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A Long Term Geospatial Investigation of Air Quality in Windsor, Ontario, Canada - Comparison to Nearby Cities and Applications of Inter-Species Ratios

by

Lindsay Miller

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A Long Term Geospatial Investigation of Air Quality in Windsor, Ontario, Canada - Comparison to Nearby Cities and Applications of Inter-Species Ratios

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DECLARATION OF PREVIOUS PUBLICATION

This thesis includes three original papers that have been published in or submitted to peer reviewed journals and one paper that has been presented and published in a conference proceeding. These papers appear in the following chapters:

Chapter	Publication Title	Publication Status and copyright permission	Co-Authors	Significant portion by a co-author
3	Intra-urban correlation and spatial variability of air toxics across an international airshed in Detroit, Michigan (USA) and Windsor, Ontario (Canada) *Corrigendum to “Intra-urban correlation and spatial variability of air toxics across an international airshed in Detroit, Michigan (USA) and Windsor, Ontario (Canada)” [Atmos. Environ. 44 (2010) 1162-1174].	Published Atmospheric Environment (2010) 44(9), 1162-1174 *Atmospheric Environment 46, 683-686 Corrected version presented in thesis Copyright permission provided in Appendix A.	Lemke, L.D, Xu, X., Molaroni, S.M., You, H., Wheeler, A.J., Booza, J., Grgicak-Mannion, A., Krajenta, R., Graniero, P., Krouse, H., Lamerato, L., Raymond, D., Reiners, J. Jr., Weglicki, L.	Section 3.3.5, Figure 3.4, 3.5, Table 3.6 completed by Larry Lemke, and Shannon Molaroni
5	Transboundary Air Pollution in Windsor, Ontario (Cananda)	Presented in 2010 at the International Society of Environmental Information Sciences (ISEIS) Procedia Environmental Sciences 2 (2010) 585–594	Farhana, S., Xu, X.	Figures 5.2-5.5 generated by Sharmeen Farhana
6	Multi-season, multi-year concentrations and correlations amongst the BTEX group of VOCs in an urbanized industrial city	Accepted for publication in Atmospheric Environment Copyright permission provided in Appendix A.	Xu, X., Grgicak-Mannion, A., Brook, J., Wheeler, A.J.	Figure 6.1 and 6.5 generated by Alice Grgicak-Mannion
8	Spatial variability and application of ratios between BTEX in two Canadian cities	Published in The Scientific World Journal (2011) 11, 2536-2549 Copyright permission provided in Appendix A.	Xu, X., Wheeler, A.J., Atari, D.O., Grgicak-Mannion, A., Luginaah, I.	Figure 8.1b by Alice Grgicak-Mannion, Table 8.6 generated by Dominic Odwa Atari

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ABSTRACT

Ambient air sampling campaigns were carried out in Windsor, Ontario, Canada as well as in Detroit, Michigan, USA and Sarnia, Ontario over a five year period. Sampling campaigns were for two-week periods in each of the four seasons of 2004-2006 in Windsor, fall 2005 in Sarnia and fall (2008) and spring (2009) for Windsor – Detroit. In Windsor, analyses of the benzene, toluene, ethylbenzene, and xylene (BTEX) species for 2004, 2005, and 2006 is reported in this thesis along with BTEX for Sarnia in 2005. Across the international airshed encompassing Windsor and Detroit, simultaneous sampling of nitrogen dioxide (NO_2), particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and BTEX is reported for 2008 and 2009.

Temporal and spatial patterns of concentrations, ratios and correlations among pollutants, as well as the effects of sampler placement, wind patterns and transboundary pollution were studied. Windsor experienced similar concentrations compared with Sarnia and lower concentrations than Detroit. Correlation and inter-specie BTEX ratio analysis identified traffic as the common source of VOCs, BTEX, and NO_2 in Windsor and Detroit. An innovative approach was applied in Sarnia using BTEX concentrations and ratios to characterize mixtures of industrial and mobile sources in different areas of the city.

Temporal and spatial variability was observed. Seasonal comparisons to annual concentrations and spatial patterns indicate that if resources are limited, fall would be preferred to conduct air quality campaigns in Windsor. The locations of hot spots in Windsor were not qualitatively associated with wind patterns during the sampling periods. Additionally there was a lack of association between air mass pathways and measured NO_2 and $PM_{2.5}$ concentrations in Windsor.

Comparisons between concentrations obtained from the sampling campaigns and those from central monitoring stations indicate that these stations are adequate for representing citywide averages. For residential exposure assessment however, these could result in misclassification up to a factor of six. Risk maps demonstrate BTEX exposure risk across Windsor.

Study design recommendations were made for future air quality campaigns. These include sampling frequency, density, and placement, exposure misclassification associated with central site measurements, and for identifying sources for pollutant reduction initiatives.

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LIST OF ACRONYMS AND SYMBOLS

AAQC – ambient air quality criteria

AGL – above ground level

ANOVA – analysis of variance

BAQS – Border Air Quality Study

BDL – below detection limit

BTEX – benzene, toluene, ethylbenzene, and xylene

CO – carbon monoxide

CV – coefficient of variation

DEARS – Detroit Exposure and Aerosol Research Study

EDAS – eta data assimilation system

EST – eastern standard time

GeoDHOC – Geospatial Determinants of Health Outcomes Consortium

HYSPLIT – Hybrid Single-Particle Langrangian Integrated Trajectory

IDW – inverse distance weighting

I-S – inter-species

LPM – litres per minute

LUR – land use regression

M+P/E – (m+p)-xylene / ethylbenzene

M+P/B – (m+p)-xylene / benzene

MDEQ – Michigan Department of Environmental Quality

MDL – method detection limit

NAPS – National Air Pollution Surveillance

NPRI – National Pollutant Reporting Inventory

N – number of samples

NO_2 – nitrogen dioxide

O/B – o-xylene / benzene

O_3 – ozone

OH – hydroxyl

PAHs – polycyclic aromatic hydrocarbons

PM – particulate matter

PM_1 – particulate matter less than one micron in diameter

$PM_{1\text{-}2.5}$ – particulate matter between 1 and 2.5 microns in diameter

$PM_{2.5\text{-}10}$ – particulate matter between 2.5 and 10 microns in diameter

PUF – polyurethane foam

SD – standard deviation

SO_2 – sulphur dioxide

T/B – toluene / benzene

US EPA – United States Environmental Protection Agency

VOC – volatile organic compound

WD – Windsor Downtown

WSU – Wayne State University

WW – Windsor West

DISSERTATION ORGANIZATION

This dissertation is organized into nine chapters. Chapter 1 and 2 consist of the introduction and literature review, respectively. Chapter 3 is an examination of a 2008 air quality study in Windsor, Ontario, Canada and Detroit, Michigan, USA and consists of a journal article published in Atmospheric Environment ('Intra-urban correlation and spatial variability of air toxics across an international airshed in Detroit, Michigan (USA) and Windsor, Ontario (Canada)', 2010, with accompanying corrigendum corrections). Chapter 4 compares the results of the Windsor-Detroit study in two separate study years, 2008 and 2009. Chapter 5 consists of a conference paper presented at the International Society of Environmental Information Sciences (ISEIS) ('Transboundary Air Pollution in Windsor, Ontario (Cananda)', 2010) which examines the frequency of transboundary air movement and its correlations with ambient concentrations in Windsor. Chapter 6 is an examination of multi-season, multi-year BTEX concentrations in Windsor which has been submitted to Atmospheric Environment ('Multi-season, multi-year concentrations and correlations amongst the BTEX group of VOCs in an urbanized industrial city'). Chapter 7 provides additional material examining the seasonal contributions to annual mean concentrations and hot spot trends of BTEX in Windsor. Chapter 8 presents a comparative study and application of inter species ratios in Windsor and Sarnia, Ontario, Canada, which has been published in a Special Issue in the Scientific World Journal ('Spatial variability and application of ratios between BTEX in two Canadian cities', 2011). Chapter 9 provides conclusions and recommendations based on all studies and outlines the engineering significance of the work presented in this dissertation.

CHAPTER 1: INTRODUCTION

1.1 Background

Air quality is an important factor in our everyday lives. Poor air quality can be linked to a number of aberrant health conditions as well as inflict damage on our ecosystem (Parra et al., 2006; Sax et al., 2006; Khoder, 2007; Whitworth et al., 2008). Recent studies have focused on the relationships between air quality and health. The results have led to regulatory agencies setting strict limits for polluting facilities as well as providing monitoring and emission reporting to the public. Exposure to air pollution is related to the area we live in and is largely unavoidable. For this reason it is imperative that facilities be required to report and regulate their emissions and that regular air monitoring for dangerous pollutants be conducted. The difficulty with achieving these objectives is the associated costs of monitoring and reporting. Determining the balance between adequate monitoring and manageable costs is a difficult task involving the determination of annual, seasonal, and spatial patterns of air pollution as well as developing models to provide estimates where comprehensive monitoring is not feasible (Tager et al., 2009).

The priority of air quality management is to implement standards to protect human health. In order to do so, relationships between exposure to air pollutants and adverse health outcomes need to be established. This allows for resources to be focused on reducing the pollutants which are most likely to cause detriment to human health. For example, several studies have pointed to air pollution contributing to hospital admissions for respiratory and cardiac disease in the Windsor area (Burnett et al., 1997; Fung et al., 2005; Luginaah et al., 2005). Exposure data are required to make the links between exposure and adverse health outcomes, preferably at the personal level. Personal monitoring, in which study participants wear equipment to monitor ambient air concentrations, provides true exposure levels on the participants. However, the time and resources required for this type of sampling are costly (Johnson et al., 2010) and it is difficult to enrol and retain a sufficient number of participants so that a desired power of statistical test is obtained to investigate the adverse outcomes (Tager et al., 2009). Researchers must recruit study participants while minimizing several confounding factors, such as smoking, and then rely on these participants to properly wear the equipment, fill out time activity diaries, and remain enrolled in the study. When personal monitoring is not possible, outdoor residential sampling campaigns may provide reasonable proxies because outdoor air is known to infiltrate into our homes (Hung et al., 2005; Ohura et al., 2006).

Government monitoring stations are set up to monitor outdoor ambient air pollution levels for selected compounds, for example, the National Air Pollutions Surveillance network (NAPS) (Environment Canada, 2011). These stations however span large areas. Windsor, located in Southwestern Ontario and covering an area of 147 km^2 with a population of 218,473 (Statistics Canada, 2010), has two central monitoring stations for some pollutants, and one for volatile organic compounds (VOCs) (Environment Canada, 2011). Many of the pollutants that have been linked to adverse health outcomes are known to show variability on a scale as low as 50 m (Hewitt et al., 1991; Tager et al., 2009). Central stations cannot adequately represent residential exposure, particularly in areas influenced by various point and mobile sources. VOC concentrations and their spatial gradients tend to be higher in urban industrialized regions such as Windsor (Srivastava et al., 2005). For this reason, if outdoor monitoring is to be used in exposure studies, more extensive spatial monitoring campaigns are required.

Recent studies have identified the need to address exposure misclassification in epidemiological studies (Sarnat et al., 2007; Sarnat et al., 2010). One way to improve exposure assessment is through spatial monitoring campaigns, which consist of a network of ambient monitoring sites deployed across a city, as applied in Windsor (Wheeler et al., 2008), Sarnia (Miller et al., 2009), Windsor – Detroit (Miller et al., 2010), Toronto (Su et al., 2010), Edmonton and Winnipeg (Allen et al., 2011), and Vancouver (Henderson et al., 2007). These campaigns provide spatial variability of concentrations which are in closer proximity to the residents. It is also important to determine the seasonal patterns of concentrations in order to evaluate seasonal variation in exposure. Furthermore, multiple season campaigns allow for the comparison between seasonal and annual means, which can identify the preferred season or seasons to represent average exposures (Henderson et al., 2007). Multiple season campaigns with high density sampling can further allow for comparison between seasonal and annual spatial patterns, thereby determining which season is best to represent annual spatial patterns. These types of conclusions provide direction for choosing the most suitable time to conduct sampling based on the desired objectives of the study.

Year to year variations in meteorology and source emissions affect concentrations levels (Tager et al., 2009). Multiple year sampling is beneficial because it provides information on how spatial and seasonal patterns change over time. The results of multiple year sampling allow investigators to decide how frequently sampling should be carried out depending on the observed variability in annual concentration measurements. For example, if little annual variability is seen in spatial patterns, then high density sampling can be carried out less frequently. Longer sampling periods are also preferred to quantify problematic pollution areas (Khoder, 2007). Multiple year sampling provides tracking of long term trends and monitors the effectiveness of pollution reduction initiatives. Sampling campaigns are costly and time consuming and the determination of how often and at what density these campaigns should be carried out depends on several factors and the study objectives (Cocheo et al., 2008). Comprehensive, long term comparisons of measurements obtained from several sampling campaigns will provide direction on this topic for future researchers.

Air quality can be influenced by many factors such as local emissions from mobile and point sources, transboundary air movement, meteorology and photochemical reactions. Although the determination of the origin of emissions and predominant sources is often a complicated and challenging task, it is a key component to implementing pollution reduction programs (Lau et al., 2010). Resources limit how many programs policy makers can implement, therefore it is necessary to identify the major contributors to the concentration levels. Polluted air masses can be carried into a city from areas near or far away. Examination of air mass trajectories is one way to assess transboundary air movement into a region (Davis et al., 2010), which is the first step toward regional or international collaborative emission control efforts.

Comparing the air quality of nearby cities allows for evaluation of the influence of local sources impacting the concentration levels. For example, Windsor and Detroit are separated by the Detroit River and share two border crossings, the Ambassador Bridge and the Windsor – Detroit Tunnel. Therefore, if sampled simultaneously, they should experience similar regional transport of pollutants and be influenced by mobile emissions resulting from the border crossing traffic. Comparing nearby cities such as Windsor and Detroit, or Windsor and Sarnia, for several pollutants can identify pollutants which are in higher concentrations in the region thus pose significant health risks to local residents. Analyses of changes in concentrations and correlation between the two cities could indicate differences in source contributions. Determining the overall picture of air quality in neighbouring cities may also lead to collaborative pollution reduction measures.

Correlations and ratios between specific air pollutants can determine whether species originate from common or separate sources. Furthermore, values of specific ratios between pollutants are indicative of mobile emissions (Khoder, 2007; Hoque et al., 2008; Buczynska et al., 2009). The determination of whether or not species originate from common sources can help to identify priority sectors, such as mobile sources, to maximize the return of pollutant reduction efforts. Long term tracking of correlations among pollutants may also identify changes in air quality that could be attributed to changes in emissions, leading to cost-effective control measures.

1.2 Objectives

The overall objective of this thesis is to provide an evaluation of air quality in Windsor, Ontario. The pollutants that will be considered include volatile organic compounds (VOCs), nitrogen dioxide (NO_2), particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs). The analysis focuses on concentration levels, major sources, and variability within and between sites, cities, seasons, and years. In addition, this study also provides recommendations that can be applied to other areas to improve both our understanding of variability and the results of future air quality studies. The analysis contained in this thesis attempts to address the following scientific questions related to air quality in this region:

1) Do Windsor and Sarnia, Ontario, and Detroit, Michigan have similar air pollutant concentrations, correlations, and spatial patterns?

2) Do concentrations vary spatially, seasonally, and annually in this region? If so, how should these be considered in deciding upon sampling frequency?

3) Is there an optimal season to sample in to represent annual concentrations values and/or spatial patterns in this region?

4) Do the air pollutants monitored have some common sources?

5) Is this region predominantly affected by local or regional sources?

6) Can inter-species ratios be applied to estimate source origins and photochemical aging in this region within and beyond the framework in the existing literature?

7) When using central site measurements to represent residential exposure, what is the level of misclassification one can estimate using spatial campaign data?

These questions are addressed through the following specific objectives:

- To evaluate and compare the concentrations and variability of VOCs, PM, NO_2, and PAHs in Windsor, Ontario, (Canada) and Detroit, Michigan (USA) over two sampling periods in 2008 and 2009.

- To examine the effect of transboundary air pollution of NO_2 and $PM_{2.5}$ in Windsor, Ontario for two sampling periods taking place in 2008 and 2009.

- To determine the spatial, seasonal and annual variability of the BTEX group of VOCs in Windsor over 2004, 2005, and 2006.

- To examine the presence of hot spots in Windsor for four seasons in 2004 and 2006 and evaluate whether wind speed and direction influence hot spot locations.

- To examine the ratios indicative of source contributions and photochemical age and the correlations between pollutants within each sampling period.

- To compare the Windsor 2005 BTEX concentrations with those obtained in Sarnia, Ontario, Canada during the same time period.

- To develop and apply an innovative approach to using concentrations and I-S ratios of BTEX in Sarnia to characterize pollutant mixtures in different areas of the city.
- To compare measurements from central monitoring stations to those obtained through saturation sampling campaigns for:
    - BTEX (Windsor 2004, 2005, 2006, 2008, 2009), Sarnia (2005)
    - NO_2 and $PM_{2.5}$ (Windsor 2008, 2009)
- To develop recommendations aimed at improving the study design of air quality monitoring campaigns, for the purpose of aiding future researchers, governments, city planners, and epidemiologists and to further the understanding of the impact of different sources on variability, exposure, and spatial patterns.

Taken together, this thesis provides analyses and recommendations for improving the understanding of air quality in urban areas and provides direction for future investigations relying on spatial campaigns to assign residential exposure. The results regarding seasonal and spatial variability provide direction as to the approximate frequency of high density sampling campaigns required to achieve adequate results. The applications of I-S ratios assist with understanding the source origins of emissions, photochemical aging, and characterization of pollutant mixtures. These objectives will be achieved through the studies documented in Chapter 3 – 8 of this thesis including three journal papers (Chapter 3, 6, and 8) and one conference paper (Chapter 5).

1.3 Chapter Contributions to Objectives

1.3.1 Air Quality in Windsor and Detroit (Chapter 3, 4, 5)

These chapters focus on comparing air quality between these two neighbouring cities as well as comparing how the concentrations and relationships change between two sampling campaigns conducted in different seasons of two different years. This analysis contributes to determining the spatial, seasonal, and annual variability of pollutants and suggests factors, such as changes in meteorology or industrial activities, which may affect these variabilities. The evaluation of I-S BTEX ratios identifies the different strength of mobile and point source contributions to the BTEX levels in the two cities. Application of HYSPLIT modelling determines to what extent transboundary air movement affects concentrations by evaluating correlations between the emissions and concentrations at the origin of an air mass and the measured concentrations at the receptor for select pollutants.

1.3.2 Long Term Concentrations and Correlations Between BTEX in Windsor (Chapters 6, 7)

This multi-year, multi-season, multi-site analysis allows for the determination of spatial, annual, and seasonal variability in Windsor. Comparison of analyses from year to year identifies both the benefits and redundancies of multiple year sampling. Comparison of the three-year seasonal and annual means identifies which seasons are best representative of annual patterns which can assist researchers in study design when resources are limited. Furthermore, evaluation of seasonal contributions to annual means on a site-by-site basis further assists in determining representative seasons. The application of I-S ratios provides preliminary source identification and estimates the photochemical age of the air mass in this city. Comparison to central government stations identifies exposure misclassification that may result if these stations were relied upon for assigning residential exposure. Additional analyses investigate whether the hot spots for BTEX remain the same from season to season, year to year, and whether there are specific factors affecting the hot spot locations. Risk maps of the Windsor area are provided based on concentrations of the BTEX species and how they compare to government standards.

1.3.3 Spatial variability and application of ratios between BTEX in two Canadian cities (Chapter 8)

This chapter compares BTEX concentrations and correlations in Windsor and Sarnia where synchronized sampling took place. Differences in concentrations lead to the identification of some predominant sources. Additionally, the I-S ratios are applied in

Sarnia as a means of characterizing pollutant mixture in different land use areas. Potential misidentification of emission sources and aging was noted through comparison of the sampling campaign ratios to those obtained at central sites. In this study I-S ratios were used in a unique way which can be applied to future studies to link these ratios with emissions, pollutant mixtures, and photochemical age. Recommendations for important considerations such as how nearby sources and concentrations may affect these ratios are also provided.

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CHAPTER 2: LITERATURE REVIEW

This literature review is meant to accompany and expand upon the introduction sections to the manuscripts (Chapters 3, 5, 6, 8) and Chapters 4 and 7 presented within this thesis. Word limits of manuscripts prevent extensive review of relevant publications; therefore this section will serve to summarize some previous investigations, point out the strengths and limitations of these studies, as well as to highlight the need of the current research presented in this thesis.

2.1 Air Quality in Windsor and Detroit

Previous studies on air quality in the Windsor and Detroit area have been conducted and have lead to interesting conclusions and questions. In 1994, Windsor was the focus of a comprehensive air quality study to measure gaseous airborne pollutants. The measurements were indicative of typical urban air quality with concentrations less than Ontario Ministry of the Environment standards (Ng and Karellas, 1994). More recently, the US and Canadian governments have developed an international agreement, the Border Air Quality Strategy (BAQS) (Health Canada, 2011) to investigate air health affects in this area. As part of the BAQS, 50 air monitors were deployed across the Windsor area for two-week periods in each of the four seasons of 2004 to assess spatial variability of residential exposure. From the winter sampling data of this study, Luginaah et al. (2006) identified key determinants of intra-urban variation of NO_2 in this city and developed an LUR model. Using the data collected in all four seasons in 2004, Wheeler et al. (2008) evaluated the intra-urban variability of NO_2, SO_2, benzene, and toluene and developed LUR models for these pollutants. The measured pollutants were found to be highly correlated with one another therefore suggesting that they were likely emitted from similar local sources. Additionally, the rank order of high to low concentrations remained consistent at each site throughout the seasons which was mentioned as a key issue to consider in the design of such sampling studies. Wheeler et al. (2008) identified important considerations when designing air sampling network studies such as whether rank order remains the same throughout different years, the representativeness of a single season and the benefits of multiple year sampling. The identification of these key components could be addressed using data collected in the three-year (2004-2006) Windsor study.

On the Detroit side, the US EPA launched the Detroit Exposure and Aerosol Research Study (DEARS) in 2004 to evaluate how their measurements obtained through spatial residential and personal monitoring compared to measurements at central sites for air toxics and particulate matter (Williams et al., 2008). Results from the DEARS study indicate spatial variability of $PM_{2.5}$ (Rodes, 2010) and the determination of factors which influence personal exposure to NO_2 (Williams, 2011). Additionally, the DEARS study data have also been used to investigate some health effects such as exposure to $PM_{2.5}$ and increases in systolic blood pressure (Brook et al., 2011) as well as adverse cardiovascular responses (Brook et al., 2008). Another recent study in Detroit utilized participant based monitoring of NO_2, VOCs, and PAHs to obtain concentrations across the city while minimizing costs (Johnson et al., 2010b). This approach of having the study participants conduct indoor and outdoor monitoring without the assistance of technicians generated spatial data which were consistent with previously reported data from technician based studies. This is something to consider for future studies where resources are limited.

Some recent air quality and health related studies also warrant further investigation into these two cities. Air pollution has been linked to contributing to hospital admissions for respiratory and cardiac disease in the Windsor area (Burnett et al., 1997; Fung et al., 2005; Luginaah et al., 2005). Similarly, investigations in Detroit have linked exposure to particulate matter with asthma (Keeler et al., 2002; Morishita et al., 2006).

Although both cities have been the focus of air quality investigations in recent years, they have not been sampled simultaneously as an international airshed since 1952 (Clayton et al., 1952). Results from the 1952 study observed high particulate matter concentrations coinciding with smog periods and with high SO_2 concentrations. Spatially, the most heavily polluted areas in Windsor were closest to the Detroit River and areas within major industrial zones. Lower concentrations were observed in areas further removed from these activities such as towards the north east border of Windsor. More highly polluted areas saw a three-fold increase in pollutant concentrations over less polluted areas, again demonstrating significant spatial variability. This study was conducted some time ago, therefore simultaneous investigation into the concentrations of several air pollutants in both Windsor and Detroit is warranted to determine the current spatial variability of air pollutants in and between the cities.

The International Air Quality Advisory Board recognizes that the spatial distribution and transport of air toxics is poorly understood in international airsheds (IAQAB, 2004). This board has recently conducted analyses on transboundary air pollution in the Detroit – Windsor area as well as the areas of Port Huron, Michigan – Sarnia, Ontario, and Sault Ste Marie, Michigan – Sault Ste Marie, Ontario (IAQAB, 2004). The analysis was based on separate reports from each city from their respective central site government monitoring. Some findings of this study consist of similar levels of NO_2 in the two cities, higher PM concentrations in Detroit and the conclusion that pollution levels are predominantly affected by area sources such as traffic and small industrial operations. The advisory board recommended that the USEPA and Environment Canada join together to provide a combined overview of air quality across these airsheds and to develop bilateral control strategies to achieve reductions in local and regional concentrations.

Few studies have undertaken sampling across an international airshed. As part of the Border Air Quality Strategy, simultaneous sampling has taken place across another US – Canada international airshed shared by Vancouver, Canada, and Seattle, Washington. This study has resulted in several publications including the investigation of transboundary air pollution and environmental justice (Su et al., 2010a), the transferability of LUR models between these two cities (Poplawski et al., 2009), and the use of spatial property assessment data in air pollution exposure assessments (Setton et al., 2005). Additional examples of international airshed studies include that between Mexico and the US (Streit, et al., 1996) and between Jordan and Israel (Sarnat, J. et al., 2010).

In summary, recent studies into air quality in Windsor and Detroit have taken place and will provide valuable information on concentrations of pollutants in these cities. However, because sampling was done for individual cities rather than them being sampled simultaneously, between city comparisons are difficult to make due to a lack of consistency in sampling design, instrumentation, and timing. Therefore there is a need to undertake synchronized sampling of these two cities to investigate the intra-urban variability in this airshed and to develop collaborative initiatives to improve air quality.

2.2 Local Scale Variability

Currently ambient air pollution levels for several pollutants are monitored by the National Air Pollution Surveillance (NAPS) network in Windsor and Sarnia (Environment Canada, 2011), and by the Michigan Department of Environmental Quality (MDEQ) in Detroit (MDEQ, 2009). These stations are useful to obtain average concentrations of pollutants, however, they have a widely spaced distribution over a large area with one monitor located in Sarnia, two monitors in Windsor, and seven monitors for Detroit. For this reason they lack the ability to address local-scale spatial variability of ambient air pollution. Recent studies have demonstrated that measurements from central stations are poorly correlated with residential ambient levels leading to exposure misclassification (Vardoulakis et al., 2005; Violante et al., 2006). Additional studies have discussed the need to address this exposure misclassification in epidemiological studies (Sarnat et al., 2007; Sarnat, S. et al., 2010). Since high ranges of concentrations within cities as well as high gradients near sources have been reported for several pollutants, additional monitoring to supplement central stations is required in order to accurately characterize the range of concentrations across a city (Touma et al., 2006).

Recent studies have conducted spatial monitoring campaigns in nearby cities to address the local scale variability of air pollutants. In Toronto, Ontario, Canada spatial variability of NO_2 concentrations were observed using 100 ambient monitors (Jerrett et al., 2007). It has previously been shown that NO_2 can display concentration differences on scales as low as 50 m (Hewitt et al., 1991). Jerrett et al. (2007) deployed 100 monitors over an area of 633 km^2, providing for the determination of small area variations which would not otherwise be seen with the three NAPS stations across the city. Similarly, spatial variability of VOCs (Miller et al., 2009) and NO_2/SO_2 concentrations (Atari et al., 2008) was observed in Sarnia, Ontario, Canada using 37 ambient monitors across the city with higher concentrations observed in the vicinity of chemical and industrial facilities. These studies further support the importance of considering local scale variability when assessing residential exposure to potentially harmful pollutants as well as suggest that the importance may be more pronounced in regions with significant industrial and chemical activity.

A limitation of the above studies is that they consist of a small number of sampling campaigns which limits the evaluation of seasonal and annual variabilities. The benefits of a high resolution sampling campaign capable of identifying local scale variability come at an increased cost and therefore are often not repeated. The method of applying an ambient air sampling campaign with extensive spatial coverage needs to be further explored to determine how spatially stable the concentrations patterns remain throughout different seasons as well as different years. This information will assist in achieving a balance between the cost of these campaigns and the extensive data they provide.

Several methods exist for selecting appropriately representative sampling sites across a study domain. Commonly applied methods include location-allocation, which requires prior knowledge of concentrations in order to generate a surface (Henderson et al., 2007), and random stratified design (Johnson et al., 2010a). Other considerations in site selection include logistics such as security and access to power, as well as achieving specific study objectives.

Due to the high costs of deployment and analysis of samples, it is important to achieve adequate spatial coverage with the fewest number of samples necessary. Cocheo et al. (2008) suggest that there is a ratio of samplers to area resulting in adequate spatial coverage. Beyond this ratio, the sampling campaign would be saturated and any further samplers would come at an increased cost with no further benefit to the study. For BTEX, Cocheo et al. found that this ratio was 1 sampling site per 3.4 km^2, with a minimum of 29 sites. They suggested that this ratio would also hold for NO_2 since the spatial distribution of this pollutant is less sensitive to the distance from the source than BTEX.

2.3 VOCs and BTEX

Of particular interest is the small scale variation of VOCs, since relatively few studies have focused on this aspect of this group of pollutants. The current health risk based air pollution literature mainly focuses on particulate matter, NO_2, CO, and O_3. Much less information is available on the spatial distribution of ambient VOCs (Su et al., 2010b). The lack of monitoring data available for ambient VOCs limits efforts to identify predominant emission sources and to evaluate potential adverse health effects related to exposure. Efforts to address this limitation have been undertaken recently with extensive VOC monitoring campaigns across 28 U.S. cities to identify and quantify the major VOC species (Baker et al., 2008).

It could be argued that people spend the majority of their time indoors, therefore outdoor concentrations may not be representative of personal exposure. Indoor air quality however, is strongly influenced by the penetration of outdoor air into buildings and outdoor concentration levels are easier to obtain for residential populations (Hung et al, 2005; Ohura et al., 2006). Indoor air pollutant concentrations have been shown to be good estimates of personal exposure (Sexton et al., 2004). Stocco et al. (2008) reported that outdoor residential concentrations were associated with personal exposure to benzene, (m+p)-xylene, and toluene in Windsor, Ontario. This was unsurprising since BTEX VOCs are known to be emitted by traffic. Additionally, vehicular traffic has been linked to the majority of intra-urban air pollution variability (Gilbert et al., 2005; Jerrett et al., 2005) suggesting that outdoor concentrations may be adequate proxies to represent the variability in residential exposure.

A cost effective method of conducting outdoor VOC sampling is with passive organic vapor monitors, which use a single charcoal sorbent wafer for collection of organic vapors via the process of diffusion. These monitors have been validated by previous studies (Chung et al., 1999; Mukerjee et al., 2004) and have been shown to perform within 5-10% of automated-gas chromatograph measurements for the BTEX species (Mukerjee et al., 2004).

Recent studies have focused on the BTEX species. Strong correlations between the BTEX species have been observed in several geographic areas such as the United States (Pankow et al., 2003), Hong Kong (Ho et al., 2004), Northern Spain (Parra et al., 2006), Greater Cairo (Khoder, 2007), Delhi, India (Hoque, 2008), Belgium (Buczynska et al., 2009), and Ontario, Canada (Wheeler et al., 2008; Miller et al., 2009). These studies conclude that the strong correlations among species are indicative of them originating predominantly from the same source. Other studies have observed that while BTEX correlations were significant, those between TEX were stronger than the correlations with benzene due to a stronger industrial component of TEX (Smith et al., 2007, Su et al., 2010b). Considering the investigations discussed above, it can be concluded that the BTEX group of species are generally well correlated with one another. This holds true regardless of geographical location, although the studies commonly took place in urban environments.

In a small sample of studies considering seasonal variability in the BTEX correlations, differences in the strength of correlations were observed (Ho et al., 2004; Parra et al., 2006). Explanations for these differences included variations in fuel evaporation rates at different temperatures, along with photochemical reactions characteristic of high solar radiation in the summer. Another study looked at how the correlations varied spatially, although it only considered four sites (Hoque et al., 2008). The site in a highly industrialized area did not experience the same strong correlations as did the three other monitors in other areas of the city. Additional multiple season, multiple site studies are warranted to further investigate the spatial and temporal variability of these correlations.

2.4 Transport of Pollutants

In addition to establishing associations between pollutant concentrations and health outcomes, another important factor in protecting human health is to identify the sources of the air pollutants. One of the approaches is the examination of transboundary air movement using back trajectory analysis to determine whether regional transport of pollutants is a significant contributor to pollution levels.

Two recent studies used the Hybrid Single-Particle Langrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003) to evaluate relationships between air flow patterns and ambient pollutant concentrations of ozone (Davis et al., 2010) and PM_{10} (Karaca et al., 2009). Both studies were able to draw associations between air flow patterns and concentrations. The PM_{10} study is particularly relevant since the results were used to determine which nearby countries influenced the PM_{10} levels in the area of the study during each season. Windsor, Ontario borders Detroit, Michigan; therefore, it is likely that pollution from Detroit is carried over to Windsor and vice versa.

2.5 Source Origins

Correlations between pollutant concentrations are often investigated to determine whether pollutant species are likely originating from common or separate sources. For some groups of pollutants, for instance the BTEX species, it has been well established that correlations between the species are generally significant and high therefore indicating common, likely vehicular, sources of these species (Pankow et al., 2003; Khoder, 2007; Hoque et al., 2008; Miller et al., 2009). Correlations among VOCs and other combustion related pollutants, for example CO (Warneke et al, 2007; Baker et al., 2008), also confirm that these species are predominantly attributed to mobile emissions. Other pollutants such as NO_2 and PM have also been observed to be well correlated suggesting a common origination, likely traffic (Brook et al., 1997; Lam et al., 1999). Another reason for establishing these correlations is to identify if one pollutant can be used as a marker for others (Brook et al., 1997, Khoder, 2007), thereby potentially limiting the need for future data collection on all species.

Another way to assess potential source contributions is the application of ratios between the BTEX species. Studies have examined the ratio between toluene and benzene, both are constituents of gasoline, and have established a range of values which may be indicative of predominantly mobile sources, based on the vehicular emission ratio of toluene and benzene and the photochemistry of these species. Brocco et al. (1997) reported that automotive exhaust has an approximate T/B ratio of 2.7 although significant variations in fuel formulations will be observed depending on geographic locations, vehicle fleets, and season. Photochemical degradation of toluene is faster than that of benzene (Gelencsr, et al., 1997) therefore, T/B ratios closer to their emission ratios are expected in areas where the monitoring stations are close to traffic sources. Deviations in (usually higher) T/B ratios are commonly attributed to source contributions from industrial activities. Benzene is predominantly used for fuels (Hoque et al., 2008) whereas TEX have stronger industrial components (Su et al., 2010b), therefore suggesting that industrial sources of toluene from painting and manufacturing facilities are the likely contributors to higher T/B ratios.

Average T/B ratios that were concluded to be indicative of predominantly traffic sources have been reported in the range of 1.3-3.4 across diverse geographical areas (Hansen and Palgrem, 1996; Gelenscr et al., 1997; Vardoulakis et al., 2002; Khoder, 2007; Bruno et al., 2008; Hoque et al., 2008; Liu et al., 2009). Other studies reported slightly higher ratios such as 4.3-4.8 in Mexico City (Bravo et al., 2002) and 3.8-4.4 in Belgium (Buczynska et al., 2009). General conclusions from these studies suggest that at sites where the ratios fall between ~ 1.5-3.0, it can be confirmed that traffic is the predominant source of these emissions. Alternatively, higher ratios; 5.1-5.3 in Belgium (Buczynska et al., 2009), 5-14 in Hong Kong (Ho et al., 2004) have been shown to be indicative of the influence of non-vehicular or industrial sources. Low ratios (0.4 – 1.3) were observed by Khoder (2007) in a rural area far away from traffic density which was the result of these pollutants being exposed to photochemical degradation. These studies generally consider an average T/B ratio over an area however could go further to consider the spatial distribution and temporal variability of ratios as well as influences from reported emissions.

Another applicable ratio is that between (m+p)-xylene and ethylbenzene which has previously been used as an indicator of photochemical age (Nelson and Quigley, 1983; Zhang et al., 2008). These two species are generally emitted from common anthropogenic sources, usually vehicle exhaust and solvent emissions, and are emitted in a set ratio of approximately 3.6:1. Deviations from the 3.6:1 ratio can be attributed to photochemical aging. The primary sink of these species from ambient air is through their reaction with OH radicals. Although the pathway for removal is the same, the rate of removal differs between species, specifically, (m+p)-xylene removal is approximately 3 times faster than the removal of ethylbenzene (Nelson and Quigley, 1983). Therefore, (M+P)/E ratios lower than the values expected for fresh emissions (3.6:1) can be attributed to the photochemical aging of these hydrocarbons.

Recent studies have confirmed higher (M+P)/E ratios in areas with fresh emissions from nearby sources and lower in areas farther removed from emission sources (Khoder, 2007, Zhang et al., 2008). Several other studies observed ratios in the range of 1.3-2.1 (Ho et al.; 2004; Liu et al., 2009; Perez-Rial et al., 2009) indicating that these species may have travelled a significant distance from the source to the receptor and have experience photochemical degradation since being emitted from the source. Although (M+P)/E is the most commonly applied ratio (Nelson and Quigley, 1983; Zhang et al., 2008) for evaluating photochemical aging, a group of additional BTEX ratios has also been applied for this purpose (Khoder 2007; Hoque et al., 2008). They are T/B, (m+p)-xylene to benzene ((M+P)/B), and o-xylene to benzene (O/B). The principle is similar to that of (M+P)/E; values closer to their expected emission ratio typically indicate fresh local emissions, whereas lower values are associated with more photochemical degradation.

A limitation of the application of ratios as previously reported is that they are not investigated further to determine the potential reasons for the high or low ratios and the role of concentration levels. The relevance of the ratios is more difficult to determine than absolute concentration levels since they depend on two species. Another limitation is that the ratios are commonly applied to areas removed from industrial sources, therefore missing the opportunity to assess how these ratios behave in the presence of a mixture of emissions from both point and mobile sources. Investigation into the impacts of different sources or land characteristics and the concentrations in these areas would improve our ability to delineate pollutant mixtures by source type.

Receptor modelling techniques such as chemical mass balance (CMB) and positive matrix factorization (PMF) have also been applied to apportion the source contributions of VOCs (Watson et al., 2001; Lau et al, 2010). These techniques allow for quantification of ambient VOC source contributions and can be applied to evaluate and improve emission inventories and air quality models (Watson et al., 2001). In CMB models, ambient data are fitted to specific source profiles. The number of sources and their profiles must be assumed in advance which is often viewed as a limitation of such models. PMF can apportion source contributions based on observations at a receptor site without knowledge of exact source profiles (Lau et al., 2010) however require a large data matrix (Brown et al., 2007). Both types of modelling have successfully been used to confirm that VOCs, including BTEX species, originate predominantly from vehicular emissions. For example, mobile exhaust was identified as the major contributor to VOCs using CMB in an extensive review of urban areas (Watson et al., 2001) and in Mexico City (Vega et al., 2000). Furthermore, PMF identified vehicle and marine exhaust as the primary contributor to VOC concentrations in Hong Kong (Lau et al., 2010) and mobile sources as the major VOC contributor in Los Angeles (Brown et al., 2007) and Santiago Chile (Jorquera and Rappengluck, 2004).

2.6 Spatial Interpolation Techniques and Land Use Regression Models

Spatial interpolation techniques are available to illustrate the variability in pollutants concentrations. Two popular choices for this application are inverse distance weighting (IDW) and kriging. IDW has been used in previous studies to demonstrate spatial concentrations in urban areas for NO_2 (Chen et al., 2010) and $PM_{2.5}$ (Wu et al., 2006). This method has the advantage of being relatively simple to apply however it is an inexact, non-interpolator method which assigns heavier weights to nearby sites (Lam, 1983). This can result in high spots which may not be representative. Kriging is another interpolation method which predicts unknown values from data observed at known points. It has been shown to be more accurate at estimating concentrations in some instances than IDW (Zimmerman et al., 1999). Sample applications of kriging include

VOC (Roukos et al., 2009; Miller et al., 2009) and $PM_{2.5}$ concentrations (Wu et al., 2006).

Another tool for estimating concentrations is land use regression modelling. Unlike spatial interpolation techniques, LUR models are developed using limited monitoring data and predictor variables, such as proximity to roads and industry, and apply the resulting spatial models to a large number of unsampled locations for prediction (Jerrett et al., 2005). These models are promising tools to provide exposure estimates at finer resolutions. LUR models provide practical applications to achieve spatial coverage of concentrations. However, high density sampling campaigns are required to develop and improve these models (Corburn, 2007).

LUR modelling has become a popular choice for estimating exposure to ambient air pollution such as NO_2 (Briggs et al., 2000; Henderson et al., 2007; Jerrett et al, 2007), $PM_{2.5}$ (Brauer et al., 2003; Ross et al., 2007), and environmental carbon (Ryan et al., 2007). Although most commonly used for these pollutants, application of LUR models for VOCs has also recently gained popularity. Seven recent studies have used LUR modelling for some BTEX species with success. For example, Carr et al., (2002) applied LUR methods to benzene for use in future epidemiological studies in Munich, Smith et al. (2006) predicted BTEX concentrations at 55 schools in Texas using LUR and Aguilera et al., (2008) used LUR modelling of BTEX to estimate exposure for pregnant women in Spain.

Three recent studies of LUR modelling of VOCs were conducted in Southwestern Ontario (Wheeler et al., 2008; Atari and Luginaah, 2009; Su et al., 2010b) and one in nearby Detroit, Michigan (Mukerjee et al., 2009). In Toronto, Ontario, Canada, benzene and total hydrocarbons were modelled in one season (Su et al., 2010b). Similarly, BTEX was modelled for one season in Sarnia, Ontario (Atari and Luginaah, 2009). In Windsor LUR modelling of benzene and toluene was carried out using monitoring data from all four seasons in 2004 (Wheeler et al., 2008). Similar BTEX LUR modelling was conducted in Detroit, Michigan using data from the summer of 2005 (Mukerjee et al., 2009). These LUR models could benefit from additional components such as annual variability and association with wind patterns. Additionally these cities are within the same geographical region which would make them good choices for the investigation of intercity transferability of LUR models as in Poplawski et al. (2008).

To summarize the findings from this literature review, further investigation into the factors that contribute to air quality variability in urban environments is warranted. Specifically, there are reasons to focus on Windsor and surrounding areas due to high pollution levels and the known health effects of air quality in the area (Fung et al., 2005; Luginaah et al., 2005). Investigation into the international airshed shared by Windsor and Detroit has been identified as a priority in order to address air quality in these cities and develop collaborative reduction initiatives (IAQAB, 2004). Furthermore, comparisons of nearby cities will determine the intra-urban variability in the region and identify whether results from one city are applicable to another geographically similar city.

There is also a concern over VOCs, especially BTEX, and the small scale variation of concentration levels so that health effect studies of these pollutants are not limited by a lack of spatial data (Su et al., 2010b). Reliance on central stations is often not adequate due to the large diverse areas these stations represent (Touma et al., 2009). Capturing the seasonal and annual variability of these pollutants is an important consideration so that sampling resources can be optimized to provide the necessary data to conduct exposure studies. Air quality is the result of a complex mixture of different emissions from regional and local sources, thus the identification of predominant and common sources can assist with implementing pollution reduction initiatives.

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CHAPTER 3: INTRA-URBAN CORRELATION AND SPATIAL VARIABILITY OF AIR TOXICS ACROSS AN INTERNATIONAL AIRSHED IN DETROIT, MICHIGAN (USA) AND WINDSOR, ONTARIO (CANADA)

3.1 Introduction

The individual and aggregate health effects of air toxics are issues of concern (Morello-Frosch et al., 2000; Turaga, 2007). One challenge in establishing the association between air pollution and health outcomes is that the spatial distribution and transport of air toxics are poorly understood, particularly in urban areas straddling international boundaries (e.g., IAQAB, 2004). The international airshed forming the domain for this study encompasses Detroit, Michigan and Windsor, Ontario, and is home to more than one million residents (Statistics Canada, 2008; US Census Bureau, 2008). Detroit and Windsor are separated by the Detroit River and connected by the Detroit-Windsor Tunnel and the Ambassador Bridge - the busiest commercial international border crossing in North America (Fig. 3.1).

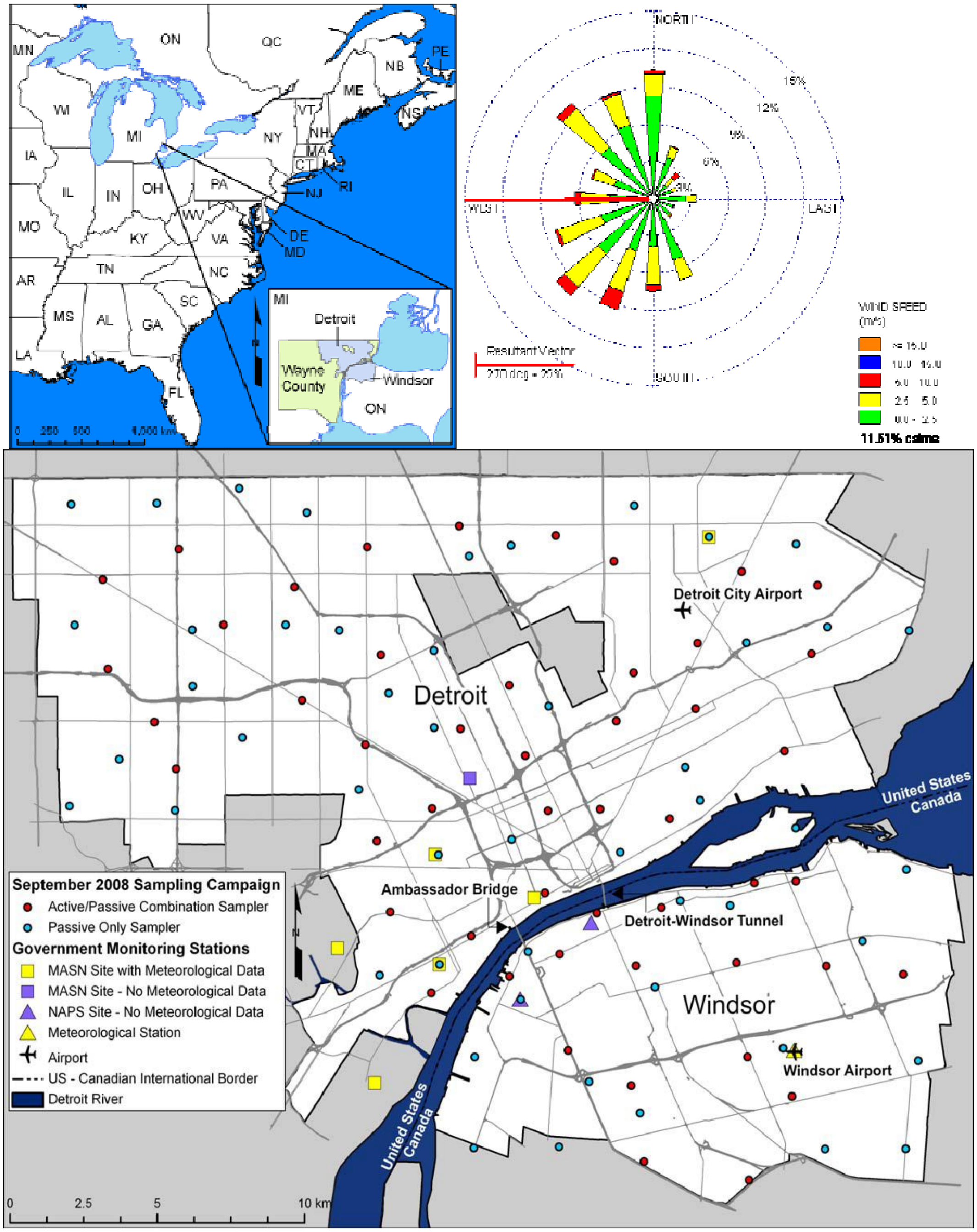

Figure 3.1. Study area showing the location of sample points, long-term monitoring stations, meteorological stations, major roads and expressways in Detroit and Windsor, and wind rose with calms excluded from resultant vector during the September 5-20, 2008 study period.

Both Detroit and Windsor are classified as high pollution zones, largely due to industrial and transportation emissions (Health Canada, 2000; Simon et al., 2005; MDEQ, 2009; USEPA, 2009). Consequently, air quality in both cities has received much attention in recent years. For example, the Detroit Exposure and Aerosol Research Study (DEARS) compared selected air pollutant concentrations measured at one community air monitoring station to those measured in six Detroit neighborhoods (Williams et al., 2008). One aim of DEARS was to evaluate the applicability of air toxic data collected at centralized monitoring sites to studies of health outcomes in neighborhoods affected by multiple sources of air pollutants. In Windsor, recent studies have examined the spatial distributions of air toxics related to land use and proximity to the Ambassador Bridge (Luginaah et al., 2006; Wheeler et al., 2008). The results of these studies are being used to assess the health impacts of air pollutants in Detroit and Windsor. However, air quality has not been addressed simultaneously in both cities since the early 1950s (Clayton et al., 1952). Although there have been numerous air quality studies in Detroit and Windsor, differences in their timing and sampling methodologies complicate efforts to combine or compare results in both cities.

Currently, the Michigan Department of Environmental Quality (MDEQ) operates seven ambient air quality monitoring stations in the vicinity of Detroit (MDEQ, 2009) (Fig. 3.1). In Windsor, two long-term monitoring sites are operated by the Ontario Ministry of the Environment (Environment Canada, 2001). Although these stations provide measurements of criteria pollutants and selected air toxics at some stations, their widely-spaced distribution across an urban area spanning 500 km^2 limits their utility for defining local-scale spatial variability in ambient air quality that can influence environmental health at a neighborhood scale (Touma et al., 2006; Corburn, 2007; Cocheo et al., 2008). Such intra-urban scale spatial variability has been documented in other cities (e.g., Jerrett et al., 2007; Atari et al., 2008; Miller et al., 2009) and is useful for epidemiological assessments quantifying differential exposures of individuals and communities with varying demographics or environmental risk factors within large urban areas (Wilson et al., 2005; Zou et al., 2009).

This study has been undertaken to investigate concentration levels and intra-urban spatial variability within the Detroit-Windsor international airshed. To this end, a simultaneous ambient air quality sampling event was undertaken in both cities during September, 2008. This study is part of a larger research project initiated by the Geospatial Determinants of Health Outcomes Consortium (GeoDHOC), a multidisciplinary, international effort aimed at improving understanding of air pollution health effects in urban environments (Weglicki et al., 2009). The central premise motivating the group's efforts is that if variability within and between Detroit and Windsor can be established, then the influence of differing population demographics, environmental regulations, and health care delivery systems on health outcomes for residents of the two cities can be investigated. Thus, an essential goal of the study is to develop a basis to assess human exposure to a suite of ambient air toxics at the neighborhood scale in both cities. An important question is whether a single spatial model of variability can be developed to include both cities or if individual models will be required to characterize ambient air quality in either city.

The specific objectives of the investigation were to: 1) simultaneously measure pollutant concentrations at 100 sites throughout Detroit and Windsor for a two-week period; 2) analyze correlation statistics within and between the two cities to evaluate contributions of common emission sources and potential contaminant measurement proxies; and 3) determine the spatial variability of pollutant concentrations within and between the two cities and begin to evaluate whether a single, unified approach can be used to model the distribution of airborne contaminants in both cities.

3.2 Experimental Methods

3.2.1 Field Campaign

Figure 3.1 shows the international study area with the locations of the field monitors, long-term air monitoring stations, and weather stations used in this study. A combination of active and passive air sampling devices was deployed for a two-week period during September 2008, at 100 sites in Windsor and Detroit (Table 3.1).

Table 3.1. Distribution of samplers.

Site	Pollutant	Windsor	Detroit	Total
Active	PM, PAH, NO_2, SO_2, VOCs	16	34	50
Passive Only	NO_2, SO_2, VOCs	16	34	50
Total		32	68	100

Time-integrated passive samples were collected for nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and volatile organic compounds (VOCs), at all 100 sites. Integrated active measurements of polycyclic aromatic hydrocarbons (PAHs) and particulate matter (PM) in three size fractions: PM_1, $PM_{1\text{-}2.5}$, and $PM_{2.5\text{-}10}$ microns were collected at a subset of 50 sites (hereafter referred to as active sites). The remaining 50 sites are hereafter referred to as passive only sites. Monitors were deployed from September 5-19, 2008 at active sites and September 6-20, 2008 at passive only sites.

3.2.2 Site Selection

A multi-criteria allocation model was used to determine the number and location of active and passive samplers deployed throughout each city. The total number of active samplers (50) was constrained by the availability of pumps and filter housings. A 3x3 km grid was established over both cities to investigate the distribution of suitable sampler locations. Locations were prioritized based on proximity to grid cell centroids while taking into consideration other factors such as the surrounding population density. Samplers were allocated in proportion to the approximate 2.5:1 ratio of land area between Detroit and Windsor. Placement of 34 samplers in Detroit and 16 samplers in Windsor (Table 3.1) resulted in an average spatial distribution of one active sampler per 10 km^2.

Fifty additional passive samplers were deployed in the same ratio as active samplers between Detroit and Windsor at positions chosen to complement active sampler locations. The final deployment of 100 samplers resulted in an approximate distribution of one passive sampler per 5 km^2 across the study area. Location coordinates were measured and recorded with global positioning systems for all monitoring sites.

3.2.3 Instrumentation

The methods employed for passive monitoring include Ogawa Samplers (Ogawa & Co. USA, Inc., Pompano Beach, FL, USA) for NO_2 and SO_2, and 3M #3500 organic vapor samplers (Guillevan, Montreal) for VOCs. At passive only sites, the monitors were installed on light poles with permission of the City of Detroit and EnWin Utilities in Windsor at a height of 3 m to prevent contamination and vandalism from pedestrians. Stainless steel rain shelters were used to protect the samplers from inclement weather.

At active sites, PM was measured using Harvard Cascade Impactors (Harvard University, Boston, MA) at a flow rate of 5.0 liters per minute (LPM). The three-stage Impactor collects PM_1 on a Teflon filter, and $PM_{1-2.5}$ and $PM_{2.5-10}$ on individual Polyurethane Foams (PUF). Vapor and particle phase PAHs were collected using URG personal pesticide samplers (Model URG-2000-25AB, URG, Chapel Hill, NC). With an operational flow rate of 2.0 LPM, the cutpoint of these samplers is 2.5 µm. Target flow rates for PM and PAH samples were obtained and maintained using an adjustable manifold and an SKC Leland Legacy sampling pump (SKC Inc., Eighty Four, PA) powered via an AC adapter. Flows were measured at both instrument setup and take down using research grade flow meters.

In field deployment, the PM and PAH samplers were enclosed in weatherproof cases where the pump, manifold, and adapter were also housed. The inlets of the samplers projected downward to minimize sample contamination by insects and precipitation. The sampling ensemble also included a shelter (identical to that in passive only sampling) attached to the exterior of the instrument case, to protect the NO_2, SO_2 and VOC samplers. Whenever feasible, active samplers were deployed at a height of 3 m above the ground on downspouts, fences, or freestanding poles. In some instances, tripod mounts were used at a height of 1.5 m above ground or above rooftop surfaces. All 100 sample locations were coded to distinguish between samplers deployed at ground (3 m or less) or elevated heights (greater than 3 m), and by site classification: i.e. active vs. passive only.

3.2.4 Laboratory Analysis of Samples

The analysis of the 3M and PAHs samples was conducted by Airzone One (Mississauga, Ontario) using gas chromatography/mass selective detector with species dependent detection limits. Twenty-six VOCs were determined (Appendix 3A). For PAH samples, 16 PAHs and seven pesticides were determined (Appendix 3A). A multi-point calibration curve ($r^2 \geq 0.99$) was used and the results were corrected with laboratory blanks and standards. The NO_2 and SO_2 samples were analyzed by Environment Canada (Egbert, Ontario) using ion chromatography. The amount of mass collected on the PM filters, which were conditioned before and after sampling, was determined using gravimetric analysis with a lab detection limit of 4 µg/filter, by the Alberta Research Council (Vegreville, Alberta).

3.2.5 QA/QC

Five percent of the passive samples were field duplicates, which were used to assess the method consistency. Field blanks, which constituted 5% of total VOC samples and 10% of total samples of other types, were deployed to quantify the sample mass attributable to handling and transportation. All NO_2 and SO_2 concentration results were corrected using the field blanks. For other analytes, no field blank corrections were necessary because the field blank values were either below laboratory method detection limits (PM and VOCs) or close to laboratory blanks (PAHs).

3.2.6 Data Screening and Analysis

Samples from individual sites were deemed invalid if physical damage, tampering, pump failure, or contamination was noted. Acceptable flow rates were required to fall within +/-20% of target rates and pump run times required to exceed 80% of the sampling period. Laboratory-reported values falling below the laboratory detection limits were replaced with ½ of the method detection limit. Individual species were excluded from further analysis when fewer than 80% of sites registered values above laboratory detection limits or when field blanks exceeded three times filter batch blanks.

Using lab-reported values, BTEX (benzene, toluene, ethylbenzene, and xylene), total VOC, and total PAH concentrations were calculated. Only species with measured values above lab detection limits at 80% or more of the sampling sites were included in the total VOC and total PAH summations.

General statistics were calculated for the entire study area and each individual city. Distributions of each pollutant were investigated using an Anderson-Darling test to validate the applicability of parametric methods. Correlation coefficient matrixes were developed to investigate pollutant associations and toluene:benzene (T/B) ratios were computed to evaluate the contribution of mobile emission sources to overall concentrations.

3.2.7 Meteorological Information

Hourly wind, barometric pressure, temperature, and relative humidity data from seven Detroit and Windsor meteorological stations (Fig. 3.1) were averaged to generate a combined data set for the study area. Hourly precipitation data were recorded at the Detroit City Airport in the central portion of the study area (Fig. 3.1). HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model 4 (Draxler and Rolph, 2003) was used to construct backward trajectories from the sampling area. Forty-eight hour backward trajectories were modeled for each day from September 5-20, 2008. The results were analyzed to identify air mass directions for regional scale and transboundary movement of pollutants.

3.2.8 Mapping of Airborne Contaminants

Simple inverse distance weighted maps were produced to illustrate spatial variability and identify the locations of high and low values within the dataset. Spatial variability of each constituent was examined further using variogram analysis and ordinary kriging to construct a set of interpolated maps that account for autocorrelation among neighboring data points. Omnidirectional experimental semivariograms (Remy et al., 2009) were generated for the entire dataset and separately for Detroit and Windsor using a 1000 m lag and a 500 m lag tolerance. Spherical models were fitted to the experimental variograms with the exception of total BTEX and total VOCs for the entire dataset, for which exponential models were employed. The nugget effect, which accounts for uncertainty attributable to short-scale spatial variability and measurement uncertainty, can have a significant influence on the agreement between interpolated (i.e., kriged) maps and measured points (Isaaks and Srivastava, 1989). Nugget variances were estimated using measurement uncertainty associated with duplicate samples for NO_2 and VOCs, following Cocheo et al. (2008). Nugget variances for PM and PAHs were estimated by extrapolating the variograms for each species back to a zero lag distance. Ordinary kriging was employed to allow for nonstationarity of the mean within local search areas across the study domain (Goovaerts, 1997). Concentration maps were constructed both for the entire data set and independently for Detroit and Windsor.

3.3 Results and Discussion

3.3.1 Meteorological Conditions

Meteorological conditions during the two-week sampling period were compared with historical meteorological conditions for the month of September. Temperature conditions were typical. The 19.1ºC sampling period mean temperature was slightly greater than the 18ºC 50-year historical average for the same period. Recorded precipitation was atypical. Average daily rainfall during the two-week period (7.3mm) exceeded the historical daily rainfall (3.0mm). Nevertheless, washout of airborne pollutants was judged to be minor because precipitation at the Detroit City Airport was only recorded during 44 of 384 hours (11.5 % of the study period) with most (78%) precipitation falling during 14 hours when rainfall exceeded 2mm/h.

The Detroit-Windsor airshed has a flat topography with elevations ranging from 175-200m and a continental climate influenced by the Great Lakes. Conditions that normally influence atmospheric stability such as the temperature and wind profiles should be similar in both cities. However, a greater number of freeways and associated overpasses and underpasses along with a greater concentration of tall buildings in downtown Detroit may contribute to different diffusion parameters in the two cities or within different segments of the same cities.

Following the initial sampler deployment on September 5, 2008, the study area was affected by high pressure systems moving in from the northwest. Approximately one week into the study, air masses flowing from the southwest became dominant as a low pressure system associated with the remnants of Hurricane Ike crossed the study area on September 13 and 14, accounting for approximately 80% of the study period rainfall. High pressure air masses moved in from the northwest during the remainder of the sampling period. Local wind directions (Fig. 3.1) reflect the synoptic pattern of air movement, with prevailing winds from the northwest-southwest during the two-week study period.

HYSPLIT backward trajectories indicate cross border air movement from Detroit to Windsor on 10 days, from Windsor to Detroit on 3 days, and parallel to the border between the cities on 3 out of 16 days during the study period. Furthermore, air masses arrived from regions with known pollution sources in Illinois, Indiana, Ohio, Pennsylvania, and New York during 11 out of 16 days, suggesting that long range transport of air pollutants was also important.

3.3.2 Data Exclusion

Data from individual sample sites were excluded on the basis of suspected tampering, physical damage, or anomalous pump readings (Table 3.2). One NO_2 sample was excluded for suspected tampering because the VOC sampler was vandalized at that site. One VOC sample was excluded due to a tear in the protective membrane and an additional NO_2 sample was excluded due to an anomalously high reading falling beyond the 75th percentile plus 20 times the interquartile range.

Table 3.2. Sampler retrieval and retention rates.

Pollutant	Planned and Deployed	Retrieved	Lost or Excluded	Included for Analysis	% Retained
NO_2	100	99	2	98	98
VOC	100	100	2	98	98
PAHs	50	50	12	38	76
PMs	50	50	12	38	76

PM and PAH data from two active sites were excluded on the basis of end flow rates outside of allowable tolerances. Data from 10 additional active sampling sites were excluded because pump run times were less than 80% of the sampling period. These insufficient pump run times resulted from widespread power outages experienced in Detroit during the sampling period.

SO_2 was excluded based on observed large variability of field duplicate measurements and high field blank values. The percent difference between duplicate samples ranged from 1.5 to 62% with an average of 25%. The field blanks registered values two to ten times higher than the filter batch blanks.

Species with fewer than 80% of sites registering values above lab detection limits were also excluded. This resulted in the exclusion of 12 of 26 VOC analytes and 16 of 23 PAH and pesticide analytes (Appendix 3A). The retained PAHs have relatively low molecular weights (i.e., four or fewer rings) and thus are likely to have been preferentially sampled from the vapor phase (Tonne et al., 2004).

3.3.3 General Statistics

Anderson-Darling test results indicated normal or near normal distributions for all species examined. Parametric tests were therefore used in statistical analysis, including Analysis of Variance (ANOVA) for comparison of means and Pearson correlation coefficients. When considering the entire sample set, comparisons by sampling method (active vs. passive) were not significantly different, indicating that sampling methodology did not bias the results. Comparison by sampling height (ground vs. elevated) did show that ground level concentrations of PM_1, BTEX, and VOCs were higher (15%, 30% and 28% respectively, statistically significant at $p<0.05$), indicative of significant contribution from ground level sources such as vehicle emissions.

A statistical summary of pollutant concentrations measured at the included sites is reported in Table 3.3. Among the seven pollutants, the coefficient of variation (CV) ranged from 14.2% for PM_{10} to 68.3% for total PAHs. The CV was higher in Windsor than Detroit for NO_2, total PAH, and $PM_{1\text{-}2.5}$, and comparable for other species in the two cities.

Table 3.3. Statistical summary of pollutants concentrations, for both cities combined (all) as well as for individual cities.

Pollutant (unit)	Sites	N	Mean	SD	CV (%)	Min	Med	Max
NO_2 (ppb)	All	98	15.3	2.9	19.2	7.3	15.7	25.2
	Detroit	66	16.5	2.4	14.3	11.6	16.6	25.2
	Windsor	32	12.8	2.4	19.0	7.3	12.7	16.7
Total VOC (µg/m^3)	All	98	13.8	5.7	41.1	3.8	13.8	46.6
	Detroit	66	16.0	5.4	34.0	4.3	15.2	46.6
	Windsor	32	9.3	2.8	30.0	3.8	9.1	14.9
Total BTEX (µg/m^3)	All	98	8.9	3.9	44.6	1.0	8.9	30.9
	Detroit	66	10.3	3.8	37.3	1.0	9.6	30.9
	Windsor	32	5.9	2.1	35.5	2.2	5.7	10.2
Total PAH (ng/m^3)	All	38	20.1	13.7	68.3	3.3	19.3	53.5
	Detroit	23	26.9	12.4	46.1	4.1	24.9	53.5
	Windsor	15	9.5	7.6	79.6	3.3	6.1	28.5
PM_1 (µg/m^3)	All	38	5.6	0.8	14.2	2.7	5.5	7.4
	Detroit	23	5.9	0.6	11.0	4.7	5.9	7.4
	Windsor	15	5.1	0.7	14.0	2.7	5.2	6.1
$PM_{2.5\text{-}10}$ (µg/m^3)	All	38	5.1	2.2	42.5	0.6	4.8	13.0
	Detroit	23	5.6	2.3	40.4	3.9	5.1	13.0
	Windsor	15	4.5	1.8	40.4	0.6	4.2	7.6
$PM_{1\text{-}2.5}$ (µg/m^3)	All	38	2.1	1.3	60.9	0.02*	1.9	7.8
	Detroit	23	2.1	0.4	19.0	1.7	2.1	3.1
	Windsor	15	2.1	2.0	94.8	0.02*	1.7	7.8

* minimum values reported at ½ detection limit values

The mean concentrations of all species except $PM_{1-2.5}$ are higher in Detroit than in Windsor; these differences were observed to be statistically significant ($p<0.05$), with the exception of $PM_{1-2.5}$. The difference is especially pronounced in the total VOCs (16.0 vs. 9.3 $\mu g/m^3$), BTEX (10.3 vs. 5.9 $\mu g/m^3$), and PAHs (26.9 vs. 9.5 $\mu g/m^3$), suggesting that a greater amount of emissions are released in Detroit than in Windsor for these species.

Of the 14 VOCs selected, 11 had measured values that were higher in Detroit than in Windsor ($p<0.05$). The mean value of total VOCs was also significantly higher in Detroit (16.0 vs. 9.3 $\mu g/m^3$ in Windsor). This may be due to the larger amount of point source emissions and traffic volume in the Detroit area. In both cities, the BTEX compounds comprise similar percentages of total VOCs (64% in Detroit and 63% in Windsor) and toluene had the highest concentration of the 14 species.

For NO_2 and PM, differences between the two cities are smaller. Because NO_2 and PM_1 are largely attributed to mobile emissions, it appears that both sides of the border experience similar effects due to border crossing traffic and other mobile sources.

3.3.4 Correlations and Ratios among Pollutants

Overall Correlations

Correlation coefficient matrixes are listed in Table 3.4. For the study area, NO_2 was correlated with PAH, BTEX, total VOC and $PM_{2.5-10}$. The two smaller size fractions of PM are also correlated (r>0.5, Table 3.4a). Previous investigators (Brook et al., 1997; Lam et al., 1999) have suggested that NO_2 may be used as a proxy for $PM_{1-2.5}$ or $PM_{2.5-10}$ based on positive correlations among these species observed in other cities where both NO_2 and PM are attributable to traffic sources. The correlation analysis suggests that one might be able to use NO_2 as a proxy for total VOC and PAH as well.

Table 3.4a. Correlation coefficients (combined and for individual cities) of active sites.

		Total PAHs	**Total VOC**	**BTEX**	**NO$_2$**	**PM$_{1-2.5}$**	**PM$_{2.5-10}$**
Both Cities (N=38)	Total VOCs	**0.472**					
	BTEX	**0.459**	**0.992**				
	NO$_2$	**0.603**	**0.529**	**0.521**			
	PM$_{1-2.5-10}$	0.018	-0.020	-0.056	0.160		
	PM$_{2.5-10}$	0.305	0.147	0.139	**0.555**	0.099	
	PM$_1$	**0.332**	0.193	0.156	**0.400**	0.150	**0.679**
Detroit (N=23)	Total VOCs	0.111					
	BTEX	0.108	**0.992**				
	NO$_2$	0.314	0.232	0.259			
	PM$_{1-2.5}$	0.262	-0.052	-0.026	**0.592**		
	PM$_{2.5-10}$	0.211	-0.036	-0.011	**0.561**	**0.909**	
	PM$_1$	0.185	-0.103	-0.105	0.255	0.702	**0.728**
Windsor (N=15)	Total VOCs	**0.663**					
	BTEX	**0.672**	**0.913**				
	NO$_2$	**0.435**	**0.545**	**0.408**			
	PM$_{1-2.5}$	-0.068	-0.049	-0.246	0.135		
	PM$_{2.5-10}$	0.048	0.024	-0.140	0.364	-0.193	
	PM$_1$	-0.309	**-0.546**	**-0.636**	-0.062	0.065	**0.540**

Bold number indicates significant at $p < 0.05$.

Table 3.4b. Correlation coefficients (combined and for individual cities) of samples at passive only sites.

		Total VOC	**BTEX**
Both Cities (N=48)	BTEX	**0.973**	
	NO$_2$	**0.652**	**0.627**
Detroit (N=32)	BTEX	**0.949**	
	NO$_2$	0.332	0.255
Windsor (N=16)	BTEX	**0.968**	
	NO$_2$	**0.550**	**0.588**

Bold number indicates significant at $p < 0.05$.

Table 3.4c. Correlation coefficients (combined and for individual cities) of all passive samplers.

		Total VOC	**BTEX**
Both Cities (N=98)	BTEX	**0.986**	
	NO_2	**0.514**	**0.496**
Detroit (N=66)	BTEX	**0.985**	
	NO_2	0.214	0.214
Windsor (N=32)	BTEX	**0.962**	
	NO_2	**0.507**	**0.490**

Bold number indicates significant at $p < 0.05$.

In Detroit, moderately positive correlations were observed between NO_2 and $PM_{1\text{-}2.5}$ and $PM_{2.5\text{-}10}$ (0.59 and 0.56, respectively). The three PM size fractions were highly positively correlated with each other, whereas in Windsor only the two smallest PM fractions were correlated. In Windsor, moderate positive correlations were also observed between total VOCs and NO_2 as well as total VOCs and total PAHs (0.55 and 0.66, respectively). Past studies have observed similar correlations and attributed their origin to common sources (e.g., Miller et al., 2009).

The anticipated PM_1 and NO_2 association, due to fuel combustion such as traffic emissions as the common source, was weak in the overall dataset ($r=0.400$, $p<0.05$) and was not significant in either city. Moreover, there were negative correlations between PM_1 and BTEX (-0.636, $p<0.05$), and VOC and PM_1 (-0.564, $p<0.05$) in Windsor, which was unexpected. Further investigation by residual analysis identified a PM_1 outlier at one of the Windsor sties. After its removal, PM_1 and NO2 were correlated in Windsor ($r=0.590$, $p<0.05$) and the correlation between PM_1 and VOC ($r=0.157$, $p=0.591$), PM_1 and BTEX ($r=0.114$, $p=0.699$) were insignificant. Nonetheless, the lack of strong correlation between NO_2 and PM, particularly in Detroit, suggests that PM absorbance instead of PM mass might be a better marker of primary emissions (e.g., Lewné et al., 2004). The correlation between NO_2 and VOC did not change significantly when the dataset included all passive samplers (Tables 3.4b and 3.4c). This finding indicates that the passive only sites served to improve the spatial resolution from 10 km^2 to 5 km^2, but did not alter the relationship between NO_2 and VOCs.

Differences in correlations between pollutants were observed in Detroit and Windsor. Such differences were expected because of the differences in the mix of pollution sources and the complexity of major roadways in the two cities. However, some significant correlations observed in the overall dataset (e.g. NO_2 and PAH) were not present in either city. These observations call into question the application of urban-scale correlations to smaller intra-urban areas, as well as the applicability of correlations observed in one city to adjacent cities, particularly across international borders.

Correlations Among the BTEX group

Table 3.5 lists the correlation coefficients among the BTEX group of VOCs. Across the entire study domain, there were positive correlations observed among the BTEX, consistent with previous studies (Pankow et al., 2003; Khoder, 2007; Hoque et al., 2008). All BTEX correlation coefficients in Detroit exceeded 0.92, indicating a strong contribution from mobile sources. Windsor showed moderate to strong correlations among the BTEX group. In contrast to Detroit and the aforementioned studies, however, toluene and benzene were not well correlated in Windsor. Correlations between toluene and other species in the BTEX group were also low, primarily due to relatively high toluene concentrations at a few sites, suggesting that, in Windsor, both mobile and other sources including industrial emitters potentially contributed to benzene and/or toluene emissions.

Table 3.5. Pearson correlation coefficients between the BTEX group (all significant at $p<0.05$).

		Benzene	**Toluene**	**Ethyl-benzene**	**(m+p)-Xylene**	**o-Xylene**	**Total VOC**
Both Cities **(N=98)**	Toluene	0.826					
	Ethylbenzene	0.925	0.858				
	(m+p)-Xylene	0.935	0.833	0.989			
	o-Xylene	0.951	0.837	0.980	0.992		
	Total VOC	0.954	0.921	0.959	0.954	0.957	
	BTEX	0.943	0.949	0.968	0.962	0.964	0.986
Detroit **(N=66)**	Toluene	0.937					
	Ethylbenzene	0.937	0.932				
	(m+p)-Xylene	0.924	0.922	0.993			
	o-Xylene	0.928	0.931	0.990	0.993		
	Total VOC	0.961	0.974	0.959	0.947	0.951	
	BTEX	0.964	0.983	0.979	0.974	0.978	0.984
Windsor (N=32)	Toluene	0.496					
	Ethylbenzene	0.690	0.529				
	(m+p)-Xylene	0.675	0.535	0.985			
	o-Xylene	0.762	0.563	0.986	0.975		
	Total VOC	0.749	0.845	0.834	0.838	0.850	
	BTEX	0.691	0.923	0.808	0.813	0.833	0.962

Toluene:Benzene Ratios

Toluene:benzene (T/B) ratios have been used to evaluate the extent to which measured concentrations can be attributed to vehicle exhaust emission sources based on the chemical make up of exhaust and the fuel burning characteristics (Hoque et al., 2008). Previous studies have found T/B ratios in the range of 1.3 – 4.8 and have indicated that when T/B ratios fall between 1.3-3.0, the majority of the toluene and benzene contribution can be attributed to mobile emissions (Gelencsr et al., 1997; Heeb et al., 2000; Khoder, 2007; Hoque et al., 2008).

The means and distributions of the T/B ratios (both and individual cities) are presented in Figure 3.2. The mean ratios observed fell within the range reported in previous investigations mentioned above. In Detroit the majority of sites (59/66) fell within the 1.3-3 range. Therefore, toluene and benzene concentrations in Detroit can be largely attributed to traffic sources. In contrast, only 3 (9%) of the 32 Windsor sites fell within the same range, with higher toluene concentrations attributable to local point sources. This may also explain the low correlations among toluene and the rest of the BTEX group (Table 3.5). The large difference in T/B ratios between the two neighboring cities suggests the need for further investigation of local toluene sources in the Windsor area.

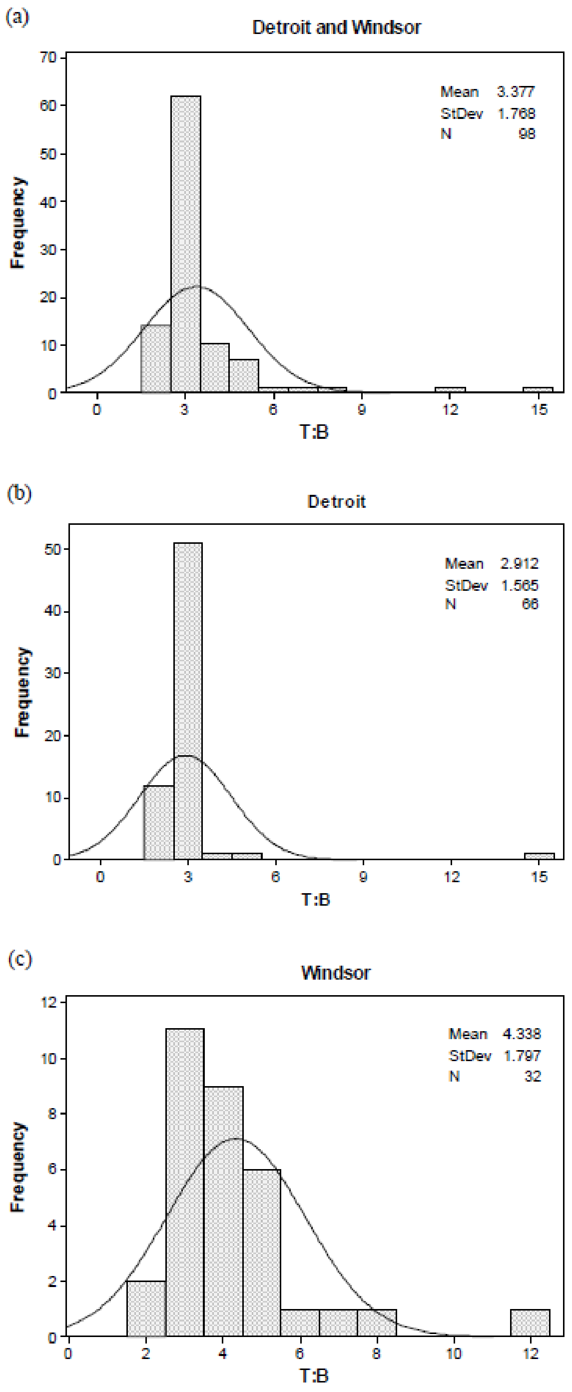

Figure 3.2. Histograms representing the toluene:benzene ratios in (a) Detroit and Windsor, (b) Detroit, and (c) Windsor.

3.3.5 Spatial Variability

The study domain encompasses 38 PM and PAH as well as 98 NO_2 and VOC measurement points across the cities of Detroit and Windsor with gross dimensions of 24 x 30 km (Fig. 3.1). Variograms and variogram models for NO_2, total VOC, total BTEX, total PAH, PM_1 and $PM_{2.5-10}$ are presented in Figure 3.3. Experimental variograms depict the average dissimilarity of data points as a function of a specified separation or lag distance. Variogram models (i.e., mathematical functions fitted to the experimental data) smooth sample fluctuations and provide a means of specifying autocovariance values at any required lag distance (Goovaerts 1997). In practice, variograms are customarily plotted for lag distances up to half the sampled domain to avoid data irregularities associated with a diminishing number of data pairs at large lag distances.

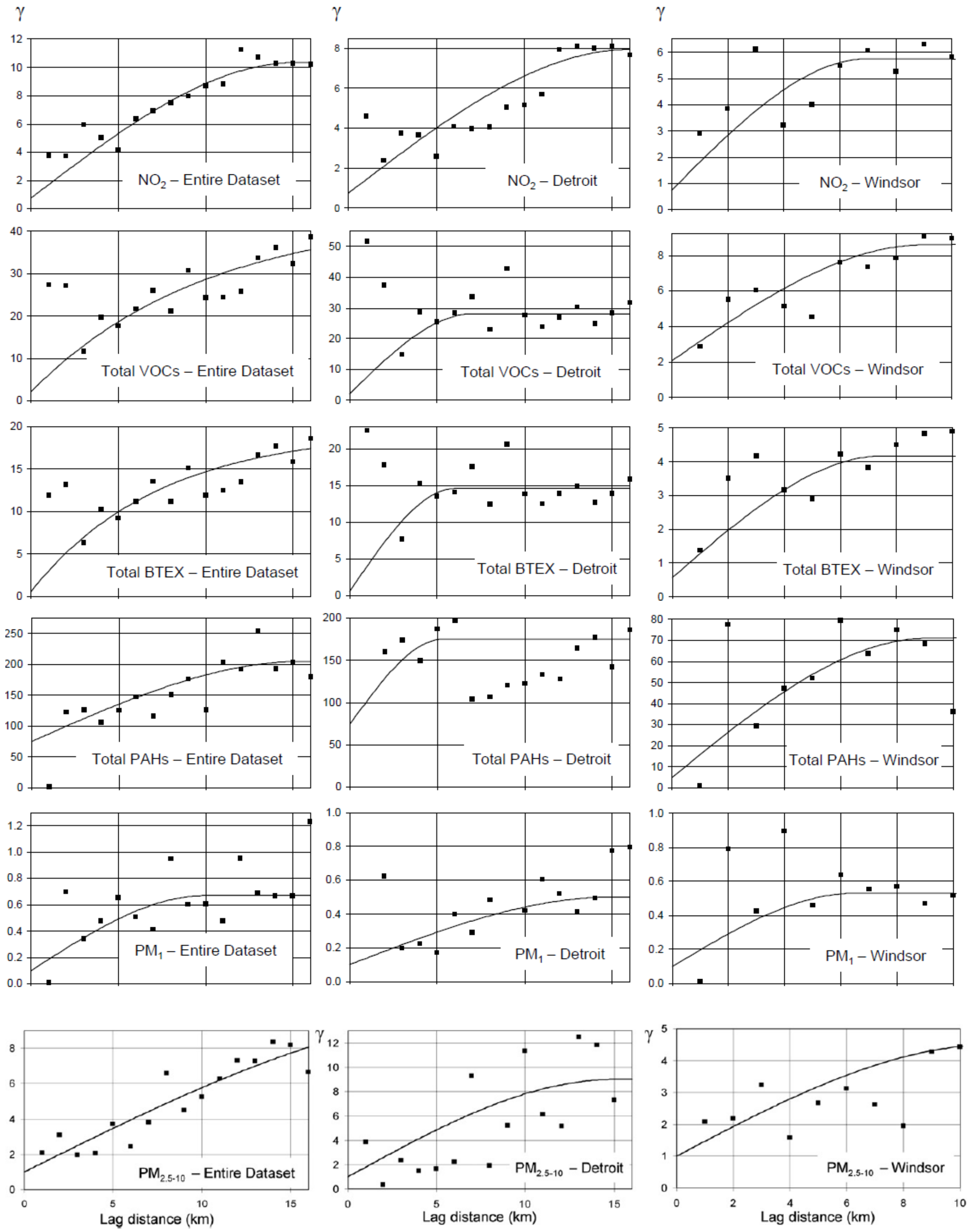

Figure 3.3. Omnidirectional experimental semivariograms (points) and variogram models (lines) by contaminant species and area.

In this study, variograms constructed using the entire dataset for total VOCs, total BTEX, and $PM_{2.5-10}$ exceed the sample variance at large lag distances and fail to reach a sill at lag distances equivalent to the extent of the model domain (Fig. 3.3). Experimental variogram sills for NO_2, total PAHs, and PM_1 also exceed the sample variance. These behaviors suggest the presence of a trend in the data (Goovaerts, personal communication, 2009). Consequently, independent variogram models were constructed for Detroit and Windsor to explore potential differences in spatial variability between the two cities (Fig. 3.3). Table 3.6 lists variogram model parameters for each of the six constituents addressed here. In most cases (NO_2, VOC, PM_1, and BTEX), variogram models for the individual cities were better defined using segregated data than combining measurements from both cities. This observation further supports the supposition of a trend in observed concentrations that may be related to the statistically different mean values observed in both cities (Table 3.3).

Table 3.6. Omnidirectional variogram model parameters.

Pollutant	**Sites**	**Model**	**Nugget**	**Range (km)**	**Sill**	**Standardized Slope (x10^{-5})**
NO_2	All	Spherical	0.75	15.2	9.6	9.0
	Detroit	Spherical	0.75	16.0	7.2	8.4
	Windsor	Spherical	0.75	7.0	5.0	17
Total VOC	All	Exponential	2.1	30.0	42	8.2
	Detroit	Spherical	2.1	7.0	26	19
	Windsor	Spherical	2.1	9.0	6.5	12
Total BTEX	All	Exponential	0.57	22.0	19	10
	Detroit	Spherical	0.57	6.0	14	22
	Windsor	Spherical	0.57	7.5	3.6	16
Total PAH	All	Spherical	75	15.6	130	5.9
	Detroit	Spherical	75	5.28	100	14
	Windsor	Spherical	5.0	9.12	66	15
PM_1	All	Spherical	0.1	10.0	0.57	12
	Detroit	Spherical	0.1	15.0	0.4	7.9
	Windsor	Spherical	0.1	6.5	0.43	17
$PM_{2.5-10}$	All	Spherical	1.0	27.0	9.0	5.0
	Detroit	Spherical	1.0	15.0	8.0	8.8
	Windsor	Spherical	1.0	11.2	3.5	10
$PM_{1-2.5}$	All	Spherical	1.0	6.0	1.2	13
	Detroit	Spherical	0.01	30.0	4.0	4.9
	Windsor	Spherical	1.0	8.0	3.8	14

To facilitate relative comparisons of spatial variability among the contaminants examined here, each variogram model was normalized to its sill variance. This process is analogous to the calculation of coefficients of variation for multiple contaminant species measurements by normalizing each standard deviation to its respective mean. The slope of each standardized variogram model, exclusive of the nugget contribution, over a lag distance of zero to 3 km (the notional sample grid spacing) can then be compared (Table 3.6). The magnitude of the standardized slope reflects the rate at which concentration measurements approach their maximum variance or sill over short distances. Thus, steeper slopes indicate greater spatial variability whereas shallower slopes indicate greater spatial continuity among observational data at short distance scales (Isaaks and Srivastava, 1989).

The population of NO_2 measurements from the two-week samples in September, 2008, has a lower coefficient of variation in the Detroit subset than in the Windsor data (Table 3.3). Comparison of variogram model values such as the range and the standardized slope confirms that spatial variability for NO_2 is greater in Windsor.

For total BTEX and total VOCs, the coefficient of variation for both constituents is greater in Detroit than in Windsor (Table 3.3). Smaller variogram ranges and steeper standardized slopes (Table 3.6) indicate that spatial variability is also greater in Detroit than Windsor for both total BTEX and total VOCs.

Variogram models for PAHs and PMs are less well constrained because there are fewer available measurement points with which to construct experimental variograms (Table 3.2). The coefficient of variation is greater in Windsor for PM_1 and $PM_{1\text{-}2.5}$ but the same for $PM_{2.5\text{-}10}$ (Table 3.3). Nevertheless, spatial variability is arguably greater in Windsor for all size fractions based on variogram characteristics (Table 3.6). Results for PAHs are mixed, however. A higher coefficient of variation is observed in Windsor, whereas the smaller variogram model range indicates that spatial variability is greater in Detroit. The standardized slope is equivalent for both cities, indicating that the relative degree of spatial variability is similar in Windsor and Detroit.

3.3.6 Patterns in Spatial Distribution

Spatial trends are observable in concentration maps made with inverse distance weighting (Fig. 3.4) and ordinary kriging (Fig. 3.5) for all pollutant species except for $PM_{1\text{-}2.5}$ (not shown). The spatial distribution of NO_2 concentrations suggests a correlation with mobile sources and, in particular, with the areas surrounding the Ambassador Bridge on both sides of the US-Canada border. Sampling sites in central and southwestern Detroit recorded the highest NO_2 concentrations with a maximum of 25.2 ppb near the freeway leading to the Ambassador Bridge. Concentrations drop below 15 ppb toward the eastern and western edges of the city and throughout Windsor except in the area of the border crossings where NO_2 concentrations of 16.7 ppb were observed nearest the Ambassador Bridge and the Detroit-Windsor Tunnel entrance. Concentrations above 15 ppb were also observed at stations along the major thoroughfare to the Ambassador Bridge and streets between the approaches to the Bridge and Tunnel. In Detroit, ongoing Gateway Project construction may have contributed to high concentration measurements for NO_2 and PM in the vicinity of the Ambassador Bridge. This two-year project (Feb 2008 – Dec 2009) involves reconstruction of portions of two interstate freeways at the approach to the Ambassador Bridge in Detroit.

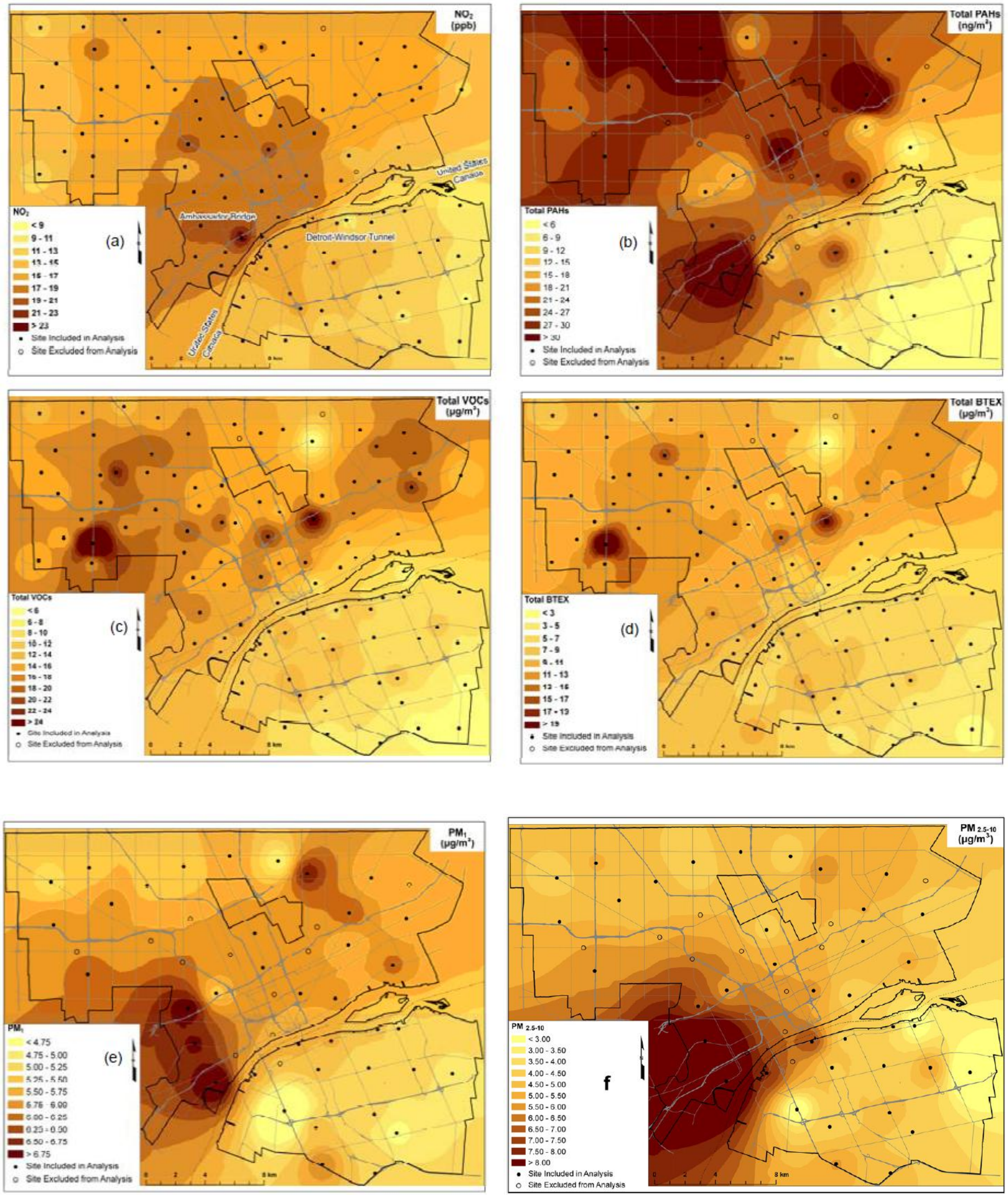

Figure 3.4. Concentrations maps interpolated using inverse distance weighting: a) NO$_2$, b) Total PAHS, c) Total VOCs, d) Total BTEX, e) PM$_1$, and f) PM$_{2.5-10}$.

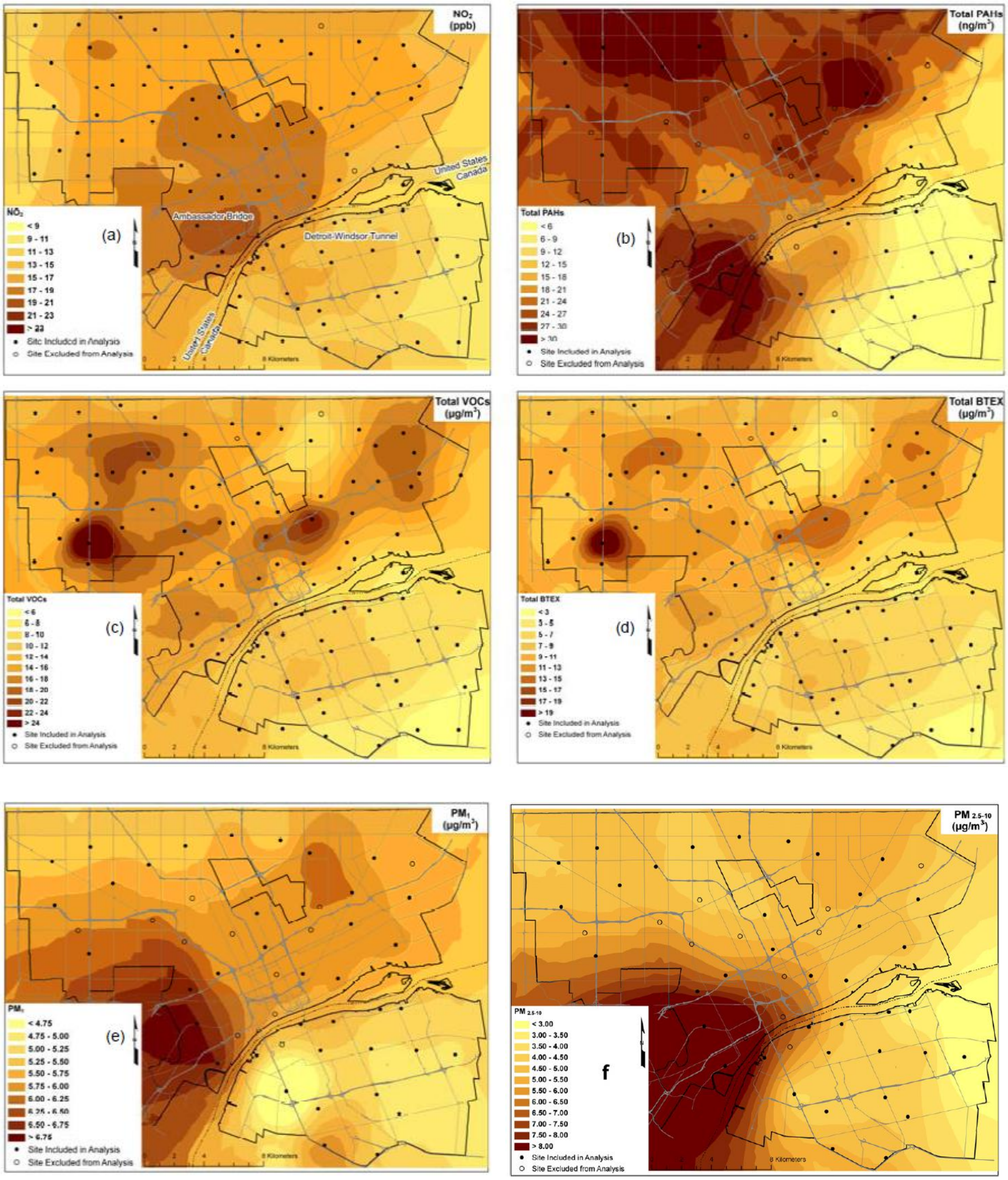

Figure 3.5. Concentration maps interpolated using ordinary kriging and omnidirectional variogram models: a) NO_2, b) Total PAHs, c) Total VOCs, d) Total BTEX, e) PM_1, and f) $PM_{2.5\text{-}10}$.

The distribution of total BTEX and total VOCs were similar. Both showed spatial map patterns with high concentrations corresponding to dense major roadways and strong statistical correlations to NO_2 (Table 3.4), indicative of mobile sources. On the other hand, greater spatial variability of VOCs and BTEX was observed in Detroit, whereas greater spatial variability was observed for NO_2 in Windsor, raising questions about the suitability of adopting NO_2 as a universal proxy for BTEX or VOCs in the study area.

The total PAH concentrations were much higher throughout Detroit, leading to a mean value of 26.9 ng/m^3 which was more than 2.5 times higher than in Windsor (9.5 ng/m^3, Table 3.3). This suggests a higher density or strength of point sources in Detroit than in Windsor.

Across the study area, PM_1 and $PM_{2.5\text{-}10}$ distributions differed. PM_1 exhibited greater localized spatial variability compared to $PM_{2.5\text{-}10}$. This is because PM_1 originates as both primary emissions from local combustion sources, as well as secondary organic aerosols produced from photochemical reactions. In contrast, long range transport of $PM_{2.5\text{-}10}$ may be significant. Southwestern Detroit had the highest levels of PM_1 and $PM_{2.5\text{-}10}$ with observed concentrations ranging up to 7.4 and 13 μg/m^3, respectively. This observation could be partially explained by the high density of industrial sources (petroleum refinery, coal fired power plant, auto factory, etc.) in southwest Detroit.

Although positive statistical correlations were observed between NO_2 and PM in Detroit (Table 3.4a), suggesting they are both originating from traffic sources, the association is not obvious on the maps (Figs. 3.4 and 3.5). For example, the highest NO_2 concentrations are found adjacent to the Ambassador Bridge, whereas the highest PM concentrations were found farther west, suggesting their association with point sources in southwestern Detroit. Furthermore, $PM_{2.5\text{-}10}$ exhibits a regional trend with concentrations decreasing away from southwest Detroit. The plume shaped pattern suggests local source contributions in southwest Detroit that are not reflected in the NO_2 concentration map. The analysis of spatial trends therefore raises questions about whether statistical correlation alone is enough to warrant the use of NO_2 as a proxy for these compounds in air quality modeling and air toxic exposure estimates.

3.3.7 Study Significance and Limitations

This study is, to the best of our knowledge, the first comprehensive intra-urban air quality investigation in an international airshed. In addition to NO_2, which is traffic-related, pollutants with multiple sources including SO_2, VOCs, PAHs, and three size fractions of PM were also measured simultaneously using identical methods in Detroit and Windsor. This provides a unique opportunity to understand the similarity and differences between the two neighboring cities in terms of concentration levels, spatial distributions, and species associations. The incorporation of both active and passive only sampling sites is also unique, which allows for a cost effective method to sample several pollutants over a large spatial area.

Sampling across an international boundary gives rise to numerous technical and logistical challenges. These include standardization of training, field, and laboratory operations, movement of equipment through customs, and the need for effective communication among international study participants. Nevertheless, the value of collecting a synchronous set of air quality measurements in two countries should make the dataset beneficial for subsequent epidemiological studies that are underway in Detroit and Windsor.

There are several important limitations to this study, however. Seasonal variability could not be addressed using a single sampling event. Moreover, the availability of a limited number of samplers coupled with budget constraints resulted in sampling densities of one site per 5 (passive only) to 10 (active) km^2 across the 500 km^2 study area. This degree of coverage is more widely spaced than a density of one site per 3.4 km^2 for BTEX and NO_2 sampling in urban settings recommended by Cocheo et al. (2008). Consequently, analysis of spatial variability at short scales, for example 100 m or less, as documented for NO_2 (e.g., Hewitt, 1991) and ultra fine particles (Zhu et al., 2002), could not be evaluated because the minimum distance between samplers in this study was approximately 2 km. The inclusion of additional sampling locations in strategically located positions during future air sampling campaigns will help to ameliorate some of these limitations. Finally, the inverse distance weighting and ordinary kriging spatial interpolation methods applied herein are relatively crude. Potential anisotropies in the spatial variability of contaminant species associated with predominant wind directions or the orientation of major roadway systems can be addressed in future studies.

3.4 Conclusions

Pollutant concentrations were measured simultaneously at 100 sites throughout Detroit and Windsor during a two-week period in September, 2008. The measurements reported here demonstrate spatial variability at a scale of 3 km which is not possible to discern using the present day network of widely-spaced air monitors. Higher concentrations of all species observed in Detroit are attributable to the greater amount of emissions in Detroit compared to Windsor.

High correlation coefficients were observed among similarly sourced air toxics across the Detroit-Windsor airshed. In Detroit, NO_2 was strongly correlated with $PM_{1-2.5}$ and $PM_{2.5-10}$. In Windsor, the strongest correlations were observed between NO_2 and VOCs, and total PAH (primarily in the vapor phase) and total VOCs. Correlations with NO_2 indicate a significant contribution from mobile sources which is consistent with the high percentage contribution of on-road sources of air toxics reported for Wayne County (US EPA, 2009), where Detroit is located. In Detroit, this conclusion is reinforced by the observed range of toluene:benzene ratios, which is consistent with traffic sources for these species.

Differences in the degree of correlation were observed in Detroit and Windsor, which reflect differences in the volume and composition of emissions between the two cities. In fact, the only consistent correlations observed in both cities were between PM_1 and $PM_{2.5-10}$. This observation suggests that pollutant correlations, and thus source identification, found in one city may not be applicable in a neighboring city, particularly when such cities are separated by an international border. Similarly, separate analysis of the correlation among pollutants in sub-regions may be required to reveal intra-urban variability in air pollution sources within large metropolitan areas.

Furthermore, statistical correlations between NO_2 and other contaminants may not provide sufficient justification for the indiscriminate use of NO_2 as a proxy for those contaminants. Such application may mask important differences related to smaller scale spatial variability that are not reflected in broader population statistics. For example, greater spatial variability was observed for NO_2 in Windsor, whereas the degree of spatial variability of BTEX and VOCs was greater in Detroit. In addition, there is a lack of consistency between mapped spatial trends of different pollutants across the Detroit-Windsor airshed. Consequently, a simple mapping of NO_2 to BTEX or VOCs is unlikely to reproduce this observed behavior.

This paper reports important findings in the concentration levels and spatial trends of air toxics in the Detroit-Windsor airshed, which will be used to support forthcoming analyses of the relationship between asthma and ambient air quality in each city. To address the need for exposure estimates at finer scales, efforts are underway to develop land use regression (LUR) models that can be used to investigate relationships between ambient concentrations and environmental factors such as traffic density and distance to major roads. In addition, air dispersion modeling is planned. LUR and dispersion modeling efforts are expected to provide additional insight into the question of whether unified models developed for the airshed can reproduce the observed differences in the magnitude and spatial variability of air toxics in Detroit and Windsor, or whether such modeling efforts will need to be conducted independently in each city.

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Appendix 3A

Table 3.A1. Volatile organic compounds with percent of sites registering values above variable method detection limits.

VOC Analyte	% Total (N=98)
(m+p)-Xylene	100%
Dichloromethane	100%
Toluene	100%
1,2,4-Trimethylbenzene	99%
Benzene	99%
Ethylbenzene	99%
Hexane	99%
o-Xylene	99%
n-Decane	98%
1,3,5-Trimethylbenzene	97%
Trichloroethylene	97%
Chloroform	90%
Tetrachloroethylene	81%
Naphthalene	80%
1,4-Dichlorobenzene	69%
a-Pinene	59%
d-Limonene	48%
1,2-Dichloroethane	27%
p-Cymene	3%
Cumene	2%
1,1,2,2-Tetrachloroethane	0%
1,2,4-Trichlorobenzene	0%
1,3-Dichlorobenzene	0%
Hexachloroethane	0%
Pentachloroethane	0%
Styrene	0%

Table 3.A2. Polycyclic aromatic hydrocarbon and pesticide species with percent of sites registering values above variable method detection limits.

PAH Analyte	% Total (N=38)
Anthracene	100%
Fluoranthrene	100%
Fluorene	100%
Phenanthrene	100%
Pyrene	100%
Acenaphthene	97%
ortho-Phenylphenol*	84%
Diazinon*	66%
Chrysene	58%
Acenaphthylene	50%
Benz(a)anthrancene	21%
Chlorpyrifos (Dursban)*	21%
Benz(k)fluoranthene	3%
Benzo(b)fluoranthrene	3%
Benzo(a)pyrene	0%
Benzo(ghi)perylene	0%
cis-Permethrin*	0%
Dibenz(a,h)anthracene	0%
Indeno(123-cd)pyrene	0%
Piperonyl butoxide*	0%
Propoxur (Baygon)*	0%
trans-Permethrin*	0%
Naphthalene**	0%

* pesticide

** excluded due to high backgrounds in sampling media

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CHAPTER 4: A COMPARISON OF RESULTS FROM TWO SAMPLING CAMPAIGNS OF AIR TOXICS IN WINDSOR AND DETROIT TAKING PLACE IN SEPTEMBER 2008 AND MAY 2009

4.1 Introduction

Air sampling was conducted during September 5th – 20th 2008 in Windsor, Ontario, (Canada) and Detroit, Michigan (USA). The results were previously published (Miller et al., 2010, Miller et al., 2012a) and presented in Chapter 3 of this thesis. A second sampling campaign was carried out from May 29th – June 13th, 2009 by the GeoDHOC team. The following is a comparison between the results from these two air sampling campaigns. Full descriptions of experimental methods as well as an introduction to this component of the GeoDHOC study and acknowledgements can be found in the preceding manuscript (Chapter 3). The methodology and the majority of sites were consistent between the two years, therefore the comparison between the two years will highlight factors that resulted in differences in the concentrations of measured pollutants such as changes in industrial emissions between the two years, or differing meteorology since sampling was conducted in different seasons. Several methods will be used to uncover the relationships between the concentrations and possible reasons of some discrepancy between the two campaigns.

The overall objective of this report is to present the results from the 2009 sampling campaign and compare these to the 2008 campaign while determining what was consistent between the two years and what varied. This will lead to some conclusions as to what new knowledge was gained from the second round of sampling and which factors resulted in variability between the two rounds of sampling.

The specific objectives are:

- To present the general statistics of the 2009 sampling campaign
- To determine whether the pattern of which city experienced higher concentrations was the same for both campaigns
- To determine which year saw higher concentrations for each of the pollutants (by each city and overall)

- To compare correlations and ratios between the two campaigns and relate these to potential emission changes
- To determine if site classifications (by equal tertiles) were preserved between the two campaigns
- To determine the correlations between sites and identify potential outlying sites

4.2 Methods

The second air sampling campaign was conducted during May 29th – June 13th, 2009 in Windsor, Ontario and Detroit, Michigan using the same experimental methods as those from the September 5th – 20th, 2008 campaign (Chapter 3) in the same cities. Sample locations were kept the same between the two periods, with the exception of one active site in Windsor and 5 passive sites in Detroit which were relocated for logistical reasons. Some additional passive sites were used for specific investigations; those data were excluded from this analysis. Data exclusions were based on the same criteria and resulted in the retention of samples as shown in Table 4.1. Laboratory and data analysis as well as QA/QC measures were kept the same between each year. Species exclusions, based on the same criteria as in 2008, resulted in 11 VOC analytes and 9 PAH analytes (See Tables 4.A1 and 4.A2 in Appendix 4A).

Table 4.1. Sampler retrieval and retention rates (2009, compare to Table 3.2).

Pollutant	Planned and Deployed	Retrieved	Lost or Excluded	Included for Analysis	% Retained	Included in paired t-test
NO_2	100	100	6	94	94	88
VOC	100	100	1	99	99	92
PAHs	50	50	13	37	74	26
PM	50	50	12	38	76	26

Methods for the determination of general statistics, 2-sample t-test between the two cites, correlations, and ratios are the same as explained in Chapter 3. The tables and figures that summarize the concentrations and correlations are presented similarly to those found in Chapter 3 for comparison purposes. Additional analysis includes cross correlation plots of the pollutants which are provided in Appendix 4B.

To assess the agreement between the concentrations measured at the same site in both years, Pearson correlation analysis and paired t–tests were conducted with sites which had data for both years. Four out of the six replacement sites were more than 50 m away from the corresponding 2008 sites, thus excluded from the comparison analysis. The remaining two sites were kept since the test results did not change regardless of their inclusion. Table 4.A3 in Appendix 4A explains specifically which sites were used for calculation of general statistics as well as which were included in the paired t-test. Scatter plots of the concentrations between the two years were generated and examined to identify sites which deviated significantly from the regression line. Another method used for comparison was site classifications. The sites in each city were split into high, medium, or low categories (equal tertiles) based on their measured concentrations of BTEX, total VOCs, and NO_2. This was repeated for both years and the classifications were compared to determine whether or not they were preserved between the two years.

4.3 Results and Discussion

4.3.1 Meteorological Conditions and Air Mass Movement

Mixed results regarding seasonal variability of air pollutants have been reported in the literature (Hansen and Palmgren, 1996; Pankow et al., 2003; Ho et al., 2004) with no clear conclusion being drawn as to whether higher or lower concentrations should be expected in one season over another. Nonetheless, comparison of meteorological conditions between the two sampling periods was undertaken to assess whether changes in concentrations may potentially be related to drastically changing weather conditions.

Analysis of the meteorological conditions in Windsor for the 2009 campaign showed slightly lower typical precipitation (mean = 1.9 mm/day) as well as mean temperatures (16.3°C) when compared to long term (30 year) averages (mean precipitation = 2.9 mm/day, mean temperature = 20.1°C) for that time of year (Environment Canada, 2011a). The 2009 temperature is slightly cooler than the mean temperature of 19.1°C during the

2008 campaign. The two-week rainfall was much higher during the 2008 sampling period (128 mm) than in 2009 (27 mm), however, the majority of the 2008 rainfall can be attributed to one day during the sampling where 75 mm of rain was reported. More importantly, rain was reported on 7 out of the 16 possible sampling days during both campaigns.

Similar to the 2008 results, HYSPLIT modelling revealed Detroit to Windsor cross border transport of air mass on the majority of the days (12/16) during which the sampling took place and during both sampling periods the air mass direction was predominantly southwest. Even though the two campaigns were conducted during different seasons, some of the meteorological characteristics known to influence pollutant concentrations were similar. Furthermore, since both campaigns took place during transition seasons (fall and spring) the concentrations obtained are more likely to be comparable and representative of annual averages, as was previously shown for VOCs (Chapter 6) and $PM_{2.5}$ (Zhao et al., 2009).

4.3.2 General Statistics, Correlations and 2008-2009 Comparison

Individual species with at least 80% of sites registered values above laboratory detection limits as described in Chapter 3, were included in the general statistics. For paired t-tests, the 2008 total VOC values were re-calculated to include only those species that were also included in 2009 (see Table 4.A1 in Appendix 4A). Comparing with Table 3.A1 in Chapter 3, a few major changes are noted for VOCs; firstly n-decane and chloroform were registering at the majority of sites in 2008 whereas at under 20% in 2009, secondly dichloromethane registered at 100% of sites in 2008 and 82% of sites in 2009, lastly naphthalene registered at 99% of sites in 2009 and at 80% in 2008. When comparing PAHs, the 2009 values were re-calculated to include only those species that were also included in 2008 (see Table 4.A2 in Appendix 4A). Comparing with Table 3.A2 in Chapter 3 a few major changes are also noted for PAHs; naphthalene had no measurements above the MDL in 2008 whereas in 2009 81% of sites registered a measurement, sites registering chlorpyrifos (dursban) were much higher in 2009 (95%) than 2008 (21%), where as 84% of sites registered ortho-Phenylphenol in 2008 but only

65% in 2009. Even though ortho-Phenylphenol was below 80% in 2009 it was included for comparison since it met the criteria in 2008 and was close in 2009.

The concentration highs and lows were found to be similar between the two sampling campaigns (Table 4.2). As with 2008, the 2009 campaign observed higher concentrations in Detroit, statistically significant (two sample t-test) for all except PM_1 and $PM_{1-2.5}$. Comparison of means and the results from paired t-tests of the sites that were at common locations and had data between the two years reveal that for both cities combined total VOC and BTEX the concentrations were significantly higher in 2008. For NO_2 and $PM_{1-2.5}$ the differences in concentrations between the two sampling campaigns were not significant. For total PAHs, PM_1, and $PM_{2.5-10}$ the concentrations were significantly higher in 2009. These differences can also be seen visually in Figure 4.1. This pattern was the same for BTEX, VOCs, and PM_1 when looking at each city individually. Windsor results show a statistically lower value of NO_2 and higher value of PAHs in 2009. Higher $PM_{1-2.5}$ and $PM_{2.5-10}$ were also observed in Windsor although not significant based on paired t-tests. In Detroit, statistically higher values of all PM fractions were observed in 2009 whereas although PAHs were higher in 2009 the difference was not significant based on the paired t-test. These mixed results may be attributed to changes in industrial activities between the two sampling campaigns or due to meteorology since the campaigns took place in different seasons. The consistent NO_2 concentrations may be linked to consistent vehicle traffic in both cities since NO_2 is largely attributable to mobile emissions. Also similar between the two years is the high CV for PAHs. Unlike in 2008, all 2009 concentrations reported in Table 4.2 were above MDL.

Table 4.2. Statistical summary of pollutant concentrations (2009), for both cities combined (all) and for individual cities. General statistics include all above MDL, paired t-test include only those which are the same for 2008. Year 2008 total VOC and total PAHs include only those species that were also included in 2009. (Compare to Table 3.3).

Pollutant (units)	**Sites**	**N**	**Mean**	**SD**	**CV (%)**	**Min.**	**Med.**	**Max.**	**Skewness**
NO$_2$ (ppb)	All	93	15.2	3.8	24.6	7.7	15.3	27.1	0.4
	Detroit	64	16.8	3.1	18.5	10.9	16.4	27.1	0.9
	Windsor	29	11.8*	2.5	21.2	7.7	11.4	15.5	0.1
Total VOC (µg/m^3)	All	98	7.7*	3.0	38.1	2.7	7.8	15.7	0.4
	Detroit	67	9.3*	2.4	25.4	3.9	9.1	15.7	0.7
	Windsor	31	4.6*	1.1	24.8	2.7	4.6	7.5	0.4
Total BTEX (µg/m^3)	All	98	5.5*	2.2	40.1	1.8	5.6	11.7	0.5
	Detroit	67	6.6*	1.8	26.8	2.9	6.4	11.7	0.8
	Windsor	31	3.2*	0.9	27.0	1.8	3.1	5.6	0.6
Total PAH (ng/m^3)	All	37	**33.5***	27.3	81.7	7.9	28.3	149.8	2.7
	Detroit	26	34.9	19.7	56.4	11.8	31.0	98.7	1.7
	Windsor	11	**30.2***	41.3	136.8	7.9	16.3	149.8	2.9
PM$_1$ (µg/m^3)	All	38	**7.0***	1.0	14.0	5.7	6.8	9.9	1.5
	Detroit	27	**7.1***	0.9	12.9	5.7	6.9	9.9	1.4
	Windsor	11	**6.7***	1.1	16.6	5.8	6.3	9.7	2.3
PM$_{1\text{-}2.5}$ (µg/m^3)	All	38	2.5	0.5	21.2	1.8	2.4	4.9	2.6
	Detroit	27	**2.6***	0.3	12.9	2.0	2.5	3.2	0.5
	Windsor	11	2.4	0.9	36.0	1.8	2.2	4.9	2.9
PM$_{2.5\text{-}10}$ (µg/m^3)	All	38	**6.3***	1.5	23.9	3.9	6.1	10.8	1.3
	Detroit	27	**6.7***	1.5	22.5	5.0	6.4	10.8	1.5
	Windsor	11	5.4	1.11	20.5	3.9	5.2	7.2	0.45

*significantly different (sites which had data for both years) from the 2008 values at $p<0.05$, higher in 2008, **higher in 2009**.

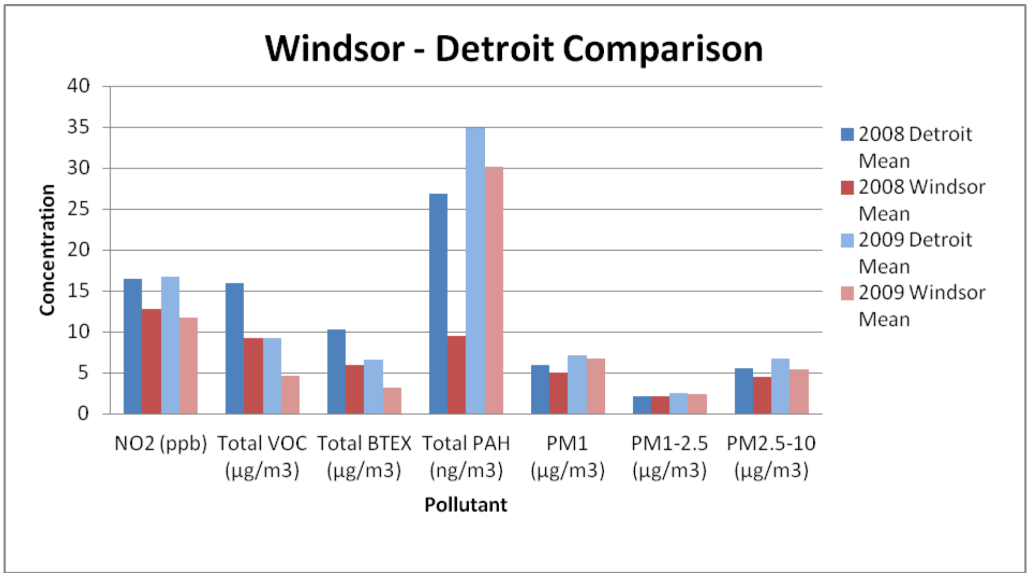


Figure 4.1. Bar graph of mean concentrations of all pollutants for each city in both years**.**

Some similarities were also observed in the correlations between pollutants, as seen in Tables 4.3 and 4.4. For both cities, significant correlations were observed between total VOCs and BTEX, between NO_2 and $PM_{2.5\text{-}10}$, as well as between PM_1 and $PM_{2.5\text{-}10}$ in both years. The significant correlations observed between the total PAHs and VOCs, BTEX, and NO_2 in 2008 were not observed in 2009. This suggests that the major sources of PAHs may have changed between years. For Detroit only, all of the significant correlations observed in 2008 were also observed in 2009 with the addition of those between NO_2 and total VOCs and BTEX. For Windsor only, correlations between total PAHs and total VOCs, total PAHs and BTEX, VOCs and NO_2, and BTEX and NO_2, were observed in both years, however some differences were observed between correlations with particulate matter. The weak correlations between PAHs and all other pollutants in Detroit and between PAHs and NO_2 and the PM size fractions in Windsor was further explored by looking at the cross correlation plots between these species (Fig 4.B1 and Fig 4.B2). A high degree of scattering was observed in these cases therefore explaining the lack of strong correlations. Similarly, cross correlations between the PM size fractions (Fig 4.B3 and 4.B4) in each city showed scattering as well as some outlying sites.

Considering the passive only sites, in 2008 significant correlations were observed between total VOC, NO_2, and BTEX for both cities and Windsor, however not for Detroit. In 2009 these significant correlations were observed for all (both cities, Windsor, and Detroit) although the strength of the NO_2 Detroit only correlations were lower than that for both cities and Windsor only. The same result described above was the case for the correlations between all passive samplers; all significant in 2009, whereas in 2008 there was no significant correlation between NO_2 and total VOC nor BTEX. Looking specifically at the correlations between the BTEX group, similar results were seen in both years with all correlations being significant and ranging from 0.496-0.993 in 2008 and from 0.754-0.993 in 2009. In both years the lowest correlation value was observed between benzene and toluene in Windsor, suggesting that these species originate from mobile and additional sources as discussed in Miller et al. (2011). Cross correlation plots of the BTEX species (Fig 4.B5) confirmed approximately linear relationships.

Table 4.3a. Correlation coefficients (combined and for individual cities, 2009) of active sites. Bold number indicates significant at $p < 0.05$. (Compare to Table 3.4a).

		Total PAHs	**Total VOCs**	**BTEX**	**NO$_2$**	**PM$_1$**	**PM$_{1-2.5}$**	**PM$_{2.5-10}$**
Both Cities	**Total VOCs**	0.293						
N = 38	**BTEX**	0.280	**0.994**					
	NO$_2$	0.226	**0.729**	**0.710**				
	PM$_1$	0.063	0.272	0.302	0.085			
	PM$_{1-2.5}$	0.048	0.146	0.169	0.174	**0.748**		
	PM$_{2.5-10}$	0.308	**0.409**	**0.410**	**0.616**	**0.384**	**0.625**	
Detroit	**Total VOCs**	0.358						
N = 27	**BTEX**	0.351	**0.992**					
	NO$_2$	0.259	**0.392**	**0.370**				
	PM$_1$	0.134	0.237	0.284	0.034			
	PM$_{1-2.5}$	0.266	0.101	0.133	**0.463**	**0.588**		
	PM$_{2.5-10}$	0.384	0.163	0.169	**0.599**	0.211	**0.795**	
Windsor	**Total VOCs**	**0.637**						
N = 11	**BTEX**	**0.718**	**0.904**					
	NO$_2$	0.401	**0.592**	**0.519**				
	PM$_1$	-0.021	0.270	0.381	-			
	PM$_{1-2.5}$	-0.054	0.172	0.313	-	**0.971**		
	PM$_{2.5-10}$	0.300	0.502	0.549	0.336	**0.792**	**0.725**	

Table 4.3b. Correlation coefficients (combined and for individual cities, 2009) of samples at passive only sites. All significant at $p < 0.05$. (Compare to Table 3.4b).

		Total VOC	**BTEX**
Both Cities	**BTEX**	0.994	
N = 45	**NO$_2$**	0.726	0.723
Detroit	**BTEX**	0.990	
N = 31	**NO$_2$**	0.476	0.459
Windsor	**BTEX**	0.983	
N = 14	**NO$_2$**	0.891	0.892

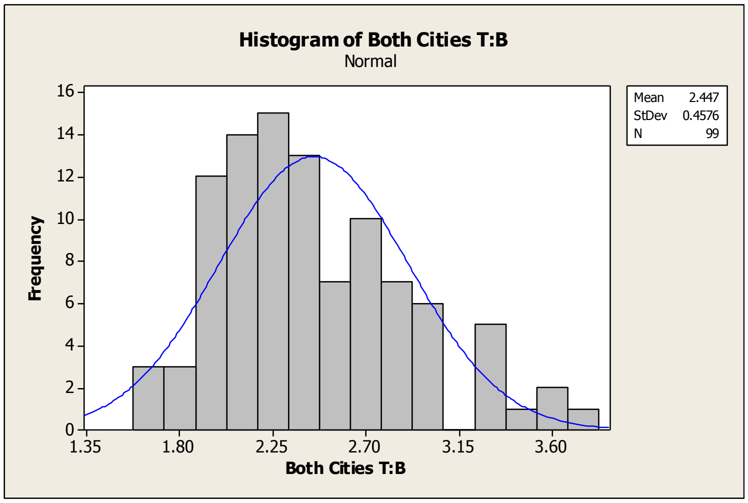
Table 4.3c. Correlation coefficients (combined and for individual cities, 2009) of all passive samplers. All significant at $p < 0.05$. (Compare to Table 3.4c).

		Total VOC	**BTEX**
Both Cities	**BTEX**	0.993	
N = 93	**NO_2**	0.724	0.706
Detroit	**BTEX**	0.991	
N = 64	**NO_2**	0.441	0.413
Windsor	**BTEX**	0.942	
N = 29	**NO_2**	0.761	0.721

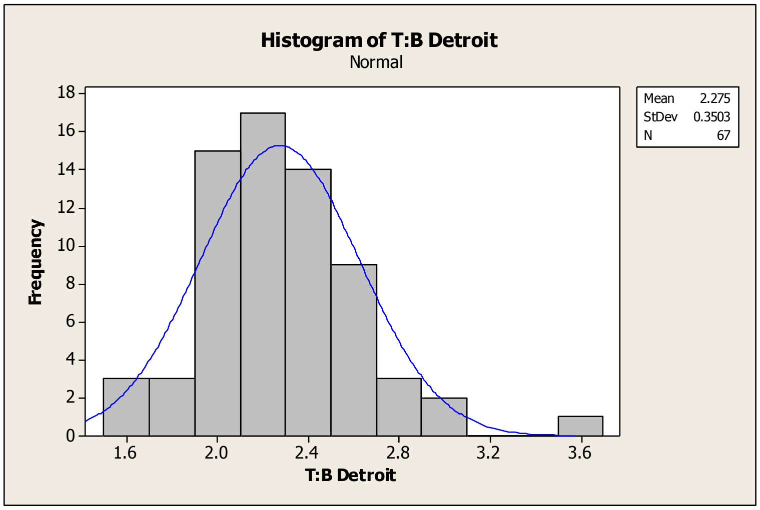
Table 4.4. Pearson correlation coefficients between the BTEX group (2009, all significant at $p < 0.05$). (Compare to Table 3.5).

		Benzene	**Toluene**	**Ethylbenzene**	**(m+p)-Xylene**	**o-Xylene**	**Total VOC**
Both	**Toluene**	0.904					
N = 98	**Ethylbenzene**	0.917	0.969				
	(m+p)-	0.890	0.972	0.990			
	o-Xylene	0.902	0.971	0.987	0.993		
	Total VOC	0.941	0.983	0.980	0.976	0.979	
	BTEX	0.937	0.990	0.989	0.988	0.988	0.993
Detroit	**Toluene**	0.821					
N = 67	**Ethylbenzene**	0.838	0.941				
	(m+p)-	0.784	0.948	0.981			
	o-Xylene	0.799	0.943	0.976	0.988		
	Total VOC	0.870	0.977	0.967	0.962	0.962	
	BTEX	0.875	0.984	0.979	0.978	0.976	0.991
Windsor	**Toluene**	0.752					
N = 31	**Ethylbenzene**	0.790	0.936				
	(m+p)-	0.764	0.940	0.983			
	o-Xylene	0.759	0.952	0.975	0.982		
	Total VOC	0.806	0.924	0.905	0.914	0.924	
	BTEX	0.828	0.980	0.978	0.980	0.980	0.942

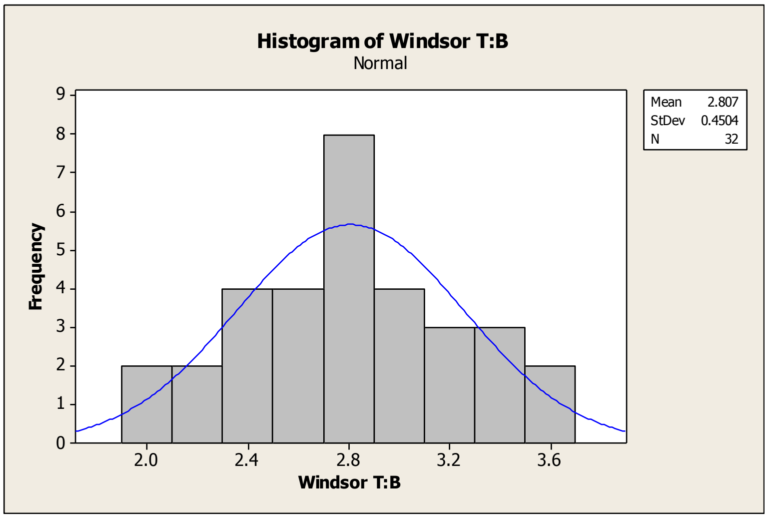
Similar to 2008, the T/B ratios were higher in Windsor than Detroit (Table 4.2 and Figure 4.2), however overall the ratios were significantly lower in 2009 than in 2008. This difference was more pronounced for Windsor (2.81 vs. 4.34) than for Detroit (2.28 vs. 2.91) and both cities (2.47 vs. 3.38). The observation of lower overall T/B ratios is consistent with other studies which have observed higher ratios in the warmer months and lower in the cooler months (Chattopadhyay et al., 1997; Ho et al., 2004; Hoque et al., 2008), although the temperature was only ~3°C cooler in the 2009 campaign. All three mean ratios are within the range commonly attributed to mobile emissions (1.3-3.0) whereas in 2008 only Detroit fell within this range. That toluene and benzene are related to mobile sources is not unexpected since both cities are subjected to vehicular emissions from the Ambassador Bridge and other roads. The distribution of the ratios changed between the two years (Figure 4.2d). Although both years follow a normal distribution, the spread was narrower in 2009 than in 2008. This is also seen for each city individually. This further suggests more consistent traffic emissions and less influence of point sources.


Histogram of Both Cities T:B
Normal
Mean 2.447
StDev 0.4576
N 99
Frequency
0
2
4
6
8
10
12
14
16
1.35
1.80
2.25
2.70
3.15
3.60
Both Cities T:B

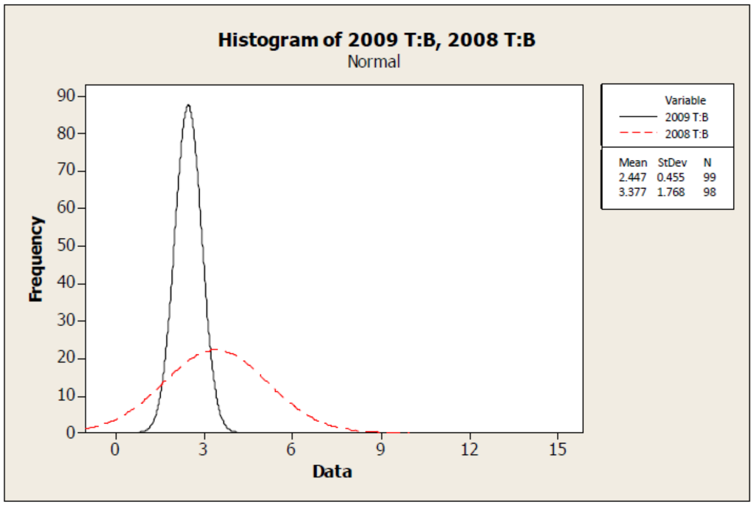
(a)


Histogram of T:B Detroit
Normal
Mean 2.275
StDev 0.3503
N 67
Frequency
0
2
4
6
8
10
12
14
16
18
1.6
2.0
2.4
2.8
3.2
3.6
T:B Detroit

(b)



(c)



(d)

Figure 4.2. Histograms representing toluene:benzene ratios in (a) Detroit and Windsor, (b) Detroit, (c) Windsor, and d) normal fit of distribution 2008/2009 both cities (Compare to Figure 3.2).

The reason for the more pronounced difference in Windsor may be due to changes in point source emissions of toluene as industrial activities in Windsor experienced some declines during the period of 2008 to 2009.

The lower T/B ratios along with the improvement in the correlation between toluene and benzene in Windsor in 2009 (0.752 vs. 0.496) suggests changes in source contributions of

one or both of those species. Since the majority of benzene emissions are from vehicular sources, the change in ratios and correlations point to a difference in toluene emissions between the two sampling periods. The mean toluene concentration observed in 2009 was less than half of the concentration in 2008 (1.52 vs. 3.17µg/m3).
The lower toluene concentration in 2009 was also confirmed by consulting the National Air Pollution Surveillance website (Environment Canada, 2011b) and considering the measured toluene concentrations on the three days closest to the sampling campaigns. For 2008, the average concentration was 2.70 µg/m^3 whereas for 2009 it was 1.57µg/m^3. This confirms that there was a significant reduction in toluene concentrations during the 2009 sampling.

The annual toluene emissions in Windsor (as reported to the National Pollutant Release Inventory (NPRI) (Environment Canada, 2011c)) were not significantly different between the two years (26 tonnes in 2008 vs. 22 tonnes in 2009), nor were the annual average concentrations of toluene (1.92 µg/m^3 vs. 1.75 µg/m^3) and benzene (0.78 µg/m^3 vs. 0.76 µg/m^3) measured at NAPS (Environment Canada, 2011b) however when considering the time period of the sampling, toluene concentrations were lower in 2009 by a factor of 2. The results of this study suggest that annual point source emissions as well as annual averages obtained from a central station could be a poor indicator of short term concentrations since factors affecting concentrations can vary across the course of a year.

The general relationships in concentrations and correlations remained the same between the two sampling periods. Concentrations were generally higher in Detroit, T/B ratios higher in Windsor, strong and consistent correlations were observed among the BTEX group as well as between BTEX, VOCs, and NO_2. In terms of absolute values some differences were observed between the two years in measured concentrations as well as in the ratios, especially for T/B in Windsor.

4.3.3 Site Classification and Correlations Between Common Sites

Site classification, based on a high / medium / low categorization (equal tertiles) remained fairly consistent between the two years. Table 4.5 depicts the percentage of sites which fall within the same classification category between the two years for BTEX,

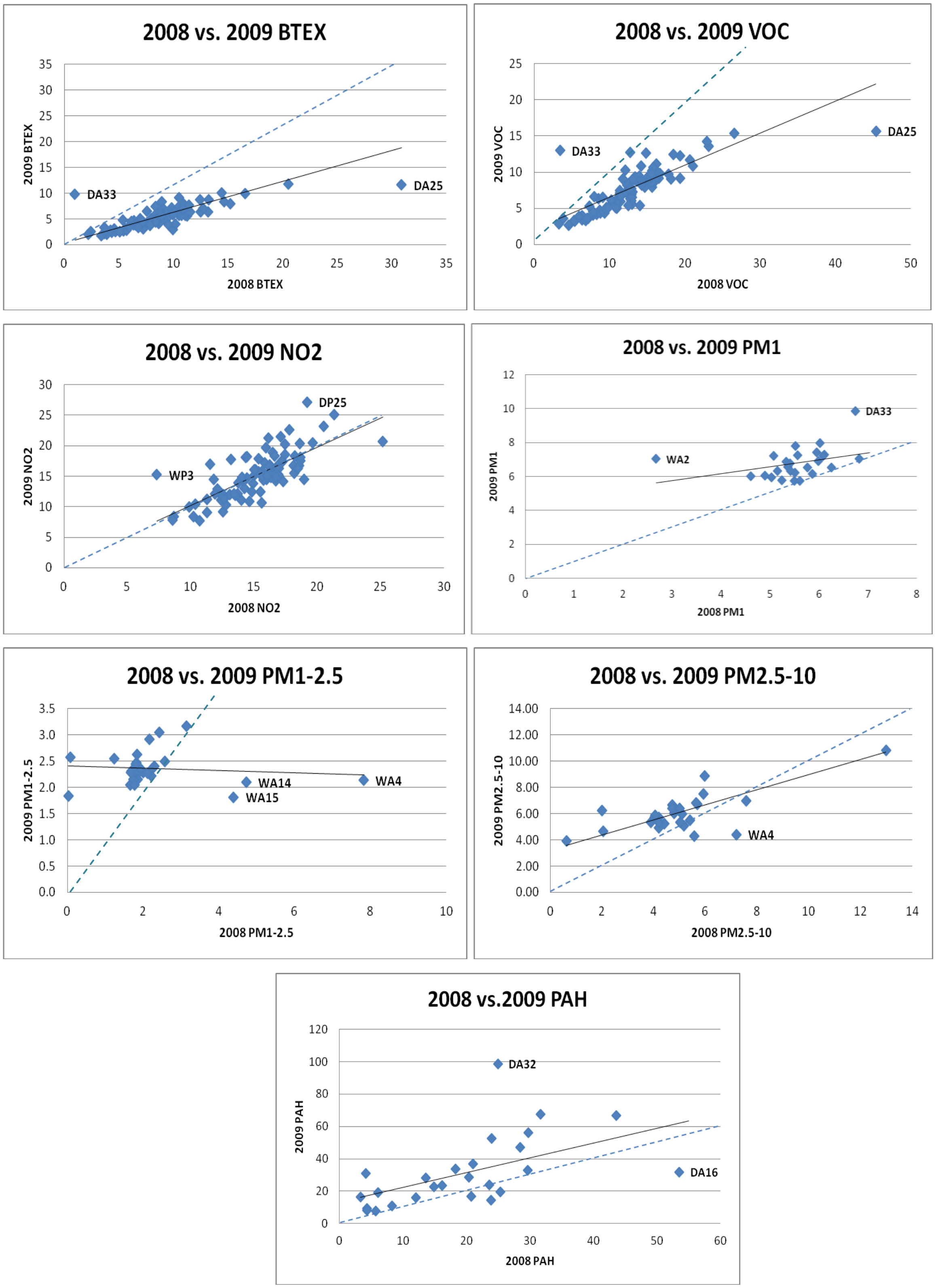
NO_2, and total VOC. The bolded numbers across the diagonal represent agreement between the 2008 and 2009 sites. These values are the highest in all cases which indicates that the majority of the sites remained in the same category from year to year. Comparing the two cities, Windsor site classification is more consistent between the two years. Only one of the Windsor sites switched from low NO_2 in 2008 to high in 2009. For Detroit, the percentage of sites switching from high to low or vice versa ranged up to 13.4% for NO_2. Similar analysis with the PMs and PAHs was difficult since there was a larger number of excluded sites each year and these sites were not the same from year to year, leaving less than half of the sites having data for both years.

Table 4.5. Site classification for (a) Detroit, (b) Windsor. Table entries are percentages falling into the same classification in the two years.

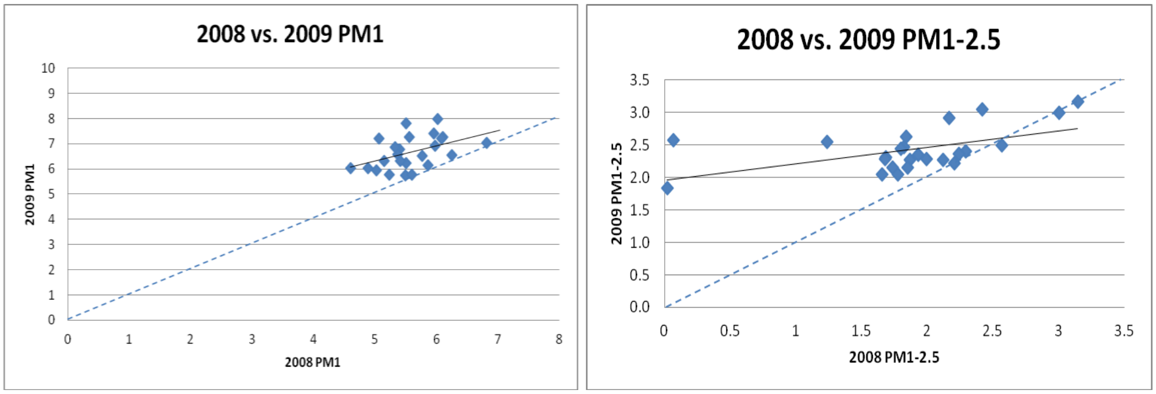
(a) Detroit		**2008**	
2009	**High**	**Medium**	**Low**
BTEX (N = 62)			
High	**22.5**	8.1	3.2
Medium	8.1	**17.7**	6.5
Low	3	6.5	**24.2**
Total VOC (N = 62)			
High	**22.5**	6.5	4.8
Medium	9.7	**19.4**	3.2
Low	1.6	6.5	**25.8**
NO_2 (N = 60)			
High	**18.3**	8.3	6.7
Medium	8.3	**16.7**	8.3
Low	6.7	8.3	**16.7**

(b) Windsor		**2008**	
2009	**High**	**Medium**	**Low**
BTEX (N = 30)			
High	**23.3**	10.0	0
Medium	10.0	**16.7**	10.0
Low	0	6.7	**23.3**
Total VOC (N = 30)			
High	**27.6**	6.9	0
Medium	6.9	**27.6**	3.4
Low	0	3.4	**31.0**
NO_2 (N = 28)			
High	**25.0**	3.6	3.6
Medium	6.5	**21.4**	3.2
Low	0	10.7	**21.4**

Figure 4.3 and Table 4.6 illustrate the agreement between the concentrations measured at the same site in each year. All of the Pearson correlations were found to be significant in Detroit. For both cities, the PM_1, and $PM_{1\text{-}2.5}$ correlations were not significant whereas for Windsor all PMs were not significantly correlated between the two years. With the exception of PM in Windsor, these results support those obtained with the site classification analysis; the pattern of highs and lows across the study area remained fairly consistent between the two sampling campaigns. Emissions and activities affecting these pollutants seem to be consistent between the two sampling periods. Comparing with BTEX, NO_2 and total VOCs, more scattering was observed for PMs and total PAHs. Moreover, there were a few sites where the concentrations were high in one year, but low in another, as shown in Figure 4.3. In some cases, those points resulted in insignificant correlations, e.g. PM_1 and $PM_{1\text{-}2.5}$. With the removal of the two most outlying sites in PM_1, and the three most outlying in $PM_{1\text{-}2.5}$ (Figure 4.3b), the ‘both city’ Pearson correlations improved to 0.462 and 0.476 (both had $p<0.05$). When looking at which sites deviated from the regression line for all pollutants, some of these points were common to more than one category. Table 4.7 lists the sites which had large deviations for at least one pollutant along with the ratio between the 2008 and 2009 concentrations. Large year to year variability at a few sites could also greatly affect the spatial distribution of pollutant concentrations in some areas. Further investigation is being conducted at Wayne State University.



(a) All sites included.



(b) PM$_1$ and PM$_{1\text{-}2.5}$ without major outliers (Table 4.7).

Figure 4.3. Scatterplots of the pollutants between the two years (both cities).

Table 4.6. Pearson correlation coefficients between the two years.

	BTEX	**VOCs**	**NO$_2$**	**PM$_1$**	**PM$_{1\text{-}2.5}$**	**PM$_{2.5\text{-}10}$**	**PAHs**
Both	0.775*	0.793*	0.745*	0.360	-0.104	0.712*	0.566*
N	92	92	88	26	26	26	26
Detroit	0.678*	0.678*	0.584*	0.534*	0.685*	0.859*	0.362*
N	62	62	60	17	17	17	17
Windsor	0.724*	0.828*	0.630*	-0.286	-0.301	0.318	0.737*
N	30	30	28	9	9	9	9

*****significant at $p<0.05$.

Table 4.7. Ratios between 2008 and 2009 values at outlier sites.

Site	**BTEX 2008/2009**	**VOCs 2008/2009**	**NO_2 2008/2009**	**PM_1 2008/2009**	**$PM_{1-2.5}$ 2008/2009**	**$PM_{2.5-10}$ 2008/2009**	**PAHs 2008/2009**
DA33	0.10*	0.27*	1.02	0.68*	0.79	0.79	0.53
DA25	2.67*	2.90*	0.79	0.84	0.74	0.67	0.90
DP25	1.12	1.18	0.71*	N/A	N/A	N/A	N/A
WP3	1.34	1.67	0.48*	N/A	N/A	N/A	N/A
WA2	3.45	2.33	1.1	0.38*	0.49	0.32	1.64
WA4	1.51	1.86	1.08	0.97	3.67*	1.63*	N/A
WA14	1.95	2.01	N/A	0.82	2.46*	0.44	0.73
WA15	1.90	2.01	1.39	0.81	2.42*	0.16	0.52
DA16	1.44	1.48	1.00	0.96	0.99	0.94	1.68*
DA32	1.80	1.77	0.89	0.97	1.00	1.20	0.25*

*large deviation from regression line for that pollutant.

Looking at the sites which showed large deviations for some pollutants there are some interesting points. DA33 was an outlier for BTEX, VOCs and PM_1 (higher in 2009), as well as showed increases in the other PM fractions and total PAHs in 2009, however no change between the years was observed for NO_2. DA16 and DA32 were significant outliers for PAHs but not for any other pollutants. The sites which showed large deviation for NO_2 (DP25, WP3) were also not outliers for any other pollutant. For DA25, BTEX and VOCs were much lower in 2009 whereas the other pollutants were higher. Overall, with the exception of BTEX and VOCs, sites which deviate for one pollutant were not seen to deviate for all, with no consistent trend as to whether the outliers were always higher in one year and lower in another. This result suggests that large variations in concentrations between the two years are largely associated with activities surrounding those few sites.

4.3.4 Comparison to NAPS

In order to test the agreement between the concentration values obtained during the spatial sampling campaigns with those obtained at the National Air Pollutions Surveillance (NAPS) (Environment Canada, 2011b) sites in Windsor some comparisons were made (Table 4.8). For NO_2 and $PM_{2.5}$ hourly concentration values were available for all of the dates at both NAPS sites in Windsor during which sampling took place; Windsor West (WW), located at the intersection of College and Prince and Windsor Downtown (WD), located at University Ave near downtown Windsor. It should be noted that $PM_{2.5}$ concentrations from the spatial sampling is calculated by adding PM_1 and $PM_{1-2.5}$ measurements since $PM_{2.5}$ was not monitored. For BTEX, one 24 hour VOC sampling takes place every six days at the WW site using canisters. The three days closest to the sampling campaigns in each year were used to estimate the average concentration obtained by NAPS over that time period. In 2008 these dates were September 9th, 15th, and 21st and in 2009 they were May 31st, June 6th, and June 12th.

For NO_2, in 2008 the NAPS values were close to the city wide mean value, more so for WD than WW which differed by 12%. In 2009 the NO_2 values obtained at both NAPS sites were similar to the city wide mean. Similarly to NO_2, the $PM_{2.5}$ concentration at WD was in better agreement with the city wide mean than the WW value, although even at WW the difference was small (18%). In 2009 the $PM_{2.5}$ concentrations at both NAPS sites were very similar but lower than the city wide average by 43-46%. For BTEX, in 2008 the city wide mean was significantly higher than the NAPS value whereas in 2008 the values were nearly identical. Some differences are expected between the central sites and the average values from across the city since different sampling methods were used and for BTEX only one in six days in used. Overall, the NAPS station does a reasonably well job capturing the average values however it cannot capture the highs and lows across the city which are often of greater interest in epidemiological studies.

Table 4.8. Comparisons between NAPS and City Wide Means for 2008 and 2009.

2008	**NAPS Windsor West**	**NAPS Windsor DT**	**City Wide Mean**
BTEX (μg/m^3)	3.9	N/A	5.9
NO2 (ppb)	14.3	12.3	12.8
PM2.5 (μg/m^3)	8.5	7.9	7.2

2009	**NAPS Windsor West**	**NAPS Windsor DT**	**City Wide Mean**
BTEX (μg/m^3)	3.3	N/A	3.2
NO2 (ppb)	12.2	12.5	11.8
PM2.5 (μg/m^3)	6.4	6.2	9.1

4.4 Conclusions

Results from the 2009 air sampling campaign carried out in Windsor, Ontario (Canada) and Detroit, Michigan (USA) show similarities to the 2008 campaign when considering which city experiences higher concentrations and in terms of correlations between pollutants. Mixed results were observed for which year saw higher concentrations of pollutants. NO_2 concentrations were slightly lower in 2009. Higher BTEX and total VOC concentrations were observed in 2008, whereas PM and PAH concentrations were higher (not all significant) in 2009. Future work could look more closely at the reasons for the differences in concentrations between the two years, for example, changes in industrial activities or mixing heights between the two campaigns.

Large significant differences in the Windsor T/B ratio suggest that point source emissions changed significantly between the two sampling campaigns. T/B ratios from both cities are within the range indicative of mobile emissions likely due to the proximity of these cities to the traffic sources including the Ambassador Bridge. Sites classifications and Pearson correlation results lead to the conclusions that the concentrations at the same sites are overall well correlated between the two years. With the exception of a few outliers, sites with high / low concentrations generally register high / low concentrations respectively in both years. In Windsor, the NAPS sites did a reasonable job of representing the city-wide values of NO_2, differing by less than 12% from the values obtained from the sampling campaign.

Changes in concentrations were observed from year to year, which was expected due to sampling being conducted in different seasons as well as year to year emission changes. Despite these differences the patterns were consistent from year to year; higher concentrations in Detroit, strong correlations amongst the BTEX group, and consistency amongst which sites were labelled as high and low concentrations. These results suggest that multiple year sampling is important when considering absolute values of concentrations but may not be necessary in cases where general areas of highs and lows are desired. Since most epidemiologic studies look at areas of highs and lows and not absolute values using site classifications from a single sampling campaign may not have a large effect on an epidemiologic study. Still, significant changes from year to year, such as the T/B ratios, and sites which show large variation between the years shine light on changes in activities in the areas which may warrant further investigation. Furthermore, the results of metal concentration on the PM_1 fraction may show a different year to year pattern.

Acknowledgements

Acknowledgments for funding, permissions, and technical support are the same as described in Chapter 3. I would also like to sincerely acknowledge the GeoDHOC team members for their contributions and their permission to include this analysis in my thesis.

Appendix 4A

Table 4.A1. Volatile organic compounds with percent of sites registering values above variable method detection limits.

VOC Analyte	% Total 2009	% Total 2008
(m+p)-Xylene	100*	100
Hexane	100*	99
Benzene	100*	99
Toluene	100*	100
Ethylbenzene	100*	99
o-Xylene	100*	99
Napthalene	99*	80
1,2,4-Trimethylbenzene	96*	99
1,3,5-Trimethylbenzene	93*	97
Tetrachloroethylene	87*	81
Dichloromethane	82*	100
n-Decane	<80	98
Chloroform	<80	90
Trichloroethylene	<80	97

*used to calculate total VOCs for comparison purposes

Table 4.A2. Polycyclic aromatic hydrocarbon and pesticide species with percent of sites registering values above variable method detection limits.

PAH Analyte	% Total 2009	% Total 2008
Fluorene	97*	100
Phenanthrene	97*	100
Fluoranthrene	97*	100
Pyrene	97*	100
Chlorpyrifos (Dursban)	95	21
Acenaphthene	92 *	97
Anthracene	92*	100
Napthalene	81	0
ortho-Phenylphenol	65*	84

*used to calculate total PAHs for comparison purposes

Table 4.A3. Inclusion / Exclusion of sites for general statistics and paired t-test.

	General Statistics				Paired T-test			
Site	**BTEX/**	**NO_2**	**PM**	**PAHs**	**BTEX/**	**NO_2**	**PM**	**PAHs**
D-A-1	Both	Both	2008	2008	Y	Y	No data	No data
D-A-2	Both	Both	Both	2008	Y	Y	Y	No data
D-A-3	Both	Both	2009	2009	Y	Y	No data	No data
D-A-4	Both	Both	2008	2008	Y	Y	No data	No data
D-A-5	Both	Both	Neither	Neither	Y	Y	No data	No data
D-A-6	Both	2008	2009	2009	Y	No data (2009)	No data	No data
D-A-7	Both	Both	Both	Both	Y	Y	Y	Y
D-A-8	Both	Both	Both	Both	Y	Y	Y	Y
D-A-9	Both	Both	Both	Both	Y	Y	Y	Y
D-A-10	Both	Both	Both	Both	Y	Y	Y	Y
D-A-11	Both	Both	2009	2009	Y	Y	No data	No data
D-A-12	Both	Both	2009	Neither	Y	Y	No data	No data
D-A-13	Both	Both	Both	Both	Y	Y	Y	Y
D-A-14	Both	Both	2009	2009	Y	Y	No data	No data
D-A-15	Both	Both	Both	Both	Y	Y	Y	Y
D-A-16	Both	Both	Both	Both	Y	Y	Y	Y
D-A-18	Both	Both	2009	2009	Y	Y	No data	No data
D-A-19	Both	Both	Neither	2009	Y	Y	No data	No data
D-A-20	Both	Both	Both	Both	Y	Y	Y	Y
D-A-21	Both	Both	Both	Both	Y	Y	Y	Y
D-A-22	Both	Both	Both	Both	Y	Y	Y	Y
D-A-23	Both	Both	Both	Both	Y	Y	Y	Y
D-A-24	Both	Both	Both	Both	Y	Y	Y	Y
D-A-25	Both	Both	Both	Both	Y	Y	Y	Y
D-A-26	Both	Both	2008	Both	Y	Y	No data	Y
D-A-27	Both	Both	Both	Both	Y	Y	Y	Y
D-A-28	Both	Both	2009	2009	Y	Y	No data	No data
D-A-29	Both	Both	2008	2008	Y	Y	No data	No data
D-A-30	Both	Both	2009	2009	Y	Y	No data	No data
D-A-31	Both	Both	2008	2008	Y	Y	No data	No data
D-A-32	Both	Both	Both	Both	Y	Y	Y	Y
D-A-33	Both	Both	Both	Both	Y	Y	Y	Y
D-A-34	Both	Both	2009	Neither	Y	Y	No data	No data
D-A-35	Both	Both	2009	2009	Y	Y	No data	No data
W-A-1	Both	Both	Both	Both	Y	Y	Y	Y
W-A-2	Both	Both	Both	Both	Y	Y	Y	Y
W-A-3	Both	Both	2009	2009	Y	Y	No data	No data
W-A-4	Both	Both	Both	Both	Y	Y	Y	Y
W-A-5	Both	Both	2008	2008	Y	Y	No data	No data
W-A-6	Both	Both	Both	Both	Y	Y	Y	Y
W-A-7	Both	Both	Both	Both	Y	Y	Y	Y
W-A-8	Both	Both	Both	Both	Excluded: Site re-location in 2009.			
W-A-9	Both	Both	2008	2008	Y	Y	No data	No data
W-A-	Both	Both	2008	2008	Y	Y	No data	No data
W-A-	Both	Both	2008	2008	Y	Y	No data	No data
W-A-	Both	Both	2008	2008	Y	Y	No data	No data
W-A-	Both	Both	Both	Both	Y	Y	Y	Y
W-A-	Both	2008	Both	Both	Y	No data	Y	Y
W-A-	Both	Both	Both	Both	Y	Y	Y	Y
W-A-	Both	Both	Both	Both	Y	Y	Y	Y
D-P-2	Both	Both	Both	Both	Y	Y		

D-P-3	Both	Both	Both	Both	Y	Y
D-P-4	Both	Both	Both	Both	Y	Y
D-P-5A	Both	Both	Both	Both	Y	Included: Site Re-location in 2009, but
D-P-6	Both	Both	Both	Both	Y	Y
D-P-7	Both	Both	Both	Both	Y	Y
D-P-8	Both	2008	Both	Both	Y	No data
D-P-9A	Both	Both	Both	Both	Y	Y
D-P-	Both	Both	Both	Both		Excluded: Site Re-location in 2009.
D-P-11	Both	Both	Both	Both	Y	Y
D-P-12	Both	Both	Both	Both	Y	Y
D-P-13	Both	Both	Both	Both	Y	Y
D-P-14	Both	Both	Both	Both	Y	Y
D-P-15	Both	Both	Both	Both	Y	Y
D-P-16	Both	Both	Both	Both	Y	Y
D-P-17	2008	2008	Both	Both	No data	No data (2009)
D-P-18	Both	Both	Both	Both	Y	Y
D-P-19	Both	Both	Both	Both	Y	Y
D-P-20	2009	Both	Both	Both	Y	Y
D-P-	Both	Both	Both	Both		Excluded: Site Relocation in 2009.
D-P-22	Both	Both	Both	Both	Y	Y
D-P-23	Both	Both	Both	Both	Y	Y
D-P-24	Both	Both	Both	Both	Y	Y
D-P-25	Both	Both	Both	Both	Y	Y
D-P-26	2009	2009	Both	Both	No data	No data (2008)
D-P-27	Both	Both	Both	Both	Y	Y
D-P-28	Both	Both	Both	Both	Y	Y
D-P-29	Both	Both	Both	Both	Y	Y
D-P-30	Both	Both	Both	Both	Y	Y
D-P-31	Both	Both	Both	Both	Y	Y
D-P-32	Both	Neither	Both	Both	Y	No data
D-P-	Both	Both	Both	Both	Y	Included: Site Re-location in 2009, but
D-P-34	Both	Both	Both	Both	Y	Y
D-P-	Both	Both	Both	Both		Excluded: Site Relocation in 2009.
W-P-1	Both	Both	Both	Both	Y	Y
W-P-2	Both	Both	Both	Both	Y	Y
W-P-3	Both	Both	Both	Both	Y	Y
W-P-4	Both	Both	Both	Both	Y	Y
W-P-5	Both	Both	Both	Both	Y	Y
W-P-6	Both	Both	Both	Both	Y	Y
W-P-7	Both	Both	Both	Both	Y	Y
W-P-8	Both	2008	Both	Both	Y	No data (2009)
W-P-9	Both	Both	Both	Both	Y	Y
W-P-	Both	Both	Both	Both	Y	Y
W-P-	Both	Both	Both	Both	Y	Y
W-P-	Both	Both	Both	Both	Y	Y
W-P-	Both	Both	Both	Both	Y	Y
W-P-	Both	Both	Both	Both	Y	Y
W-P-	Both	Both	Both	Both	Y	Y

Appendix 4B

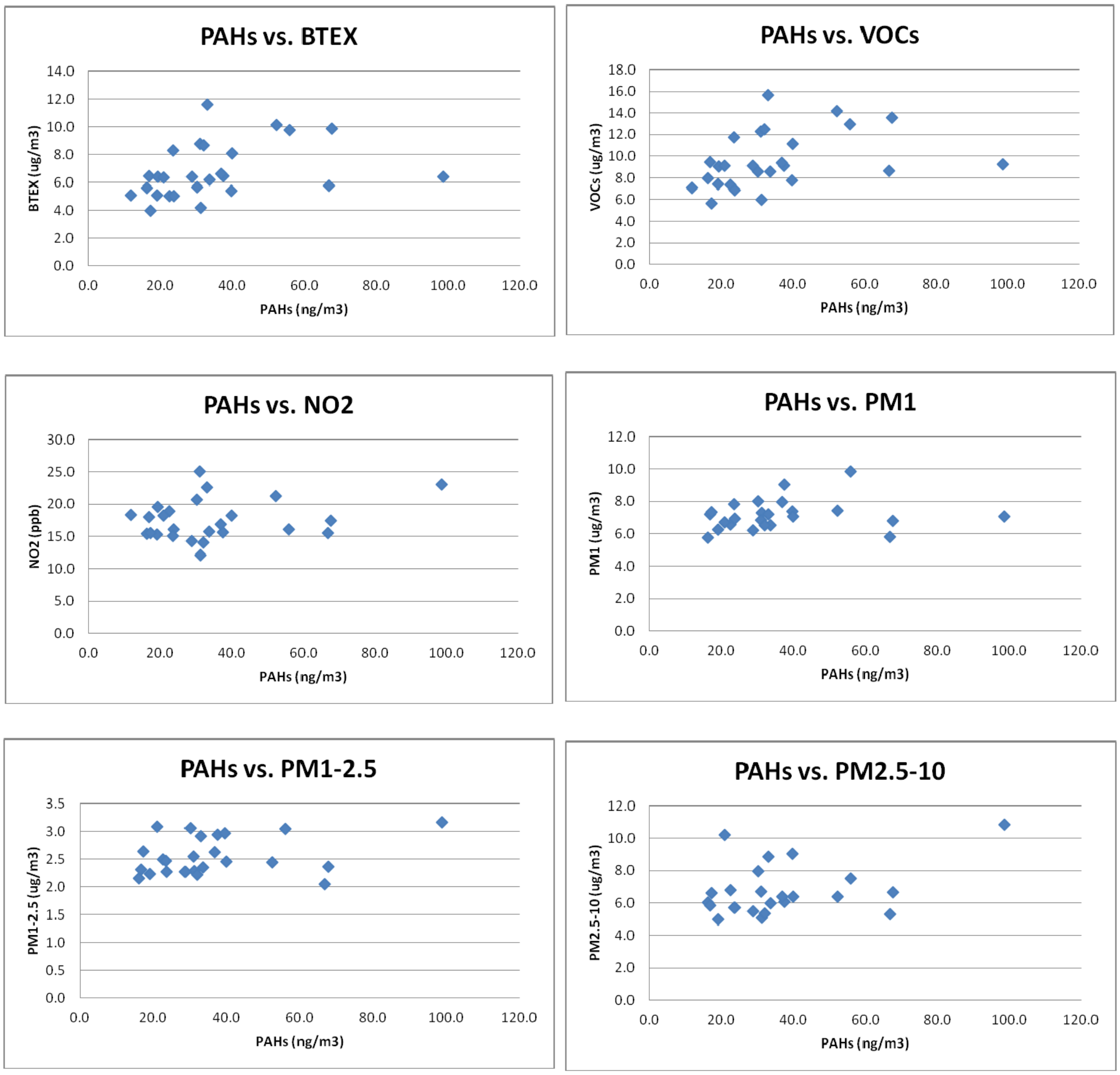


Figure 4.B1. PAHs vs. other pollutants in Detroit (2009).

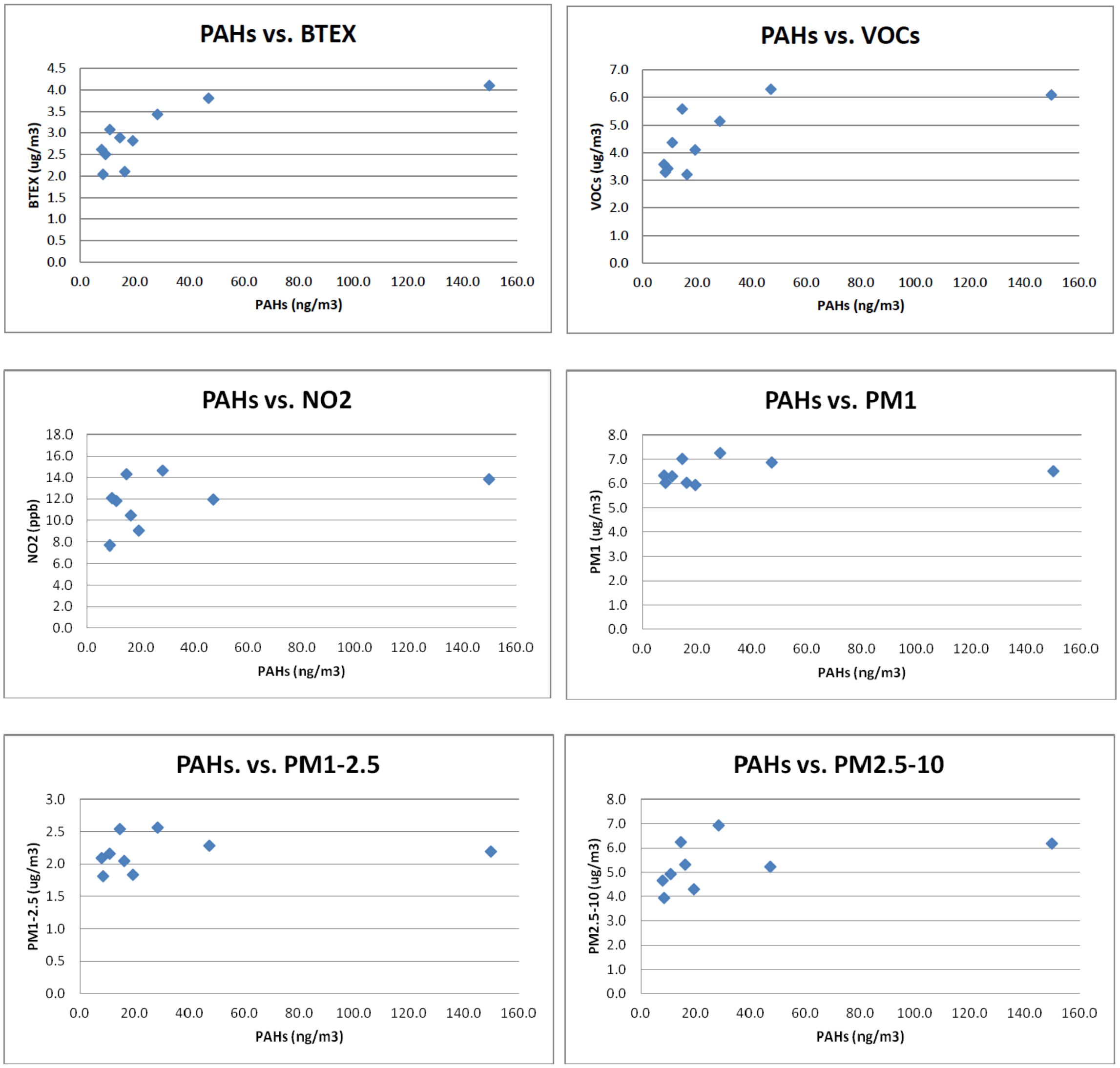


Figure 4.B2. PAHs vs. other pollutants in Windsor (2009).

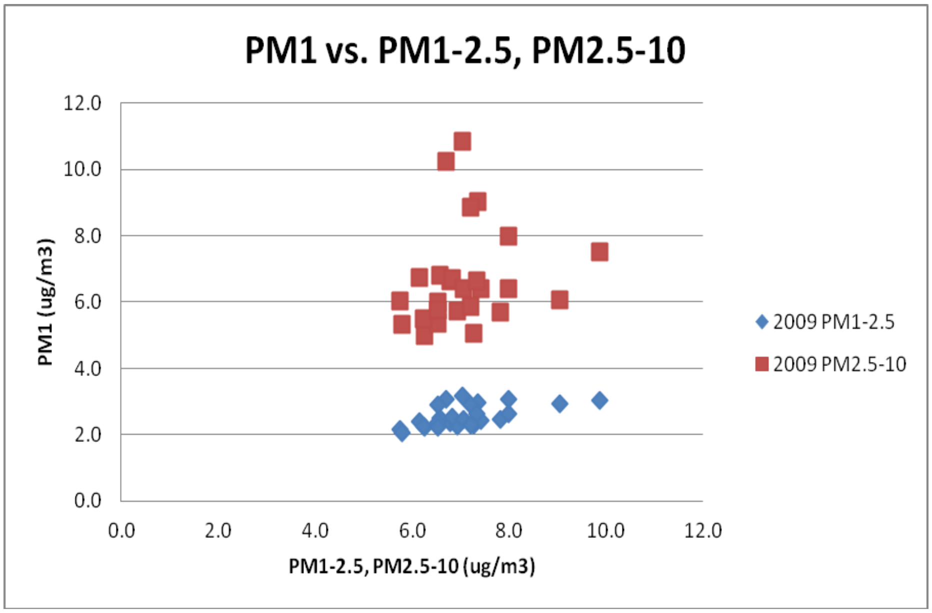


Figure 4.B3. PM size fractions in Detroit (2009).

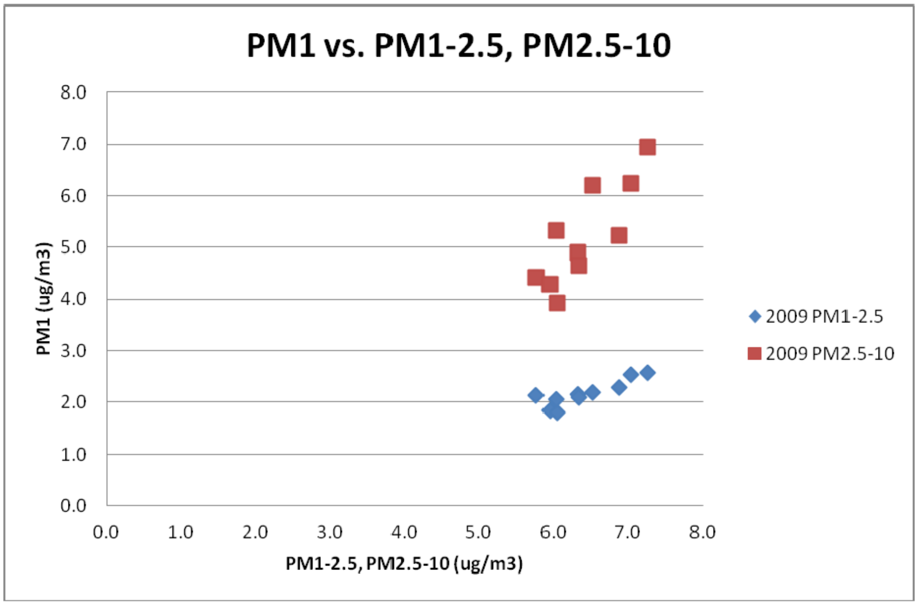


Figure 4.B4. PM size fractions in Windsor (2009).

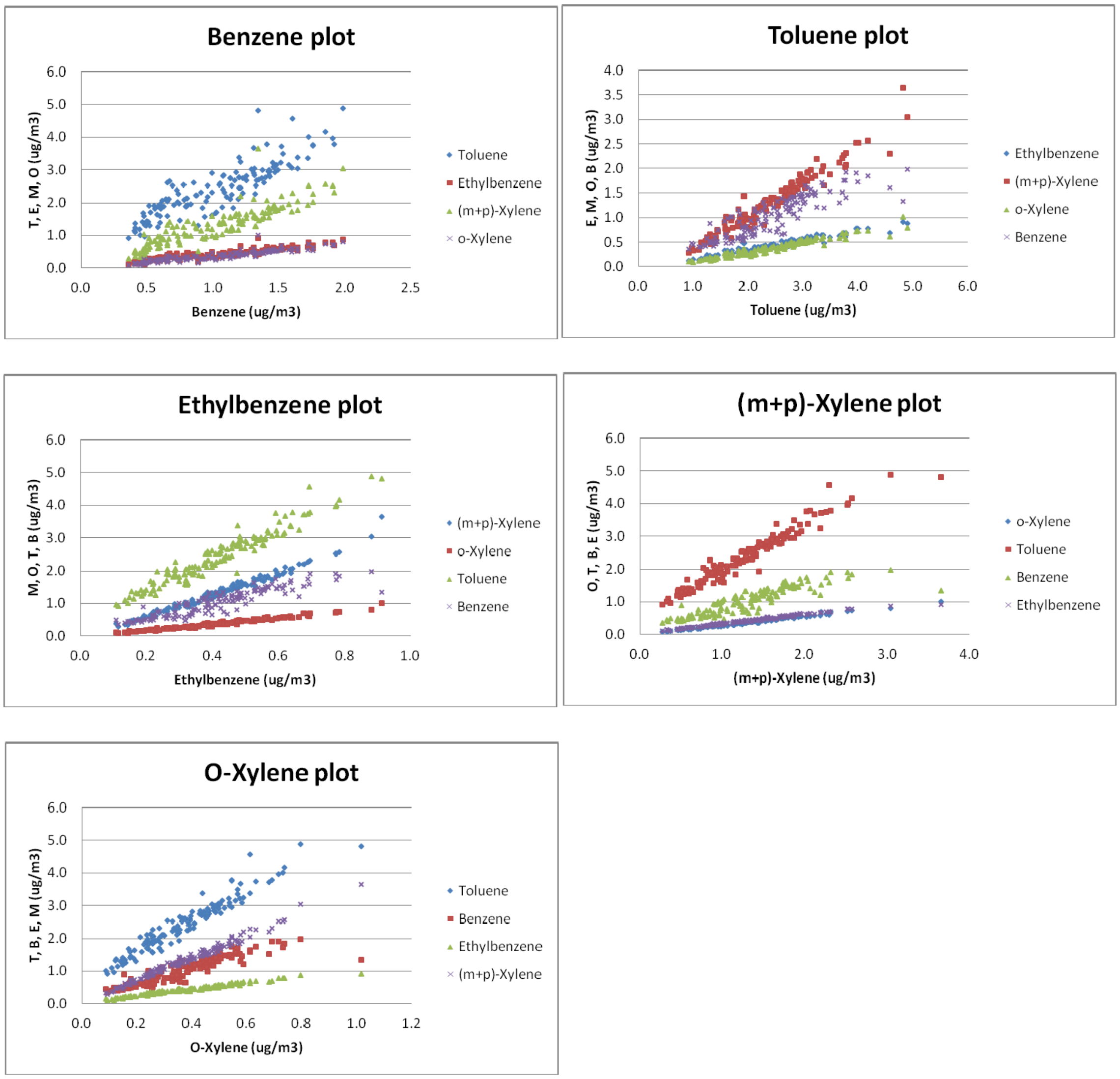


Figure 4.B5. BTEX for both cities combined (2009).

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CHAPTER 5: TRANSBOUNDARY AIR POLLUTION IN WINDSOR, ONTARIO (CANADA)

5.1 Introduction

Air pollution in a particular city is not only influenced by local emission sources but also by sources in the region around the city as air movement does not respect any geo-political boundaries. Air mass movement is influenced by meteorological conditions and the geography of the region. Analysis of frequency distribution of air mass movements provides useful insights about the effect of non-local emissions on local air quality.

Windsor (Ontario) is located on the Canada-US border. Some believe that the heavy industrial facilities such as power generation and automobile production in the neighbouring regions of US greatly affect Windsor’s air quality. This study examines the 48 hr and 24 hr back trajectories over two years using the Hybrid Single-Particle Langrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003). HYSPLIT has been used in previously published research as a means to investigate the impact of long range transport of pollutants (Karaca et al., 2009; Davis et al., 2010). Observation of the sources and directions of air masses arriving at a receptor provides an idea about the influence of neighbouring regions on the local air quality, but it does not necessarily mean that a particular region is the ‘culprit’ for bad local air quality. Several others factors are involved such as the presence of emission sources along the air mass trajectory, the time it takes for the air mass to reach the receptor and the height of air mass when it approaches the receptor.

To further analyze whether the travel path of the air mass influences the measured concentration at the receptor, the emission densities of the pollutants of interest and the ambient concentrations of these pollutants along the pathway was investigated to determine whether significant correlations exist. This analysis was performed for a two-week sample period during each year and the pollutants considered are nitrogen dioxide (NO_2) and particulate matter less than 2.5 microns ($PM_{2.5}$). This expanded analysis should provide a better understanding of whether or not the origin and the pathway of an air mass and the strength of the sources encountered along the path can be expected to influence the measured concentrations at the receptor.

5.2 Methods

5.2.1 Modeling

The backward trajectories were modelled using Hybrid Single-Particle Langrangian Intergrated (Trajectory HYSPLIT) Model 4 (Draxler and Rolph, 2003). Two calendar years, 2008 and 2009, were modeled thus, seasonal and inter-annual variations would be observed. Modeling resolution was three days a week, i.e. Tuesday, Thursday and Saturday. Two-day (48 hr) and one-day (24 hr) HYSPLIT back trajectories were run using Windsor airport as the starting point. The simulation parameters are shown in Table 5.1.

Table 5.1. Parameters used for all modeling runs.

MODEL PARAMETER	SETTING
Meteorological dataset	EDAS 40km, 2004-Present
Trajectory direction	Backward
Total run time (trajectory duration)	48hr & 24hr
Start point	Windsor Airport (42.27 N,
Start time	00:00 UTC (7 pm EST)
Start height	500m AGL

5.2.2 Analysis of Simulation Results

The back trajectories obtained from the modeling simulation were categorised based on the origin of air mass: 48 h and 24 h; the direction of air mass (N, E etc) just before entry into Windsor, and trans-boundary movement of air mass: Windsor-Detroit, Detroit-Windsor or parallel to the border. For this purpose, eight directions were chosen with a 45 degree tolerance band for each direction. A picture of the compass divided into eight directions was overlaid on the trajectory image to precisely determine the direction of air mass movement. Figure 5.1 shows an example trajectory with origin in the US and direction of entry into Windsor as southwest. In discussion concerning seasonal variability, the seasons were defined as follows, Spring: March, April, May; Summer: June, July, August; Fall: September, October, November; Winter: December, January, February.

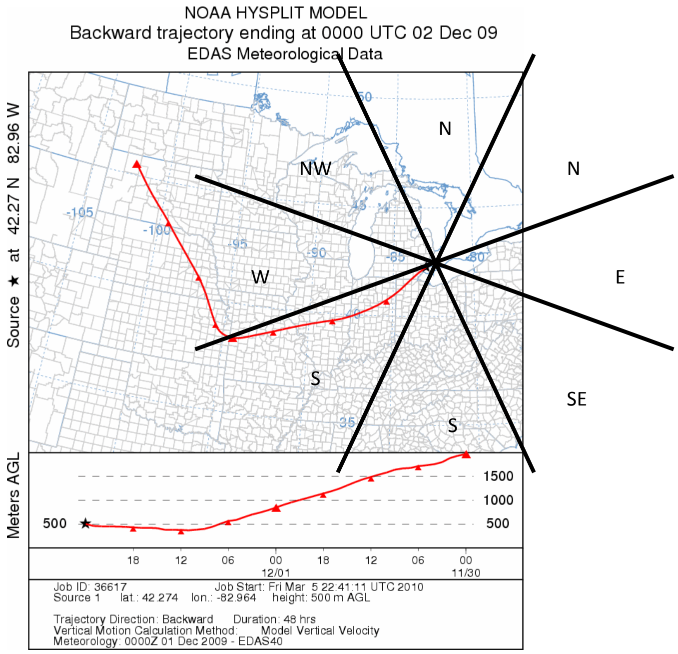

Figure 5.1. Sample trajectory with compass image overlay. Air mass source is US and direction of entry in Windsor is southwest.

5.2.3 Correlations Between Concentration at Receptor and Trajectory Pathway

In order to investigate whether the origin or pathway of an air mass is correlated with the measured concentration at the receptor, two sample periods were subjected to further analysis. The sample periods were each two weeks in length; September 5th-20th, 2008 and May 29th- June 13th, 2009. The measures that were investigated were the emissions encountered along the air mass pathway, and the ambient annual average concentrations encountered along the air mass pathway.

The 24 hour backward air mass trajectories for each day during the study periods were analyzed to determine which regions they passed through before arriving at the receptor site (Windsor, Ontario). Once the regions for all dates were identified, the total NO_2 and $PM_{2.5}$ emissions for these states/provinces were calculated by consulting the US Environmental Protection Agency (EPA, 2010) and the Environment Canada (EC, 2010) online emission inventories and were then normalized based on the square kilometers of the state or province. If an air mass passed through more than one state or province a weighted average emission rate value was calculated based on the travelled path and the approximate time spent in each region.

The average ambient concentrations of NO_2 and $PM_{2.5}$ for each state/province were determined by consulting the US EPA (EPA, 2010) and the Environment Canada (Ontario) websites (EC, 2010). Using the same weighted average method, an ambient concentration value for each pollutant was assigned to the air mass on each day based on the time spent in each region.

Using scatter plots and Pearson correlation, analyses were performed to determine if there were any correlations between the path of the trajectory and the level of NO_2 and $PM_{2.5}$ concentration measured at the National Air Pollution Surveillance (NAPS, 2010) Windsor West site on a given day.

5.3 Results and Discussion

5.3.1 Origins of Air Masses

Table 5.2 shows the percentage of air mass movement between the two countries for 2008 and 2009 based on the 48 hr and 24 hr trajectories. When considering the 48 hr trajectories, a slightly higher proportion of air masses originated in the US for both 2008 and 2009. However, when considering the 24 hr trajectories, this difference is much more pronounced with over 80% of air masses originating in the US.

The annual variability between the two years is very small. When considering both the 48 hr and 24 hr trajectories, the variability between 2008 and 2009 does not exceed two percent. This suggests that the movement of air masses between the two countries is consistent on an annual basis.

Table 5.2. Percentage of 48 and 24 hr trajectories originating in Canada and US.

	48 hr		**24 hr**	
	2008	**2009**	**2008**	**2009**
Canada	45%	47%	18%	19%
US	55%	53%	82%	81%

Figure 5.2 shows that a higher percentage of air masses entering Windsor during the winter season of both 2008 (64%) and 2009 (58%) were from US. In the other three seasons of 2009 the percentage of air mass coming from Canada and US were almost equal. In contrast, in 2008 summer and fall have different patterns with 72% of air masses originating from US in summer and 38% in fall. Figure 5.3 shows that regardless of season and year a higher percentage of air masses arriving in Windsor were originated in the US when considering the 24 hr trajectories, especially during winter.

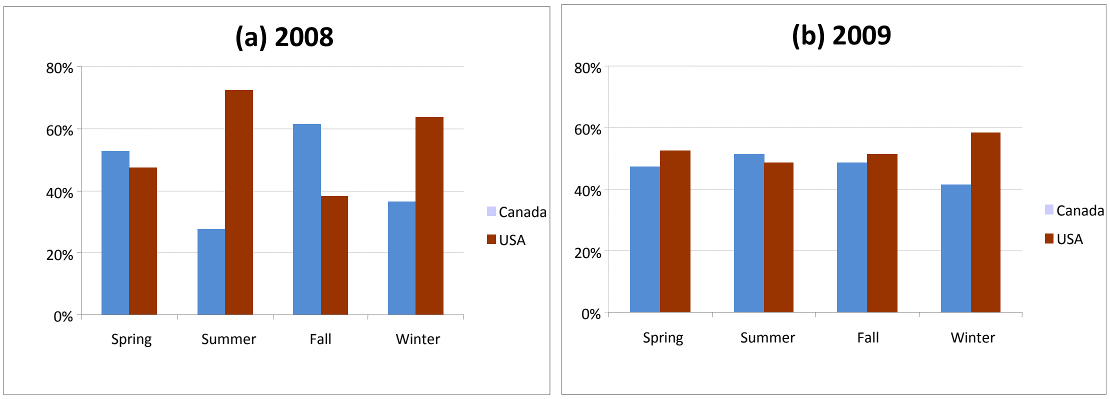

Figure 5.2. Seasonal patterns of 48-hr Trajectory originating from Canada and US, (a) 2008, (b) 2009.

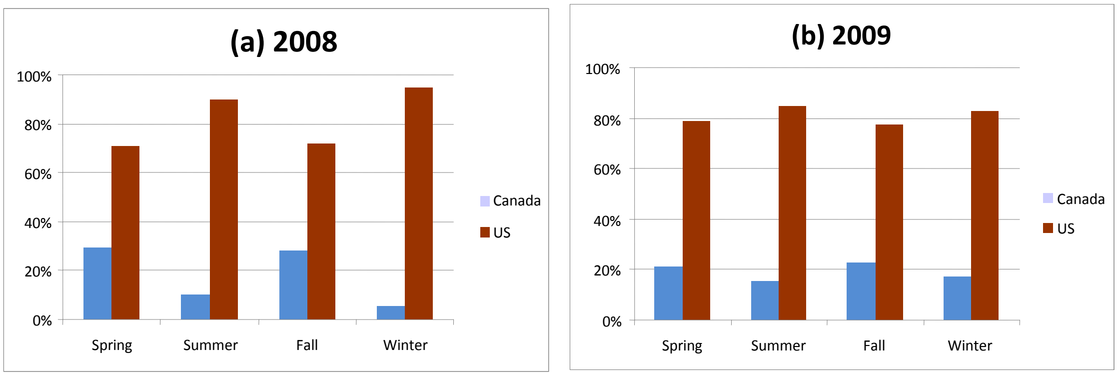

Figure 5.3. Seasonal patterns of 24-hr trajectory originating from Canada and US, (a) 2008, (b) 2009.

Figure 5.4 shows the direction of air mass movement with respect to the Windsor-Detroit border. In all four seasons of both years a higher percentage of air masses entering Windsor were from the US, especially during summer 2009. On average 30% of the air masses entering Windsor were parallel to the border during 2008 followed by 20% during 2009. A much lower percentage of air masses entering parallel to the border was observed in summer and winter 2009 due to the lower frequency of south and south-westerly air flows during that time.

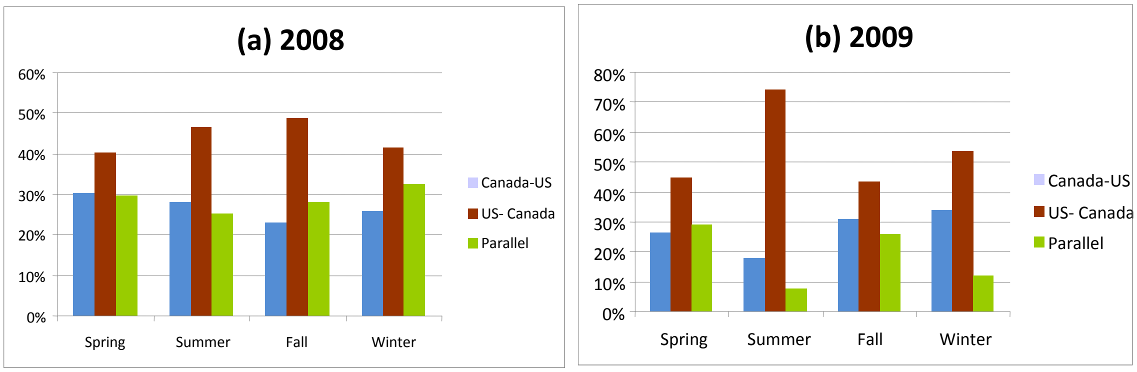

Figure 5.4. Seasonal patterns of trans-boundary movement of air mass, (a) 2008, (b) 2009.

5.3.2 Directions of Air Masses

Figure 5.5 shows the direction of air mass entry into Windsor. For both 2008 and 2009, westerly flow is the most frequent. The combined flow from the southwest, west, and northwest directions accounted for 61% in 2008 and 55% in 2009.

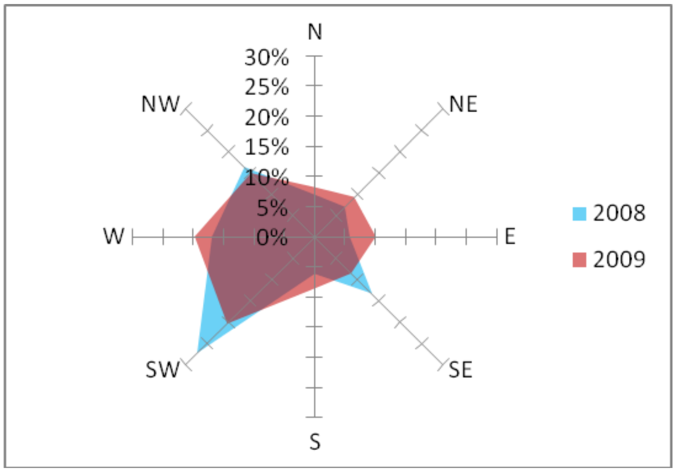

Figure 5.5. Percentage of occurrence of air mass path direction.

Seasonal comparison of air mass flow directions for 2008 and 2009 is shown in Figure 5.6. In 2008, the most common air mass flow direction during spring, summer, and winter was from the southwest. In fall, the percentage of air mass flow direction for both southwest and northwest was equal. In 2009, the most common air mass flow directions during each season were as follows, spring and fall: southwest, summer: northwest, and winter: west. These seasonal trends corroborate the annual observations by showing that the most frequent directions of air mass entry to Windsor are the ones from the direction of the US.

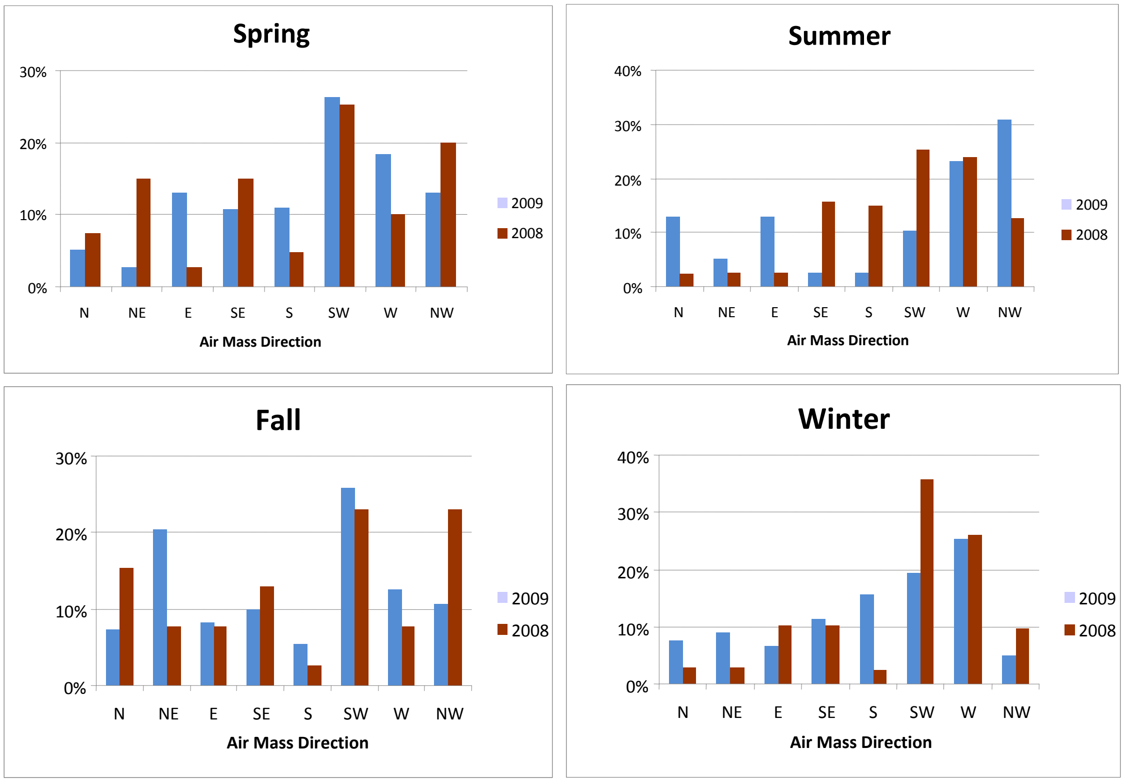

Figure 5.6. Seasonal variation of air mass flow directions**.**

5.3.3 Air Mass Pathways for Sample Periods

Reverse geo-coding and examination of the 24-hr backward trajectories for each day during the two-week sample periods were used to determine the origin of the trajectories as well as the regions that the air mass passed through prior to arrival at the receptor. Air masses arrived from as far away as Missouri and travelled through as many as four states/provinces prior to arrival in Windsor. From the models, a total of eight states and one province were predicted to have possibly affected the measured pollutant concentrations during the study period. Results suggest that Windsor is exposed to trans-boundary air pollution on nearly a daily basis (13/16 days during the 2008 sample period and 12/16 days for 2009).

5.3.4 Effect of Emission Densities Encountered along Air Mass Pathway

Annual emissions of NO_2 and $PM_{2.5}$ for each state/province were determined by consulting the US EPA (US States) and the EC (Ontario) websites. The most recent year in which data was available for the US was 2005, whereas for Ontario 2007 data was available (2005 data was not available for Ontario). The annual emissions from all sources were then divided by the area of each region in order to obtain an emissions/area value, reported in tons/km^2 of NO_2 or $PM_{2.5}$. An emissions/square kilometer value was calculated for each day in the sample period based on the 24 hour air mass trajectory for that day. On days where the air mass passed through more than one region, a weighted average was taken. This was carried out as a means of finding a rough estimate of the emissions that a given air mass was exposed to prior to arriving at the receptor site.

Scatter plots and Pearson correlation analysis revealed that there was no observable correlation between the projected emissions encountered along the pathway of an air mass and the measured concentration at the receptor. An exception to this was the Pearson correlation between the average air mass exposure to $PM_{2.5}$ and the concentration at the receptor during the 2008 sample period ($r = 0.44$, $p<0.05$). Since this trend was not observed during the 2009 sample period, further analysis, including longer sampling periods may be required in order to determine whether or not a significant correlation exists between the two measures. Scatter plots did not reveal any significant relationships. An example of the scatter plots for 2008 (24 hr trajectories) is shown Figure 5.7.

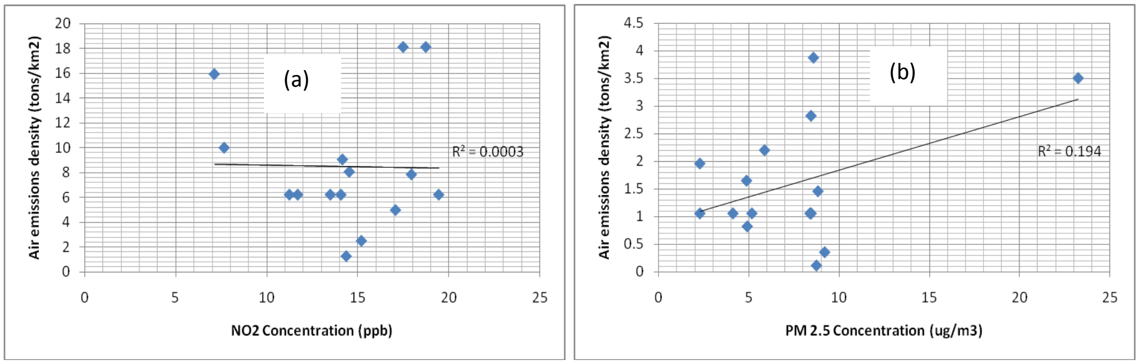

Figure 5.7. Observed concentrations vs. weighted average air emissions density for the 24 hr trajectories for (a) NO_2, (b) $PM_{2.5}$.

5.3.5 Effect of Ambient Concentrations along Air Mass Pathway

The annual average ambient concentrations of NO_2 and $PM_{2.5}$ for each area are shown in Table 5.3. Similar to the previous analysis, scatter plots between the annual ambient concentration of the pollutants in the regions that the air mass has travelled through and the measured concentrations at the Windsor West NAPS site on a given day were not seen to be significant. This is likely due to the large area and long timeframe over which the concentrations have been averaged. Pearson correlation analysis confirmed the lack of correlation between these measures for both sampling periods.

Table 5.3. Annual average ambient concentrations**.**

State/Province	**NO_2 (ppb)**	**$PM_{2.5}$ (µg/m3)**
Ontario	11	7.00
Michigan	12	11.29
Ohio	13	12.46
Illinois	18.5	11.58
Indiana	9.2	11.71
Missouri	9.3	12.22
Kentucky	8.3	12.08
Wisconsin	7.5	10.06
Pennsylvania	11.2	13.90

5.4 Conclusions

Observation of 48-hr backward air mass trajectories during both 2008 and 2009 reveal that although a higher percentage of backward trajectories originate from US, the difference is not significant when compared with the percentage of trajectories originating from Canada. However, the results of the 24-hr trajectories showed a much higher percentage of US to Canada air movement. The time period over which the air mass movement is modelled is a significant factor which points to further research into which time period (24-hr or 48-hr) is the most relevant when considering the movement of pollutants. For both trajectory time periods the inter-annual variability in air mass movement was small.

Analysis of the air mass directions supports the 24-hr trajectory results. Most of the air masses flow is from the southwest, west and northwest. These are the directions in which the US states are located around Windsor. Windsor is located on the border and these air masses entering Windsor may potentially bring pollutants from the US. The direction of air mass flow just before entering Windsor may be more important than the origin of the air mass trajectory. An air mass may originate in Canada, but enter Windsor after passing through US. Such an air mass can still bring pollutants from the US.

When the 24-hr trajectories for the two sample periods were broken down by how many regions they passed through and by the time spent in each region, it was seen that an air mass arriving in Windsor may be a result of emissions occurring as far away as Missouri and may have had emissions from as many as four states/provinces contributing to the measured concentrations. The emissions/km^2 values for each trajectory were compared to the concentrations obtained at the receptor site for each day. Results from this analysis suggest a moderate positive correlation between the $PM_{2.5}$ emissions encountered along the path of the air mass trajectory and the measured $PM_{2.5}$ concentration at the receptor for 2008, however similar correlations were not observed during 2009. Therefore, further investigation over longer sample periods is required in order to make a conclusion.

Strong correlations between emission densities and measured concentrations were not observed for NO_2 during either year. When comparing the annual ambient concentrations along the pathway of an air mass to the concentrations obtained at the receptor site no significant correlations were observed during both sample periods for either pollutant. This may be due to the large area over which the concentrations were averaged. For example, in Michigan there are 31 $PM_{2.5}$ monitors with ambient annual concentrations ranging from 6.59 $\mu g/m^3$ to 15.54 $\mu g/m^3$. Once these values are averaged over the entire state the concentration obtained is 11.29 $\mu g/m^3$. An air mass may have passed though an area where the concentration was higher (lower) than the average but this would not be reflected in the correlation.

In conclusion, although the backward air mass trajectory origins as well as the analysis of the direction from which the air masses enter suggests that Windsor is frequently exposed to air mass arriving from the US, this alone does not suggest that the air quality in Windsor is in fact a result of this air mass movement. Analysis considering emission density and ambient concentrations did not show strong and consistent correlations. Further research is required to investigate whether or not the pathway of an air mass has a considerable effect on the measured concentration at the receptor.

An important future consideration would be to further break down the areas into smaller segments, allowing for more accurate determination of emissions density and ambient concentrations. Additionally, future investigations should consider longer sample periods and possibly more pollutants. More thorough consideration of weather patterns and their relationship to long range transport of pollutants should also be further explored.

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CHAPTER 6: MULTI-SEASON, MULTI-YEAR CONCENTRATIONS AND CORRELATIONS AMONGST THE BTEX GROUP OF VOCS IN AN URBANIZED INDUSTRIAL CITY

6. 1 Introduction

Volatile organic compounds (VOCs) are abundant in the atmosphere in urban, industrialized regions with anthropogenic sources such as vehicle exhaust and solvent and gas emissions from manufacturing and chemical facilities as the major contributors (Srivastava et al., 2005). Windsor, Ontario (42.267º N, 82.95º W), covering an area of 147 km^2 and a population of 218,473 (Statistics Canada, 2008), experiences high concentrations of air pollutants, including VOCs, from the large number of manufacturing facilities (mainly automotive) and from vehicle emissions from the border crossings, i.e. the Ambassador Bridge and the Windsor – Detroit Tunnel connecting Windsor to Detroit, Michigan (Wheeler et al., 2008). Research has focused on monitoring these compounds as exposure to VOCs poses significant health risks (Parra et al., 2006; Khoder, 2007), including adverse birth outcomes (Aguilera et al., 2008) and cancer (Sax et al., 2006). A lack of ambient VOC monitoring data has been identified as limiting efforts to evaluate associations between exposure and adverse health outcomes (Su et al, 2010).

Recent studies have focused on BTEX VOCs, including benzene, toluene, ethylbenzene, o-xylene, and (m+p)-xylene, due to their carcinogenic potential and abundance in urban ambient air. These pollutants are well correlated with each other (Pankow et al., 2003; Ho et al., 2004; Parra et al., 2006; Khoder, 2007; Bruno et al., 2008; Hoque et al., 2008; Miller et al., 2009; Miller et al., 2010) suggesting vehicular emissions as common sources since VOCs in vehicle exhaust are present in fixed ratios. Source apportionment studies in other urban areas have confirmed that mobile emissions are the dominant source of aromatic hydrocarbons (Srivastava et al., 2005).

BTEX ratios can be indicative of sources or photochemical age. Studies have looked at toluene to benzene (T/B) ratios as an indicator of emission sources in North America (Miller et al., 2010; Miller et al., 2011) and internationally (Hansen and Palmgren, 1996;

Khoder, 2007; Hoque et al., 2008; Buczynska et al., 2009). These studies reported T/B values from 1.5-4.0 in urban areas impacted by mobile sources. Similarly, the ratio of (m+p)-xylenes to ethylbenzene ((M+P)-X/E) has been identified as an indicator of photochemical age (Zhang, et al., 2008). These species are typically emitted in a ratio of approximately 3.6 in urban areas regardless of geographic location (Monod et al., 2001) and are removed from the air by dispersion, deposition, and chemical reaction. However, the removal of (m+p)-xylene via chemical reaction is approximately 3 times faster than that of ethylbenzene. Therefore, the (M+P)-X/E ratio typically decreases with photochemical aging (Nelson and Quigley, 1983).

Air pollutant concentrations can vary significantly between seasons and within an urban airshed. Additionally, year to year variations in meteorology and source emissions affect concentrations levels (Tager et al., 2009). Due to the high cost of deployment and sequential chemical analysis of dense network samples, previous investigations have been limited in the number of sites, seasons, and years during which air sampling was conducted. Previous studies have obtained data from 1-12 sites during one or two-weeks of a single season (Ho et al., 2004; Khoder, 2007; Smith et al., 2007; Bruno et al., 2008; Hoque et al., 2008; Zhang et al., 2008; Buczynska et al., 2009; Ho et al., 2009), which does not allow for the comparison of seasonal trends. Others sampled in multiple years for the same season (Chattopadhyay et al., 1997) or multiple seasons of one year (Hansen and Palmgren, 1996; Ho et al., 2004; Parra et al., 2006). Pankow et al. (2003) sampled during multiple seasons over a 29 month period however the study was limited to 13 monitoring sites. Atmospheric processes vary temporally and changes in meteorology affect pollutant dispersion and atmospheric reactions leading to misclassification in exposure estimation when using one sampling period to represent population exposure.

Two nearby comprehensive studies have been conducted which consider seasonal and intra-urban spatial variability in air pollution sampling; the Detroit Exposure and Aerosol Research Study (DEARS) funded by the US EPA, and the Border Air Quality Strategy (BAQS) study funded by Health Canada. Both studies took place over three years (2004-2006) and included spatial monitoring over summer and winter (DEARS) (Williams et al., 2008) and over all four seasons (BAQS) (Health Canada, 2010; Wheeler et al., 2008).

Moreover, high density sampling of VOCs has been undertaken internationally (Aguilera et al., 2008, Bruno et al., 2008), in Southwestern Ontario (Wheeler et al., 2008; Miller et al., 2009; Su et al., 2010) and in Detroit, Michigan (Mukerjee et al., 2009; Miller et al., 2010).

Recent studies have pointed out the need to address exposure misclassification in epidemiological studies (Sarnat et al., 2010) that may result from reliance on central ambient monitoring station measurements for exposure assignment. For example, in Windsor (Ontario, Canada) there is one government monitoring station (Windsor West) which measures ambient VOCs for 24-hours, once every six days although VOC spatial variability can be observed at a scale of 4-50 km (Tager et al., 2009). Measurements at central stations may not adequately represent exposure for residents living some distance away from the stations or in close proximity to industry or traffic sources. This can be evaluated by comparing central site measurements with those obtained across the sampling domain.

This study examined BTEX concentrations and correlations from a multi-season (four per year), multi-year (2004, 2005, 2006), multi-site (approximately 50) perspective. To the best of our knowledge, this study is one of the first to utilize a multiple year, multiple season network. This unique BTEX dataset allows for comprehensive investigation of intra-city variability by considering factors such as major sources, photochemical age, spatial and temporal trends, which lead to changes in ambient concentrations and exposure levels. The specific objectives of this paper are as follows:

- Characterize seasonal and inter-annual variability of BTEX concentrations
- Determine how well the spatial network from this study represents the seasonal means obtained at the long term monitoring station
- Identify whether any single season best represents an annual mean for multiple locations
- Investigate inter-species correlations for seasonal and annual trends
- Use BTEX ratios to characterize major sources and photochemical age

- Examine spatial variability and assess potential exposure misclassification by comparing the concentrations measured at multiple sampling sites to those from a fixed monitoring station

6.2 Methods

6.2.1 Field Campaigns

This study was carried out in all four seasons (winter, spring, summer, fall) over a three-year period (2004-2006), for a total of 12 sessions. Figure 6.1 shows the locations of the sites across the study area. Each sampling session consisted of a two-week integrated period, during which 3M Model 3500 Organic Vapor Passive Samplers (Guillevan, Montreal) were used to measure the concentrations of VOCs. During each sampling period, approximately 50 monitors were located across the city for a total of 162 sites over the three-year period. The sites were not in identical locations from year to year, however they remained the same for each season within a given year and were selected to represent the majority of the residential population. Sampler spacing in each year (maximum distance of 2.1 km in 2004, 2.3 km in 2005, and 3.3. km in 2006) was less than the variogram range of 7.5 km for total BTEX in Windsor (Miller et al., 2010) and the density was 1 sampler / 3 km^2 as recommended by Cocheo et al. (2008) for BTEX sampling. The calculated average distance between all the monitoring sites in a year and the highways (Fig. 6.1) were 2.5 km, 1.9 km and 2.3 km in 2004, 2005 and 2006 respectively. For major roads, the average distances were 127 m, 145 m and 151 m, in 2004, 2005 and 2006 respectively. Therefore it was assumed that despite the change in site locations from one year to another, the sites would provide similar representation and adequate spatial coverage of the study. In 2004, the VOC samplers, equipped with rain shelters, were installed on light poles at an approximate height of 2.5 meters, to prevent contamination and vandalism. In 2005 and 2006, most samplers were installed on tripods (1.5 m) in residential backyards. Additional considerations in 2005 and 2006 included accessibility to alternating-current (AC) electric power due to the collocation of other active samplers (results not reported in this paper) and site security. Two of these sites were collocated with the two National Air Pollution Surveillance (NAPS)

(Environment Canada, 2010a) stations: Windsor West and Windsor Downtown (Fig 6.1) in all three years. However, NAPS only measured VOCs at the Windsor West site. Location coordinates were measured and recorded with global positioning systems for all monitoring sites.

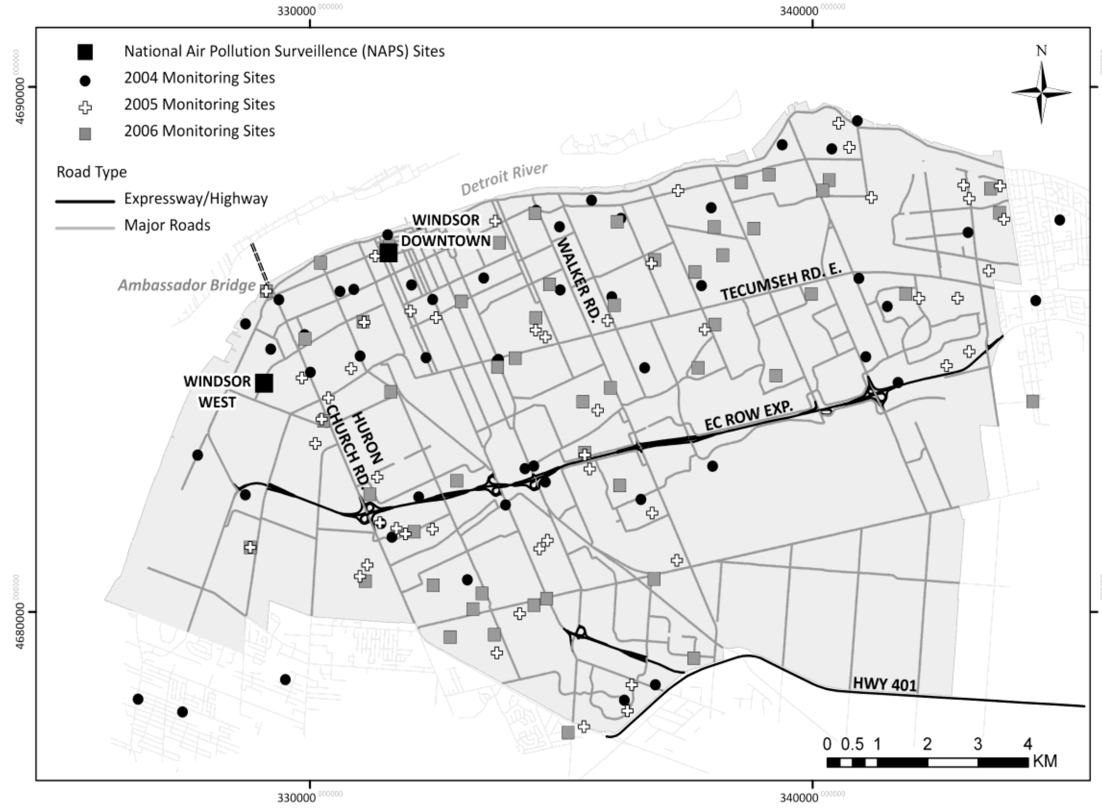

Figure 6.1. Study area, highway/express way and major roads, locations of sampling site and government monitoring stations Windsor West and Windsor Downtown. Shaded area is the city of Windsor.

6.2.2 Laboratory Analysis of Samples

Analysis of the 3M Samplers was conducted by Airzone One (Mississauga, ON), using gas chromatography/mass selective detector. Additional information about the analytical procedure can be found in Wheeler et al. (2008).

6.2.3 Data Screening and Analysis

VOC concentrations were field and lab blank corrected along with assessments of precision using duplicate samples as per Wheeler et al. (2008). Briefly, sample concentrations below the method detection limit (MDL) were replaced with ½ MDL. Extreme observations, defined as ± six standard deviations from the mean values, were excluded from analysis; this led to the omission of two values. Seasonal and annual means were calculated using all sites in the corresponding period. Annual means of each species were calculated using data from all seasons with available concentrations, with a minimum of two seasons being required. The data analysis includes the general descriptive statistics of the BTEX species by season and by year.

6.2.4 Seasonal and Annual Trends

The three-year seasonal means from the spatial network in this study were compared to the seasonal mean concentrations obtained from four years (2003, 2004, 2006, 2007) of data from the Windsor West NAPS site. To minimize the effect of meteorological variations that would occur over a given 2-week period and to achieve representativeness of seasonal conditions, the mean values for each season were calculated using all three years of measurements (e.g. spring mean = average of spring 2004, spring 2005, and spring 2006).

6.2.5 Correlation and Ratios

Spearman rank correlation coefficients among the BTEX group of VOCs were calculated for each season. T/B ratios and (M+P)-X/E ratios of each sample were calculated.

6.2.6 Spatial Variability and Exposure Misclassification

Variability among the sites within each season was considered by calculating the coefficient of variation (CV) for each species. Spearman rank correlation coefficients among seasons were also calculated for each species in each year to assess the stability of observed spatial patterns. Concentration maps were generated in ArcGIS 9.3 for visualization of the spatial distribution. The inverse distance weighting (IDW) interpolation method was utilized to develop independent raster layers for each pollutant for each season. The Raster Calculator function was then used to overlay each layer to produce yearly average maps and finally three-year average maps.

The NAPS Windsor West Station, shown in Figure 6.1, measures VOCs using a 6L Summa canister which was analyzed with a gas chromatography / mass spectrometry system. Twenty-four hour samples are taken once every six days. A 3M sampler was collocated at this site and the concentrations obtained were compared to the distribution of concentrations across the study area. Specifically, the upper range of values obtained across the 50 sites was compared to the collocated NAPS value to determine the order of magnitude that the two values differed.

6.3 Results and Discussion

6.3.1 BTEX Concentrations

In the summer of 2005, all of the benzene and o-xylene values were reported as 'below the detection limit', therefore these species in this season have been excluded from further analysis. The BTEX concentrations from the remaining seasons and species from all sites are presented in Figure 6.2. Toluene had the highest concentrations (three-yr mean among all sites and all four seasons = 2.75 µg/m^3), followed by (m+p)-xylene (1.36 µg/m^3), and benzene (0.76 µg/m^3). Ethylbenzene (0.45µg/m^3) and o-xylene (0.47 µg/m^3) were present at lower concentrations. The three-yr mean of total BTEX was 5.64 µg/m^3.

Several other studies have reported toluene as having the highest concentrations in urban areas for these pollutants (Ho et al., 2004; Srivasta et al., 2005; Parra et al., 2006; Smith et al., 2007; Hoque et al., 2008, Johnson et al., 2010). The concentration levels observed in this study are comparable to those observed in Texas (Smith et al., 2007) and in Sarnia, Ontario (Miller et al., 2009). Smith et al. (2007) reported the highest concentration of toluene (2.27 µg/m^3), followed by benzene (2.04 µg/m^3), (m+p)-xylene (1.42 µg/m^3), o-xylene (0.52 µg/m^3) and ethylbenzene (0.51 µg/m^3). The rank order observed in this study was similar to that reported by Miller et al. (2009) with toluene being the highest (2.51 µg/m^3), followed by (m+p)-xylene (1.28 µg/m^3), benzene (0.98 µg/m^3), ethylbenzene (0.48 µg/m^3), and o-xylene (0.48 µg/m^3). The reported benzene concentration is also consistent with that reported in Toronto, Ontario (0.68 µg/m^3) (Su et al., 2010). In Detroit, Michigan the pattern was similar however the concentration values were approximately double those reported for Windsor (Johnson et al., 2010).

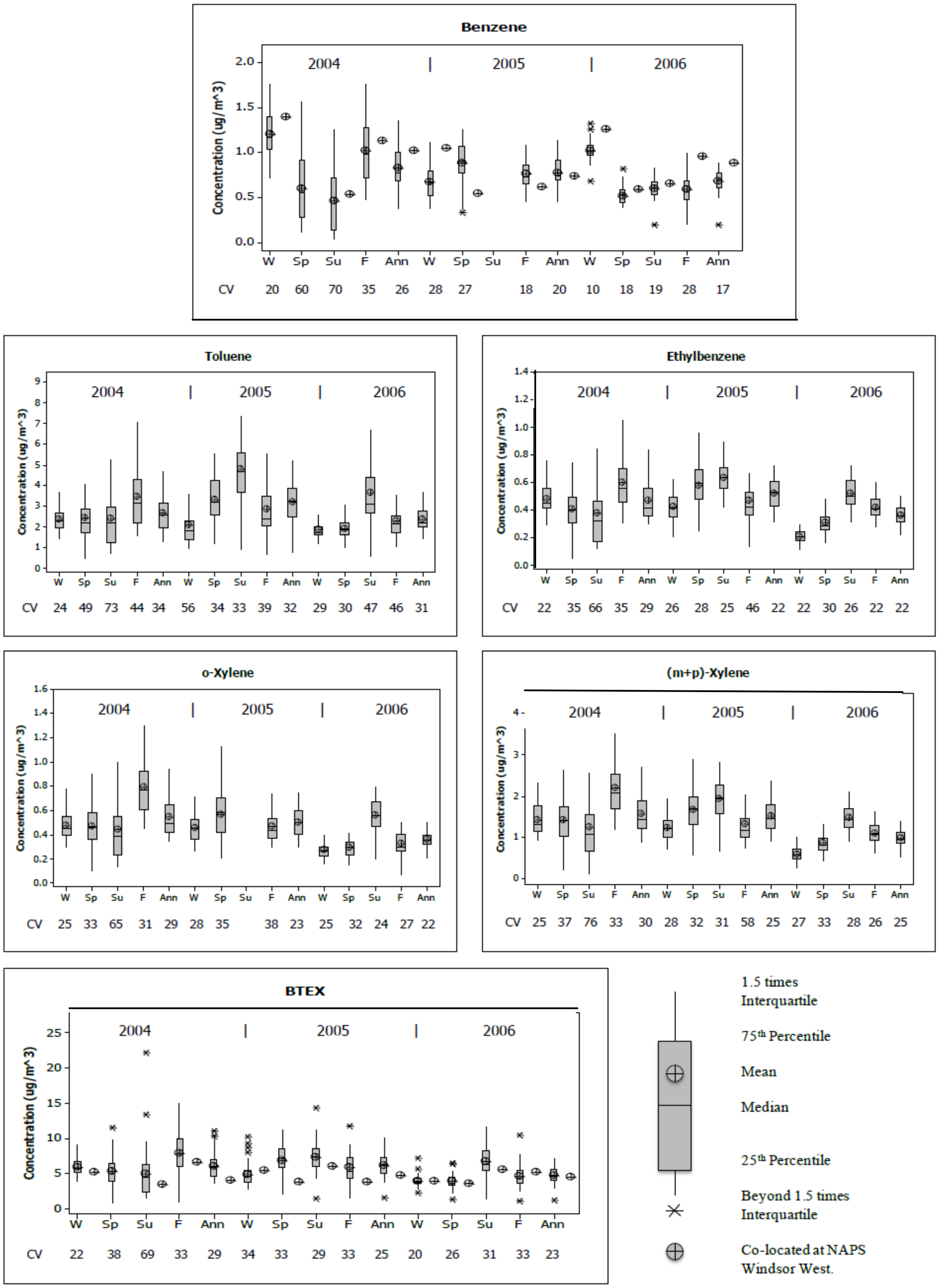

Figure 6.2. Boxplots of individual and total BTEX concentrations (CV=coefficient of variation, %. Points beyond 1.5 times interquartile shown for benzene and total BTEX only).

6.3.2 Seasonal and Annual Trends

Observations from the three-year sampling network reveal that for toluene and benzene, the fall season is most representative of the annual mean, whereas for ethylbenzene, xylenes, and BTEX it is the spring season (Fig 6.2). Considering the measurement data from the NAPS station, for benzene and o-xylene the fall season is most representative of long term annual average concentrations, whereas for toluene, (m+p)-xylene, and BTEX it is spring, and for ethylbenzene it is summer. For four out of the six species, the spatial network predicted the same season as the NAPS station, as well as revealed the same overall trend; that measurements made during the transition seasons (spring and fall) are more representative of long term annual means.

When comparing how well the spatial network sampling measurements represent the long term seasonal means obtained at the NAPS station, for toluene, o-xylene, (m+p)-xylene, and BTEX, the measurements obtained from both methods were similar and followed the general trend of summer highs, winter lows, and fall and spring values falling in between. For benzene although the measurements from the two methods differed by a factor of two, the concentrations followed the same general trend. For ethylbenzene, the NAPS station identified summer as being representative of annual concentrations whereas the spatial network identified spring.

Previous studies have observed mixed seasonal effects on BTEX concentrations. Hansen and Palmgren (1996) observed minor seasonal variations in VOC concentrations in Copenhagen with lower concentrations occurring in the warmer months. Pankow et al. (2003) observed higher benzene and toluene concentrations in the winter throughout the United States, whereas Ho et al. (2004) observed higher xylene concentrations in the summer, no seasonal variability of ethylbenzene and toluene, and lower summer benzene concentrations in Hong Kong. A possible explanation for such mixed seasonal variability observed in both the literature and our study is that although sampling was performed over every season, a given 2-week monitoring period in a season (the design followed in this study) may experience meteorology that is not consistent with seasonal averages. For example, the average temperature during each of the winter sampling sessions was within +/- 1.1°C of the long term (30 years) seasonal temperature, however for the remaining seasons the range was larger; +/- 2.5°C for spring, +/- 4.7°C for summer, and +/-9.5°C for fall. Future studies should consider how such variations affect the representativeness of discrete concentration measurements to the full season of study.

Overall, the three-year spatial network which essentially provides a snapshot of seasonal measurements was fairly representative of the concentrations and seasonal patterns obtained at the NAPS station. Both methods reveal that measurements made during the transition seasons were most representative of annual mean concentrations and therefore, when resources are limited to single season sampling these seasons would provide the best estimation of annual concentrations. Transition seasons were also observed to provide the best estimates of nitrogen oxides in Vancouver, Canada (Henderson et al., 2007).

Each seasonal mean was compared to the corresponding three-year seasonal average (i.e. spring 2004 compared with spring three-year) and the percent difference between the two was calculated in order to assess how much variability can be attributed to meteorology. Among the six compounds (B, T, E, (M+P)-X, O-X, BTEX), the variability was lower for toluene and BTEX (24 and 25%, respectively) and higher for benzene, ethylbenzene, o-xylene, and (m+p)-xylene (30, 31, 39, 40% respectively). The four seasons showed similar results with upper limits averaged among six compounds ranging from 28-38%. This demonstrates that although spring and fall campaigns may be more representative of annual averages they can still be off by a factor of 33% (fall) or 38% (spring), due to meteorological variability from year to year. On average the highest seasonal mean concentrations were approximately double the lowest seasonal means (i.e. BTEX, 8.71 $\mu g/m^3$ in fall 2004 vs. 4.97 $\mu g/m^3$ in fall 2006). Ho et al. (2004), considering two seasons (winter and summer), observed comparable patterns with the highest seasonal benzene concentrations being 1.7-6.5 times the lowest seasonal means at the three sites.

Overall 2005 had slightly higher BTEX concentrations than 2004, with 2006 having the lowest concentrations. Although the land use patterns remained fairly consistent, some variability is expected since weather conditions can change significantly from year to year. Considering ozone concentrations, Brook et al. (2000) recommend considering a minimum of five years in order to have confidence in representing average meteorological conditions.

6.3.3 Correlations and Ratios

The Spearman rank correlation coefficients indicative of consistency in spatial patterns for each season are provided in Table 6.1. The majority of the BTEX species displayed a strong positive correlation with one another. This is consistent with previous studies that observed strong correlations amongst BTEX in the United States (Pankow et al., 2003), Greater Cairo (Khoder, 2007), India (Hoque et al., 2008) and Canada (Miller et al., 2010). Correlations between ethylbenzene and the two xylene species were the highest ($r > 0.74$). The high correlations suggest that the species were originating from common sources. The lower correlation coefficients ($r < 0.60$) were mainly seen between benzene and the other BTEX species; a trend that was also observed by Parra et al. (2006), Smith et al. (2007), and Su et al. (2010) likely due to benzene being emitted almost solely from vehicles whereas the other four species were likely emitted from both vehicles and industrial activities. The strongest correlations were observed in 2004. The decline in the strength of the correlations in 2005 and 2006 could be attributed to the change in sampling strategy; backyard instead of roadside in 2004. With roadside sampling the majority of pollutant concentration contributions are from fresh mobile sources which have a relatively consistent ratio of species in their composition whereas residential backyards may receive a mix of varying photochemically aged emissions from nearby roads and other more distant sources. In 2004, the summer season exhibited the highest correlations (bold numbers in Table 6.1), whereas in 2005 it was fall and in 2006 it was spring.

Table 6.1. Spearman rank correlation coefficients among species within each period (bold numbers indicate the highest correlation coefficients among the 4 seasons in each year). All coefficients significant at the p<0.01 level.

Season	Pollutant	Benzene	Toluene	Ethylbenzene	o-Xylene	(m+p)-Xylene
Winter	Toluene	0.70				
2004	Ethylbenzene	0.57	0.77			
	o-Xylene	0.68	0.83	0.950		
	(m+p)-	0.65	0.83	0.90	0.95	
	Total BTEX	0.79	0.94	0.88	0.94	**0.94**
Spring	Toluene	0.70				
2004	Ethylbenzene	0.57	0.77			
	o-Xylene	0.51	0.83	0.93		
	(m+p)-	0.46	0.74	0.95	0.92	
	Total BTEX	0.74	0.95	0.90	0.90	0.87
Summer	Toluene	**0.88**				
2004	Ethylbenzene	**0.91**	**0.94**			
	o-Xylene	**0.91**	**0.95**	**0.98**		
	(m+p)-	**0.77**	**0.87**	0.84	0.86	
	Total BTEX	**0.91**	**0.98**	**0.96**	**0.96**	0.92
Fall	Toluene	0.68				
2004	Ethylbenzene	0.65	0.63			
	o-Xylene	0.68	0.62	0.94		
	(m+p)-	0.64	0.64	**0.97**	**0.96**	
	Total BTEX	0.76	0.93	0.81	0.80	0.83
Winter	Toluene	0.66				
2005	Ethylbenzene	0.56	0.55			
	o-Xylene	0.57	0.62	0.82		
	(m+p)-	0.66	0.74	0.84	0.90	
	Total BTEX	0.73	0.96	0.68	0.72	0.83
Spring	Toluene	0.64				
2005	Ethylbenzene	**0.69**	**0.77**			
	o-Xylene	0.69	0.77	0.94		
	(m+p)-	**0.73**	**0.79**	0.95	0.96	
	Total BTEX	0.71	0.94	0.88	0.88	0.84
Summer[1]	Ethylbenzene		0.69			
2005	(m+p)-		0.58	0.93		
	Total BTEX		**0.98**	0.79		0.71
Fall	Toluene	**0.78**				
2005	Ethylbenzene	0.69	0.73			
	o-Xylene	**0.71**	**0.78**	**0.96**		
	(m+p)-	0.68	0.74	**0.98**	**0.99**	
	Total BTEX	**0.76**	0.93	**0.88**	**0.91**	**0.89**

Winter 2006	Toluene	0.56				
	Ethylbenzene	0.59	0.59			
	o-Xylene	0.59	0.50	0.74		
	(m+p)-	**0.65**	0.65	0.90	0.77	
	Total BTEX	0.75	0.91	0.79	0.70	**0.85**
Spring 2006	Toluene	0.41				
	Ethylbenzene	0.65	0.73			
	o-Xylene	**0.67**	0.68	**0.93**		
	(m+p)-	0.63	0.72	**0.97**	**0.95**	
	Total BTEX	0.58	0.95	**0.86**	**0.80**	0.85
Summer 2006	Toluene	0.44				
	Ethylbenzene	0.63	0.59			
	o-Xylene	0.51	0.50	0.81		
	(m+p)-	0.65	0.55	0.94	0.88	
	Total BTEX	0.60	**0.96**	0.70	0.59	0.68
Fall 2006	Toluene	**0.77**				
	Ethylbenzene	**0.66**	**0.75**			
	o-Xylene	0.65	**0.77**	0.78		
	(m+p)-	0.57	**0.78**	0.90	0.89	
	Total	**0.82**	0.95	0.82	0.79	0.81

[1]-benzene and o-Xylene data not available

Boxplots of the T/B ratios are presented in Figure 6.3. The seasonal mean T/B ratio ranged from 2.0 – 6.9 with a three-year average of 3.9. The annual T/B ratios was slightly higher in 2004 (4.4) and almost identical in 2005 (3.5) and 2006 (3.7). The T/B ratios are in good agreement with the values reported in the literature (Table 6.A1). There were consistent patterns observed over all three years; the lowest T/B ratios were observed in the winter season, highest in the summer (2004 & 2006 – no data for 2005), and the fall and spring seasons were the closest to the annual means. The two-week moving average T/B ratios from the Windsor West NAPS station canister measurements (not shown) followed a similar seasonal pattern to that observed in this investigation with the highest mean T/B ratio occurring in summer (4.3) and the lowest occurring in the winter (2.2). This result is consistent with several previous studies (Chattopadhyay et al., 1997; Ho et al., 2004; Hoque et al., 2008) that observed higher T/B ratios in the summer and lower in the winter. Factors affecting seasonal changes in the T/B ratios include photochemistry, meteorology and emissions. For example, fuel formulations in Canada vary seasonally and are blended to be more volatile in the winter in order to achieve a better cold start. Activities at industrial facilities may also have seasonal patterns which affect the ratios across the area.

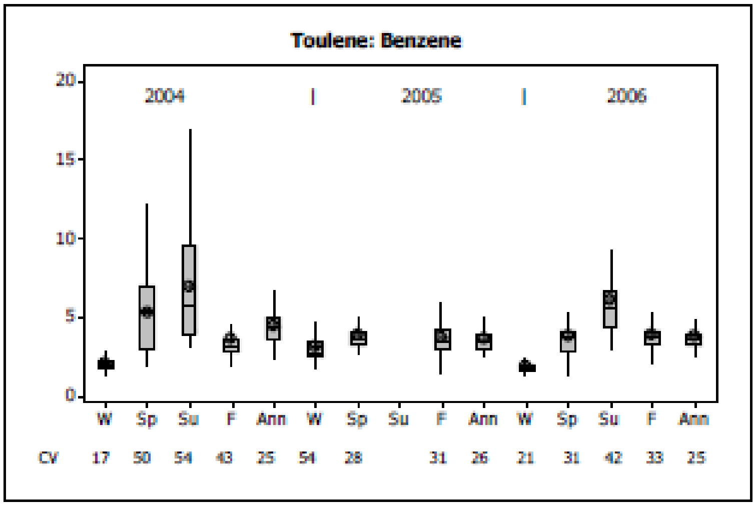

Figure 6.3. Boxplots of T/B ratios. (CV=coefficient of variation, %)

Spatial variability was also observed in the range of T/B values across the study area. In areas where the ratios are within the range of 1.5-4.3, as reported by previous studies (Hoque et al., 2008), traffic is more likely to have been the main source since benzene and toluene are constituents of vehicular emissions which are found in consistent ratios specific to that source. As suggested by Buczynska et al. (2009) in areas where the ratio is higher than the accepted 'traffic range' (>4.3) nearby point sources may be the main contributor to emissions in that area. Because benzene is primarily used in fuels, the likely contributors to the higher T/B ratios would be the nine industrial facilities in Windsor that reported toluene emissions to the National Pollutant Release Inventory (NPRI) (Environment Canada, 2010b). Spearman rank correlation coefficients of T/B ratios (not shown) were used to assess the spatial stability of the ratio across seasons. The correlations between seasons were moderate to high (r>0.50) and statistically significant (p<0.05) indicating that the sources are relatively consistent over all four seasons. In other words, the areas of highest T/B values largely remain that way throughout the year suggesting that the industrial source impacts can be discerned over and above the ‘ever-present’ traffic signal.

Figure 6.4 presents the (M+P)-X/E ratios along with the CV values for each season. The range of seasonal mean ratios observed over four seasons of the three-year study period was 2.6-3.7 with a three-year mean value of 3.0, which is at the upper range of previously observed ratios in urban settings (Table 6.A2) indicating that the photochemical age in the study area is relatively young. This can be expected due to the continual fresh emissions experienced in this city. In 2004 some seasonal variability was observed, however, in 2005 and 2006 little variability was observed between the seasons. The 2004 mean ratio was higher (3.4) than in 2005 (2.9) and 2006 (2.8). This may again be attributable to the location of the samplers over the three years. The spatial variability associated with the (M+P)-X/E ratios, as indicated by the CV, was lower than that associated with the T/B ratios. Small day to day variability in this ratio has been reported based on NAPS measurements in Windsor (Xu and Wang, 2012). Therefore, the low CV is indicative of a homogeneous environment in the study area in terms of photochemical age, rather than the photochemical aging being averaged out over the two-week sampling period.

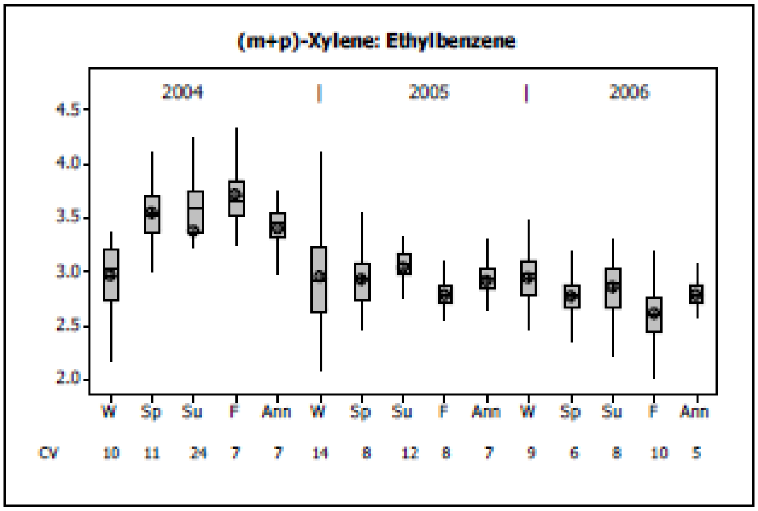

Figure 6.4. Boxplots of (M+P)/E ratios. (CV=coefficient of variation, %).

6.3.4 Spatial Variability and Exposure Misclassification

To demonstrate spatial variability in this study, the seasonal and annual CV, derived across the 50 measurement locations for each species are shown in Figure 6.2. There was a consistent pattern as to which species had greater spatial variability, with the greatest spatial variability being observed for toluene, followed by (m+p)-xylene, ethylbenzene, o-xylene, and benzene. The variability in the winter season was the most representative of the annual variability. The year with the greatest spatial variability was 2004, with 2005 and 2006 being lower and similar. This indicates, not surprisingly, that the larger relative number of roadside sampling sites in 2004 resulted in greater spatial variability. Based on a small subset of five common sites between 2005 and 2006 a high degree of correlation between the concentrations at the same site from year to year was observed (Appendix 6B and Fig 6.B1). This suggests that the general spatial pattern of concentrations remains stable from year to year.

The three-year average concentration maps of total BTEX and benzene are represented in Figure 6.5 to illustrate spatial variability. The highest benzene concentrations were typically found along the northwest of the city and the concentrations diminished towards the southeast (Fig 6.5a). This can be expected due to several factors. First, Huron Church Road (Fig 6.1) which carries cars and trucks towards and from the Ambassador Bridge is located in this area and therefore, high vehicular emissions are expected. Over the study period, the Bridge traffic averaged 5.4 million cars and 3.6 million trucks annually (Transport Canada, 2008). Secondly, this area is adjacent to urban and industrialized areas of Detroit, Michigan and therefore may experience greater impacts from Detroit emissions. Finally, the downtown Windsor core (Fig 6.1), associated with high traffic volume, is located in this area. The total BTEX map (Fig 6.5b) follows a similar spatial pattern to that of benzene. Wheeler et al. (2008) showed a similar general pattern of higher concentrations of benzene and toluene in the northwest of the city using land use regression (LUR) models, however their maps showed the highest concentrations occurring along major transportation corridors and intersections. This suggests that the methods used to generate the maps in Figure 6.5 are representative of what is happening at a broad urban scale but not of the concentration patterns at a smaller neighbourhood scale that LUR models are designed to resolve.

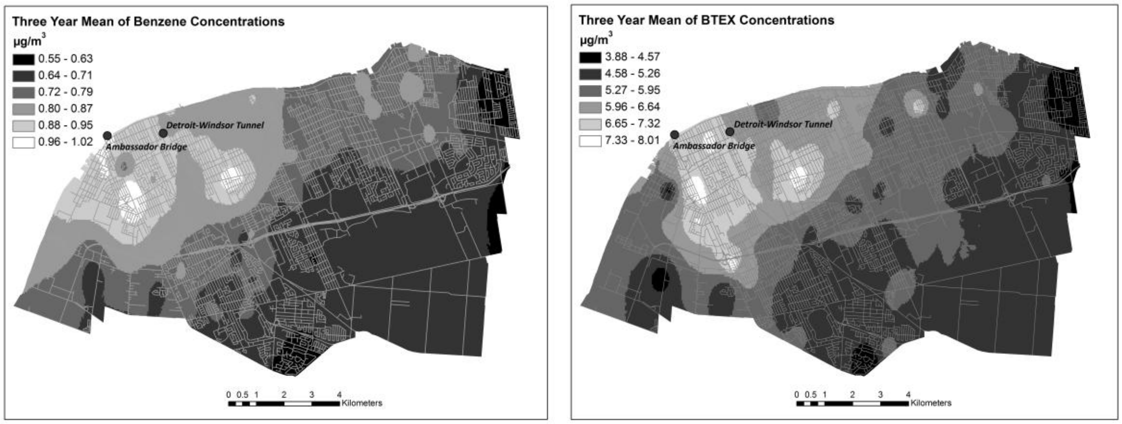

Figure 6.5. Concentration maps of average Benzene (a) and BTEX (b) concentrations over the three year period of 2004-2006.

The concentrations were ranked from high to low by site and the Spearman rank correlation coefficients among seasons for each species in each year are presented in Table 6.2 to examine whether the spatial ranking of concentrations was consistent between seasons. In the majority of cases, significant correlations were observed suggesting that the spatial pattern remains relatively consistent. When comparing the correlations between seasonal and annual means, the difference was small but noticeable among the four seasons. As indicated in Table 6.2 the fall season typically had the highest correlations with the annual means, therefore is best representative of the annual rank order of concentrations, followed by winter and summer, with spring being the least representative. This was confirmed by examining the seasonal maps (not shown here). This result reveals another factor in sampling design consideration. Although the seasonal to annual mean comparisons (Section 6.3.2) suggest that fall or spring are the best seasons for representing annual means, spring may not be a good choice to present the annual spatial pattern.

Table 6.2. Spearman rank correlation coefficients among seasons (bold numbers indicate the highest correlation coefficients between seasonal and annual means, among the 4 seasons in each year).

Year	Pollutant	Season	Annual	Winter	Spring	Summer
2004	Benzene	Winter	**0.89****			
		Spring	0.24	0.06		
		Summer	0.72**	0.74**	-0.32*	
		Fall	0.86**	0.70**	-0.08	0.71**
	Toluene	Winter	0.79**			
		Spring	0.61**	0.31*		
		Summer	0.77**	0.78**	0.14	
		Fall	**0.90****	0.60**	0.50**	0.56**
	Ethylbenzene	Winter	0.78**			
		Spring	0.62**	0.45**		
		Summer	**0.80****	0.63**	0.17	
		Fall	0.80**	0.50**	0.43**	0.55**
	o-Xylene	Winter	**0.83****			
		Spring	0.70**	0.60**		
		Summer	0.81**	0.74**	0.36**	
		Fall	0.82**	0.53**	0.45**	0.55**
	(m+p)-	Winter	**0.84****			
		Spring	0.70**	0.55**		
		Summer	0.77**	0.70**	0.33*	
		Fall	0.80**	0.58**	0.50**	0.42**
	BTEX	Winter	0.84**			
		Spring	0.57**	0.35**		
		Summer	0.78**	0.77**	0.11	
		Fall	**0.86****	0.60**	0.43**	0.53**
2005	Benzene	Winter	0.79**			
		Spring	**0.86****	0.41**		
		Summer[1]	-	-	0.65**	
		Fall	0.72**	0.44**	0.86**	-
	Toluene	Winter	0.68**			
		Spring	0.83**	0.41**		
		Summer	**0.86****	0.50**	0.61**	
		Fall	**0.86****	0.69**	0.68**	0.71**
	Ethylbenzene	Winter	0.57**			
		Spring	0.74**	0.36*		
		Summer	0.82**	0.52**	0.58**	
		Fall	**0.88****	0.56**	0.50**	0.68**
	o-Xylene	Winter	0.60**			
		Spring	**0.82****	0.36*		
		Summer	-	-	-	

		Fall	0.79**	0.49**	0.46**	-
	(m+p)-	Winter	0.59**			
		Spring	0.70**	0.41**		
		Summer	0.82**	0.51**	0.37*	
		Fall	**0.87****	0.61**	0.49**	0.73**
	BTEX	Winter	0.70**			
		Spring	0.80**	0.37*		
		Summer	0.83**	0.56**	0.51**	
		Fall	**0.86****	0.59**	0.51**	0.70**
2006	Benzene	Winter	0.83**			
		Spring	0.57**	0.31		
		Summer	0.78**	0.60**	0.33	
		Fall	**0.87****	0.67**	0.38*	0.69**
	Toluene	Winter	0.73**			
		Spring	0.66**	0.72**		
		Summer	**0.79****	0.52**	0.26	
		Fall	0.58**	0.54**	0.62**	0.25
	Ethylbenzene	Winter	0.70**			
		Spring	0.68**	0.60**		
		Summer	**0.78****	0.40*	0.34	
		Fall	0.77**	0.57**	0.67**	0.51**
	o-Xylene	Winter	0.54**			
		Spring	0.63**	0.51**		
		Summer	0.66**	0.00	0.23	
		Fall	**0.73****	0.51**	0.58**	0.36*
	(m+p)-	Winter	0.80**			
		Spring	0.75**	0.66**		
		Summer	0.73**	0.48**	0.36*	
		Fall	**0.82****	0.74**	0.70**	0.64**
	BTEX	Winter	**0.79****			
		Spring	0.67**	0.66**		
		Summer	0.76**	0.52**	0.20	
		Fall	0.77**	0.73**	0.69**	0.37*

[1] benzene and o-Xylene data not available

* significant at $p<0.05$

** significant at $p<0.01$

As shown in Figure 6.2, the mean benzene and total BTEX concentrations from ~50 sites are fairly close to the collocated NAPS site concentrations in the majority of cases; however the concentrations varied significantly across the monitoring sites with maximum concentrations of benzene (> 2x) and total BTEX (> 6x) greater than the measured concentration at the NAPS site. Those peak concentrations (Fig 6.5) were observed in sites along the northwest border of the city and within the densely populated downtown area (Fig 6.1). Consequently, exposure assignment based on NAPS monitoring could result in misclassification of (up to) a factor of six for total BTEX and a factor of two for benzene among residents living in those areas. These findings demonstrate that measurements at the NAPS station do not adequately reflect exposure to BTEX pollution among Windsor residents. Some recent studies have demonstrated this by comparing observed associations between central monitoring ambient concentrations and health outcomes to associations obtained by more extensive sampling (Ebelt et al., 2005; Koenig et al., 2005).

6.4 Conclusions

This study examined BTEX concentrations and correlations from a multi-season, multi-year, and multi-site perspective. Results of this study demonstrate seasonal, annual, and spatial variability in BTEX concentrations. The levels and rank order of the concentration values was in agreement with previously reported studies in urban cities. Comparisons between seasonal and annual values obtained by the spatial network and long term observations at the NAPS station revealed that the fall or spring season was most representative of annual concentrations. These conclusions may be specific to the area and may not apply to other regions that do not have similar seasonal patterns. Seasonal trends in concentration values were observed with summer highs and winter lows for toluene and xylenes. The spatial network represented the seasonal concentrations and pattern obtained at the NAPS station for the majority of the monitored species.

Strong and consistent correlations were observed between the BTEX species suggesting that these VOCs originated from common sources in the Windsor area. Consistent T/B ratios were observed from year to year and suggest that mobile emissions are the predominant sources of these compounds in Windsor with toluene from point sources also contributing. Seasonal variation in the T/B ratios was observed, consistent with previous studies. Spatial variability of T/B ratios points to some areas being dominated by traffic sources while other areas have additional contributing sources. Areas of the high or low T/B values were stable over the seasons suggesting that the T/B ratios could be useful to discern the industrial source impacts over and above the traffic signal. Future studies are planned to map these ratios in relation to the NPRI reported industrial sources in the area, as in Miller et al. (2011). The (M+P)-X/E ratios indicate a relatively young and homogenous photochemical age across the study area. In a city such as Windsor with several industrial sources and given the sampling design of this study it was not easy to see the impact of aging on this ratio.

Throughout the study several differences were seen between the roadside and backyard monitoring. The interspecies correlation, spatial variability, and (M+P)-X/E ratio analysis show that roadside monitors are more representative of fresh mobile emissions. While adequate spatial coverage and operational logistics may remain as primary considerations in site selection, our finding suggests that site characteristics should be considered as well in both site selection and comparison between studies.

The concentration maps generated across the study area were able to discern that the high traffic areas and those in close vicinity to Detroit experienced higher benzene and total BTEX levels however they could not depict the situation at a smaller scale consistent with previous LUR maps (Wheeler et al., 2008, Su et al., 2010). The consistent high correlation of concentrations between seasons suggests that spatial patterns, i.e. the rank order of high to low concentrations, remained relatively consistent from season to season within a given year, for all three years despite changing of monitoring sites from one year to another. Comparison of the range of concentrations obtained across the multiple sampling sites to that obtained at the NAPS site confirms the need for multiple sampling sites to reduce exposure misclassification, which could be up to a factor of six for these species in Windsor.

All sources of variability considered in the study (seasonal, annual, and spatial) are significant in air monitoring investigations and should be considered when assigning exposure for health based investigations. The use of multiple sampling sites provides comparison to the central monitoring station and quantifies potential exposure misclassification that could result from reliance on the NAPS data for health based studies. In regions such as Windsor which experiences variable meteorology between and within seasons, observed seasonal variability in BTEX concentrations indicates multiple season sampling better accounts for the changes in pollutant concentrations attributed to meteorology and photochemistry within a year. When resources are limited sampling during transition seasons, i.e. fall or spring, will provide a better estimate of annual concentrations. The benefit of multiple year sampling can be seen in the variability observed in the measurements, with respect to which season had the highest and lowest concentrations within a year, and which season best represented the annual pattern. The three-year data also allowed for quantification of the inherent uncertainty of employing two-week sampling, which was primarily designed to gain insight on spatial variability, as a snapshot to obtain long term seasonal means. However, results from this study indicate that the benefit of multiple year sampling diminishes when considering quantities indicative of major sources, photochemical age, spatial variability by species, and the rank order of high to low concentrations in the study area, since the observed inter-annual variability was low based on the correlations among the seasons, and the interspecies correlation and ratios.

This study only considers ambient concentrations, however since BTEX are known to be emitted by traffic, outdoor concentrations may be reasonable proxies of personal exposure. Stocco et al. (2008) reported that personal exposure to traffic related VOCs were predicted by outdoor concentrations in Windsor homes although indoor concentrations did provide better estimates. A limitation of the study is the reliance on two-week measurements to represent seasonal concentrations. Due to variable weather patterns, a given two-week period may not be characteristic of typical seasonal weather. A further limitation is the small number of consistent sites from year to year due to logistic reasons. Future studies should have a higher number of common sites to allow for spatial pattern comparison on an inter-annual basis. Moreover, the spatial analysis of measurements could be enhanced by incorporating site classification including residential, industrial, proximity to major and minor roads, and to compare the years to determine the extent to which the same range of site classifications and frequency representation of these classes. Additionally, the concentration maps could be further investigated to provide more insight into point source contributions, into regional pollution trends, particularly those of a transboundary nature between Detroit and Windsor, and into the locality of hot spots and whether these hot spots changed significantly between seasons and years. Furthermore, the ratios between BTEX could be more closely examined to determine whether there are distinct changes in the ratios based on the area of the city as in Miller et al. (2011). The multi-season, multi-year extensive spatial data obtained in this study could also be used to develop VOC LUR models for the region as in Wheeler at al. (2008) and Su et al. (2010).

Significance of this work includes air quality management and epidemiological study design. The within and between season, year and site comparisons are valuable to improving our understanding of intra-urban BTEX temporal and spatial patterns. The knowledge gained and research directions identified in this work can be applied to future studies to decide upon sampling frequency, timing, and potential misclassification when relying on central stations measurements to represent citywide averages. Those measurement and modeling initiatives can lead to policies to reduce health risks associated with VOC exposures.

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Appendix 6A.

Table 6.A1. Toluene/Benzene ratios reported in previous studies.

Study area (setting)	Season (year of study)	T/B Ratio	Source
Copenhagen (urban)	February (1994) – March (1995)*	Avg. = 2.2	Hansen and Palmgren, 1996
Various cities in Hungary (rural/urban)	Not specified	Avg. = 2.02 +/- 0.073	Gelencsr et al., 1997
Mexico City (urban)	Aug. – Oct. (1999), Jul. (2000) – Feb (2001) $^{1, 2}$	4.3-4.8	Bravo et al., 2002
Paris (urban)	Winter/Summer (1998/1999) ^{1}	2.9-3.4	Vardoulakis et al., 2002
Hong Kong (urban)	Winter/Summer (2000/2001) ^{1}	3-8	Ho et al., 2004
Great Cairo (urban and rural area)	Summer (2004)	1.29 (rural) – 2.45 (urban)	Khoder, 2007
Canosa di Puglia, Italy (urban)	Fall (2006)	Avg. = 3.4	Bruno et al., 2008
Delhi, India (urban)	Year round (2001-2002) ^{1}	1.8 – 2.54	Hoque et al., 2008
Belgium (urban)	June/September (2003), and September/October (2005) ^{3}	3.8 – 4.4	Buczynska et al., 2009
Windsor, Ontario and Detroit, Michigan (urban)	September (2008)	Avg. = 4.3 Windsor) Avg. = 2.9 (Detroit)	Miller et al., 2010
Beijing, China (urban)	July – October (2008) ^{3}	1.5-2.2	Liu et al., 2009

^{1} multi-season
^{2} multi-year
^{3} before and after a particular event

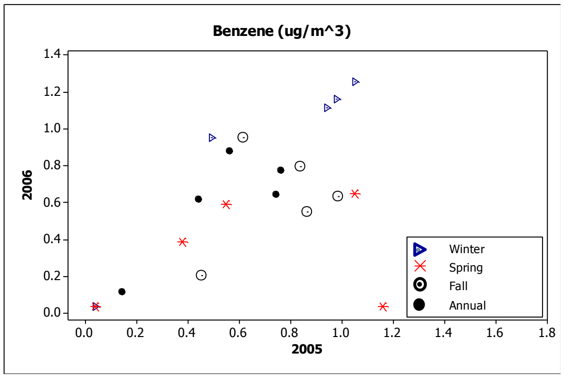
Table 6.A2. (m+p)-Xylene/Ethylbenzene ratios reported in previous studies**.**

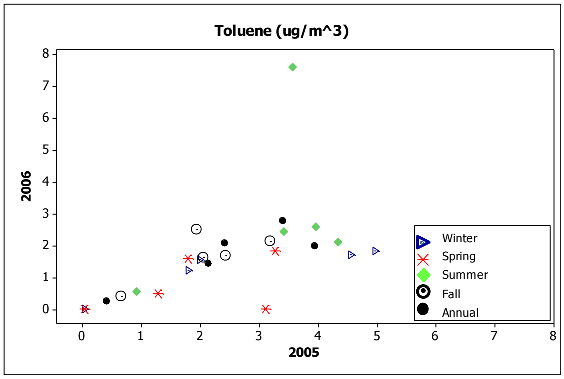
Study area	Site	(M+P)/E Ratio	Source
Central Taiwan [1]	One upwind of major city Two downwind	2.56 1.75-1.89	Chen et al., 2010
Beijing, China[1]	One urban site (20 m above ground level)	1.30-1.85	Liu et al., 2009
Hong Kong	1 urban 1 industrial 3 rural	1.65 1.7 1.1-1.3	Zhang et al., 2008
Hong Kong[2]	1 urban 1 rural 2 suburban	1.9 1.3 1.6-1.9	Guo et al., 2007
Yokohama, Japan[3]	3 industrial 1 residential 1 commercial 1 urban	1.24-1.44 1.45 1.53 1.13	Tiwari et al., 2010
Haifa, Israel	1 urban 1 industrial-commercial	5.64 ±1.21 4.31 ±1.46	Zalel et al., 2008
Australia, Austria, Brazil, Bulgaria, Chile, China, Croatia, Czech Republic, France, Germany, Greece, Hungary, Italy, Japan, Poland, Romania, Taiwan, Thailand, UK, US	12 urban 3 suburban 2 industrial	1.3-4.48 2-3.36 2.47-2.7	Monod et al., 2001
China, Greece, India, Italy, Japan, Korea, Taiwan, Turkey[4]	4 urban 8 industrial	0.6-4.68 0.38-4.2	Tiwari et al., 2010
Shing Mun Tunnel, Hong Kong	2 monitoring stations	2.61± 0.30	Ho et al., 2009
Australia, Austria, Brazil, Bulgaria, Chile, China, Croatia, Czech Republic, France, Greece, Hungary, Italy, Japan, Poland, Romania, Taiwan, Thailand, UK, US	Source samples	2.81-4.63	Monod et al.,

[1] E/(M+P) ratios reported, inversed to get (M+P)/E ratios
[2] E/(M+P) ratios obtained from graphs
[3] Results of their study
[4] Reported as results of previous studies

Appendix 6B.

A subset of 8 sampling sites that were common in 2005 and 2006 were investigated to gain some insight regarding whether the concentration patterns were similar on a site to site basis between the years. Of the eight sites that were in a consistent location in 2005 and 2006, only five had measurements that were above the detection limit for at least three seasons in each year. These five were used to generate scatter plots of the concentrations at these sites, presented in Figure 6.B1. The ranges of concentrations observed across those 5 sites are fairly close to that of all sites. A high degree of correlation can be seen between the concentrations at the same site from year to year, suggesting that the general spatial pattern of concentrations portrayed by this collection of locations remains consistent from year to year. Although this is a small subset of the total sites, the results are encouraging. Future studies could consider keeping a larger subset of sites consistent from year to year so that these results can be confirmed. Thus one year of sampling could be used to represent multiple years while maintaining representative spatial patterns.





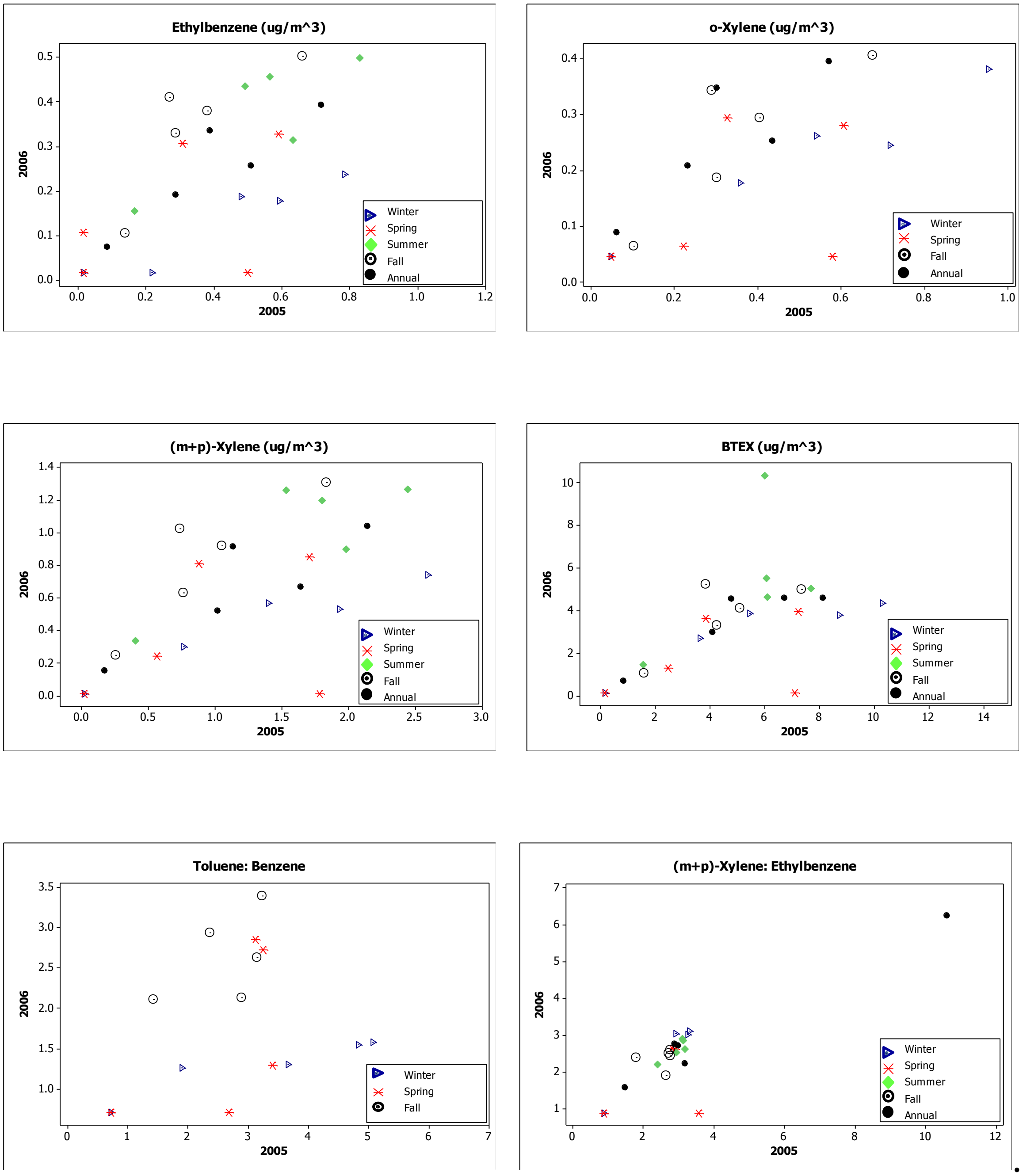


Figure 6.B1. Scatter plots of individual and total BTEX concentrations, Toluene: Benzene and (m+p)-Xylene: Ethylbenzene ratios, 2005 vs.2006.

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CHAPTER 7: SEASONAL CONTRIBUTIONS, HOT SPOT TRENDS, AND OVERALL HAZARD QUOTIENT OF BTEX IN WINDSOR

7.1 Introduction

BTEX species have been the focus of several recent studies (Ho et al., 2004; Khoder, 2007; Smith et al, 2007; Hoque et al., 2008; Miller et al., 2009). Although studies have demonstrated that BTEX concentrations exhibit seasonal variation (Ho et al., 2004; Hoque et al., 2008), less is known about how spatial patterns of concentrations vary seasonally and from year to year. Recent investigations have looked at how high concentration areas, referred to as ‘hot spots’, vary. In New Jersey, USA, spatial variability was seen to be higher for VOCs in a hot spot area than in an urban neighbourhood. Over three sampling campaigns, two in the summer and one in the winter, multiple hot spots were observed although the main high concentration zones remained the same (Zhu et al., 2008). Hung et al. (2005) investigated the VOC concentrations at several sites in the vicinity of an industrial park in Taiwan over the course of 10 months and noted that the spatial pattern of high concentration sites remained the same over the time period. However, Touma et al. (2006) demonstrated that four seasons of monitoring data are necessary to adequately represent spatial patterns of annual concentration averages for VOCs.

Pollutant concentrations at receptors can be affected by sources that originate significant distances away and are carried in with air mass movement. Hung et al., (2005) observed an association between lower wind speed and more uniformly distributed concentrations and also noted that concentration patterns changed depending on the predominant wind direction. Smith et al. (2007) also reported associations between wind direction and BTEX concentrations, consistent with the location of emission sources, in Texas. Furthermore, Tomlin et al. (2009) concluded that wind patterns play a role in determining where pollutant hot spots will occur. Other studies, using GIS techniques have noted associations between BTEX and wind patterns (Kwon et al, 2006; Arain et al., 2007). Alternatively, Ohura et al. (2006) noted that the distribution of ambient VOCs was independent of wind patterns.

Risk maps have been developed as a means to assess risk of disease based on residential exposure to specific pollutants. For example, Ohura et al. (2006) evaluated inhalation cancer risks from ambient VOC concentrations in an industrialized harbour area of Shizuoka, Japan. They reported seasonal differences in risk levels and identified benzene as a major contributor to this risk.

In order to investigate the association between spatial concentration patterns and wind direction as well as the risk due to exposure to BTEX, additional components were analysed using the 2004 and 2006 BTEX data from Chapter 6. The objectives are:

- To determine how the relative concentrations in each season contribute to the overall annual average (each season has an equal weight in the annual mean calculation), for each species, on a site-by-site basis, and to what degree those contributions change by location within a season.
- To determine which season was a better proxy of the annual mean and whether this was consistent among species and between the two years.
- To assess whether hot spots, or clustering of high concentration sites, remained the same among species and from season to season or year to year and whether these changes support the necessity of multiple season / multiple year sampling.
- To investigate qualitative associations between the spatial pattern of concentrations and the predominant wind directions, using wind roses.
- To develop a potential exposure risk map in Windsor using the observed concentrations and the Ambient Air Quality Criteria (AAQC) for Ontario.

7.2 Methods

BTEX concentrations for 2004 and 2006 were used in the analyses in this chapter. Data from 2005 were excluded due to a large number of BDL readings for summer. For 2004 and 2006, only sites which had valid data (i.e. >MDL) in all four seasons were included. Annual mean concentrations are calculated based on equally weighted contributions from each season, however, high or low concentrations in one season may bias the interpretation of the annual mean. To determine whether one season was more likely to govern the annual means, seasonal contribution analyses were carried out for the BTEX species. Bar graphs were generated for each species in each year depicting which percentage each season contributed to the annual means. Additionally, the general statistics of seasonal contributions to annual concentrations were calculated. Both were done on a site by site basis.

For the hot spot analysis, proportional concentration maps were generated for 2004 and 2006 for all four seasons for benzene and toluene. This was done by mapping the sites in ArcGIS 9.3. The concentration ranges were divided into ten natural break points, represented by different size circles with areas proportional to the concentration levels. As reported in Chapter 6, the sites did not remain in the same location between years; however, both years had a similar number of sites (approximately 50) resulting in a sampling density in the range of 1 sampler / 3.4 km^2 as recommended by Cocheo et al. for BTEX sampling. The sites were selected to provide adequate spatial coverage of the city based on objective criteria as described in Wheeler et al. (2008). To compare sampler spacing for both campaigns, the distance to the nearest neighbours for each site was calculated. In 2004 the average spacing was 1.4 km and in 2006 it was 1.5 km. The maximum distance between sites did not exceed 4 km in either year. Because these distances are less than the variogram range of 7.5 km for total BTEX in Windsor reported by Miller et al. (2010) (Chapter 3) it was assumed that clusters of high concentration sites across the city should be discernible regardless of the change in sampler locations. Benzene and toluene were chosen because toluene was highly correlated with ethylbenzene and the xylenes (Chapter 6), therefore these two species would be representative of the pattern for all (i.e. benzene, and toluene for TEX). Wind roses for each two-week sampling period were generated using hourly wind speed and direction collected at Windsor Airport (Environment Canada, 2011a) and WRPLOT View Software (Lakes Environmental, 2011).

The AAQCs for Ontario (Ontario Ministry of the Environment, 2011) were compared to the two-year mean and maximum two-week concentrations among all sites from the sampling campaign as well as the NAPS (Environment Canada, 2011) data. Specifically, the concentrations at each site were divided by the AAQC values and summed for BTEX to generate an overall hazard quotient (HQ) as described in equation 7.1.

$$HQ = \left(\frac{C_B}{AAQC_B} + \frac{C_T}{AAQC_T} + \frac{C_E}{AAQC_E} + \frac{C_X}{AAQC_X}\right) \qquad \textbf{(7.1)}$$

Annual 2004 and 2006 exposure risk maps were then generated using inverse distance weighting (IDW), with a power of two, of the HQ values across the sampling area to illustrate the distribution of risk in the city (Figure 7.1). The maps were generated using ArcGIS 9.3 by assigning each site an HQ value and then applying inverse distance weighting (IDW) to obtain a gradient map with a 10 m X 10 m grid. The exposure risk maps presented in this study do not consider a particular disease but are simply based on the limits of the criteria in place to protect human health set forth by the government.

The yearly maps were further investigated to determine whether the data could be justifiably combined to generate a two-year average map. The sampling area was divided into uniform grids to obtain a resolution which would provide a reasonable amount of cells having sites from each year present. Figure 7.2 illustrates the 1.5 km X 1.5 km grids with 19 cells containing measurements from at least one site from each year. For each of these 19 cells, the mean values for 2004 and 2006 were calculated using sites within the cell. Results from a paired t-test of 2004 and 2006 cell means showed a statistically insignificant (p<0.001) difference between the two years. Additionally the percent difference in annual means between the two years was small (2004 mean = 0.35, 2006 mean = 0.30, % difference in means = 16%), therefore justifying combining the 2004 and 2006 maps to generate a two-year average map. The two-year average map was generated by converting each yearly IDW map to raster format and using the raster calculator function to obtain the two-year average values which were used to produce a two-year average HQ map for the city.

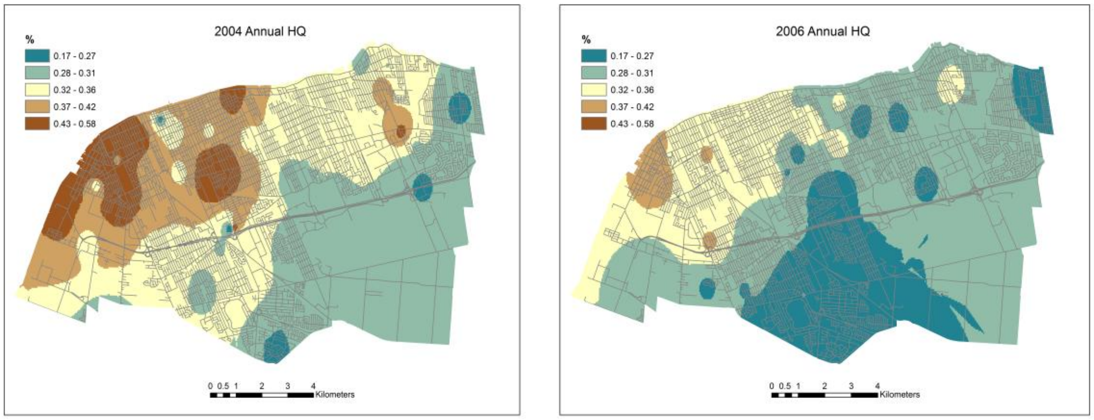


Figure 7.1. Risk maps based on the HQ values for 2004 and 2006**.**

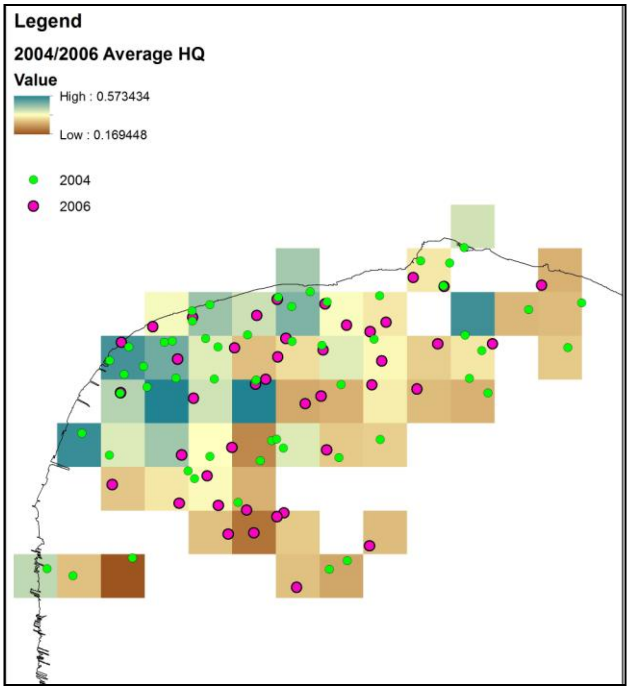
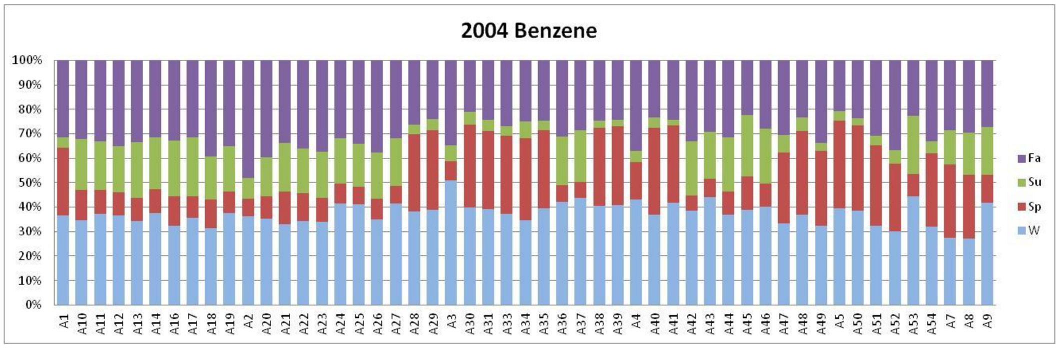


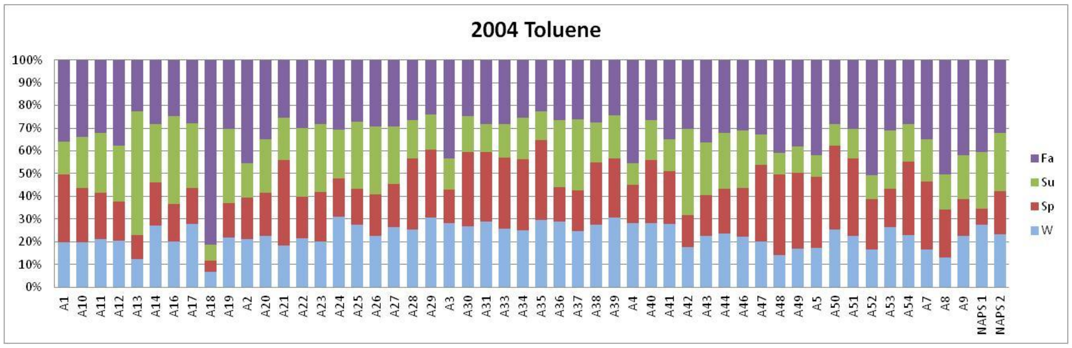
Figure 7.2. Grids (1.5 km X 1.5 km) with the locations of sampling sites.

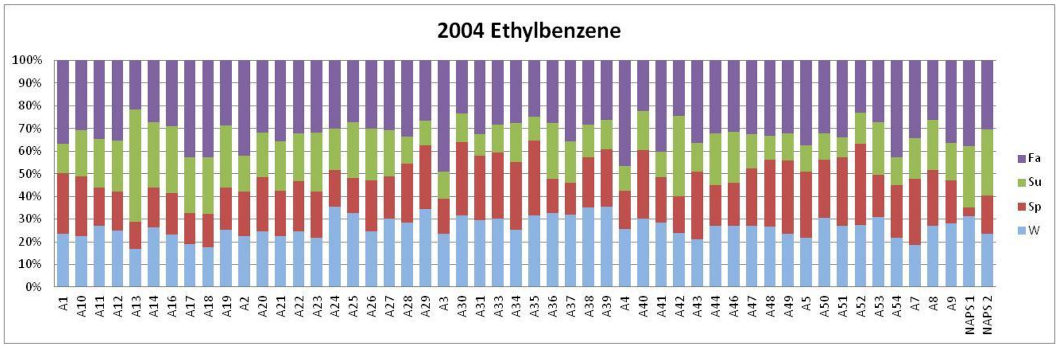
7.3 Results

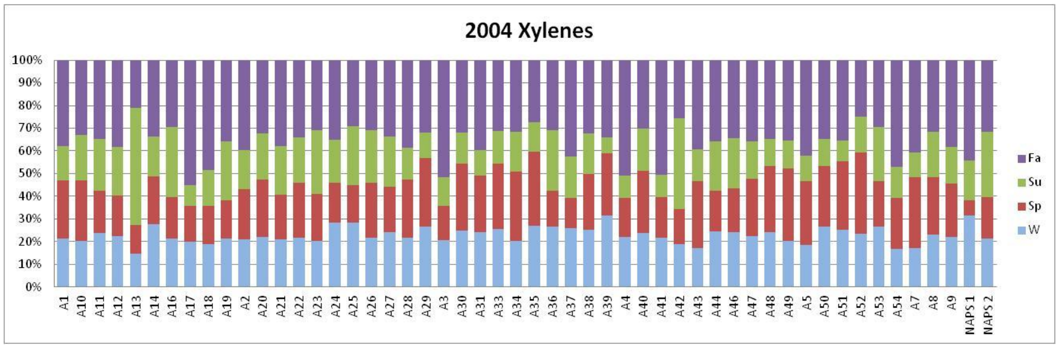
7.3.1 Seasonal Contributions to Annual Means

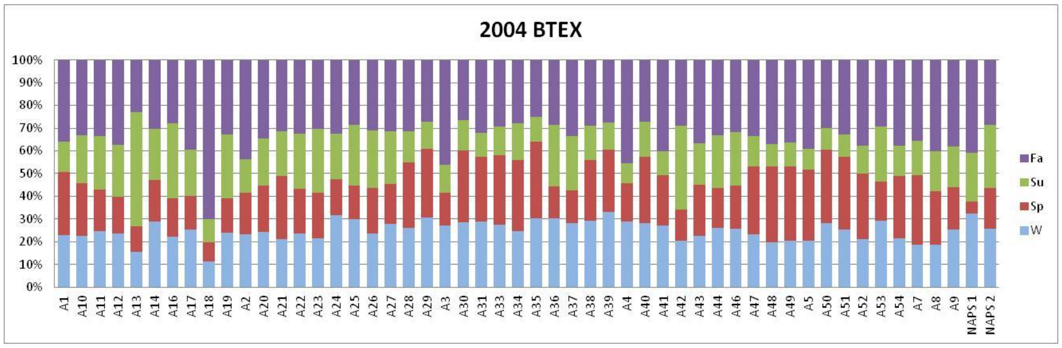
Figure 7.3 and Table 7.1 depict the relative seasonal contributions for each species in 2004 and 2006. They illustrate what percentage of the annual mean was determined by the mean concentrations from each season, which is important for selecting representative seasons. Seasons which contribute close to 25% towards the annual mean would provide measurements representative of annual exposure. The bold values in Table 7.1 indicate representative seasons. The shaded values indicate seasons which had large site by site contribution variability. Differences were seen between the two years with the exception of benzene which had the largest contribution coming from the winter season (37%) in both years. Spring and summer had smaller contributions in 2004 for benzene whereas the remaining three seasons were approximately equal in 2006. In 2004, for TEX and total BTEX fall made the largest contributions to the annual mean (32-36%), followed by winter (25-37%), spring (22-23%) and summer (19-21%). In 2006, for TEX and total BTEX summer made a larger contribution (36-39%) with the other three seasons approximately equal (20-29%) except for ethylbenzene where winter makes a small contribution (13%).

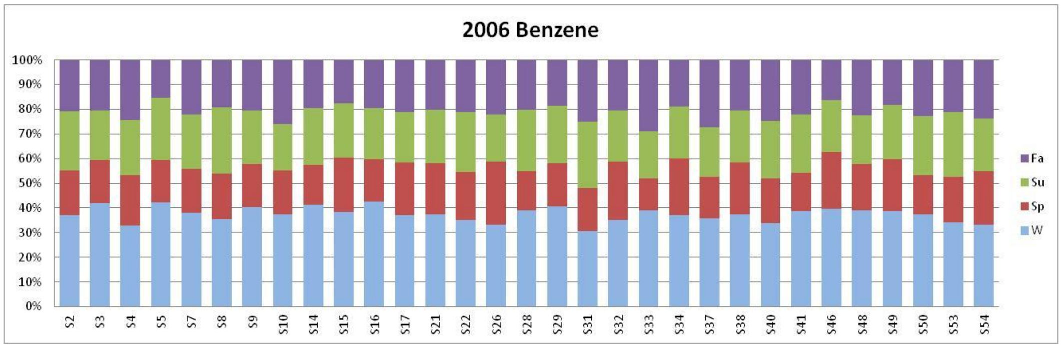

2004 Benzene
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
A1
A10
A11
A12
A13
A14
A16
A17
A18
A19
A2
A20
A21
A22
A23
A24
A25
A26
A27
A28
A29
A3
A30
A31
A33
A34
A35
A36
A37
A38
A39
A4
A40
A41
A42
A43
A44
A45
A46
A47
A48
A49
A5
A50
A51
A52
A53
A54
A7
A8
A9
Fa
Su
Sp
W

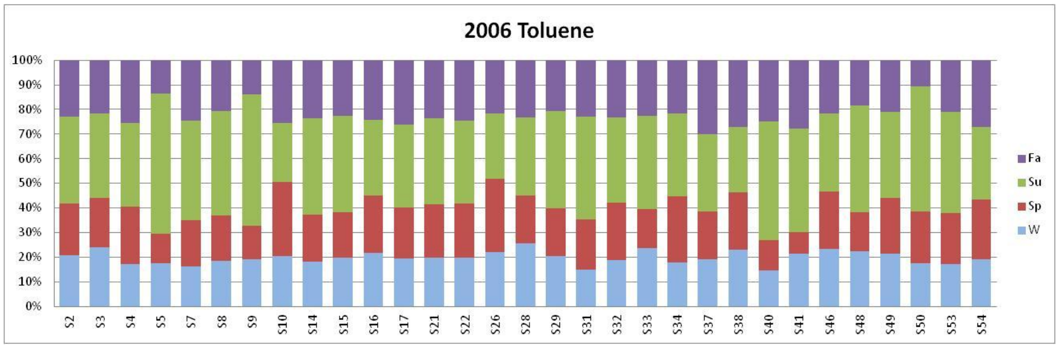

2004 Toluene
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
A1
A10
A11
A12
A13
A14
A16
A17
A18
A19
A2
A20
A21
A22
A23
A24
A25
A26
A27
A28
A29
A3
A30
A31
A33
A34
A35
A36
A37
A38
A39
A4
A40
A41
A42
A43
A44
A46
A47
A48
A49
A5
A50
A51
A52
A53
A54
A7
A8
A9
NAPS 1
NAPS 2
Fa
Su
Sp
W

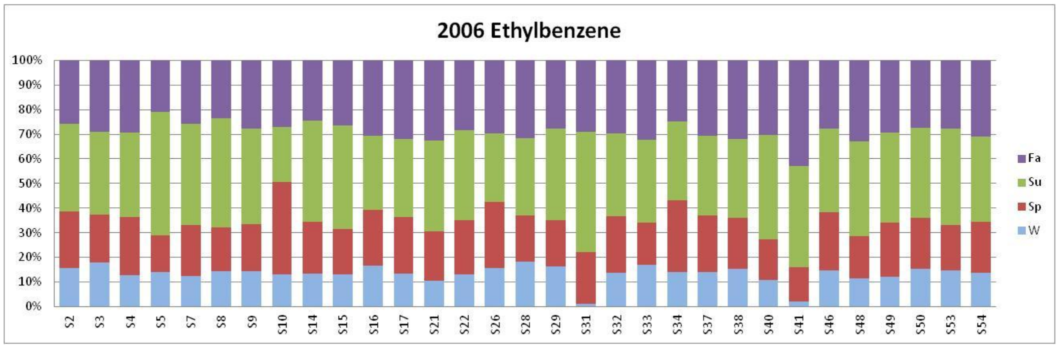

2004 Ethylbenzene
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
A1
A10
A11
A12
A13
A14
A16
A17
A18
A19
A2
A20
A21
A22
A23
A24
A25
A26
A27
A28
A29
A3
A30
A31
A33
A34
A35
A36
A37
A38
A39
A4
A40
A41
A42
A43
A44
A46
A47
A48
A49
A5
A50
A51
A52
A53
A54
A7
A8
A9
NAPS 1
NAPS 2
Fa
Su
Sp
W


2004 Xylenes
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
A1
A10
A11
A12
A13
A14
A16
A17
A18
A19
A2
A20
A21
A22
A23
A24
A25
A26
A27
A28
A29
A3
A30
A31
A33
A34
A35
A36
A37
A38
A39
A4
A40
A41
A42
A43
A44
A46
A47
A48
A49
A5
A50
A51
A52
A53
A54
A7
A8
A9
NAPS 1
NAPS 2
Fa
Su
Sp
W


2004 BTEX
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
A1
A10
A11
A12
A13
A14
A16
A17
A18
A19
A2
A20
A21
A22
A23
A24
A25
A26
A27
A28
A29
A3
A30
A31
A33
A34
A35
A36
A37
A38
A39
A4
A40
A41
A42
A43
A44
A46
A47
A48
A49
A5
A50
A51
A52
A53
A54
A7
A8
A9
NAPS 1
NAPS 2
Fa
Su
Sp
W


2006 Benzene
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
S2
S3
S4
S5
S7
S8
S9
S10
S14
S15
S16
S17
S21
S22
S26
S28
S29
S31
S32
S33
S34
S37
S38
S40
S41
S46
S48
S49
S50
S53
S54
Fa
Su
Sp
W


2006 Toluene
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
S2
S3
S4
S5
S7
S8
S9
S10
S14
S15
S16
S17
S21
S22
S26
S28
S29
S31
S32
S33
S34
S37
S38
S40
S41
S46
S48
S49
S50
S53
S54
Fa
Su
Sp
W


2006 Ethylbenzene
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
S2
S3
S4
S5
S7
S8
S9
S10
S14
S15
S16
S17
S21
S22
S26
S28
S29
S31
S32
S33
S34
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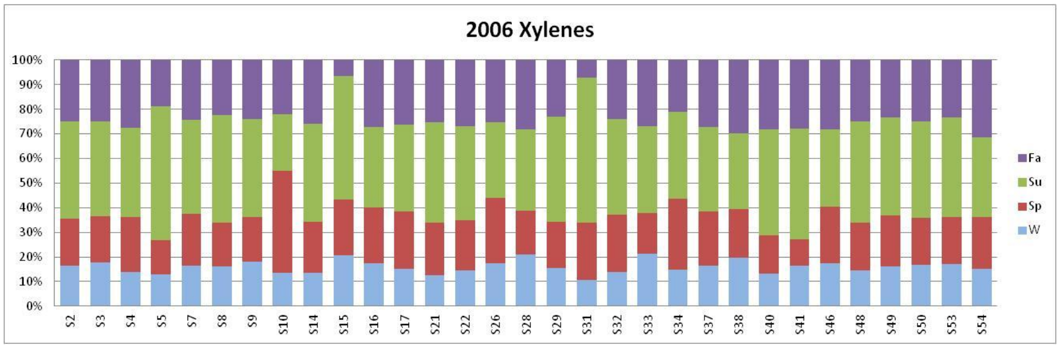
S38
S40
S41
S46
S48
S49
S50
S53
S54
Fa
Su
Sp
W



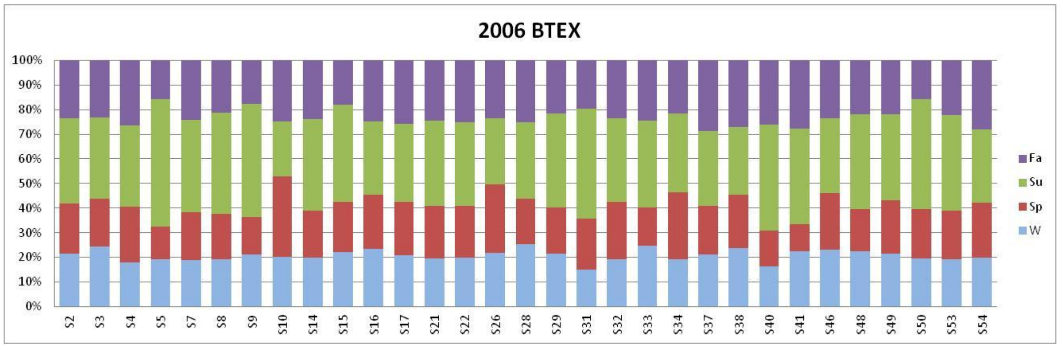


Figure 7.3. Seasonal contributions to annual means with site identification labels along the x-axis.

Table 7.1. General statistics of seasonal contributions to annual concentrations, 2004 and 2006. Mean and median values closest to 25% in that year are bolded, CV greater than 40% are shaded.

2004		**Mean**	**Min**	**Max**	**Median**	**SD**	**CV**
Benzene	% Winter	37	27	51	37	5	12
	% Spring	19	6	36	12	11	59
	% Summer	13	2	25	17	8	62
	% Fall	**30**	21	48	**31**	6	19
Toluene	% Winter	**23**	7	31	**23**	5	23
	% Spring	**23**	5	38	**21**	8	35
	% Summer	21	7	54	19	9	43
	% Fall	33	23	81	30	10	29
Ethylbenzene	% Winter	**27**	17	35	**27**	5	17
	% Spring	**22**	4	36	**21**	7	30
	% Summer	19	9	49	18	8	41
	% Fall	32	22	49	32	6	19
Xylenes	% Winter	**23**	15	32	**22**	4	15
	% Spring	**23**	7	36	**23**	6	27
	% Summer	19	7	52	18	8	43
	% Fall	36	21	55	35	7	19

BTEX	% Winter	**25**	11	33	**25**	4	17
	% Spring	**22**	5	34	**20**	7	33
	% Summer	19	9	50	18	8	43
	% Fall	34	23	70	33	7	21
2006							
Benzene	% Winter	37	31	43	37	3	8
	% Spring	19	13	26	18	3	15
	% Summer	**22**	19	27	**22**	2	10
	% Fall	**21**	15	29	**21**	3	14
Toluene	% Winter	20	15	25	20	3	13
	% Spring	20	9	30	21	5	23
	% Summer	37	24	57	35	8	21
	% Fall	**23**	11	30	**23**	4	18
Ethylbenzene	% Winter	13	1	18	14	4	27
	% Spring	**21**	14	38	**21**	4	21
	% Summer	37	22	50	37	6	16
	% Fall	**29**	21	43	**29**	4	13
Xylenes	% Winter	16	11	21	16	3	16
	% Spring	21	11	41	21	5	25
	% Summer	39	23	59	39	7	18
	% Fall	**24**	6	31	**25**	5	22
BTEX	% Winter	21	15	25	21	2	11
	% Spring	20	11	33	20	4	21
	% Summer	36	23	52	35	6	18
	% Fall	**23**	16	29	**24**	3	14

As seen in Table 7.1, spring and winter were most representative of the annual mean (~25%) in 2004 whereas in 2006 it is fall. Considering both years together, fall and spring were the most representative seasons. This supports the previous conclusions in Chapter 6 that these transition seasons would be the best proxies of annual means.

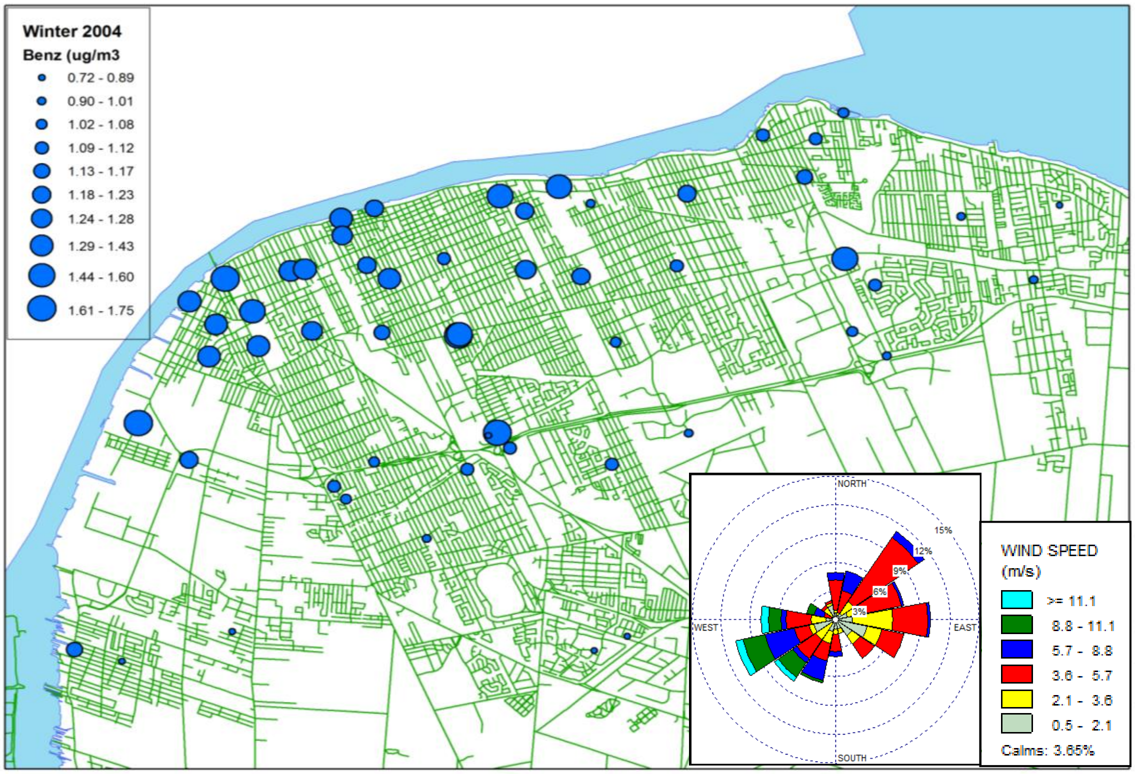
Considering whether the seasonal contributions changed based on location, the percent contributions within a season were much more consistent in 2006 than 2004 (see total BTEX in both years, Table 7.1 and Figure 7.3). In 2004, percent contributions within a season did change with location; for benzene these changes were more pronounced in spring and summer than the other two seasons, whereas for the TEX species variability is seen across all seasons however the majority of the significant changes are limited to ~ 20% of the sites. Based on the CVs (Table 7.1), summer had the highest with winter and fall having lower variability among sites in 2004. In 2006 the CV was more consistent (<30%) in all seasons, with relatively high variability in spring and low in winter.

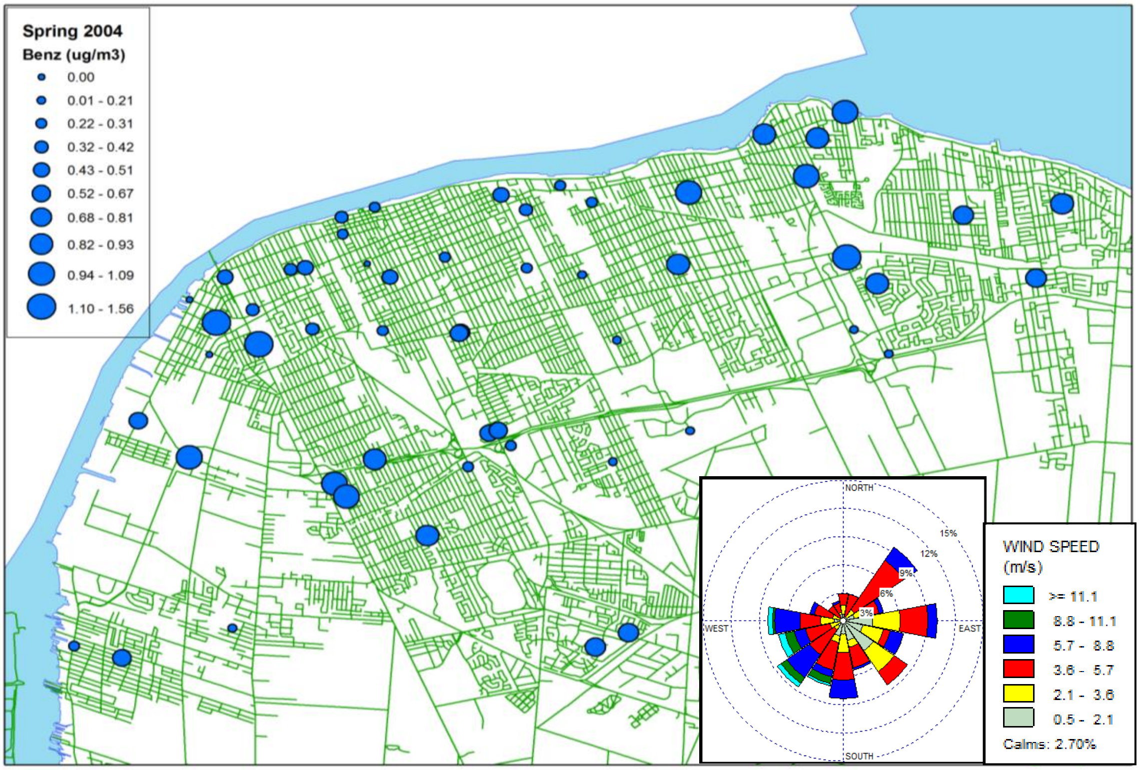
Comparing total BTEX to each species, BTEX most resembles toluene (Fig 7.3 and Table 7.1). This is expected because toluene is the greatest contributor to total BTEX concentrations. Moreover, the seasonal rank order of contributions was consistent among T, E and X and BTEX in both years (Table 7.1). Comparing the two years, more consistency was seen in percent contributions by location in 2006 than 2004. Consistency was observed between the two years in terms of the rank order of contributions and which season would be a better proxy of annual means for benzene. For the remaining species, the same consistency was not observed in terms of proxy seasons as well as in terms of which season makes larger contributions.

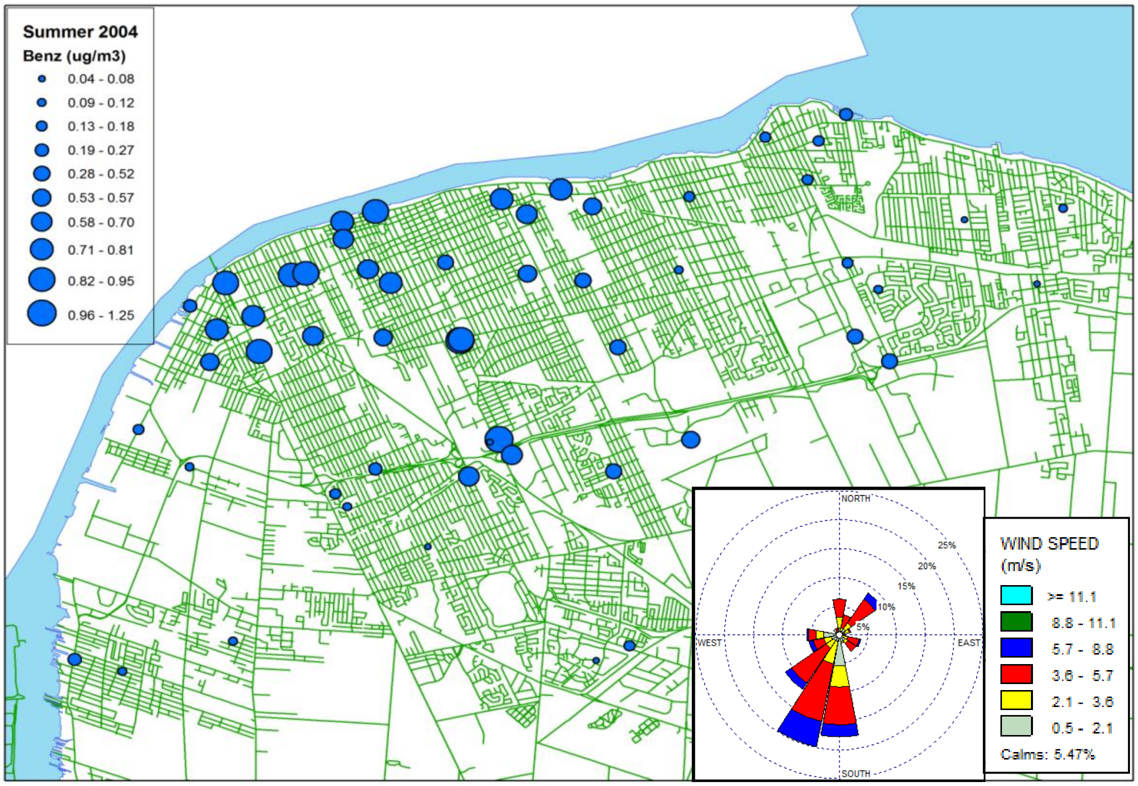
The seasonal analysis is useful to highlight how one season contributes to the annual means on a site-by-site basis and the need to consider this in assigning exposure estimates relying on a single season. However, this analysis alone could not provide accurate information on where the hot spots are and how hot spots change with season and year, because the percent contribution is in reference to the four seasons at the same site, not a comparison of all sites in a particular season. For example, for toluene in 2004 it would appear that fall would have a high concentration site not seen in the other two seasons, which is true. However, for benzene 2004 it appears that site A2 (Figure 7.3) would be high in fall and although it does have a high concentration (1.55 µg/m^3), site A22 has a higher concentration (1.60 µg/m^3) however does not look to be as much of a high concentration site based on Figure 7.3.

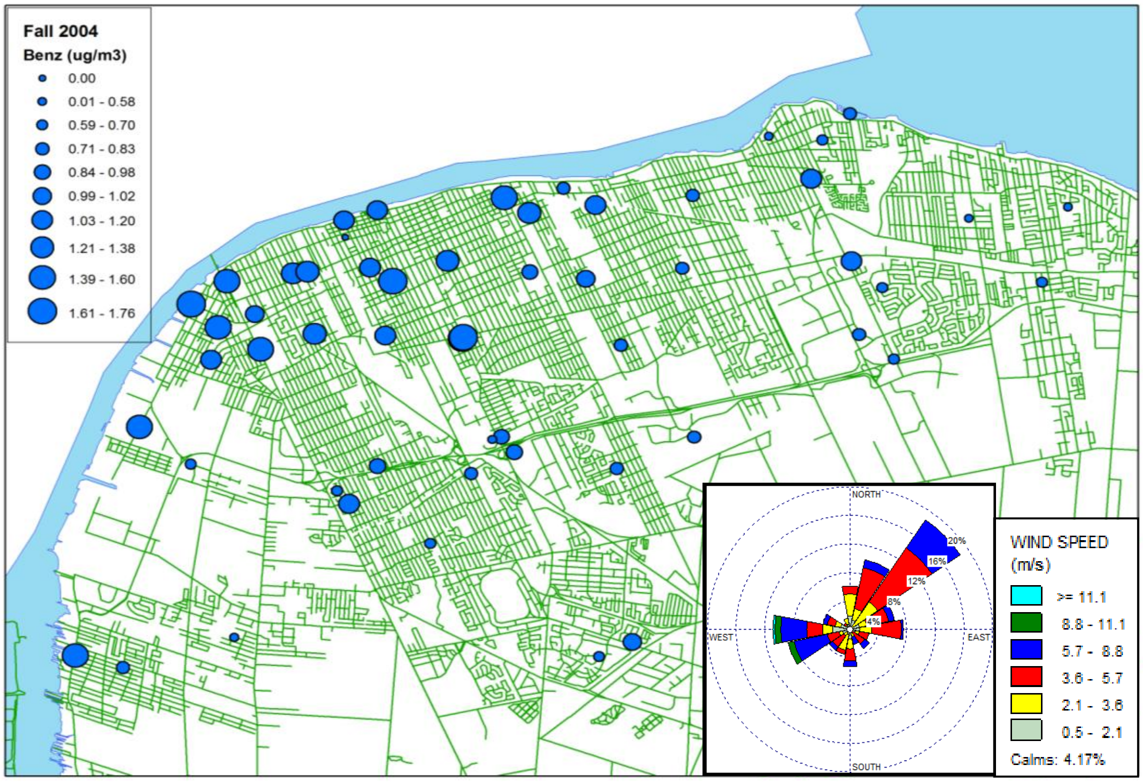
7.3.2 Spatial Distribution of Hot Spots

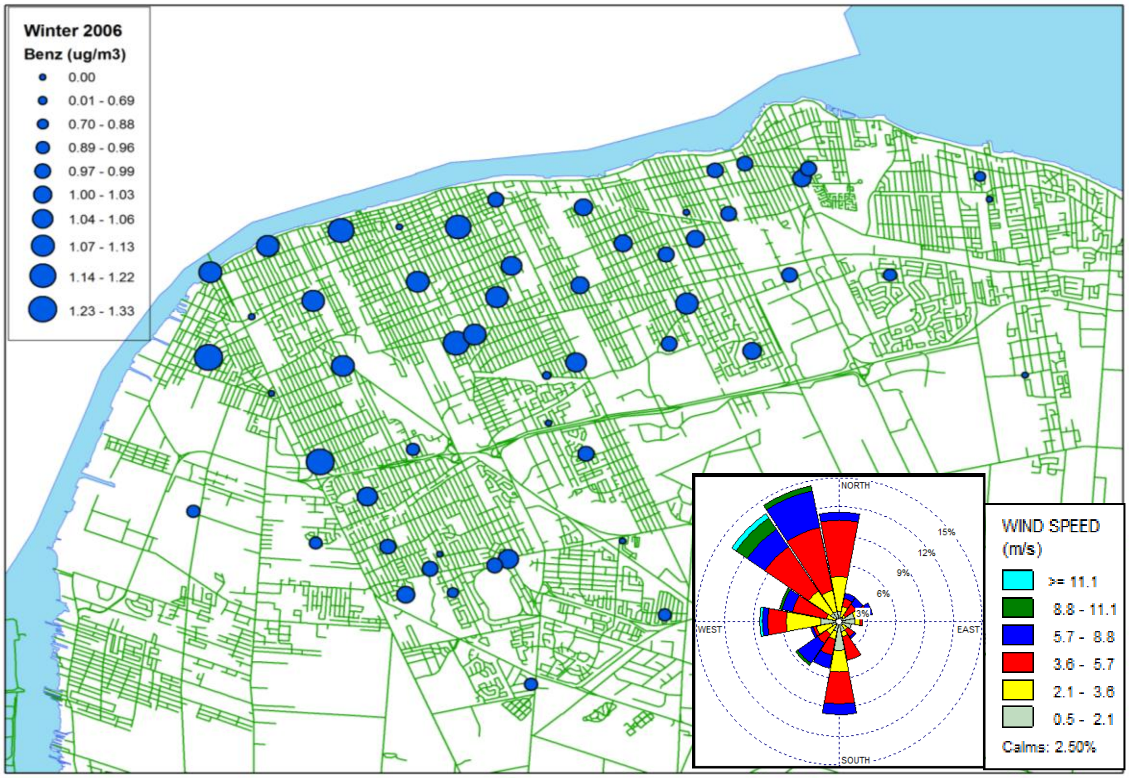
For this analysis hot spots are defined as a clustering of relatively high concentration sites as identified by the proportional concentration maps presented in Figure 7.4. Season to season and year to year comparisons are summarized in Table 7.2. Looking at benzene in 2004, a distinct cluster of high concentration sites exists towards the NW of the city in winter, summer, and fall. This pattern however, was not observed in spring where instead some high concentration sites were observed along Huron Church Road and towards the NE of the city. Additionally, fall had a hot spot towards the west edge of the city which was not seen in the other seasons. In the same year, a similar clustering of medium to high sites along the NW was observed for toluene for all seasons. Winter and spring had some additional high sites further east which were not observed in summer or fall. Fall had two additional high sites not observed in the other seasons.

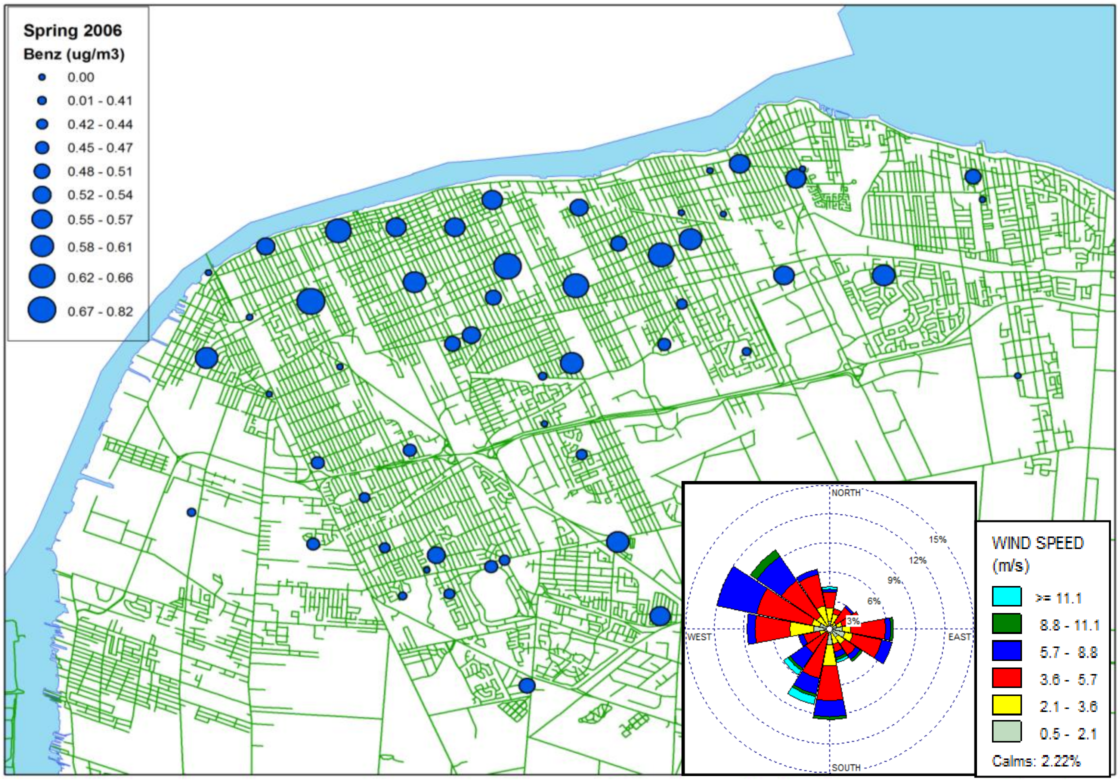

Winter 2004
Benz (ug/m3
0.72 - 0.89
0.90 - 1.01
1.02 - 1.08
1.09 - 1.12
1.13 - 1.17
1.18 - 1.23
1.24 - 1.28
1.29 - 1.43
1.44 - 1.60
1.61 - 1.75
NORTH
SOUTH
WEST
EAST
3%
6%
9%
12%
15%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 3.65%

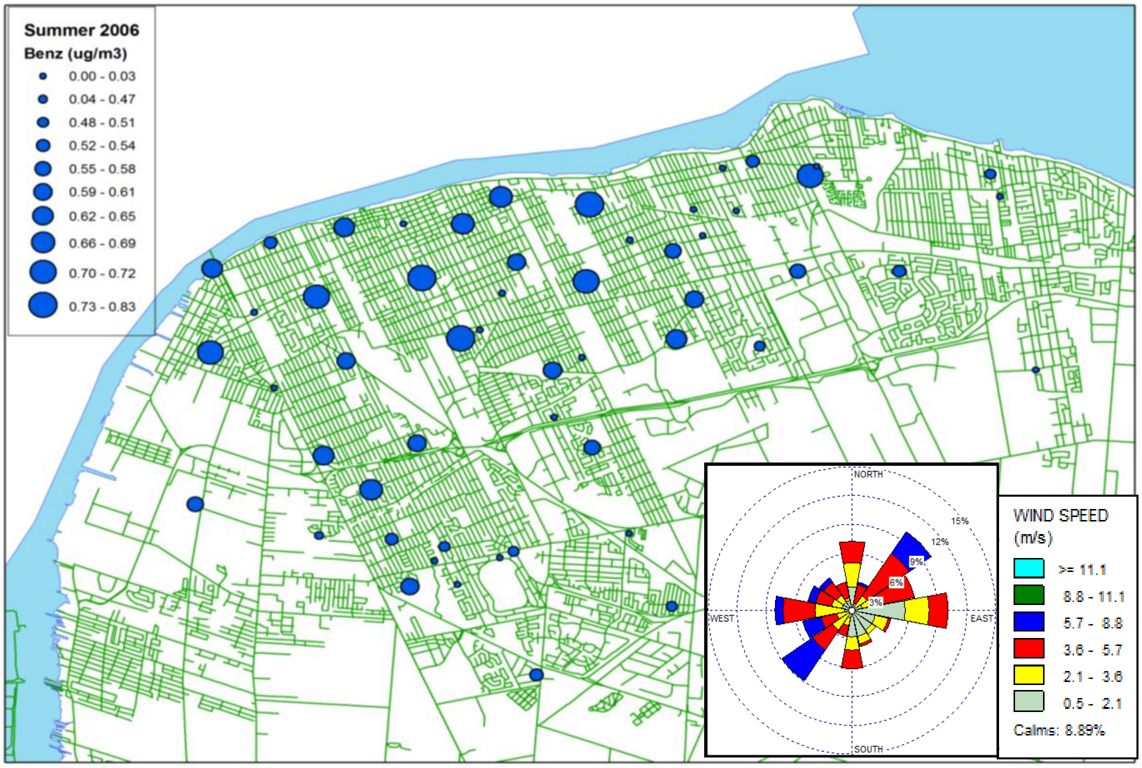

Spring 2004
Benz (ug/m3)
0.00
0.01 - 0.21
0.22 - 0.31
0.32 - 0.42
0.43 - 0.51
0.52 - 0.67
0.68 - 0.81
0.82 - 0.93
0.94 - 1.09
1.10 - 1.56
NORTH
SOUTH
WEST
EAST
3%
6%
9%
12%
15%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 2.70%

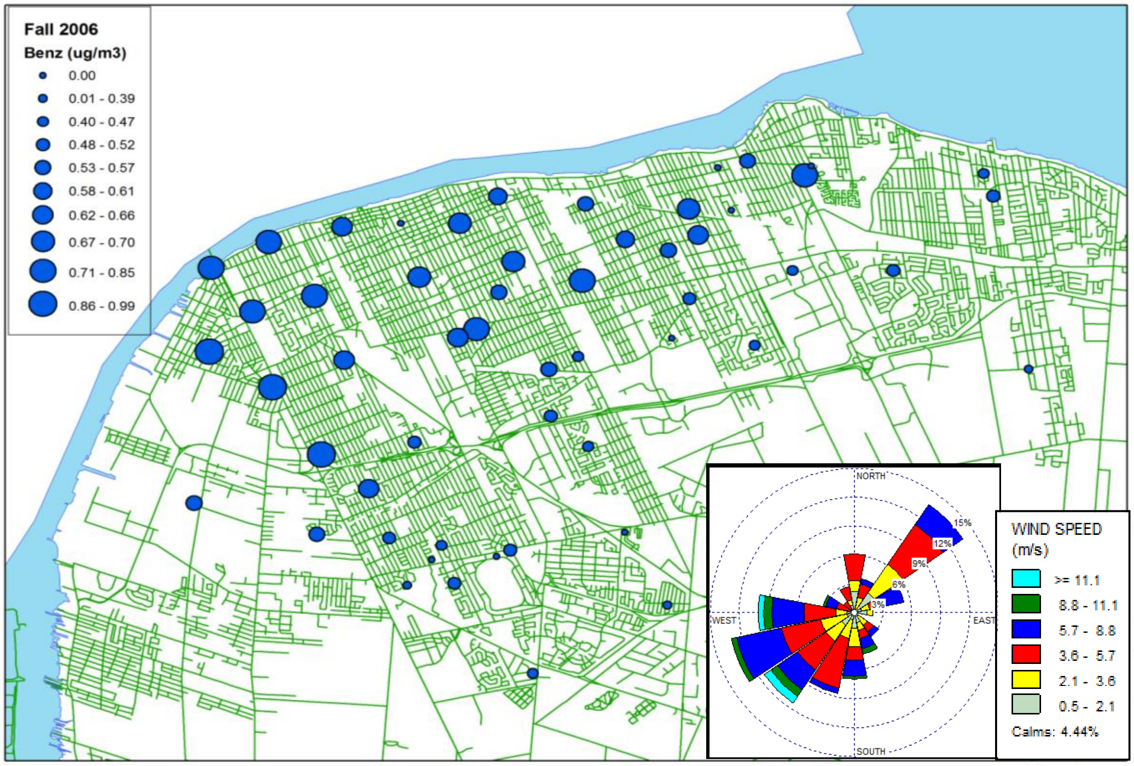

Summer 2004
Benz (ug/m3)
0.04 - 0.08
0.09 - 0.12
0.13 - 0.18
0.19 - 0.27
0.28 - 0.52
0.53 - 0.57
0.58 - 0.70
0.71 - 0.81
0.82 - 0.95
0.96 - 1.25
NORTH
WEST
EAST
SOUTH
5%
10%
15%
20%
25%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 5.47%

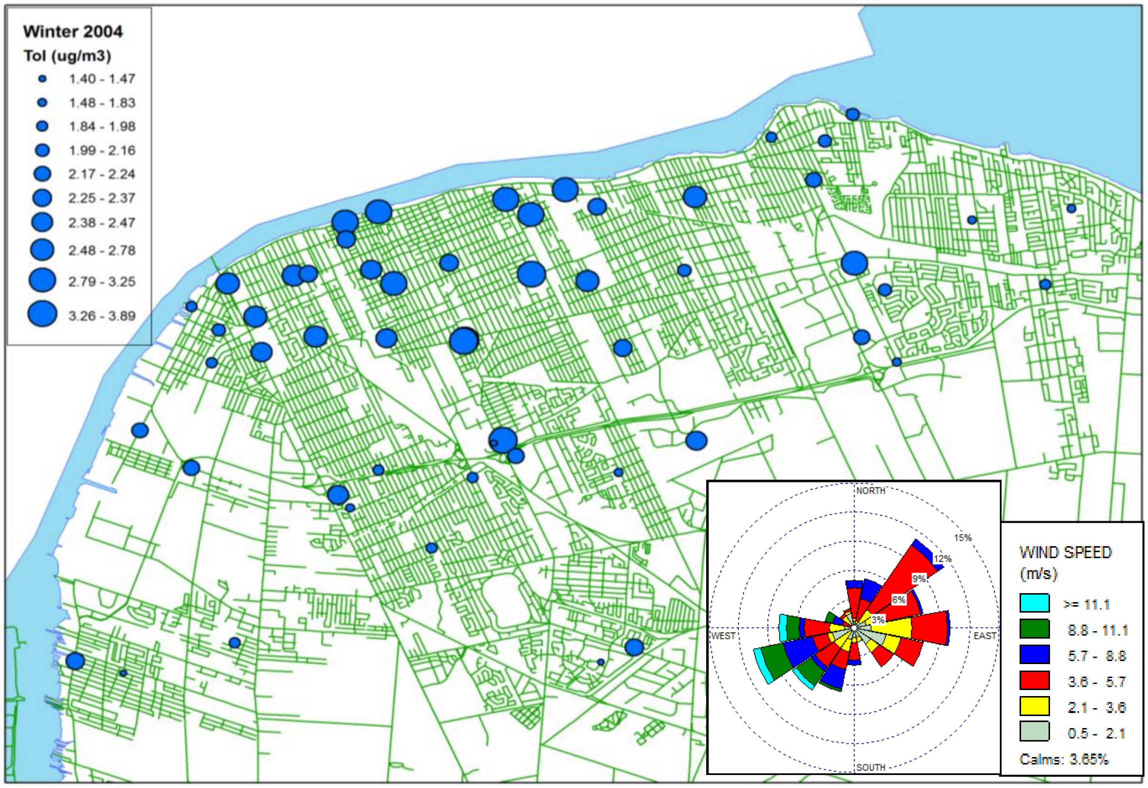

Fall 2004
Benz (ug/m3)
0.00
0.01 - 0.58
0.59 - 0.70
0.71 - 0.83
0.84 - 0.98
0.99 - 1.02
1.03 - 1.20
1.21 - 1.38
1.39 - 1.60
1.61 - 1.76
NORTH
WEST
EAST
SOUTH
4%
8%
12%
16%
20%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 4.17%

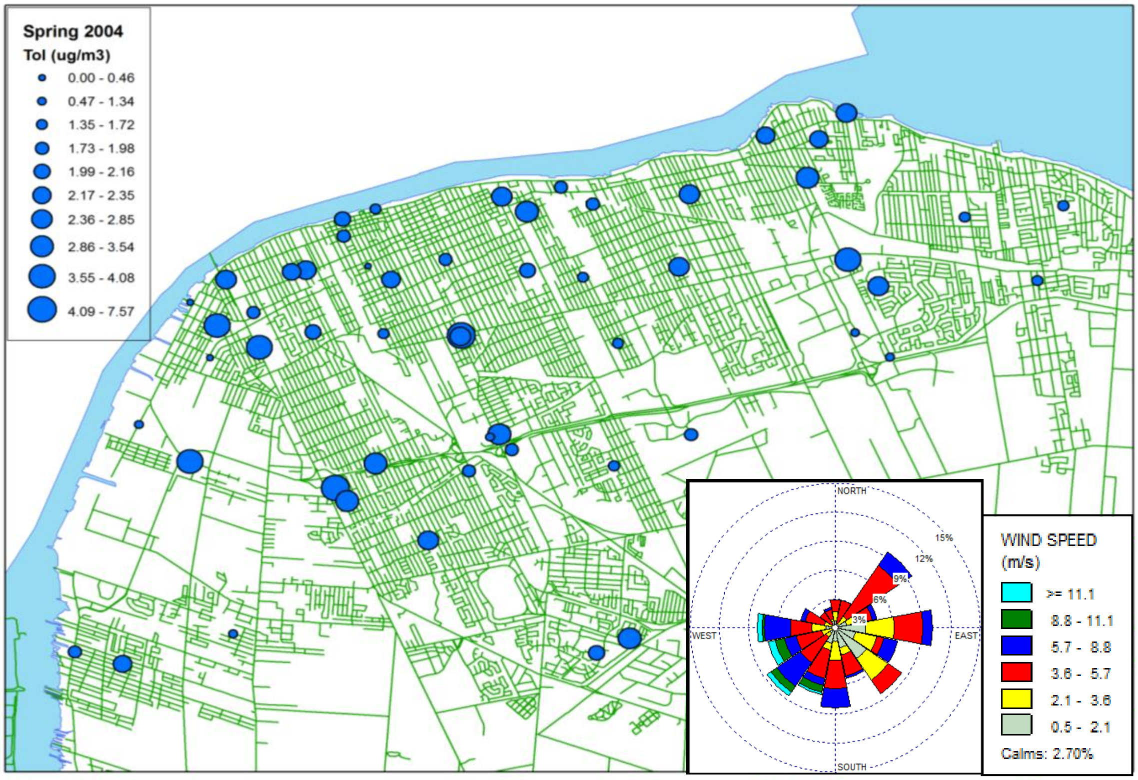

Winter 2006
Benz (ug/m3)
0.00
0.01 - 0.69
0.70 - 0.88
0.89 - 0.96
0.97 - 0.99
1.00 - 1.03
1.04 - 1.06
1.07 - 1.13
1.14 - 1.22
1.23 - 1.33
NORTH
SOUTH
WEST
EAST
3%
6%
9%
12%
15%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 2.50%

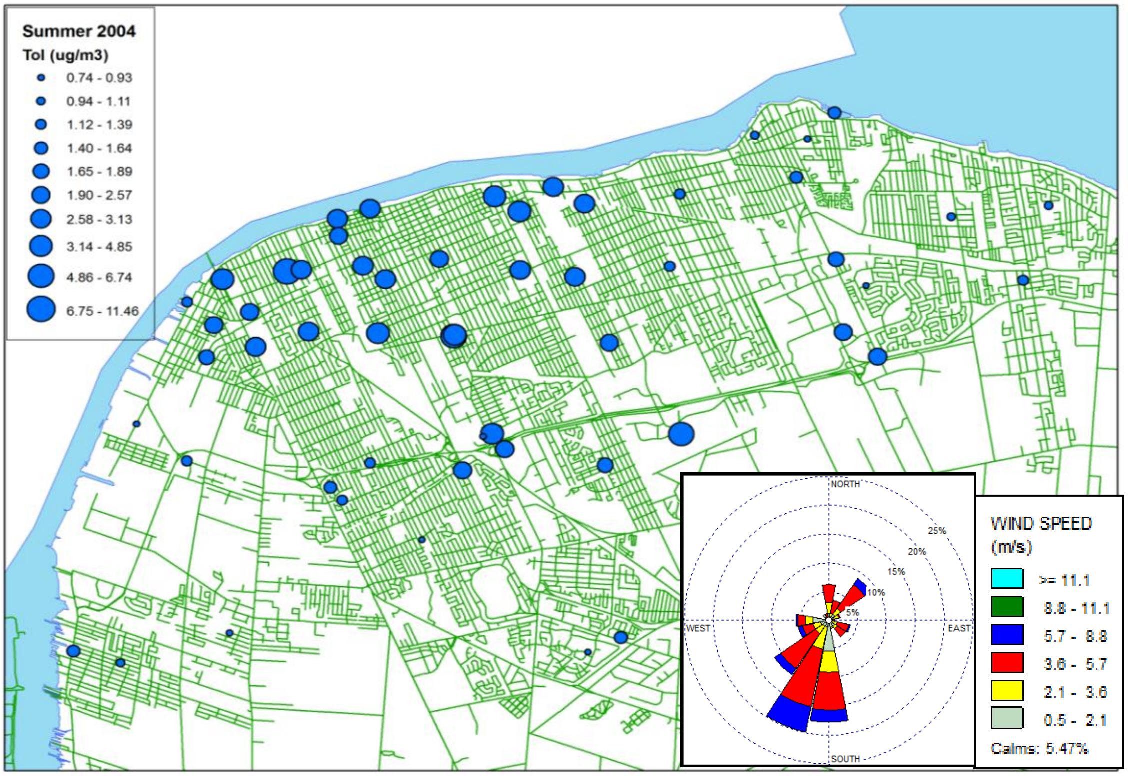

Spring 2006
Benz (ug/m3)
0.00
0.01 - 0.41
0.42 - 0.44
0.45 - 0.47
0.48 - 0.51
0.52 - 0.54
0.55 - 0.57
0.58 - 0.61
0.62 - 0.66
0.67 - 0.82
NORTH
SOUTH
WEST
EAST
3%
6%
9%
12%
15%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 2.22%

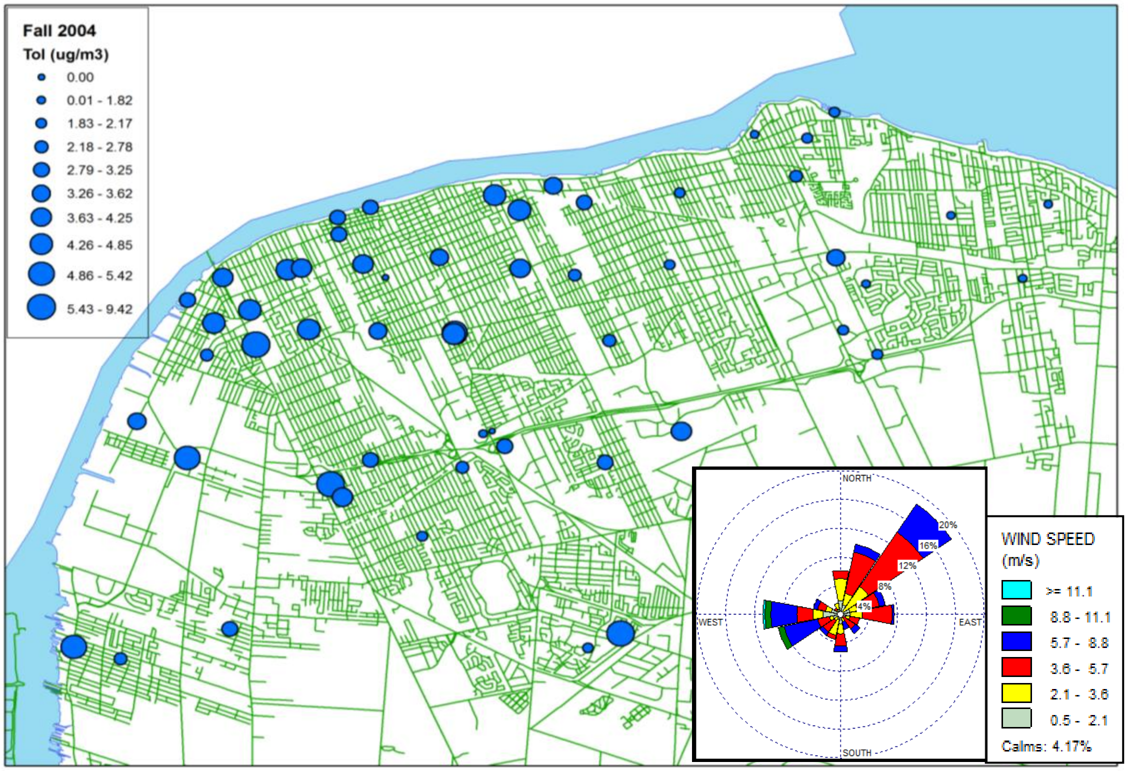

Summer 2006
Benz (ug/m3)
0.00 - 0.03
0.04 - 0.47
0.48 - 0.51
0.52 - 0.54
0.55 - 0.58
0.59 - 0.61
0.62 - 0.65
0.66 - 0.69
0.70 - 0.72
0.73 - 0.83
NORTH
WEST
EAST
SOUTH
3%
6%
9%
12%
15%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 8.89%

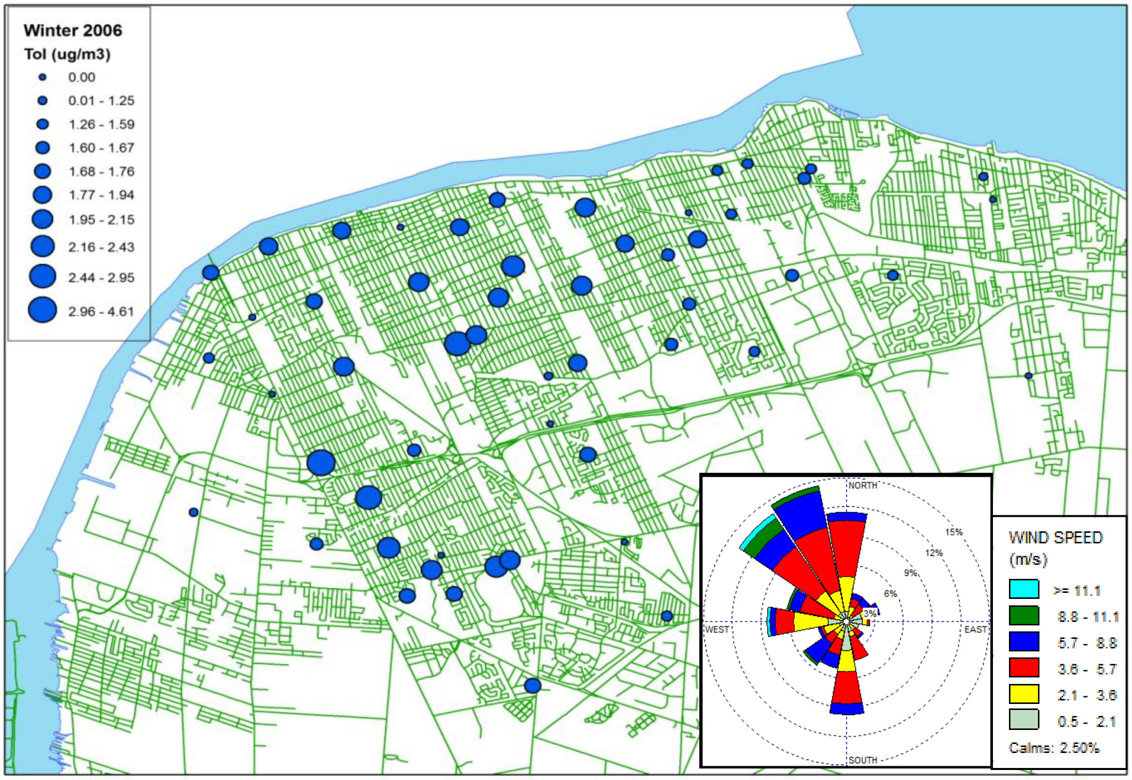

Fall 2006
Benz (ug/m3)
0.00
0.01 - 0.39
0.40 - 0.47
0.48 - 0.52
0.53 - 0.57
0.58 - 0.61
0.62 - 0.66
0.67 - 0.70
0.71 - 0.85
0.86 - 0.99
NORTH
WEST
EAST
SOUTH
3%
6%
9%
12%
15%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 4.44%

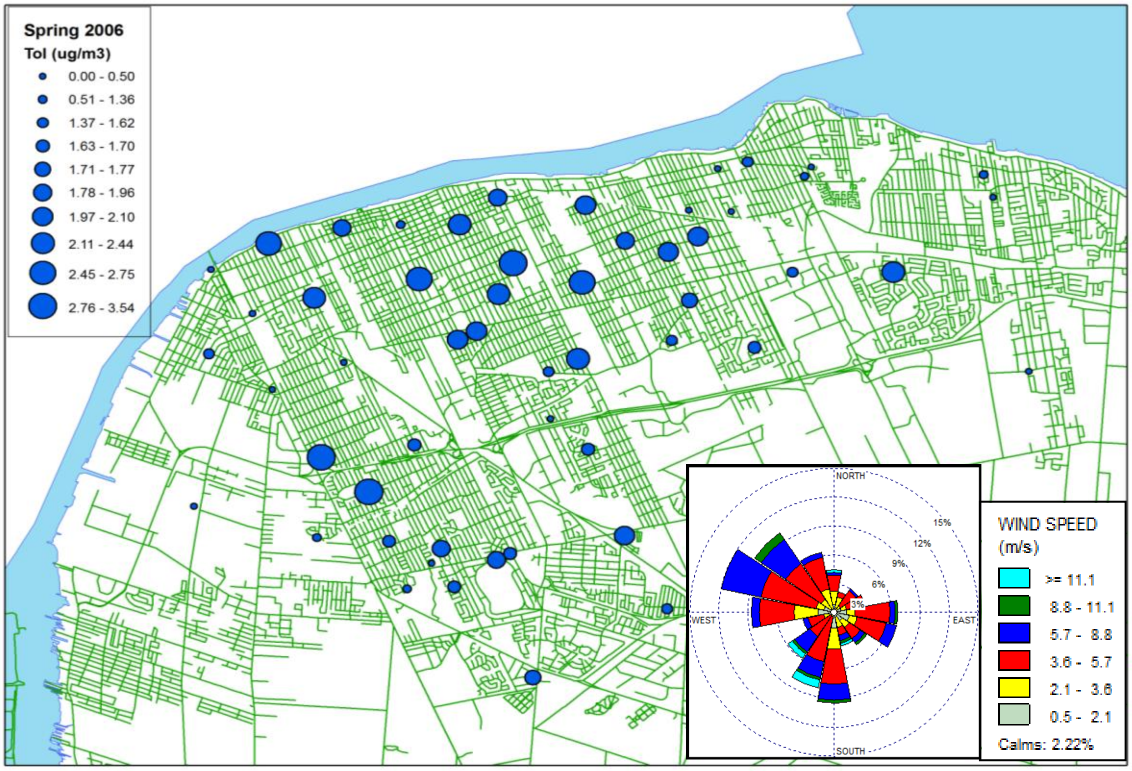

Winter 2004
Tol (ug/m3)
1.40 - 1.47
1.48 - 1.83
1.84 - 1.98
1.99 - 2.16
2.17 - 2.24
2.25 - 2.37
2.38 - 2.47
2.48 - 2.78
2.79 - 3.25
3.26 - 3.89
NORTH
SOUTH
WEST
EAST
3%
6%
9%
12%
15%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 3.65%


Spring 2004
Tol (ug/m3)
0.00 - 0.46
0.47 - 1.34
1.35 - 1.72
1.73 - 1.98
1.99 - 2.16
2.17 - 2.35
2.36 - 2.85
2.86 - 3.54
3.55 - 4.08
4.09 - 7.57
NORTH
SOUTH
WEST
EAST
3%
6%
9%
12%
15%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 2.70%


Summer 2004
Tol (ug/m3)
0.74 - 0.93
0.94 - 1.11
1.12 - 1.39
1.40 - 1.64
1.65 - 1.89
1.90 - 2.57
2.58 - 3.13
3.14 - 4.85
4.86 - 6.74
6.75 - 11.46
NORTH
SOUTH
WEST
EAST
5%
10%
15%
20%
25%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 5.47%


Fall 2004
Tol (ug/m3)
0.00
0.01 - 1.82
1.83 - 2.17
2.18 - 2.78
2.79 - 3.25
3.26 - 3.62
3.63 - 4.25
4.26 - 4.85
4.86 - 5.42
5.43 - 9.42
NORTH
SOUTH
WEST
EAST
4%
8%
12%
16%
20%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 4.17%


Winter 2006
Tol (ug/m3)
0.00
0.01 - 1.25
1.26 - 1.59
1.60 - 1.67
1.68 - 1.76
1.77 - 1.94
1.95 - 2.15
2.16 - 2.43
2.44 - 2.95
2.96 - 4.61
NORTH
WEST
EAST
SOUTH
3%
6%
9%
12%
15%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 2.50%


Spring 2006
Tol (ug/m3)
0.00 - 0.50
0.51 - 1.36
1.37 - 1.62
1.63 - 1.70
1.71 - 1.77
1.78 - 1.96
1.97 - 2.10
2.11 - 2.44
2.45 - 2.75
2.76 - 3.54
NORTH
WEST
EAST
SOUTH
3%
6%
9%
12%
15%
WIND SPEED
(m/s)
>= 11.1
8.8 - 11.1
5.7 - 8.8
3.6 - 5.7
2.1 - 3.6
0.5 - 2.1
Calms: 2.22%

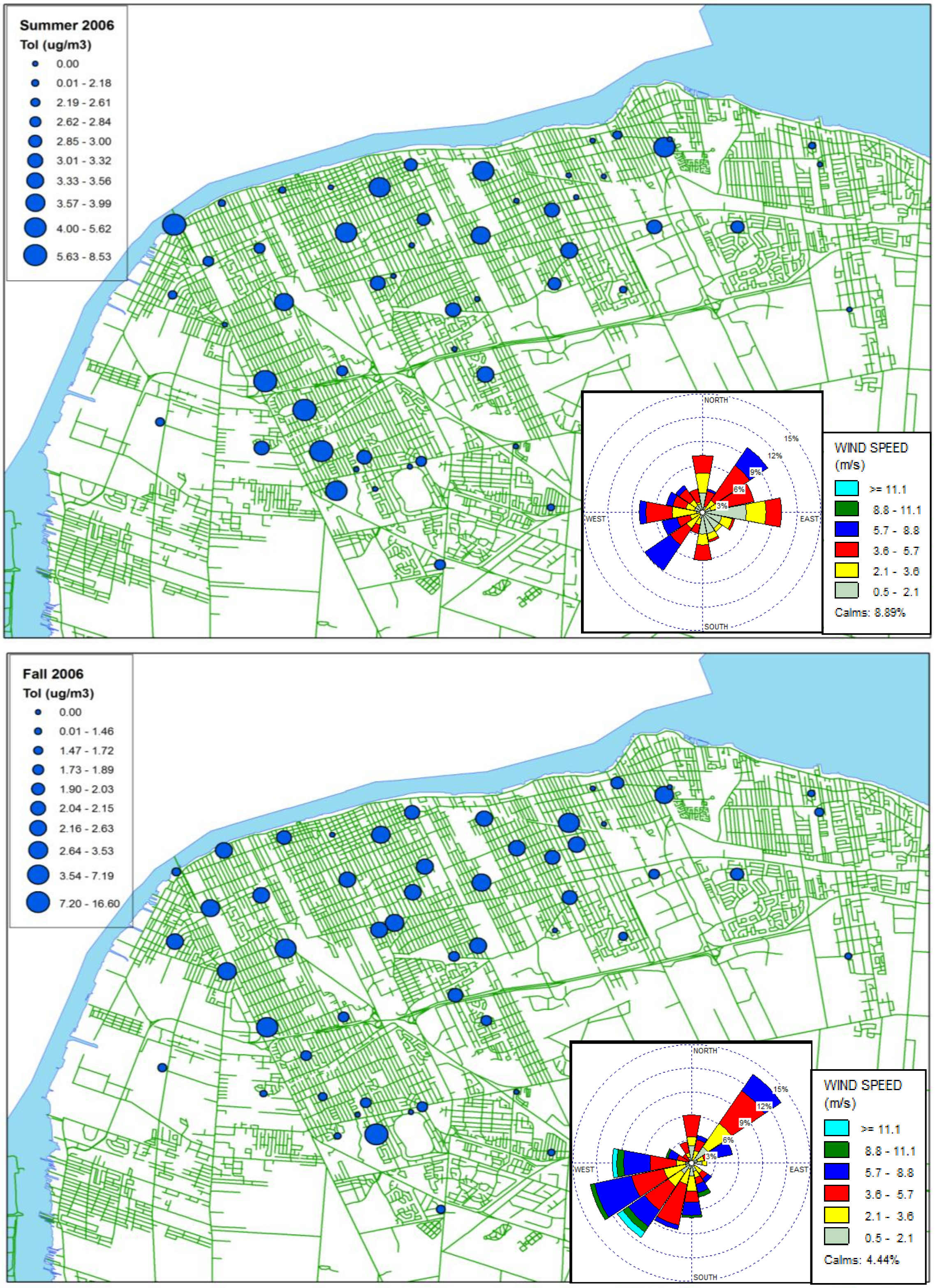


Figure 7.4. Proportional concentration maps and wind roses for benzene 2004, benzene 2006, toluene 2004, and toluene 2006.

Table 7.2. Qualitative summary of season to season and year to year comparisons for (a) benzene and (b) toluene.

(a) benzene

Year / Season	**Winter**	**Spring**	**Summer**	**Fall**	**Season to season**
2004	High sites along NW of city	High sites along Huron Church and towards E of city	High sites along NW of city	High sites along NW of city	Consistent with the exception of Spring
2006	High sites along NW and along Huron Church	High sites along NW of city	Moderate to high sites along NW and Huron Church	High sites along NW and Huron Church	Consistent
Year to year	Variable: consistent highs along NW, highs along Huron Church seen in 2006 which were not seen in 2004	Inconsistent	Consistent	Consistent	Overall, benzene saw more year to year consistency than toluene

(b) toluene

Year / Season	**Winter**	**Spring**	**Summer**	**Fall**	**Season to season**
2004	Medium to high sites along NW of city	High sites more widely spread throughout the city	Medium to high sites along NW of city	Medium to high sites along NW of city	Consistent with the exception of spring
2006	High sites along South side of Huron Church, moderate towards NW	High sites along South side of Huron Church, also moderate to high sites towards NW	High sites along South side of Huron Church, also moderate to high sites spread throughout the city	Moderate to high sites distributed across the city	Consistent with the exception of fall
Year to year	Inconsistent	Some consistency	Some consistency	Consistent	Overall, toluene saw less year to year consistency than benzene

In 2006, clustering of high concentrations was observed along the NW for benzene in all seasons with an additional two high concentration sites towards the south of the city in spring. For toluene a distinct clustering was not as evident, although consistent low points were observed towards the east and south of the city. Some hot spots were observed along Huron Church Road for all seasons and summer had an additional high site towards the east which was not seen in the other seasons.

Comparing year to year benzene in any given season, similar clustering was observed in winter 2004 and winter 2006 with two additional high sites in 2004. For spring however, there were very different patterns; in 2004 clustering of highs were observed towards the east and hot spots were also seen along Huron Church Road, whereas in 2006 clustering was observed towards NW with two additional high sites towards the south. This conclusion confirms the results presented in Chapter 6, that spring would not be an ideal season to represent annual spatial patterns. Similar patterns of clustering of highs along the NW were seen in 2004 and 2006 summer and fall with one additional high site in summer 2006 and another in fall 2004.

For toluene, in winter, the grouping of hot spots seen along the SW in 2006 was not observed in 2004, and the cluster of hot spots in 2004 along the NW was not observed in 2006. For spring, higher points towards the east in 2004 were not seen in 2006, as well as there was an additional high site towards the west in 2004. For summer, hot spots along Huron Church Road and towards the east observed in 2006 were not seen in 2004, whereas hot spots along NW in 2004 were not observed in 2006. A similar pattern was observed for fall between the two years, with two additional hot spots along the south in 2004 not seen in 2006.

In some cases, a high concentration site appeared in very close proximity to a low site and this was consistent between several seasons of sampling. For example, winter benzene 2004, a high spot is directly located next to a low spot in the middle of the map (intersection of E.C. Row Expressway with Howard Avenue). This was also seen in summer and spring of this year as well as for winter and summer toluene in this year. Upon further investigation, it was noted that a scrap metal yard which is a known high polluter in the province is located on the north side of this intersection, where the high sites are seen. In other cases, no conclusive reasons for the high / lows were noted however it is expected that these gradients would be present in a city of diverse point sources.

Overall, even though the ranges of concentrations vary, generally the pattern of highs and lows is similar between seasons within a given year. This is consistent with results presented in Chapter 6 and in previous studies (Hung et al., 2005; Zhu et al., 2008). However, some high sites are seen in one season and not in another which would lead to misclassification if one season were relied on as a proxy for the entire year. Comparing the same seasons from different years showed more variability with different high sites appearing between the two years. Future studies could look more in depth at the factors contributing to localised hot spots such as regional pollution trends, nearby point sources, and proximity to major roads.

7.3.3 Spatial Distribution of Benzene

As will be further discussed in section 7.3.5, benzene is the only species whose values approach the AAQCs set forth by the government. For the TEX species, even at their maximum measured values they are well below the AAQCs. Therefore, of the species sampled, relatively high concentrations of benzene are presumed to be harmful to residents. The inverse distance weighting maps were generated for this pollutant (Figure 7.5) to provide a thematic illustration of interpolated concentrations across the city, which complements the proportional concentration maps identifying areas of high concentrations (Figure 7.4).

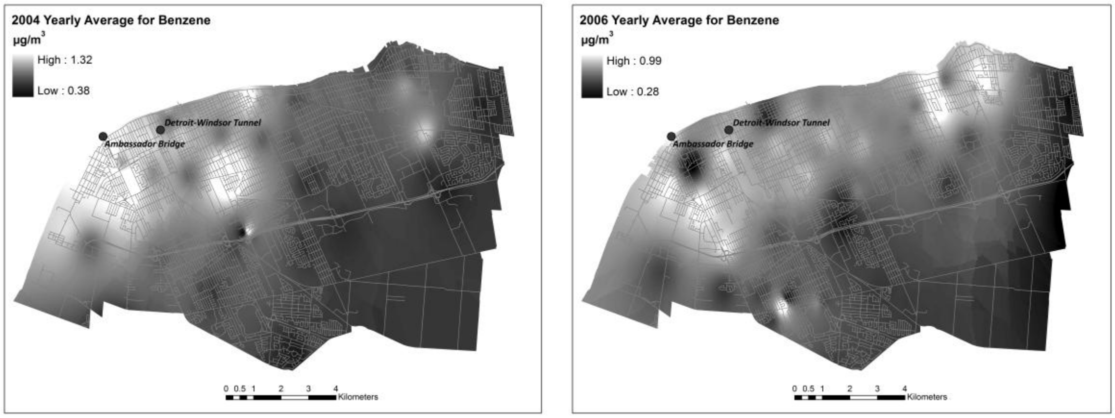


Figure 7.5. IDW maps of benzene for 2004 and 2006.

As can be seen from Figure 7.5, the gross concentration pattern is similar between the two years, with higher concentrations occurring along the northwest of the city which is in the vicinity of Huron Church Road and the Ambassador Bridge crossing where traffic emissions are high. These maps are also similar to those presented in Figure 7.1, since the HQ value is governed by the benzene concentrations. As seen in the proportional concentration maps, although the general highs and lows are consistent, there are some areas where a high site is located in an otherwise low area and vice versa. This demonstrates the usefulness of frequent spatial sampling to identify high concentration areas, however, as reported in Chapter 6 the benefits of multiple year sampling diminish when general spatial patterns are desired.

7.3.4 Association with Wind Directions

Wind roses generated for each sampling period (Fig 7.4) were evaluated in conjunction with the proportional concentration maps to determine if the spatial patterns changed with predominant wind direction from each of the two-week study periods. If significant changes in concentrations maps were observed when the predominant wind direction changed, then this may indicate a strong regional transport of pollutants into the city. Qualitative observations did not reveal any correlations between the wind direction and the location of hot spots. This suggests that local emissions are the predominant contributors to concentration levels in this area rather than regional sources which would be carried in by air mass movement and be expected to show an association with wind direction. For example, spring benzene 2004 and winter benzene 2004 had nearly identical wind roses yet a very different spatial pattern. Conversely, winter benzene 2004 and summer benzene 2004 had a very similar spatial pattern but very different wind roses. This is consistent with Ohura et al., (2006), but contrary to other studies (Hung et al., 2005; Smith et al, 2007), where associations with wind directions were observed. This is likely due to the lack of a segregated industrial core in Windsor, whereas the studies which did observe associations were investigating concentrations downwind from distinct industrial areas. There were emissions from traffic on Huron Church Road and the Ambassador Bridge, however higher concentrations downwind of these were not evident from the wind association analysis. Another possible explanation for the lack of correlation could be strong temporal/seasonal alterations to emission strength which is variable among the sites, although analysis in Chapter 6 suggested limited temporal variability in the spatial concentration patterns within a year.

7.3.5 Exposure Risk Map

The ambient air quality criteria for Ontario (Ontario Ministry of the Environment, 2011) were compared with measured BTEX concentrations on a site by site basis, leading to the depiction of the spatial distribution of exposure risk. The AAQCs for the contaminants considered are presented in Table 7.3 along with the city-wide mean concentrations obtained during these sampling periods as well as the two-week maximum concentrations among all sites. Because the averaging time for the AAQCs is 24 hours, the two-week mean values could be lower than any 24 hour maximum that would occur during the sampling time, therefore leading to an underestimation of the HQ. However, the general conclusions are likely still applicable.

As can be seen from Table 7.3, the only species that would significantly contribute to an overall AAQC risk based index would be benzene, which, at its maximum measured concentration reaches 77% of the recommended AAQC. Our methods estimate the concentrations from two-week sampling periods and use different methodology than the government sites, therefore, the BTEX concentrations measured at the NAPS (Environment Canada, 2011) Windsor-West Station were also considered. The NAPS measurements confirm that only benzene would be a contributor to potential risk based on the AAQCs. Based on the annual average concentrations for 2004 and 2006, the TEX species registered maximum concentrations less than 2% of the AAQC values. In contrast, the maximum two-week benzene concentration is 77% of the AAQC in 2004 and 47% in 2006.

Table 7.3. AAQCs and mean concentrations for BTEX in Windsor.

Species	**2-year mean concentration (μg/m3)**	**Annual NAPS concentration (μg/m3) 2004/2006**	**Maximum two- week concentration among all sites (μg/m3)**	**AAQC (μg/m3)**	**% of AAQC (max concentration)**
Benzene	0.70	1.75/1.07	1.8	2.3	76.5
Toluene	2.84	3.67/3.75	16.6	2000	0.8
Ethylbenzene	0.44	0.56/0.52	1.7	1000	0.2
Xylenes	1.76	2.08/2.05	8.2	730	1.1

Even though benzene is the only species whose value approaches the AAQC value, an exposure risk map based on all BTEX species is useful to illustrate which areas of the cities are more at risk for air quality related illnesses. Figure 7.6 is an IDW surface of the two-year average risk in terms of the hazard quotient (with Windsor boundary shown). As expected, the pattern for potential risk is similar to that for benzene concentrations (Fig 7.5); higher along the northwest of the city and diminishing towards the east and south. In Figure 7.6, the high area represents a two-year average HQ in the range of 0.37-0.58, which may still be unsettling for residents since this value is almost solely attributable to benzene, a known carcinogen. The World Health Organization states that there is no safe level of exposure to benzene and that exposure to 1.7 μg/m^3 of benzene will result in 10 cases of leukemia per 1 million residents (WHO, 2000). This calls for further investigation into benzene pollution in Windsor since it is likely that 24 hour maximum concentrations could approach the AAQC values in the high areas of the city, putting residents at an increased risk of cancer.

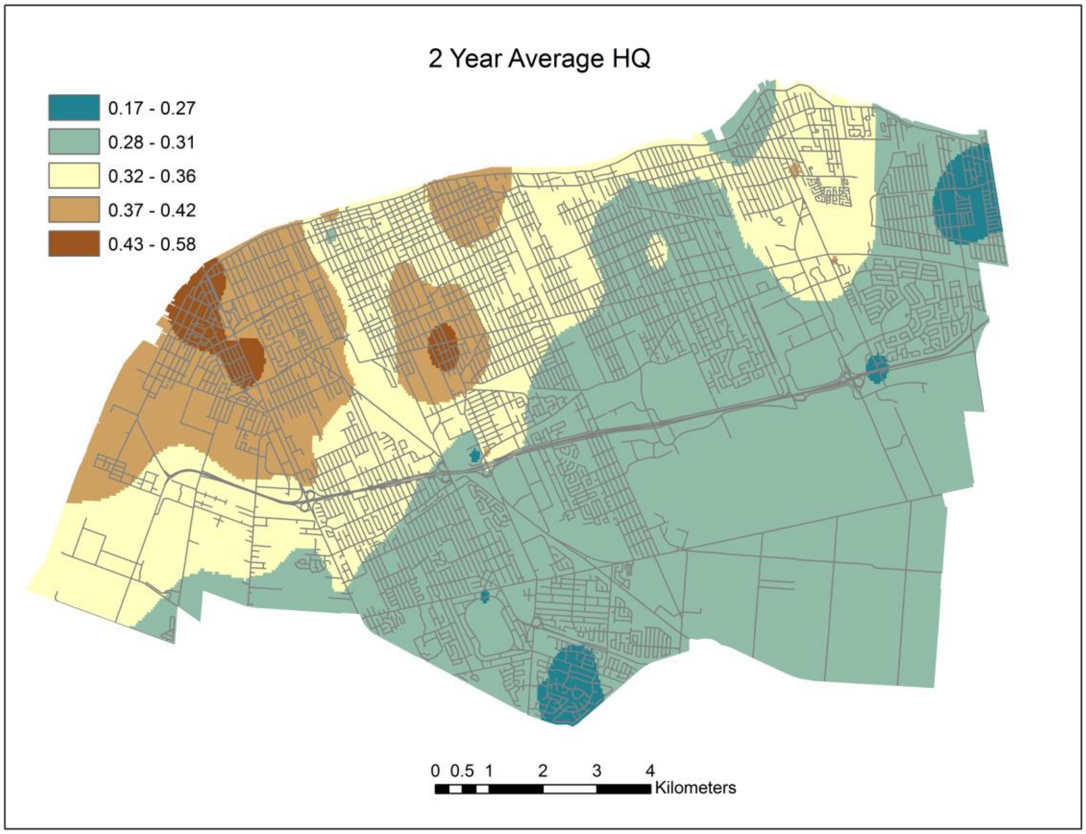


Figure 7.6. IDW surface of two-year average BTEX hazard quotient based on AAQCs**.**

7.4. Conclusions

These analyses expanded on some conclusions regarding spatial and temporal variability reported in Chapter 6 and additionally considered correlations between wind direction and hot spot locations and residential BTEX exposure risk for Windsor. The importance of sampling in every season was confirmed, through evaluation of the seasonal contributions to annual mean concentrations, in order to obtain an accurate annual exposure estimate, as has been presented in Chapter 6 of this thesis and reported previously (Touma et al., 2006). The percent contribution of a single season to the annual mean can be as low as 13% (benzene, summer 2004, ethylbenzene, winter 2006) and as high as 39% (xylenes, summer, 2006) and also varies by location. For example, data in both years suggest that sampling in winter only for benzene would likely result in overestimation of annual exposure. In both 2004 and 2006, toluene, ethylbenzene, xylenes and BTEX behaved the same as each other, with spring and winter contributing the most representative amounts to the annual mean in 2004 and fall in 2006. For benzene, fall contributed the most representative amount in 2004 whereas it was fall and summer in 2006. Overall, spring and fall were most likely to contribute representative amounts, consistent with the findings that these seasons are best to represent city-wide annual concentrations presented in Chapter 6. Additionally, this analysis confirms that benzene behaves slightly differently than TEX in this city as reported in Chapters 3 and 4 of this thesis and as reported previously (Smith, et al., 2007; Su et al., 2010).

Overall the general patterns of clustering of high concentrations remain relatively stable over the course of a year suggesting that despite changing meteorology and concentration levels, high concentration areas are consistent, likely due to nearby point or mobile emissions. More variability is observed when comparing the same season from two different years, and more so for toluene than benzene which may be attributable to a stronger industrial component of toluene as has been previously reported (Su et al., 2010). Also, spring displayed a different pattern than the other seasons in 2004 especially for benzene, which is consistent with the correlation analysis in Chapter 6 concluding that the spring season, particularly for benzene 2004 ($r = 0.24$) was least representative of annual spatial patterns.

There were no evident associations observed between the spatial patterns of the proportional concentration maps and the wind roses generated for the sampling periods based on qualitative observations. Further investigation into the correlation between wind patterns and spatial concentrations should be undertaken for this area. Although some previous studies did report associations between these measures, their study areas were specifically down or upwind of a clustering of industrial sources whereas no such distinct cluster exists in Windsor. Exposure risk maps, based on the AAQC values, identified areas of highest benzene concentrations located in northwest Windsor, calling for further investigation into benzene pollution and its health effects in that area.

A limitation of this study is the change in sampler locations between the two years. This may affect the inter-annual comparisons and could be addressed in future studies by keeping a larger portion of the sites in consistent locations. Another limitation is the use of two-week averages to represent seasonal mean concentrations as was explored further in Chapter 6. Furthermore, due to some species registering values below the detection limits in 2005, the year to year comparisons span two years, i.e. 2004 compared to 2006. The origin of the grids for comparison of cell means was randomly selected. This comparison could be improved by testing several grid systems in order to further justify combining the two years of data.

IDW maps were generated to aid an assessment of spatial distribution. IDW is an inexact method which assigns heavier weights to nearby samples and can therefore result in high spots which may not be truly representative at a neighbourhood level. Therefore, the exposure risk map is somewhat dependent on the interpolation method and these maps should be interpreted at a broader scale. Other interpretative mapping techniques, such as kriging, could be explored in further investigations.

Acknowledgements

The maps presented in this chapter were generated with the assistance of Alice Grigcak-Mannion and Hassan Mohseni.

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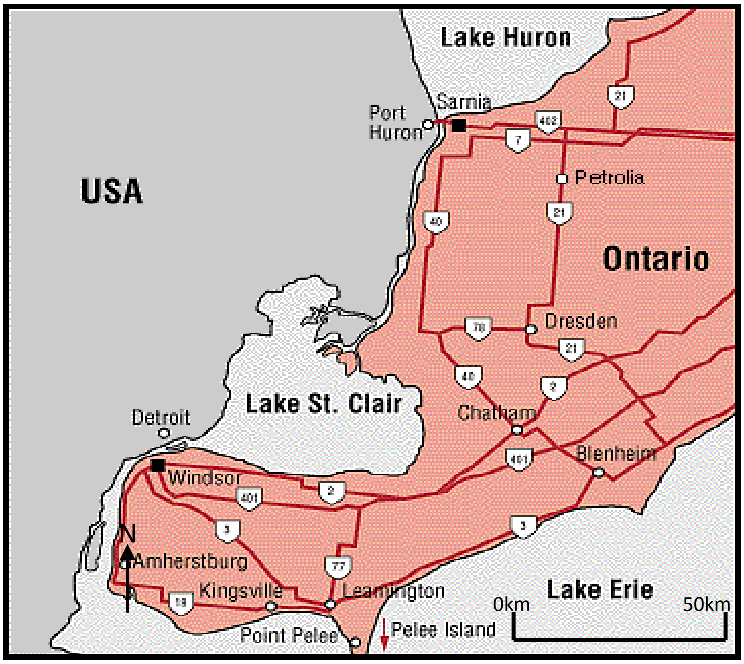
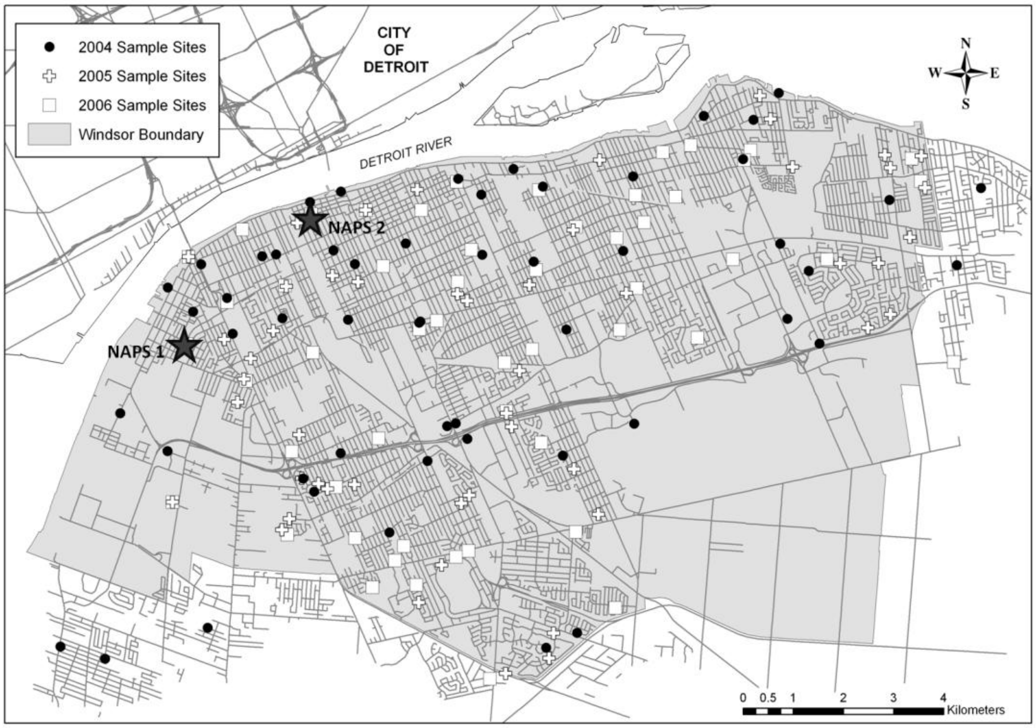
CHAPTER 8: SPATIAL VARIABILITY AND APPLICATION OF RATIOS BETWEEN BTEX IN TWO CANADIAN CITIES

8.1 Introduction

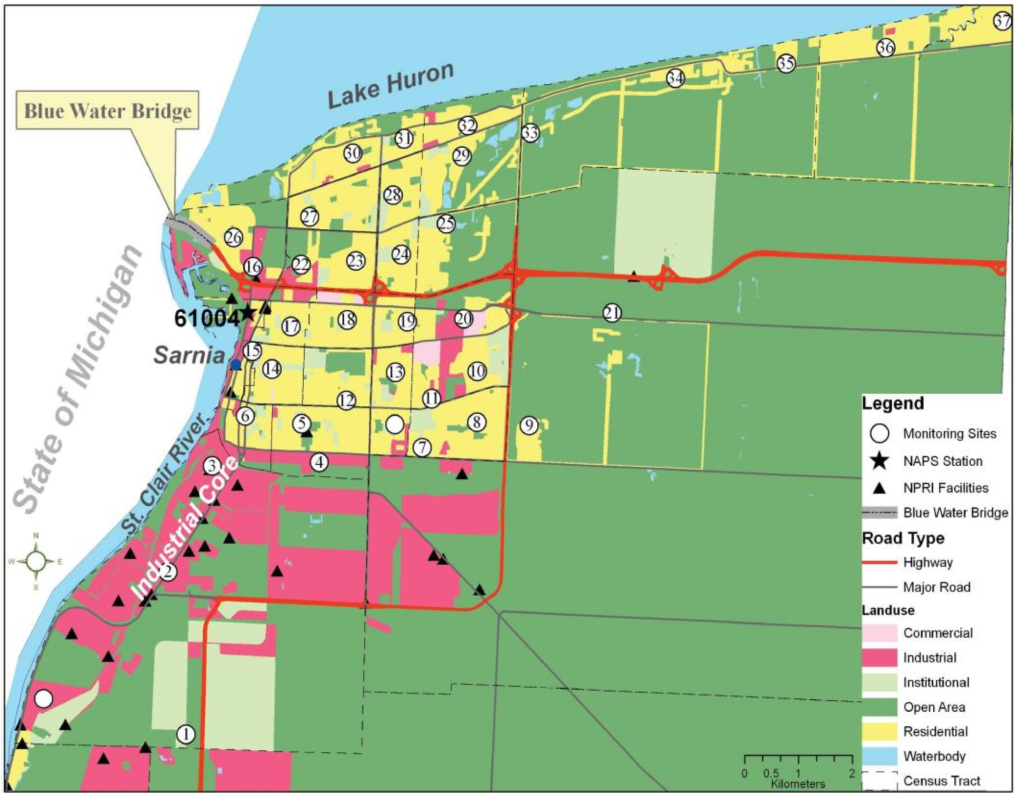
Volatile organic compounds (VOCs), specifically benzene, toluene, ethylbenzene, o-xylene, and (m+p)-xylene (BTEX), have been the focus of several recent studies (Parra et al., 2006; Sax et al., 2006; Khdoer, 2007; Whitworth et al., 2008) due to the adverse health effects, including cancer, associated with their exposure. Spatial monitoring campaigns were done in two similarly sized urban industrial cities in southwestern Ontario, Canada: Windsor (42° 16’N, 82° 58’W) and Sarnia (42° 58’N, 82° 23’W). Windsor has an area of 147 km^2, and a population of 218,473, while Sarnia has an area of 165 km^2 and a population of 70, 876 (Statistics Canada, 2008). The two study areas are shown in Figure 8.1. The geography of both cities is relatively flat, with elevations above sea level of 190 and 191 m, respectively. Sarnia is located approximately 100 km northeast of Windsor (Figure 8.1a) and is subject to similar weather conditions. In 2005, the annual average temperatures differed by 3% between the two cities and the relative humidity by 16% (with Sarnia experiencing higher humidity levels). The long-term (30 years) average wind speed is 16 km/h in both cities. The wind is predominantly from the north and south for Sarnia and from the south and southwest for Windsor (Environment Canada, 2011a). The two cities are comparable in terms of land use, climate, and geography.


Lake Huron
Sarnia
Port Huron
USA
21
402
7
Petrolia
40
21
Ontario
78
Dresden
21
40
2
Lake St. Clair
Chatham
Detroit
401
Blenheim
Windsor
2
401
3
3
N
Amherstburg
77
Kingsville
Leamington
18
Lake Erie
0km
50km
Point Pelee
Pelee Island

(a)


● 2004 Sample Sites
✚ 2005 Sample Sites
☐ 2006 Sample Sites
▨ Windsor Boundary
CITY OF DETROIT
DETROIT RIVER
N
W
E
S
NAPS 2
NAPS 1
0 0.5 1 2 3 4
Kilometers

(b)



(c)

Figure 8.1. Maps of (a) study areas (ontournet.com), (b) Sampling locations and NAPS stations in Windsor , and (c) Sampling locations, NAPS station, and land use in Sarnia (taken from Miller et al., 2009).

Both study areas are known to experience poor air quality due in part to high VOC emissions. In Windsor, VOC emissions are likely attributable to the large number of manufacturing facilities and the high vehicle traffic emissions generated by the bridge crossing between Windsor, Ontario and Detroit, Michigan. Sarnia has been labelled ‘Chemical Valley’ due to the large number of chemical companies that operate in the area. Sarnia is also the location of a large sanitary landfill and has a major bridge crossing to the US with high vehicle volumes. These industrial and transportation activities are emitters of VOCs, specifically of BTEX.

To investigate how exposure to BTEX compounds can cause adverse health effects, it is important to capture local scale spatial variability, which cannot be accomplished with central monitoring stations such as those provided by the National Air Pollution Surveillance (NAPS) network (Environment Canada, 2011b). Spatial variability of VOCs has been observed in several previous studies (Srivastava et al., 2005; Parra et al., 2006; Smith et al, 2007; Miller et al., 2009; Miller et al., 2010), where some factors (e.g., proximity to roads, industries, and wind direction) have been shown to influence their spatial distribution. In cities such as Windsor and Sarnia, point sources can exert a significant impact on residential exposure, as their concentration levels can show a strong spatial variability across the cities. For this reason, dense spatial networks are better suited to provide data at a resolution that may be linked with exposure and ultimately, illness, or disease. However, such dense networks are not always feasible due to the associated high cost of deployment and analysis. High costs also prohibit long-term, year-round sampling. Therefore, often one or several (across all seasons) short-term campaigns are used to estimate the spatial pattern of pollutants.

Recent studies have examined how the ratios between the BTEX species can provide insight into source origins as well as the photochemical age of the air mass. A specific range of the toluene to benzene ratio (T/B) has been used as an indicator of traffic emissions (Barletta et al., 2005; Hoque et al., 2008; Buczynska et al., 2009; Miller et al., 2010). The values are in the range of 1.5 – 3.0 (Chiang et al., 1996; Barletta et al., 2005; Khoder, 2007; Hoque et al., 2008; Liu et al., 2009), with variations likely attributable to different vehicle types and fuel composition in different regions. As pointed out by Gelencsr et al. (1997), toluene and benzene concentrations are reduced through their reaction with OH radicals with the rate constant of toluene being approximately 5 times larger than that of benzene. Therefore, ambient T/B ratios that are significantly lower than vehicular emission ratios are expected to have travelled and degraded, whereas higher T/B ratios may reflect relatively fresh vehicular emission sources. For example, this ratio was used to identify predominant hydrocarbon sources in 43 Chinese cities (Barletta et al., 2005). The B/T ratios of 10 cities were seen to be affected more by vehicular emissions as the main source of hydrocarbons. This was further confirmed by correlations between some traffic markers (benzene, toluene, and 1,3-butadiene) with ethyne and ethane, indicating the ability of T/B ratio to differentiate traffic emission dominated areas.

Due to the known rates of chemical reaction removal, the (m+p)-xylene to ethylbenzene ((m+p)/E) ratio can act as an indicator of the photochemical age of the air mass (Nelson and Quigley, 1983; Zhang et al., 2008). A ratio of 3.6:1 for (m+p)/E has been reported as the typical emission ratio for these species (Nelson and Quigley, 1983). Studies have also identified a group of ratios that can indicate photochemical age. In addition to T/B and (m+p)/E, (m+p)-xylene to benzene ((m+p)/B), and o-xylene to benzene (O/B) have also been used for such purpose (Khoder, 2007; Hoque et al., 2008). Higher values of these ratios (those closer to their expected emission ratio) typically indicate fresh local emissions, whereas lower values are associated with more photochemical degradation and therefore suggest that a sampling site is being influenced by emissions originated some distance away. Values of ratios reported as 'high' in a previous study are as follows: 2.45 (T/B), 1.61 (m+p)/B, 0.85 (O/B), and 3.28 (m+p)/E (Khoder, 2007). Furthermore, B:T:E:X ratios are useful for comparing sites across a city to identify areas influenced more strongly by one of the emission sources (Khoder, 2007). The degree to which the inter-species (I-S) ratios vary is also dependent on several factors including land use and climate, which are similar for the two cities that are the focus of this study.

This paper discusses synchronized VOC datasets from two cities to identify the factors that influence the BTEX concentrations and to characterize relationships between BTEX species. Additionally, this study investigates the use of specific ratios to estimate photochemical age and to differentiate different areas within a study area. Windsor and Sarnia were selected as they exhibit similar characteristics in terms of geographic location, weather patterns, degree of industrialization, and traffic. Furthermore, both cities had VOC data collected in the fall of 2005. The Sarnia BTEX data reported in this article have previously been evaluated as part of a larger VOC dataset (10 species). It was shown that concentrations levels and patterns were strongly influenced by industrial sources (Miller et al., 2009). In the current study, this analysis is expanded through comparison to another city (Windsor), consideration of inter-species ratios, and the impact of land use on these ratios.

8.2 Methods

8.2.1 Data Collection

For Windsor, data were obtained for 27 VOCs for all four seasons (winter, spring, summer, and fall) over a three-year period (2004, 2005, and 2006) for a total of 12 sampling sessions. Sampling in Sarnia took place in the fall of 2005. In both cities, passive sampling was done using 3M #3500 organic vapor samplers (Guillevan, Montreal) at approximately the same sampling density (1 passive sampler per 5 km^2). However, the sampling design differed for the two cities. In Sarnia, the 37 sampling locations (Figure 8.1) were selected to ensure that there was at least one site in or near every census tract and were more focused in residential areas than in industrial areas. In Windsor, locations were selected based on approximately even spatial distribution over the city, while also considering population density, with 52 sites in 2005 and 162 sites over the three years. Samplers were installed on light poles (in Windsor in 2004 and in Sarnia in 2005) or in residential backyards (Windsor 2005-2006) with shelters to protect them from inclement weather. Each sampling campaign was a 2-week integrated period. The fall 2005 sampling took place from October 4 to 18 in Sarnia and from October 5 to 19 in Windsor. The laboratory analysis of samples was conducted at the same facility (Airzone One, Mississauga, Ontario). Details of laboratory analyses and data screening have been previously documented in (Wheeler et al., 2008; Miller et al., 2009). Benzene, toluene, ethylbenzene, o-xylene, and (m+p)-xylene concentrations were used in this study. Samples with any of the five concentrations below the method detection limit were excluded, since the I-S ratios would not be representative.

8.2.2 Data Analysis

Statistical analyses were conducted in each city using Minitab Version 16. Pearson correlation coefficients between benzene and TEX were obtained. The rank (i.e., highest to lowest) order of concentrations and correlations were also determined. The I-S ratios relative to benzene, the B:T:E:X ratio, and (m+p)/E ratio were calculated using fall 2005 data as well as three years of fall data from Windsor. These ratios were further examined to determine if they could differentiate different areas within Sarnia. Furthermore, land use variables, including distance to open and industrial areas as well as length of highway and dwelling counts, were used to investigate any associations with the concentration ratios in Sarnia. The land use variables were generated within circular buffers that extended from the sampling locations. The set of variables used in correlation analysis were selected as the predictors having significant correlation with BTEX concentrations and low collinearity with other predictor variables. More information on the generation and selection of those variables can be found in (Atari et al., 2009). Finally, the same sets of ratios were calculated based on emissions reported to the National Pollutant Release Inventory (NPRI) (Environment Canada, 2011c), as well as based on the concentrations reported by the NAPS stations (Environment Canada, 2011b).

8.3 Results and Discussion

8.3.1 Concentrations

Pollutant concentrations, including descriptive statistics, have been reported elsewhere for Sarnia (Miller et al., 2009), and will be reported elsewhere for Windsor. The average fall concentrations for both cities are reported in Table 8.1. The concentration ranking was the same for both cities with toluene being the highest and ethylbenzene the lowest, which is also consistent with a 2006 study in the nearby city of Detroit, Michigan, USA (Johnson et al., 2010). In Windsor, the fall 2005 values were similar to the 3-year average fall values, indicating that fall 2005 was representative of typical seasonal concentrations. The mean values for each species were similar between the two cities, the differences varying from 22% (benzene), 14% (toluene), to less than 5% for other BTEX concentrations (ethylbenzene, xylenes and total BTEX).

Table 8.1. Mean fall concentration values and standard deviation (in parenthesis) in Windsor and Sarnia (µg/m^3).

	Benzene	Toluene	Ethylbenzene	(m+p) - xylene	o – xylene	BTEX
Windsor 3 yrs Fall (N = 144)	0.79	2.87	0.49	1.54	0.53	6.12
	(0.38)	(1.92)	(0.24)	(0.91)	(0.31)	(3.21)
Windsor Fall 2005 (N= 43)	0.76	2.87	0.47	1.33	0.47	5.89
	(0.14)	(1.13)	(0.21)	(0.76)	(0.18)	(1.93)
Sarnia Fall 2005 (N = 37)	0.98	2.51	0.48	1.28	0.49	5.73
	(0.54)	(1.31)	(0.22)	(0.59)	(0.24)	(2.78)

8.3.2 Inter-Species Correlations

The I-S correlations with benzene for the fall season in both cities are presented in Table 8.2. Strong correlations ranging from 0.63 – 0.85 were observed between benzene and TEX in both cities. This is consistent with previous studies in urban areas (Ho et al., 2004; Parra et al., 2006; Khoder, 2007; Bruno et al., 2008; Hoque et al., 2008; Miller et al., 2010). The correlation coefficient observed between benzene and toluene in Sarnia was slightly higher (0.85 vs. 0.67 in Windsor), which indicates that these pollutants likely originate from common sources. Investigation into which sources were high emitters in each city revealed that the manufacturing and industrial activities differed. In Windsor, the major VOC emitters were automotive manufacturing and supplier facilities, tool, mould and metal stamping facilities, and paint manufacturing. In Sarnia, oil refineries and large chemical companies were the major emitters. Despite the different activities, both cities were highly industrialized at the time of sampling and the types of VOCs being emitted were similar for their industries. Overall, the correlations support the conclusion that, in both cities, the emissions from this group of VOCs can be attributed to their respective industrial and mobile emissions.

Table 8.2. Pearson correlation coefficients between benzene and TEX in Windsor and Sarnia (all significant at $p < 0.05$).

	Toluene	**Ethylbenzene**	**(m+p)-Xylene**	**o-Xylene**
Windsor 2004-2006 fall average (N=144)	0.75	0.67	0.63	0.68
Windsor fall 2005 (N=42)	0.67	0.72	0.69	0.72
Sarnia fall 2005 (N=37)	0.85	0.81	0.66	0.67

8.3.3 Inter-Species Ratios in Both Cities

The means and medians of four specific inter-specie ratios, T/B, (m+p)/B, O/B, and (m+p)/E, averaged over all sites for each city are presented in Table 8.3. Those ratios are commonly used as indicators of photochemical age or predominant emission sources. The intra-city variability was low for all ratios in Windsor and for all except T/B in Sarnia, with less than 25% of the sites falling outside of the range of the mean value +/- 1 standard deviation. For the T/B ratio in Sarnia, up to 38% of sites fell beyond the same range, indicating the impact of numerous point sources of benzene and toluene (8 and 12 facilities respectively (Environment Canada, 2011c)).

Table 8.3. Mean, median, and coefficient of variation (CV) of inter-species ratios in Windsor and Sarnia**.**

		T/B	**E/B**	**(m+p)/B**	**O/B**	**(m+p)/E**
Windsor 3 years fall	Mean	3.91	0.59	2.02	0.68	3.03
(N=144)	Median	3.42	0.60	1.90	0.61	2.86
	CV (%)	30	22	25	28	22
Windsor Fall 2005	Mean	3.72	0.58	1.60	0.59	2.76
(N=42)	Median	3.44	0.59	1.65	0.60	2.77
	CV (%)	31	21	21	21	7
Sarnia Fall 2005	Mean	2.92	0.52	1.40	0.56	2.63
(N=37)	Median	2.89	0.52	1.38	0.55	2.70
	CV (%)	27	28	33	33	9

The mean ratios were similar in the two cities with the exception of T/B, which was significantly higher in Windsor (3.72 vs. 2.92 in Sarnia), indicating higher local emissions of toluene. The mean T/B ratio in Sarnia was in the upper range of 1.5 – 3.0, which is indicative of strong contributions from mobile sources (Khoder 2007; Hoque et al., 2008). In Windsor, the mean T/B ratios were outside of this range (3.7 for fall 2005, and 3.9 for fall 2004, 2005 and 2006), indicating that industrial activities were also large contributors to toluene. The high T/B ratios observed in Windsor are consistent with results reported for fall 2008 (Miller et al., 2010). The mean ratio of 4.3 observed in 2008 was well outside of the traffic range (1.5 – 3.0) and higher than that observed in this study (3.7), further confirming the influence of point sources of toluene in Windsor.

As with the concentrations, the rank order of the I-S ratios remained the same in both cities. The city-wide mean ratios were also similar for fall 2005, although less so for the T/B ratios which differed by 32%. The higher ratios in Windsor can be linked to higher reported emissions from the NPRI (Environment Canada, 2011c). For Windsor, 180 tonnes of toluene were emitted in 2005 with no reported benzene emissions, whereas for Sarnia, 86 tonnes of toluene were reported and 52 tonnes of benzene. This observation gives insight as to why the T/B ratios were higher in Windsor; benzene was emitted by vehicular sources and toluene was released from both mobile and point sources. This also explains the lower correlation between benzene and toluene in Windsor since different sources are emitting these species.

The emission ratios were not indicative of the concentration ratios. For example, in Windsor the T/B ratio would be extremely high (estimated at 180/1) due to having zero reported point source emissions of benzene, indicating that benzene is originating from sources other than industry in Windsor. In Sarnia, the T/B emission ratio was much lower (1.65) than the mean concentration ratio (2.92). In the B:T:E:X ratios for both cities (Table 8.4), toluene was in higher concentration ratios than would normally be attributable to traffic emissions (3:4:1:4) (Chiang et al., 1996). However, toluene is not high in the B:T:E:X emission ratios (0:2.3:1:1.3 for Windsor, and 1.7:2.6:1:2.1 for Sarnia). Differences in emissions of the other species such as higher ethylbenzene and xylenes in Windsor were not reflected in the concentrations (Table 8.1) or ratios (Table 8.3). However, it is difficult to decipher since the NPRI reports all xylene isomers into one category. Overall, low agreement was seen between the emission and concentration ratios, which can be expected since the emission ratios did not account for photochemical age and did not include mobile source emissions.

Table 8.4. B:T:E:X ratios in Windsor, Sarnia and previous literature**.**

	Site	**B:**	**T:**	**E:**	**X**
Windsor	N = 42	1.80	6.47	1	3.77
Sarnia	N = 37	2.05	5.58	1	3.68
Greater Cairo (Khoder, 2007)	Site 1(urban)	2.01	4.94	1	4.95
	Site 2 (urban)	2.03	4.91	1	4.87
	Site 3 (rural)	2.31	2.98	1	2.59
China (Wang et al., 2002)	City of Guangzhou	2.9	4.3	1	4.6
Taiwan-vehicle exhaust (Chiang et al., 1996)	Tunnel	3	4	1	4

The four concentration ratios (T/B, (m+p)/B, O/B, and (m+p)/E) were in agreement with one another in Sarnia. If one of these ratios was low (lowest quartile) or high (highest quartile), the chances of at least two of the other ratios being in the same quartile were

89% and 100%, respectively. The agreement in Windsor between the ratios was not as high; 50% for low sites, and 40% for high sites, with the T/B ratio being responsible for the majority of the discrepancies. This is likely due to the quantity or location of point source emissions of toluene or influences from transboundary pollution.

The mean B:T:E:X ratios were also calculated and compared with other studies (Table 8.4). Sarnia compares well with the two urban sites in Greater Cairo and sites in China, although toluene is higher for Sarnia and the xylenes are lower. For Windsor, toluene is even higher, although the other ratios are comparable to the previous studies. Compared with the ratios obtained in Taiwan, which are indicative of vehicle emissions, it is clear that there are other activities in Windsor and Sarnia contributing to the BTEX emissions, particularly toluene.

Pearson correlations between the ratios in each city also shed light on how different emissions affect the ratios. Although all ratios were significantly correlated ($0.510<r<0.996$, $p<0.05$) in both cities, the T/B, O/B, and (m+p)/B were more highly correlated in Sarnia ($r>0.943$), indicating that these are likely governed by benzene emissions. Low correlations between T/B and others ratios in Windsor ($0.510<r<0.585$) suggest that toluene emissions govern the T/B ratios. Correlations between (m+p)/B, O/B, (m+p)/E were similar in both cities.

8.3.4 Intra-city Variability of Relationships Between the BTEX Species Within Sarnia

Unlike Windsor, the majority of emitting facilities in Sarnia are located in a distinct industrial core (Fig 8.1c) that is separated from residential areas. The sites that were commonly identified as having high and low photochemical age ratios (T/B, (m+p)/B, O/B, (m+p)/E) in Sarnia are identified in Table 8.5. As indicated in Figure 8.1, the high-ratio sites were within the residential area, whereas most of the low-ratio sites were found in areas away from the residential area. This finding is consistent with that in Khoder (2007) where maximum T/B, (m+p)/B, and O/B ratios were observed in high traffic areas and lower ratios in areas less influenced by traffic.

Table 8.5. High and low ratio sites in Sarnia and characterization of pollutant mixtures.

Site	T/B	(m+p)/B	O/B	(m+p)/E	Characterization of pollutant mixtures	B:	T:	E:	X
Lows Group A					**Industry**				
1	1.65	0.58	0.23	2.20	High	3.82	6.32	1	3.06
2	1.43	0.58	0.22	1.67	concentration of	2.88	4.12	1	2.32
3	2.05	0.67	0.28	2.14	benzene from	3.18	6.52	1	3.02
Mean	1.71	0.61	0.24	2.01	industry leads to low ratios	3.30	5.65	1	2.80
Relatively Lows Group B					**Background (Open Area)**				
34	1.88	0.86	0.37	2.55		2.96	5.56	1	3.63
35	1.92	0.97	0.38	2.72	Low	2.81	5.41	1	3.79
36	1.98	1.03	0.43	2.67	concentrations	2.59	5.13	1	3.77
37	2.02	1.00	0.40	2.71	and relatively low	2.71	5.47	1	3.78
Mean	1.95	0.96	0.39	2.66	ratios	2.77	5.39	1	3.75
Highs Group C					**Traffic**				
12	4.59	2.33	0.94	2.91	Higher T,E,X	1.25	5.74	1	4.10
21	4.57	2.80	1.10	3.07	concentrations	1.10	5.00	1	4.27
30	3.98	1.87	0.75	2.80	and high ratios	1.50	5.97	1	3.92
31	4.03	1.96	0.78	2.79		1.42	5.75	1	3.90
Mean	4.29	2.24	0.89	2.90		1.32	5.62	1	4.05

Further examination of these ratios in Sarnia illustrates the ability of these ratios to differentiate areas within a city. There appear to be two areas where lower ratios were observed; within the industrial core (Group A - industry) and in the area near Lake Huron (Group B - clean). The reasons for these two low ratio areas are different. Near the industrial core (sites 1, 2, 3), benzene concentrations were higher (ranked 1, 4, and 5) and therefore the T/B, O/B, and (m+p)/B ratios were lower. In the area near Lake Huron (sites 34, 35, 36, 37), the low ratios were due to low concentration values of all species (less than half of the mean values for TEX and approximately two-thirds the mean value for benzene). This is an important finding with respect to how BTEX ratios can be used in cities with fresh industrial emissions. Although both groups of sites were in areas less influenced by traffic, the reason for the low ratio values is not the same. This should be considered when attempting to group sites by photochemical age through reliance on these ratios. One difference is in the (m+p)/E ratio, which is less consistent amongst the low ratios in the industrial core but more consistent amongst the low ratios experienced near Lake Huron. This suggests that the ratios at the sites near the lake were truly indicative of photochemical age - lower ratios due to dispersion and degradation of pollutants as they reached this area. On the other hand, the ratios obtained at the sites in the industrial core may not actually be related to photochemical age but more related to the quantities of emissions at nearby point sources. Therefore, the simple use of these ratios to indicate photochemical age may only be appropriate in areas away from point sources which may bias the ratios. In areas with significant point sources, this analysis may become more complex and could be broken down into more categories, for examples: low concentration/low ratios indicative of regional background influence; and high concentration/low ratios indicative of fresh sources.

As for the high photochemical age ratios (Group C – traffic) these were all found in the residential area and could be attributed to traffic. Sites 12, 21, 30, and 31 were high for all four ratios, whereas these, plus sites 4, 5, 7, 8, 12, 14, 22, 23, and 28, were high for the T/B, O/B, and (m+p)/B. Since these sites were located near highways or major roads, the higher ratios were likely due to fresh traffic emissions. Even though some distinct differences were seen in the ratios in the different areas (industrial, clean, traffic), these differences were small. Higher variability in the ratios is likely when larger areas with different land uses are considered, as was the case in Greater Cairo (Khoder, 2007). Significant differences were observed between the high- and low-ratios relative to benzene however this difference was small for (m+p)/E, while the differences between the two low-ratio groups were small, especially for T/B, indicating the importance of considering all ratios when making conclusions about their relevance. Looking at one ratio in isolation may lead to false conclusions regarding photochemical age and emission source origins.

Table 8.5 also shows the B:T:E:X ratios at the low and high photochemical ratio sites. The T/E ratios showed little variation amongst the three areas. The values were greater than 4, which was reported to be indicative of traffic (Chiang et al., 1996), suggesting toluene emissions from point sources. Furthermore, lower T/E ratio at the rural site as reported in Khoder (2007) was not observed at these sites, indicating once again, toluene emissions from non traffic sources. Higher X/E and E/B ratios were observed in the traffic area (Group C) and lower ratios in the industrial area (Group B). The B/E pattern is consistent with Khoder (2007). The low X/E ratio in the industrial area is due to low concentrations of xylenes, which may be predominantly emitted from vehicles and not point sources in this city.

In summary, relatively low T/B, (m+p)/B, O/B, E/B, (m+p)/E, ratios were observed in the clean areas, and the high ratios were observed in the traffic areas. However, low ratios were also observed in the industrial areas. When considering these ratios, concentration levels, proximity to known sources, and correlations between species should be taken into consideration when determining whether the air pollutants are aged or freshly emitted.

Land use variables were investigated to determine whether any of these were correlated with the concentration ratios in Sarnia. The land use variables selected are listed in Table 8.6. Significant correlations were observed between several of the B:T:E:X ratios and proximity to industry; specifically the xylenes to ethylbenzene ratios. The negative correlations indicate more industrial land use leads to lower X/E ratios, consistent with results presented in Table 8.5. The correlation becomes weaker with increasing buffer radian, suggesting diminishing effects of industrial emissions on the observed concentration ratios. Furthermore, positive correlation between the X/E ratio and dwelling counts indicates that this ratio is able to distinguish between residential and industrial areas. The (m+p)/B ratio was also marginally negatively correlated with industrial land use within 1600 m, but not so for greater distances.

Table 8.6. Pearson correlation coefficients between pollutant ratios and land use variables.

	Pollution ratios								
Land Use Variables	**B/E**	**T/E**	**(m+p)/E**	**O/E**	**X/E**	**T/B**	**E/B**	**(m+p)/B**	**O/B**
Open Area within 600m	0.173	-0.089	0.108	0.014	0.081	-0.064	-0.015	0.048	0.021
Industrial Area within 1600m	0.262	0.017	**-0.614*****	**-0.512*****	**-0.591*****	-0.210	-0.214	**-0.289***	-0.265
Industrial Area within 2500m	0.137	-0.093	**-0.453*****	**-0.374****	**-0.435*****	-0.097	-0.062	-0.128	-0.104
Industrial Area within 2800m	0.102	-0.089	**-0.403****	**-0.319***	**-0.383****	-0.064	-0.029	-0.091	-0.064
Length of Highway within 800m	0.014	0.150	0.008	-0.057	-0.012	-0.008	-0.039	-0.030	-0.049
Length of Highway within 900m	-0.009	0.126	0.030	-0.040	0.009	0.003	-0.016	-0.006	-0.027
Dwelling Counts within 1200m	**-0.407****	0.000	**0.341****	**0.383****	**0.358****	0.265	0.269	0.261	**0.284***
Dwelling Counts within 1400m	**-0.330****	**0.277***	0.273	**0.329****	**0.293***	**0.281***	0.195	0.184	0.204

*** Significant at $p<0.01$; ** Significant at $p<0.05$; * Significant at $p<0.10$

Significant positive correlations were observed between the B:T:E:X ratios and dwelling counts within 1200 and 1400 m, with the exception of B/E where negative correlations were observed. These correlations are likely attributable to local traffic in these residential areas. Significant correlations were not observed between any of the ratios and open areas or length of highway. This may be due to the small study area used to obtain the ratios. There is not as much variability in the age of the air masses as would be expected in a larger city or region. Overall, the correlations with the land use variables confirms that these ratios change depending on location within a city and can indeed be indicative of the activities or land use types nearby. Future research in larger areas is needed to further explore the utility of these ratios and their association with land use.

8.3.5 Inter-Species Ratios at the NAPS Stations

In both cities there is one NAPS station (NAPS 1 for Windsor, shown in Figure 8.1b) to sample VOCs approximately once every six days (Environment Canada, 2011b). Previously, NAPS concentrations have been reported to be representative of concentrations averaged across city-wide monitors in Sarnia (Miller et al., 2009).

However, small differences in concentrations could lead to large differences in ratios. Therefore, the NAPS station may not represent city-wide average ratios well. Furthermore, there could be significant differences in ratios between each site and the NAPS station.

In Sarnia, there were four dates when sampling data was available around the same time as the monitoring campaign in this study; October 1, 7, 19, and 25, 2005. Ratios from concentrations reported on these individual dates, as well as those averaged over all four dates, are provided in Table 8.7. Among the five ratios, the three ratios involving benzene were significantly different than the average ratios from the 37 monitors across the city. On the contrary, the (m+p)/E and B:T:E:X ratios were similar to that of the city-wide averages. In addition, the median percent differences between the four-day NAPS average photochemical ratios and those obtained at each of the sites across the monitoring campaign ranged from 22% ((m+p)/E) to 139% (O/B), with the positive values indicating that the NAPS ratios were lower than most ratios obtained from the spatial campaign. The percent differences indicate significant variability between the two sets of ratios, but more for some ratios than others. This is also evidenced by the percent differences up to 377% (O/B). The ratios on the four separate dates were fairly consistent, suggesting that the monitoring site does a reasonable job of determining the relationship between the species in that one specific area. However, it is not applicable across the city. Further investigation examined the three sites (Sites 15-17, Fig 8.1c) that were closest to the NAPS station. The ratios from these sites were significantly different from those obtained at the NAPS site, with percent differences ranging from 15 – 117%, suggesting that differing sampling methodology and frequency of measurements were likely some of the causes for the discrepancy. The ratios from these nearby sites fell in between the high and low ratio groups (Table 8.5) and were very similar to the city-wide means (Tables 8.3 and 8.5), differing by less than 13% for all ratios. The reason for these ratios falling in between the high and low ratios was likely due to this area being influenced by traffic and, to a lesser degree, by industry as well as their locations along the St. Clair River.

Table 8.7. Ratios calculated using three nearby monitoring sites in Sarnia and NAPS data in Sarnia and Windsor.

	T/B	**(m+p)/B**	**O/B**	**(m+p)/E**	**B: T: E: X**
Sarnia					
NAPS October 1	1.92	0.78	0.23	2.22	2.86:5.50:1:2.88
NAPS October 7	1.82	0.76	0.29	2.60	3.40:6.20:1:3.6
NAPS October 19	1.80	0.45	0.15	1.40	3.11:5.59:1:1.88
NAPS October 25	1.67	0.74	0.26	2.63	3.55:5.94:1:3.54
October 1, 7, & 19, 25 mean	1.80	0.68	0.23	2.21	3.23:5.81:1:2.98
Site 15	3.21	1.43	0.57	2.59	1.87:5.83:1:3.62
Site 16	2.53	1.00	0.41	2.42	2.42:6.11:1:3.42
Site 17	2.74	1.30	0.53	2.62	2.01:5.51:1:3.68
3 nearby sites mean	2.83	1.24	0.50	2.54	2.10:5.82:1:3.57
% Difference between NAPS					
Median	60.4	102	139	22.0	
Min	-20.7	-15.2	-2.56	-24.5	
Max	154	312	377	39.0	
Windsor					
NAPS October 25	2.60	1.88	0.53	3.00	1.59:4.15:1:3.85
% Difference between NAPS					
Median	32.4	-0.26	12.5	-7.64	
Min	-45.3	-1.50	-56.9	-40.2	
Max	163	0.82	78.4	3.07	

In Windsor, data from the NAPS station was available for only one sampling date around the time of the monitoring campaign- October 25, 2005. With the exception of T/B, these were similar to those mean values obtained from the spatial monitoring campaign. In both cities, the (m+p)/E ratios exhibited the least deviation from the single NAPS station, indicating relatively uniform photochemical aging across each city. T/B ratios observed at NAPS were poor indicators in both cities due to point source emissions. Large differences were observed between NAPS and the spatial network (m+p)/B and O/B ratios in Sarnia, with relatively small differences observed in Windsor. This is due to the presence of numerous stationary benzene sources in Sarnia, whereas there are no point sources in Windsor. The maximum percent differences between the NAPS T/B, (m+p)/B, O/B, (m+p)/E ratios and those obtained from the 42 Winsor sites ranged from -57% (O/B) to 163% (T/B). These differences are less than those observed in Sarnia. For Sarnia, the one central station was located in a residential area near the international bridge, which did not capture the high and low ratios due to it being some distance away from the industrial and open areas. In Windsor, it seems that the central station did a better job representing the concentration ratios across the city, possibly due to the fact that the industrial sites were spread across the city rather than situated in a concentrated area. Due to the limitation of having only one day of NAPS data for the sampling period in Windsor, future work should consider these comparisons over a longer timeframe.

8.4 Conclusions

The overall rank order and values of the BTEX concentrations, correlations, and ratios were found to be similar in two southwestern Ontario cities, Windsor and Sarnia. However, some significant differences were noted, leading to the determination of predominant sources in each city. With the exception of vehicular emissions, the sources of BTEX differed between the two cities. Windsor was highly influenced by automotive manufacturing activities while Sarnia was mainly exposed to emissions from petroleum processing sources. Since Windsor borders Detroit and Sarnia borders Port Huron, both cities may have been influenced by trans-boundary pollution. Despite these differences, the I-S ratios relative to benzene and ethylbenzene were found to be similar for both cities, suggesting that BTEX species were emitted in relatively set ratios, regardless of the nature of industrial activities. Whether this is true in other regions with different industries should be explored in future studies.

The inter-species ratios suggest fresh mobile sources as in previous urban studies, although both cities had significant non-vehicular air emissions of BTEX. This study led to new findings. First, the inter-species concentration ratios were successfully used to identify contributions of point source emissions in both cities. The B:T:E:X ratios indicate higher toluene emissions in Sarnia and Windsor. In Sarnia, large variability was observed in the T/B ratios, indicating large contributions of these two compounds from point sources. The four photochemical age ratios (T/B, (m+p)/B, O/B, and (m+p)/E) were found to be in better agreement with each other in Sarnia than in Windsor. In Windsor, the T/B ratio did not agree as well with the other ratios. Also, the mean T/B ratio was found to be higher and outside the range normally indicative of traffic. Furthermore, lower correlations between T/B and the other photochemical age ratios, and between toluene concentrations and other species were observed in Windsor. All of these results suggest that there were significant emissions of toluene and benzene from non-vehicular sources in Windsor and Sarnia respectively, which was confirmed by consulting the NPRI reporting.

Second, the quantity of point source air emissions, i.e., higher benzene in Sarnia and more toluene in Windsor, was consistent with the higher benzene concentrations in Sarnia and higher toluene concentrations in Windsor. However, the emission ratios were not in agreement with the concentration ratios found in either city, or indicative of the difference in concentration ratios between the two cities. Future studies could make accurate estimates of BTEX emissions from vehicular sources in these areas, thus making it possible to compare emission profiles of, and properly apportion of, the relative contributions from mobile and point sources respectively.

Third, it was observed that specific ratios representing photochemical age varied significantly for the different areas in Sarnia. These ratios could differentiate between clean, traffic, and industrial areas in Sarnia (however, the differences were small due to the relatively small study area). When using these ratios, caution is needed to ensure that they are not being biased by nearby point source emissions. Considering all ratios together leads to better conclusions regarding photochemical aging of these pollutants within the city. In addition, these ratios can be low or high for different reasons; either due to true photochemical aging or due to close proximity of emissions. In Sarnia, proximity to industry was the most significant influence on the X/E ratios, whereas B:T:E:X was also associated with dwelling counts.

Last, the reliance on central monitoring stations likely leads to misclassification of exposure assessment and emission source identification, and more where there is a greater number of point sources concentrated in one area far removed from a central monitoring station. This was evidenced by less agreement between the NAPS ratios and the spatial monitoring campaign ratios in Sarnia than in Windsor. Also, in Sarnia the

NAPS ratios were not able to differentiate areas of the city by land use in the way that the sampling campaign ratios might.

The insights gained may benefit future air quality spatial analyses and epidemiological studies. Despite the challenges, the use of ratios to identify photochemical aging and potential source origins is promising. However, the applications of these ratios may not be as simple as claimed in previous studies. These ratios will work differently depending on their area of application and consideration must be given to nearby sources.

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CHAPTER 9: CONCLUSIONS, RECOMMENDATIONS AND ENGINEERING SIGNIFICANCE

9.1 Conclusions and Engineering Significance

The studies contained within this thesis are meant to provide evaluation of air quality in Windsor, Detroit, and Sarnia while focusing on study components and applications that can be improved and applied to future air quality studies. This is achieved through the evaluation of results from several high density sampling campaigns and those obtained from current central site monitoring, leading to assessment of variability in urban air quality and recommendations for future study design and data analysis. Taken together, these studies provide an extensive analysis of air quality in the region for several pollutants. For Windsor, sampling was carried out over five years. In 2004, 2005, and 2006 passive sampling for NO_2 and SO_2 and VOCs took place at approximately 50 sites across the city for all four seasons, while only BTEX VOCs are reported on in this thesis. Furthermore the fall 2005 Windsor campaign was coordinated with simultaneous sampling at 37 sites in Sarnia. In 2008 and 2009 passive and active sampling of VOCs, PAHs, NO_2, and three PM size fractions was carried out at 32 sites (16 active/16 passive) across Windsor while simultaneously sampling the same pollutants at 68 (34 active/34 passive) sites across Detroit. Simultaneous sampling across an international border provides a unique opportunity to analyze the variability within and between the two cities. Few studies exist to provide an opportunity to consider the large number of factors and variabilities made possible by this multi city, multi site, multi pollutant, multi year, multi season, investigation. Significant conclusions and recommendations were made from the results of this comprehensive study.

9.1.1 Spatial and Temporal Variability and Exposure Assessment

Three sources of variability were addressed in this thesis; seasonal, annual, and spatial. Each was significant to varying degrees. Seasonal variability in concentrations and ratios was observed in the three-year BTEX study. Both the spatial monitoring campaigns and NAPS station recorded generally higher concentrations in the summer and lower concentrations in the winter. Spring and fall values generally fell in between.

Additionally, these seasons were the most likely to contribute representative amounts (i.e. 25%) on a site-by-site basis to the annual mean concentrations. In other words the transition seasons (fall and spring) were most representative of annual mean concentrations in both city-wide and city-by-site aspects. In terms of spatial patterns, fall had the strongest correlations with annual patterns while the spring season was the least correlated. Year to year variability was observed when considering which season was most representative of annual averages. This is likely due to the seasons being represented by a two-week period, during which meteorology may differ compared to seasonal averages.

T/B ratios were observed to be highest in the summer and lowest in the winter in all three years of the study. Correlations among BTEX also varied seasonally but these variations were not consistent. Those results point to the need of seasonal sampling to capture the variability observed throughout these studies. If resources limit sampling to a single season, fall followed by spring will generally provide better estimates of annual exposures.

Annual variability was assessed both in the three-year BTEX Windsor study and in the two-year Windsor-Detroit comparison. In terms of concentration values and the locations of distinct hot spots, variability between years was observed. Mixed results were observed for which species had higher or lower concentrations in a given year. This may indicate that point sources are more likely the source of variability rather than mobile emissions which have a consistent species mixture. General patterns such as the rank order of high to low concentrations in the study area and site classification based on high / medium / low concentration categorization were fairly consistent from year to year. Photochemical age, correlations among BTEX species, and spatial patterns were also seen to be fairly consistent, with the exception of large annual variations in the T/B ratio in Windsor. Overall, although annual variability was significant in some aspects, it is concluded that multiple year sampling may not be necessary, since the benefit of multiple year sampling may not justify the associated costs.

For all pollutants monitored, spatial variability was seen in Windsor and Detroit in the 2008-2009 study, the degree of which was similar between the two cities. Some species experienced greater variability than others but the relative order of variability was consistent among the two sampling campaigns. The observed patterns in spatial variability were somewhat expected; higher concentrations of NO_2 and BTEX near the Ambassador Bridge and in the vicinity of industrialized areas. Spatial variability was also observed in the three-year Windsor BTEX study with the highest benzene concentrations located along the northwest of the city in the vicinity of Huron Church road and the Ambassador Bridge. The significant spatial variability observed in Windsor (2004, 2005, 2006, 2008, 2009) and Detroit (2008, 2009) is in agreement with high spatial variability reported in Sarnia for VOCs (Miller et al., 2009) and for NO_2 and SO_2 (Atari et al., 2008) in 2005.

Hot spot analysis of the Windsor benzene and toluene data from 2004 and 2006 also demonstrated spatial variability. High concentration clusters were observed and the spatial patterns of these clusters remained fairly consistent throughout the year however showed more variability between years (2004 compared to 2006). The general pattern consisted of a clustering of high concentrations sites along the northwest of the city, consistent with the concentration maps. Despite the general patterns being similar, additional high sites were often observed in one season that were not present in another. The pattern for spring in 2004 was very different than for the other three seasons. Year to year comparison of the spatial patterns demonstrated that toluene experienced more variability than benzene.

A high degree of correlation was observed where sites remained in the same locations between the 2005-2006 Windsor sampling campaigns, suggesting that the spatial patterns remained relatively consistent from one year to another. In the Windsor – Detroit 2008/2009 study correlations between common sites were significant for all pollutants in Detroit and for all except PM in Windsor. These are encouraging findings with implications for adequate sampling with limited resources. If spatial variability remains fairly consistent between years, it may not be necessary to conduct such extensive sampling annually, but rather determine an appropriate sampling frequency to provide reasonable spatial patterns.

Overall, the studies on variability lead to some conclusions. Seasonal variability is significant with fall and spring being preferred seasons to sample in order to represent annual concentrations, and fall being preferred to represent annual spatial patterns. Spatial variability is significant and important to capture with high density sampling. Inter-annual variability is present however the degree of variability may not justify the cost for most sampling purposes.

Throughout the analysis reported in this thesis, emphasis was placed on comparing the concentrations of measured pollutants and ratios among toluene and benzene obtained from the spatial sampling campaigns with those reported from central monitoring stations. Results from the three-year Windsor BTEX study suggest that reliance on the NAPS data could lead to significant exposure misclassification for these species since values measured at sites across the city varied by up to a factor of six. In terms of citywide average concentrations however, Windsor NAPS station did a reasonable job of estimating average concentrations of NO_2, total BTEX and $PM_{2.5}$ in 2008 and 2009. NAPS also revealed the same seasonal BTEX trends from 2004-2006 that were observed in the sampling campaigns. This serves to provide researchers and government officials with information regarding the utility of central stations for different purposes. It also provides ranges of exposure misclassification associated with reliance on these measurements. It is concluded that the implementation of additional high density spatial monitoring campaigns for NAPS monitored pollutants could lead to reduced exposure misclassification by providing valuable spatial concentration data. Results from these campaigns can lead to the development of models such as LUR which can be applied to estimate concentrations with finer spatial resolutions for exposure assessment.

9.1.2 Determination of Contributing Sources

Statistical correlations between measured pollutants were calculated for all study periods. Correlations among the BTEX species were generally all high and significant regardless of city, season, or year, indicating that these species originate from predominantly common sources, likely traffic, in this region. Total VOCs, BTEX and NO_2 were also well correlated with each other in Windsor and Detroit, further suggesting predominantly vehicular sources of these pollutants.

I-S BTEX ratios were investigated in all three cities to identify major sources. In Windsor and Sarnia the ratios were also used to estimate the photochemical age of the air mass in these cities. These applications of ratios are of engineering significance. These ratios identified significant differences between the cities despite their similarities in geography, meteorology, and degree of industrialization. The higher T/B ratios observed in Windsor, compared with Sarnia and Detroit, suggest that Windsor may be predominantly exposed to industrial sources of toluene compared to mobile in the other cities. For Sarnia, the ratios are indicative of predominantly mobile emissions which is consistent with the high proportion of samplers being located within the residential area of the city. T/B ratios were also a useful tool in identifying possible changes in toluene and benzene emissions in Windsor in 2009 compared with 2004-2006 and 2008. Similarly (M+P)/E ratios identified a relatively young photochemical age of the air masses in both Windsor and Sarnia. This result was expected due to the documented presence of numerous emission sources in these areas.

In Sarnia, the chemical valley of Canada, a combination of four ratios known to be indicative of photochemical age were used to successfully differentiate pollutant mixtures of mobile and industrial sources between different areas of the city. This application of ratios was unique in two ways. First, the ratios were applied in areas near industrial sources which has rarely been reported in past investigations. Secondly, it considered both the ratios and the concentration levels in different areas which lead to an important conclusion. The ratios were observed to experience lows for two separate reasons; (1) due to high concentrations of one species from nearby industrial facilities, and (2) due to relatively low concentrations of all species. The latter is a common explanation for low ratios reported in the literature whereas the relation to impact of high concentrations has not been previously reported. These applications can be useful to further investigate spatial sampling data to delineate contributing sources. The consideration of how concentration levels affect ratio values in places with different source impacts highlights the need to evaluate both when identifying the mixture of sources affecting the area.

The utility of pollutant release inventories in relation to air quality studies was evaluated. The point source emission quantities reported to the NPRI were not seen to be indicative of concentrations or I-S BTEX ratios in Windsor or Sarnia. However, NPRI data did explain some differences such as higher T/B ratios in Windsor. Annual emission quantities did not explain the higher T/B ratios in Windsor in 2008 compared with 2009. It is difficult to associate concentrations with quantities from reporting inventories due to the lack of temporal and mobile emissions components. Reporting industries are not adequately representative of concentrations or ratios and should not be used for exposure purposes. On the other hand, when large year to year or city to city differences are observed, these inventories may serve to identify potential reasons for these variations.

The pathways of the back trajectories of air masses arriving in Windsor during the 2008 and 2009 sampling campaigns were not seen to be correlated with the emissions and concentrations of NO_2 or $PM_{2.5}$ encountered along the air mass pathway. This application was meant to identify whether or not Windsor is affected by transboundary air pollution. For the short time frame considered, Windsor was predominantly affected by local sources.

9.1.3 Air Quality in Windsor

Air quality in Windsor was assessed through the evaluation of concentrations and correlations obtained from a total of 14 two-week sampling campaigns, data from the central monitoring sites, and through comparison to nearby cities. Windsor experiences lower concentrations of air pollutants than Detroit and similar concentrations to Sarnia. Based on the (M+P)/E ratio analysis the photochemical age of the air mass in Windsor (2004-2006) and in Sarnia (2005) was comparable. The use of I-S BTEX ratios, correlations among BTEX and between VOCs and NO_2, HYSPLIT modelling, and wind associations has lead to the conclusion that Windsor is predominantly influenced by local point and mobile sources. This is likely due to the number of manufacturing facilities which emit air pollutants in this area and vehicular emissions from local traffic and the border crossings. Unlike Detroit, Michigan, and Sarnia, Ontario where T/B ratios and correlations indicate that these two compounds originate from a common source, likely traffic, Windsor had higher T/B ratios outside of the range normally attributed to traffic. This suggests that Windsor experiences significant contributions of toluene from industrial sources which was confirmed by consulting the NPRI. Additionally, the lack of association between high concentration sites for benzene and toluene (2004 and 2006) and wind patterns, further suggests that local sources are the predominant contributors of the BTEX species.

Risk maps illustrate that some areas of the city are more susceptible to illness related to BTEX exposure than others. Specifically, benzene, a known carcinogen largely governs the hazard quotient for exposure with the TEX species registering measurements significantly below the AAQC standards. The deviation from the typically high benzene – toluene correlations, along with benzene values approaching the AAQC for the city warrants further investigation into the emissions of toluene and benzene and implementation of control measures.

A lack of correlation between any PM size fraction and NO_2 in Windsor was noted, whereas significant correlations were observed between NO_2 and $PM_{2.5\text{-}10}$ in Detroit and NO_2 has previously been suggested to be a good proxy for PM (Brook et al., 1997). In Windsor, however, NO_2 as a proxy for PM would not be justified based on the 2008 and 2009 data and further investigation into this correlation in the city is warranted.

Taken together, the between city comparisons highlight significant differences in concentrations of most pollutants and correlations between NO_2 and PM (Windsor – Detroit), and between T/B ratios (Windsor – Detroit and Windsor – Sarnia). Spatial variability was observed and correlations among BTEX species were generally high in all cities. Although similar in terms of meteorology and geography, these cities have distinct differences such as an industrial core in Sarnia and higher emissions from diverse industrial operations and high traffic volumes in Detroit. These differences affect the variabilities related to exposure as well as the ability of central stations to represent citywide concentrations. Additionally, the establishment of proxy variables in one city may not be applicable to a nearby city. For these reasons, sampling in all major cities is recommended to capture the unique differences related to source contributions.

9.2 Recommendations

9.2.1 Recommendations for Future Sampling Campaigns

Sampling at multiple sites, over multiple years, in all four seasons, across different cities, and at different sampling locations provided information to evaluate sources of variability which are essential in exposure assessment. Taken together, the results of the studies presented herein can be generalized to formulate recommendations to improve future air quality campaigns for exposure assessment and the estimation of source contributions and origins in other urban areas. In a city such as Windsor that experiences four distinct seasons, seasonal sampling is recommended to capture the changes in concentration ranges attributable to changing meteorology and to some degree emissions. If resource limitations render seasonal sampling infeasible, then sampling during a transition season (i.e., spring or fall) will yield better estimates of annual concentrations than sampling in summer or winter. Annual sampling is beneficial to identify changes in annual concentration values, hot spots, or spatial patterns however the benefits diminish when general concentration patterns or exposure classifications are desired. It is recommended that researchers exercise discretion to determine the accuracy level required consistent with study objectives and decide whether multiple year sampling is necessary.

Sampling density is an important design consideration. Sampling densities for the Windsor, Detroit, and Sarnia campaigns examined in this thesis ranged from approximately 1 sample per 3 km^2 to 1 sample per 5 km^2 for passive sampling, and 1 sample per 10 km^2 for active. Variability observed at this level of sampling density suggests that future exposure studies should be sampled at similar or greater spatial densities. This recommendation is consistent with the sampling density of 1 sample per 3.4 km^2 recommended by Cocheo et al. (2008) to achieve adequate spatial coverage for BTEX. If resources are feasible, future studies could sample at finer scales (i.e. greater sample densities) to achieve more accurate exposure estimates.

The placement of samplers should also be controlled. Differences between I-S correlations, spatial variability, and (M+P)/E ratios were observed in the Windsor BTEX analysis when samplers were placed roadside as opposed to in residential backyards. Roadside monitors were seen to be more representative of fresh mobile emissions. Additionally, comparison by sampling height (1.5 m vs. 3 m) in the Windsor – Detroit 2008 study noted significant differences, with higher concentrations of vehicular related emissions being observed at the lower height. These are important findings when comparing outdoor passive monitoring studies. Often times, placement throughout the city or sampler height is overlooked which could be an important factor in interpreting results.

Site selection methods differed from year to year (Sarnia 2005 and Windsor 2004-2006) based on the objectives of the projects. One limitation to the three-year, four-season, BTEX study was the lack of consistency between sampling locations from year to year. Future multi season or multi year studies could keep an appropriate proportion, e.g. one-third, of the sites common between sampling campaigns to minimize variability associated with changes in the sampling locations. This will also facilitate the evaluation of the temporal stability of spatial patterns. When the study design calls for a large portion of the sites to change locations between years, it is recommended that site classifications such as the number of residential or industrial sites, and the distribution of proximity to roads remain consistent. This will reduce the variability due to changes in site classifications.

Regarding the application of BTEX I-S ratios in future studies it is important to consider multiple ratios, concentration levels and proximity to known sources, in addition to considering the range of ratios, when making conclusions regarding source contributions. One ratio alone may be biased due to nearby sources. Moreover, the range of T/B ratios used to identify the influence of mobile emissions is large. These identifications should be further investigated by considering other factors such as concentration levels and proximity to roads at these sites. Further refinement of the traffic range could also include sampling in areas known to be almost solely influenced by traffic, such as tunnel studies (i.e. Ho et al., 2009).

Reliance on concentrations obtained from central monitoring stations will result in exposure misclassification due to their widely spaced geographical distribution. In urban areas where point and mobile sources are abundant and diverse, central stations cannot capture residential exposure at a level required for health investigations. In most cases, values from these stations were found to be representative of citywide means in Windsor and Sarnia, but the range of concentrations obtained across the city was significant and could not be derived from central monitoring data. The overall recommendation regarding use of these central stations is that they are adequate to represent average concentrations but lack the ability to provide spatial data for accurate exposure assessment. Analysis based on reliance on concentrations from these stations should be accompanied by a range of potential misclassification if applied over a large and diverse area.

These recommendations for study design will improve the efficacy of future air monitoring campaigns. Furthermore, the comparisons between spatial campaign and central station measurements will provide potential degrees of misclassification for studies relying on data from government monitoring stations. This will result in better exposure estimates that will improve understanding of the linkages between air quality and human health. Several groups of people can benefit from the recommendations provided:

Air Quality Researchers:

The evaluation of the different sources of variability and how they affect air quality studies will assist researchers when selecting important field study design components. The application of I-S ratios is also useful for future researchers to provide information such as source and photochemical age estimation. Reported concentration values, ratios and correlations serve as an air quality assessment of the region. These also provide a basis for comparison for future studies taking place in the same, or comparable urban areas.

City Planners:

The impact of point and mobile sources on the spatial patterns and hot spots of concentrations and high risk locations within the study areas are demonstrated. This will allow city planners to better establish adequate buffering distance between industrial areas or transportation corridors and residential settings as well as institutions such as schools and nursing homes.

Governments:

Throughout this thesis comparison are made between concentrations obtained at central stations and those from the spatial sampling campaigns. It was concluded that one or two central monitoring stations in a city cannot estimate exposure for a large population due to the large area and the diverse activities occurring over this area. This finding will hopefully encourage governments to undertake more extensive monitoring, at least occasionally, to adequately represent spatial patterns. Governments can also apply the BTEX I-S ratios method in conjunction with concentration levels to delineate source impacts, leading to the identification of problem areas, such as air releases from stationary sources. This information can be used to determine where to focus their pollution reduction resources, thus ultimately improving air quality. Further pollution reduction initiatives could be based on the concentrations in relation to the AAQC values and the determination of which pollutants pose potential health risks, for example, benzene in Windsor and Sarnia.

Epidemiologists:

These studies illustrate what level of data collection is required depending on the objectives of the study. For instance, if general high and low concentration areas are sufficient then multiple season or multiple year sampling may not be required. However, if more details are required such as intra-annual and inter-annual variability in concentration values, ratios, or hot spots, it would be necessary to consider increased sampling frequency. The recommendations regarding central stations also aid epidemiologists by demonstrating the need to account for misclassification when choosing to use such data for their health studies and how to use spatial campaign data to estimate the level of misclassification they can expect.

9.2.2 Recommendations for Future Research

Time and resource limitations did not permit for some additional components to be addressed which could therefore be investigated in future research. Future work could consider the long term variability in measurements from the Windsor West NAPS station to determine if the temporal variability is comparable to the observed spatial variability. Spatial analyses at finer scales, for example 100 m or less, has been documented but was not possible to discern with the studies contained within due to resource limitations. Future studies could employ greater sampling densities to depict the fine scale spatial variability for the three cities considered. Hot spots in concentration were seen to vary to a lesser degree between seasons than between years. These changes in hot spot locations were not associated with wind patterns. Further investigation into the causes of these hot spots should be undertaken to determine potential reasons for their occurrence such as changes in industrial activities, construction projects, or traffic patterns.

Other sampling methods such location-allocation and stratified random sampling could be employed to capture key land use as well as population and concentration characteristics. Future research could also assess the role of site selection in the outcome of the studies. For example, the spatial analysis could further incorporate site classifications such as residential, industrial, and proximity to roads, based on correlations and ratios. These classifications could then be investigated to determine whether they are stable over time and how they impact hot spot locations. For the use of ambient datasets for exposure estimates, indoor, outdoor, and personal monitoring data collected in Windsor (Wheeler et al., 2011) could be used to investigate any correlations between outdoor and personal exposure for this region and whether the relationship is pollutant specific.

For evaluation of the effects of transboundary air movement on Windsor concentration levels, longer study periods should be considered to evaluate the correlation between emissions and concentrations encountered along the air mass pathway and the concentration at the receptor, or to identify reasons of the lack of such correlations. Also, the areas encountered along the pathway could be subdivided, rather than considering an entire state or province, to refine the associations.

Point source emission inventories, such as the NPRI, were not indicative of concentrations, ratios, or transboundary air movement, although did explain some differences in concentrations and ratios between cities. These inventories only account for point source emissions and do not have a temporal component, therefore, do not provide enough information in relation to two-week concentrations. Future analysis could combine the point source emission quantities with mobile emissions for a city to determine if this would provide better associations with concentration levels. Source apportionment studies (e.g. Lau, 2010) could also be carried out, with both the three-year Windsor dataset and the two-year Detroit-Windsor data. Receptor models, such as Chemical Mass Balance and Positive Matrix Factorization could be applied to identify contributions from each source, such as vehicular and refinery, during each sampling campaign and evaluate any seasonal and annual variability in source contributions.

The extensive concentration data could also be used to develop multi pollutant LUR models for the region. This could include the development of spatial models encompassing the international airshed of Windsor and Detroit to determine whether single or unified modelling efforts would be better able to represent the spatial variability within and between cities. The development of multi season and multi year LUR models would also be a significant contribution. This could help in determining how frequently these models would need to be updated, as well as evaluate the transferability of LUR models between seasons and years, and between cities. Some of the accompanying analysis such as the wind speed and directional analyses for the hot spot maps could also be used to resolve some of the variance in LUR models for the region.

An extensive evaluation of statistical and spatial correlations between pollutants is also warranted to investigate any differences between the two and to determine which pollutants can act as proxies for others in this region. Differences were observed between which pollutants were statistically correlated with each other and which had similar spatial patterns in Detroit and Windsor, therefore suggesting that both should be considered when selecting proxy pollutants.

Furthermore, benzene pollution in Windsor could be the focus of future research and reduction initiatives due to the concentration levels approaching the public health based AAQC value. Sarnia could also benefit from benzene reduction initiatives as the average benzene concentration in fall 2005 was higher than in Windsor, due to an abundance of industrial and chemical facilities, and values in Sarnia would also approach the AAQC standard.

9.3 References

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APPENDIX A. Copyright information from relevant journals

The following copyright information pertains to the following publications:

- Intra-urban correlation and spatial variability of air toxics across an international airshed in Detroit, Michigan (USA) and Windsor, Ontario (Canada)
- Transboundary air pollution in Windsor, Ontario (Canada)
- Multi-season, multi-year concentrations and correlations amongst the BTEX group of VOCs in an urbanized industrial city

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