 2001; Sapkota & Buckley, 2003). Despite high concentrations of VOCs, effective environmental regulations can lower concentrations in ambient air. Han et al. (2006) have attributed reduction in VOC levels observed over the past decade in Mexico City to the implementation of traffic emission controls there (Han, X. & Naeher, L. P., 2006). However, VOC levels in Mexico City are still higher than many other cities around the world (Gee, I. L. & Sollars, C. J., 1998).

The second category, stationary sources, includes industries, power plants and small industries including dry cleaners. Pollutants from industries and power plants are discharged into the atmosphere from smokestacks. Mintz and McWhinney attributed 85% and 89% of VOCs observed in Fort Saskatchewan, Western Canada, to the industry in those areas (Mintz, R. & McWhinney, R. D., 2008). In a separate study conducted in Spain, researchers reported traffic emissions accounted for 60% of ambient VOCs while those from industrial emissions accounted for 32% (Montserrat, C. & Baldasano, J. M., 1996). Likewise, interesting data are available from Korea, which has undergone a rapid industrial growth, especially in petrochemical industries in the past 30 years. Na et al. reported higher VOC concentrations in Korean cities located near petrochemical industries (Na, K., Kim, Y. P., Moon, K. C., Moon, I. & Fung, K., 2001).

2.3 VOCs and Health

The extent to which VOCs affect human health is not well understood. Most of the health effects identified are from occupational settings where exposures tend to be an order of magnitude higher than those observed in environmental settings. In most cases, VOCs act as irritants, causing acute effects such as watery eyes, itchy throat, sneezing, and skin rash (US-EPA). These acute symptoms are usually temporary and cease once the source of exposure has been identified and removed (EPA, 2009). But in severe cases, VOCs can trigger exacerbation of asthma (Delfino et al., 2003), and, in the case of chronic exposures, can lead to various adverse health outcomes including kidney failure, liver failure, central nervous system damage, and cancer (Ashley, D. L., Bonin, M. A., Cardinali, F. L., McCraw, J. M. & Wooten, J. V. , 1996). Individuals with respiratory complications such as asthma, young children, elders, and individuals highly sensitive to chemicals face greater risk for irritation and health complications from exposure to VOCs.

2.3.1 ***VOC Exposures and Asthma***

Asthma is an inflammatory disorder of the lungs characterized by episodic and reversible symptoms of air-flow obstruction, and random airway hyperactivity. Asthma affects all age groups, with millions of children suffering from this condition (Mannino, D. M., Homa, D. M. & Petrowski, C. A., 1998). Though the rate of mortality from asthma has decreased, ambulatory care has continued to grow since 2000 (Akinbami, 2006).

Exposure to mixtures of VOCs has been shown to increase neutrophils, a type of white blood cells in the immune system, in nasal passages among non-smoking young adult men (Koren, H. S. & Delvin, R. B., 1992). Delfino et al. (2003) who observed an increase in asthma symptoms among Hispanic teenagers with high concentrations of selected VOCs in breath and ambient air suggested that acute and chronic exposure to air toxics may contribute to a decline in lung function and an increase in exacerbation symptoms among asthmatics (Delfino et al., 2003). The EPA defines air toxics as pollutants confirmed or suspected to be harmful to human health. A recent study by Elliott et al. (2006) reported decrease in lung function with increase exposure to VOCs from air fresheners, mothballs, and cleaning products (Elliott, L., Longnecker, M. P., Kissling, G. E. & London, S. J., 2006). Biomarkers, biological indicators such as biomechanical metabolites from exposure to a chemical agent, have also been used as strong indicators of VOCs exposure.

Recently several epidemiological studies have established association between exposure to automobile exhaust and asthma. The findings suggested that asthmatic children living close to roads with high traffic density experienced higher rates of asthma exacerbation (Edwards et al., 1994; vanVliet, P., Knape, M., de Hartog, J., Janssen, N., Harssema, H, & Bunekreef, B., 1997; Carbajal-Arroyo et al., 2007). Although the observed association may have also resulted from exposures to other compounds such as particulate matter (PM) (Morgenstern et al., 2007; Brauer et al., 2002) and nitrogen dioxide (NO_2) (Gauderman et al., 2005; Nicolai et al., 2003) also found in automobile exhausts, the possibility of VOC contribution cannot be ruled out.

A case study investigated exposure to high VOC concentrations in a residential area in Mont Chanin, France where industrial waste was dumped in the mid 1980s. Results showed VOC levels as high as 433 $\mu g/m^3$, inside homes. Investigators also observed several health complications such as psychological disorders and pulmonary irritation among the local residents and attributed such outcomes to the unusually high levels of VOCs observed (Deloraine, A., Zmirou, D. Tillier, C., Boucharlat, A. & Bouti, H., 1995).

2.3.2 ***VOC Exposures and Cancer***

Cancer is characterized by uncontrolled growth, invasion, and sometimes metastasis of a group of cells. In the uncontrolled growth, the cells undergo division beyond the normal division limits (American Cancer Society, 2009). Cells intruding and destroying adjacent tissues characterize the invasion. Metastasis, which mostly occurs in advanced stages of the disease, is the spreading of cancerous cells to other locations in the body via lymph or blood. Cancer can affect all age groups, but this risk increases with age. Cancer can result from mutations from chemical carcinogens, ionizing radiation, heredity, immune system dysfunction, and other causes that still remain unknown (American Cancer Society).

Early studies focused on cancer and inherited genetic disorders, chemotherapeutic agents, and ionizing radiation (Reynolds, P., Von Behren, J., Gunier, R. B., Goldberg, D. E., Hertz, A. & Smith, D. F., 2003). It is only in the past decades that researchers have included toxic agents from emission sources in studies on cancer (Pearson, R. L., Watchel, H. & Ebi, K. L., 2000). Despite the decrease in cancer deaths in the U.S. (by 18.4% in men, and 10.5% in women), cancer of the lungs and bronchus are among the most common types of cancer in both men and women, with smoking having been shown as the most contributing risk factor (Doll, R., Peto, R., Boreham, J. & Sutherland, I., 2005). Cancer has also been reported as the second leading cause of death among children under the age of fourteen (American Cancer Society, 2008).

Woodruff et al. (2000) estimated cancer risk with ambient concentrations of toxic substances, using the EPA Cumulative Exposure Project (Woodruff et al., 2000). Most of the cancer cases were attributable to exposure to VOCs (benzene, 1,3-butadiene), and other toxic agents (chromium, formaldehyde). Similar findings were observed in Great Britain in geographical clustering of children with leukemia living near industries (oil refineries, oil storage sites, paper manufacturing) releasing large emissions containing VOCs (Knox, 1997). This study suggested that childhood cancer was associated with geographical location, later supported by a follow-up study by Knox and Gilman (1998), who reported that the increase in cancer risk was primarily attributable to exposures to benzene, 1,3-butadiene, NO_x, and benz(a)pyrene (Knox, E. G. & Gilman, E. A., 1998; Knox, 2005). On the other hand, Wilkinson et al. (1999) who followed the same study design as Knox and Gilman (1998), did not find any association between cancer risk among children and exposure to oil refineries (Wilkinson et al., 1999). With scarce data on adverse health outcomes from exposure to mixed agents, one cannot conclude whether VOCs were the primary contributors to cancer outcomes from studies such as Knox and Gilman's or if the observed outcomes were associated with some confounding variables that were not accounted for.

To date, most studies have brought more focus on single chemicals as opposed to mixed exposures from indoor and outdoor air. Moreover, investigations have taken place in areas such as workplaces, home, and stores near traffic arteries. However, little has been done on outdoor VOCs air assessment near schools, where children spend significant amounts of time. Therefore, it is important to evaluate the air around these schools for VOCs to understand if there is an increased risk of adverse health outcomes among the schoolchildren.

CHAPTER 3: METHODS

3.1 Instrument

3.1.1 *Gas Chromatograph Mass-Spectrometer*

The Gas Chromatograph Mass-Spectrometer (GC-MS) is an instrument used for qualitative as well as quantitative analyses. During analysis, samples are introduced into the system via injection through a heated injection port. Samples are separated using a capillary column and introduced into the mass spectrometer, where they get ionized. The ions are detected based on their mass to charge ratios (m/z). Each chemical has a unique m/z, which enables the instrument to detect them with high accuracy.

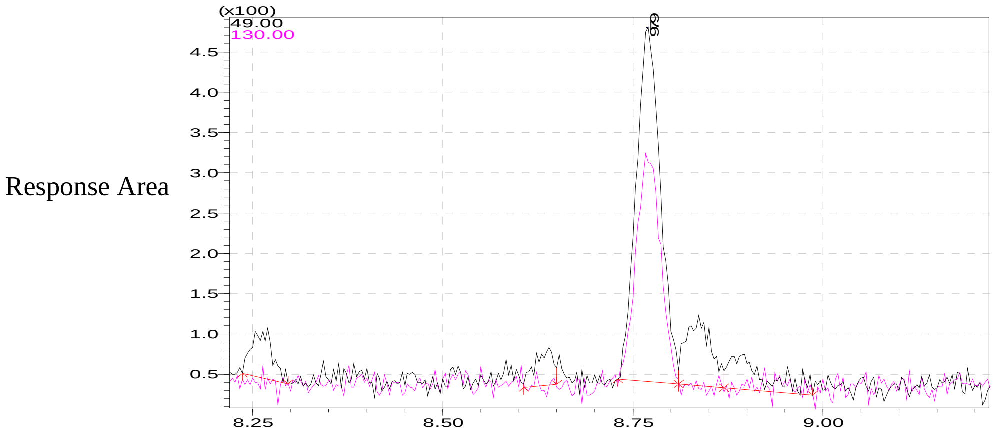
For this thesis, samples were analyzed with a Schimadzu GC-MS model QP2010 (Shimadzu Scientific, Columbia, MD). Samples were analyzed in Selective Ion Monitoring (SIM) mode.

3.1.2 *Calibration*

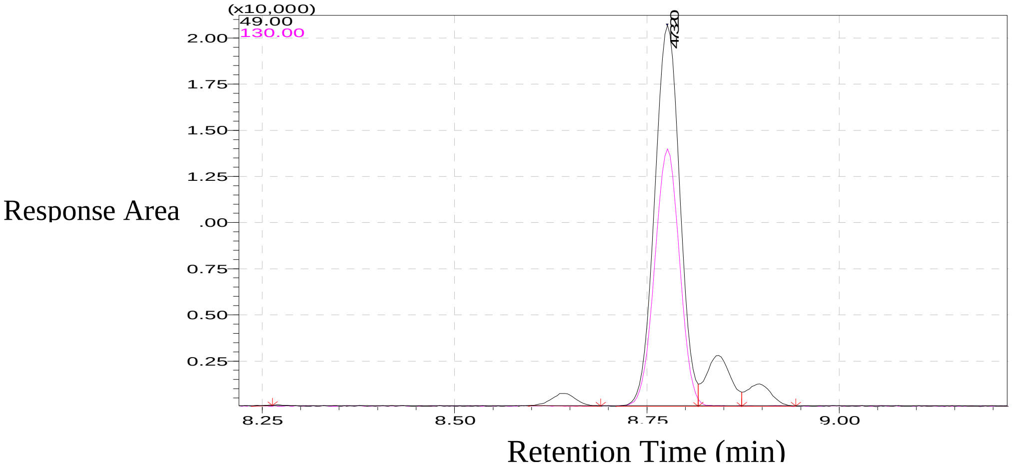
The GC-MS was calibrated to assess the GC-MS response and accuracy in identifying compounds. The calibration would be used as a reference when quantifying unknown agents by measuring the response of the unknown and using the calibration curve to determine the concentration of the unknown. Seven calibration standards were prepared using a method of serial dilution, with concentration ranging from 0-2,000 ng/mL for each standard. A working stock solution of 40 µg/mL of VOC mixture was prepared using 200 µg/mL VOC mixture with MTBE 55 analytes stock solution (Ultra Scientific, Cat# DWM-596-1). Calibration standards were prepared diluting known amounts of the compound of interest with calculated amounts of carbon disulfide and acetone.

Exactly 10 µL of internal standards of volatile monitoring spiking solution was added to each calibration standard. These standards were prepared in 1.5 mL screw thread amber vials. A 1 µL aliquot was injected into the GC-MS using an auto sampler injector (50^{o}C, helium flow, 1.00 mL/min for 26 minutes). The 7-point calibration curves were prepared each week. The GC-MS underwent a total of 8 calibrations. All calibration curves had a linear response with r-square greater than 0.98.

Figure 1. Spectral Peak for Chloroform with 50 ng/mL Concentration



Spectral Peak for Chloroform with 2,000 ng/mL Concentration



Calibration Curve for 6 Standards and One Blank (**r^2= 0.99994**)

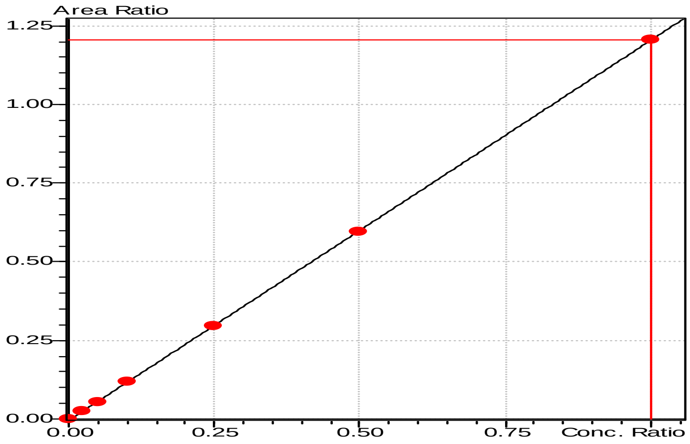


Figure 1 shows one calibration curve done during this study. The first two figures representing spectral peaks for chloroform, the standard with the highest concentration (2,000 ng/mL) having a greater area within its spectral peak. This calibration curve had an r-square equal to 0.99994.

3.2 Chemicals

Solvents - carbon disulfide (OmniSolv Cat# EM-CX0396-6), acetone, and methanol (Burdick & Jackson Cat# BJ010-4, BJAH230-4 respectively) were purchased from VWR International, Bridgeport, New Jersey. Internal standards and VOC standards containing 55 different VOCs (Cat# STM-262, DWM-596-1 respectively) were purchased from Ultra Scientific, Kingstown, Rhode Island.

3.3 Air Sampling

3.3.1 *Study Site*

Reporters of the USA-TODAY were interested in issues of VOCs near schools throughout the U.S. Investigators at the University of Maryland, College Park, and the Johns Hopkins University, Baltimore, were approached by the reporters to provide expert guidance on VOC sample collection and analysis. Representatives of the USA-TODAY and affiliated newspaper and television stations collected 85 samples. Sites for sample collection were from proximity to schools identified as being highly exposed to industrial emissions (elementary, middle, or high-school) from different geographical locations throughout the U.S. These sites differed by type of location: rural vs. urban, distance from and presence of pollution sources (mobile and stationary). Air samples were collected using 3M-3500 passive organic vapor monitors (OVMs). The 3M-3500 OVMs are comprised of one charcoal adsorbent pad to collect organic vapors in the air. Air samples are absorbed by the OVMs by the process of diffusion where organic vapors move from high (ambient air) to low concentration (into monitor).

3.3.2 ***Sample Collection***

Once a location was identified, field staff placed OVM samplers within 100 yards from schools and 7-8 feet above the ground. A pail was used to protect the samplers from excessive wind and rain. To ensure sufficient airflow for the diffusion process, samplers were placed at least 3 feet from any walls.

At sampling location samplers were removed from their containers. The airtight cap of the samplers was removed and replaced by a clear cap, the diffusive cover. Samplers' identification number, opening date and time were recorded in sample log sheet. Samplers were then hung above ground level, and protected from rain and/or high winds. Additional items recorded in the log sheet included location of sampling, presence/absence of industries, major roads in the neighborhood, population size of the town for subsequent evaluations. Sampling periods were 4 or 7 days. Periodical visits were done at collection sites to check monitors for any possible damages, and any relevant observations were reported. If not properly stored, OVMs can adsorb additional agents in the ambient air after the collection period. Thus, protection of the OVMs after sampling is critical. At the end of collection period, field staff removed and replaced samplers' diffusive cover by the airtight cap. The samplers were then placed in their original containers. Field staffs then recorded ending date and time of sample collection in the log sheet. Sealed samplers were shipped with ice packs in a zip lock bag to the lab.

Once delivered to the lab, samplers were removed from zip-lock bags, observed for any physical damage, recorded, and placed in a freezer at -20 degrees Celsius. To minimize contamination by other chemicals in the laboratory, all monitors were assigned to one freezer free of other items.

3.4 Sample Analysis

3.4.1 *Sample Extraction*

For extraction, monitors were taken out of freezer, placed under the fume hood and allowed to equilibrate to room temperature for one hour with airtight covers in place. The airtight covers were removed, and replaced by the clear cap. The monitors were spiked with 10 µL of internal standard (200 µg/mL), which consisted of 1,2-dichloroethane-D4, toluene-D8, and 4-bromofluorobenzene in methanol through a tab located on the clear cap. Tabs were closed immediately after each spiking. Spiked monitors sat under fume hood at room temperature for an additional hour. After the second hour, clear caps were removed, and using tefflon tweezers, activated charcoal pads from the monitors were removed from the monitors and placed into 12x32 screw thread amber vials with PTFE/Silicone caps. With a 100-1000 µL pipette, 1mL of solvent mix (carbon disulfide and acetone, 1:2 v/v) was added to each vial containing the charcoal pads spiked with 10 µL of internal standards. Vials were put in a Bransonic sonication bath and sonicated for 45 minutes. Solution in the vials was drawn using a 146-millimeter (mm) Pasteur Pipette, and transferred onto a new vial. Chromatographic separation was achieved using a Restek-1 column, 60 mm X 0.25 mm internal diameter (ID) with 1.00 µm thickness (Restek Corp., catalog no. 10156).

3.4.2 *Sample Recovery*

We used a new set of blank monitors from our laboratory to determine sample recovery. Nine monitors were injected with 20 µL of 40 µg/mL VOC mixture and left at room temperature for one hour with the clear caps in place. The monitors were then put back in their original containers and transferred to the assigned freezer. The following morning, monitors were removed from the freezer and let sit at room temperature for one hour. The monitors were then spiked with 15 µL internal standards with a concentration of 200 µg/mL using a 2500 µg/mL volatile system monitoring spiking solution with 3 analytes: 1,2-dichloroethane-D4, toluene-D8, and 4-bromofluorobenzene in methanol (Ultra Scientific, Cat# STM-262). Spiked monitors sat at room temperature for one hour under the fume hood. Clear caps were removed, and using tefflon tweezers the activated charcoal pads from the monitors were transferred into 1.5mL screw thread amber vial, then extracted with 1.5mL solvent mix (carbon disulfide and acetone, 1:2, v/v). All vials were sonicated for 45-minutes using Bransonic sonicator. Sonicated solutions were then transferred into new vials, using a new Pasteur pipette for each vial transfer. Sample recovery was calculated as the percent of analyte recovered with respect to the spiked amount by dividing the extracted concentration to the injected concentration.

3.4.3 *Limit of Detection*

Limit of Detection (LOD) refers to the lowest amount of an analyte that can be distinguished from the background (absence) with a certain degree of confidence. When an analyte was present at detectable levels on blank samples, LOD was calculated using the blanks. When the analytes were not present at detectable level on the blank samples, a lowest level spike was used for calculating LOD. In either case, the samples allocated for LOD determination were handled the same way as badges with actual samples in terms of transportation and delivery to and storage in the laboratory. LOD was calculated by multiplying the field blank standard deviation by three. Measured concentrations below the LOD were replaced with a value equal the LOD divided by two. Seven monitors previously stored in the lab freezer, sat at room temperature under the laboratory fume hood for one hour. Each monitor was then spiked with 15uL internal standards of volatile system monitoring spiking solution with 1,2-dichloroethane-D4, toluene-D8, 4-bromofluorobenzene in methanol, recapped and sat for one hour. Charcoal films from monitors were rolled, transferred into 1.5mL screw thread amber vials using teflon tweezers, and then extracted with 1.5mL solvent mix (carbon disulfide and acetone, 1:2, v/v). All vials were sonicated for 45-minutes using Bransonic sonicator. Sonicated solutions were then transferred into new vials, using a new Pasteur pipette for each vial transfer. The level of analyte was calculated using the calibration curve. Following this step, the limit of detection (LOD) was calculated by multiplying the standard deviation (SD) of the seven blank samples by the Student's t -value associated with 99% confidence interval with 6 degrees of freedom. For those compounds that were not detected on the blank samples, 7 badges were spiked with low level of the analytes and the process was repeated to calculate LOD. All samples that were below the LOD were assigned a value that was ½ the LOD. All reported values were corrected for field blanks.

3.5 Statistical Methods

All statistical analyses were performed using the Intercooled Stata, version 10.0 for Windows (Stata Corp., TX). Differences in VOC concentrations by region were tested using the paired t-test. Correlations between compounds were tested using the Spearman's rank correlation. Statistical significance was associated with $p<0.05$.

CHAPTER 4: RESULTS

Table 1- Sample Location Description by State

State	Total Samples	Rural	Semi-Urban	Urban	Unspecified
Arkansas	1	0	1	0	0
California	13	0	4	7	2
Colorado	2	0	1	1	0
Delaware	3	3	0	0	0
Georgia	2	0	2	0	0
Illinois	4	1	1	2	0
Indiana	5	1	1	3	0
Iowa	2	0	2	0	0
Louisiana	5	0	5	0	0
Maryland	4	1	1	2	0
Massachusetts	1	0	1	0	0
Michigan	3	0	3	0	0
Missouri	4	1	3	0	0
New Jersey	1	0	0	1	0
New York	1	0	0	1	0
Ohio	5	2	2	1	0
Oklahoma	1	0	1	0	0
Oregon	3	0	0	3	0
Pennsylvania	6	1	4	1	0
South Carolina	1	0	0	0	1
South Dakota	2	0	0	2	0
Tennessee	4	1	1	2	0
Utah	1	0	1	0	0
Vermont	1	0	1	0	0
Virginia	4	0	3	1	0
Washington	2	0	1	1	0
West Virginia	2	1	1	0	0
Wisconsin	2	0	1	1	0
United States	**85**	**12**	**41**	**29**	**3**

4.1 General Characteristics of the Samples Collected

All samples were collected between August and October of 2008. The characteristics of the locations where samples were collected are summarized in Table 1. A total of eighty-five samples from 75 towns in 27 states were collected throughout the US. Of the 85 samples, 12 were from rural areas and 28 were from urban areas while 44 were from semi urban or non-specified areas. The majority of the samples was collected in the vicinity of elementary schools (70), while a few were collected around middle (5), and high (10) schools.

4.2 Recovery Rate

The recovery rate varied significantly across the different analytes and ranged from 16.9% to 129.3%. Ten compounds had recovery rates above 100% (chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, carbon tetrachloride, 1,1,2-trichloroethane, ethylbenzene, m,p-xylene, o-xylene, 2-chlorotoluene, chlorotoluene).

4.3 Limit of Detection (LOD)

The limit of detection (LOD) calculated from field blanks for the 18 VOCs are provided in Table 2. Of the 18 VOCs sampled, four of the compounds (1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, and bromoform) were below the LOD in all instances. Likewise, compounds such as benzene, carbon tetrachloride, toluene, m,p-xylene, and chlorotoluene were above LOD in majority of the samples.

Table 2-Compound Retention Time (RT), and Limit of Detection (LOD)

Analyte	Ion 1 (m/z)	Ion 2 (m/z)	RT (min)	LOD (µg/m^3)	% >LOD
Chloroform	83	85	8.88	0.29	11%
Ethane, 1,2-dichloro	62	27	9.44	0.38	0%
Ethane, 1,1,1-trichloro-	97	99	9.65	0.38	0%
Benzene	78	77	10.2	0.50	66%
Carbon Tetrachloride	117	119	10.15	0.56	80%
1,1,2-Trichloroethane	97	83	12.36	0.51	0%
Toluene	91	92	12.66	0.35	100%
Chlorobenzene	112	77	14.71	0.44	33%
Ethylbenzene	91	106	15.12	0.45	48%
m,p-Xylene	91	106	15.95	0.45	80%
Bromoform	173	252	15.53	0.93	0%
Styrene	104	78	15.81	0.64	2%
o-Xylene	91	106	15.95	0.72	33%
1,2,3-Trichloropropane	75	110	16.12	0.68	24%
2-Chlorotoluene	91	126	17.45	0.59	4%
Chlorotoluene	91	126	17.53	0.59	58%
Dichlorobenzene	146	148	18.77	1.11	5%
Naphthalene	128	102	22.8	0.80	4%

The average distance of samplers from schools was 57.86 yards. Forty schools were reported to be in proximity to industries with an average distance of 1.28 miles. Fifteen schools were near highways with an average distance of 0.50 miles. Twenty-four schools were near major roads with an average distance of 0.19 miles.

Altogether, eighteen VOCs were identified in this study. The descriptive characteristics of the samples, including the mean, standard deviation, minima, maxima, median, 25th, and 75% percentiles are in Table 3. Out of all samples, the highest upper limit concentration was observed for benzene, chlorobenzene, and toluene (76.36, 43.71, and 30.51 µg/m^3 respectively). Likewise, the highest average concentration was observed for toluene and benzene (4.86, and 2.28 µg/m^3, respectively).

Table 3-Total VOC average concentration (µg/m3)

Compounds	Mean	Std. Dev.	Min	Max	P50[1]	IQR[2]	P25[3]	P75[4]
Chloroform	0.18	0.13	0.14	0.99	0.14	0.00	0.14	0.14
Ethane, 1,2-dichloro	0.19	0.00	0.19	0.19	0.19	0.00	0.19	0.19
Ethane, 1,1,1-trichloro-	0.19	0.00	0.19	0.19	0.19	0.00	0.19	0.19
Benzene	2.28	8.39	0.25	76.36	0.85	1.79	0.25	2.04
Carbon Tetrachloride	0.69	0.50	0.28	4.71	0.66	0.15	0.60	0.75
1,1,2-Trichloroethane	0.25	0.00	0.25	0.25	0.25	0.00	0.25	0.25
Toluene	4.86	4.72	0.36	30.51	3.50	2.60	2.28	4.88
Chlorobenzene	1.07	4.77	0.22	43.71	0.22	0.37	0.22	0.59
Ethylbenzene	0.59	0.61	0.23	3.33	0.23	0.41	0.23	0.64
M,p-Xylene	1.05	1.00	0.22	5.21	0.79	0.59	0.50	1.09
Bromoform	0.47	0.00	0.47	0.47	0.47	0.00	0.47	0.47
Styrene	0.34	0.13	0.32	1.39	0.32	0.00	0.32	0.32
o-Xylene	0.73	0.71	0.36	3.76	0.36	0.44	0.36	0.80
1,2,3-Trichloropropane	0.68	0.95	0.34	7.76	0.34	0.00	0.34	0.34
2-Chlorotoluene	0.33	0.19	0.30	1.60	0.30	0.00	0.30	0.30
Chlorotoluene	1.14	1.03	0.30	5.32	0.84	1.27	0.30	1.57
Dichlorobenzene	0.60	0.25	0.55	2.00	0.55	0.00	0.55	0.55
Naphthalene	0.45	0.37	0.40	3.74	0.40	0.00	0.40	0.40

[1] Median
[2] Interquartile Ratio
[3] 25% percentile
[4] 75% percentile

4.3 Concentration Differences in Rural and Urban Areas

Figure 2 illustrates the distribution of mean concentration in rural and urban areas. For all compounds, the mean concentrations measured were higher in the urban areas than rural areas. In urban locations, toluene, benzene, and chlorobenzene were the most dominant compounds, with concentrations of 6.40, 4.04, and 2.14 $\mu g/m^3$ respectively. In rural locations, the concentrations of these compounds were 2.60, 0.95, and 0.49 $\mu g/m^3$. The mean concentrations observed in the urban locations were significantly higher then those observed for the rural locations ($p<0.0001$), as determined by the two-tailed statistical t-test.

4.4 Concentration Differences by Presence of Industries

We compared VOC concentrations based on presence of industries. Figure 3 demonstrates the variation of concentrations for all compounds in areas with and without industries. Overall average concentrations were higher in schools within proximity to industries than schools without industries in their surroundings. Toluene, benzene, chlorobenzene and m,p-xylene were the most dominant VOCs for schools that were close to industries. For schools that were not near industries, the most dominant VOCs were toluene, chlorotoluene, and benzene, although the concentrations were much lower. We observed almost 3-fold higher benzene concentrations in schools that were closer to the industries compared to those that had no known industries in nearby areas.

Figure 2.

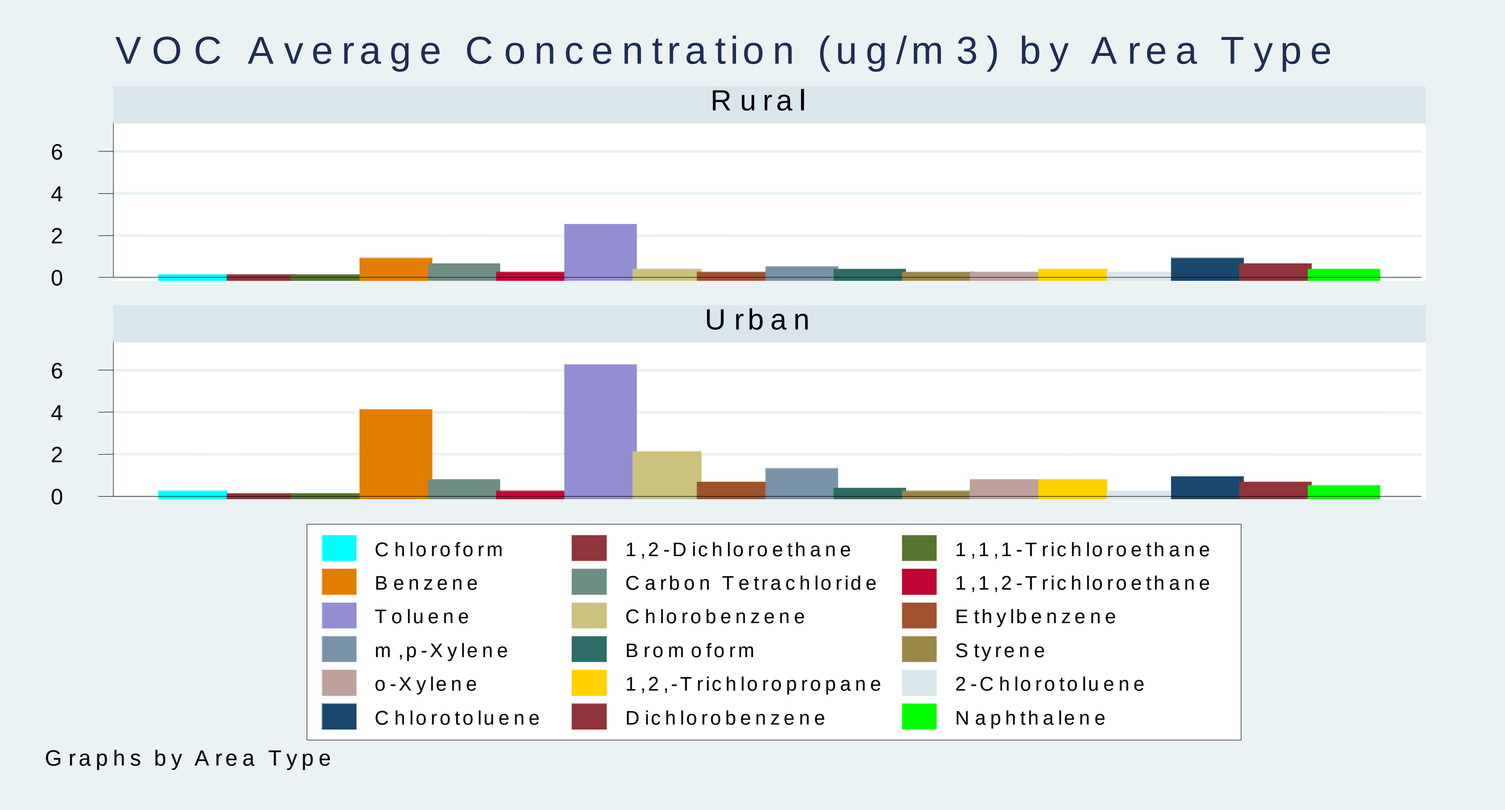
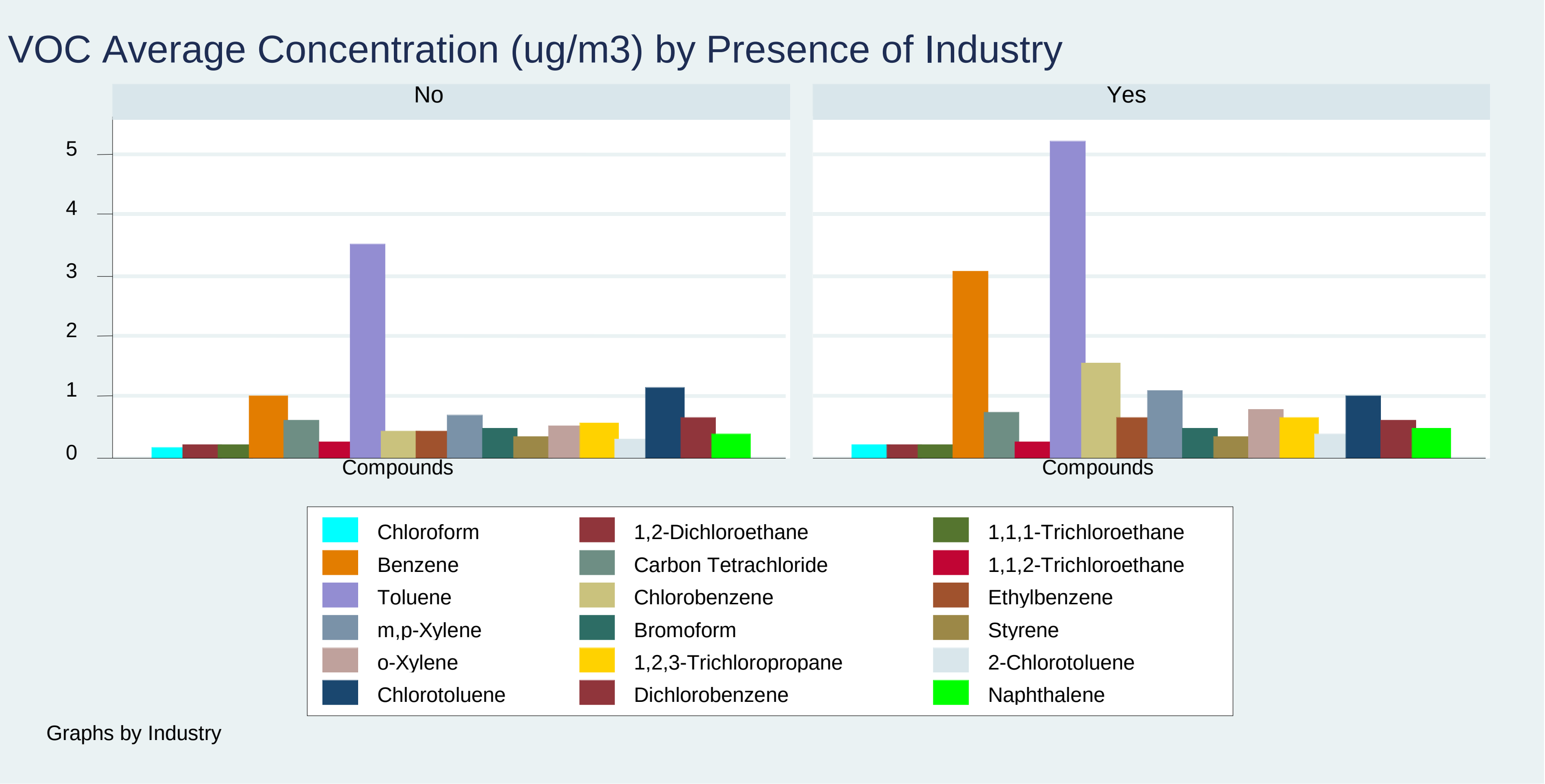

VOC Average Concentration (ug/m3) by Area Type
Rural
Urban
0
2
4
6
Chloroform
1,2-Dichloroethane
1,1,1-Trichloroethane
Benzene
Carbon Tetrachloride
1,1,2-Trichloroethane
Toluene
Chlorobenzene
Ethylbenzene
m,p-Xylene
Bromoform
Styrene
o-Xylene
1,2,-Trichloropropane
2-Chlorotoluene
Chlorotoluene
Dichlorobenzene
Naphthalene
Graphs by Area Type

Figure 3.

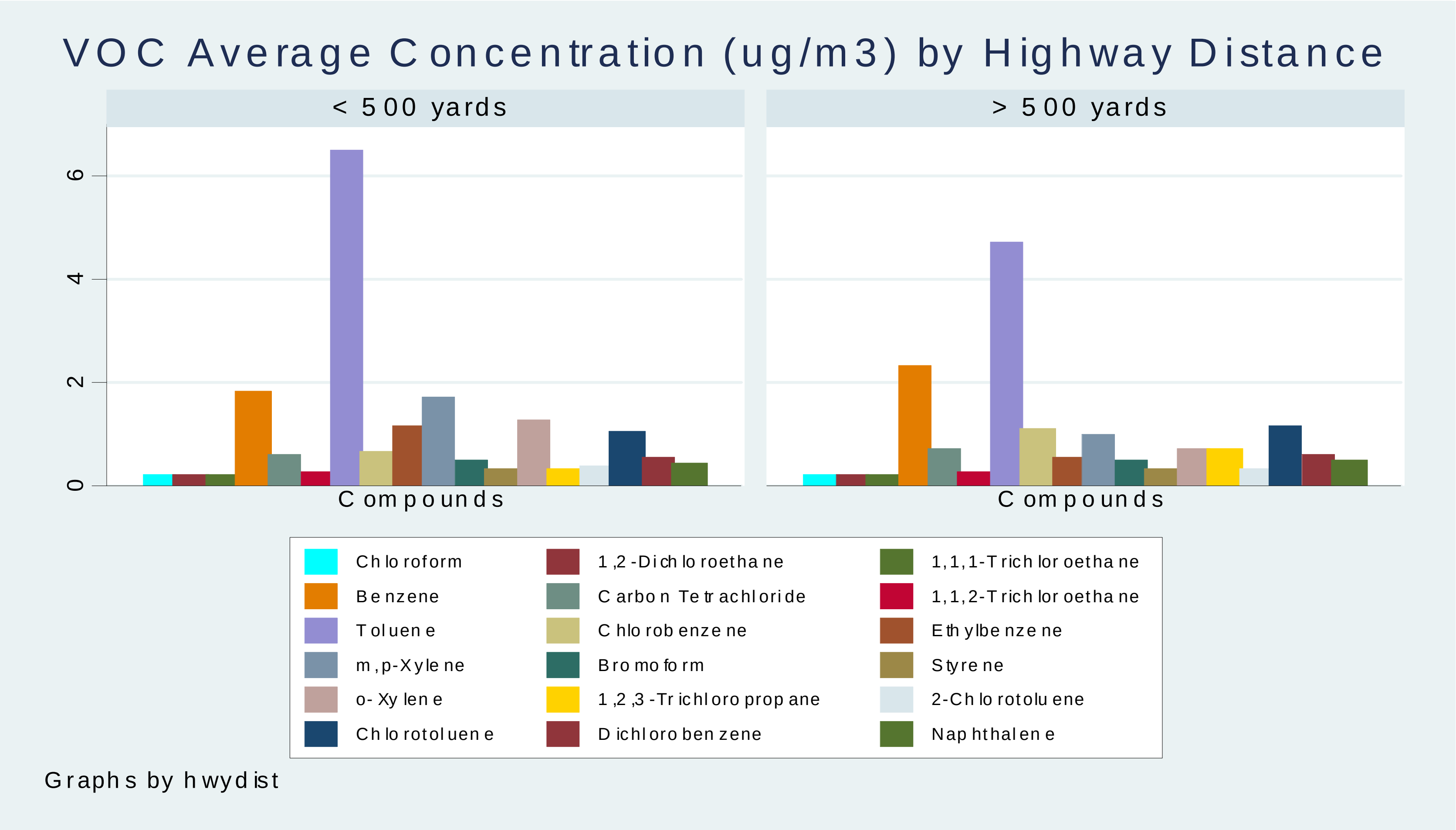

VOC Average Concentration (ug/m3) by Presence of Industry
No
Yes
0
1
2
3
4
5
Compounds
Compounds
Chloroform
1,2-Dichloroethane
1,1,1-Trichloroethane
Benzene
Carbon Tetrachloride
1,1,2-Trichloroethane
Toluene
Chlorobenzene
Ethylbenzene
m,p-Xylene
Bromoform
Styrene
o-Xylene
1,2,3-Trichloropropane
2-Chlorotoluene
Chlorotoluene
Dichlorobenzene
Naphthalene
Graphs by Industry

4.5 Concentration differences by traffic

Information on presence of major roads near schools was available for thirty-eight schools. Out of those thirty-eight schools, twenty-four schools were near major roads. The distance of major roads from schools ranged from 10-1000 yards. Toluene and chlorotoluene were the most dominant among schools less than 300 yards from major roads. Toluene and benzene were the most dominant among schools more than 300 yards away from major roads. Toluene and benzene concentrations from schools over 300 yards away from major roads were also higher than that of schools less than 300 yards away from major roads.

We also looked into presence of highways. Information on highways was given for forty-three schools. Out of the forty-three reports, fourteen schools were close to highways. Highway distances from schools were within 3600 yards. When we observed VOCs concentrations between schools less than and over 500 yards from highways, toluene and benzene were the most dominant compounds in both categories (Fig. 4). Toluene was higher in the category less than 500 yards (6.5 $\mu g/m^3$) compared to the category over 500 yards (3.42 $\mu g/m^3$) away from highways. Benzene was also higher in the category less than 500 yards (1.81 $\mu g/m^3$) compared to the category over 500 yards (1.73 $\mu g/m^3$) away from highways.

Figure 4.


VOC Average Concentration (ug/m3) by Highway Distance
< 500 yards
> 500 yards
0
2
4
6
Compounds
Compounds
Chloroform
Benzene
Toluene
m,p-Xylene
o-Xylene
Chlorotoluene
1,2-Dichloroethane
Carbon Tetrachloride
Chlorobenzene
Bromoform
1,2,3-Trichloropropane
Dichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Ethylbenzene
Styrene
2-Chlorotoluene
Naphthalene
Graphs by hwydist

4.5 Concentration differences across regions

We also compared VOC concentrations by region where sampling locations were divided into West, Midwest, South and Northeast (Fig. 5). In all regions, toluene and benzene were the most dominant VOCs. Benzene concentration was the highest in the Northeast. For the Northeast, benzene, toluene, and chlorobenzene had average concentrations above 2 $\mu g/m^3$, and these concentrations were above the total average concentration for all 85 samples combined.

Table 4 describes the significance in regional concentration from total concentration average. Chlorobenzene was significantly lower that the total average in the Midwest, South and West regions. Benzene was significantly lower than the total average in the South, and West regions. Toluene was significantly lower than the total average in the South region. However, it is difficult to make a meaningful interpretation of these results as the sampling sites were not randomly selected.

Figure 5.

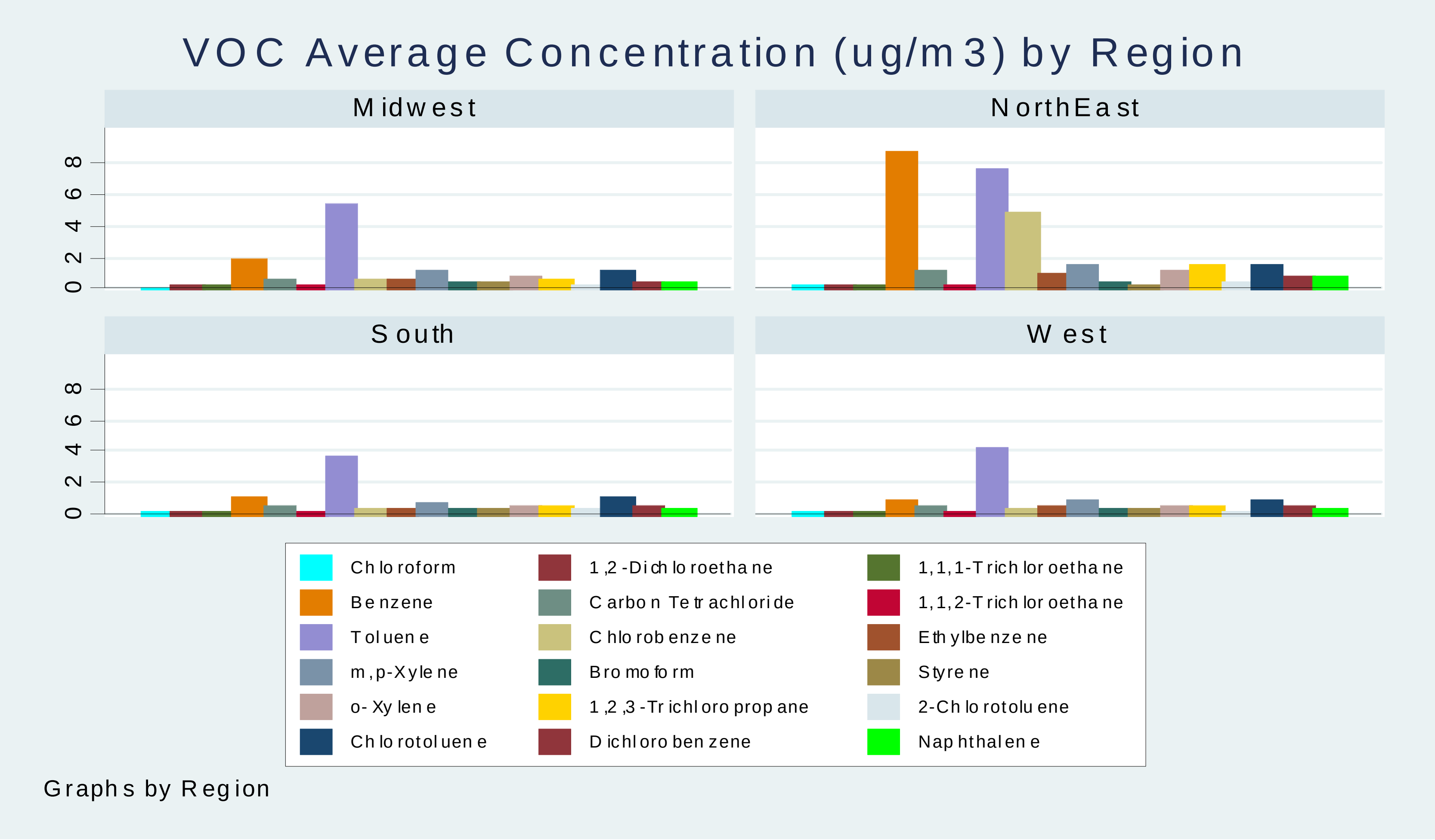

VOC Average Concentration (ug/m3) by Region
Midwest
NorthEast
South
West
0
2
4
6
8
Chloroform
1,2-Dichloroethane
1,1,1-Trichloroethane
Benzene
Carbon Tetrachloride
1,1,2-Trichloroethane
Toluene
Chlorobenzene
Ethylbenzene
m,p-Xylene
Bromoform
Styrene
o-Xylene
1,2,3-Trichloropropane
2-Chlorotoluene
Chlorotoluene
Dichlorobenzene
Naphthalene
Graphs by Region

Table 4- Regional average concentration ($\mu g/m^3$) vs. Total average concentration ($\mu g/m^3$) for all 85

Region	Variable	Obs	Mean[1]	Std.Err.	Std. Dev.	[95% Conf. Interval]	Ho[2]	P-value[3]
Midwest	Chloroform	26	0.15	0.01	0.06	0.13-0.18	0.18	0.03
	Ethane, 1,2-dichloro	26	0.19	0.00	0.00	0.19-0.19	0.19	.
	Ethane, 1,1,1-trichloro-	26	0.19	0.00	0.00	0.19-0.19	0.19	.
	Benzene	26	1.87	0.52	2.59	0.80-2.94	2.28	0.44
	Carbon Tetrachloride	26	0.70	0.04	0.20	0.62-0.78	0.69	0.78
	1,1,2-Trichloroethane	26	0.25	0.00	0.00	0.25-0.25	0.25	.
	Toluene	26	5.35	0.94	4.78	3.42-7.28	4.86	0.61
	Chlorobenzene	26	0.57	0.14	0.69	0.29-0.85	1.07	0.001
	Ethylbenzene	26	0.66	0.13	0.67	0.39-0.93	0.59	0.59
	m,p-Xylene	26	1.21	0.22	1.11	0.77-1.66	1.05	0.46
	Bromoform	26	0.47	0.00	0.00	0.47-0.47	0.47	.
	Styrene	26	0.34	0.02	0.11	0.30-0.39	0.34	0.92
	o-Xylene	26	0.83	0.17	0.84	0.49-1.17	0.73	0.57
	1,2,3-Trichloropropane	26	0.58	0.11	0.56	0.36-0.81	0.68	0.38
	2-Chlorotoluene	26	0.31	0.01	0.06	0.29-0.34	0.33	0.12
	Chlorotoluene	26	1.12	0.19	0.98	0.72-1.52	1.14	0.92
	Dichlorobenzene	26	0.55	0.00	0.00	0.55-0.55	0.61	.
	Naphthalene	26	0.43	0.03	0.13	0.37-0.48	0.45	0.34

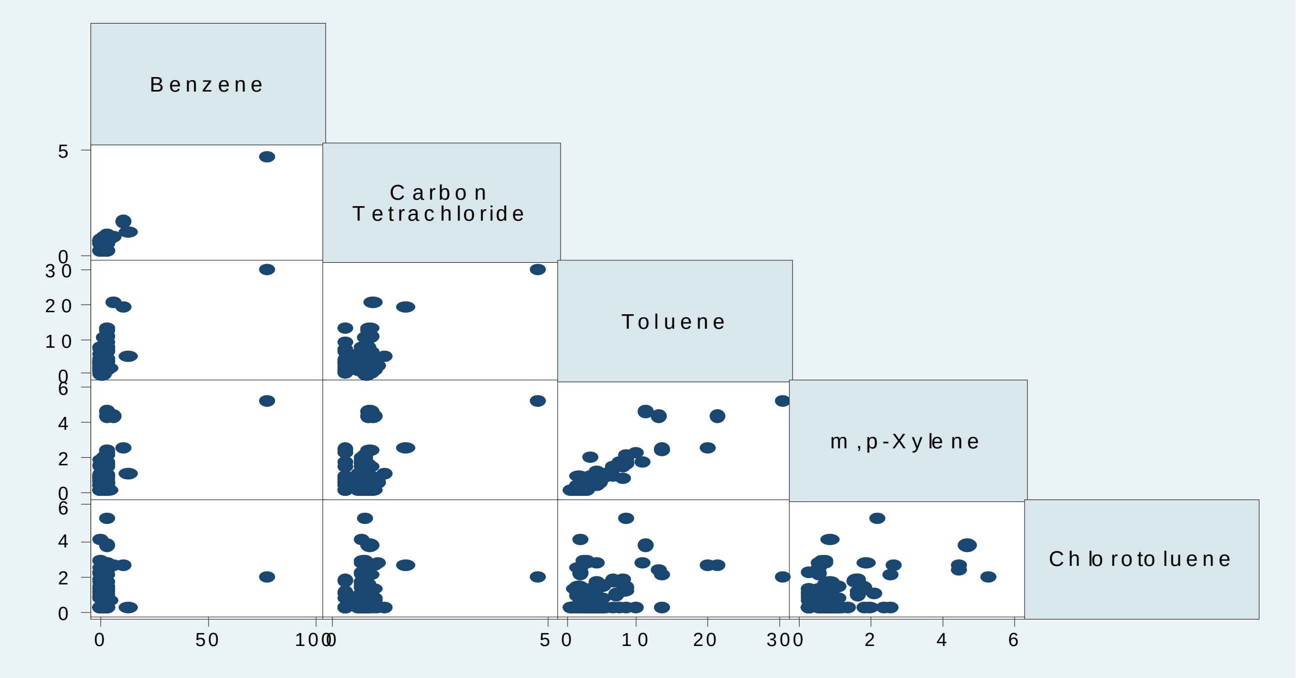
Region	Variable	Obs	Mean[1]	Std.Err.	Std. Dev.	[95% Conf. Interval]	Ho[2]	P-value[3]
Northeast	Chloroform	11	0.25	0.08	0.26	0.08-0.43	0.18	0.37
	Ethane, 1,2-dichloro	11	0.19	0.00	0.00	0.19-0.19	0.19	.
	Ethane, 1,1,1-trichloro-	11	0.19	0.00	0.00	0.19-0.19	0.19	.
	Benzene	11	8.72	6.82	22.62	-6.48-23.92	2.28	0.37
	Carbon Tetrachloride	11	1.16	0.37	1.21	0.34-1.97	0.69	0.23
	1,1,2-Trichloroethane	11	0.25	0.00	0.00	0.25-0.25	0.25	.
	Toluene	11	7.66	2.84	9.43	1.33-13.99	4.86	0.35
	Chlorobenzene	11	4.97	3.93	13.02	-3.77-13.72	1.07	0.34
	Ethylbenzene	11	0.99	0.34	1.14	0.22-1.75	0.59	0.28
	m,p-Xylene	11	1.52	0.56	1.84	0.28-2.76	1.05	0.42
	Bromoform	11	0.47	0.00	0.00	0.47-0.47	0.47	.
	Styrene	11	0.32	0.00	0.00	0.32-0.32	0.34	.
	o-Xylene	11	1.10	0.36	1.19	0.30-1.90	0.73	0.33
	1,2,3-Trichloropropane	11	1.45	0.67	2.21	-0.03-2.94	0.68	0.27
	2-Chlorotoluene	11	0.42	0.12	0.39	0.15-0.68	0.33	0.47
	Chlorotoluene	11	1.53	0.34	1.14	0.77-2.29	1.14	0.28
	Dichlorobenzene	11	0.84	0.15	0.49	0.50-1.17	0.61	0.16
	Naphthalene	11	0.76	0.30	1.01	0.09-1.44	0.45	0.33

Region	Variable	Obs	Mean[1]	Std.Err.	Std. Dev.	[95% Conf. Interval]	Ho[2]	P-value[3]
South	Chloroform	27	0.14	0.00	0.00	0.14-0.14	0.18	.
	Ethane, 1,2-dichloro	27	0.19	0.00	0.00	0.19-0.19	0.19	.
	Ethane, 1,1,1-trichloro-	27	0.19	0.00	0.00	0.19-0.19	0.19	.
	Benzene	27	1.15	0.16	0.82	0.83-1.48	2.28	0.0000
	Carbon Tetrachloride	27	0.61	0.04	0.20	0.53-0.69	0.69	0.05
	1,1,2-Trichloroethane	27	0.25	0.00	0.00	0.25-0.25	0.25	.
	Toluene	27	3.72	0.47	2.47	2.74-4.69	4.86	0.02
	Chlorobenzene	27	0.47	0.07	0.39	0.32-0.63	1.07	0.0000
	Ethylbenzene	27	0.44	0.06	0.31	0.32-0.56	0.59	0.02
	m,p-Xylene	27	0.77	0.11	0.55	0.55-0.99	1.05	0.01
	Bromoform	27	0.47	0.00	0.00	0.47-0.47	0.47	.
	Styrene	27	0.36	0.04	0.21	0.28-0.44	0.34	0.62
	o-Xylene	27	0.61	0.08	0.44	0.43-0.78	0.73	0.15
	1,2,3-Trichloropropane	27	0.53	0.09	0.45	0.35-0.70	0.68	0.09
	2-Chlorotoluene	27	0.34	0.04	0.22	0.26-0.43	0.33	0.77
	Chlorotoluene	27	1.19	0.23	1.18	0.72-1.65	1.14	0.84
	Dichlorobenzene	27	0.60	0.05	0.28	0.49-0.71	0.61	0.91
	Naphthalene	27	0.40	0.00	0.00	0.40-0.40	0.45	.

Region	Variable	Obs	Mean[1]	Std.Err.	Std. Dev.	[95% Conf. Interval]	Ho[2]	P-value[3]
West	Chloroform	21	0.21	0.03	0.15	0.14-0.28	0.18	0.33
	Ethane, 1,2-dichloro	21	0.19	0.00	0.00	0.19-0.19	0.19	.
	Ethane, 1,1,1-trichloro-	21	0.19	0.00	0.00	0.19-0.19	0.19	.
	Benzene	21	0.85	0.18	0.82	0.48-1.22	2.28	0.0000
	Carbon Tetrachloride	21	0.54	0.05	0.21	0.45-0.64	0.69	0.005
	1,1,2-Trichloroethane	21	0.25	0.00	0.00	0.25-0.25	0.25	.
	Toluene	21	4.26	0.53	2.41	3.16-5.36	4.86	0.27
	Chlorobenzene	21	0.41	0.10	0.47	0.19-0.62	1.07	0.0000
	Ethylbenzene	21	0.50	0.06	0.29	0.37-0.64	0.59	0.19
	m,p-Xylene	21	0.95	0.12	0.56	0.70-1.21	1.05	0.44
	Bromoform	21	0.47	0.00	0.00	0.47-0.47	0.47	.
	Styrene	21	0.32	0.00	0.00	0.32-0.32	0.34	.
	o-Xylene	21	0.59	0.08	0.38	0.42-0.77	0.73	0.11
	1,2,3-Trichloropropane	21	0.58	0.13	0.58	0.31-0.84	0.68	0.42
	2-Chlorotoluene	21	0.30	0.00	0.00	0.30-0.30	0.33	.
	Chlorotoluene	21	0.89	0.18	0.82	0.52-1.27	1.14	0.18
	Dichlorobenzene	21	0.55	0.00	0.00	0.55-0.55	0.61	.
	Naphthalene	21	0.40	0.00	0.00	0.40-0.40	0.45	.

[1] Regional average concentration
[2] Total average concentration for all 85 samples
[3] Significance of difference in concentration ($p<0.05$)

Figure 6- Association among Five Selected VOCs



4.5 Correlation between VOC Levels Concentrations

For the VOCs that were routinely detected (50% of samples over LOD), we investigated the relationship between individual VOCs using simple linear regression (Figure 6). The Spearman's correlation coefficients for these VOCs are provided in Table 5. Most of the correlation coefficients were small (R^2<0.45), with the exception of benzene and carbon tetrachloride, benzene and toluene, and toluene and m,p-xylene. The highest correlation was observed with toluene and m,p-xylene with R^2= 0.87 . When additional VOCs were considered (<50 % of samples above LOD) strong correlations were observed between toluene and selected other VOCs (ethylbenzene, o-xylene, m,p-xylene and o-xylene) with correlation coefficients ranging from 0.76 to 0.87. When we broke down this correlation of compounds by region, we observed a much stronger correlations for toluene and m,p-xylene in the South (0.91) and West (R^2=0.94 respectively). Likewise a strong correlation was observed between benzene and carbon tetrachloride in the West (R^2=0.78), and Northeast (R^2=0.75 respectively).

Table 5- Correlation Between VOCs Using Spearman’s Rank Test

	Chloroform	Benzene	Carbon Tetrachloride	Toluene	Chloro benzene	Ethyl benzene	m,p-Xylene	Styrene	o-Xylene	1,2,3-Trichloro propane	2-Chloro toluene	Chlorotoluene	Dichloro benzene	Naphthalene
Chloroform	1.00													
Benzene	0.06	1.00												
Carbon Tetrachloride	0.00	0.53	1.00											
Toluene	0.33	0.50	0.19	1.00										
Chlorobenzene	0.01	0.42	0.72	0.14	1.00									
Ethylbenzene	0.37	0.42	0.16	0.81	0.06	1.00								
m,p-Xylene	0.34	0.44	0.15	0.87	0.05	0.91	1.00							
Styrene	-0.05	-0.06	0.05	0.04	0.17	0.00	-0.08	1.00						
o-Xylene	0.31	0.50	0.20	0.76	0.14	0.87	0.82	-0.10	1.00					
1,2,3-Trichloropropane	0.16	0.14	0.23	-0.02	0.22	-0.08	-0.07	-0.09	-0.10	1.00				
2-Chlorotoluene	0.24	0.05	0.21	0.03	0.11	0.08	0.03	-0.02	0.11	0.19	1.00			
Chlorotoluene	-0.04	0.26	0.74	0.22	0.22	0.19	0.22	0.12	0.28	-0.05	0.01	1.00		
Dichlorobenzene	0.31	0.05	0.13	0.16	0.15	0.22	0.16	-0.05	0.26	0.18	0.32	0.22	1.00	
Naphthalene	0.90	0.31	0.31	0.18	0.22	0.17	0.18	-0.03	0.20	0.38	0.41	0.15	0.54	1.00

CHAPTER 5: DISCUSSION

This thesis tested the hypotheses that schools in urban areas have higher VOCs concentration than in rural areas, and that schools near industries have higher VOCs concentration than those away from industries. Relatively few studies have looked into all the variables in this study and VOC concentrations simultaneously. Data on outdoor VOC concentrations near schools are also limited. To address this data gap, a total of 85 samples were collected from across the country, using passive organic vapor monitors.

Of all the VOCs measured, toluene had the highest mean concentration, followed by benzene. These findings are consistent with what has been previously reported on ambient environments (Gee & Sollars, 1999; Payne-Sturges, D. C., Burke, T. A., Breysse, P., Diener-West, P. & Buckley, T. J., 2004). Likewise, styrene, 2-chlorotoluene, dichlorobenzene, and naphthalene were the least frequently detected. The compounds for which most samples were below the LOD could be explained by the absence of sources where sampling occurred.

This study indicates that urban areas had the highest VOC average concentrations. Concentration levels were much higher for benzene, toluene, and chlorobenzene. Toluene concentrations were higher in urban areas, areas closer to highways, and areas with industries. These findings support the hypothesis that traffic and industrial emissions are major sources of ambient toluene. Previous studies have shown the level of toluene to vary closely with vehicle flow in areas characterized by heavy traffic density (Sapkota &

Buckley 2003). The high concentrations for benzene and toluene observed in the urban areas are consistent with previous observations in El Paso (urban), Texas, and Underhill (rural), Vermont (Mohamed, M. F., Kang, D. & Aneja, V. P., 2002), and Izmir, Turkey (Muezzinoglu et al., 2001).

Our results are also consistent with the observed variation of VOCs in the urban atmosphere (Yamamoto, N., Okayasu, H., Murayama, S., Mori, S., Hunahashi, K. & Suzuki, K., 2000), suggesting that traffic activities contribute increased VOC concentrations. Kwon et al. (2006), who observed outdoor-residential VOCs concentrations, also reported similar findings. The highest mean VOCs concentrations in that study were toluene (6.82 $\mu g/m^3$), methyl tert-butyl ether (MTBE) (5.75 $\mu g/m^3$), and m,p-xylene (3.25 $\mu g/m^3$). Burstyn et al. (2007) observed benzene levels in rural areas in Western Canada (Burnstyn, I., You, X. I., Cherry, N. & Senthilselvan, A., 2007). Their findings suggested that benzene maximum concentration level occurred in the winter compared to the minimal concentration observed during summer months. The U.S. Census Bureau defines an urban area as a community with a population density of 1,000 of more people per square mile. Son et al. (2003) examined two cities in Korea: Asan, a medium city, with a population of about 200,000 and Seoul, the capital metropolitan city, with a population of about 10 million people. Using the Spearman's coefficient test, outdoor/personal exposure had a strong correlation for benzene (r= 0.829) in Seoul, and for ethylbenzene (r= 0.724) in Asan. These findings also reported strong indoor/outdoor correlation with great significance for benzene (r= 0.653) and toluene (r= 0.605) in Seoul. Our results also showed highest VOCs concentrations in the Northeast. The Northeast has the highest population density (U.S. Census Estimates, 2006), with increase in traffic and overcrowded cities, which may explain the high VOCs concentrations in our results. Some of these concentrations have been shown to vary according to traffic flow and hours of the day (Muezzinoglu et al., 2001).

Out of all eighteen compounds, higher concentrations of toluene followed by benzene were observed. These results are in agreement with Mintz and McWhinney (2008) who assessed VOCs concentrations in two towns from proximity to a highly industrialized zone in the western area of Canada. In one site, situated downwind from the industrialized zone, toluene and benzene were the highest concentrations. On the other hand, the second site, which was closer to the city, had toluene and m,p-xylene with the highest concentrations, toluene having levels about three times higher than that of the first site. Na et al. (2001) observed VOCs concentration variation in Ulsan, Korea in industrial areas, one near a petrochemical complex (industrial site) and the other near residential and commercial (downtown site) areas. When VOCs concentrations were combined, the industrial site had the greater total concentration. Benzene, p-xylene, and styrene were much higher in the industrial site. Toluene and m-xylene had the same average concentration in both industrial and downtown sites. These findings on toluene contradicts our and Mintz and McWhinney results. This suggests that certain industries may release higher concentrations of specific compounds.

The differences in VOCs concentration observed across the geographical areas suggest that some health outcomes related to exposure may be more dominant in some geographical locations compared to others. These adverse outcomes may also vary by frequency, duration of exposure.

The Spearman's coefficient test was performed and high correlations (r>0.80) were detected for toluene and ethylbenzene, toluene and m,p-xylene, chloroform and naphthalene, ethylebenzene andm,p-xylene, ethylbenzene and o-xylene, and m,p-xylene and o-xylene (r=0.81; 0.87; 0.90; 0.91; 0.87; 0.82 respectively). The strength of the observed correlation between compounds is consistent with those reported by Muezzinoglu et al. (2001). Benzene primarily originated from traffic emissions in that study, so any strong correlation with other compounds would suggest they also were originating form traffic emission. Benzene correlated well with toluene, m,p-xylene, o-xylene, and ethylbenzene (r^2= 0.50; 0.65; 0.73; and 0.55 respectively) in locations near highway. The strong correlations that we observed in our study suggest that these compounds may also be originating from the same sources.

This study provided a snapshot of VOCs concentrations at a given point in time. We established possible associations with several aspects influencing VOCs concentrations. However, this study has several limitations. First, sampling locations were not selected at random. Higher concentrations observed in the Northeast could be explained by an increase in number of industries compared to other regions. Second, data on presence of industry, major roads, and highways were available for only half of the samples. We collected samples at one point in time over one season. Third, collected samples included both weekdays and weekends. Variation in traffic flow over a full week may have altered VOC concentrations, considering that weekends would have less traffic flow than weekdays. Weather variation could have revealed different concentrations as shown in previous studies. There was also a lack of data on industry smokestack height, emission rate that would allow assessing how these emissions were distributed and possibly affecting the community.

CHAPTER 6: CONCLUSION

Despite the limitations, this study provides the first quantitative estimates of ambient VOCs concentrations near schools. Concentration levels were much higher in the urban area compared to the rural area, area close to industries, and highways. Overall, toluene and benzene had the highest average concentrations. The distribution of compounds varied and suggests that some of these compounds might be originating from different emission sources. The findings suggest that school children in some areas may be exposed to high levels of VOCs. As a result of this study with the USA-TODAY, the US-EPA announced an air-monitoring plan near 62 schools in 22 states that include small towns and large cities throughout the U.S.

Standard of Procedure: Calibration Curve
using Working Stock [40 µg/mL]

1. Creating 7 stocks for calibration curve with following final concentrations:

Stock-1= 2,000 ng/mL
Stock-2= 1,000 ng/mL
Stock-3= 500 ng/mL
Stock-4= 200 ng/mL
Stock-5= 100 ng/mL
Stock-6= 50 ng/mL
Stock-7= 0 ng/mL

2. An additional stock (STD-A) with [2,000 ng/mL] will be made using working stock [40 ug/mL] to make stocks 3-6 considering that using working stock [40 ug/mL] instead of STD-A would result in extracting really small volume of the working stock which could lead to possible inaccuracy in making stocks 3-6.

3. Stocks will be made using :

Working stock [40 ug/mL]
+
Solvent Mix (1:2 CS2:ACN)
+
10 uL surrogate [200 ug/mL]

Final volume or V2 of new stock (volume from working stock + volume solvent) prior to adding surrogate will equal to 1,000 uL

4. Making Stocks: C1V1=C2V2

Stock-1= 2,000 ng/mL C1= 40 ug/mL= 40,000ng/mL V1= ? C2= 2,000 ng/mL V2= 1,000 uL

$$V1 = \frac{2{,}000 \text{ ng/mL} \times 1{,}000 \text{ uL}}{40{,}000 \text{ ng/mL}}$$

V1= 50 uL of working stock
+
950 uL solvent mix
+
10 uL surrogate

Stock-2= 1,000 ng/mL C1= 40,000 ng/mL V1= ? C2= 1,000 ng/mL V2= 1,000 uL

$$V1 = \frac{1{,}000 \text{ ng/mL} \times 1{,}000 \text{ uL}}{40{,}000 \text{ ng/mL}}$$

V1= 25 uL of working stock
+
975 uL solvent mix
+
10 uL surrogate

Making STD-A to create stocks 3-6 using working stock [40 ug/mL]

STD-A= 2,000 ng/mL C1= 40,000 ng/mL V1= ? C2= 2,000 ng/mL V2= 1,000 uL

V1= 2,000 ng/mL x 1,000 uL
40,000 ng/mL

V1= 50 uL of working stock
\+
950 uL solvent mix

Stock-3= 500 ng/mL C1= 2,000 ng/mL V1= ? C2= 500 ng/mL V2= 1,000 uL

V1= 500 ng/mL x1,000 uL
2,000 ng/mL

V1= 250 uL of STD-A
\+
750 uL solvent mix
\+
10 uL surrogate

Stock-4= 200 ng/mL C1= 2,000 ng/mL V1= ? C2= 200 ng/mL V2= 1,000 uL

V1= 200 ng/mL x1,000 uL
2,000 ng/mL

V1= 100 uL of STD-A
\+
900 uL solvent mix
\+
10 uL surrogate

Stock-5= 100 ng/mL C1= 2,000 ng/mL V1= ? C2= 100 ng/mL V2= 1,000 uL

V1= 100 ng/mL x1,000 uL
2,000 ng/mL

V1= 50 uL of STD-A
\+
950 uL solvent mix
\+
10 uL surrogate

Stock-6= 50 ng/mL C1= 2,000 ng/mL V1= ? C2= 50 ng/mL V2= 1,000 uL

$$V1 = \frac{50\ \text{ng/mL} \times 1{,}000\ \text{uL}}{2{,}000\ \text{ng/mL}}$$

V1= 25 uL STD-A **+** 975 uL solvent mix **+** 10 uL surrogate

Stock-7= 0 ng/mL C1= 2,000 ng/mL V1= ? C2= 0 ng/mL V2= 1,000 uL

Stock-7 will comprise of 1,000 uL of solvent mix and 10 uL surrogate

1,000 uL solvent mix **+** 10 uL surrogate

All 7 stocks are transferred to GCMS, sorting vials from least to most concentrated.

Extraction Procedure for Calculating Recovery Rate

Materials used: working stock [40 ug/mL]**
100 uL syringe
Internal Standard (IS) [200 ug/mL surrogate]
OVM badge (7)

Badges are spiked with 20 uL of working stock [40 ug/mL]
using syringe previously used to spike blanks

After first spike, tightly sealed badges sit for 10 mins

After 10 minutes, spike badges with 10 uL IS using 2-20 uL pipette

After second spike, tighly sealy badges sit for 3.5 hours

SONICATION

1. Badges are removed from plastic container in vial by rolling them using tefflon tweezers

2. Once in vials, add 1mL of solvent mix using 100-1000 uL pipette

3. Tightly sealed vials are placed in sonicator for 45 mins.

EXTRACTION

1. Extract sonicated solution and tranfer into fresh vial using Pasteur pipette.

ANALYSIS

**Mass for badges extracted with working stock

20 uL of working stock **x** 40 ug/mL
= 20 uL x 40 ng/uL
= 800 ng

+

10 uL IS x 200 ug/mL
= 10 uL x 200 ng/uL
= 2000 ng

Bibliography

Adgate, J. L., Church, T. R., Ryan, A. D., Ramachandran, G., Fredrickson, A. L., Stock, T. H. et al. (2004). Outdoor, Indoor, and Personal Exposure to VOCs in Children. *Environmental Health Perspectives, 112*, 1386-1392.

Adgate, J. L., Eberly, L. E., Stroebel, C., Pellizzari, E. D., & Sexton, K. (2004). Personal, indoor, and outdoor VOCs exposures in a probability sample of children. *Journal of Exposure Analysis and Environmental Epidemiology, 14,* S4-S13.

Akinbami, L. J. (2006). The state of childhood asthma, United States, 1980-2005. Advance Data from Vital and Health Statistics, 381, Retrieved January 15, 2009, from the U.S Department of Health and Human Services, Centers for Disease Control and Prevention National Center for Health Statistics database.

American Cancer Society. (2009). Cancer facts and figures 2009. Retrieved February 10, 2009, from http://www.cancer.org/docroot/stt/stt_0.asp?from=fast

American Chemistry Council (2009). Federal regulations on ground-level ozone. Retrieved February 15, 2009, from http://www.americanchemistry.com/s_acc/sec_solvents.asp?CID=1515&DID=5801

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

Ashley, D. L., Bonin, M. A., Cardinali, F. L., McCraw, J. M & Wooten, J. V. (1996). Measurement of volatile organic compounds in human blood. *Environmental Health Perspectives*, *104,* 871-877.

Boeglin, M. L., Wessels, D., & Henshel, D. (2006). An investigation of the relationship between air emissions of volatile organic compounds and the incidence of cancer in Indiana counties. *Environmental Research, 100,* 242-254.

Brauer, M., Hoek, G., Van Vliet, P., Meliefste, K., Fischer, P. H., Wijga, A. et al. (2002). Air Pollution from Traffic and the Development of Respiratory Infections and Asthmatic and Allergic Symptoms in Children. *American Journal of Respiratory and Critical Care Medicine, 166,* 1092-1098.

Burstyn, I., You, X. I., Cherry, N. & Senthilselvan, A. (2007). Determinants of airborne benzene concentration in rural areas of Western Canada. *Atmospheric Environment, 41,* 7778-7787.

Carbajal-Arroyo, L., Barraza-Villarreal, A., Durand-Pardo, R., Moreno-Macías, H., Espinoza-Lain, R., Chiarella-Ortigosa, P. et al. (2007). Impact of traffic flow on the asthma prevalence among school children in Lima, Peru. *Journal of Asthma, 44,* 197-202.

Carter, W. P. L. (1994). Development of ozone reactivity scales for volatile organic compounds. *Journal of the Air & Waste Management Association*, *44,* 881-899.

Cohen,A. J., & Pope III, C.A. (1995). Lung cancer and air pollution. *Environmental Health Perspectives, 103,* 219-224.

Delfino, R. J., Gong, H., Linn, W. S., Hu, Y., & Pellizzari, E. D. (2003).

Respiratory symptoms and peak expiratory flow in children with asthma in relation to volatile organic compounds in exhaled breath and ambient air. *Journal of Exposure Analysis and Environmental Epidemiology, 13*, 348-363.

Deloraine, A., Zmirou, D., Tillier, C., Boucharlat, A., & Bouti, H. (1995). Case-Control Assessment of the Short-Term Health Effects of an Industrial Toxic Waste Landfill. *Environmental Research, 68,* 124-132.

Dockery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E. et al. (1993). An association between air pollution and mortality in six U.S. cities. *The New England Journal of Medicine, 329,* 1753-1759.

Doll, R., Peto, R., Boreham, J. & Sutherland, I. (2005). Mortality from cancer in relation to smoking: 50 years observations on British doctors. *British Journal of Cancer, 92,* 426-429.

D'Amato, G., Liccardi, G., D'Amato, M., & Cazzola, M. (2001). The role of outdoor air pollution and climatic changes on the rising trends in respiratory allergy. *Respiratory Medicine, 95,* 606-611.

Edwards, J., Walters, S. & Griffiths, R. K. (1994). Hospital admissions for asthma in preschool children: relationship to major roads in Birmingham, United Kingdom. *Archives of Environmental Health, 49,* 223-227.

Edwards, R. D., Iurvelin, J., Saarela, K., & Jantunen, M. (2001). Volatile organic compound concentrations measured in personal samples and residential indoor, outdoor and workplace microenvironments in EXPOLIS-Helinski, Finland. *Atmospheric Environment, 35,* 4531-4543.

Elliott, L., Longnecker, M. P., Kissling, G. E., & London, S. J. (2006). Volatile organic compounds and pulmonary function in the Third National Health and Nutrition Examination Survey, 1988-1994. *Environmental Health Perspectives, 114,* 1210-1214.

Fischer, P. H., Hoek, G., van Reeuwijk, H., Briggs, D. J., Lebret, E., van Wijnen, J. H. et al. (2000). Traffic-related differences in outdoor and indoor concentrations of particles and volatile organic compounds in Amsterdam. *Atmospheric Environment, 34,* 3713-3722.

Fondelli, M. C., Bavazzano, P., Grechi, D., Gorini, G., Miligi, L., Marchese, G. et al. (2008). Benzene exposure in a sample of population residing in a district of Florence, Italy. *Science of The Total Environment, 392,* 41-49.

Gauderman, W. J., Avol, E., Lurmann, F., Kuenzli, H., Gilliland, F., Peters, J. et al. (2005). Childhood asthma and exposure to traffic and nitrogen dioxide. *Epidemiology, 16,* 737-743.

Gee, I. L., & Sollars, C. J. (1998). Ambient air levels of volatile organic compounds in Latin American and Asian cities. *Chemosphere, 36,* 2497-2506.

Guo, H., Lee, S. C., Chan, L. Y., & Li, W. M. (2004). Risk assessment of exposure to volatile organic compounds in different indoor environments. *Environmental Research, 94,* 57-66.

Han, X., & Naeher, L. P. (2006). A review of traffic-related air pollution exposure assessment studies in the developing world. *Environment International, 32,* 106-120.

Jones, A. P. (1999). Indoor air quality and health. *Atmospheric Environment, 33,* 4535-4564.

Katsouyanni, K., & Pershagen, G. (1997). Ambient air pollution and cancer. *Cancer Causes and Control, 8,* 284-291.

Khan, F. I., & Ghoshal, A. (2000). Removal of Volatile Organic Compounds from polluted air. *Journal of Loss Prevention in the Process Industries, 13,* 527-545.

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.

Klepeis, N. E., Nelson, W. C., Ott, W. R., Robinson, J. P., Tsang, A. M., Switzer, P. A. U. L. et al. (2001). The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. *J Expo Anal Environ Epidemiol, 11,* 231-252.

Knox, E. G., & Gilman, E. A. (1997). Hazard proximities of childhood cancers in Great Britain from 1953-80. *Journal of Epidemiology and Community Health, 51,* 151-159.

Knox, E. G., & Gilman, E. A. (1998). Migration patterns of children with cancer in Britain. *Journal of Epidemiology and Community Health, 52,* 716-726.

Knox, E. G. (2005). Childhood cancers and atmospheric carcinogens. *Journal of Epidemiology and Community Health, 59,* 101-105.

Koren, H. S. & Delvin, R. B. (1992). Exposure of humans o a volatile organic mixture. III. Inflammatory response. *Archives of Environmental Health, 47,* 39-44.

Kuo, H.-W., Chiang, T.-F., Lo, I.-I., Lai, J.-S., Chan, C.-C., & Wang, J.-D. (1998). Estimates of cancer risk from chloroform exposure during showering in Taiwan. *The Science of The Total Environment, 218,* 1-7.

Kwon, J., Weisel, C. P., Turpin, B. J., Zhang, J., Korn, L. R., Morandi, M. T. et al. (2006). Source proximity and outdoor-residential VOC concentrations: results from the RIOPA study. *Environmental Science & Technology, 40,* 4074-4082.

Lee, S. C., Chiu, M. Y., Ho, K. F., Zou, S. C., & Wang, X. (2002). Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong. *Chemosphere, 48,* 375-382.

Lin, Y. S., Egeghy, P. P., & Rappaport, S. M. (2008). Relationships between levels of volatile organic compounds in air and blood from the general population. *Journal of Exposure Science and Environmental Epidemiology, 18,* 421-429.

Loyo-Berrios, N. I., Irizarry, R., Hennessey, J. G., Tao, X. G., & Matanoski, G. (2007). Air Pollution Sources and Childhood Asthma Attacks in Catano, Puerto Rico. *American Journal of Epidemiology, 165*, 927-935.

Mannino, D. M., Homa, D. M. & Petrowski, C. A. (1998). Surveillance for asthma—United States, 1960-1995. MMWR CDC Surveillance Summary, 47, 1-27.

McConnell, R., Berhane, K., Yao, L., Jerrett, M., Lurmann, F., Gilliland, F. et al. (2006). Traffic, susceptibility, and childhood asthma. *Environmental Health Perspectives, 114*, 766-772.

Mintz, R., & McWhinney, R. D. (2008). Characterization of volatile organic compound emission sources in Fort Saskatchewan, Alberta using principal compound analysis. *J Atmos Chem, 60,* 83-101.

Mohamed, M. F., Kang, D., & Aneja, V. P. (2002). Volatile organic compounds in some urban locations in United States. *Chemosphere, 47,* 863-882.

Montserrat, C. & Baldasano, J. M. (1995). Development of a source emission model for atmospheric pollutants in the Barcelona area. *Atmospheric Environment, 30,* 309-318.

Morgenstern, V., Zutavern, A., Cyrys, J., Brockow, I., Gehring, U., Koletzko, S. et al. (2007). Respiratory health and individual estimated exposure to traffic-related air pollutants in a cohort of young children. *Occupational and Environmental Medicine, 64,* 8-16.

Muezzinoglu, A., Odabasi, M., & Onat, L. (2001). Volatile organic compounds in the air of Izmir, Turkey. *Atmospheric Environment, 35,* 753-760.

Na, K., Kim, Y. P., Moon, K. C., Moon, I., & Fung, K. (2001). Concentrations of volatile organic compounds in an industrial area of Korea. *Atmospheric Environment, 35,* 2747-2756.

Nicolai, T., Carr, D., Weiland, S. K., Duhme, H., von Ehrenstein, O., Wagner, C. et al. (2003). Urban traffic and pollutant exposure related to respiratory outcomes and atopy in a large sample of children. *European Respiratory Journal, 21,* 956-963.

Oftedal, B., Nafsad, P., Magnus, P., Bjørkly, S., & Skrondal, A. (2003). Traffic related air pollution and acute hospital admission for respiratory diseases in Drammen, Norway 1995-2000. *European Journal of Epidemiology, 18,* 671-675.

Paul, J. (1997). Improved air quality on Turkish roads: fuels and exhaust gas treatment. *Environmental Research Forum, 7-8,* 145-152.Paustenbach, D. J. (2000). The practice of exposure assessment: a state-of-the-art review. *Journal of Toxicology and Environmental Health, 3,* 179-291.

Payne-Sturges, D. C., Burke, T. A., Breysse, P., Diener-West, P., & 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,* 589-598.

Pearson, R. L., Watchel, H. & Ebi, K. L. (2000). Distance-weighted traffic density in proximity to a home is a risk factor for leukemia anad other childhood cancers. *Journal of Air Waste Management Association, 50,* 175-180.

Peng, C. Y., & Lin, T. S. (2007). Volatile organic compound exposure of suburban elementary students in taiwan. *Bulletin of Environmental Contamination and Toxicology, 78,* 85-88.

Phillips, M., Herrera, J., Krishnan, S., Zain, M., Greenberg, J., & Cataneo, R. N. (1999). Variation in volatile organic compounds in the breath of normal humans. *Journal of Chromatography B: Biomedical Sciences and Applications, 729,* 75-88.

Rappaport, S. M., & Kupper, L. L. (2004). Variability of environmental exposures to volatile organic compounds. *Journal of Exposure Analysis and Environmental Epidemiology, 14,* 92-107.

Reynolds, P., Von Behren, J., Gunier, R. B., Goldberg, D. E., Hertz, A., & Smith, D. F. (2003). Childhood Cancer Incidence Rates and Hazardous Air Pollutants in California: An Exploratory Analysis. *Environmental Health Perspectives, 111,* 330.

Rumchev, K., Spickett, J., Bulsara, M., Phillips, M. & Stick, S. (2004). Association of domestic exposure to volatile organic compounds with asthma in young children. *Thorax, 59,* 746-751.

Sapkota, A., & Buckley, T. (2003). The mobile source effect on curbside 1,3-butadiene, benzene, and particle-bound polycyclic aromatic hydrocarbons assessed at a tollbooth. *Journal of Air & Waste Management Association, 53,* 740-748.

Sapkota, A., Williams, D., & Buckley, T. J. (2005). Tollbooth workers and mobile source-related hazardous air pollutants: how protective is the indoor environment? *Environmental Science & Technology, 39,* 2936-2943.

Sax, S. N., Bennett, D. H., Chillrud, S. N., Kinney, P. L., & Spengler, J. D. (2004). Differences in source emission rates of volatile organic compounds in inner-city residences of New York City and Los Angeles. *J Expo Anal Environ Epidemiol, 14,* S95-S109.

Sexton, K., Adgate, J. L., Ramachandran, G., Pratt, G. C., Mongin, S. J., Stock, T. H. et al. (2004). Comparison of personal, indoor, and outdoor exposures to hazardous air pollutants in three urban communities. *Environmental Science & Technology, 38,* 423-430.

Skov, H., Hansen, A. B., Lorenzen, G., Andersen, H. V., Løfstrøm, P., & Christensen, C. S. (2001). Benzene exposure and the effect of traffic pollution in Copenhagen, Denmark. *Atmospheric Environment, 35,* 2463-2471.

Son, B., Breysse, P., & Yang, W. (2003). Volatile organic compounds concentrations in residential indoor and outdoor and its personal exposure in Korea. *Environment International, 29,* 79-85.

U.S. Census Bureau. (2009). Population estimates. Retrieved February 10, 2009, from U.S. Census Bureau database.

U.S. Environmental Protection Agency. (2009). Assessing outdoor air near schools. Retrieved April 1, 2009, from
http://www.epa.gov/schoolair/index.html

van Vliet, P., Knape, M., de Hartog, J., Janssen, N., Harssema, H, & Bunekreef, B. (1997). Motor vehicle exhaust and chronic respiratory symptoms in children living near freeways. Environmental Research, 74, 122-132.

Vineis, P., Forastiere, F., Hoek, G., & Lipsett, M. (2004). Outdoor air pollution and lung cancer: recent epidemiologic evidence. *International Journal of Cancer, 111,* 647-652.

United Nation Environment Program (1994). Air pollution in the world's megacities. *Environment, 36,* 5-37.

Wallace, L. (1986). Personal exposures, indoor and outdoor air concentrations, and exhaled breath concentration of selected volatile organic compounds measured for 600 residents of New Jersey, North Dakota, North Carolina and California. *Toxicological and Environmental Chemistry, 12,* 215-236.

Wallace, L. (1987). The total exposure assessment methodology (TEAM) study. United States: Environmental Protection Agency. Office of Research and Development.

Wallace, L. (1989). Major sources of benzene exposure. *Environmental Health Perspectives, 82,* 165-169.

Wallace, L. (1991). Comparison of risks from outdoor and indoor exposure to toxic chemicals. *Environmental Health Perspectives, 95,* 7-13.

Wallace, L. (1996). Environmental exposure to benzene: an update. *Environmental Health Perspectives, 104,* 1129-1136.

Wallace, L. A. (2001). Human exposure to volatile organic pollutants: Implications for Indoor Air Studies1. *Annual Review of Energy and the Environment, 26,* 269-301.

Wilkinson, P., Thakrar, B., Walls, P., Landon, M., Falconer, S., Grundy, C. et al. (1999). Lymphohaematopoeitic malignancy around all industrial complexes that include major oil refineries in Great Britain. Occupational & Environmental Medicine, 56, 577-580.

Woodruff, T. J., Caldwell, J., Cogliano, V. J., & Axelrad, D. A. (2000). Estimating Cancer Risk from Outdoor Concentrations of Hazardous Air Pollutants in 1990. *Environmental Research, 82*, 194-206.

Yamamoto, N., Okayasu, H., Murayama, S., Mori, S., Hunahashi, K. & Suzuki, K. (2000). Measurement of volatile organic compounds in the urban atmosphere of Yokohama, Japan, by an automated gas chromatography system. *Atmospheric Environment, 34*, 4441-4446.

Zhao, W., Hopke, P. K., & Karl, T. (2004). Source Identification of Volatile Organic Compounds in Houston, Texas. *Environmental Science & Technology, 38,* 1338-1347.