SOURCES AND EXPOSURES OF AMBIENT AIR POLLUTANTS AND THEIR RELATIONSHIP TO ADVERSE BIRTH OUTCOMES AND RESPIRATORY DISEASE

by

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Dedication

This dissertation is dedicated to my parents, Hai Van Le and Lang Ngoc Luong, all my siblings and their families, and D.C. Rompf in appreciation of their enduring supports and encouragements.

Acknowledgements

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Chapter 1

Introduction

Exposure to ambient air pollutants has been associated with both morbidity[1,2] and mortality.[3,4] Many studies have shown that ambient air pollutants, at concentrations well below U.S. EPA and WHO guidelines, can adversely affect fetal growth and development as well as contribute to acute childhood respiratory-related illness.[2,5,6]

The research in this dissertation investigates the effects of criteria and toxic ambient air pollutants on adverse birth outcomes and childhood respiratory-related illness, respectively. The research examines the following topics: (1) the effects of criteria air pollutants on adverse birth outcomes, as adjusted for race, smoking and social economic status (SES) and long-term trends in pollutant concentrations; (2) the effects of multiple pollutants, modeled as source classes, on acute respiratory-related illness among children; (3) the evaluation of the reproducibility of air toxic data and different methods to handle missing air quality data for health effects studies; and (4) the use of receptor modeling for deriving source class contributions as pollutant exposure indicators for health effect studies.

1.1 Dissertation organization

This dissertation is organized into five chapters and two appendices. This chapter (Chapter 1) summarizes the current literature for the main topics of the research, and presents the objectives and hypotheses. Chapters 2 through 4, the research chapters, and Appendix 1 have been written as stand-alone sections, in anticipation of submission to journals as article manuscripts.[*] Chapter 2 investigates the association

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[*] Chapter two has been submitted, and chapter four has been published.

between exposures to criteria air pollutants and adverse birth outcomes. Chapter 3 investigates associations between exposures to air toxics, identified as different source classes, and emergency department (ED) visits for respiratory problems among children. Chapter 4 examines the reproducibility of air toxics data and evaluates two imputation methods in handling missing air quality data. Chapter 5 summarizes the findings of all of the research questions. Appendix 1 identifies source classes of air toxics data using receptor modeling. The apportionment results are used as exposure estimates in the third objective described in Chapter 3. Finally, Appendix 2 is the published paper based on Chapter 4.

1.2 Background

1.2.1 Ambient air pollutants

The 1990 Clean Air Act Amendments focused attention on two classes of air pollutants: criteria pollutants and hazardous or "toxic" air pollutants (HAPs). Criteria pollutants, which have been routinely monitored and regulated for many years, include particulate matter (PM), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3), carbon monoxide (CO) and lead (Pb). In contrast, monitoring and regulation of HAPs are still in their infancy. Although there are an estimated 189 HAPs, U.S. EPA (1998) focuses on a subset of 33 pollutants called urban air toxics (UATs).[7] UATs include several classes of pollutants: volatile organic compounds (VOCs), very volatile compounds, semivolatile organic compounds, metals, and mixtures. Monitoring of UATs is relatively uncommon and typically only a few pollutants are measured on an intermittent basis. This study focuses on selected short term health effects of the UATs, specifically acute respiratory-related illness among children, and several long term health effects, specifically adverse birth outcomes, of the criteria air pollutants.

1.2.2 Air pollution and adverse birth outcomes

Many studies have examined the relationship between air pollutants and adverse birth outcomes (Table 1). Associations between criteria air pollutants and low birth weight (LBW; birth weight < 2500g) have been studied more extensively than other birth outcomes, such as small-for-gestational-age (SGA; birth weight <10th percentiles by

gestational age and sex) and preterm (PTB; birth < 37 gestational weeks) births. Only three studies examined SGA directly[8-10], although five other studies have examined intra uterine growth restriction (IUGR), in which SGA is a measure of IUGR.[11-15] In the U.S., the only studies on SGA or IUGR measures were conducted in California, and they obtained inconsistent results.[10,15] For the sample taken across the entire California population, exposure to $PM_{2.5}$ was positively associated with SGA, and exposure to CO was negatively associated with SGA.[10] However, in the southern California sample, exposures to CO, NO_2, O_3, and PM_{10} were not associated with IUGR (a SGA measure).[15] For PTB, associations with SO_2 and PM_{10} are fairly well established, while results are inconsistent for CO and NO_2.[8,11,13,15-22]

The strength of these relationships differs dramatically between studies, which constitutes a major weakness in the current literature. For example, three California studies examined the association between CO and LBW and obtained varying results: the early study (1975-1987) with 24-hr inter-quartile range exposures between 1.2 to 1.4 ppm reported no effect for all trimesters of pregnancy[15]; a later study (1989-1993) with relatively high CO exposures (3-hr trimester average ≥5.5 ppm versus <2.2 ppm) showed increased risk of LBW among mothers residing within 3.2 km of air quality monitors in single pollutant models[23]; and the latest study (1994-2000) in the same area showed effects with much lower CO exposures (third trimester mean of 1.4 ppm).[21] Positive CO-LBW associations have been shown in studies conducted in the northeast U.S.[24] and South Korea[25,26], but not in Taiwan[27], Nevada, U.S.[28] and Vancouver, Canada.[13] The literature examining LBW with respect to NO_2 and PM_{10} exposure is also inconsistent. Two Korean studies[25,26] found positive NO_2-LBW associations, but this was not seen in studies from southern California[15], Taiwan[27] and Vancouver.[13] Positive PM_{10}-LBW associations were found in one southern California study[21] and in a South Korea study[26], but not in another southern California study[15], northeast U.S.[24], and Taiwan.[27]

There are several possible reasons for these mixed results. First, the studies differed with respect to exposure concentrations of air pollutants, periods over which measurements were averaged, and cut-off concentrations. As examples: the northeast U.S. study compared CO exposures above and below 1.46 ppm; the Korean studies examined 0.5 and 4.2 ppm changes in 24-hr exposures; the Nevada study used tertiles of

8-hr exposures (<0.6, 0.6-1.4, and >1.4 ppm); and the Taiwan study used three categorical 24-hr exposures that reached very high levels (<1.3, 1.3-15, >15 ppm). Given that CO-LBW associations have been found at both low and high concentrations, other factors may better explain study outcomes. A second inconsistency among the studies is the control of covariates and potential confounders. Among the nine CO-LBW studies, only three[15,24,28] controlled for maternal smoking, a well-known risk factor. Only three of the ten SO_2-LBW studies[24,29,30] adjusted for maternal smoking status. A third difference between the studies is the control of long term trends in pollutant exposures. In the single study examining long term trends[29], the SO_2-LBW and PM_{10}-LBW associations lost significance when adjusted for trend in the models. A fourth difference is the varying exposure windows used by different studies. For example, exposures to SO_2 in all three trimesters were associated with increased risks of LBW reported in the Czech Republic and South Korea studies[11,26]; however, such risks were found only the first month of pregnancy in Vancouver[13], the first trimester in South Korea[25], the second trimester in northeast U.S.[24], and the third trimester in Beijing, China.[31]

Yet another problem arises from the ways in which multiple pollutant models, which are key to understanding the effects of simultaneous exposure to several pollutants, are constructed across studies. A recent California study found a positive CO-LBW association in a single pollutant model but a positive PM_{10}-LBW association in a multi-pollutant model (CO, NO_2, O_3 and PM_{10}).[21] A final problem arises from temporal and geographic variability of the studies. Not only can pollutant compositions and concentrations differ geographically, decreases in SO_2 and CO over the past few decades mean that findings from earlier studies with higher pollution levels may not represent the health effects for current levels of exposure. Similarly, rates of LBW, PTB and term SGA births have declined in the U.S., possibly due to trends in ambient pollutant levels or individual risk factors.[21,23,29,32,33]

In summary, the inconsistent strength of associations across studies may reflect methodological differences including exposure misclassification (e.g., distance to air monitoring site), and biases related to study duration (e.g., long-term trend), model structure (e.g., single versus multiple pollutant models), and the measurement and control of confounding factors (e.g., smoking, SES). Additional research on adverse birth

outcomes at recent and current levels of air pollutant exposures for different populations, including minority populations, is needed to address these gaps in the literature.

1.2.3   Air pollution and acute childhood respiratory-related illness

Associations between criteria air pollutants and exacerbation of childhood asthma are fairly well established.[2,34] Given the lack of data, associations concerning HAPs, however, have received minimal attention. There are even fewer studies investigating associations between air toxics and acute respiratory-related illness among children and minority populations.[35]

Those studies that have examined linkages between HAPs and respiratory-related illness have been conducted mainly in occupational settings where exposure levels are much higher than ambient levels.[36-40] A review found that although solvent-mediated respiratory toxicity was biologically plausible, occupational epidemiologic studies were unable to demonstrate respiratory symptoms or changes in pulmonary function associated with organic solvent exposure.[41] This was due to the nature of cross sectional study designs, the failure to adequately account for mixed exposures, potential response biases (i.e., past exposures) and the absence of exposure data.

Among the few non-occupational studies of children's exposure to HAPs, the focus has been primarily on single pollutant analyses, although most exposures occur as mixtures. For example, in Germany, exposure to benzene estimated within 50 m radius of a child's home was associated with asthma, wheezing and coughing, even after the adjustment for environmental tobacco smoke (ETS) at the child's residence.[42] Another study of German children also found an increased prevalence of morning cough and bronchitis associated with a 1 $\mu g/m^3$ increase in benzene exposure.[43] Furthermore, a study in Belfast (Northern Ireland) concluded that benzene was the only pollutant associated with emergency-department asthma admissions.[44] The study considered benzene and other criteria pollutants (SO_2, PM_{10}, O_3, NO_x, NO, NO_2 and CO) but did so only in two-pollutant Poisson regression models. These models may have failed to capture exposure of mixtures which then lead to the inability to determine the independent association between benzene exposure and asthma admission.

In the U.S., few studies have examined toxic exposures and respiratory-related problems among children. In West Virginia, a 10 µg/m^3 increase in petroleum-related compounds (toluene, m,p-xylene, benzene, o-xylene, decane) was associated with bronchitis, persistent wheezing, asthma, lower respiratory symptoms, and chronic lower respiratory response.[45] The same study found that a 2 µg/m^3 increase in process-related compounds (1,1,1-trichloroethane, carbon tetrachloride, 1-butantol, chloroform, perchloroethylene, methyl isobutyl ketone, etc) was associated with lower respiratory symptoms and chronic lower respiratory response in fifth grade children. In a more recent study, exposures to outdoor polar VOCs in the previous two days were associated with hospital/emergency-room visits due to asthma among Atlanta children 18 years and under.[46] In Los Angeles, ambient petroleum-related VOCs (toluene, m,p-xylene, o-xylene, and benzene) measured on the same person-day as breath VOCs were associated with mild asthma symptoms in Hispanic children.[47] However, the study concluded that only ambient benzene was associated with asthma symptom episodes; therefore, ambient measurements may serve as better indicators of true causal air pollutants in ambient air than breath VOCs, which may less accurately reflect pulmonary doses during the time frame relevant to acute responses.

All of these U.S. studies attempted to identify the source classes of air toxics in their study designs; however, using total concentrations and grouping compounds (i.e. sum of related compounds) as one single source class might not be representative of the actual sources. Individual compounds can be emitted from different sources. For example, ambient formaldehyde is formed from multiple sources, including photochemical oxidation of VOCs present in vehicle exhaust, incomplete combustion of gasoline and diesel fuels, and other combustion processes (e.g. burning of forests, cigarettes, and coal).[48] Source-resolved exposure estimates, in which the major sources are identified and quantified, are needed to address this gap. Recent panel studies have shown that the use of source apportionment methods for particulate matter can yield robust results in epidemiological analyses[49-51], suggesting that there is significant potential in using apportionment results as exposure measures in epidemiological investigations. (Information regarding source apportionment is described in Section 1.2.5

and Appendix 1.) Currently, only a few studies have investigated associations between source contributions of air pollutants and health effects.[51-53]

1.2.4 Quality of ambient air quality data

Quality assurance (QA) issues are frequently encountered in ambient air quality datasets. These issues tend to be especially important for UATs, more so than for criteria air pollutants, for several reasons. First, air toxic measurements may reflect low concentrations that fall below method detection limits (MDLs). For some species, concentrations may rarely, if ever, exceed the MDLs. Such 'sparse' data patterns can occur because a specific toxic pollutant simply may not be present or because the MDL is too high to allow frequent detection.[54] This situation rarely occurs for criteria pollutants, both because these pollutants are ubiquitous due to emissions from numerous sources, and because monitoring instruments have been highly refined and are very sensitive.

Second, high concentration values may be encountered on occasion, even for rarely detected pollutants. These detections (or "hits") may be real and significant, or they may be false positives due to contamination, chemical reactions forming artifacts on the sampling adsorbent, interferences, chromatographic shifts, laboratory errors, or some other reason. Third, it is difficult to characterize the measurement precision and accuracy for commonly-detected toxic pollutants, and exceedingly difficult for rarely detected pollutants. Compared to criteria pollutants where relative precisions and accuracies are well-characterized and in the 10% range (or lower), the few available estimates for air toxic suggest much greater variability.[55]

Historically, air monitoring data have been collected for compliance and regulatory purposes, but with the growing importance of environmental epidemiology, such data now serve multiple purposes. Given that quality assurances checks (instrument flow, zero and span checks) and calibrations require that instruments must be taken off-line, another issue concerning air quality data is missing data due to these planned events. Further, other pollutants are monitored intermittently, e.g., many particulate matter and toxics measurements are collected only every third or sixth day. Missing data can cause problems in environmental epidemiological studies that attempt to link air pollution and health effects as models in these studies generally require complete data sets.

A range of methods for handling missing data are available but their application to air pollution applications remains limited. Most applications have been in models aimed at pollutant forecasts and often for compliance purposes. For example, forecasting ground level O_3 is motivated by numerous studies reporting increased in mortality rates[56-58] during episodes of high ground level ozone concentrations as well as associations between acute respiratory symptoms in children and summer air pollution.[59] This type of forecasting information is aimed at warning the public to avoid exposure to unhealthy air and to encourage people to voluntarily reduce activities (e.g., driving cars to work) that emit precursor substances (e.g., Oxides of nitrogen; NO_x). While epidemiological studies require year-round and continuous measurements of air pollutants, forecasting focuses only on specific seasonal periods with high level of pollutants (e.g., summer smog). In the U.S., monitoring of O_3 is required during "high" ozone season (April to September); therefore, O_3 data is not available for the other half of the year.

The most common approach to handle missing data and values below MDLs is the use of *ad hoc* single-imputation (SI) method.[60] This method replaces the fully missing values with a single value, such as a sample mean of the fully observed data for that variable. SI is simple and allows the use of the standard analysis methods for complete data. However, SI methods do not account for imputation uncertainty, representing a significant disadvantage.[61] Thus, standard errors estimated from imputed data are systematically underestimated, and statistical inference is biased by erroneously small p-values and narrow confidence intervals.[61]

Another technique in handling missing data is multiple imputation (MI) technique, first proposed by Rubin (1987).[62] MI has been shown to yield valid statistical inferences, shares the advantages of SI, and corrects for the disadvantages of SI.[61] Here, each missing value is replaced with a vector of m $\geq$ 2 plausible values resulting in m datasets, each of which is analyzed using standard complete-data software to yield "complete-data" statistics.[63] Although MI methods were first developed for social science studies to minimize the bias in the study inference, its application in other research areas, specifically air pollution epidemiology, is growing.

Evaluations of the above techniques have been very limited. A summary of techniques to deal with missing data (as well as forecasting) in air pollution research is

shown in Table 2. For example, one study evaluated imputation methods, including SI and MI methods, for criteria air pollutions (NO_x, NO_2, O_3, PM_{10}, SO_2, and CO) in Helsinki and Belfast for the year 1998.[64] The study suggested that SI methods underestimated the error variance of missing data while MI methods considerably improved accuracy. Better performance was obtained using the MI procedure which accounts for the uncertainty associated with the missing data. In contrast, SI procedures do not account for this uncertainty.[61] Currently, few studies have addressed the problems of quality assurance and missing air toxics data, a prerequisite for obtaining unbiased results in health effect studies.

1.2.5   Receptor modeling

Receptor modeling (RM) utilizes monitoring information to identify and quantify the contributions of emission sources (or classes of emission sources) that are responsible for observed pollutant levels monitored at the "receptor." While receptor models have been widely used for particulate matter, relatively few applications have been reported for VOCs and carbonyls.[65-73] Fewer still have used receptor models in epidemiological investigations, in which the derived source contributions or composite scores from the receptor model are used as exposure measures in the same or similar statistical framework used to associate exposure measures with health outcomes.[49]

Epidemiologic studies using source-apportioned exposure measures from RM are potentially attractive for several reasons: they offer increased statistical power since the exposure measures may be more strongly associated with health impacts; the correlation in the larger data set is used to derive a smaller number of robust exposure measures; and they offer enhanced biological plausibility and relevance of the exposure measure. Most air pollutants originate or are derived from many emission sources and most sources emit multiple pollutants. Thus the toxicity of the exposure mixture can vary. Focusing on source types rather than simply selected pollutants may lead to better assessments of impacts as well as enhance the ability to implement effective interventions. These outcomes are advantageous to both regulatory and health service agencies.

1.3   Research hypotheses

This research evaluates several methods to improve exposure estimates of air pollution epidemiological studies. The methods are then applied to exposures in the Detroit metropolitan area to determine adverse effects on birth outcomes and acute respiratory illness in children. This research addresses the following topics. First, associations between criteria air pollutants and the frequency of several adverse birth outcomes are examined. Second, multivariate receptor models are used to derive source apportionments as exposure estimates to investigate associations with respiratory illness in children. Third, statistical approaches to handling missing air quality data as well as the reproducibility of air toxics are evaluated.

The research tests the following three hypotheses:

1. Exposure to ambient air pollutants, including CO, NO$_2$, PM$_{10}$ and SO$_2$, is associated with low birth weight (LBW), small-for-gestational-age (SGA) and preterm birth (PTB) in Detroit, Michigan. As mentioned, recent epidemiological studies that have attempted to link adverse birth outcomes and criteria air pollutants have yielded inconsistent results. This research helps to address this gap in the literature as well as to investigate several key topics, including the effects of long term trends, maternal race, smoking and SES on the associations of air pollutants and adverse birth outcomes.

2. Exposures to ambient air toxics, identified from different source classes, are associated with emergency department visits for respiratory-related illness among Medicaid children in Dearborn, Michigan. As noted, most ambient air pollutant health effect studies have focused on single pollutant models, although two or three pollutant models have been used to help account for mixtures of air pollutants. The work in this hypothesis is aimed at deriving exposure estimates that can potentially represent many related compounds and their sources.

3. Methods to evaluate, clean, impute and otherwise enhance the reproducibility of air toxics data are essential prior to its use in apportionment, exposure and health effect studies. This hypothesis is aimed at evaluating two imputation approaches, SI (optimal linear estimation; OLE) and MI using a comprehensive set of performance indicators. In addition, the reproducibility of air toxics data is examined.

1.4 Importance and novelty

This research addresses several important gaps in the current literature regarding the adverse health effects of ambient air pollutants, including reproductive health and acute respiratory related illness. This study is one of the few studies in the U.S. that examines the relationship between all three adverse indicators of reproductive health (LBW, PTB and SGA) and ambient air pollutants using both single and multiple pollutant models, and accounting for the effects of race, long-term trends, smoking and SES simultaneously. Previous studies rarely focus on SGA and very little on PTB in comparison to LBW. In addition, only one study (from Nova Scotia, Canada[29]) has evaluated effects of long-term trends in associating criteria pollutants with adverse birth outcomes. There is a need for this type of evaluation given that both levels of outdoor air concentrations and rates of adverse birth outcomes have been declining, due to stricter regulations, better health care, and possibly other reasons. Further, effects of race, smoking and SES on the associations between air pollutants and adverse birth outcomes have not been examined extensively in currently literature due to the homogeneity of the studied population and lacking of individual level information in the previous studies.

As noted earlier, much of the research on air toxics and adverse health outcomes has been based on occupational settings that might not reflect actual exposures of the general population, especially for children. Furthermore, there are few if any epidemiological studies that have focused on air toxics, much less apportionments derived using air toxics data, despite considerable promise and advantage of this approach. Linking exposures to air toxics in terms of source classes derived from receptor models can help to improve the effectiveness of both public health interventions and policy implementations. This study is novel in that not only does it examine associations between UATs exposures and acute respiratory-related illnesses in children, but it does so using apportionments, source classes, and receptor modeling.

Finally, issues associated with quality assurance and missing air pollutant exposure data have been only rarely addressed. Such issues can influence both the design and interpretation of air pollution exposure and epidemiological studies. Inadequate treatment of missing values may bias inferences in epidemiological studies. It is believed

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that research findings evaluating the reproducibility of air toxics data and the
performance of imputation methods will have numerous applications in the field.

Table 1-1. Summary of the literature on adverse birth outcomes

First author	Year	Study design (duration, site)	Outcomes	Pollutants	Exposure windows	Exposure categories	Covariates	Findings
Xu	1995	Prospective cohort (1988, Beijing)	PTB	SO_2, TSP	Entire pregnancy	Quartiles; 100 µg/m^3 ↑ TSP; ln µg/m^3 ↑ SO_2	Quntiles of weather covariates (temperature, humidity), day of the week, season, residential area, maternal age, and infant sex	Increased odds of PTB for SO_2 and TSP exposures (continous exposure measures)
Wang	1997	Ecological (1988-1991, Beijing)	Term LBW (37-44 wk)	TSP, SO_2	Trimesters	Quintile; 100 µg/m^3 ↑ TSP and SO_2	gestational age, season, residential area, maternal age, infant gender	Increased odds of LBW for highest quintiles and for each 100 µg/m^3 ↑ in TSP or SO_2 exposures; and for 4th quintile of SO_2 exposure
Bobak	1999	Ecological (1986-1988, Czech Republic)	LBW	NO_x, SO_2, TSP	Trimesters	IQR	Births outside marriage, abortions, divorces, mean income, mean savings, people per car	Increased odds of LBW for SO_2 exposure in both single and 3 pollutant models; No effects found for NO_x and TSP
Dejmek	1999	Ecological (1994-1996, Teplice Dist, N. Bohemia)	IUGR	PM_{10}, $PM_{2.5}$	Months	Tertiles	Maternal height, prepregnancy weight, completed high school, currently married, month-specific smoking habits, year, and season	Increased odds of IUGR for PM_{10} (2nd and 3rd tertiles) and $PM_{2.5}$ (highest tertiles) exposures
Ritz	1999	Ecological (1989-1993, S. California)	Term LBW (37-44 wk)	CO	Trimesters	<2.2, 2.2-5.5, >5.5 ppm CO	Gestational age, maternal age, race, education, parity, interval before previous birth, prenatal care, infant sex	Increased odds of LBW for CO (>5.5 vs. <2.2 ppm; last trimester) exposures among subjects living within 2-5 miles radius of air monitoring sites
Bobak	2000	Ecological (1990-1991, Czech Republic)	LBW, PTB, IUGR	NO_x, SO_2, TSP	Trimesters	50 µg/m^3↑ NO_2, SO_2 and TSP;	maternal age, education, marital status, race/ethnicity, parity and birth month	Increased odds of LBW for SO_2 (all trimesters) and TSP (1st & 2nd trimesters) exposures; and of PTB for SO_2 (all trimesters) & TSP (1st trimester) exposures; IUGR was not associated with any pollutants; No effects found for Nox; Significant effects for LBW were removed after adjustment for gestational age
Ritz	2000	Ecological (1989-1993, S. California)	PTB (26-44 wk)	CO, NO_2, O_3, PM_{10}	1st month, last 6th week	Quartiles	Maternal age, race, education, parity, interval since previous birth, prenatal care, infant sex, previous low weight or preterm births, and tobacco smoke during pregnancy	Increased odds of PTB for CO (1st month and last 6th week) and PM_{10} (last 6th week) exposures. Results were site dependent
Rogers	2000	Case-control (1986-1988, Georgia)	VLBW	TSP+SO_2	Annual	Percentiles (50, 50-75, 75-95, >95)	Race, Toxemia, smoking status, maternal weight gain, maternal age, prenatal care, income, mother's education, father's education, drug use, infant sex, alcohol use, stress.	Increased odds of VLBW for SO_2+TSP (>95 vs. 50) exposures

Table 1-1 (Cont.)

First author	Year	Study design (duration, site)	Outcomes	Pollutants	Exposure windows	Exposure categories	Covariates	Findings
Ha	2001	Ecological (1996-1997, S. Korea)	Term LBW (≥ 37 wk)	CO, NO_2, O_3, SO_2, TSP	Trimesters	IQR	Gestational age, maternal age, parental education level, parity, gender	Increased odds of LBW for CO (1st trimester), NO_2 (1st trimester), O_3 (3rd trimester) and SO_2 (1st trimester) exposures; No effects found for TSP
Maisonet	2001	Ecological (1994-1996, N.E. US)	Term LBW (37-44 wk)	CO, SO_2, PM_{10}	Trimesters	1 ppm↑ CO; 10 µg/m³ ↑ PM_{10}; 10 ppm ↑ SO_2; Percentiles (<25, 25-50, 50-75, 75-95, ≥ 95)	Gestational age, gender, birth order, maternal age, race, yrs of education, marital status, prenatal care, previous abortions, weight gain during pregnancy, maternal prenatal smoking, and alcohol consumption.	Increased odds of LBW for CO (1 ppm ↑, 3rd trimester), PM_{10} (≥ 95 vs. <25, 1st & 2nd trimesters) and SO_2 (25-50, 50-75, 75-95 vs. <25, 2nd trimester) exposures; LBW was inversersly associated with SO_2 exposure (≥ 95 vs. <25, 2nd trimester)
Chen	2002	Ecological (1991-1999, Nevada)	Term LBW (37-44 wk)	PM_{10}, CO, O_3	Trimester, entire pregnancy	Percentiles (<10, 10-90, >90)	infant sex, maternal residential, education, medical risk factors, tobacco use, drug use, alcohol use, prenatal care, mother's age, race, and weight gain of mothers	LBW was not associated with any pollutants
Lee	2003	Ecological (1995-1998, S. Korea)	Term LBW (37-44 wk)	CO, NO_2, SO_2, PM_{10}	Trimesters, entire pregnancy	IQR change	Infant sex, birth order, maternal age, parental education, time trend and gestational age	Increased odds of LBW for CO (1st trimester & entire pregnancy), NO2 (2nd trimester), SO2 (2nd trimester & entire pregnancy), and PM10 (entire pregnancy) exposures
Liu	2003	Ecological (1985-1998, Vancouver, Canada)	Term (37-42) LBW, IUGR, PTB	CO, NO_2, O_3, SO_2	months & trimesters	1 ppm ↑ CO; 10 ppb ↑ NO_2; 5 ppb ↑ SO_2	Maternal age, parity, infant sex, birth weight, and season of birth	Increased odds of LBW for SO_2 exposure during 1st month, of PTB for SO_2 and CO exposures during last month, and of IUGR for SO_2, CO and NO_2 exposures during 1st month
Gouveia	2004	Cross sectional (1997, Brazil)	Term LBW (≥ 37wk)	SO_2, PM_{10}, NO_2, O_3, CO	Trimesters	Quartiles; 1 ppm ↑ CO; 10 µg/m³ ↑ in PM_{10} and SO_2	infant sex, gestaional age, maternal age, education, antenatal care, parity, type of deliveries	Increased odds of LBW for PM_{10} (highest quartile) exposure during 2nd trimester; Inverse associations were found for 2nd quartile of SO_2 (1st trimester) and O_3 (3rd trimester) exposures
Lin	2004	Ecological (1995-1997, Taiwan)	Term LBW (37-44 wk)	CO, NO_2, O_3, SO_2, PM_{10}	Trimesters; entire pregnancy	Categorical: low, medium, high	Gestational age, gender, birth order, maternal age, educational level, birth season, concentrations of other air pollutants; (1.4 to 3.3 km radius around air monitoring sites)	Increased odds of LBW for SO_2 (high & med vs. low, entire preg.), for SO_2 (high vs. low, 3rd trimester); Inverse association between LBW and CO (high vs. low, entire preg.)
Salam	2005	Ecological (1975-1987, Southern California)	Term LBW (37-44 wk), IUGR	O_3, NO_2, CO, PM_{10}	Months, trimesters, entire pregancy	CO: 1.4 ppm ↑; O_3: 16-33 ppm ↑; PM_{10}: 20 µg/m³ ↑	Maternal age, months since last live birth, parity, maternal smoking status, SES, marital status, gestational diabetes, infant sex, race/ethnicity, and schoold grades, seasonal terms (6) with b-spline.	Increased odds of LBW for O_3 exposures during 3rd trimester; No associations found for IUGR with any pollutants.

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Table 1-1. (Cont.)

First author	Year	Study design (duration, site)	Outcomes	Pollutants	Exposure windows	Exposure categories	Covariates	Findings
Mannes	2005	Ecological (1998-2000, Sydney, Australia)	SGA	CO, NO_2, O_3, $PM_{2.5}$, PM_{10}	Last month, trimesters	Continuous (1 unit increase)	Maternal age, smoking, indigenous status, SES, gestational age, parity and season of birth	Increased odds for SGA ((>2 SD below the mean birth weight) for NO_2 and $PM_{2.5}$ exposures during 2nd trimester
Parker	2005	Ecological (California)	SGA (40 wk)	CO, $PM_{2.5}$	Trimesters	Quartile	Maternal race, education, marital status, age, parity, and season of delivery	Increased odds of SGA for $PM_{2.5}$ exposures during all trimesters; CO was inversely associated with SGA.
Sagiv	2005	Time series analysis (1997-2001, Pennsylvania)	PTB (20-44 wk)	SO_2, PM_{10}	Last 6th weeks	Quartile	Long-term trends in PTB and weather	Increased odds of PTB (<36 wk) for PM_{10} and SO_2 exposures
Wilhelm	2005	Ecological (1994-2000)	Term LBW (≥37 wk)	CO, NO_2, O_3, PM_{10}	Trimesters	Quartile; 1 ppm ↑ CO; 10 µg/m³ ↑ PM_{10}; 0< Distance (d) ≤ 4 mi	Maternal age, infant sex, maternal race/ethnicity, prenatal care information, maternal education, birth season, previous LBW, interval since previous live birth	Increased odds of LBW for CO (d≤1 mi, ≥75th vs. <25th), CO (2<d≤4 mi, 1 ppm ↑), CO (0<d≤2 mi, 1 ppm↑), CO (0<d≤2 mi, 50th-75th vs <25th), CO (0<d≤2 mi, ≥75th vs <25th) and PM_{10} (d≤1 mi) exposures; In 3-pollutant models (PM_{10}, CO, O_3), only PM_{10} (d≤1 mi) was associated with LBW
Dugandzic	2006	Ecological (1988-2000, NovaScotia, Canada)	Term LBW (≥37 wk)	O_3, SO_2, PM_{10}	Trimesters	Quartile; IQR	Maternal age, parity, prior fetal death, neonatal death, prior LBW, smoking status, income, infant sex, gestational age, weight change, birth year	Increased odds of LBW for highest quartile of SO_2 and PM_{10} exposures during 1st trimester; Significant effects were removed after adjustment for birth year.
Hansen	2006	Ecological (2000-03, Brisbane, Australia)	Term SGA	bsp, NO_2, O_3, PM_{10}	Trimester	IQR	Gestational age (with quadratic term), neonate gender, mother's age, parity, indigenous status, member of antenatal visits, marital status, previous abortions/miscarriages, type of delivery, index of SEX, season of birth	No strong evidence suggesting associations between SGA and any of these pollutants.
Hansen	2006	Ecological (2000-03, Brisbane, Australia)	PTB (>22 wk)	bsp, NO_2, O_3, PM_{11}	Trimester	IQR	(with quadratic term), neonate gender, mother's age, parity, indigenous status, member of antenatal visits, marital status, previous abortions/miscarriages, type of delivery, index of SEX, season of birth	Increased odds of PTB for PM_{10} and O_3 exposures during 1st trimester

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Table 1-1. (Cont.)

First author	Year	Study design (duration, site)	Outcomes	Pollutants	Exposure windows	Exposure categories	Covariates	Findings
Huynh	2006	Matched case-control (1999-2000, S. California)	PTB (24-44 wk)	CO, $PM_{2.5}$	First month, last 2 weeks, entire gestation	Quartiles; 1 ppm ↑ CO ; 10 μg/m^3 ↑ $PM_{2.5}$	maternal age, race/ethnicity, education, marital status and parity	Odds of PTB increased for $PM_{2.5}$ exposures (all exposure windows and measures) but not for CO exposures.
Leem	2006	Ecological (2001-02, Incheon, Korea)	PTB	CO, NO_2, SO_2, PM_{10}	First & third trimesters	Quartiles	maternal age, parity, sex, season of birth, education level of both parents	Increased in odds of PTB for CO, NO_2, SO_2, and PM_{10} exposures during 1st trimester, and of PTB for CO and NO_2 exposures during 3rd trimester
Bell	2007	Ecological (1999-2002)	LBW (32-44 wk)	CO, NO_2, SO_2, PM_{10}, $PM_{2.5}$	Trimesters	IQR, county averages	Gestational length, prenatal care, type of delivery, child's sex, birth order, weather, year, and mother's race, education, marital status, age and tobacco use	Increased odds of LBW for CO (1st & 3rd trimesters), NO_2 (1st trimester), SO_2 (1st trimester), PM_{10} (3rd trimester) and $PM_{2.5}$ (2nd & 3rd trimesters) exposures; Effect estimates for PM2.5 were higher for infants of balck mothers than those of white mothers
Liu	2007	Ecological (1985-2000, Calgary, Edmonton and Montreal)	IUGR	CO, NO_2, SO_2, O_3, $PM_{2.5}$	Months, trimesters	1 ppb ↑ CO; 20 ppb ↑ NO_2; 3 ppb ↑ SO_2; 15 ppb ↑ O_3; 10 μg/m^3 $PM_{2.5}$	Maternal age, parity, infant sex, season of birth, residence of city	Increased odds of IUGR for CO, NO_2 and $PM_{2.5}$ exposures during all trimester in single pollutant models; In 3-pollutant models (CO, NO_2 and $PM_{2.5}$), only CO exposures were associated with IUGR
Ritz	2007	Case-control (2003, S. California)	PTB	CO, NO_2, O_3, $PM_{2.5}$	1st trimester, last 6th weeks, entire pregnancy	Categorical: 5 even spaced intervals	Birth season, parity, mother's age, race, education, and covariates from environment and pregnancy outcomes survey (active and passive smoking, marital status and alcohol use during pregnancy)	Increased odds of PTB for CO (1st trimester & last 6th month) and $PM_{2.5}$ (1st trimester) exposures

Abbreviations and symbols: bsp, visibility reducing particles; ↑, increase; ↓, decrease; IQR, inter-quartile range; LBW, low birth weight; IUGR, intra uterine growth restriction; SGA, small-for-gestational-age; PTB, preterm birth; ppm, part per million; ppb, part per billion; wk, week.

Table 1-2. Summary of methods for estimating and forecasting ozone

Input data	Time scales	Data basis	Modelling approach	Reference
Daily 8hr max ozone concentration, temperature, relative humidity, pressure, wind speed, wind direction	Hourly, daily	Summer season (1999)	Hierarchical Bayesian modeling	McMillan et al., 2005
8hr ozone, NO, NO2, temperature, relative humidity, wind velocity, wind direction, solar radiation, day of the week, day length	Hourly	4 years	Generalize additive model (GAM)	Schlink et al., 2005
Ozone concentration, wind speed, wind direction, temperature, relative humidity	Hourly	One year (1998)	Multiple imputation, linear, spline and univariate nearest neighbour interpolations, regression-based imputation, multivariate nearest neighbor, self-organizing maps, multilayer back-propagation nets	Junninen et al., 2004
8hr Ozone concentration, nonlinear term, atmospheric transmittance, trend term (year), relative humidity, daily min. temperature departure, wind speed, cloud cover	Daily max 8-hr avg.	Several years (1998-2001)	Non-linear regression model	Cobourn and Lin, 2004
Ozone concentration	Hourly	July-March 1999	ARIMA modeling	Kumar et al., 2004
Ozone concentration, CO, NO2, SO2, surface and upper wind direction, surface and upper wind speed, surface and upper temperature, relative humidity, solar radiation,	Hourly	1989-1999	Fuzzy expert and neural network systems	Heo and Kim, 2004
Ozone concentration	Hourly	Summer season	Non-linear dynamical systems	Chen et al., 1998, 2000
Ozone concentration	Hourly	Summer season	Grey-box and component models	Schlink and Volta, 2000
Ozone concentration	Hourly	Several years	Attractor embedding	Kocak et al., 2000
Ozone concentration, wind, temperature, pressure, humidity, global solar radiation	Hourly	Summer season	Linear regression, regression tree, multilayer perceptron neural networks	Gardner and Dorling, 2000a
Ozone concentration, wind, temperature, pressure, humidity, global solar radiation	Daily max., daily avg.	Several years	Cluster analysis, generalized additive models (GAM)	Davies et al., 1998, 1999
Ozone concentration, temperature, total daily sunshine, mean daily wind speed, vapour pressure, total cloud cover	Daily max., daily avg.	Several years	Multilayer perceptron neural network	Gardner and Dorling, 1999
Ozone concentration	Hourly	Several years	Neural networks	Arena et al., 1998
Ozone concentration, wind, temperature, pressure, humidity, global solar radiation	Hourly	Summer season	Grey-box stochastic model, neural network model	Finzi et al., 1998

Table 1-2 (Cont.)

Input data	Time scales	Data basis	Modelling approach	Reference
Ozone concentration, wind, temperature, pressure, humidity, global solar radiation	Hourly	Summer season	Grey-box stochastic model, neural network model	Nunnari et al., 1998
Ozone concentration, length of the day, day of the week, UV-index, previous day Ozone, meteorological data	Daily max., daily avg.	Summer season	Multiple-linear regression model	Hubbard and Cobourn, 1998
Pollutants and meteorological data	Daily max., daily avg.	Several years	Linear time series, artificial neural network, fuzzy models	Jorquera et al., 1998
Ozone concentration, wind, temperature, pressure, humidity, global solar radiation	Hourly	Summer season	Cluster analysis, regression models	Bel et al., 1997
Ozone concentration, wind, temperature, pressure, humidity, global solar radiation	Daily max. of hourly avg.	Summer season	Neural networks, multiple regression	Comrie, 1997
Ozone concentration, wind, temperature, pressure, humidity, global solar radiation	Daily max., daily avg.	Several years	Long range dependence, fractional autoregressive, fractional co-integration	Anh et al., 1996
Ozone concentration, wind, temperature, pressure, humidity, global solar radiation	Daily max., daily avg.	Several years	Cluster analysis, generalized additive models (GAM)	Anh et al., 1996
Pollutants and meteorological data	Hourly	Case study for May 25th 1990	Photochemical dispersion model	Moussiopoulos et al., 1995
Ozone concentration, conc. of NO and NO2	Hourly	Two years	Vector autoregressive	Hsu, 1992
O_3 and TSP	Hourly & 24hr	1-4 months, high ozone season	Optimal estimators	Batterman, 1992
Ozone, max. daily temp.			Maximum likelihood,	Davison, 1987

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Chapter 2

Air Pollutant Exposure and Low Birth Weight, Preterm and Small-for-Gestational-Age Births in Detroit, Michigan: Long-term Trends and Associations

2.1 Abstract

A growing number of studies have reported associations between ambient air pollutants and adverse birth outcomes such as low birth weight (LBW), preterm birth (PTB) and, to a lesser extent, small for gestational age (SGA). These studies have limitations, including incomplete control of temporal trends in exposure and maternal smoking and their results are often inconsistent.

The relationship between ambient air pollutants and LBW, SGA and PTB outcomes among 155,000 singleton births in Detroit, Michigan between 1990 and 2001 was investigated. SO_2, CO, NO_2 and PM_{10} exposures were estimated using measurements from three air monitoring sites in Detroit and used in single and multiple pollutant logistic regression models to estimate odds ratios (OR) for these outcomes, adjusting for the infant's sex and gestational age; the mother's race, age group, education level, smoking status and prenatal care; the birth season; site of residence; and long-term exposure trends.

SGA was associated with NO_2 (OR=1.10, 95% confidence interval=1.01-1.19) and CO (1.14, 1.02-1.27) exposures in the first month and with PM_{10} exposures in the third trimester (1.22, 1.04-1.44). Maternal exposure to SO_2 was associated with PTB (1.07, 1.01-1.14) in the last month and LBW (1.16, 1.04-1.30) in the first month.

This appears to be the first U.S. study to associate SGA with air pollutant exposures, and effects were observed at concentrations below current air quality standards. The study design addresses many of the limitations in the earlier studies, and it highlights the importance of accounting for long-term trends and individual risk factors.

2.2 Introduction

Low birth weight (LBW), small for gestational age (SGA) and preterm birth (PTB) are important indicators of fetal health during pregnancy, as well as predictors of infant mortality and morbidity.[1-3] Animal studies have shown that exposure to air pollutant can adversely affect fetal development, and epidemiological studies have associated air pollutant exposure with adverse birth outcomes, especially LBW. [4-12] However, few studies have investigated the relationship between air pollution exposure and preterm birth (live birth at <37 weeks gestation), and none have examined growth restriction as indicated by SGA status (birth weights <10th percentile for the same gestational age).

The literature relating air pollution to birth outcomes has a number of inconsistencies, which may reflect differences across populations, exposure misclassification, statistical power issues, confounding, and biases related to study duration, design, and model structure. Pollutant compositions and concentrations differ geographically, which can cause study results to differ. Further, given the decreases in sulfur dioxide (SO_2) and carbon monoxide (CO) concentrations over the past few decades, findings from earlier studies with higher pollution levels may no longer represent current health impacts. Rates of PTB and term SGA also have declined in the U.S., possibly due to trends in ambient pollutant levels or individual risk factors,[10,12-15] and these trends must be carefully controlled. Additional research is needed on the health effects of pollutants at recent exposure levels and to identify critical exposure windows during pregnancy. [16-18]

This study evaluates effects of four ambient air pollutants on adverse birth outcomes in three industrialized and urban areas in metropolitan Detroit, Michigan. We use a long study period (1990 to 2001), multiple exposure periods during pregnancy, and

both SGA and PTB as indicators of adverse birth outcomes. (A parallel analysis for LBW in the same population is reported in the supplemental materials.)

2.3   Method

2.3.1   Study group, health outcomes, and covariates

The study group consisted of all live, singleton births for mothers living in three areas (Allen Park, East 7 Mile and Linwood) of Detroit occurring between January 1, 1990 and December 31, 2001. Birth certificate data, obtained from the Michigan Department of Community Health, were used to determine gestational age, infant sex, date of birth, maternal age, race, smoking status, education level, and level of prenatal care, all used as individual-level covariates. Eligible residences were in ZIP codes that were wholly or partially contained within a 4 km radius surrounding an air quality monitoring station, based on previous investigations that have shown stronger risk estimates for subjects living within this distance.[12,19] The study was restricted to birth weights 750-4000 g, gestational ages 22-42 weeks, and mothers 16-45 years of age. Teenage mothers less than 16 years of age are more likely to deliver preterm and to have cesarean deliveries than mothers 16-19 years of age and adult mothers aged 20 years and older.[20] For women 45 years and older, the rate of spontaneous conception is low and the risk of hypertension is high; and hypertension can complicate pregnancies by restricting fetal growth and may trigger premature delivery.[21] Births >4000 g that may have resulted from poorly controlled maternal diabetes,[22] and births <750 g that are rarely viable[23] and unlikely to be affected by air pollutant exposure were excluded. Gestational age was based on the date of the last menstrual period (LMP) if available, or the clinically estimated weeks of gestation. These criteria excluded 21,055 births out of 185,960.

For the study outcomes, a term SGA birth was defined as an infant whose birth weight fell below the 10th percentile by sex and gestational week, based on the distribution of the study population and restricted to gestational ages between 37 and 42 weeks, and a PTB was defined as a birth with <37 weeks gestation. Assessing only term SGA can avoid the colinearity of multiple outcomes between SGA and PTB.

2.3.2 Exposure assessment

We selected three monitoring sites located in densely populated areas that measured multiple air pollutants over extended periods. These sites are approximately 20 km apart (Figure 2.1). Monitoring was consistent with federal reference methods and Michigan Department of Environmental Quality protocols.[24] CO measurements were available at the Allen Park and Linwood sites for the entire study period; however, due to vandalism in July 1997 and quality assurance (QA) issues, CO data at Linwood were restricted to 1990-1996. SO_2 measurements were available at each site but only through 1997 at Allen Park. Nitrogen dioxide (NO_2) was available for the entire study period at the East Seven Mile site and at Linwood; however, several periods were omitted due to QA issues (September 1996 at Linwood, March, April, and September through November 1997 at East Seven Mile). Hourly measurements falling below method detection limits (MDL) were replaced by one-half the MDL. Daily (24-hr) averages were computed from hourly data, and monthly and trimester (3 month) averages were computed from daily averages. Running monthly and trimester averages were computed from the every-6th-day PM_{10} measurements at Allen Park. Because ozone (O_3) was monitored only during the high O_3 season (April to September), and $PM_{2.5}$ measurements (collected every-3rd-day) were only available from May 1999 forward, these pollutants were not used as exposure variables. Daily, monthly, and trimester averages each required the availability of ≥75% of all possible measurements, e.g., daily averages required at least 18 (of 24 possible) hourly values. The gestational period and LMP were used to estimate exposures for each pregnancy in five time windows: the first and last months of gestation, and each trimester (using divisions of 1-13 weeks, 14-26 weeks, and 27 weeks to birth).[25]

2.3.3 Statistical methods

Adjusted odds ratios (AORs) and 95% confidence intervals (CIs) were estimated for each outcome and exposure window using logistic regression models. In the case of PTB, only the first and last months' exposures were examined.[8,9] Although exposure to air pollutants for the entire pregnancy have been associated with PTB but stronger associations were found for the earlier (e.g. first month or first trimester) and the later

period of pregnancy (e.g. last two weeks or six weeks).[26-28] SGA and PTB outcomes were dichotomous variables and pollutant concentrations were expressed in quartiles. The AORs represent associations for the second, third and fourth quartiles of exposure relative to the first quartile.

Covariates included infant sex (for PTB), maternal race (Black, White, other), maternal education level (<12, 12, >12 years), maternal smoking status during pregnancy (yes/no), use of prenatal care (yes/no), late prenatal care (starting after the fourth month of pregnancy; yes/no) and residence location (Allen Park, Linwood, East Seven Mile). To adjust for seasonality, models included variables for birth season, defined as spring (March-May), summer (June-Aug.), fall (Sept.-Nov.), and winter (Dec.-Feb.). To examine long-term trends in pollutant levels, a locally-weighted regression smoother was applied to air pollutant concentrations. To control for potential biases associated with temporal changes in the study population and environment, models were adjusted for birth year using consecutive 4-year periods (1990-1993, 1994-1997 and 1998-2001). Single pollutant models were constructed by pooling data across all sites, with analytic control for site in the models, and multiple pollutant models were restricted to Linwood where CO, SO_2 and NO_2 were measured. PM_{10} measured at Allen Park was assigned to Linwood mothers since PM_{10} concentration gradients in the region are modest.[29,30] Additional analyses stratified by race and maternal smoking status were conducted to help discern effects arising from both exposures and covariates. ("Other" races were excluded due to small sample sizes.)

2.4   Results

2.4.1   Study population

The study population included 164,905 eligible births between 1990 and 2001. Due to missing exposure data, the final sample size was 155,094 (94% of all eligible births). Infant and maternal characteristics by birth outcome and race are shown in Table 1. Both SGA and PTB outcomes were slightly more common among male births. Race was associated with many risk factors and outcomes. Whites had fewer births to teenage mothers (16-19 yrs), fewer mothers who had not completed high school, and more mothers who had obtained prenatal care. Infants born to Black mothers had an

approximately 2-fold increased risk of SGA and PTB compared to White mothers. Maternal smoking was associated with large effects on all the birth outcomes, and White mothers were more likely to be smokers than Black mothers. Additional results, as well as the parallel analyses for LBW, are shown in Supplemental Tables S2-1 to S2-17.

Several long-term trends were observed. First, the overall birth rate and rates of adverse birth outcomes declined, with the greatest change occurring between the 1990-3 and 1994-7 periods (Table 2.1). Second, most but not all risk factors also showed a downward trend, with some differences by race (Table S2-1). For example, the rate of teenage mothers declined from 19% in 1990 to 15% in 2001, largely due to decreases among Black mothers (from 25 to 18%) rather than among White mothers, which were relatively stable (11.2 to 11.4%). Many of these patterns, e.g., teenage pregnancies and smoking during pregnancy, followed national trends.[31,32]

2.4.2 Air pollutant exposures

Exposures for 3-hr CO, 24-hr, first month and first trimester averaging periods are shown in Table 2.2. (Other periods had similar statistics.) Concentrations were below the U.S. National Ambient Air Quality Standards (NAAQS), although maximum 3-hr CO levels (8.8 ppm) approached the 8-hr NAAQS (9 ppm). For SO_2, 24-hr levels reached 50 ppb, far below the 24-hr standard (140 ppb). 24-hr and annual NO_2 levels reached 77 and 26 ppb, respectively, compared to the annual standard of 53 ppb. 24-hr PM_{10} levels reached 131 $\mu g\ m^{-3}$, slightly below the (former) 24-hr standard (150 $\mu g\ m^{-3}$).

Over the study period, average concentrations as well as the amplitude of concentration fluctuations declined for CO and SO_2 (Figures 2.2a, b), trends not seen for NO_2 and PM_{10} (Figures 2.2c, d). Considering the monthly pollutant averages used in the birth outcomes models, we found SO_2 had low-to-moderate correlation with CO (r=0.35) and NO_2 (r=0.27); CO and NO_2 had low correlation (r≤0.27); and PM_{10} had negligible correlation with both CO and SO_2 (r≤0.11). The correlation coefficients varied little across different pregnancy windows (Table S2-2). These correlations are lower than those reported in other studies, and although they capture only pair-wise relations, they suggest that colinearity would not be a problem in multi-pollutant models.

2.4.3   Single pollutant models

Associations between air pollutants and birth outcomes in single pollutant models are shown in Table 2.3. Multiple adverse birth outcomes, exposure windows and pollutants were examined. The presentation focused on results that were consistent, e.g., associations in which all three quartiles of exposures (2nd, 3rd and 4th) were in the same direction, either negative or positive, compared to the first quartile of exposure. Association at the 4th quartile (highest) of exposure that were statistically significant were also considered.

CO was positively associated with SGA for all exposure windows, and odds of a SGA birth increased by 5-20% for women with higher CO levels (>0.56 ppm; 2nd through 4th quartiles). (Table S2-3 shows associations with covariates; Table S2-4 shows air pollutant concentrations by window and quartile of exposures.) After adjusting for long-term trends, the statistical significance of CO-SGA associations persisted only for exposures in the first month at α=0.05. Women in the top quartile of first-month CO exposures (>0.75 ppm) showed the greatest odds of a SGA birth (AOR=1.14; 95% CI: 1.02-1.27). In analyses stratified by race, the CO-SGA associations in the first month were stronger for infants of Black mothers compared to that of White mothers (Table S2-5). In analyses stratified by smoking, the positive CO-SGA associations in the first month were consistent with the pooled results, although AORs obtained for smokers were attenuated (Table S2-5).

For SO_2, only first trimester exposures showed consistent patterns in increasing odds of SGA births both with and without trend-adjustments, however, AORs obtained from trend-adjusted models were attenuated (Table S2-6). The largest AOR of 1.09 (1.00-1.18) was seen for top quartile of first trimester exposure (SO_2>6.63 ppb). NO_2 was positively associated with SGA for first-month and first trimester exposures and results did not change after trend adjustment. Odds of SGA births increased by 2-10% for women with higher NO_2 levels (>18.7 ppb; 2nd through 4th quartiles). Women with highest quartile first-month NO_2 exposures (>23.6 ppb) had the highest AOR of 1.10 (1.01-1.19). Similar NO_2-SGA associations were found among infants of Black mothers and mothers who smoked (Table S2-7).

Maternal exposure to PM_{10} during all three trimesters was positively associated with SGA, and the results were unaffected by the trend adjustment. Odds of SGA birth increased by 1-22% for women with higher PM_{10} levels (>22.8 µg m^{-3}; 2nd through 4th quartiles). Women with highest quartile third trimester PM_{10} exposures (>35.8 µg m^{-3}) had the strongest increase in odds for SGA birth (AOR=1.22; 1.04-1.44). Similar PM_{10}-SGA associations were found among infants of White mothers and non-smoking mothers (Table 2S-8).

For PTB, SO_2 exposure only during the last month was positively associated with PTB, both with and without adjustment of long-term trends. Odds of PTB birth increased by 7-11% for women with SO_2 levels >4.5 ppb (2nd through 4th quartiles). These positive SO_2-PTB associations were consistent with those for infants of Black and non-smoking mothers (Table S2-6). No associations were seen for PTB with CO, NO_2 and PM_{10}.

2.4.4 Multiple pollutant models

Table 2.4 summarizes the results for the four-pollutant models (CO, SO_2, NO_2 and PM_{10}) for SGA and PTB outcomes. (Detailed results are in Tables S2-9 to S2-12.) All models were adjusted for long-term trends and are restricted to Linwood mothers. The multi-pollutant models showed consistent patterns of increased odds of SGA births for CO (first and second trimester), SO_2 (all trimesters), NO_2 (first month and all trimesters), and PM_{10} (first month and first trimester), and increased odds of PTB births for first-month SO_2 and NO_2 exposures. Overall, these results did not differ from those obtained using single-pollutant models. Furthermore, the patterns of associations among infants of Linwood mothers did not differ appreciably from associations among mothers from Allen Park and East Seven Mile, suggesting that the multi-pollutant model results may be representative of the entire study population. However, the multi-pollutant models yielded wider confidence intervals due to the decreased sample size (n=67,577) compared to the single pollutant models that used all three sites (n=155,094) and colinearity among pollutants.

2.5 Discussion

This study highlights the importance of individual risk factors as well as temporal changes in air pollutant concentrations on associations with adverse birth outcomes.

After controlling for trends and covariates, we observed consistent patterns of increase in the odds of SGA with CO, NO_2 and PM_{10} exposures, and of PTB and LBW with SO_2 exposures.

2.5.1 Possible mechanisms

The biological pathways linking pollutant exposure to SGA and PTB are not well understood.[8,33,34] SGA may be triggered by an abnormal reaction between trophoblast and uterine tissues in the first few weeks of pregnancy[33], which is consistent with the timing of the CO-SGA and NO_2-SGA associations found in this study. CO reduces the oxygen-carrying capacity of maternal hemoglobin, which decreases oxygen delivery to the fetus. Further, CO can cross the placental barrier and interfere with oxygen binding to fetal hemoglobin, which has a higher affinity for CO than adult hemoglobin.[35,36] Both effects may induce tissue hypoxia and reduce fetal growth. Alternatively, CO may be a proxy for particles emitted by vehicles and other sources that contain polycyclic aromatic hydrocarbons (PAHs) that can induce DNA adducts, which have been associated with increased risks of LBW.[37-39] Exposure to NO_2 increases lipid peroxidation in both maternal and cord blood, which could interfere with normal intrauterine growth development via oxidative stress.[40] PM_{10} is a complex toxicant. It includes mixtures of different substances, including fine particles, metals and organic matter (e.g., PAHs), and compositions are source-specific.[33] Several mechanisms have been proposed for PM_{10}, one of which is the DNA adducts pathway discussed above. Alveolar inflammation or systemic infection associated with air pollutants may play a role in PTB.[17,41] Other possible mechanisms include oxidative stress, reactive nitrogen or sulfur species, bacterial infections, and unfavorable metabolic processes that result in growth-arrested cells during early embryogenesis.[42] The first two months of pregnancy have been identified as the critical period for PTBs associated with exposures to coal combustion toxics.[42] However, we found that only the last month's SO_2 exposure was associated with PTB births.

2.5.2 Comparison with previous studies

The current literature on air pollution and SGA is limited. SGA has been linked to $PM_{2.5}$ in California[25] and to PM_{10}, $PM_{2.5}$ and NO_2 in Sydney, Australia.[43] These

studies did not find associations between CO exposures and SGA. Higher risk of intrauterine growth restriction (IUGR; for which SGA is a measure) has been shown for CO, NO_2 and $PM_{2.5}$ exposures in Vancouver,[8] in a second Canadian study in Calgary, Edmonton, and Montreal,[44] and for PM_{10} exposure in the Czech Republic.[33] No associations were seen between IUGR and CO, NO_2 or PM_{10} exposures in a southern California study.[45] These divergent results could arise for several reasons. First, the studies differed with respect to exposures, averaging periods, and cut-off concentrations. For example, the Vancouver study examined 1 ppm and 10 ppb increases in CO and NO_2 exposures, respectively, while the southern California study used inter-quartile ranges of 1.2 ppm and 25 ppb of monthly average CO and NO_2, respectively.[8,45] A second difference is the control of covariates and potential confounders. The southern California study[45] controlled for both SES and maternal smoking, a well-known risk factor; the Canadian studies[8,44] controlled for neither. A third difference is the control of long-term trends in pollutant exposures. We demonstrated that this is critical for CO and SO_2. Fourth, the studies differed in their ability to construct multi-pollutant models, essential in understanding effects of simultaneous exposure to several pollutants. Only the recent Canadian study used multi-pollutant models (NO_2, CO and $PM_{2.5}$).[44] Finally, the studies differed significantly with respect to sample size, model structure, and geographic location.

For PTB, SO_2 increased risks in five studies,[8,34,46-48] as did PM_{10} in four studies,[11,26,46,48] and total suspended particulates in two studies.[34,47] PTB associations with CO and NO_2 exposures are inconsistent. Studies in southern California,[11,12,26] Vancouver,[8] and South Korea[48] found positive associations between CO exposure and PTB, but another southern California study[27] found an inverse association. Positive NO_2-PTB associations were found in studies in Korea[48] and southern California,[28] but not in Vancouver[8] or Australia.[26]

In this study, increased odds of SGA birth found for CO and NO_2 are consistent with the Canadian studies.[8,44] SO_2 was associated with increased risk of PTB which is also consistent with most of the previous studies. Unlike many of the earlier studies, this study controlled for many individual risk factors, including maternal smoking and SES,

both important confounders for adverse birth outcomes.[49,50] This study also controlled for temporal trends, which had a large effect, as discussed below.

2.5.3 Effects of temporal trend

With a few exceptions, the previous adverse birth effect studies have been short in duration, and effects of long-term temporal trends were not examined extensively. A 13-yr Canadian study (in Nova Scotia) found that birth year confounded the association between SO_2 and PM_{10} and LBW.[14] In this study, after accounting for long-term trends, specifically the declines in CO and SO_2 concentrations, the CO-SGA and SO_2-SGA associations were attenuated, probably due to declining rates of both adverse birth outcomes and associated risk factors, e.g. smoking. This study also examined CO-LBW associations using trend-adjusted (Tables S2-13 to S2-15) and de-trended CO data (data not shown). In both cases, the CO-LBW associations were also attenuated. Based on these results, time trend adjustments seem justified when analyzing long time periods. Associations for NO_2 and PM_{10}, which did not show such patterns, were insensitive to this adjustment.

2.5.4 Race and social economic status

In southern California, traffic-related pollution exposure (indicated by distance-weighted traffic density) in winter was associated with PTB among the low SES population,[51] suggesting that SES might modify exposure or interact with air pollutants. The effect estimates did not differ by maternal education levels (Table S2-16), however, odds of SGA birth increased for CO exposures among mothers with ≤12 years of education; and decreased for CO exposures among mothers with >12 years of education. On the other hand, the odds of PTB birth for SO_2 exposures increased among mothers with different education levels. These results suggest maternal education may be an inadequate proxy for SES if there is true heterogeneity in the effects caused by maternal SES.

In analyses stratified by race, CO-SGA, NO_2-SGA and SO_2-PTB associations were statistically significant for infants of Black mothers, but not White mothers. This may reflect effects of neighborhood: Linwood (measured CO_2, NO_2 and SO_2) and East Seven Mile (NO_2 and SO_2) sites are predominantly Black areas; Allen Park (CO and SO_2)

is a predominantly White area. Over the past several decades, Detroit has experienced increased race-based residential segregation,[52] which has been associated with higher rates of LBW, prematurity and fetal growth restriction. Such outcomes might result from exposures as well as many other neighborhood-level factors, e.g., lack of access to health care and intra-group diffusion of harmful health behaviors.[53]

2.5.5 Smoking

Studies have long associated cigarette smoking and environmental tobacco smoke exposure with adverse birth outcomes.[54-56] Smoking was a very strong risk factor for all outcomes. The odds of SGA were both consistent and statistically significant for all quartiles of first month NO_2 exposures among smokers, and for third trimester PM_{10} exposures among non-smokers. A possible speculation is that smoking mothers were already getting large pollutant doses, diminishing the significance of the ambient contribution; additionally that smoking may have increased the variability of the response. In models accounting for trend but not controlling for smoking (Table S2-17), odds of SGA increased for SO_2 exposures in the second trimester, which was not seen in models that controlled for smoking. This is consistent with smoking confounding SO_2-SGA associations. In a recent analysis examining traffic-related pollutants (CO and $PM_{2.5}$) and PTB in southern California, maternal smoking apparently did not confound the odds ratios, however, this conclusion was restricted to a subsample of the study with a low response rate (40%) from the survey, and it applied to only the second exposure quartile.[28] We believe that maternal smoking should be considered as a possible effect modifier of the associations between air pollutants and adverse birth outcomes.

2.5.6 Strengths and limitations of this study

Specific strengths of this study included a large sample size (n=155,094), a long duration (7-12 years), and individual-level information on residence location, race, smoking status, pregnancy and SES indicators. This study accounted for time trends in pollutant concentrations, which apparently affected SO_2 and CO results, and we examined exposures to several pollutants simultaneously. A large Black population in our study sample allowed us to examine possible heterogeneity by race. Finally, we

examined births of mothers residing quite close (≤4 km) to air monitors, potentially minimizing exposure measurement error.[12]

There are a number of study weaknesses. Geocoding of individual residences was unavailable, thus residences (and subjects) were selected if their ZIP code area was either within or partially within 4 km of an air quality monitor. In the worst case, a residence could have been as far as 12 km from the monitor, which could have led to exposure misclassification and attenuation of our estimates, however, most homes were much closer since most of the studied areas were densely populated. Further, air pollution exposures at the ZIP code level can yield reasonable exposure estimates.[57] Pollutant levels in Detroit generally fell below those in other studies, and low exposures may be subject to greater exposure measurement error. Exposure misclassification is possible for subjects living near major traffic routes (more likely near Linwood and East Seven Mile sites), which could increase exposures above levels measured at the monitoring sites, which were located in residential areas at least several blocks from major roads. Limiting the study area to a relatively small radius around the monitor should minimize such errors.

Because this study examined multiple health outcome and multiple exposure windows, Type I error rates might have inflated; however, minimal effect was anticipated. The main health outcomes were term LBW, term SGA and PTB. (Since SGA and LBW are overlapping by definition, LBW is included for only discussion purposes.) By definition, term SGA and PTB are not correlated; therefore, the effects of multiple health outcomes comparison should be irrelevant. On the other hand, the multiple exposure windows examined in this study might have inflated the Type I error rate. There are two options to address this issue: (1) select a single exposure window; and (2) apply the Bonferroni correction. The first option is not desirable because the actual mechanism and exposure window with the highest risk were still unclear. The Bonferroni correction (method to adjust for the smallest p-value for significant tests on multiple comparisons.[58]) only works reasonably well for moderately correlated variables because the conservatism of Bonferroni increases when the correlation between variables increases.[58] The exposure windows examined in this study were highly correlated (e.g., first trimester exposure included first month exposure); therefore, the correction approach

was not applied. Besides, the overall patterns of associations strongly suggested effects of pollutant exposures on adverse birth outcomes, e.g., the positive associations were found for CO exposure and SGA for three out of five exposure windows in models with trend-adjusted (Table 2-3). (The effects were found at $\alpha=0.05$ for only the first month exposure.)

The time-trend adjustment used might have resulted in overly adjusted models because other covariates in the models also captured the time-trend effects (e.g., the decline of smoking rate among mothers). However, this should not be a concern because the effects were substantial, especially in the case of CO-SGA association in which AORs reduced from 1.20 to 1.14 (or 5%) after adjustment for time-trend (Table 2-3), indicating there were other effects associated with time-trend that were not captured by the covariates included in the models.

Missing pollutant data may have influenced results, although the results using a single monitor (Linwood) were consistent with those using all three sites, suggesting any bias was minimal. Additional information on potential covariates and confounders not contained in the birth certificate database may have been helpful, e.g., alcohol consumption, although we suspect that effects of many such factors would likely be correlated with other individual-level risk factors that were available, thus minimizing confounding. Finally, measurements of personal or indoor exposures were unavailable, a limitation of all studies that rely on ambient measures of exposure.[59-61] Further research using individual-level exposure monitoring would help to quantify the relative contribution of ambient versus localized exposures to the occurrence of adverse birth outcomes.

2.6 Conclusions

CO, NO_2 and PM_{10} exposures were associated with increased risk of SGA, and SO_2 exposure was associated with increased risk of LBW and PTB. This study highlights the importance of the early period of pregnancy for the CO-SGA, NO_2-SGA and SO_2-LBW associations, and the late pregnancy period for SO_2-PTB and PM_{10}-SGA associations. Our results suggest that air pollution may have more harmful effects on infants of Black mothers, as compared with infants of White mothers. This study

highlights the importance of accounting for long-term trends and maternal smoking status in evaluating the relations between air pollutant exposures and adverse birth outcomes.

Figure 2-1. Map of the Detroit area showing the three air quality monitoring sites, 4 km radius and intersecting Zip codes.
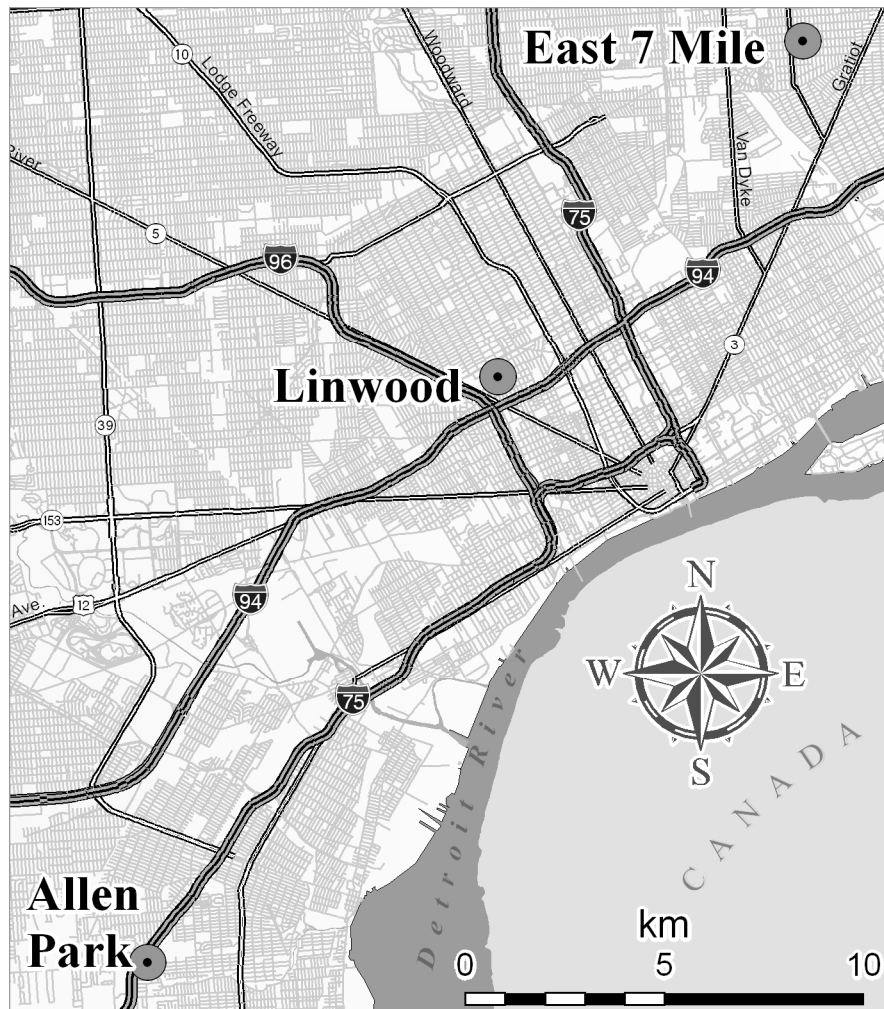
Figure 2-2. Trends of monthly averages of pollutant concentrations. Results of LOESS smoother shown as dashed line for trend.
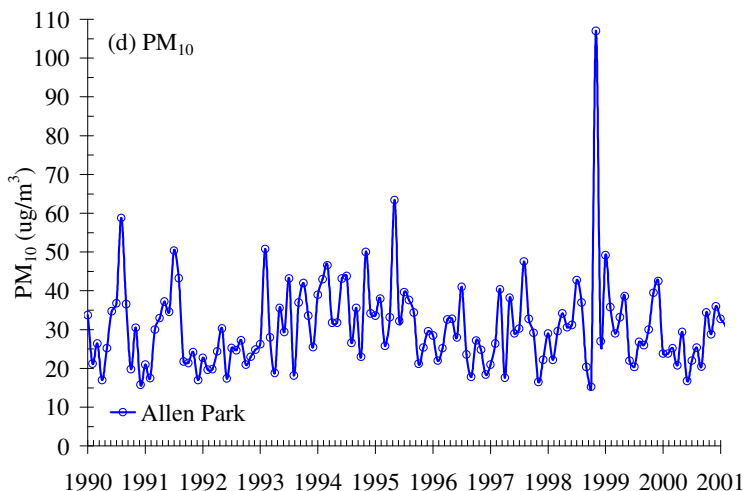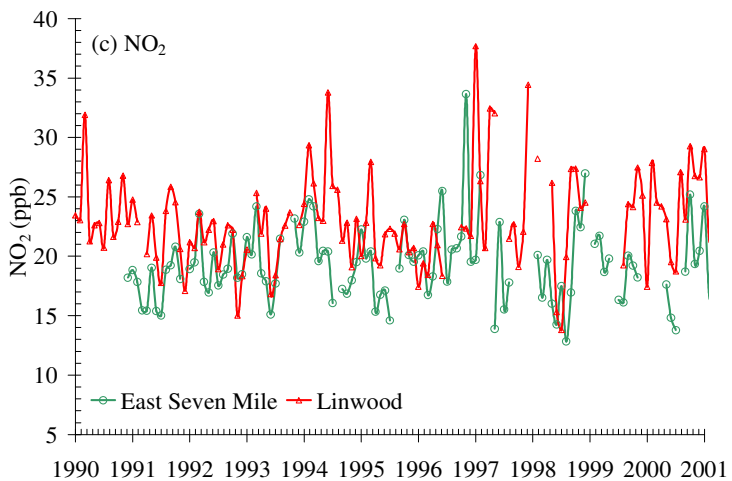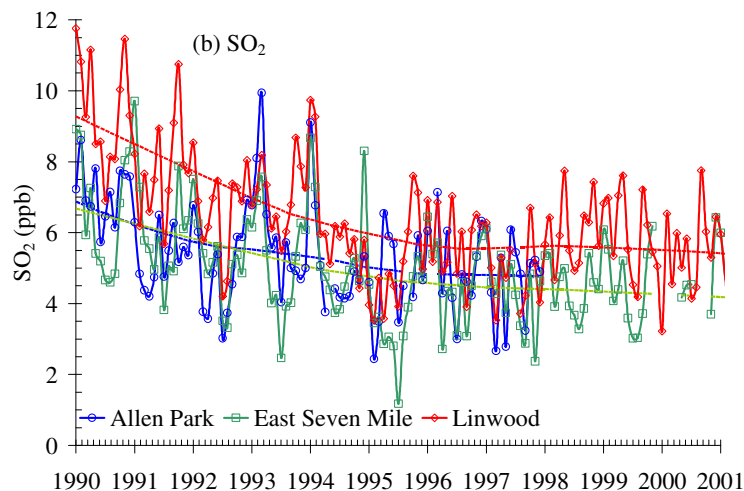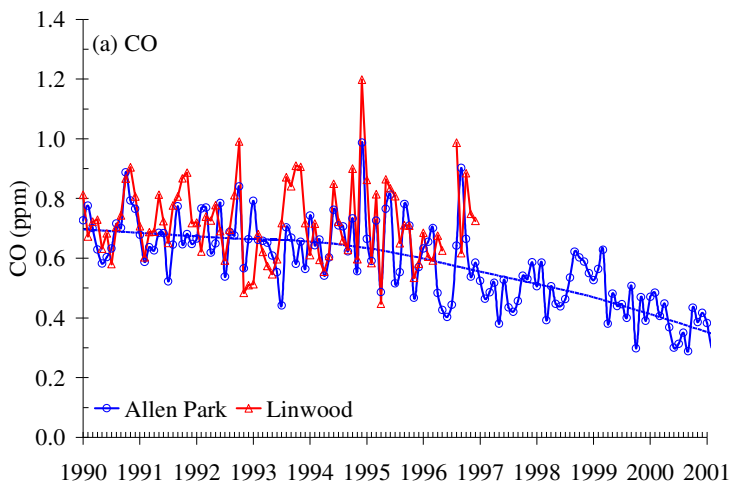
Table 2-1. Infant and maternal characteristics by birth outcomes and ethnicity, 1990-2001.

Characteristics		All births* N=164905 (%)	SGA N=13754 (%)	PTB N=24954 (%)	Term births N=139951 (%)	Black N=93078 (%)	White N=68164 (%)
Infant sex	Female	49.1	49.1	47.8	49.3	49.3	48.8
	Male	50.9	51.0	52.2	50.7	50.6	51.2
Race	Black	56.4	69.1	71.1	53.8	-	-
	White	41.3	28.6	27.1	43.9	-	-
	Other	2.2	2.3	1.8	2.3	-	-
Age (yrs)	16-19	17.4	19.8	19.8	17.0	22.0	11.6
	20-29	58.1	55.4	54.0	58.8	57.4	59.1
	≥30	24.5	24.8	26.2	24.2	20.6	29.3
Education (yrs)	0-11	32.9	40.5	39.5	31.7	36.2	28.4
	12	40.0	38.5	38.9	40.2	39.0	41.9
	≥13	27.1	21.0	21.7	28.1	24.8	29.7
Tobacco use	Smoker	21.8	35.7	27.0	20.9	19.3	26.0
Prenatal care	None	3.4	5.4	7.5	2.7	4.8	1.7
	Late (after 4th month)	26.0	31.8	35.9	24.3	32.7	17.2
Birth season	Spring (Mar-May)	25.2	24.8	25.1	25.3	25.0	25.7
	Summer (Jun-Aug)	26.1	26.2	25.7	26.2	26.0	26.3
	Fall (Sept-Nov)	24.1	23.7	23.8	24.2	23.8	24.5
	Winter (Dec-Feb)	24.6	25.3	25.5	24.4	25.2	23.6
Birth period	1990-1993	39.5	43.4	40.6	39.3	41.1	37.7
	1994-1997	31.3	29.7	31.0	31.3	31.0	31.5
	1998-2001	29.3	26.9	28.5	29.4	28.0	30.8

Abbreviations: SGA, small for gestational age; PTB, preterm births; (*) All births included Blacks, Whites and others.

Table 2-2. Statistics of air pollutant concentrations.

Pollutants	Average time	Site	N	Mean	SD	Min	25th	50th	75th	Max
CO (ppm)	3-hr	All	6674	0.84	0.72	0.05	0.40	0.63	1.03	8.77
		AP	4266	0.80	0.69	0.05	0.40	0.60	0.97	8.77
		LW	2408	0.91	0.76	0.05	0.43	0.70	1.13	7.23
	24-hr	All	6695	0.62	0.38	0.05	0.37	0.53	0.77	5.18
		AP	4278	0.56	0.33	0.05	0.35	0.49	0.70	4.01
		LW	2417	0.72	0.44	0.05	0.43	0.62	0.90	5.18
	Month*	All	66182	0.66	0.15	0.26	0.57	0.67	0.76	1.18
	Trimester*	All	66905	0.66	0.12	0.28	0.61	0.67	0.73	0.93
SO₂ (ppb)	24-hr	All	11194	5.6	4.8	0.5	2.2	4.1	7.4	49.5
		AP	2826	5.4	4.1	0.5	2.4	4.3	7.2	31.7
		E7M	4108	4.9	4.1	0.5	2.0	3.7	6.5	31.4
		LW	4260	6.3	5.7	0.5	2.2	4.5	8.7	49.5
	Month*	All	140092	5.8	1.8	1.0	4.5	5.5	6.8	12.5
	Trimester*	All	141016	5.8	1.5	2.2	4.7	5.5	6.6	11.0
NO₂ (ppb)	24-hr	All	7169	21.2	9.3	0.5	14.7	20.1	26.3	76.7
		E7M	3418	19.2	8.5	0.5	13.2	18.1	24.0	76.7
		LW	3751	23.0	9.6	0.5	16.4	21.9	27.9	76.5
	Annual	All	12	21.3	1.2	19.6	20.6	21.0	21.9	23.5
		E7M	12	19.1	1.1	17.6	18.6	18.9	19.4	21.6
		LW	12	23.0	1.6	20.9	21.6	23.2	24.0	26.1
	Month*	All	99442	21.3	4.1	8.2	18.7	21.0	23.6	41.7
	Trimester*	All	100163	21.2	3.1	14.1	19.1	21.0	23.2	30.8
PM₁₀ (µg/m³)	24-hr	AP	661	29.9	16.1	4.0	19.0	27.0	37.0	131.0
	Month*	AP	27178	30.0	9.3	12.8	23.0	29.0	35.8	63.4
	Trimester*	AP	27376	30.0	6.4	17.5	24.3	30.1	35.2	46.0

Abbreviations: AP, Allen Park; E7M, East Seven Mile; LW, Linwood; SD, standard deviation; 25th, 50th, 75th are percentiles; (*) Month and trimester averages are subjects' exposure estimates.

Table 2-3. Adjusted odds ratio and 95% confident interval (95% CI) for each window of exposure to air pollutants for small for gestational age (SGA) and preterm birth (PTB).

Statistically significant estimates are in bold.

Windows and quartiles of exposures	CO Adjusted[a] OR (95% CI)	CO Time trend[b] OR (95% CI)	SO_2 Adjusted[a] OR (95% CI)	SO_2 Time trend[b] OR (95% CI)	NO_2 Adjusted[a] OR (95% CI)	NO_2 Time trend[b] OR (95% CI)	PM_{10} Adjusted[a] OR (95% CI)	PM_{10} Time trend[b] OR (95% CI)
SGA								
1st month								
2nd	**1.17 (1.06-1.29)**	1.11 (1.00-1.24)	0.98 (0.92-1.04)	0.96 (0.90-1.03)	1.06 (0.99-1.14)	1.07 (0.99-1.14)	1.06 (0.91-1.24)	1.07 (0.92-1.25)
3rd	1.07 (0.97-1.18)	1.00 (0.89-1.12)	1.03 (0.97-1.10)	1.00 (0.94-1.07)	1.06 (0.98-1.14)	1.06 (0.98-1.14)	0.99 (0.84-1.16)	1.01 (0.85-1.20)
4th	**1.20 (1.09-1.33)**	**1.14 (1.02-1.27)**	**1.11 (1.04-1.18)**	1.04 (0.97-1.13)	**1.10 (1.01-1.19)**	**1.11 (1.03-1.21)**	1.15 (0.98-1.36)	1.16 (0.98-1.38)
Last month								
2nd	1.06 (0.97-1.17)	1.00 (0.90-1.11)	1.03 (0.97-1.09)	1.01 (0.95-1.07)	1.00 (0.93-1.07)	1.00 (0.93-1.07)	0.99 (0.85-1.15)	1.00 (0.86-1.17)
3rd	1.10 (1.00-1.20)	1.02 (0.91-1.13)	0.98 (0.92-1.04)	0.94 (0.88-1.01)	1.00 (0.93-1.07)	1.00 (0.93-1.07)	1.07 (0.92-1.25)	1.09 (0.93-1.28)
4th	1.05 (0.96-1.16)	0.98 (0.88-1.09)	1.07 (1.00-1.14)	0.98 (0.91-1.05)	0.93 (0.86-1.01)	0.95 (0.88-1.03)	1.08 (0.92-1.26)	1.07 (0.91-1.26)
1st trimester								
2nd	**1.15 (1.04-1.27)**	1.11 (0.98-1.25)	1.04 (0.98-1.11)	1.02 (0.96-1.09)	1.02 (0.95-1.10)	1.03 (0.96-1.11)	1.02 (0.87-1.19)	1.06 (0.90-1.25)
3rd	**1.17 (1.06-1.29)**	1.10 (0.98-1.24)	1.04 (0.97-1.11)	1.01 (0.94-1.09)	1.04 (0.95-1.12)	1.05 (0.97-1.14)	1.01 (0.86-1.20)	1.06 (0.89-1.27)
4th	**1.16 (1.04-1.28)**	1.10 (0.97-1.25)	**1.15 (1.08-1.23)**	1.09 (1.00-1.18)	1.02 (0.93-1.12)	1.06 (0.97-1.16)	1.11 (0.94-1.32)	1.14 (0.95-1.36)
2nd trimester								
2nd	1.07 (0.97-1.18)	1.01 (0.90-1.13)	1.00 (0.94-1.06)	0.98 (0.92-1.05)	0.98 (0.91-1.05)	0.98 (0.91-1.06)	1.16 (0.99-1.37)	**1.23 (1.04-1.45)**
3rd	1.10 (1.00-1.21)	1.01 (0.90-1.14)	0.97 (0.91-1.03)	0.94 (0.88-1.01)	0.97 (0.90-1.06)	0.99 (0.91-1.08)	1.17 (0.99-1.38)	**1.22 (1.02-1.45)**
4th	1.10 (0.99-1.23)	1.02 (0.90-1.15)	**1.12 (1.05-1.20)**	1.05 (0.96-1.14)	0.96 (0.88-1.05)	1.01 (0.92-1.11)	1.04 (0.88-1.23)	**1.05 (0.87-1.26)**
3rd trimester								
2nd	1.08 (0.98-1.19)	1.00 (0.90-1.11)	**1.07 (1.01-1.13)**	1.04 (0.98-1.11)	0.93 (0.87-1.00)	0.94 (0.88-1.01)	1.03 (0.88-1.22)	1.05 (0.89-1.25)
3rd	1.05 (0.95-1.15)	0.96 (0.86-1.07)	1.02 (0.95-1.08)	0.98 (0.92-1.05)	0.98 (0.91-1.06)	0.99 (0.92-1.07)	**1.20 (1.02-1.42)**	**1.25 (1.05-1.49)**
4th	1.06 (0.96-1.17)	0.97 (0.87-1.09)	**1.12 (1.05-1.20)**	1.03 (0.96-1.12)	0.98 (0.90-1.06)	1.01 (0.93-1.09)	**1.22 (1.04-1.44)**	**1.22 (1.03-1.46)**
PTB								
1st month								
2nd	**0.90 (0.84-0.97)**	0.96 (0.88-1.04)	1.00 (0.96-1.05)	0.99 (0.94-1.04)	1.03 (0.97-1.08)	1.03 (0.97-1.09)	0.99 (0.87-1.12)	0.97 (0.86-1.10)
3rd	**0.92 (0.86-0.99)**	0.98 (0.90-1.07)	1.00 (0.95-1.05)	0.97 (0.93-1.02)	1.03 (0.97-1.09)	1.03 (0.97-1.09)	1.10 (0.97-1.24)	1.07 (0.94-1.22)
4th	**0.89 (0.83-0.97)**	0.95 (0.87-1.03)	1.03 (0.98-1.09)	0.98 (0.92-1.04)	1.00 (0.95-1.07)	1.02 (0.96-1.08)	1.06 (0.93-1.20)	1.05 (0.92-1.20)
Last month								
2nd	0.97 (0.91-1.04)	1.04 (0.96-1.13)	**1.08 (1.03-1.13)**	**1.08 (1.03-1.13)**	0.98 (0.93-1.04)	0.98 (0.93-1.03)	0.98 (0.87-1.10)	0.96 (0.85-1.08)
3rd	**0.89 (0.83-0.96)**	0.96 (0.89-1.04)	**1.11 (1.05-1.16)**	**1.11 (1.05-1.16)**	0.99 (0.94-1.05)	0.99 (0.94-1.05)	0.91 (0.80-1.02)	0.88 (0.78-1.00)
4th	**0.96 (0.89-1.04)**	1.04 (0.95-1.13)	**1.07 (1.02-1.13)**	**1.07 (1.01-1.14)**	0.98 (0.92-1.04)	0.98 (0.92-1.04)	0.95 (0.84-1.07)	0.95 (0.84-1.08)

([a]) Adjusted for sex, gestational age, race, maternal age groups, education levels, tobacco use, prenatal care, birth seasons and site of residency; ([b]) Adjusted for variables in a and birth periods.

Table 2-4. Results of the multipollutant models (including CO, SO_2, NO_2 and PM_{10}) for the Linwood area.

Otherwise as Table 2.3.

Windows and quartiles of exposures			CO	SO_2	NO_2	PM_{10}
			OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
SGA	1st month	2nd	1.04 (0.89-1.21)	1.00 (0.83-1.20)	1.14 (0.97-1.33)	1.02 (0.87-1.19)
		3rd	0.90 (0.77-1.05)	0.99 (0.83-1.17)	1.12 (0.97-1.31)	1.07 (0.90-1.28)
		4th	1.02 (0.87-1.19)	0.93 (0.78-1.11)	**1.28 (1.09-1.49)**	1.08 (0.90-1.30)
	Last month	2nd	0.93 (0.80-1.08)	0.99 (0.83-1.18)	1.09 (0.93-1.26)	1.00 (0.86-1.15)
		3rd	1.03 (0.89-1.20)	0.97 (0.82-1.15)	1.04 (0.90-1.20)	0.98 (0.83-1.16)
		4th	0.98 (0.84-1.14)	1.03 (0.86-1.23)	0.99 (0.85-1.16)	0.88 (0.75-1.04)
	1st trimester	2nd	**1.22 (1.02-1.46)**	1.18 (0.92-1.51)	1.04 (0.83-1.31)	1.11 (0.92-1.33)
		3rd	1.20 (1.00-1.45)	1.01 (0.83-1.23)	1.04 (0.83-1.31)	1.16 (0.95-1.42)
		4th	1.16 (0.96-1.41)	1.05 (0.87-1.28)	1.14 (0.91-1.44)	1.16 (0.95-1.41)
	2nd trimester	2nd	1.14 (0.95-1.36)	**1.30 (1.01-1.69)**	1.06 (0.81-1.40)	1.15 (0.94-1.42)
		3rd	1.19 (0.98-1.44)	1.12 (0.91-1.37)	1.03 (0.78-1.35)	0.97 (0.79-1.19)
		4th	**1.22 (1.01-1.47)**	1.11 (0.90-1.36)	1.12 (0.85-1.48)	1.13 (0.92-1.40)
	3rd trimester	2nd	0.97 (0.83-1.14)	1.17 (0.94-1.45)	1.10 (0.92-1.33)	0.89 (0.74-1.07)
		3rd	0.98 (0.83-1.16)	**1.24 (1.02-1.50)**	1.07 (0.88-1.29)	0.87 (0.72-1.05)
		4th	0.99 (0.84-1.17)	**1.31 (1.06-1.60)**	1.04 (0.85-1.26)	**0.82 (0.69-0.98)**
PTB	1st month	2nd	0.94 (0.84-1.06)	**1.27 (1.11-1.47)**	1.06 (0.94-1.19)	1.00 (0.92-1.09)
		3rd	1.00 (0.90-1.13)	1.14 (0.99-1.30)	1.08 (0.97-1.21)	1.01 (0.91-1.11)
		4th	0.95 (0.85-1.06)	1.13 (0.98-1.30)	1.05 (0.94-1.18)	1.08 (0.98-1.19)
	Last month	2nd	1.01 (0.90-1.13)	1.04 (0.91-1.19)	0.92 (0.82-1.03)	1.06 (0.97-1.15)
		3rd	0.94 (0.84-1.05)	1.06 (0.93-1.21)	0.99 (0.89-1.11)	0.98 (0.89-1.08)
		4th	1.03 (0.92-1.16)	0.99 (0.86-1.14)	1.01 (0.90-1.14)	0.92 (0.84-1.01)

Adjusted for infant sex, maternal race, age groups, education levels, tobacco use, prenatal care, birth seasons, site of residency and birth periods. (*Note: SGA models do not include infant sex.*)

Table S2- 1. Annual descriptive statistics for covariates for all eligible births

Year	16-19 yrs			≥30 yrs			<High school			High school			>High school			Smoker			No prenatal care		
	All	Black	White	All	Black	White	All	Black	White	All	Black	White	All	Black	White	All	Black	White	All	Black	White
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
1990	19.4	25.2	11.2	22.3	18.6	27.5	33.7	38.3	26.6	42.8	40.3	47.3	23.5	21.3	26.1	26.3	24.2	30.2	4.1	5.6	2.0
1991	19.4	24.7	11.9	22.4	19.0	27.2	34.8	39.0	28.5	41.6	39.3	45.5	23.6	21.7	26.1	26.2	23.0	31.5	4.2	5.7	2.2
1992	18.9	24.2	11.3	23.0	19.4	28.0	34.4	38.6	28.3	40.8	39.2	43.6	24.8	22.3	28.1	24.6	21.6	29.5	4.2	5.6	2.3
1993	18.1	23.1	11.1	23.6	19.1	30.1	35.6	40.3	28.3	39.2	37.0	43.0	25.3	22.7	28.7	23.2	20.1	28.5	4.5	6.5	1.8
1994	18.3	22.5	12.6	24.1	20.0	29.7	33.3	37.1	27.6	40.0	38.2	43.2	26.8	27.7	29.3	22.1	18.9	27.5	3.7	5.2	1.7
1995	17.4	22.1	11.6	25.2	20.6	30.7	32.4	36.8	26.6	39.0	37.2	42.1	28.6	26.0	31.3	20.8	18.0	25.2	3.7	5.3	1.8
1996	17.3	22.0	11.6	25.5	20.9	30.9	31.6	35.3	27.1	38.6	37.7	40.5	29.8	27.0	32.5	21.2	18.0	26.2	2.3	3.3	1.3
1997	16.8	20.8	12.1	25.6	22.0	29.8	31.2	33.7	28.0	39.5	38.4	41.2	29.4	27.9	30.8	19.9	17.3	24.3	2.1	2.9	1.2
1998	16.2	19.7	12.0	25.3	21.8	29.4	30.7	32.5	28.3	39.1	39.1	39.9	30.2	28.4	31.8	18.8	16.7	22.3	2.9	4.1	1.6
1999	15.7	19.4	11.4	25.8	22.2	29.6	30.6	32.1	28.7	39.6	40.8	39.0	29.7	27.2	32.3	18.0	15.9	21.4	3.1	4.4	1.7
2000	14.4	17.7	10.6	26.2	22.7	29.8	32.4	33.1	31.5	38.7	40.0	37.9	28.9	26.9	30.6	18.4	16.4	21.5	1.9	2.9	0.9
2001	14.8	18.0	11.4	27.2	24.3	30.1	31.8	31.6	32.1	38.9	41.1	36.8	29.3	27.3	31.1	16.9	15.2	19.6	2.4	3.4	1.3

Table S2- 2. Pearson correlation coefficients by window of exposure to pollutants, 1990-2001

Pollutants	1st Month				Last Month				1st Trimester				2nd Trimester				3rd Trimester			
	CO	SO_2	NO_2	PM_{10}	CO	SO_2	NO_2	PM_{10}	CO	SO_2	NO_2	PM_{10}	CO	SO_2	NO_2	PM_{10}	CO	SO_2	NO_2	PM_{10}
CO	1.00				1.00				1.00				1.00				1.00			
SO_2	0.35	1.00			0.32	1.00			0.36	1.00			0.37	1.00			0.33	1.00		
NO_2	0.27	0.35	1.00	-	0.27	0.37	1.00	-	0.19	0.39	1.00	-	0.17	0.41	1.00	-	0.19	0.39	1.00	-
PM_{10}	0.07	0.03	-	1.00	0.11	0.04	-	1.00	0.07	-0.08	-	1.00	0.08	-0.01	-	1.00	0.05	-0.08	-	1.00

Abbreviations: CO, carbon monoxide; SO_2, sulfur dioxide; NO_2, nitrogen dioxide; PM_{10}, particulate matter aerodynamic diameter <10 μm

Table S2- 3. Associations between covariates and birth outcomes.

Model included all covariates. Statistical significant estimates are in bold.

Covariates		SGA (N=122494)			PTB (N=145296)		
		ORs	95% CI		ORs	95% CI	
Male		-	-	-	**1.07**	**(1.03-**	**1.10)**
Race	Black	**2.10**	**(2.00-**	**2.21)**	**1.94**	**(1.87-**	**2.02)**
	Other	**1.86**	**(1.63-**	**2.13)**	**1.29**	**(1.15-**	**1.44)**
Age	16-19 yrs	**1.13**	**(1.07-**	**1.19)**	1.04	(1.00-	1.08)
	≥30 yrs	**1.16**	**(1.11-**	**1.22)**	**1.27**	**(1.22-**	**1.31)**
Education	<12 yrs	**1.33**	**(1.26-**	**1.41)**	**1.34**	**(1.28-**	**1.40)**
	12 yrs	**1.18**	**(1.12-**	**1.25)**	**1.19**	**(1.14-**	**1.24)**
Smoker		**2.39**	**(2.29-**	**2.49)**	**1.36**	**(1.31-**	**1.41)**
No perinatal care		**1.49**	**(1.35-**	**1.64)**	**1.87**	**(1.75-**	**2.00)**
Late perinatal care		**1.12**	**(1.07-**	**1.17)**	**1.31**	**(1.27-**	**1.36)**
Birth season	Fall	0.98	(0.93-	1.03)	1.01	(0.97-	1.06)
	Winter	1.01	(0.95-	1.06)	1.04	(1.00-	1.09)
	Spring	0.96	(0.91-	1.02)	1.03	(0.99-	1.07)
Site	Linwood	**1.23**	**(1.15-**	**1.32)**	**1.21**	**(1.14-**	**1.27)**
	East Seven Mile	**1.15**	**(1.08-**	**1.23)**	**1.14**	**(1.08-**	**1.20)**
Birth period	1990-1993	**1.12**	**(1.07-**	**1.18)**	1.01	(0.97-	1.04)
	1994-1997	1.01	(0.96-	1.07)	1.00	(0.96-	1.04)

Abbreviations: SGA, small for gestational age; PTB, preterm birth; ORs, odds ratio.

Reference groups: Female, White, age group 20-29, >12 yrs of education, non-smoker,

summer, Allen Park, and birth period 1998-2001.

Table S2- 4. Air pollutant concentrations by window and quartile of exposures

Window of exposure/ Quartile of exposure			CO (ppm)	SO$_2$ (ppb)	NO$_2$ (ppb)	PM$_{10}$ ($\mu g/m^3$)
SGA	1st month	1st	≤0.56	≤4.53	≤18.65	≤22.80
		2nd	0.57-0.66	4.54-5.53	18.66-20.98	22.81-28.80
		3rd	0.67-0.75	5.54-6.80	20.99-23.56	28.81-35.75
		4th	>0.75	>6.80	>23.56	>35.8
	Last month	1st	≤0.56	≤4.47	≤18.57	≤23.00
		2nd	0.57-0.66	4.48-5.47	18.58-20.94	23.01-29.20
		3rd	0.67-0.75	5.48-6.76	20.96-23.46	29.21-35.75
		4th	>0.75	>6.76	>23.46	>35.75
	1st trimester	1st	≤0.61	≤4.67	≤19.06	≤24.21
		2nd	0.62-0.67	4.68-5.49	19.07-21.03	24.22-30.06
		3rd	0.68-0.73	5.50-6.62	21.04-23.2	30.07-35.19
		4th	>0.73	>6.63	>23.2	>35.19
	2nd trimester	1st	≤0.61	≤4.67	≤19.02	≤24.54
		2nd	0.62-0.67	4.68-5.50	19.03-21.01	24.55-30.29
		3rd	0.68-0.73	5.51-6.56	21.03-23.12	30.30-34.59
		4th	>0.73	>6.56	>23.12	>34.59
	3rd trimester	1st	≤0.59	≤4.57	≤18.79	≤24.00
		2nd	0.60-0.67	4.58-5.48	18.80-21.01	24.01-29.54
		3rd	0.68-0.74	5.49-6.66	21.03-23.12	29.55-35.23
		4th	>0.74	>6.66	>23.12	>35.23
PTB	1st month	1st	≤0.57	≤4.54	≤18.67	≤22.80
		2nd	0.58-0.67	4.55-5.55	18.68-21.00	22.81-28.80
		3rd	0.68-0.76	5.56-6.83	21.01-23.56	28.81-35.75
		4th	>0.76	>6.83	>23.56	>35.76
	Last month	1st	≤0.56	≤4.49	≤18.59	≤23.00
		2nd	0.57-0.66	4.50-5.49	18.61-20.96	23.01-29.20
		3rd	0.67-0.75	5.50-6.79	20.97-23.47	29.21-35.60
		4th	>0.75	>6.79	>23.47	>35.61

Abbreviations: SGA, small for gestational age; PTB, preterm birth; ppm, part per million; ppb, part per billion.

Table S2- 5. Adjusted odds ratio and their 95% confident interval (95% CI) at each window of exposure to CO for small for gestational age (SGA) and preterm birth (PTB). Statistical significant estimates are in bold.

Windows and quartiles of exposures		All Subjects	Maternal race		Maternal smoking status	
		Trend-adjusted	Black	White	Smoker	Non-smoker
		OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
SGA						
1st Month	2nd	1.11 (1.00-1.24)	1.15 (0.98-1.36)	1.08 (0.93-1.27)	**1.23 (1.05-1.45)**	1.07 (0.94-1.21)
	3rd	1.00 (0.89-1.12)	1.08 (0.92-1.26)	0.93 (0.78-1.11)	1.08 (0.91-1.28)	0.98 (0.86-1.11)
	4th	**1.14 (1.02-1.27)**	**1.20 (1.03-1.41)**	1.08 (0.90-1.30)	1.15 (0.97-1.38)	**1.16 (1.02-1.32)**
Last Month	2nd	1.00 (0.90-1.11)	0.92 (0.79-1.07)	1.10 (0.95-1.28)	1.07 (0.91-1.25)	1.00 (0.88-1.12)
	3rd	1.02 (0.91-1.13)	0.98 (0.85-1.14)	1.03 (0.88-1.21)	1.14 (0.97-1.34)	0.98 (0.87-1.11)
	4th	0.98 (0.88-1.09)	0.96 (0.83-1.11)	0.97 (0.81-1.16)	1.12 (0.94-1.32)	0.94 (0.83-1.07)
1st Trimester	2nd	1.11 (0.98-1.25)	1.30 (1.09-1.55)	0.95 (0.80-1.13)	**1.19 (1.01-1.40)**	1.06 (0.94-1.21)
	3rd	1.10 (0.98-1.24)	1.19 (1.00-1.41)	1.08 (0.90-1.29)	1.17 (0.99-1.39)	1.08 (0.94-1.23)
	4th	1.10 (0.97-1.25)	**1.24 (1.05-1.47)**	0.95 (0.77-1.17)	1.07 (0.89-1.28)	1.13 (0.99-1.30)
2nd Trimester	2nd	1.01 (0.90-1.13)	1.11 (0.93-1.32)	0.98 (0.83-1.15)	0.97 (0.83-1.14)	1.10 (0.97-1.24)
	3rd	1.01 (0.90-1.14)	1.07 (0.90-1.27)	1.02 (0.85-1.21)	0.98 (0.83-1.16)	1.09 (0.95-1.24)
	4th	1.02 (0.90-1.15)	1.13 (0.96-1.34)	0.90 (0.73-1.11)	0.96 (0.80-1.15)	1.11 (0.97-1.28)
3rd Trimester	2nd	1.00 (0.90-1.11)	1.11 (0.94-1.30)	0.94 (0.80-1.09)	1.05 (0.90-1.23)	1.03 (0.91-1.17)
	3rd	0.96 (0.86-1.07)	1.12 (0.96-1.31)	**0.82 (0.70-0.97)**	0.97 (0.82-1.14)	1.00 (0.89-1.14)
	4th	0.97 (0.87-1.09)	1.07 (0.91-1.25)	0.93 (0.77-1.11)	1.03 (0.87-1.22)	0.99 (0.87-1.13)
PTB						
1st Month	2nd	0.96 (0.88-1.04)	0.93 (0.83-1.04)	0.93 (0.84-1.03)	0.90 (0.78-1.04)	**0.91 (0.83-0.99)**
	3rd	0.98 (0.90-1.07)	0.98 (0.88-1.10)	0.91 (0.81-1.02)	0.99 (0.86-1.15)	**0.90 (0.82-0.99)**
	4th	0.95 (0.87-1.03)	0.93 (0.83-1.04)	0.89 (0.78-1.01)	0.91 (0.79-1.06)	**0.89 (0.81-0.98)**
Last Month	2nd	1.04 (0.96-1.13)	1.03 (0.92-1.15)	0.98 (0.88-1.08)	1.03 (0.90-1.18)	0.97 (0.89-1.05)
	3rd	0.96 (0.89-1.04)	0.97 (0.87-1.09)	0.87 (0.78-0.98)	0.92 (0.80-1.06)	**0.90 (0.83-0.99)**
	4th	1.04 (0.95-1.13)	1.04 (0.93-1.16)	0.93 (0.82-1.05)	0.99 (0.85-1.14)	0.98 (0.89-1.07)

Adjusted for sex, gestational age, race, maternal age groups, education levels, tobacco use, prenatal care, birth seasons, site of residency and birth periods.

Table S2- 6. Adjusted odds ratio and their 95% confident interval (95% CI) at each window of exposure to SO_2 for small for gestational age (SGA) and preterm birth (PTB). Otherwise as Table S2-5.

Windows and quartiles of exposures		All Subjects	Maternal race		Maternal smoking status	
		Trend-adjusted	Black	White	Smoker	Non-smoker
		OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
SGA						
	2nd	0.96 (0.90-1.03)	0.92 (0.85-1.00)	1.04 (0.94-1.16)	0.93 (0.83-1.04)	0.98 (0.91-1.06)
1st Month	3rd	1.00 (0.94-1.07)	0.98 (0.90-1.06)	1.05 (0.94-1.19)	0.97 (0.86-1.09)	1.02 (0.94-1.11)
	4th	1.04 (0.97-1.13)	0.99 (0.90-1.09)	1.12 (0.98-1.29)	1.06 (0.93-1.22)	1.03 (0.94-1.14)
	2nd	1.01 (0.95-1.07)	1.00 (0.93-1.08)	1.01 (0.91-1.13)	1.03 (0.93-1.15)	1.00 (0.93-1.07)
Last Month	3rd	0.94 (0.88-1.01)	0.95 (0.88-1.03)	0.95 (0.85-1.07)	0.94 (0.84-1.06)	0.94 (0.87-1.02)
	4th	0.98 (0.91-1.05)	0.96 (0.88-1.05)	1.01 (0.88-1.15)	1.06 (0.94-1.21)	0.94 (0.86-1.03)
	2nd	1.02 (0.96-1.09)	1.04 (0.96-1.13)	1.01 (0.90-1.12)	0.99 (0.88-1.11)	1.04 (0.96-1.13)
1st Trimester	3rd	1.01 (0.94-1.09)	1.03 (0.94-1.12)	1.00 (0.88-1.13)	1.00 (0.88-1.13)	1.02 (0.94-1.11)
	4th	1.09 (1.00-1.18)	1.13 (1.01-1.26)	1.00 (0.86-1.15)	1.03 (0.89-1.20)	1.12 (1.00-1.24)
	2nd	0.98 (0.92-1.05)	0.96 (0.89-1.04)	1.00 (0.90-1.12)	0.93 (0.83-1.04)	1.01 (0.93-1.09)
2nd Trimester	3rd	0.94 (0.88-1.01)	**0.91 (0.83-0.99)**	1.00 (0.89-1.13)	0.90 (0.80-1.02)	0.95 (0.88-1.04)
	4th	1.05 (0.96-1.14)	1.01 (0.91-1.13)	1.08 (0.93-1.25)	0.99 (0.86-1.15)	1.07 (0.97-1.19)
	2nd	1.04 (0.98-1.11)	1.03 (0.96-1.12)	1.06 (0.96-1.18)	0.97 (0.87-1.08)	1.08 (1.00-1.16)
3rd Trimester	3rd	0.98 (0.92-1.05)	0.98 (0.90-1.06)	1.00 (0.88-1.12)	0.95 (0.85-1.07)	1.00 (0.92-1.08)
	4th	1.03 (0.96-1.12)	1.02 (0.92-1.12)	1.06 (0.92-1.22)	1.06 (0.93-1.22)	1.02 (0.92-1.12)
PTB						
	2nd	0.99 (0.94-1.04)	0.98 (0.92-1.04)	1.01 (0.93-1.10)	0.99 (0.89-1.09)	0.99 (0.94-1.05)
1st Month	3rd	0.97 (0.93-1.02)	0.97 (0.91-1.03)	1.00 (0.91-1.09)	1.00 (0.90-1.11)	0.97 (0.91-1.03)
	4th	0.98 (0.92-1.04)	0.98 (0.91-1.05)	0.96 (0.86-1.07)	0.95 (0.84-1.06)	0.99 (0.93-1.06)
	2nd	**1.08 (1.03-1.13)**	**1.12 (1.06-1.19)**	1.02 (0.94-1.11)	1.07 (0.98-1.18)	**1.08 (1.03-1.14)**
Last Month	3rd	**1.11 (1.05-1.16)**	**1.16 (1.09-1.23)**	1.01 (0.92-1.10)	**1.12 (1.01-1.23)**	**1.10 (1.04-1.17)**
	4th	**1.07 (1.01-1.14)**	**1.11 (1.03-1.19)**	1.02 (0.92-1.13)	1.06 (0.95-1.19)	**1.08 (1.01-1.15)**

Adjusted for sex, gestational age, race, maternal age groups, education levels, tobacco use, prenatal care, birth seasons, site of residency and birth periods.

Table S2- 7. Adjusted odds ratio and their 95% confident interval (95% CI) at each window of exposure to NO_2 for small for gestational age (SGA) and preterm birth (PTB). Otherwise as Table S2-5.

Windows and quartiles of exposures		All Subjects	Maternal race		Maternal smoking status	
		Trend-adjusted	Black	White	Smoker	Non-smoker
		OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
SGA						
	2nd	1.07 (0.99-1.14)	**1.09 (1.01-1.19)**	1.01 (0.87-1.17)	**1.17 (1.03-1.33)**	1.02 (0.94-1.11)
1st Month	3rd	1.06 (0.98-1.14)	**1.10 (1.01-1.20)**	0.97 (0.82-1.14)	**1.22 (1.06-1.39)**	0.99 (0.91-1.09)
	4th	**1.11 (1.03-1.21)**	**1.17 (1.06-1.28)**	0.99 (0.84-1.18)	**1.25 (1.08-1.44)**	1.06 (0.96-1.16)
	2nd	1.00 (0.93-1.07)	1.01 (0.93-1.09)	0.99 (0.86-1.14)	0.96 (0.85-1.08)	1.02 (0.94-1.11)
Last Month	3rd	1.00 (0.93-1.07)	1.00 (0.92-1.09)	0.97 (0.83-1.14)	0.96 (0.85-1.10)	1.01 (0.92-1.11)
	4th	0.95 (0.88-1.03)	0.96 (0.88-1.04)	0.93 (0.79-1.10)	0.94 (0.82-1.07)	0.96 (0.87-1.05)
	2nd	1.03 (0.96-1.11)	1.03 (0.95-1.13)	1.00 (0.86-1.17)	1.09 (0.95-1.24)	1.01 (0.92-1.10)
1st Trimester	3rd	1.05 (0.97-1.14)	1.07 (0.97-1.18)	1.01 (0.85-1.21)	1.06 (0.91-1.23)	1.05 (0.95-1.16)
	4th	1.06 (0.97-1.16)	1.10 (0.99-1.22)	0.90 (0.74-1.09)	1.10 (0.94-1.30)	1.03 (0.92-1.15)
	2nd	0.98 (0.91-1.06)	1.00 (0.92-1.09)	0.97 (0.84-1.13)	0.97 (0.85-1.11)	0.98 (0.90-1.08)
2nd Trimester	3rd	0.99 (0.91-1.08)	1.00 (0.91-1.11)	1.00 (0.83-1.19)	0.89 (0.77-1.04)	1.04 (0.94-1.15)
	4th	1.01 (0.92-1.11)	1.06 (0.95-1.18)	0.86 (0.70-1.05)	0.99 (0.84-1.17)	1.02 (0.91-1.14)
	2nd	0.94 (0.88-1.01)	0.95 (0.87-1.02)	0.90 (0.78-1.04)	0.95 (0.84-1.08)	0.93 (0.86-1.01)
3rd Trimester	3rd	0.99 (0.92-1.07)	0.99 (0.91-1.08)	0.97 (0.83-1.14)	1.03 (0.90-1.17)	0.98 (0.90-1.07)
	4th	1.01 (0.93-1.09)	0.99 (0.90-1.09)	1.06 (0.89-1.26)	1.02 (0.88-1.18)	1.00 (0.91-1.11)
PTB						
	2nd	1.03 (0.97-1.09)	1.03 (0.97-1.09)	1.02 (0.91-1.15)	0.99 (0.89-1.11)	1.04 (0.97-1.10)
1st Month	3rd	1.03 (0.97-1.09)	1.03 (0.96-1.10)	1.08 (0.95-1.22)	0.99 (0.89-1.11)	1.05 (0.98-1.12)
	4th	1.02 (0.96-1.08)	1.03 (0.96-1.10)	0.97 (0.85-1.11)	1.03 (0.92-1.17)	1.01 (0.95-1.09)
	2nd	0.98 (0.93-1.03)	0.97 (0.91-1.03)	1.03 (0.92-1.15)	1.00 (0.90-1.11)	0.98 (0.92-1.04)
Last Month	3rd	0.99 (0.94-1.05)	1.00 (0.93-1.06)	0.98 (0.87-1.11)	0.96 (0.86-1.08)	1.00 (0.93-1.06)
	4th	0.98 (0.92-1.04)	1.00 (0.93-1.07)	0.94 (0.82-1.07)	0.94 (0.84-1.06)	0.99 (0.93-1.06)

Adjusted for sex, gestational age, race, maternal age groups, education levels, tobacco use, prenatal care, birth seasons, site of residency and birth periods.

Table S2- 8. Adjusted odds ratio and their 95% confident interval (95% CI) at each window of exposure to PM_{10} for small for gestational age (SGA) and preterm birth (PTB).

Otherwise as Table S2-5.

Windows and quartiles of exposures		All Subjects	Maternal race		Maternal smoking status	
		Trend-adjusted	Black	White	Smoker	Non-smoker
		OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
SGA						
	2nd	1.06 (0.91-1.24)	1.05 (0.62-1.78)	1.06 (0.90-1.26)	0.99 (0.78-1.26)	1.13 (0.92-1.39)
1st Month	3rd	0.99 (0.84-1.16)	0.87 (0.49-1.54)	1.02 (0.85-1.22)	0.90 (0.69-1.18)	1.10 (0.88-1.38)
	4th	1.15 (0.98-1.36)	0.77 (0.42-1.40)	1.17 (0.98-1.40)	1.12 (0.87-1.45)	1.22 (0.97-1.52)
	2nd	0.99 (0.85-1.15)	1.35 (0.79-2.33)	0.96 (0.82-1.13)	1.02 (0.81-1.29)	0.99 (0.81-1.21)
Last Month	3rd	1.07 (0.92-1.25)	1.07 (0.59-1.95)	1.11 (0.94-1.31)	1.05 (0.82-1.35)	1.12 (0.91-1.38)
	4th	1.08 (0.92-1.26)	1.41 (0.77-2.59)	1.03 (0.87-1.23)	1.12 (0.88-1.43)	1.04 (0.84-1.29)
	2nd	1.02 (0.87-1.19)	0.92 (0.52-1.64)	1.09 (0.91-1.30)	0.93 (0.71-1.20)	1.20 (0.96-1.49)
1st Trimester	3rd	1.01 (0.86-1.20)	0.88 (0.48-1.62)	1.08 (0.89-1.30)	0.97 (0.74-1.27)	1.17 (0.92-1.48)
	4th	1.11 (0.94-1.32)	0.87 (0.46-1.64)	1.14 (0.94-1.39)	1.06 (0.80-1.39)	1.22 (0.96-1.56)
	2nd	1.16 (0.99-1.37)	1.20 (0.65-2.20)	**1.23 (1.03-1.47)**	1.08 (0.83-1.41)	**1.35 (1.08-1.68)**
2nd Trimester	3rd	1.17 (0.99-1.38)	1.38 (0.75-2.53)	1.19 (0.98-1.43)	1.19 (0.91-1.56)	1.23 (0.97-1.56)
	4th	1.04 (0.88-1.23)	1.43 (0.76-2.70)	0.99 (0.81-1.21)	0.84 (0.63-1.12)	1.22 (0.96-1.56)
	2nd	1.03 (0.88-1.22)	0.79 (0.44-1.41)	1.05 (0.88-1.25)	0.95 (0.73-1.24)	1.13 (0.91-1.42)
3rd Trimester	3rd	**1.20 (1.02-1.42)**	1.16 (0.64-2.10)	**1.22 (1.01-1.47)**	1.15 (0.88-1.50)	**1.33 (1.05-1.68)**
	4th	**1.22 (1.04-1.44)**	0.93 (0.50-1.73)	**1.23 (1.02-1.48)**	1.14 (0.87-1.49)	**1.31 (1.03-1.65)**
PTB						
	2nd	0.99 (0.87-1.12)	0.69 (0.43-1.10)	1.01 (0.88-1.15)	1.01 (0.80-1.27)	0.95 (0.82-1.11)
1st Month	3rd	1.10 (0.97-1.24)	0.98 (0.62-1.55)	1.10 (0.96-1.26)	1.07 (0.84-1.36)	1.07 (0.91-1.24)
	4th	1.06 (0.93-1.20)	1.04 (0.66-1.66)	1.07 (0.93-1.23)	1.04 (0.81-1.32)	1.06 (0.90-1.24)
	2nd	0.98 (0.87-1.10)	0.87 (0.57-1.33)	0.97 (0.86-1.10)	0.97 (0.79-1.19)	0.96 (0.83-1.10)
Last Month	3rd	0.91 (0.80-1.02)	0.64 (0.40-1.03)	0.92 (0.80-1.05)	0.82 (0.65-1.03)	0.92 (0.79-1.07)
	4th	0.95 (0.84-1.07)	0.99 (0.63-1.56)	0.96 (0.84-1.09)	0.81 (0.64-1.02)	1.02 (0.88-1.19)

Adjusted for sex, gestational age, race, maternal age groups, education levels, tobacco use, prenatal care, birth seasons, site of residency and birth periods.

Table S2- 9. Adjusted odds ratio and their 95% CIs at each window of exposure to CO and adverse birth outcomes for Linwood from single and multiple pollutant models including CO, SO_2, NO_2 and PM_{10} in the model.

Otherwise as Table S2-5.

Windows and quartiles of exposures		CO	CO and SO_2	CO and NO_2	CO and PM_{10}	All pollutants
		OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
SGA						
	2nd	1.07 (0.92-1.24)	1.07 (0.92-1.24)	1.04 (0.89-1.21)	1.07 (0.92-1.25)	1.04 (0.89-1.21)
1st Month	3rd	0.98 (0.85-1.13)	0.98 (0.85-1.14)	0.92 (0.78-1.07)	0.96 (0.83-1.11)	0.90 (0.77-1.05)
	4th	1.11 (0.96-1.27)	1.10 (0.95-1.27)	1.04 (0.89-1.21)	1.08 (0.94-1.25)	1.02 (0.87-1.19)
	2nd	0.95 (0.82-1.09)	0.95 (0.82-1.10)	0.93 (0.80-1.07)	0.95 (0.82-1.10)	0.93 (0.80-1.08)
Last Month	3rd	1.01 (0.88-1.16)	1.02 (0.88-1.17)	1.03 (0.89-1.19)	1.02 (0.88-1.17)	1.03 (0.89-1.20)
	4th	0.98 (0.85-1.12)	0.98 (0.85-1.13)	0.98 (0.84-1.14)	0.98 (0.85-1.13)	0.98 (0.84-1.14)
	2nd	**1.22 (1.04-1.44)**	**1.22 (1.03-1.44)**	1.19 (1.00-1.42)	**1.25 (1.05-1.47)**	**1.22 (1.02-1.46)**
1st Trimester	3rd	**1.18 (1.01-1.39)**	**1.19 (1.01-1.40)**	1.14 (0.95-1.35)	**1.23 (1.04-1.46)**	1.20 (1.00-1.45)
	4th	**1.19 (1.02-1.39)**	**1.19 (1.01-1.39)**	1.13 (0.94-1.35)	**1.20 (1.02-1.42)**	1.16 (0.96-1.41)
	2nd	1.17 (0.98-1.38)	1.16 (0.98-1.38)	1.14 (0.95-1.36)	1.16 (0.97-1.38)	1.14 (0.95-1.36)
2nd Trimester	3rd	1.15 (0.98-1.35)	1.16 (0.98-1.37)	1.11 (0.93-1.32)	1.19 (1.00-1.42)	1.19 (0.98-1.44)
	4th	1.17 (0.99-1.37)	1.17 (1.00-1.38)	1.12 (0.94-1.34)	**1.23 (1.04-1.46)**	**1.22 (1.01-1.47)**
	2nd	1.02 (0.87-1.18)	1.02 (0.87-1.18)	1.01 (0.87-1.18)	0.99 (0.84-1.16)	0.97 (0.83-1.14)
3rd Trimester	3rd	1.02 (0.88-1.18)	1.02 (0.88-1.19)	1.01 (0.86-1.17)	1.00 (0.85-1.17)	0.98 (0.83-1.16)
	4th	1.00 (0.86-1.15)	1.02 (0.88-1.18)	0.99 (0.85-1.15)	0.98 (0.84-1.15)	0.99 (0.84-1.17)
PTB						
	2nd	0.97 (0.87-1.08)	0.96 (0.86-1.07)	0.94 (0.84-1.05)	0.98 (0.88-1.10)	0.94 (0.84-1.06)
1st Month	3rd	1.03 (0.93-1.15)	1.03 (0.92-1.14)	1.00 (0.89-1.12)	1.04 (0.93-1.16)	1.00 (0.90-1.13)
	4th	0.96 (0.86-1.06)	0.95 (0.86-1.06)	0.95 (0.85-1.06)	0.95 (0.86-1.06)	0.95 (0.85-1.06)
	2nd	1.04 (0.93-1.16)	1.04 (0.93-1.15)	1.04 (0.93-1.16)	1.02 (0.91-1.13)	1.01 (0.90-1.13)
Last Month	3rd	0.97 (0.87-1.08)	0.97 (0.87-1.08)	0.95 (0.85-1.06)	0.97 (0.87-1.08)	0.94 (0.84-1.05)
	4th	1.04 (0.93-1.16)	1.04 (0.94-1.16)	1.03 (0.92-1.16)	1.05 (0.94-1.17)	1.03 (0.92-1.16)

Table S2- 10. Adjusted odds ratio and their 95% CIs at each window of exposure to SO_2 and adverse birth outcomes for Linwood from single and multiple pollutant models including CO, SO_2, NO_2 and PM_{10} in the model.

Otherwise as Table S2-5.

Windows and quartiles of exposures		SO_2	SO_2 and CO	SO_2 and NO_2	SO_2 and PM_{10}	All pollutants
		OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
SGA						
1st Month	2nd	0.91 (0.81-1.03)	0.98 (0.81-1.17)	0.92 (0.81-1.04)	0.92 (0.82-1.03)	1.00 (0.83-1.20)
	3rd	0.96 (0.86-1.07)	0.97 (0.82-1.15)	0.95 (0.84-1.07)	0.97 (0.87-1.08)	0.99 (0.83-1.17)
	4th	0.94 (0.84-1.05)	0.98 (0.83-1.15)	0.89 (0.78-1.01)	0.93 (0.82-1.05)	0.93 (0.78-1.11)
Last Month	2nd	1.01 (0.90-1.13)	0.99 (0.83-1.17)	1.03 (0.91-1.16)	1.01 (0.90-1.13)	0.99 (0.83-1.18)
	3rd	0.94 (0.85-1.05)	0.96 (0.82-1.12)	0.95 (0.84-1.07)	0.96 (0.86-1.07)	0.97 (0.82-1.15)
	4th	0.98 (0.87-1.10)	0.99 (0.85-1.17)	1.01 (0.89-1.15)	0.99 (0.88-1.12)	1.03 (0.86-1.23)
1st Trimester	2nd	1.11 (0.97-1.28)	1.16 (0.91-1.47)	1.13 (0.97-1.31)	1.13 (0.98-1.30)	1.18 (0.92-1.51)
	3rd	1.06 (0.93-1.21)	1.02 (0.85-1.23)	1.08 (0.94-1.24)	1.08 (0.95-1.24)	1.01 (0.83-1.23)
	4th	1.10 (0.95-1.27)	1.11 (0.91-1.34)	1.13 (0.97-1.32)	1.12 (0.96-1.31)	1.05 (0.87-1.28)
2nd Trimester	2nd	**1.20 (1.03-1.39)**	1.23 (0.96-1.59)	**1.22 (1.04-1.44)**	**1.21 (1.04-1.41)**	**1.30 (1.01-1.69)**
	3rd	1.06 (0.91-1.22)	1.11 (0.91-1.34)	1.07 (0.92-1.24)	1.08 (0.93-1.25)	1.12 (0.91-1.37)
	4th	1.09 (0.94-1.28)	1.14 (0.94-1.39)	1.11 (0.94-1.31)	1.10 (0.94-1.30)	1.11 (0.90-1.36)
3rd Trimester	2nd	1.10 (0.97-1.25)	1.13 (0.92-1.38)	1.10 (0.96-1.26)	1.10 (0.97-1.25)	1.17 (0.94-1.45)
	3rd	1.05 (0.93-1.19)	1.21 (1.00-1.46)	1.05 (0.92-1.19)	1.07 (0.95-1.21)	**1.24 (1.02-1.50)**
	4th	1.11 (0.97-1.27)	**1.24 (1.02-1.51)**	1.11 (0.96-1.28)	1.15 (1.00-1.32)	**1.31 (1.06-1.60)**
PTB						
1st Month	2nd	1.06 (0.97-1.16)	**1.26 (1.10-1.45)**	1.07 (0.98-1.18)	1.05 (0.96-1.15)	**1.27 (1.11-1.47)**
	3rd	1.04 (0.96-1.13)	1.12 (0.99-1.28)	1.04 (0.95-1.14)	1.05 (0.96-1.14)	1.14 (0.99-1.30)
	4th	1.06 (0.97-1.16)	1.14 (1.00-1.30)	1.06 (0.96-1.17)	1.05 (0.96-1.15)	1.13 (0.98-1.30)
Last Month	2nd	1.03 (0.94-1.12)	1.06 (0.93-1.21)	1.03 (0.93-1.13)	1.03 (0.95-1.13)	1.04 (0.91-1.19)
	3rd	1.06 (0.98-1.15)	1.07 (0.95-1.21)	1.05 (0.95-1.14)	1.08 (0.99-1.17)	1.06 (0.93-1.21)
	4th	1.06 (0.97-1.15)	1.02 (0.90-1.16)	1.00 (0.91-1.11)	1.05 (0.95-1.15)	0.99 (0.86-1.14)

Table S2- 11. Adjusted odds ratio and their 95% CIs at each window of exposure to NO_2 and adverse birth outcomes for Linwood from single and multiple pollutant models including CO, SO_2, NO_2 and PM_{10} in the model.

Otherwise as Table S2-5.

Windows and quartiles of exposures		NO_2 OR (95% CI)	NO_2 and CO OR (95% CI)	NO_2 and SO_2 OR (95% CI)	NO_2 and PM_{10} OR (95% CI)	All pollutants OR (95% CI)
SGA						
1st Month	2nd	**1.19 (1.05-1.36)**	1.14 (0.98-1.33)	**1.18 (1.04-1.35)**	**1.20 (1.05-1.36)**	1.14 (0.97-1.33)
	3rd	1.13 (1.00-1.28)	1.11 (0.96-1.29)	1.13 (1.00-1.28)	**1.14 (1.01-1.29)**	1.12 (0.97-1.31)
	4th	**1.23 (1.09-1.39)**	**1.24 (1.07-1.45)**	**1.25 (1.11-1.41)**	**1.24 (1.10-1.40)**	**1.28 (1.09-1.49)**
Last Month	2nd	1.06 (0.93-1.19)	1.08 (0.93-1.25)	1.05 (0.93-1.19)	1.07 (0.94-1.21)	1.09 (0.93-1.26)
	3rd	1.04 (0.93-1.17)	1.05 (0.91-1.21)	1.04 (0.93-1.17)	1.04 (0.93-1.17)	1.04 (0.90-1.20)
	4th	0.99 (0.88-1.11)	1.00 (0.86-1.16)	0.99 (0.88-1.11)	1.00 (0.89-1.12)	0.99 (0.85-1.16)
1st Trimester	2nd	1.17 (0.98-1.40)	1.07 (0.85-1.34)	1.17 (0.98-1.41)	1.17 (0.97-1.40)	1.04 (0.83-1.31)
	3rd	**1.22 (1.02-1.45)**	1.06 (0.85-1.33)	**1.22 (1.03-1.45)**	**1.23 (1.03-1.47)**	1.04 (0.83-1.31)
	4th	**1.26 (1.06-1.49)**	1.18 (0.94-1.48)	**1.26 (1.06-1.49)**	**1.25 (1.05-1.49)**	1.14 (0.91-1.44)
2nd Trimester	2nd	**1.29 (1.05-1.59)**	1.15 (0.88-1.49)	**1.29 (1.05-1.59)**	**1.30 (1.06-1.60)**	1.06 (0.81-1.40)
	3rd	**1.27 (1.03-1.55)**	1.12 (0.86-1.46)	**1.26 (1.03-1.55)**	**1.26 (1.03-1.55)**	1.03 (0.78-1.35)
	4th	**1.31 (1.07-1.61)**	1.17 (0.90-1.54)	**1.31 (1.07-1.61)**	**1.31 (1.07-1.61)**	1.12 (0.85-1.48)
3rd Trimester	2nd	1.09 (0.93-1.26)	1.10 (0.92-1.32)	1.09 (0.94-1.27)	1.09 (0.94-1.27)	1.10 (0.92-1.33)
	3rd	1.07 (0.93-1.24)	1.07 (0.89-1.28)	1.07 (0.92-1.24)	1.09 (0.94-1.27)	1.07 (0.88-1.29)
	4th	1.11 (0.96-1.28)	1.11 (0.92-1.33)	1.10 (0.95-1.27)	1.10 (0.95-1.28)	1.04 (0.85-1.26)
PTB						
1st Month	2nd	1.05 (0.95-1.16)	1.05 (0.93-1.17)	1.05 (0.95-1.16)	1.06 (0.96-1.16)	1.06 (0.94-1.19)
	3rd	1.03 (0.95-1.13)	1.08 (0.97-1.21)	1.03 (0.94-1.13)	1.04 (0.95-1.14)	1.08 (0.97-1.21)
	4th	1.07 (0.98-1.17)	1.07 (0.95-1.20)	1.07 (0.98-1.17)	1.07 (0.98-1.17)	1.05 (0.94-1.18)
Last Month	2nd	0.92 (0.83-1.01)	0.92 (0.82-1.03)	0.92 (0.83-1.01)	0.92 (0.83-1.01)	0.92 (0.82-1.03)
	3rd	0.96 (0.88-1.04)	0.98 (0.88-1.10)	0.96 (0.88-1.04)	0.95 (0.87-1.04)	0.99 (0.89-1.11)
	4th	0.96 (0.88-1.05)	0.98 (0.87-1.09)	0.96 (0.88-1.05)	0.97 (0.89-1.06)	1.01 (0.90-1.14)

Table S2- 12. Adjusted odds ratio and their 95% CIs at each window of exposure to PM_{10} and adverse birth outcomes for Linwood from single and multiple pollutant models including CO, SO_2, NO_2 and PM_{10} in the model.

Otherwise as Table S2-5.

Windows and quartiles of exposures		PM_{10} OR (95% CI)	PM_{10} and CO OR (95% CI)	PM_{10} and SO_2 OR (95% CI)	PM_{10} and NO_2 OR (95% CI)	All pollutants OR (95% CI)
SGA						
1st Month	2nd	1.02 (0.90-1.15)	0.98 (0.84-1.14)	1.01 (0.89-1.15)	1.04 (0.91-1.18)	1.02 (0.87-1.19)
	3rd	1.01 (0.88-1.15)	1.05 (0.88-1.24)	1.00 (0.87-1.15)	1.01 (0.87-1.16)	1.07 (0.90-1.28)
	4th	1.05 (0.92-1.21)	1.12 (0.95-1.32)	1.04 (0.91-1.20)	1.06 (0.91-1.22)	1.08 (0.90-1.30)
Last Month	2nd	1.01 (0.90-1.13)	0.99 (0.87-1.14)	1.00 (0.89-1.13)	1.03 (0.91-1.17)	1.00 (0.86-1.15)
	3rd	0.97 (0.86-1.11)	0.95 (0.81-1.11)	0.97 (0.86-1.11)	0.99 (0.86-1.14)	0.98 (0.83-1.16)
	4th	0.95 (0.83-1.07)	0.88 (0.75-1.02)	0.94 (0.83-1.08)	0.96 (0.84-1.10)	0.88 (0.75-1.04)
1st Trimester	2nd	1.06 (0.93-1.21)	1.14 (0.96-1.36)	1.03 (0.90-1.18)	1.09 (0.95-1.25)	1.11 (0.92-1.33)
	3rd	1.13 (0.98-1.30)	**1.25 (1.04-1.50)**	1.07 (0.92-1.25)	1.16 (1.00-1.35)	1.16 (0.95-1.42)
	4th	**1.16 (1.01-1.34)**	**1.25 (1.04-1.49)**	1.11 (0.95-1.30)	1.15 (0.99-1.34)	1.16 (0.95-1.41)
2nd Trimester	2nd	1.08 (0.94-1.23)	1.12 (0.93-1.35)	1.07 (0.93-1.23)	1.10 (0.96-1.27)	1.15 (0.94-1.42)
	3rd	0.97 (0.84-1.11)	0.99 (0.82-1.19)	0.96 (0.83-1.12)	0.98 (0.85-1.14)	0.97 (0.79-1.19)
	4th	**1.25 (1.09-1.44)**	**1.23 (1.03-1.47)**	**1.24 (1.06-1.45)**	**1.23 (1.06-1.43)**	1.13 (0.92-1.40)
3rd Trimester	2nd	0.98 (0.87-1.12)	0.90 (0.76-1.07)	0.98 (0.86-1.11)	0.98 (0.86-1.12)	0.89 (0.74-1.07)
	3rd	0.95 (0.82-1.09)	0.89 (0.75-1.07)	0.92 (0.80-1.07)	0.95 (0.82-1.10)	0.87 (0.72-1.05)
	4th	0.92 (0.80-1.05)	0.87 (0.74-1.02)	0.90 (0.78-1.04)	0.89 (0.77-1.04)	0.82 (0.69-0.98)
PTB						
1st Month	2nd	0.98 (0.91-1.04)	0.99 (0.91-1.07)	0.97 (0.91-1.04)	0.97 (0.91-1.04)	1.00 (0.92-1.09)
	3rd	0.98 (0.92-1.05)	1.01 (0.92-1.11)	0.97 (0.91-1.04)	0.97 (0.90-1.04)	1.01 (0.91-1.11)
	4th	1.02 (0.95-1.10)	1.07 (0.98-1.17)	1.02 (0.95-1.10)	1.01 (0.93-1.09)	1.08 (0.98-1.19)
Last Month	2nd	1.06 (0.99-1.13)	1.05 (0.97-1.14)	1.05 (0.98-1.12)	1.06 (0.99-1.13)	1.06 (0.97-1.15)
	3rd	1.03 (0.96-1.10)	0.99 (0.91-1.08)	1.01 (0.94-1.08)	1.00 (0.93-1.08)	0.98 (0.89-1.08)
	4th	1.00 (0.94-1.07)	0.93 (0.85-1.01)	0.98 (0.91-1.05)	0.96 (0.89-1.04)	0.92 (0.84-1.01)

Table S2- 13. Adjusted odds ratio (ORs) for SGA and PTB at each window of exposure to air pollutants by maternal education levels.

Otherwise as Table S2-5.

Windows and quartiles of exposures		SGA			PTB		
		<12 yrs	12 yrs	>12 yrs	<12 yrs	12 yrs	>12 yrs
		OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
CO (ppm)							
1st Month	2nd	**1.24 (1.03-1.49)**	1.13 (0.95-1.34)	0.94 (0.76-1.17)	0.98 (0.86-1.12)	0.97 (0.87-1.10)	**0.74 (0.64-0.85)**
	3rd	1.11 (0.92-1.34)	1.03 (0.86-1.23)	0.82 (0.65-1.03)	1.03 (0.90-1.17)	0.95 (0.84-1.08)	**0.78 (0.67-0.91)**
	4th	1.19 (0.99-1.44)	**1.22 (1.02-1.47)**	0.95 (0.75-1.20)	0.94 (0.83-1.08)	0.94 (0.83-1.06)	**0.80 (0.69-0.94)**
Last Month	2nd	0.99 (0.83-1.17)	0.97 (0.83-1.14)	1.06 (0.87-1.31)	0.97 (0.85-1.10)	1.03 (0.92-1.15)	0.94 (0.82-1.08)
	3rd	1.03 (0.86-1.22)	1.00 (0.84-1.17)	1.02 (0.82-1.27)	0.93 (0.81-1.05)	0.91 (0.81-1.03)	0.87 (0.75-1.01)
	4th	1.03 (0.86-1.23)	0.97 (0.81-1.15)	0.90 (0.72-1.14)	1.01 (0.88-1.15)	1.05 (0.92-1.18)	**0.83 (0.71-0.97)**
1st Trimester	2nd	**1.46 (1.19-1.80)**	0.97 (0.80-1.17)	0.94 (0.74-1.20)	-	-	-
	3rd	**1.42 (1.15-1.75)**	1.01 (0.84-1.22)	0.90 (0.70-1.15)	-	-	-
	4th	**1.31 (1.06-1.62)**	1.03 (0.85-1.26)	0.99 (0.77-1.28)	-	-	-
2nd Trimester	2nd	1.07 (0.88-1.31)	1.10 (0.91-1.32)	0.80 (0.63-1.00)	-	-	-
	3rd	1.10 (0.90-1.34)	1.06 (0.88-1.28)	0.83 (0.65-1.05)	-	-	-
	4th	1.14 (0.93-1.39)	1.04 (0.85-1.27)	0.84 (0.65-1.08)	-	-	-
3rd Trimester	2nd	1.05 (0.87-1.26)	0.95 (0.80-1.12)	1.03 (0.84-1.28)	-	-	-
	3rd	1.17 (0.97-1.40)	**0.80 (0.68-0.96)**	0.92 (0.74-1.16)	-	-	-
	4th	1.06 (0.88-1.28)	0.96 (0.81-1.15)	0.87 (0.69-1.10)	-	-	-
SO$_2$ (ppb)							
1st Month	2nd	0.97 (0.87-1.07)	1.02 (0.92-1.13)	**0.87 (0.76-0.99)**	0.97 (0.89-1.05)	1.02 (0.95-1.11)	0.97 (0.88-1.07)
	3rd	0.98 (0.88-1.09)	1.06 (0.95-1.18)	0.95 (0.83-1.09)	1.05 (0.96-1.14)	0.96 (0.89-1.04)	**0.88 (0.79-0.98)**
	4th	1.06 (0.94-1.19)	1.10 (0.97-1.24)	0.94 (0.79-1.10)	1.02 (0.93-1.12)	0.97 (0.88-1.07)	0.93 (0.82-1.05)
Last Month	2nd	1.01 (0.92-1.11)	0.98 (0.89-1.08)	1.04 (0.92-1.18)	**1.10 (1.02-1.19)**	1.05 (0.98-1.13)	**1.11 (1.01-1.22)**
	3rd	**0.86 (0.78-0.96)**	0.98 (0.89-1.09)	1.02 (0.89-1.17)	**1.13 (1.05-1.23)**	1.08 (1.00-1.17)	1.12 (1.00-1.24)
	4th	0.96 (0.86-1.08)	1.00 (0.89-1.12)	0.97 (0.82-1.13)	**1.12 (1.02-1.23)**	1.02 (0.93-1.12)	1.09 (0.96-1.23)
1st Trimester	2nd	1.01 (0.90-1.12)	1.05 (0.95-1.17)	1.01 (0.88-1.16)	-	-	-
	3rd	1.00 (0.89-1.11)	1.02 (0.91-1.15)	1.02 (0.88-1.19)	-	-	-
	4th	1.10 (0.95-1.26)	1.10 (0.95-1.26)	1.05 (0.88-1.26)	-	-	-
2nd Trimester	2nd	0.95 (0.86-1.06)	0.97 (0.88-1.08)	1.04 (0.91-1.19)	-	-	-
	3rd	0.90 (0.81-1.01)	0.94 (0.84-1.05)	1.01 (0.87-1.17)	-	-	-
	4th	0.98 (0.86-1.13)	1.08 (0.95-1.24)	1.09 (0.91-1.31)	-	-	-
3rd Trimester	2nd	1.01 (0.91-1.11)	1.05 (0.95-1.15)	1.09 (0.96-1.24)	-	-	-
	3rd	0.95 (0.86-1.06)	0.97 (0.87-1.08)	1.06 (0.92-1.21)	-	-	-
	4th	1.02 (0.90-1.16)	1.02 (0.90-1.16)	1.08 (0.91-1.28)	-	-	-

Table S2-13 (Cont.)

Windows and quartiles of exposures		SGA			PTB		
		<12 yrs	12 yrs	>12 yrs	<12 yrs	12 yrs	>12 yrs
		OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
NO_2 (ppb)							
1st Month	2nd	1.05 (0.94-1.17)	1.10 (0.97-1.23)	1.04 (0.89-1.22)	1.00 (0.92-1.09)	1.06 (0.97-1.16)	1.02 (0.90-1.14)
	3rd	1.10 (0.98-1.24)	1.09 (0.96-1.23)	0.93 (0.78-1.10)	1.04 (0.95-1.14)	1.03 (0.94-1.13)	1.01 (0.89-1.14)
	4th	1.08 (0.96-1.22)	1.13 (0.99-1.29)	1.16 (0.97-1.38)	1.08 (0.98-1.18)	1.01 (0.91-1.11)	0.93 (0.81-1.06)
Last Month	2nd	1.00 (0.90-1.11)	1.01 (0.90-1.13)	0.97 (0.83-1.13)	1.05 (0.96-1.14)	0.92 (0.85-1.01)	0.97 (0.87-1.09)
	3rd	0.93 (0.83-1.04)	0.99 (0.88-1.11)	1.16 (0.99-1.37)	1.05 (0.96-1.15)	0.93 (0.84-1.01)	1.00 (0.89-1.14)
	4th	0.95 (0.84-1.07)	0.90 (0.79-1.02)	1.05 (0.88-1.24)	1.05 (0.96-1.15)	0.90 (0.82-1.00)	0.99 (0.88-1.13)
1st Trimester	2nd	1.06 (0.94-1.19)	1.03 (0.92-1.17)	0.98 (0.83-1.16)	-	-	-
	3rd	1.10 (0.96-1.25)	0.99 (0.87-1.13)	1.08 (0.90-1.30)	-	-	-
	4th	1.10 (0.95-1.26)	1.02 (0.88-1.18)	1.05 (0.86-1.29)	-	-	-
2nd Trimester	2nd	0.96 (0.85-1.08)	1.04 (0.92-1.17)	0.92 (0.78-1.09)	-	-	-
	3rd	0.94 (0.82-1.07)	1.04 (0.90-1.19)	1.03 (0.86-1.25)	-	-	-
	4th	0.94 (0.82-1.09)	1.04 (0.90-1.21)	1.09 (0.89-1.34)	-	-	-
3rd Trimester	2nd	0.91 (0.82-1.02)	0.97 (0.87-1.08)	0.93 (0.80-1.09)	-	-	-
	3rd	0.97 (0.86-1.09)	0.98 (0.87-1.11)	1.06 (0.90-1.25)	-	-	-
	4th	0.97 (0.86-1.10)	1.00 (0.88-1.14)	1.07 (0.90-1.28)	-	-	-
PM_{10} ($\mu g/m^3$)							
1st Month	2nd	1.12 (0.81-1.54)	0.96 (0.76-1.22)	1.18 (0.89-1.56)	1.17 (0.90-1.52)	0.96 (0.79-1.15)	0.86 (0.69-1.08)
	3rd	1.12 (0.79-1.59)	0.96 (0.75-1.23)	1.01 (0.74-1.38)	1.28 (0.97-1.69)	0.99 (0.82-1.21)	1.04 (0.83-1.31)
	4th	1.34 (0.95-1.90)	1.16 (0.91-1.49)	1.04 (0.76-1.42)	1.12 (0.84-1.50)	1.02 (0.84-1.25)	1.04 (0.83-1.32)
Last Month	2nd	1.23 (0.91-1.67)	1.00 (0.79-1.25)	0.85 (0.65-1.12)	0.81 (0.64-1.03)	1.00 (0.84-1.19)	1.02 (0.83-1.25)
	3rd	1.20 (0.87-1.67)	1.25 (0.99-1.59)	0.83 (0.62-1.11)	**0.74 (0.56-0.96)**	0.83 (0.68-1.00)	1.09 (0.87-1.35)
	4th	1.21 (0.87-1.68)	1.10 (0.86-1.40)	0.96 (0.72-1.28)	0.89 (0.68-1.16)	0.97 (0.80-1.17)	0.97 (0.77-1.22)
1st Trimester	2nd	0.92 (0.66-1.29)	0.92 (0.71-1.18)	**1.57 (1.15-2.14)**	-	-	-
	3rd	0.87 (0.61-1.25)	1.12 (0.86-1.45)	1.25 (0.89-1.74)	-	-	-
	4th	0.98 (0.68-1.39)	1.10 (0.84-1.44)	**1.44 (1.02-2.04)**	-	-	-
2nd Trimester	2nd	0.94 (0.67-1.33)	1.27 (0.98-1.64)	**1.44 (1.06-1.96)**	-	-	-
	3rd	0.98 (0.68-1.40)	**1.40 (1.08-1.82)**	1.18 (0.85-1.64)	-	-	-
	4th	0.97 (0.67-1.41)	0.99 (0.75-1.31)	1.19 (0.85-1.67)	-	-	-
3rd Trimester	2nd	0.97 (0.69-1.36)	1.16 (0.90-1.49)	1.00 (0.73-1.35)	-	-	-
	3rd	1.23 (0.87-1.74)	**1.36 (1.04-1.76)**	1.13 (0.82-1.56)	-	-	-
	4th	1.06 (0.74-1.50)	**1.34 (1.03-1.75)**	1.23 (0.89-1.69)	-	-	-

Table S2- 14. Infant and maternal characteristics by birth outcomes and ethnicity, 1990-2001.

Characteristics		All births* N=164905 (%)	LBW N=6106 (%)	SGA N=13754 (%)	PTB N=24954 (%)	Term births N=139951 (%)	Black N=93078 (%)	White N=68164 (%)
Infant sex	Female	49.1	58.8	49.1	47.8	49.3	49.3	48.8
	Male	50.9	41.3	51.0	52.2	50.7	50.6	51.2
Race	Black	56.4	71.4	69.1	71.1	53.8	-	-
	White	41.3	26.7	28.6	27.1	43.9	-	-
	Other	2.2	1.9	2.3	1.8	2.3	-	-
Age (yrs)	16-19	17.4	19.2	19.8	19.8	17.0	22.0	11.6
	20-29	58.1	52.9	55.4	54.0	58.8	57.4	59.1
	≥30	24.5	27.9	24.8	26.2	24.2	20.6	29.3
Education (yrs)	0-11	32.9	41.2	40.5	39.5	31.7	36.2	28.4
	12	40.0	38.4	38.5	38.9	40.2	39.0	41.9
	≥13	27.1	20.4	21.0	21.7	28.1	24.8	29.7
Tobacco use	Smoker	21.8	38.3	35.7	27.0	20.9	19.3	26.0
Prenatal care	None	3.4	6.9	5.4	7.5	2.7	4.8	1.7
	Late (after 4th month)	26.0	32.8	31.8	35.9	24.3	32.7	17.2
Birth season	Spring (Mar-May)	25.2	25.2	24.8	25.1	25.3	25.0	25.7
	Summer (Jun-Aug)	26.1	26.0	26.2	25.7	26.2	26.0	26.3
	Fall (Sept-Nov)	24.1	23.2	23.7	23.8	24.2	23.8	24.5
	Winter (Dec-Feb)	24.6	25.6	25.3	25.5	24.4	25.2	23.6
Birth period	1990-1993	39.5	43.7	43.4	40.6	39.3	41.1	37.7
	1994-1997	31.3	29.2	29.7	31.0	31.3	31.0	31.5
	1998-2001	29.3	27.1	26.9	28.5	29.4	28.0	30.8

Abbreviations: LBW, low birth weight; SGA, small for gestational age; PTB, preterm births; (*) All births included Blacks, Whites and others.

Table S2- 15. Adjusted odds ratio and 95% confident interval (95% CI) for each window of exposure to air pollutants for low birth weight (LBW).

Windows and quartiles of exposures		CO Adjusted[a]	CO Trend-adjusted[b]	SO$_2$ Adjusted[a]	SO$_2$ Trend-adjusted[b]	NO$_2$ Adjusted[a]	NO$_2$ Trend-adjusted[b]	PM$_{10}$ Adjusted[a]	PM$_{10}$ Trend-adjusted[b]
1st month	2nd	**1.23 (1.07-1.43)**	1.11 (0.94-1.31)	1.03 (0.94-1.13)	1.01 (0.92-1.11)	1.05 (0.95-1.17)	1.06 (0.95-1.17)	0.89 (0.69-1.15)	0.91 (0.70-1.17)
	3rd	1.15 (0.99-1.33)	1.01 (0.85-1.19)	**1.12 (1.02-1.23)**	1.09 (0.99-1.20)	**1.14 (1.02-1.27)**	**1.14 (1.03-1.28)**	1.07 (0.83-1.38)	1.08 (0.83-1.40)
	4th	**1.20 (1.03-1.39)**	1.07 (0.90-1.26)	**1.24 (1.13-1.37)**	**1.16 (1.04-1.30)**	1.09 (0.97-1.22)	1.12 (1.00-1.26)	1.19 (0.92-1.54)	1.17 (0.90-1.52)
Last month	2nd	1.06 (0.92-1.21)	0.96 (0.82-1.11)	1.06 (0.97-1.15)	1.02 (0.94-1.12)	0.98 (0.89-1.09)	0.99 (0.89-1.09)	**1.28 (1.01-1.62)**	1.28 (1.00-1.62)
	3rd	1.13 (0.99-1.30)	1.01 (0.86-1.17)	1.00 (0.92-1.10)	0.95 (0.86-1.04)	0.95 (0.85-1.05)	0.95 (0.85-1.05)	1.14 (0.89-1.47)	1.12 (0.86-1.45)
	4th	1.11 (0.96-1.29)	0.99 (0.85-1.16)	**1.11 (1.01-1.22)**	0.98 (0.88-1.09)	**0.88 (0.79-0.99)**	0.91 (0.81-1.01)	1.22 (0.95-1.58)	1.15 (0.89-1.50)
1st trimester	2nd	**1.21 (1.05-1.41)**	1.12 (0.94-1.34)	1.10 (1.00-1.21)	1.08 (0.98-1.19)	0.99 (0.89-1.10)	1.00 (0.90-1.12)	1.02 (0.79-1.32)	1.00 (0.76-1.32)
	3rd	**1.20 (1.03-1.39)**	1.07 (0.90-1.28)	1.06 (0.96-1.17)	1.03 (0.93-1.15)	1.06 (0.94-1.19)	1.08 (0.96-1.22)	0.91 (0.69-1.20)	0.90 (0.67-1.20)
	4th	1.10 (0.94-1.29)	1.00 (0.84-1.20)	**1.29 (1.17-1.42)**	**1.23 (1.08-1.39)**	0.95 (0.83-1.08)	1.01 (0.88-1.15)	1.21 (0.93-1.57)	1.11 (0.83-1.47)
2nd trimester	2nd	1.15 (0.99-1.34)	1.06 (0.89-1.26)	0.93 (0.85-1.02)	0.91 (0.83-1.00)	0.94 (0.84-1.04)	0.94 (0.84-1.05)	1.17 (0.90-1.51)	1.17 (0.89-1.54)
	3rd	**1.18 (1.02-1.37)**	1.06 (0.89-1.26)	0.93 (0.85-1.03)	**0.89 (0.81-0.99)**	0.97 (0.86-1.10)	1.00 (0.88-1.13)	1.12 (0.85-1.47)	1.10 (0.83-1.47)
	4th	**1.24 (1.06-1.45)**	1.12 (0.93-1.34)	**1.16 (1.05-1.28)**	1.05 (0.93-1.19)	0.97 (0.85-1.10)	1.04 (0.91-1.19)	1.09 (0.84-1.42)	0.97 (0.73-1.30)
3rd trimester	2nd	1.05 (0.91-1.21)	0.93 (0.80-1.08)	1.09 (1.00-1.19)	1.06 (0.97-1.16)	**0.90 (0.81-0.99)**	0.91 (0.82-1.00)	0.95 (0.74-1.23)	0.91 (0.70-1.18)
	3rd	1.07 (0.93-1.23)	0.93 (0.80-1.08)	1.04 (0.95-1.14)	0.99 (0.90-1.09)	**0.87 (0.78-0.97)**	**0.88 (0.79-0.98)**	0.96 (0.74-1.26)	0.92 (0.69-1.21)
	4th	1.07 (0.92-1.24)	0.94 (0.80-1.10)	**1.21 (1.10-1.33)**	1.08 (0.96-1.21)	0.90 (0.80-1.01)	0.94 (0.84-1.06)	1.17 (0.91-1.50)	1.03 (0.79-1.36)

[a]*Adjusted for sex, gestational age, race, maternal age groups, education levels, tobacco use, prenatal care, birth seasons and site of residency.*

[b]*Adjusted for variables above and birth periods.*

Table S2- 16. Results of the multipollutant model (including CO, SO_2, NO_2 and PM_{10}) for LBW at the Linwood area.

Otherwise as Table 2S-14.

Window of exposure/ Quartile of exposure		CO	SO_2	NO_2	PM_{10}
		OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
1st month	2nd	1.05 (0.84-1.31)	1.05 (0.80-1.39)	1.14 (0.91-1.44)	1.02 (0.87-1.19)
	3rd	0.91 (0.72-1.14)	1.16 (0.89-1.50)	1.21 (0.97-1.50)	1.07 (0.90-1.28)
	4th	0.93 (0.75-1.16)	1.16 (0.89-1.52)	**1.30 (1.04-1.63)**	1.08 (0.90-1.30)
Last month	2nd	0.96 (0.78-1.19)	1.17 (0.90-1.51)	1.04 (0.84-1.28)	1.00 (0.86-1.15)
	3rd	1.05 (0.85-1.30)	1.04 (0.81-1.33)	1.01 (0.82-1.23)	0.98 (0.83-1.16)
	4th	1.01 (0.82-1.25)	1.09 (0.84-1.41)	1.05 (0.85-1.30)	0.88 (0.75-1.04)
1st trimester	2nd	**1.35 (1.04-1.76)**	1.30 (0.91-1.87)	0.92 (0.67-1.28)	1.11 (0.92-1.33)
	3rd	**1.32 (1.01-1.73)**	1.02 (0.77-1.36)	0.95 (0.69-1.30)	1.16 (0.95-1.42)
	4th	1.17 (0.89-1.54)	1.25 (0.94-1.66)	0.94 (0.68-1.30)	1.16 (0.95-1.41)
2nd trimester	2nd	1.20 (0.92-1.55)	0.98 (0.67-1.44)	1.22 (0.82-1.81)	1.15 (0.94-1.42)
	3rd	1.14 (0.87-1.50)	0.99 (0.74-1.33)	1.29 (0.87-1.91)	0.97 (0.79-1.19)
	4th	1.22 (0.93-1.59)	1.00 (0.75-1.34)	1.49 (1.00-2.24)	1.13 (0.92-1.40)
3rd trimester	2nd	0.96 (0.76-1.20)	1.11 (0.82-1.52)	1.19 (0.93-1.53)	0.89 (0.74-1.07)
	3rd	1.01 (0.81-1.27)	1.17 (0.88-1.54)	1.03 (0.80-1.34)	0.87 (0.72-1.05)
	4th	0.99 (0.79-1.24)	1.24 (0.92-1.66)	1.12 (0.86-1.46)	**0.82 (0.69-0.98)**

Table S2- 17. Adjusted odds ratio and 95% confidence interval (95% CI) for each window of exposure to air pollutants for small for gestational age (SGA) and preterm birth (PTB). No adjustment for maternal smoking.

Windows and quartiles of exposures			CO	SO$_2$	NO$_2$	PM$_{10}$
			OR (95% CI)	OR (95% CI)	OR (95% CI)	OR (95% CI)
SGA	1st month	2nd	**1.13 (1.01-1.25)**	0.96 (0.90-1.02)	1.06 (0.99-1.14)	1.09 (0.93-1.27)
		3rd	1.01 (0.90-1.13)	1.00 (0.94-1.07)	1.06 (0.99-1.15)	1.02 (0.87-1.21)
		4th	**1.15 (1.02-1.28)**	1.06 (0.98-1.14)	**1.11 (1.02-1.20)**	1.18 (1.00-1.40)
	Last month	2nd	1.02 (0.92-1.13)	1.01 (0.95-1.07)	0.99 (0.93-1.06)	1.00 (0.86-1.16)
		3rd	1.03 (0.93-1.15)	0.94 (0.88-1.00)	1.01 (0.94-1.08)	1.07 (0.92-1.26)
		4th	1.00 (0.90-1.12)	0.99 (0.92-1.07)	0.95 (0.88-1.03)	1.09 (0.93-1.28)
	1st trimester	2nd	1.11 (0.99-1.25)	1.03 (0.96-1.09)	1.02 (0.95-1.10)	1.06 (0.90-1.25)
		3rd	1.11 (0.98-1.25)	1.02 (0.95-1.09)	1.05 (0.96-1.14)	1.07 (0.90-1.28)
		4th	1.11 (0.98-1.26)	**1.11 (1.02-1.21)**	1.05 (0.96-1.15)	1.15 (0.96-1.37)
	2nd trimester	2nd	1.02 (0.91-1.14)	0.98 (0.92-1.04)	0.97 (0.91-1.05)	**1.25 (1.06-1.48)**
		3rd	1.03 (0.91-1.15)	0.93 (0.87-1.00)	1.00 (0.92-1.08)	**1.24 (1.04-1.48)**
		4th	1.04 (0.92-1.18)	1.05 (0.97-1.14)	1.00 (0.92-1.10)	1.07 (0.89-1.28)
	3rd trimester	2nd	1.02 (0.92-1.13)	1.05 (0.98-1.11)	0.93 (0.87-1.00)	1.05 (0.89-1.24)
		3rd	0.98 (0.88-1.09)	0.98 (0.92-1.05)	0.99 (0.92-1.07)	**1.24 (1.05-1.48)**
		4th	1.01 (0.91-1.13)	1.05 (0.97-1.14)	1.01 (0.93-1.09)	**1.22 (1.03-1.45)**
PTB	1st month	2nd	0.97 (0.90-1.06)	0.99 (0.94-1.04)	1.02 (0.97-1.08)	0.97 (0.86-1.10)
		3rd	1.00 (0.92-1.09)	0.97 (0.93-1.03)	1.03 (0.98-1.10)	1.06 (0.93-1.21)
		4th	0.96 (0.88-1.05)	0.99 (0.93-1.05)	1.02 (0.96-1.08)	1.05 (0.92-1.20)
	Last month	2nd	1.05 (0.97-1.13)	**1.08 (1.03-1.13)**	0.98 (0.93-1.03)	0.95 (0.85-1.07)
		3rd	0.97 (0.89-1.05)	**1.11 (1.05-1.16)**	0.99 (0.94-1.05)	**0.87 (0.77-0.99)**
		4th	1.04 (0.96-1.13)	**1.08 (1.02-1.15)**	0.98 (0.92-1.04)	0.94 (0.83-1.06)

Adjusted for sex, gestational age, race, maternal age groups, education levels, prenatal care, birth season, site of residency and birth periods.

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Chapter 3

Apportionment of Air Toxics and Emergency Department Visits for Respiratory Illness among Dearborn, Michigan Children

3.1   Abstract

Asthma morbidity has been associated with exposure to a number of ambient air pollutants; however, effects of exposure to urban air toxics (UATs) remain poorly understood. Monitoring for this class of pollutants has been limited, and available data are generally inadequate to support epidemiological studies. This study uses exposure measures for UATs, derived using source apportionment techniques, to evaluate acute effects of UATs on health care utilization of children living near an ambient air quality monitoring site in the Dearborn, Michigan area.

Health outcomes investigated included emergency department (ED) visits for asthma and respiratory problems of 7,863 children living within 10 km of the Dearborn monitoring site and enrolled in Medicaid for the one year study period. After an analysis of quality assurance issues of the daily UAT data, based largely on 122 pairs of replicate samples, missing data were imputed, and exposures were expressed as concentrations of individual pollutants as well as scores derived from factor analysis and positive matrix factorization (PMF) models that represented contributions from source classes. Rate ratios (RR) of ED visits for exposures to source-specific UATs for the current and previous 1, 2, 3 and 4 days were estimated using Poisson regression models adjusted for temperature, pressure, relative humidity, season, day-of-week, and $PM_{2.5}$ concentration.

Of the 71 UAT compounds measured, only 23 were frequently detected or had at least fair reproducibility. These measurements were distilled to five source classes using

PMF. The rate of ED visits for respiratory problems increased among those children in the highest exposure quartile for fuel combustion sources (RR=1.44 and 95% confidence interval=1.03-2.01), photochemical pollutants (1.48, 1.15-1.90), and gasoline exhaust/evaporated gasoline (1.35, 1.05-1.74) compared to those in the lowest exposure quartile. Effects were stronger for subjects living closer (within 4 km) of the air monitoring site. No statistically significant associations were found between exposures to criteria pollutants, or between UAT exposures and injury, an outcome used as a control. This study suggests that respiratory health effects are caused by exposure to pollutants associated with several common sources, and that the use of exposure measures based on source apportionments can provide a powerful technique for investigating health effects of toxic air pollutants.

3.2 Introduction

Many studies have linked exacerbations of asthma to exposures of "criteria" air pollutants, including particulate matter ($PM_{2.5}$ and PM_{10}), ozone (O_3), carbon monoxide (CO), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2).[1-6] In contrast, very few studies have examined or linked asthma (and respiratory health in general) with exposure to a group of pollutants known as urban air toxics (UAT),[7] which include carbonyls, volatile organic compounds (VOC), semivolatile organic compounds, metals, and several pollutant mixtures. Exposures to several UATs have been estimated to increase risks of adverse respiratory system effects for nearly all (92%) of the U.S. population.[8] Most of our understanding of the health impacts of UATs is based on occupational studies, which likely have limited applicability to environmental exposures for several reasons, e.g., the high concentrations, simple exposures (i.e., single pollutant) and healthy worker effect.

UAT monitoring is uncommon, and typically integrated 24-hour measurements are taken on a periodic basis, e.g., every 6th day. Hourly measurements of UAT are rarely available. Further, each type or class of air toxics requires a different sampling and analysis approach.

The lack of continuous UAT data makes it difficult for epidemiological studies to investigate these pollutants in relation to health risks. Current occupational and community-based studies are limited by the accuracy of self-reported information about

exposures (i.e. job-exposure matrices) and inability to capture mixed pollutant exposure.[9]

For most individuals, UAT exposures occur as mixtures at low concentrations. Given the importance of mixtures, exposure indicators for UATs might utilize source class contributions derived using receptor models which utilize a mass balance analysis to identify and apportion sources of ambient air pollutants. In comparison to the use of one or possibly several pollutants, such indicators may provide greater ability to ascertain impacts as well as enhance the ability to implement effective interventions, advantageous to both regulatory and health service agencies. For example, exposures to benzene, a common and well-known toxicant and carcinogen, may be reduced by controlling automobile exhaust. It is possible that indicators of automobile exhaust may be more strongly correlated with health impacts than benzene alone..

This chapter presents a study of the relationship between UAT exposures and utilization of urgent care facilities for asthma and respiratory disease. A time-series analysis is used to link daily health care utilization to both source-apportioned exposure measures and individual pollutant concentrations. Information regarding quality assurance, reproducibility and imputation of missing UAT data is discussed in Chapter 4 and in a published paper (Appendix 2).[10] Detailed information regarding receptor modeling and the source apportionments used in this chapter is discussed in Appendix 1.

3.3   Background

3.3.1   Sources, characteristics, and types of urban air toxics

The 1990 Clean Air Act Amendments listed 188 hazardous air pollutants (HAPs), also known as "air toxics," which include several classes of pollutants.[7] UATs, one of these classes defined by the U.S. Environmental Protection Agency, include volatile organic compounds (VOCs), very volatile organic compounds, semivolatile organic compounds, aldehydes, metals, and several mixtures including diesel exhaust. Ambient air quality monitoring for UATs is relatively uncommon, and typically only a few species are measured on an intermittent basis, e.g., every sixth day.

The origin, transport, and behavior of UATs in the atmosphere can be complex. UATs originate from both natural (e.g., volcano, ocean spray, wind erosion, biogenic activity) and anthropogenic (industrial, domestic, agricultural) processes.[11] Most UATs

originate from man-made sources, which include mobile (e.g., cars, trucks, aircraft) and stationary sources (e.g., power plants, refineries, factories). In cases, natural sources (e.g., volcanic eruption, forest fires) can be important. In the U.S., about 4.7 million tons of HAPs were emitted in 1996, with 51% from mobile sources, 25% from area sources, and 24% from industrial sources.[12] Since most sources emit multiple pollutants, exposures nearly always represent mixture of pollutants. As noted below, the toxicity of UATs and UAT mixtures vary, depending on the concentration and the chemical and physical composition.

3.3.2 Urban air toxics and respiratory health effects

Respiratory health effects due to environmental exposures of air toxics have not been extensively studied, especially in children. In large part, this is due to the lack of UAT data at appropriate spatial and temporal scales for epidemiological studies.

Most of the existing studies examining respiratory health effects and UATs have focused on VOCs. Among a representative U.S. adult population studied in the National Health and Nutrition Examination Survey (1999-2000), personal exposures to aromatic VOCs were associated with physician-diagnosed asthma and wheezing attacks.[13] In their review, Schenker and Jacobs (1996) concluded that exposures to organic solvents may cause respiratory symptoms or impaired pulmonary function in the general population, and that exposure to formaldehyde above 5 ppm in occupational settings was associated with asthma.[9] In a randomized, crossover-design study of controlled adult human exposures to VOCs mixtures (including 21 compounds) similar to those found indoors, Pappas et al. (2000) found that 4 hr exposures to concentrations >25 mg/m^3 increased both lower and upper respiratory symptoms.[14] Ambient VOC exposures were associated with respiratory health effects in school age children (third to fifth grade) in Kanawha County, West Virginia.[15] This study found that a 10 μg/m^3 increase in petroleum-related compounds (toluene, m,p-xylene, benzene, o-xylene and decane) was associated with bronchitis, persistent wheezing, physician's diagnosis of asthma, lower respiratory symptoms, and chronic lower respiratory response, while a 2 μg/m^3 increase in process-related compounds (1,1,1-trichloroethane, carbon tetrachloride, 1-butanol, chloroform, perchloroethylene, methyl isobutyl ketone, etc.) was associated with lower respiratory

symptoms and chronic lower respiratory response. In a more recent study among children between 10 to 15 yrs of age with mild asthma in a Los Angeles community, petroleum-related VOCs (toluene, m,p-xylene, o-xylene and benzene) were associated with self-reported asthma symptoms (peak expiratory flow rate was also measured by the children).[16] Although this study found that VOCs monitored in breath were weakly correlated to ambient levels, ambient VOCs can be used to indicate exposure to combustion-related compounds. Using a survey instrument, a study in Anchorage, Alaska, young children (5-7 yrs) exposed to traffic-related air pollutants (VOCs and coarse fraction particulate matter) showed increased risk of asthma.[17] In Atlanta, Georgia, children less than 18 yrs of age with diagnosed asthma made more frequent visits to an ambulatory care setting after earlier (past 2 days) exposures to outdoor polar VOCs.[18] In Belfast, Northern Ireland, ambient benzene levels were associated with ED admissions for children with asthma, after controlling for exposures to criteria air pollutants (SO_2, NO_2, NO, CO, O_3), temperature and rainfall.[19] This study did not account for exposure to other air toxics. In a case-control study in Perth, Australia, young children (1/2 – 3 years of age) experiencing indoor VOC at concentrations above 60 $\mu g/m^3$ were four times more likely to have asthma compared to children with lower exposures.[20]

Most of the exposure measures used in the literature, including the studies just mentioned, have utilized individual pollutant species, groups of related pollutants, or total concentrations of all pollutants in the class. Such measures may not adequately reflect the actual health effects of mixed pollutant exposures. For example, the West Virginia study identified two source indicators for VOC exposure, namely, petroleum-related and process-related compounds, by grouping together a small number of pollutants from similar sources.[15] This approach may have the advantage of utilizing *a priori* information, but it may not be efficient because collinearity is not accounted for and the source(s) must be known. Another limitation in using *a priori* source identification are the inconsistencies that result between studies. For example, traffic-related exposures were defined in the Los Angeles study[16] using a few VOCs, while the Alaskan study[17] included both VOCs and coarse particulate matter. Another problem is the varying composition of toxic pollutants emitted from different sources types, which may alter the

toxicity of the mixture.

UAT exposures also occur due to indoor sources, and the types and concentrations of pollutants can vary between indoor and outdoor microenvironments.[21] For example, in inner-city New York City, formaldehyde and acetaldehyde indoor (home) levels exceeded outdoors, but vehicle-related VOCs (benzene, toluene, ethylbenzene, xylenes, and tert-butyl ether) were consistent in both environments.[22]

Health effects studies could benefit from exposure assessment approaches that identify the sources of UATs and help capture exposures to mixtures. The use of receptor model-based apportionments, described next, provides a promising approach for this task.

3.3.3 Receptor modeling

The fundamental principle of receptor modeling (RM) is that a mass balance analysis can be used to identify and apportion sources of ambient air pollutants.[23] This allows source-specific contributions to be identified and quantified on the basis of matching ambient concentrations with the chemical (and sometimes physical) characteristics of source emissions. While RMs have been widely used for apportioning ambient particulate matter, there are relatively few applications for VOCs and carbonyls, and fewer still using RM results in epidemiological investigations.

There are two types of receptor models, chemical mass balance (CMB) and multivariate. In CMB models, information of the composition of emissions, the source "profile," from all contributing source types is required. This need for complete (and accurate) profiles is a limitation associated with CMB models.[24] Additionally, CMB models do not treat profiles that change between source and receptor.[25] Sometimes, CMB models are viewed as complementing rather than replacing other analysis and modeling methods. So called "multivariate" models provide an alternative to CMB models. These models estimate the number and composition of sources, as well as their contributions to measured concentrations of air pollutants. Multivariate models utilize factor analysis, eigenvector analysis and related methods. A popular technique, called positive matrix factorization (PMF), ensures that derived source profiles are non-negative, which is required for physical interpretation.[26,27] PMF also allows the use of weights or uncertainties for individual data points. PMF has been used successfully to

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apportion particulate matter and VOCs.[28-32] Further information regarding this method is presented in Appendix 1.

3.3.4 Receptor modeling and epidemiology

Very few epidemiological studies have used source apportionment techniques, although it has been suggested that these methods can provide insight into those sources that affect health.[32-34] The use of source-apportioned exposures is attractive for several reasons: increased statistical power since the exposure measures may be more strongly associated with health impacts; the correlation in the larger pollutant data set is used to derive a smaller number of potentially more robust exposure measures; and the enhanced biological plausibility and relevance of the exposure measure since most toxic exposures occur as mixtures from a variety of sources.

3.3.5 Case study area

Asthma is the number one reason for preventable hospitalizations among Michigan children,[35] and it has an even greater impact on the city of Detroit.[36,37] The overall pediatric hospitalization rate in Detroit (70/10,000) was three times higher than the state rate (23/10,000) in 2001, and over four times higher than the Healthy People 2010 target (17/10,000). Also in 2001, the rate of emergency department visits for asthma among Medicaid-only beneficiaries less than 14 years of age in Wayne County was 352/10,000 and the rate of hospital admissions for asthma was 96/10,000. Detroit experiences a greater burden of asthma than the state as a whole in part due to its demographic and socioeconomic composition, since low socioeconomic status and minority race are risk factors for asthma. A recent pilot study at an inner-city children's hospital in Detroit reported 61,443 and 71,044 visits by children to the ED in 2001 and 2002, respectively, representing 50.83%, 9.43% and 39.74% of the children enrolled in Medicaid, children who were uninsured, and children with other insurance.[38] Detroit's population is 81.6% African American, over 21% of families with children <18 years live in poverty, and over 30% of the population aged 25 and older have not received their high school diploma.

The Detroit area contains major industries, e.g., the 1,100 acre Ford Rouge facility (one of the world's largest industrial complexes with foundries, casting,

machining, coating, and fabrication plants), and numerous other industries, e.g., chemical, refinery, plastics production, specialty steel production, waste disposal, chemicals, trucking, meat packing, etc. Due to high pollutant levels (based on 2004-2006 measurements), the area was designated as non-attainment for the annual PM_{10} and annual $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS).[39,40] The Toxic Release Inventory System shows that Michigan ranks ninth among states for air emissions of benzene. In Wayne County, the ten facilities with the largest toxic releases are located within a single zip code (48121) in the "South End" of Dearborn, in which total emissions of toxic air pollutants exceeded 1.5 M lbs in 1995. The study area also includes sizable train and truck traffic, including intermodal activities, and, in the last several years, its proximity to the international border and additional security checks have caused considerable concern regarding emissions from the large number of diesel trucks idling on freeways ramps near the bridge and tunnels to Canada. Based on EPA's 1999 National Air Toxics Assessment (NATA), Wayne County and the greater Detroit area were ranked in the highest 5% of counties in the country with regard to risks from air toxics and diesel particulate matter.

3.4 Methods

3.4.1 Health outcomes data

In-patient hospital admissions and emergency department/urgent care (ED) visits for asthma and respiratory problems between 4/19/2001 and 4/18/2002 for children residing near the Dearborn monitoring site were identified from the Medicaid beneficiary database using an adaptation of the Healthcare Effectiveness Data and Information Set (HEDIS) case definition for persistent asthma.[41] HEDIS is widely used by Medicaid and commercial health plans as well as health outcomes studies to measure performance on important dimensions of care and service.[42,43] ED visits for injury, representing claims believed to be unrelated to air pollutants, were identified and used as a control case. Out-patient visits, which include both unscheduled/urgent care visits and scheduled check-ups/well-child visits, were excluded because the purpose of these visits could not be distinguished.

Claims were classified using the primary diagnosis into two categories: respiratory disease, including symptoms involving the respiratory system (ICD-9 codes 460-519 and 786.x); and injury (ICD-9 codes 800-999). Additional claimant information available in and obtained from the Medicaid files included an encrypted identifier for the child, child age, sex, race/ethnicity, date of service, residence location (street address and geocoded coordinates), and provider information (e.g., address).

ZIP codes in which 60% of the population fell within a 10 km radius of the Dearborn air monitor were determined using a geographic information system. This monitor was selected for this study because a special year-long study took daily measurements – daily measurements of air toxics are highly unusual. Duplicates were removed and data was collapsed into a SAS file. Place of residence was mapped within ZIP codes to remove records that fell outside the study area. Urgent care visits that occurred within 7 days of the initial visit were removed to obtain a set of independent urgent events. Visits that occurred within 7 days for the same individual could be related to the same trigger and were regarded as possible "treatment failures".

Criteria for eligibility in the study included living within 10 km of the Dearborn monitoring site (using the geocoded home location) during the study period, being less than or equal 18 years of age, and having medical insurance provided solely by Medicaid. (Children having health insurance in addition to Medicaid were excluded.) To investigate effects of residential proximity to the air-monitoring site, a second analysis was restricted to children residing within 4 km of the monitoring site. Eligible claims were further processed to exclude services received at out-of-state locations (based upon provider location), and to remove duplicate claims. Counts of the daily number of hospital admission and ED visits were then determined for each diagnosis category.

Health care data utilization for the year following the main study period (April 2002 – April 2003) were also collected and processed as described above in order to determine whether the study year was representative, i.e., whether counts were typical on an annual and seasonal level.

3.4.2 Exposure assessment

Dearborn, Detroit is a diverse airshed that contains many types of point and

mobile emission sources. The area also experiences highly variable meteorology patterns, strong shifts in seasonal heating and cooling requirements, and a high population density.[44] These features tend to increase concentrations of toxic pollutants, and also produce substantial temporal variation in daily exposures. Many of these features are paralleled at other sites in the U.S. and elsewhere, although the density of the interspersed industry and population is somewhat unusual.

Daily air quality data were obtained from the Dearborn, Michigan monitoring site (Site ID: 261630033), which was operated by Michigan Department of Environmental Quality (MDEQ), for the period from 4/19/2001 to 4/18/2002. The site is located in a residential neighborhood near an elementary school and industrial area of automobile and steel manufacturing. The site also lies within approximately 2 km of I-75 and I-94 interstate highways, two of the largest commuter and trucking routes in the region, and it formed part of the Detroit Air Toxics Pilot Project.[39]

Volatile organic compounds (VOCs) were collected in canisters following EPA method TO-15,[45] and carbonyl compounds were collected using DNPH cartridges and analyzed by HPLC following EPA method TO-11A.[46] Most samples were shipped to the Eastern Research Group (ERG, Research Triangle Park, NC, USA) for analysis. The monitoring program included extensive quality assurance (QA) activities, including the collection of co-located samples every third day during the sampling period, with analysis by the MDEQ laboratory (Lansing, MI, USA).

Our previous analysis indicated several issues regarding QA and intra- and inter-laboratory reproducibility for many of the compounds measured at Dearborn.[10] In brief, we saw good agreement for only one compound (benzene), moderate agreement for several other VOCs (e.g., trimethylbenzene, xylenes, ethylbenzene, dichlorodifluoromethane, tetrachloroethylene, and toluene), and poor-to-fair agreement for the remaining VOCs and all carbonyls (Appendix 1). To help ensure that the measurements used in the present study were meaningful, we selected 16 of the 59 VOCs and 7 of the 13 carbonyls measured using four screens: (1) overall detection frequency $\geq 20\%$; (2) identification and elimination of outliers using the maximum Gumbell distribution; (3) intra-laboratory agreement demonstrated by a Spearman rank correlation

coefficient $\geq$0.2; and (4) inter-laboratory reproducibility demonstrated by a Spearman rank correlation coefficient $\geq$0.2. Duplicate samples were averaged, and measurements falling below the method detection limit (MDL) were set to ½ MDL. Table 3-1 lists descriptive statistics of the toxics dataset used in this study.

To help evaluate the receptor modeling, we also obtained ambient metals data (arsenic, beryllium, cadmium, chromium, lead, manganese and nickel), which were monitored every 6th day at the Dearborn site. Due to sampling schedule and relatively small sample size, these data were not used in the final health models.

Because exposures to criteria air pollutants have been linked to respiratory problems among children and adults,[1-6] parallel analyses were conducted using criteria pollutants as exposure measures and both single and multiple pollutant models. Criteria air pollutant data were obtained for three nearby sites (within 20 km): Allen Park (CO, O_3 and $PM_{2.5}$), East Seven Mile (NO_2, O_3 and SO_2), and Linwood (CO, NO_2, O_3, $PM_{2.5}$ and SO_2). These pollutants are monitored by MDEQ using federal reference methods. In Michigan, O_3 is monitored for only 6 months (the so-called O_3 season from April to September). Therefore, hourly O_3 data from downtown Windsor, Canada (within 20 km of the Dearborn site), which is monitored year-round, were obtained. The annual health models for O_3 used the Windsor data. Daily (24-hr) averages were computed for hourly CO, NO_2 and SO_2 data, and 8-hr moving averages were computed for hourly O_3, if $\geq$75% of hourly observations were available and considered valid. $PM_{2.5}$ is measured in 24-hr increments and does not require 24-hr average calculations. In addition, daily meteorological data (temperature, relative humidity, barometric pressure) at Detroit Metro Airport were obtained from the National Oceanic and Atmospheric Administration through online electronic sources.[47]

3.4.3   Receptor modeling

Source apportionments of the toxics dataset used positive matrix factorization (PMF) version 1.1.[48]   (Complete modeling details are provided in Appendix 1.) Based on previous work apportioning $PM_{2.5}$, a pollutant species was considered as "bad," "weak" or "good" if its signal/noise (S/N) ratio was <0.2, between 0.2 and 2, or $\geq$2, respectively.[49-51] Bad species were excluded from analysis, and weak species were

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down-weighted. A total of 20 random starting points were performed to determine the global minimum. The optimum run was selected by examining the robust Q values of all the random runs. (The Q value is the sum of square measures used to quantify model fit.)

The final number of sources was selected using PMF, principal component analysis (PCA), annual and seasonal modeling, and modeling incorporating the additional metals information. Initially, the number of eigenvalues exceeding one obtained from PCA was used as a guideline to determine the number of sources. The final number of sources was based on the overall model fit (measured by the root mean square error [RMSE] and the coefficient of determination [R^2]). For example, if the R^2 and RMSE values of the five- and six-source models were similar, then the five-source model was considered as the final model.

Daily contributions estimated for each source class in the PMF model were expressed in quartiles for the health models. Five exposure windows were used to account for possible time lags between exposure and health response: (1) no lag (same day as the health outcome); (2) prior day; (3) average of the two prior days, called average 2-day lag; (4) average 3-day lag; and (5) average 4-day lag. Each of the lagged exposure estimates required at least one valid exposure score during the lag period.

3.4.4 Statistical analyses

After merging the daily source class-specific exposure scores and the daily counts of health outcomes for children residing near the Dearborn site, adjusted rate ratios (ARRs) and 95% confidence intervals (CIs) for each outcome were estimated using Poisson regression models. Each ARR represents the effect of a source-specific UAT exposure in the second, third and fourth (highest) exposure quartiles relative to the first (lowest) exposure quartile.

To control for covariates and possible confounding, models were adjusted for day-of-week, calendar month, and daily meteorology (ambient temperature, relative humidity and pressure). Day-of-week may influence the caregiver's decision to bring their children to the emergency room if the condition is not life threatening. Due to the study's short duration (one year) and relatively small sample size, control for calendar month was intended to control for seasonal adjustments. Daily meteorological variables

were detrended by subtracting the monthly mean from the daily values.

Initially, single source/pollutant models were constructed. Next, $PM_{2.5}$ data (from Allen Park) were included in the model, since this is a recognized risk factor for respiratory outcomes.[2] $PM_{2.5}$ and meteorological variables used the same five exposure windows as the UAT exposure scores to account for possible lag times, with a separate analysis for each exposure window. These windows were used separately. Multiple source models were constructed using all source classes, again using five time windows.

The Poisson distribution assumes that the mean and variance are equal, however, this is rarely found in real data.[52] A higher incidence of zero counts in the data will increase the variance, which is considered as "overdispersed" data.[52] To examine whether the health outcome data in this study was not Poisson distributed, the final health models was analyzed using negative binomial regression, a standard method to model overdispersed Poisson data, which can also be viewed as an extension to the Poisson-gamma mixture model.[52]

As part of a sensitivity analysis, associations between selected pollutants (formaldehyde, MEK, benzene, CO, NO_2, O_3, $PM_{2.5}$, PM_{10} and SO_2) and ED visits for respiratory problems were examined using both single and multiple pollutant models and the same exposure windows (lag structures) described previously. Additionally, single and multiple source models were constructed using imputed data, obtained from single imputation as suggested by Polissar et al. (1998).[53] For imputed data, replicates from the two laboratories were averaged. Finally, all models were repeated using ED visits for injury as the outcome, a control case that was not expected to show associations with pollutant variables.

SAS version 9 was used to format and aggregate Medicaid claims data, and SAS PROC GENMOD was used for the health models.[54] Institutional review boards at both Michigan Department of Community Health (MDCH) and the University of Michigan reviewed and approved study protocols.

3.5 Results

Results are presented by main tables (Tables 3-1 to 3-10) and figure (Figure 3-1)

followed by supplemental tables (Tables S3-1 to S3-10).

3.5.1 Source apportionment

Five source classes were identified using PMF with the UAT dataset (Figure 3-1): (1) Fuel combustion, suggested by aldehyde, benzaldehyde, hexaldehyde, iso-butyraldehyde, propionaldehyde and tolualdehyde (mass of species apportioned to sources: 40-100%); (2) photochemical pollutants by formaldehyde (>90%); (3) gasoline exhaust/evaporated gasoline by benzene, 1,3-butadiene, ethylbenzene, m,p-xylene, o-xylene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene and toluene (40-70%); (4) combined industrial sources by acetylene, n-octane, propylene, dichlorodifluoromethane, tetrachloroethylene, trichlorofluoromethane and trichlorotrifluoroethane (30-65%); and (5) industrial solvents by methyl ethyl ketone (>80%). (Detailed receptor modeling results, using PMF as well as PCA, are presented in Appendix 1.) The overall fit for the 5-source model was reasonable for most compounds, e.g., aromatic and carbonyl compounds had R^2 values above 0.7 in both seasonal and annual analyses. Lower R^2 values (<0.4) were obtained for chlorinated and fluorinated VOCs and for propylene, most likely due to reproducibility problems and the small variation in the concentrations of these compounds.

Compared to individual pollutants, which were highly correlated among carbonyls ($0.64 \leq r \leq 0.89$) and among aromatic VOCs ($0.68 \leq r \leq 0.77$), the correlation between source classes was generally lower ($-0.61 \leq r \leq 0.43$) (Tables S3-1 and S3-2). The correlation coefficients between source classes and criteria pollutants were low-to-moderate (Table S3-3). All pollutants were moderately correlated with industrial solvent ($-0.42 \leq r \leq 0.51$). Other noticeable correlations occurred between CO and gasoline exhaust (r=0.47), NO_2 and photochemical pollutants (r=0.36), and O_3 (Windsor) and fuel combustion (r=0.38). These correlations help to affirm that the 5-source apportionment results reflected actual sources in the Detroit area.

Season differences were modest. Source classes for spring and winter seasons were unchanged. Variability during the summer and fall seasons affected only a few sources. For example, MEK, which is the key species of industrial solvent sources in the annual model, was apportioned together with key species of combined industrial sources, and hexaldehyde was a key species for a new source (fraction of species apportioned to

sources: >97%) in summer models. The change in summer results might be due to a reduction in MEK emissions caused by shutdowns in nearby automobile assembly facilities. Higher rates of photochemical reactions and the consumption of reactive compounds during the summer season also might contribute to this variability.

The 6-source models only marginally improved fit. Thus, results from the 5-source annual model (using observed data) are used in subsequent analyses. Analyses using imputed data are also presented as part of sensitivity analyses.

3.5.2   Characteristics of the study population

Daily counts of ED visits for asthma, respiratory problems and injury for subjects in the study area are shown in Table 3-2. An unusually large number (n=23) of ED visits for asthma occurred on July 11, 2001 among subjects living within the 10 km buffer. On this same day, there were no unusual number of ED visits for respiratory problem (n=20) and injury (n=20) nor hospital admission for asthma (n=1) and injury (n=1).   No unusual circumstances were noted in the air pollution and meteorological data around that time. High concentrations of several trace metals were detected on the July 4, 2001 due to fireworks; however, this was a full week earlier and is unlikely to be connected to the ED visits. The health outcome model was run both with and without the July 11, 2001 data.

For the 10 km radius, the numbers of ED visits for asthma, respiratory and injury reasons (1166, 4042 and 4617, respectively) were sufficient for analysis. However, the number of hospital admissions for the three outcomes (328, 251 and 356, respectively) was too small to obtain adequate statistical power. For the 4 km radius, the number of ED visits for asthma (192) was also too small for analysis. The numbers of ED visits for respiratory (853) and injury (773) reasons were considered marginal for analysis. Given these sample sizes, the analyses were focused on ED visits for respiratory effects.

Due to the study design for air toxics, about 22% of the possible exposure measurements were missing. This has the potential to influence the study results; however, chi-square and Fisher's exact tests comparing counts of ED visits of all three health outcomes (asthma, respiratory problems and injury) on days with and without air toxics exposure data were not statistically different (p-value>0.05).

Health care utilization data for the year following the study period (April 2002–

April 2003) is shown in Table S3-4. Both periods showed similar counts; therefore, the data obtained for the study period appears to be representative.

3.5.3 Single source models

ED visits for respiratory problems

Adjusted risk ratios of ED visits for respiratory problems for each of the five source class contributions (using a separate analysis for each source class) are shown in Table 3-3. For the 4 km buffer, exposures to photochemical pollutants lagged 2 to 4 days increased the rate of ED visits, and a dose-response relationship was seen for the 3-day lag. Rate of ED visits increased by 16 to 48% for exposure in the 2nd, 3rd and 4th quartiles compared to the lowest quartile. Results for the fuel combustion source class were similar, and again, there was some evidence of a dose-response relationship for the 3-day lag. The ARR of ED visits with fuel combustion exposure increased by 36 to 44%. For the gasoline exhaust/evaporated gasoline source class, 3 and 4 day lagged exposures consistently increased odds of ED visits. Some evidence of a dose-response relationship for the 4-day lag was seen, and the ARR of ED visits increased by 7 to 35% at higher exposures. For the combined industrial/industrial solvent source class, the ARRs were either statistically insignificant or weakly negative.

Results for children living within the larger (10 km) buffer tended to follow a pattern similar to that seen for the 4 km buffer, although many associations were attenuated toward the null, statistically insignificant, or weakly negative (Table 3-3). The only exception was the photochemical source class in which the ARR of ED visits increased by 6 to 19% for the 1-day lag, an association not seen for the 4 km radius.

ED visits for asthma

Results for ED visits for asthma in the 10 km radius are shown in Table 3-4. Only exposures to the combined industrial source class, lagged 4 days, showed a consistent pattern and increased odds. While statistically significant, this result appears to be an artifact of the anomalously large number of ED visits on July 11, 2001. After this observation was removed, this association became statistically insignificant (Table 3-5). Outcomes for ED visits for respiratory problems were unaffected by this observation; therefore, only the asthma count was removed.

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Exposure to pollutants identified as fuel combustion lagged 4 days showed negative associations with ED visits, however, the confidence interval approached the null value, suggesting spurious associations.

Single pollutant models

Results of analyses using selected pollutants are shown in Tables 3-6 and 3-7 for ED visits for respiratory problems in 4 and 10 km radius buffers, respectively. The analyses used data from the Linwood site, which measured most of the criteria pollutants. O_3 analyses used data from both Linwood (April to September) and downtown Windsor (annual). Three UATs were selected for the single pollutant models (formaldehyde, benzene and MEK), in order to reflect the key species of the source classes identified by PMF.

For children residing in the 4 km buffer, exposures to CO lagged 4 days and NO_2 lagged 3 and 4 days increased the odds of ED visits for respiratory problems (Table 3-6). However, the CO association was considered to be spurious because statistically significant associations were not found at the highest exposure quartile. NO_2 results resembled those found for photochemical pollutant sources, which might reflect the formation of photochemical pollutants.[55] For air toxics, only exposures to formaldehyde, lagged 1 to 4 days, showed an increased risk of ED visits for respiratory problems. These results resembled those for the photochemical source in which formaldehyde is the key species. No statistically significant associations were found for the other criteria air pollutants, benzene or MEK. Results for the 10 km radius were similar. While several associations were negative, these appeared spurious because they occurred in only the lower exposure quartiles.

For the 10 km buffer, only exposures to $PM_{2.5}$, CO and SO_2 showed an increase in the risk of ED asthma visits (Table 3-7). However, the CO and SO_2 associations were considered to be spurious because significant associations occurred only at the 2nd exposure quartile. For $PM_{2.5}$, the odds of ED asthma visits increased by 25% for the same day exposure.

3.5.4 Multiple source models

Results of the multiple source models for ED visits for respiratory problems and

asthma are shown in Tables 3-8 and 3-9, respectively. The patterns of associations were similar to those seen earlier in the single source models (Tables 3-3 and 3-4), however, associations were attenuated and confidence intervals were broader. Only exposure to pollutants identified as fuel combustion lagged 3 and 4 days showed an increase in odds of ED visits for respiratory effects (7 to 27%) among children in the 10 km buffer. This suggests that models using multiple source factors encounter the same problems as "conventional" multi-pollutant health models, namely, multicollinearity that tends to reduce statistical significance of the estimated coefficients. It may be possible to simultaneously use two or possibly three factors without detrimental effects; however, five source profiles are too many.

3.5.5   Sensitivity analyses

Tests using the control outcome, ED visits for injury, showed no statistically significant associations for exposures to any of the source classes for both 4 and 10 km buffers, and for single and multiple source class models (Tables S3-5 to S3-7). Results from the negative binomial regression models were similar to those from the Poisson regression models (Tables S3-9 to S3-10), indicating that any possible deviations from the Poisson distribution assumption did not cause biases.

For receptor modeling, results using observed and imputed data were similar for four of the five source classes. The photochemical pollutant source class was replaced by petrochemical pollutant source, indicated by propylene. Formaldehyde, the key species of the former photochemical pollutant source, merged together with other carbonyls identified as fuel combustion source. These results indicate that the PMF method can be sensitive to the use of imputed data. Analyses re-run using the single imputation dataset are shown in Table S3-8. The results did not differ significantly between observed and imputed data. The major difference was that the petrochemical pollutant source class lagged 4 days (with propylene as the key species) increased the ARR of ED visits for respiratory effects in the 10 km buffer. Since propylene was not highly correlated with any other compound ($r \leq 0.32$) (Table S3-2), this might be an artifact or spurious result, e.g., a result of a small sample size.

3.6   Discussion

This work used receptor modeling (RM) to derive an exposure indicator which was then used in an epidemiological analysis examining exacerbation of asthma and other respiratory diseases in Dearborn, Michigan. Using PMF, five source classes were identified, primarily on the basis of carbonyl and volatile organic compounds. Unsurprisingly, traffic-related emission sources were dominant, consistent with a previous study.[56] The results suggest that exposures to traffic-related air toxics, emission sources identified as secondary pollutants, fuel combustion, and gasoline exhaust/evaporated gasoline increased the rate of ED visits for respiratory problems among children living within a 4 km radius of the Dearborn air monitor. Risks were attenuated for children living in the larger (10 km) buffer as compared to the smaller (4 km) region nearer the monitor.

3.6.1   Mechanisms

Volatile organic compounds are irritants that can affect the airways and induce inflammation and airway obstruction,[57,58] and can have chronic effects such as cancer.[59,60] Two examples of acute effects are provided. First, formaldehyde causes inflammation and the release of cytokines, which leads to the up-regulation of induced nitric oxide (NO), itself a marker for lower airway inflammation.[61-63] Second, human respiratory epithelial cells exposed *in vitro* to 1,3-butadiene and its photochemical-generated products (acrolein, acetaldehyde, formaldehyde, furan and O_3) induced significant increases in cytotoxicity, however, the equivalent levels of O_3 exposure did not induce the same level of inflammatory cytokine release,[64] also suggesting that respiratory health effects occur via the inflammatory pathway from 1,3-butadiene exposure.

3.6.2   Comparison to previous studies

As noted, few studies have focused on UAT exposure and respiratory illness in children. Petroleum- and process-related VOCs were associated with bronchitis, persistent wheezing, physician's diagnostic of asthma, lower respiratory symptoms, and chronic lower respiratory response in school age children in Kanawha County, West Virginia.[15] Traffic-related VOCs were associated with asthma symptoms in children with mild asthma in Los Angeles[16], and exposures to outdoor (polar) VOCs lagged 2 days

were associated with acute visits to an ambulatory care setting for asthma among children in Atlanta.[18] In Germany, benzene exposure was associated with asthma, wheeze and cough in children.[65] In Belfast, Northern Ireland, benzene exposures were associated with ED visits for acute asthma among children.[19] This Belfast study is interesting in that in the two pollutant Poisson regression models (using benzene and SO_2, PM_{10}, O_3, NO_x, NO, NO_2, or CO), benzene was the only variable independently associated with ED asthma admissions, suggesting that benzene might be a more reliable indicator of vehicle exhaust than the criteria pollutants.

In the present study, associations between benzene and ED visits for respiratory effects were not found (Table 3-6). Notably, benzene levels were relatively low (geometric mean of 0.55 ppbv; maximum of 2.20 ppbv), suggesting small impacts from traffic and other sources even though the Dearborn site is located in a heavily industrialized area. Low benzene levels might be influenced by other traffic-related pollutants (including many VOCs) which have sharp spatial gradient.[66] For an example, benzene is highly correlated with acetylene (r=0.69, Table S3-1), which is also emitted by gasoline combustion. Thus, benzene (or some other VOCs) by themselves may not be a strong or sufficient indicator of vehicular emissions, as suggested by the Belfast study.[19]

Only a few studies have examined formaldehyde and asthma in nonoccupational settings.[67] Indoor exposure has been linked to physician-diagnosed asthma, however, these studies were likely confounded by unmeasured factors (i.e., environmental tobacco smoke) and by the parents' history of asthma and allergy.[68,69] In this study, exposures to formaldehyde, but not MEK, increased ED visits for respiratory problems (Table 3-6). Additionally, the risks estimated using the PMF exposure scores were smaller and had narrower CIs compared to those estimated for formaldehyde, suggesting improved precision of the estimate as well as adjustment for other pollutants.

Criteria air pollutants have been associated with respiratory illness in many epidemiological studies.[5,6] In Dearborn, ED visits for respiratory problems were linked to concentrations of several criteria pollutants (Table 3-6). The pattern of results was quite consistent for CO and NO_2 in the single pollutant models. However, in two-pollutant models (CO and NO_2) and for the 4 km radius, the statistically significant associations between NO_2 and ED visits diminished (Table 3-10). In five-pollutant

models (CO, NO_2, SO_2, O_3 and $PM_{2.5}$) and for the 10 km radius, associations between NO_2 and ED visits for respiratory problems remained statistically significant, however, the CIs were wider, suggesting some loss in precision. There is a greater chance of exposure misclassification for analyses involving the criteria air pollutants since these pollutants were measured at a different site, which tends to complicate interpretation of results.

In summary, this study found exposures to source contributions from photochemical pollutants, fuel combustion, and gasoline exhaust/evaporated gasoline source classes were associated with ED visits for respiratory problems among children.

3.6.3   Study strengths

One key strength of this study lies in its exposure assessment, which is unique in its use of source-apportioned exposure measures. In brief, the derived source contributions or scores from the RM are used as exposure measures in the same or similar statistical framework used to associate conventional exposure measures and health outcomes. As noted above, this approach is attractive because these exposure measures may be more strongly associated with health impacts (thus increasing statistical power), and because the correlation in the exposure dataset is used to derive a smaller number of exposure measures that may be more robust than any single pollutant. Additionally, the approach may be more realistic as people experience exposures to most air pollutants as mixtures, not as individual pollutants. Finally, exposures using source classes may be biologically more plausible and relevant.

While current epidemiological studies examining toxics have focused on VOC exposures, our study examined both VOCs and carbonyls, important since carbonyls appear to be stronger indicators of vehicle-related sources. Dose-response relationships were obtained for the associations between exposure to carbonyls identified as photochemical pollutants and fuel combustion source classes and ED visits for respiratory problems, suggesting strong associations.

The use of geo-coded Medicaid data also has several advantages. First, families of lower social economic status (SES) more commonly utilize urgent care facilities for asthma as compared to families of higher SES.[70] By examining only the Medicaid

pediatric population, results from the current study should not be confounded by SES. Second, the approach potentially could encompass a very large sample size, especially if pollutants are measured at multiple sites. As discussed below, sample size was an issue in Dearborn, in part because daily UAT data were available at a single site.

3.6.4 Limitations

As further discussed in the following chapter, due to detection frequency and reproducibility issues, many of the 71 measured air toxics did not appear usable. Ideally, each source class (or factor) would represent a single and correctly identified source class that is uncorrelated with other source classes. However, in complicated systems, these classes may consist of features from several sources.[29] Combined source factors are also more likely in samples using longer averaging periods, e.g., the 24-hr samples collected at Dearborn (as compared to 1-hr data)[29] since winds from multiple directions are likely and may transport pollutants from several source types to the monitor site. In such situations, separate sources in effect become correlated. A further complication arises as several aldehydes (e.g., formaldehyde, acetaldehyde) and VOCs (e.g., 1,3-butadiene) can be chemically reactive, and their concentration and lifetime will be affected by photochemistry, temperature, sunlight, and the other reactive species present. Thus, measurements of these compounds can reflect both primary emissions (directly from the source) and secondary production. Such effects will "blur" profiles and can create new profiles that primarily reflect secondary sources, as suggested for formaldehyde which formed its own profile in several seasons. This problem is not present in $PM_{2.5}$ or PM_{10} apportionments that utilize (unreactive) elemental concentration data. While the breakdown into source factors by receptor models is imperfect and may not isolate single sources or source types, the use of source factors is a valid approach for representing the pattern of exposures, and its use in epidemiological analyses can help to identify those pollutants and pollutant mixtures associated with adverse health effects.

An important limitation was the relatively small size of the study population, which did not permit assessment of certain exposure-outcome relationships, including asthma exacerbation (ED visits) among children in the smaller (4 km) buffer around the monitoring site. Also, daily air toxics data were available for only one year, which also affected sample size, as well as the ability to investigate long-term trends.

Effects of exposure misclassification can be seen as the buffer's radius increased from 4 to 10 km, which tended to force risk ratios towards the null. We had no personal or indoor exposure data, despite known indoor sources, e.g., formaldehyde concentrations in residences may exceed outdoor concentrations.[71] However, contributions from indoor sources are likely uncorrelated with outdoor formaldehyde levels, thus only non-differential bias in exposure classification is expected. Finally, there was the potential that the exposure scores were affected by unmeasured confounding variables and unknown uncertainties, given that these scores were derived from daily measurements using receptor modeling, neither of which were accounted for in this study. Future study might address these issues using several approaches, e.g., instrumental variable regression.[72] While measurement uncertainties were incorporated in the PMF method, further analysis is recommended to determine the sensitivity of results to these effects.

3.7 Conclusions

This study appears to be the first to utilize source-apportioned exposure measures of urban air toxics (UATs), specifically VOCs and carbonyls, to investigate the relationship of exposure to respiratory illness in children. The children in the study population making respiratory-related Medicaid claims and living within 10 km of the Dearborn, Michigan air quality monitor made 1,166 and 4,617 emergency department (ED) visits for asthma and respiratory problems, respectively, during the study year. Exposures to UAT source classes identified as fuel combustion, photochemical pollutants, and gasoline exhaust/evaporated gasoline were associated with increased the rate of ED visits for respiratory problems. Effects were stronger for subjects living closer (within 4 km) to the air monitoring site. Due to the limitations and uncertainties in the ambient air toxics data and model predictions, as well as the novelty of this study, follow-up studies to help confirm results are suggested.

Figure 3- 1. Mass of species apportioned to sources for observed urban air toxics

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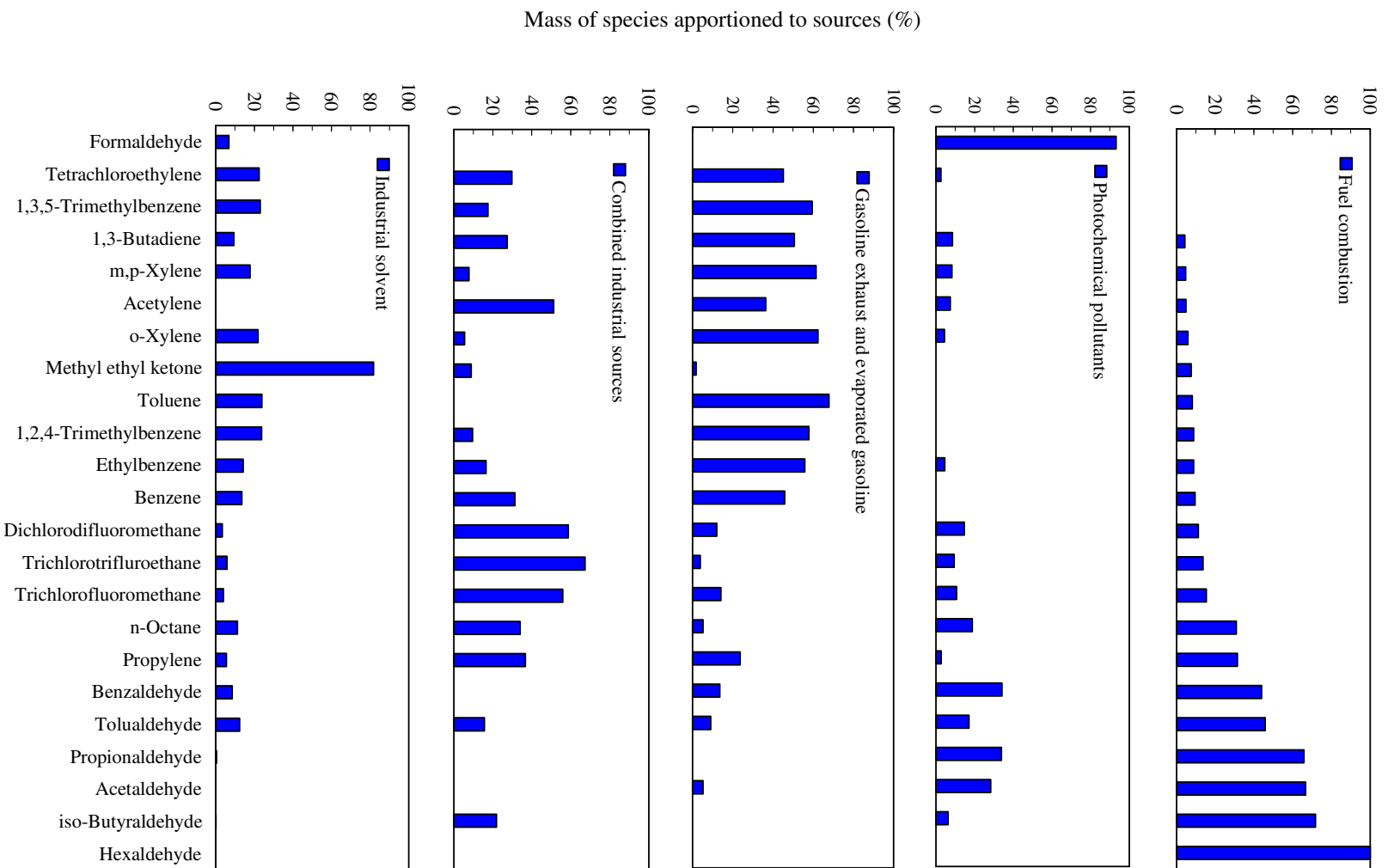
Table 3- 1. Summary of the species measurements

(BDL, below detection measurements; Ms, missing values; S/N, ratio of signal to noise; GM, geometric mean; ppb, part per billion)

Compounds	Ms (%)	BDL (%)	S/N	GM (ppb)
Carbonyls				
Acetaldehyde	22	0	44.70	0.73
Benzaldehyde	22	2	0.39	0.04
Formaldehyde	22	0	46.81	1.47
Hexaldehyde	22	1	1.99	0.05
iso-Butyraldehyde	22	1	2.93	0.14
Propionaldehyde	22	10	3.19	0.08
Tolualdehyde	22	7	0.31	0.03
VOCs				
Acetylene	17	1	7.74	1.52
Benzene	17	0	4.08	0.55
1,3-Butadiene	17	73	0.73	0.05
Dichlorodifluoromethane	17	0	3.68	0.63
Ethylbenzene	18	2	2.52	0.15
Methyl ethyl ketone	17	26	7.68	0.39
m,p-Xylene	18	0	3.07	0.43
n-Octane	18	66	0.47	0.04
o-Xylene	18	3	5.18	0.18
Propylene	17	0	3.48	0.82
Tetrachloroethylene	17	66	2.46	0.05
Trichlorofluoromethane	17	0	3.57	0.31
Trichlorotrifluoroethane	17	0	0.12	0.11
1,2,4-Trimethylbenzene	17	9	1.03	0.17
1,3,5-Trimethylbenzene	18	61	0.45	0.05
Toluene	18	0	14.73	0.88

Table 3- 2. Study population size and number of Medicaid visits, 4/19/2001-4/18/2002

Variable	Study population	Hospital admission			Emergency department visit			Outpatient visit		
		Asthma	Respiratory	Injury	Asthma	Respiratory	Injury	Asthma	Respiratory	Injury
	N (%)	n	n	n	n	n	n	n	n	n
4 km buffer										
N	4733	50	76	46	192	853	773	617	9638	1076
Gender										
Female	2310 (49)	13	42	34	69	390	341	257	4800	449
Male	2423 (51)	37	34	12	123	463	432	360	4838	627
Race										
Black	698 (15)	5	6	8	43	125	128	85	406	92
White	2240 (47)	19	33	27	82	467	443	312	6559	732
Others	1795 (38)	26	37	11	67	261	202	220	2673	252
Age group (yrs)										
0 to 4	1697 (36)	29	43	16	93	516	284	302	4956	296
5 to 9	1407 (30)	11	17	16	57	204	234	186	2840	305
10 to 14	1052 (22)	4	5	4	30	94	176	102	1365	339
15 to 18	577 (12)	6	11	10	12	39	79	27	477	136
10 km buffer										
N	7863	328	251	356	1166	4042	4617	2483	3966	27345
Gender										
Female	3850 (49)	140	112	162	504	1701	2225	1021	1632	13515
Male	4013 (51)	188	139	194	662	2341	2392	1462	2334	13830
Race										
Black	2685 (34)	247	158	225	864	2458	3003	1374	1813	7107
White	2595 (33)	41	70	67	176	1207	1140	764	1734	16167
Others	2583 (33)	40	23	64	126	377	474	345	419	4071
Age group (yrs)										
0 to 4	2458 (31)	158	89	211	550	1326	2600	1076	1082	13416
5 to 9	2195 (28)	77	76	60	340	1166	1097	744	1098	7987
10 to 14	1894 (24)	57	49	54	214	1069	645	541	1316	4552
15 to 18	1316 (17)	36	37	31	62	481	275	122	470	1390

Table 3- 3. Single source models - Associations between exposures to pollutants identified as 5 source classes and ED visits for respiratory problems (observed data).

Statistical significant estimates are in bold. RR, relative risk; covariates: day of week, calendar month, $PM_{2.5}$, ambient temperature, relative humidity and pressure; reference groups: 1st quartile exposure, Friday and April.

Exposures	Photochemical RR (95%CI)	Fuel Combustion RR (95%CI)	Combined industrial RR (95%CI)	Gasoline exhaust RR (95%CI)	Industrial solvent RR (95%CI)
4 km buffer					
Current day					
4th quartile	0.85 (0.64- 1.12)	0.76 (0.52- 1.12)	1.17 (0.83- 1.66)	0.89 (0.67- 1.18)	1.12 (0.77- 1.64)
3rd quartile	0.85 (0.66- 1.09)	1.07 (0.82- 1.40)	1.21 (0.86- 1.70)	1.05 (0.82- 1.35)	1.07 (0.77- 1.49)
2nd quartile	1.00 (0.79- 1.26)	1.00 (0.79- 1.27)	1.27 (0.94- 1.70)	**0.75 (0.58- 0.96)**	1.11 (0.87- 1.41)
1 day lag					
4th quartile	**1.41 (1.08- 1.84)**	1.19 (0.82- 1.73)	0.87 (0.61- 1.24)	1.09 (0.82- 1.44)	0.69 (0.46- 1.02)
3rd quartile	0.96 (0.74- 1.23)	**1.34 (1.03- 1.73)**	1.16 (0.83- 1.62)	1.08 (0.84- 1.39)	**0.70 (0.51- 0.98)**
2nd quartile	1.05 (0.83- 1.33)	0.92 (0.72- 1.17)	1.24 (0.92- 1.66)	0.88 (0.69- 1.13)	0.95 (0.75- 1.20)
2-day-lag average					
4th quartile	**1.39 (1.08- 1.79)**	1.34 (0.96- 1.87)	0.76 (0.55- 1.04)	1.16 (0.91- 1.47)	0.92 (0.64- 1.32)
3rd quartile	1.19 (0.95- 1.49)	1.28 (1.00- 1.65)	0.89 (0.66- 1.20)	1.19 (0.95- 1.51)	0.75 (0.55- 1.02)
2nd quartile	1.02 (0.82- 1.27)	1.10 (0.89- 1.37)	0.80 (0.61- 1.04)	0.91 (0.73- 1.14)	0.93 (0.74- 1.15)
3-day-lag average					
4th quartile	**1.48 (1.15- 1.90)**	**1.44 (1.03- 2.01)**	0.85 (0.60- 1.21)	1.28 (0.99- 1.65)	0.74 (0.51- 1.08)
3rd quartile	**1.31 (1.04- 1.66)**	**1.42 (1.08- 1.86)**	0.90 (0.65- 1.25)	**1.45 (1.15- 1.83)**	**0.69 (0.50- 0.95)**
2nd quartile	1.16 (0.93- 1.44)	**1.36 (1.10- 1.68)**	1.01 (0.77- 1.32)	1.12 (0.90- 1.38)	0.93 (0.75- 1.16)
4-day-lag average					
4th quartile	**1.33 (1.04- 1.71)**	**1.74 (1.19- 2.54)**	0.73 (0.50- 1.07)	**1.35 (1.05- 1.74)**	0.83 (0.55- 1.24)
3rd quartile	1.09 (0.86- 1.38)	1.28 (0.98- 1.68)	0.90 (0.64- 1.26)	1.29 (1.00- 1.66)	0.75 (0.54- 1.04)
2nd quartile	1.15 (0.92- 1.42)	1.15 (0.93- 1.42)	0.95 (0.72- 1.25)	1.07 (0.86- 1.33)	0.82 (0.65- 1.04)
10 km buffer					
Current day					
4th quartile	1.02 (0.90- 1.15)	1.03 (0.87- 1.21)	0.98 (0.84- 1.15)	1.03 (0.91- 1.16)	1.08 (0.91- 1.27)
3rd quartile	0.93 (0.84- 1.04)	**1.14 (1.01- 1.28)**	1.02 (0.87- 1.18)	**1.17 (1.05- 1.30)**	1.02 (0.88- 1.17)
2nd quartile	1.02 (0.92- 1.13)	1.04 (0.94- 1.15)	1.00 (0.88- 1.14)	1.01 (0.91- 1.12)	1.08 (0.97- 1.19)
1 day lag					
4th quartile	**1.19 (1.05- 1.34)**	1.07 (0.91- 1.26)	1.00 (0.86- 1.17)	1.03 (0.91- 1.16)	0.99 (0.84- 1.17)
3rd quartile	1.06 (0.95- 1.18)	**1.13 (1.01- 1.27)**	1.03 (0.89- 1.19)	1.00 (0.90- 1.12)	0.94 (0.82- 1.08)
2nd quartile	**1.13 (1.02- 1.26)**	1.07 (0.97- 1.19)	1.05 (0.93- 1.20)	0.96 (0.86- 1.07)	1.02 (0.93- 1.13)
2-day-lag average					
4th quartile	1.10 (0.98- 1.23)	1.12 (0.97- 1.29)	0.92 (0.80- 1.05)	1.01 (0.91- 1.12)	0.91 (0.77- 1.06)
3rd quartile	**1.11 (1.01- 1.23)**	1.09 (0.98- 1.21)	0.99 (0.86- 1.12)	1.06 (0.96- 1.17)	0.93 (0.82- 1.06)
2nd quartile	1.00 (0.91- 1.10)	1.08 (0.99- 1.18)	0.98 (0.87- 1.10)	0.97 (0.89- 1.06)	0.95 (0.87- 1.05)
3-day-lag average					
4th quartile	1.08 (0.97- 1.20)	1.13 (0.98- 1.30)	1.04 (0.89- 1.21)	1.00 (0.89- 1.11)	**0.84 (0.71- 0.98)**
3rd quartile	**1.12 (1.02- 1.24)**	1.09 (0.97- 1.22)	1.05 (0.91- 1.21)	1.03 (0.93- 1.14)	**0.86 (0.76- 0.99)**
2nd quartile	1.06 (0.97- 1.17)	**1.11 (1.02- 1.22)**	1.00 (0.89- 1.13)	0.99 (0.91- 1.08)	0.95 (0.86- 1.04)
4-day-lag average					
4th quartile	1.07 (0.96- 1.19)	1.17 (1.00- 1.38)	1.00 (0.85- 1.18)	1.03 (0.93- 1.15)	**0.82 (0.69- 0.98)**
3rd quartile	1.06 (0.96- 1.17)	1.04 (0.92- 1.16)	1.02 (0.88- 1.19)	1.02 (0.92- 1.14)	**0.81 (0.70- 0.93)**
2nd quartile	1.01 (0.92- 1.10)	1.09 (1.00- 1.19)	1.03 (0.92- 1.16)	1.04 (0.95- 1.14)	**0.88 (0.79- 0.97)**

Table 3- 4. Single source models - Associations between exposures to pollutants identified as 5 source classes and ED visits for asthma among children living within 10 km buffer (observed data).

Otherwise as Table 3-3.

Exposures	Photochemical	Fuel Combustion	Combined industrial	Gasoline exhaust	Industrial solvent
	RR (95%CI)	RR (95%CI)	RR (95%CI)	RR (95%CI)	RR (95%CI)
Current day					
4th quartile	1.09 (0.86- 1.38)	0.89 (0.65- 1.21)	1.30 (0.96- 1.76)	0.92 (0.73- 1.16)	0.99 (0.71- 1.38)
3rd quartile	1.06 (0.85- 1.31)	0.98 (0.78- 1.24)	1.14 (0.85- 1.53)	**0.77 (0.62- 0.97)**	1.12 (0.84- 1.49)
2nd quartile	0.93 (0.75- 1.16)	1.01 (0.81- 1.26)	1.18 (0.93- 1.51)	0.97 (0.78- 1.19)	1.06 (0.85- 1.32)
1 day lag					
4th quartile	1.15 (0.91- 1.47)	0.99 (0.73- 1.34)	1.00 (0.74- 1.34)	1.13 (0.89- 1.43)	0.99 (0.71- 1.38)
3rd quartile	1.12 (0.89- 1.39)	1.13 (0.89- 1.43)	0.93 (0.71- 1.23)	0.98 (0.78- 1.24)	1.02 (0.77- 1.36)
2nd quartile	1.12 (0.90- 1.40)	1.26 (1.01- 1.57)	1.07 (0.85- 1.36)	**1.28 (1.03- 1.58)**	1.00 (0.80- 1.25)
2-day-lag average					
4th quartile	0.84 (0.67- 1.05)	0.91 (0.69- 1.19)	1.01 (0.77- 1.33)	1.11 (0.90- 1.37)	0.99 (0.72- 1.35)
3rd quartile	0.95 (0.78- 1.16)	0.94 (0.75- 1.17)	1.03 (0.80- 1.32)	1.04 (0.84- 1.27)	0.88 (0.67- 1.14)
2nd quartile	0.84 (0.69- 1.02)	0.96 (0.79- 1.16)	0.98 (0.79- 1.21)	1.15 (0.95- 1.39)	0.93 (0.75- 1.15)
3-day-lag average					
4th quartile	0.89 (0.71- 1.12)	1.00 (0.76- 1.30)	1.11 (0.82- 1.49)	0.97 (0.78- 1.19)	1.05 (0.77- 1.43)
3rd quartile	1.11 (0.90- 1.37)	0.91 (0.72- 1.14)	0.98 (0.74- 1.28)	1.05 (0.86- 1.29)	0.94 (0.72- 1.24)
2nd quartile	1.07 (0.88- 1.30)	0.93 (0.76- 1.13)	0.99 (0.81- 1.22)	1.01 (0.84- 1.22)	0.90 (0.73- 1.11)
4-day-lag average					
4th quartile	0.86 (0.68- 1.07)	**0.73 (0.55- 0.99)**	**1.43 (1.03- 1.97)**	0.83 (0.67- 1.03)	1.14 (0.82- 1.60)
3rd quartile	1.01 (0.82- 1.24)	0.87 (0.69- 1.09)	1.30 (0.98- 1.73)	0.95 (0.77- 1.17)	0.98 (0.74- 1.30)
2nd quartile	0.94 (0.78- 1.14)	0.87 (0.72- 1.06)	**1.36 (1.11- 1.68)**	0.95 (0.79- 1.14)	0.95 (0.76- 1.19)

Table 3- 5. Single source models - Associations between exposures to pollutants identified as 5 source classes and ED visits for respiratory problems and asthma with exclusion of health events on July 11, 2001.

Otherwise as Table 3-3.

Health outcomes/Exposures	Photochemical RR (95%CI)		Fuel Combustion RR (95%CI)		Combined industrial RR (95%CI)		Gasoline exhaust RR (95%CI)		Industrial solvent RR (95%CI)	
Respiratory										
Current day										
4th quartile	1.02	(0.90- 1.15)	1.03	(0.87- 1.21)	0.98	(0.84- 1.15)	1.03	(0.91- 1.16)	1.08	(0.91- 1.27)
3rd quartile	0.93	(0.84- 1.04)	**1.14**	**(1.01- 1.28)**	1.02	(0.87- 1.18)	**1.17**	**(1.05- 1.30)**	1.02	(0.88- 1.17)
2nd quartile	1.02	(0.92- 1.13)	1.04	(0.94- 1.15)	1.00	(0.88- 1.14)	1.01	(0.91- 1.12)	1.08	(0.97- 1.19)
1 day lag										
4th quartile	**1.19**	**(1.05- 1.34)**	1.07	(0.91- 1.26)	1.00	(0.86- 1.17)	1.03	(0.91- 1.16)	0.99	(0.84- 1.17)
3rd quartile	1.06	(0.95- 1.18)	**1.13**	**(1.01- 1.27)**	1.03	(0.89- 1.19)	1.00	(0.90- 1.12)	0.94	(0.82- 1.08)
2nd quartile	**1.13**	**(1.02- 1.26)**	1.07	(0.97- 1.19)	1.05	(0.93- 1.20)	0.96	(0.86- 1.07)	1.02	(0.93- 1.13)
2-day lag average										
4th quartile	1.10	(0.98- 1.23)	1.12	(0.97- 1.29)	0.92	(0.80- 1.05)	1.01	(0.91- 1.12)	0.91	(0.77- 1.06)
3rd quartile	**1.11**	**(1.01- 1.23)**	1.09	(0.98- 1.21)	0.99	(0.86- 1.12)	1.06	(0.96- 1.17)	0.93	(0.82- 1.06)
2nd quartile	1.00	(0.91- 1.10)	1.08	(0.99- 1.18)	0.98	(0.87- 1.10)	0.97	(0.89- 1.06)	0.95	(0.87- 1.05)
3-day lag average										
4th quartile	1.07	(0.96- 1.19)	1.08	(0.93- 1.24)	1.05	(0.91- 1.23)	0.99	(0.89- 1.10)	**0.83**	**(0.70- 0.97)**
3rd quartile	**1.12**	**(1.01- 1.23)**	1.08	(0.97- 1.22)	1.06	(0.92- 1.22)	1.01	(0.92- 1.12)	0.87	(0.76- 1.00)
2nd quartile	1.05	(0.95- 1.15)	**1.11**	**(1.02- 1.22)**	1.03	(0.92- 1.16)	0.99	(0.91- 1.08)	0.94	(0.86- 1.04)
4-day lag average										
4th quartile	1.07	(0.96- 1.19)	1.18	(1.00- 1.38)	0.98	(0.83- 1.15)	1.03	(0.93- 1.15)	**0.81**	**(0.68- 0.96)**
3rd quartile	1.06	(0.96- 1.17)	1.02	(0.91- 1.14)	1.00	(0.86- 1.16)	1.03	(0.92- 1.14)	**0.81**	**(0.71- 0.94)**
2nd quartile	1.00	(0.91- 1.09)	1.09	(1.00- 1.19)	1.01	(0.89- 1.14)	1.03	(0.94- 1.13)	**0.87**	**(0.79- 0.97)**
Asthma										
Current day										
4th quartile	1.09	(0.86- 1.38)	0.89	(0.65- 1.21)	1.30	(0.96- 1.76)	0.92	(0.73- 1.16)	0.99	(0.71- 1.38)
3rd quartile	1.06	(0.85- 1.31)	0.98	(0.78- 1.24)	1.14	(0.85- 1.53)	**0.77**	**(0.62- 0.97)**	1.12	(0.84- 1.49)
2nd quartile	0.93	(0.75- 1.16)	1.01	(0.81- 1.26)	1.18	(0.93- 1.51)	0.97	(0.78- 1.19)	1.06	(0.85- 1.32)
1 day lag										
4th quartile	1.15	(0.91- 1.47)	0.99	(0.73- 1.34)	1.00	(0.74- 1.34)	1.13	(0.89- 1.43)	0.99	(0.72- 1.35)
3rd quartile	1.12	(0.89- 1.39)	1.13	(0.89- 1.43)	0.93	(0.71- 1.23)	0.98	(0.78- 1.24)	0.88	(0.67- 1.14)
2nd quartile	1.12	(0.90- 1.40)	**1.26**	**(1.01- 1.57)**	1.07	(0.85- 1.36)	**1.28**	**(1.03- 1.58)**	0.93	(0.75- 1.15)
2-day lag average										
4th quartile	0.84	(0.67- 1.05)	0.91	(0.69- 1.19)	1.01	(0.77- 1.33)	1.11	(0.90- 1.37)	0.99	(0.72- 1.35)
3rd quartile	0.95	(0.78- 1.16)	0.94	(0.75- 1.17)	1.03	(0.80- 1.32)	1.04	(0.84- 1.27)	0.88	(0.67- 1.14)
2nd quartile	0.84	(0.69- 1.02)	0.96	(0.79- 1.16)	0.98	(0.79- 1.21)	1.15	(0.95- 1.39)	0.93	(0.75- 1.15)
3-day lag average										
4th quartile	0.85	(0.68- 1.07)	0.80	(0.61- 1.05)	1.16	(0.86- 1.56)	0.94	(0.76- 1.16)	1.01	(0.74- 1.39)
3rd quartile	1.06	(0.86- 1.30)	0.90	(0.71- 1.13)	1.02	(0.78- 1.34)	0.96	(0.78- 1.18)	0.99	(0.75- 1.29)
2nd quartile	0.97	(0.79- 1.18)	0.93	(0.76- 1.13)	1.12	(0.90- 1.38)	1.01	(0.84- 1.22)	0.88	(0.71- 1.09)
4-day lag average										
4th quartile	0.83	(0.66- 1.04)	0.75	(0.56- 1.00)	1.29	(0.94- 1.78)	0.84	(0.68- 1.04)	1.05	(0.74- 1.47)
3rd quartile	0.97	(0.79- 1.19)	0.80	(0.63- 1.00)	1.17	(0.89- 1.55)	0.97	(0.78- 1.20)	1.00	(0.75- 1.33)
2nd quartile	0.87	(0.71- 1.05)	0.86	(0.71- 1.05)	1.24	(1.00- 1.53)	0.87	(0.72- 1.05)	0.93	(0.74- 1.16)

Table 3- 6. Single pollutant models - Associations between exposures to selected pollutants (criteria and air toxics) and ED visits for respiratory problems (observed data).

Criteria pollutants monitored at Linwood otherwise indicate by site name; (#), restricted to April to September months. Otherwise as Table 3-3.

Sources	PM2.5 RR (95%CI)	CO RR (95%CI)	NO2 RR (95%CI)	SO2 RR (95%CI)	O3# RR (95%CI)	O3 (Windsor) RR (95%CI)	Formaldehyde RR (95%CI)	Benzene RR (95%CI)	MEK RR (95%CI)
4 km buffer									
Current day									
4th quartile	1.03 (0.80- 1.33)	0.95 (0.77- 1.19)	1.06 (0.83- 1.35)	1.18 (0.94- 1.49)	1.27 (0.78- 2.06)	1.13 (0.77- 1.68)	0.79 (0.58- 1.08)	1.10 (0.86- 1.40)	0.58 (0.27- 1.29)
3rd quartile	1.11 (0.89- 1.40)	0.83 (0.67- 1.03)	0.98 (0.77- 1.24)	1.13 (0.91- 1.40)	1.06 (0.70- 1.59)	1.19 (0.87- 1.61)	0.99 (0.77- 1.28)	0.95 (0.75- 1.21)	1.01 (0.52- 1.94)
2nd quartile	1.03 (0.83- 1.29)	0.89 (0.73- 1.09)	0.93 (0.75- 1.16)	1.07 (0.86- 1.34)	0.88 (0.60- 1.29)	1.05 (0.83- 1.32)	0.92 (0.73- 1.16)	0.81 (0.64- 1.02)	0.74 (0.42- 1.29)
1 day lag									
4th quartile	0.92 (0.72- 1.18)	1.03 (0.82- 1.28)	1.09 (0.86- 1.39)	0.87 (0.69- 1.10)	1.11 (0.67- 1.82)	0.92 (0.68- 1.24)	**1.50 (1.12- 2.02)**	1.03 (0.80- 1.32)	0.66 (0.31- 1.42)
3rd quartile	0.89 (0.71- 1.12)	0.91 (0.74- 1.12)	1.01 (0.79- 1.28)	0.88 (0.71- 1.09)	1.36 (0.90- 2.05)	0.97 (0.77- 1.21)	1.06 (0.82- 1.37)	0.99 (0.78- 1.25)	**0.50 (0.26- 0.98)**
2nd quartile	0.88 (0.71- 1.09)	0.86 (0.70- 1.05)	0.92 (0.73- 1.14)	0.85 (0.68- 1.07)	1.21 (0.83- 1.76)	0.94 (0.71- 1.26)	0.95 (0.75- 1.20)	0.88 (0.70- 1.10)	0.90 (0.53- 1.55)
2-day-lag average									
4th quartile	1.01 (0.78- 1.30)	1.05 (0.83- 1.33)	1.11 (0.86- 1.42)	0.80 (0.63- 1.02)	1.12 (0.67- 1.89)	1.01 (0.80- 1.29)	**1.37 (1.04- 1.81)**	1.04 (0.81- 1.33)	1.11 (0.53- 2.31)
3rd quartile	1.05 (0.83- 1.32)	0.92 (0.74- 1.14)	0.90 (0.71- 1.15)	0.94 (0.76- 1.16)	1.02 (0.67- 1.54)	0.96 (0.72- 1.28)	1.14 (0.89- 1.46)	1.06 (0.85- 1.32)	0.64 (0.33- 1.24)
2nd quartile	1.03 (0.83- 1.29)	0.90 (0.73- 1.10)	0.97 (0.77- 1.21)	0.83 (0.67- 1.03)	1.25 (0.88- 1.78)	1.09 (0.83- 1.45)	1.09 (0.88- 1.34)	1.09 (0.89- 1.34)	0.96 (0.58- 1.59)
3-day-lag average									
4th quartile	1.09 (0.85- 1.38)	1.16 (0.90- 1.50)	**1.37 (1.05- 1.78)**	0.88 (0.69- 1.13)	1.00 (0.57- 1.74)	0.95 (0.71- 1.26)	**1.64 (1.25- 2.16)**	0.93 (0.73- 1.20)	1.12 (0.50- 2.47)
3rd quartile	1.10 (0.88- 1.39)	1.12 (0.90- 1.40)	1.03 (0.80- 1.32)	1.02 (0.81- 1.27)	1.25 (0.81- 1.92)	1.09 (0.83- 1.44)	1.25 (0.98- 1.60)	1.15 (0.93- 1.43)	0.98 (0.50- 1.92)
2nd quartile	1.09 (0.88- 1.35)	1.06 (0.86- 1.31)	1.17 (0.93- 1.47)	1.00 (0.80- 1.24)	0.97 (0.67- 1.39)	0.99 (0.75- 1.31)	**1.35 (1.09- 1.67)**	0.97 (0.79- 1.20)	0.86 (0.51- 1.44)
4-day-lag average									
4th quartile	1.10 (0.86- 1.41)	1.28 (0.98- 1.67)	**1.46 (1.11- 1.93)**	0.90 (0.70- 1.15)	0.77 (0.44- 1.36)	1.08 (0.82- 1.42)	**1.36 (1.03- 1.80)**	1.15 (0.89- 1.49)	1.59 (0.71- 3.55)
3rd quartile	0.99 (0.79- 1.26)	**1.29 (1.02- 1.62)**	1.14 (0.88- 1.48)	0.94 (0.75- 1.18)	0.90 (0.58- 1.38)	0.98 (0.75- 1.30)	1.07 (0.83- 1.38)	1.04 (0.83- 1.30)	1.15 (0.57- 2.31)
2nd quartile	1.06 (0.85- 1.32)	**1.30 (1.05- 1.61)**	**1.42 (1.13- 1.79)**	0.89 (0.71- 1.10)	0.91 (0.64- 1.29)	0.92 (0.69- 1.22)	1.11 (0.90- 1.37)	1.13 (0.92- 1.39)	1.10 (0.64- 1.89)
10 km buffer									
Current day									
4th quartile	1.04 (0.93- 1.16)	1.03 (0.94- 1.14)	1.02 (0.92- 1.13)	1.05 (0.95- 1.16)	0.96 (0.78- 1.19)	0.89 (0.75- 1.05)	0.98 (0.85- 1.12)	1.11 (0.99- 1.24)	0.98 (0.84- 1.15)
3rd quartile	1.02 (0.93- 1.13)	0.94 (0.85- 1.03)	1.03 (0.93- 1.14)	1.05 (0.95- 1.15)	0.95 (0.80- 1.13)	0.94 (0.83- 1.07)	1.00 (0.90- 1.12)	**1.13 (1.01- 1.25)**	0.98 (0.86- 1.11)
2nd quartile	1.02 (0.93- 1.12)	1.00 (0.92- 1.09)	0.94 (0.86- 1.04)	1.05 (0.96- 1.16)	0.93 (0.79- 1.09)	1.03 (0.94- 1.14)	1.02 (0.92- 1.13)	0.97 (0.87- 1.07)	1.05 (0.95- 1.16)
1 day lag									
4th quartile	1.05 (0.94- 1.17)	1.08 (0.98- 1.19)	1.04 (0.94- 1.16)	1.04 (0.94- 1.15)	1.20 (0.97- 1.49)	0.93 (0.81- 1.06)	1.12 (0.98- 1.28)	1.10 (0.98- 1.23)	0.99 (0.84- 1.15)
3rd quartile	1.08 (0.98- 1.20)	1.00 (0.91- 1.09)	1.04 (0.94- 1.15)	1.00 (0.91- 1.09)	**1.26 (1.06- 1.51)**	1.02 (0.93- 1.13)	1.10 (0.99- 1.23)	1.04 (0.93- 1.15)	0.90 (0.79- 1.02)
2nd quartile	1.03 (0.93- 1.13)	1.02 (0.94- 1.11)	0.93 (0.84- 1.02)	0.94 (0.85- 1.03)	1.12 (0.95- 1.32)	1.13 (1.00- 1.27)	1.05 (0.95- 1.16)	1.00 (0.90- 1.10)	1.09 (0.98- 1.20)
2-day-lag average									
4th quartile	1.07 (0.96- 1.19)	1.10 (0.99- 1.21)	**1.15 (1.04- 1.29)**	0.97 (0.87- 1.07)	1.19 (0.96- 1.49)	1.01 (0.91- 1.12)	1.11 (0.98- 1.25)	1.05 (0.95- 1.17)	0.90 (0.77- 1.05)
3rd quartile	1.10 (0.99- 1.21)	1.00 (0.91- 1.10)	1.01 (0.91- 1.12)	0.98 (0.89- 1.07)	0.99 (0.83- 1.19)	**1.14 (1.01- 1.28)**	1.04 (0.94- 1.16)	1.04 (0.95- 1.14)	0.92 (0.82- 1.04)
2nd quartile	1.07 (0.98- 1.18)	0.98 (0.90- 1.07)	1.01 (0.92- 1.11)	**0.86 (0.78- 0.94)**	1.10 (0.95- 1.28)	1.12 (0.99- 1.26)	1.06 (0.97- 1.15)	1.02 (0.93- 1.11)	0.94 (0.86- 1.03)
3-day-lag average									
4th quartile	1.04 (0.94- 1.15)	1.10 (0.98- 1.23)	**1.18 (1.05- 1.32)**	1.03 (0.93- 1.14)	1.00 (0.78- 1.27)	1.12 (1.00- 1.27)	1.08 (0.96- 1.21)	1.01 (0.91- 1.13)	0.85 (0.72- 1.00)
3rd quartile	1.06 (0.96- 1.17)	1.06 (0.96- 1.16)	1.10 (0.99- 1.22)	0.99 (0.90- 1.09)	0.94 (0.78- 1.14)	1.11 (0.98- 1.25)	1.07 (0.97- 1.19)	1.03 (0.93- 1.13)	0.89 (0.78- 1.01)
2nd quartile	1.04 (0.95- 1.14)	1.01 (0.92- 1.11)	1.05 (0.95- 1.16)	0.99 (0.90- 1.09)	0.96 (0.82- 1.12)	1.06 (0.94- 1.19)	1.06 (0.97- 1.17)	1.04 (0.96- 1.14)	**0.91 (0.83- 0.99)**
4-day-lag average									
4th quartile	1.10 (0.99- 1.23)	1.10 (0.98- 1.23)	**1.26 (1.12- 1.42)**	0.96 (0.87- 1.07)	0.92 (0.72- 1.17)	1.08 (0.96- 1.22)	1.03 (0.91- 1.16)	1.01 (0.90- 1.12)	0.85 (0.72- 1.00)
3rd quartile	**1.14 (1.03- 1.26)**	**1.14 (1.03- 1.25)**	1.11 (1.00- 1.24)	1.02 (0.93- 1.13)	0.87 (0.72- 1.05)	1.03 (0.92- 1.16)	1.05 (0.95- 1.17)	1.02 (0.93- 1.12)	**0.84 (0.74- 0.96)**
2nd quartile	**1.14 (1.04- 1.26)**	**1.11 (1.01- 1.22)**	**1.16 (1.05- 1.28)**	**0.89 (0.81- 0.98)**	0.96 (0.82- 1.12)	1.02 (0.91- 1.15)	0.99 (0.91- 1.08)	0.98 (0.90- 1.07)	0.93 (0.85- 1.03)

Table 3- 7. Single pollutant models - Associations between exposures to selected pollutants (criteria and air toxics) and ED visits for asthma among children residing within 10 km radius of the air monitoring site (observed data).

Otherwise as Table 3-6.

Exposures	PM2.5		CO		NO2		SO2		O3#		O3 (Windsor)		Formaldehyde		Benzene		MEK	
	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)
10 km buffer																		
Current day																		
4th quartile	**1.25**	**(1.01- 1.56)**	0.89	(0.73- 1.07)	0.86	(0.69- 1.08)	0.88	(0.72- 1.08)	0.83	(0.57- 1.22)	0.79	(0.57- 1.11)	1.02	(0.78- 1.32)	1.13	(0.92- 1.40)	1.04	(0.76- 1.42)
3rd quartile	1.05	(0.85- 1.29)	0.96	(0.80- 1.16)	1.07	(0.87- 1.31)	0.97	(0.80- 1.17)	0.75	(0.53- 1.05)	1.17	(0.90- 1.52)	0.98	(0.78- 1.22)	1.05	(0.84- 1.30)	1.12	(0.86- 1.47)
2nd quartile	1.21	(1.00- 1.46)	1.06	(0.89- 1.26)	0.98	(0.81- 1.19)	1.00	(0.82- 1.22)	0.91	(0.68- 1.21)	1.01	(0.83- 1.24)	0.91	(0.73- 1.12)	0.98	(0.80- 1.20)	1.04	(0.84- 1.30)
1 day lag																		
4th quartile	1.10	(0.89- 1.37)	1.05	(0.87- 1.28)	0.96	(0.77- 1.19)	1.22	(0.99- 1.49)	0.99	(0.67- 1.45)	0.87	(0.67- 1.14)	0.98	(0.76- 1.28)	1.16	(0.94- 1.44)	1.01	(0.74- 1.39)
3rd quartile	1.00	(0.82- 1.22)	1.07	(0.89- 1.29)	1.06	(0.86- 1.30)	1.05	(0.86- 1.29)	0.99	(0.71- 1.38)	1.12	(0.92- 1.37)	1.04	(0.83- 1.30)	1.11	(0.90- 1.37)	1.04	(0.80- 1.36)
2nd quartile	1.00	(0.83- 1.21)	**1.24**	**(1.04- 1.48)**	1.06	(0.87- 1.29)	**1.31**	**(1.07- 1.60)**	0.94	(0.70- 1.26)	1.11	(0.87- 1.41)	1.14	(0.92- 1.41)	0.97	(0.79- 1.19)	1.09	(0.87- 1.36)
2-day-lag average																		
4th quartile	0.95	(0.77- 1.17)	1.07	(0.87- 1.31)	1.10	(0.89- 1.38)	1.17	(0.95- 1.44)	1.04	(0.69- 1.56)	0.97	(0.79- 1.21)	0.95	(0.74- 1.20)	1.04	(0.85- 1.28)	1.03	(0.76- 1.39)
3rd quartile	0.94	(0.77- 1.15)	1.19	(0.99- 1.44)	1.07	(0.87- 1.33)	1.02	(0.84- 1.24)	0.84	(0.60- 1.17)	1.13	(0.89- 1.45)	0.92	(0.74- 1.15)	1.00	(0.83- 1.21)	0.96	(0.74- 1.24)
2nd quartile	0.86	(0.71- 1.04)	1.08	(0.90- 1.30)	1.05	(0.86- 1.28)	1.21	(1.00- 1.46)	0.96	(0.73- 1.28)	1.08	(0.85- 1.38)	0.99	(0.81- 1.20)	1.04	(0.87- 1.26)	1.05	(0.86- 1.29)
3-day-lag average																		
4th quartile	0.96	(0.78- 1.19)	1.02	(0.83- 1.27)	1.13	(0.89- 1.42)	0.96	(0.78- 1.19)	1.03	(0.66- 1.62)	1.12	(0.88- 1.43)	0.87	(0.68- 1.10)	1.00	(0.81- 1.23)	0.95	(0.69- 1.31)
3rd quartile	0.94	(0.77- 1.14)	0.99	(0.81- 1.20)	1.02	(0.83- 1.27)	1.03	(0.84- 1.25)	0.96	(0.67- 1.37)	1.06	(0.83- 1.36)	1.01	(0.81- 1.25)	1.06	(0.87- 1.28)	0.91	(0.69- 1.19)
2nd quartile	0.88	(0.73- 1.06)	1.01	(0.84- 1.21)	1.10	(0.90- 1.35)	0.96	(0.79- 1.17)	1.04	(0.78- 1.39)	1.10	(0.86- 1.40)	0.97	(0.80- 1.18)	1.06	(0.88- 1.27)	0.85	(0.69- 1.05)
4-day-lag average																		
4th quartile	1.01	(0.82- 1.26)	0.94	(0.76- 1.17)	0.91	(0.72- 1.14)	0.98	(0.79- 1.21)	1.04	(0.66- 1.64)	1.00	(0.79- 1.27)	0.86	(0.67- 1.09)	0.89	(0.72- 1.11)	1.06	(0.76- 1.47)
3rd quartile	0.87	(0.71- 1.06)	0.96	(0.79- 1.16)	0.93	(0.75- 1.14)	1.05	(0.86- 1.28)	0.92	(0.64- 1.33)	1.04	(0.82- 1.31)	0.98	(0.78- 1.22)	0.91	(0.75- 1.10)	0.94	(0.71- 1.25)
2nd quartile	1.02	(0.85- 1.23)	0.94	(0.78- 1.13)	0.82	(0.67- 1.01)	0.94	(0.77- 1.14)	1.06	(0.79- 1.41)	0.97	(0.76- 1.23)	0.87	(0.72- 1.06)	1.03	(0.86- 1.24)	0.84	(0.67- 1.05)

Table 3- 8. Multiple source models - Associations between exposures to pollutants identified as 5 source classes and ED visits for respiratory problems (observed data).

Otherwise as Table 3-3.

Sources/Exposures	Current day		1-day-lag avg		2-day-lag avg		3-day-lag avg		4-day-lag avg	
	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)
4 km buffer										
Photochemical										
4th quartile	0.76	(0.52- 1.10)	1.23	(0.85- 1.78)	1.21	(0.86- 1.70)	1.19	(0.84- 1.67)	1.09	(0.77- 1.54)
3rd quartile	0.76	(0.53- 1.07)	0.86	(0.61- 1.22)	1.06	(0.79- 1.42)	1.11	(0.83- 1.48)	0.98	(0.74- 1.30)
2nd quartile	0.85	(0.62- 1.15)	1.02	(0.75- 1.39)	0.92	(0.69- 1.22)	1.03	(0.79- 1.35)	1.10	(0.85- 1.43)
Fuel combustion										
4th quartile	0.94	(0.57- 1.54)	1.30	(0.79- 2.16)	1.06	(0.67- 1.66)	1.20	(0.75- 1.91)	1.52	(0.90- 2.58)
3rd quartile	1.22	(0.84- 1.77)	1.28	(0.89- 1.86)	1.29	(0.92- 1.81)	1.37	(0.95- 1.98)	1.21	(0.84- 1.74)
2nd quartile	1.14	(0.83- 1.57)	0.97	(0.70- 1.33)	1.17	(0.89- 1.55)	**1.35**	**(1.02- 1.77)**	1.13	(0.87- 1.48)
Combined industrial										
4th quartile	1.06	(0.70- 1.62)	1.10	(0.72- 1.67)	0.85	(0.58- 1.24)	0.90	(0.59- 1.36)	0.92	(0.60- 1.42)
3rd quartile	1.10	(0.73- 1.66)	1.47	(0.97- 2.22)	0.92	(0.65- 1.31)	0.85	(0.58- 1.25)	1.08	(0.73- 1.59)
2nd quartile	1.15	(0.80- 1.67)	1.35	(0.93- 1.95)	0.81	(0.59- 1.10)	1.02	(0.75- 1.40)	1.14	(0.83- 1.57)
Gasoline exhaust										
4th quartile	0.99	(0.73- 1.35)	1.05	(0.78- 1.42)	1.02	(0.79- 1.33)	1.24	(0.94- 1.64)	1.27	(0.96- 1.67)
3rd quartile	1.11	(0.85- 1.46)	1.04	(0.79- 1.36)	1.09	(0.86- 1.39)	**1.35**	**(1.05- 1.73)**	1.16	(0.88- 1.54)
2nd quartile	0.79	(0.60- 1.03)	0.93	(0.72- 1.21)	0.86	(0.69- 1.08)	1.04	(0.83- 1.30)	0.98	(0.77- 1.24)
Industrial solvent										
4th quartile	1.28	(0.85- 1.92)	0.71	(0.46- 1.08)	0.82	(0.56- 1.21)	0.68	(0.45- 1.03)	0.72	(0.47- 1.10)
3rd quartile	1.04	(0.73- 1.48)	**0.67**	**(0.47- 0.95)**	**0.66**	**(0.47- 0.91)**	**0.64**	**(0.45- 0.90)**	**0.69**	**(0.49- 0.98)**
2nd quartile	1.09	(0.85- 1.41)	0.86	(0.67- 1.10)	0.86	(0.68- 1.08)	0.87	(0.69- 1.10)	**0.76**	**(0.59- 0.97)**
10 km buffer										
Photochemical										
4th quartile	0.85	(0.73- 1.01)	1.17	(0.99- 1.37)	1.02	(0.88- 1.19)	0.99	(0.85- 1.15)	0.99	(0.85- 1.15)
3rd quartile	**0.77**	**(0.66- 0.90)**	1.02	(0.88- 1.19)	1.05	(0.93- 1.19)	1.06	(0.94- 1.20)	1.01	(0.90- 1.14)
2nd quartile	**0.87**	**(0.76- 0.99)**	1.12	(0.98- 1.28)	0.94	(0.84- 1.06)	1.03	(0.92- 1.15)	0.97	(0.87- 1.08)
Fuel combustion										
4th quartile	1.10	(0.89- 1.37)	1.01	(0.81- 1.25)	1.08	(0.89- 1.31)	**1.24**	**(1.02- 1.52)**	**1.27**	**(1.02- 1.59)**
3rd quartile	1.28	(1.09- 1.51)	1.07	(0.91- 1.26)	1.09	(0.94- 1.26)	1.15	(0.98- 1.34)	1.07	(0.92- 1.25)
2nd quartile	1.18	(1.03- 1.36)	1.03	(0.90- 1.18)	1.09	(0.97- 1.23)	1.12	(0.99- 1.25)	1.12	(1.00- 1.25)
Combined industrial										
4th quartile	1.00	(0.83- 1.20)	1.07	(0.89- 1.28)	0.94	(0.80- 1.11)	1.07	(0.90- 1.29)	1.04	(0.87- 1.26)
3rd quartile	1.05	(0.88- 1.26)	1.09	(0.91- 1.30)	0.99	(0.85- 1.16)	1.07	(0.90- 1.26)	1.06	(0.89- 1.26)
2nd quartile	0.98	(0.84- 1.16)	1.05	(0.89- 1.23)	0.97	(0.85- 1.11)	1.02	(0.89- 1.16)	1.10	(0.96- 1.26)
Gasoline exhaust										
4th quartile	1.07	(0.94- 1.23)	1.03	(0.90- 1.18)	0.97	(0.87- 1.09)	0.98	(0.87- 1.10)	1.00	(0.89- 1.13)
3rd quartile	**1.21**	**(1.07- 1.36)**	0.97	(0.86- 1.09)	1.03	(0.93- 1.14)	0.98	(0.88- 1.09)	0.96	(0.85- 1.08)
2nd quartile	1.07	(0.95- 1.19)	0.96	(0.86- 1.08)	0.95	(0.87- 1.05)	0.95	(0.87- 1.04)	0.99	(0.90- 1.09)
Industrial solvent										
4th quartile	1.16	(0.97- 1.38)	1.00	(0.84- 1.19)	0.88	(0.74- 1.03)	**0.78**	**(0.65- 0.93)**	**0.81**	**(0.67- 0.97)**
3rd quartile	1.02	(0.88- 1.18)	0.92	(0.79- 1.06)	0.89	(0.78- 1.02)	**0.82**	**(0.71- 0.95)**	**0.80**	**(0.69- 0.92)**
2nd quartile	1.08	(0.97- 1.20)	0.99	(0.89- 1.10)	0.94	(0.85- 1.03)	0.91	(0.83- 1.01)	**0.87**	**(0.78- 0.97)**

Table 3- 9. Multiple source models - Associations between exposures to pollutants identified as 5 source classes and ED visits for asthma among children living within 10 km radius (observed data).

Events on July 11, 2001 were excluded. Otherwise as Table 3-3.

Sources/Exposures	Current day		1-day-lag avg		2-day-lag avg		3-day-lag avg		4-day-lag avg	
	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)
Photochemical										
4th quartile	1.30	(0.95- 1.79)	1.08	(0.79- 1.48)	0.80	(0.59- 1.07)	0.94	(0.70- 1.27)	0.92	(0.69- 1.22)
3rd quartile	1.22	(0.91- 1.63)	0.95	(0.70- 1.27)	0.87	(0.68- 1.13)	1.18	(0.92- 1.52)	1.07	(0.84- 1.35)
2nd quartile	1.02	(0.78- 1.34)	1.04	(0.79- 1.36)	0.78	(0.61- 1.00)	1.15	(0.91- 1.45)	0.98	(0.79- 1.22)
Fuel combustion										
4th quartile	0.87	(0.58- 1.30)	0.88	(0.59- 1.31)	1.02	(0.70- 1.47)	1.08	(0.74- 1.57)	0.96	(0.64- 1.43)
3rd quartile	0.86	(0.62- 1.18)	1.13	(0.83- 1.56)	1.11	(0.83- 1.49)	0.93	(0.69- 1.25)	0.94	(0.71- 1.26)
2nd quartile	0.92	(0.70- 1.21)	1.27	(0.96- 1.69)	1.10	(0.86- 1.42)	0.89	(0.70- 1.14)	0.91	(0.72- 1.15)
Combined industrial										
4th quartile	1.33	(0.94- 1.88)	0.96	(0.68- 1.36)	0.98	(0.70- 1.35)	1.15	(0.81- 1.62)	1.34	(0.94- 1.91)
3rd quartile	1.10	(0.78- 1.55)	0.91	(0.65- 1.27)	1.03	(0.76- 1.38)	1.03	(0.75- 1.41)	1.26	(0.92- 1.73)
2nd quartile	1.19	(0.89- 1.60)	0.98	(0.74- 1.31)	0.98	(0.76- 1.26)	1.05	(0.83- 1.34)	**1.35**	**(1.06- 1.73)**
Gasoline exhaust										
4th quartile	0.94	(0.72- 1.21)	1.22	(0.93- 1.59)	1.09	(0.87- 1.37)	0.96	(0.76- 1.21)	0.90	(0.71- 1.13)
3rd quartile	0.80	(0.63- 1.01)	0.97	(0.76- 1.25)	1.04	(0.84- 1.29)	1.05	(0.85- 1.30)	0.98	(0.78- 1.24)
2nd quartile	0.96	(0.77- 1.20)	**1.33**	**(1.06- 1.67)**	1.15	(0.94- 1.40)	1.01	(0.83- 1.22)	0.98	(0.80- 1.19)
Industrial solvent										
4th quartile	1.01	(0.71- 1.44)	1.00	(0.70- 1.43)	0.97	(0.70- 1.36)	1.06	(0.75- 1.50)	1.29	(0.91- 1.85)
3rd quartile	1.12	(0.83- 1.52)	0.98	(0.72- 1.33)	0.87	(0.65- 1.16)	0.96	(0.71- 1.29)	1.05	(0.78- 1.42)
2nd quartile	1.08	(0.86- 1.36)	0.98	(0.77- 1.25)	0.93	(0.74- 1.16)	0.93	(0.74- 1.17)	0.97	(0.76- 1.23)

Table 3- 10. Multiple pollutant models - Associations between exposures to selected criteria pollutants and ED visits for respiratory problems (observed data).

Otherwise as Table 3-6.

Sources	CO		NO2		SO2		O3 (Windsor)		PM2.5	
	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)
4 km buffer										
Current day										
4th quartile	0.93	(0.68- 1.27)	1.15	(0.83- 1.60)	-	-	-	-	-	-
3rd quartile	0.81	(0.62- 1.07)	1.04	(0.80- 1.35)	-	-	-	-	-	-
2nd quartile	0.90	(0.72- 1.13)	0.98	(0.77- 1.24)	-	-	-	-	-	-
1 day lag										
4th quartile	1.14	(0.83- 1.56)	0.01	(0.91- 0.00)	-	-	-	-	-	-
3rd quartile	0.92	(0.70- 1.21)	0.04	(0.85- 0.00)	-	-	-	-	-	-
2nd quartile	0.90	(0.72- 1.13)	0.56	(0.45- 0.00)	-	-	-	-	-	-
2-day-lag average										
4th quartile	0.95	(0.69- 1.32)	1.10	(0.80- 1.51)	-	-	-	-	-	-
3rd quartile	0.92	(0.70- 1.19)	0.92	(0.70- 1.21)	-	-	-	-	-	-
2nd quartile	0.88	(0.70- 1.11)	0.99	(0.78- 1.26)	-	-	-	-	-	-
3-day-lag average										
4th quartile	1.08	(0.77- 1.53)	1.28	(0.94- 1.76)	-	-	-	-	-	-
3rd quartile	1.11	(0.85- 1.44)	0.98	(0.74- 1.29)	-	-	-	-	-	-
2nd quartile	1.08	(0.86- 1.36)	1.12	(0.89- 1.43)	-	-	-	-	-	-
4-day-lag average										
4th quartile	1.29	(0.89- 1.86)	1.27	(0.92- 1.76)	-	-	-	-	-	-
3rd quartile	**1.34**	**(1.01- 1.78)**	1.03	(0.78- 1.36)	-	-	-	-	-	-
2nd quartile	**1.31**	**(1.02- 1.67)**	**1.29**	**(1.01- 1.65)**	-	-	-	-	-	-
10 km buffer										
Current day										
4th quartile	0.93	(0.79- 1.10)	1.10	(0.89- 1.36)	1.09	(0.93- 1.29)	**0.81**	**(0.65- 0.99)**	1.00	(0.83- 1.20)
3rd quartile	0.87	(0.75- 1.00)	1.09	(0.93- 1.28)	1.09	(0.95- 1.25)	**0.84**	**(0.72- 0.99)**	0.97	(0.83- 1.13)
2nd quartile	0.94	(0.84- 1.06)	0.96	(0.84- 1.09)	1.10	(0.96- 1.25)	0.96	(0.85- 1.08)	0.99	(0.87- 1.13)
1 day lag										
4th quartile	1.08	(0.92- 1.28)	0.97	(0.79- 1.20)	1.06	(0.91- 1.25)	0.91	(0.74- 1.13)	1.03	(0.86- 1.25)
3rd quartile	0.96	(0.83- 1.10)	0.99	(0.85- 1.16)	0.99	(0.87- 1.13)	0.87	(0.74- 1.03)	1.02	(0.87- 1.19)
2nd quartile	1.07	(0.95- 1.20)	0.94	(0.82- 1.07)	0.92	(0.81- 1.05)	0.96	(0.85- 1.08)	1.03	(0.90- 1.18)
2-day-lag average										
4th quartile	1.08	(0.91- 1.28)	1.15	(0.96- 1.39)	0.86	(0.72- 1.02)	0.83	(0.66- 1.06)	1.00	(0.85- 1.17)
3rd quartile	1.02	(0.89- 1.18)	1.00	(0.87- 1.16)	0.89	(0.78- 1.02)	0.86	(0.71- 1.04)	1.05	(0.91- 1.20)
2nd quartile	0.99	(0.88- 1.13)	1.02	(0.90- 1.16)	0.81	(0.72- 0.92)	0.97	(0.85- 1.10)	1.04	(0.93- 1.18)
3-day-lag average										
4th quartile	1.03	(0.87- 1.21)	**1.23**	**(1.02- 1.47)**	1.06	(0.90- 1.25)	0.94	(0.74- 1.19)	0.94	(0.80- 1.11)
3rd quartile	1.02	(0.89- 1.16)	1.11	(0.96- 1.28)	1.03	(0.89- 1.20)	0.91	(0.75- 1.10)	1.00	(0.86- 1.15)
2nd quartile	1.00	(0.89- 1.12)	1.10	(0.98- 1.25)	1.02	(0.90- 1.16)	0.98	(0.86- 1.12)	1.01	(0.90- 1.13)
4-day-lag average										
4th quartile	1.02	(0.86- 1.21)	**1.23**	**(1.02- 1.49)**	0.91	(0.78- 1.07)	1.01	(0.77- 1.31)	1.04	(0.88- 1.24)
3rd quartile	1.08	(0.94- 1.23)	1.12	(0.97- 1.30)	1.01	(0.88- 1.16)	0.92	(0.74- 1.14)	1.05	(0.91- 1.22)
2nd quartile	1.10	(0.97- 1.24)	1.13	(1.00- 1.28)	**0.86**	**(0.76- 0.98)**	1.08	(0.92- 1.26)	1.12	(0.99- 1.27)

Table S3- 1. Pearson correlation coefficients between air toxics and criteria air pollutants. Criteria air pollutants were measured at Linwood otherwise stated by site name.

Pollutants	Acetaldehyde	Benzaldehyde	Formaldehyde	Hexaldehyde	iso-Butyraldehyde	Propionaldehyde	Tolualdehyde	Acetylene	Benzene	1,3-Butadiene	Dichlorodifluoromethane	Ethylbenzene	Methyl ethyl ketone	m,p-Xylene	n-Octane	o-Xylene	Propylene	Tetrachloroethylene	Trichlorofluoromethane	Trichlorotrifluoroethane	1,2,4-Trimethylbenzene	1,3,5-Trimethylbenzene	Toluene	PM10 (Dearborn)	PM2.5	CO	NO2	SO2	O3 (Apr-Sept)	O3 (Windsor)
N	284	284	283	284	284	284	283	302	302	302	302	300	302	300	301	301	300	302	302	302	302	301	300	361	324	357	298	334	180	320
Acetaldehyde	1.00																													
Benzaldehyde	0.64	1.00																												
Formaldehyde	0.80	0.77	1.00																											
Hexaldehyde	0.69	0.62	0.54	1.00																										
iso-Butyraldehyde	0.89	0.60	0.68	0.68	1.00																									
Propionaldehyde	0.84	0.74	0.81	0.66	0.79	1.00																								
Tolualdehyde	0.64	0.68	0.58	0.69	0.61	0.73	1.00																							
Acetylene	0.31	0.25	0.27	0.07	0.19	0.23	0.16	1.00																						
Benzene	0.45	0.39	0.31	0.28	0.31	0.32	0.27	0.69	1.00																					
1,3-Butadiene	0.35	0.28	0.31	0.13	0.23	0.24	0.18	0.73	0.63	1.00																				
Dichlorodifluoromethane	0.44	0.21	0.31	0.35	0.37	0.32	0.26	0.29	0.34	0.34	1.00																			
Ethylbenzene	0.42	0.34	0.35	0.30	0.30	0.29	0.31	0.63	0.68	0.71	0.38	1.00																		
Methyl ethyl ketone	0.43	0.44	0.35	0.46	0.38	0.35	0.37	0.22	0.50	0.26	0.38	0.45	1.00																	
m,p-Xylene	0.43	0.35	0.37	0.31	0.31	0.29	0.32	0.63	0.69	0.71	0.40	0.99	0.45	1.00																
n-Octane	0.29	0.20	0.21	0.19	0.20	0.21	0.20	0.34	0.37	0.48	0.24	0.37	0.30	0.35	1.00															
o-Xylene	0.42	0.37	0.36	0.30	0.29	0.29	0.33	0.67	0.73	0.75	0.41	0.96	0.45	0.97	0.40	1.00														
Propylene	0.28	0.12	0.23	0.11	0.21	0.18	0.11	0.32	0.26	0.32	0.17	0.23	0.17	0.23	0.22	0.24	1.00													
Tetrachloroethylene	0.08	0.05	0.06	0.10	0.07	0.07	0.11	0.19	0.21	0.20	0.03	0.20	0.16	0.20	0.10	0.20	-0.01	1.00												
Trichlorofluoromethane	0.26	0.08	0.14	0.23	0.23	0.18	0.15	0.12	0.16	0.17	0.54	0.19	0.15	0.22	0.15	0.24	0.09	-0.03	1.00											
Trichlorotrifluoroethane	0.13	-0.12	0.03	-0.03	0.16	0.08	0.01	0.04	-0.02	0.14	0.14	0.03	-0.05	0.01	0.17	0.00	0.20	-0.06	0.01	1.00										
1,2,4-Trimethylbenzene	0.46	0.37	0.36	0.35	0.35	0.34	0.37	0.67	0.75	0.78	0.44	0.94	0.49	0.95	0.41	0.93	0.25	0.24	0.24	0.02	1.00									
1,3,5-Trimethylbenzene	0.43	0.35	0.33	0.30	0.31	0.31	0.36	0.67	0.72	0.79	0.40	0.89	0.44	0.90	0.44	0.90	0.22	0.25	0.21	0.00	0.95	1.00								
Toluene	0.40	0.38	0.31	0.32	0.28	0.27	0.30	0.62	0.77	0.65	0.34	0.82	0.51	0.81	0.34	0.84	0.21	0.20	0.16	-0.07	0.85	0.82	1.00							
PM10 (Dearborn)	0.14	0.14	0.20	0.11	0.09	0.13	0.16	0.03	0.07	-0.07	0.01	0.04	0.25	0.04	0.08	0.02	0.15	-0.09	-0.03	-0.03	0.03	0.04	0.02	1.00						
PM2.5	0.18	0.19	0.15	0.19	0.14	0.16	0.18	0.15	0.32	-0.05	0.03	0.14	0.37	0.13	0.01	0.13	0.25	-0.02	-0.01	-0.02	0.15	0.11	0.17	0.56	1.00					
CO	0.20	0.16	0.20	0.09	0.15	0.17	0.13	0.48	0.43	0.42	0.08	0.46	0.27	0.45	0.19	0.44	0.06	0.06	0.00		0.45	0.42	0.41	0.29	0.30	1.00				
NO2	0.25	0.21	0.29	0.16	0.18	0.26	0.24	0.37	0.33	0.16	0.03	0.27	0.26	0.26	0.11	0.27	0.39	0.02	-0.04	0.02	0.29	0.23	0.21	0.47	0.51	0.64	1.00			
SO2	0.16	0.10	0.12	0.14	0.11	0.15	0.16	0.22	0.26	0.10	0.07	0.08	0.22	0.07	0.09	0.12	0.44	-0.03	0.01	0.08	0.16	0.11	0.14	0.27	0.46	0.33	0.58	1.00		
O3 (Apr-Sept)	0.09	0.16	0.15	0.36	0.03	0.05	0.26	-0.04	0.18	-0.18	0.11	0.10	0.37	0.10	-0.02	0.09	-0.07	-0.02	0.06	-0.30	0.03	0.02	0.13	0.55	0.53	0.21	0.15	0.15	1.00	
O3 (Windsor)	0.36	0.42	0.31	0.60	0.35	0.39	0.47	-0.16	0.14	-0.12	0.30	0.09	0.50	0.10	0.02	0.11	-0.08	0.05	0.06	-0.17	0.14	0.10	0.17	0.34	0.35	-0.06	0.15	0.19	0.96	1.00

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Table S3- 2. Pearson correlation coefficients between 5 source classes and air toxics.

Sources/Pollutants	Photochemical pollutants	Fuel combustion	Combined industrial	Gasoline exhaust	Industrial solvent	Acetaldehyde	Benzaldehyde	Formaldehyde	Hexaldehyde	iso-Butyraldehyde	Propionaldehyde	Tolualdehyde	Acetylene	Benzene	1,3-Butadiene	Dichlorodifluoromethane	Ethylbenzene	Methyl ethyl ketone	m,p-Xylene	n-Octane	o-Xylene	Propylene	Tetrachloroethylene	Trichlorofluoromethane	Trichlorotrifluoroethane	1,2,4-Trimethylbenzene	1,3,5-Trimethylbenzene	Toluene
N	265	265	265	265	265	284	284	283	284	284	284	283	302	302	302	302	300	302	300	301	301	300	302	302	302	302	301	300
Photochemical pollutants	1.00																											
Fuel combustion	0.43	1.00																										
Combined industrial	-0.48	-0.61	1.00																									
Gasoline exhaust	0.24	0.22	-0.36	1.00																								
Industrial solvent	0.19	0.38	-0.54	0.15	1.00																							
Acetaldehyde	0.56	0.98	-0.64	0.29	0.39	1.00																						
Benzaldehyde	0.66	0.67	-0.69	0.38	0.50	0.64	1.00																					
Formaldehyde	0.93	0.73	-0.61	0.26	0.31	0.80	0.77	1.00																				
Hexaldehyde	0.29	0.72	-0.56	0.14	0.47	0.69	0.62	0.54	1.00																			
iso-Butyraldehyde	0.38	0.92	-0.54	0.17	0.36	0.89	0.60	0.68	0.68	1.00																		
Propionaldehyde	0.60	0.91	-0.60	0.24	0.37	0.84	0.74	0.81	0.66	0.79	1.00																	
Tolualdehyde	0.42	0.65	-0.56	0.22	0.40	0.64	0.68	0.58	0.69	0.61	0.73	1.00																
Acetylene	0.30	0.18	-0.06	0.80	0.17	0.31	0.25	0.27	0.07	0.19	0.23	0.16	1.00															
Benzene	0.20	0.36	-0.38	0.77	0.46	0.45	0.39	0.31	0.28	0.31	0.32	0.27	0.69	1.00														
1,3-Butadiene	0.30	0.23	-0.24	0.81	0.20	0.35	0.28	0.31	0.13	0.23	0.24	0.18	0.73	0.63	1.00													
Dichlorodifluoromethane	0.19	0.43	-0.06	0.27	0.37	0.44	0.21	0.31	0.35	0.37	0.32	0.26	0.29	0.34	0.34	1.00												
Ethylbenzene	0.30	0.37	-0.52	0.88	0.43	0.42	0.34	0.35	0.30	0.30	0.29	0.31	0.63	0.68	0.71	0.38	1.00											
Methyl ethyl ketone	0.23	0.39	-0.52	0.17	1.00	0.43	0.44	0.35	0.46	0.38	0.35	0.37	0.22	0.50	0.26	0.38	0.45	1.00										
m,p-Xylene	0.31	0.38	-0.53	0.88	0.43	0.43	0.35	0.37	0.31	0.31	0.29	0.32	0.63	0.69	0.71	0.40	0.99	0.45	1.00									
n-Octane	0.17	0.23	-0.17	0.36	0.32	0.29	0.20	0.21	0.19	0.20	0.21	0.20	0.34	0.37	0.48	0.24	0.37	0.30	0.35	1.00								
o-Xylene	0.32	0.37	-0.53	0.92	0.45	0.42	0.37	0.36	0.30	0.29	0.29	0.33	0.67	0.73	0.75	0.41	0.96	0.45	0.97	0.40	1.00							
Propylene	0.19	0.24	-0.06	0.24	0.15	0.28	0.12	0.23	0.11	0.21	0.18	0.11	0.32	0.26	0.32	0.17	0.23	0.17	0.23	0.22	0.24	1.00						
Tetrachloroethylene	0.06	0.05	-0.17	0.19	0.14	0.08	0.05	0.06	0.10	0.07	0.07	0.11	0.19	0.21	0.20	0.03	0.20	0.16	0.20	0.10	0.20	-0.01	1.00					
Trichlorofluoromethane	0.03	0.25	0.03	0.13	0.14	0.26	0.08	0.14	0.23	0.23	0.18	0.15	0.12	0.16	0.17	0.54	0.19	0.15	0.22	0.15	0.24	0.09	-0.03	1.00				
Trichlorotrifluoroethane	-0.02	0.14	0.21	-0.04	-0.04	0.13	-0.12	0.03	-0.03	0.16	0.08	0.01	0.04	-0.02	0.14	0.14	0.03	-0.05	0.01	0.17	0.00	0.20	-0.06	0.01	1.00			
1,2,4-Trimethylbenzene	0.30	0.37	-0.52	0.89	0.45	0.46	0.37	0.36	0.35	0.35	0.34	0.37	0.67	0.75	0.78	0.44	0.94	0.49	0.95	0.41	0.93	0.25	0.24	0.24	0.02	1.00		
1,3,5-Trimethylbenzene	0.29	0.33	-0.47	0.88	0.40	0.43	0.35	0.33	0.30	0.31	0.31	0.36	0.67	0.72	0.79	0.40	0.89	0.44	0.90	0.41	0.90	0.22	0.25	0.21	0.00	0.95	1.00	
Toluene	0.24	0.36	-0.54	0.84	0.50	0.40	0.38	0.31	0.32	0.28	0.27	0.30	0.62	0.77	0.65	0.34	0.82	0.51	0.82	0.34	0.84	0.21	0.20	0.16	-0.07	0.85	0.82	1.00

Table S3- 3. Pearson correlation coefficients between 5 source classes and criteria air pollutants.

Sources/Pollutants	Photochemical pollutants	Fuel combustion	Combined industrial	Gasoline exhaust	Industrial solvent	PM10 (Dearborn)	PM2.5	CO	NO2	SO2	O3 (Apr-Sept)	O3 (Windsor)
N	265	265	265	265	265	361	324	357	298	334	180	320
Photochemical pollutants	1.00											
Fuel combustion	0.43	1.00										
Combined industrial	-0.48	-0.61	1.00									
Gasoline exhaust	0.24	0.22	-0.36	1.00								
Industrial solvent	0.19	0.38	-0.54	0.15	1.00							
PM10 (Dearborn)	0.22	0.15	-0.14	-0.08	0.23	1.00						
PM2.5	0.09	0.18	-0.12	0.05	0.34	0.56	1.00					
CO	0.23	0.15	-0.21	0.47	0.26	0.29	0.30	1.00				
NO2	0.36	0.18	-0.24	0.25	0.29	0.47	0.51	0.64	1.00			
SO2	0.11	0.12	-0.08	0.10	0.23	0.27	0.46	0.33	0.58	1.00		
O3 (Apr-Sept)	0.10	0.13	-0.20	0.01	0.41	0.55	0.53	0.21	0.15	0.15	1.00	
O3 (Windsor)	0.17	0.38	-0.42	-0.07	0.51	0.34	0.35	-0.06	0.15	0.19	0.96	1.00

Table S3- 4. Study population size and number of Medicaid visits, 4/19/2002-4/18/2003

Variable		Study population	Hospital admission			Emergency department visit			Outpatient visit		
			Asthma	Respiratory	Injury	Asthma	Respiratory	Injury	Asthma	Respiratory	Injury
		N (%)	n	n	n	n	n	n	n	n	n
4 km buffer											
N		4731	49	33	41	156	826	597	536	1213	9067
Gender											
	Female	2287 (48)	16	15	26	57	330	281	218	452	4536
	Male	2444 (52)	33	18	15	99	496	316	318	761	4531
Race											
	Black	642 (14)	8	8	5	28	116	80	57	125	344
	White	2312 (49)	19	12	16	72	491	306	301	802	6234
	Others	1777 (38)	22	13	20	56	219	211	178	286	2489
Age group (yrs)											
	0 to 4	1562 (33)	22	8	20	67	283	289	243	285	4178
	5 to 9	1418 (30)	14	13	10	52	237	173	167	355	2945
	10 to 14	1134 (24)	6	10	8	25	204	96	90	417	1437
	15 to 18	617 (13)	7	2	3	12	102	39	36	156	507
10 km buffer											
N		8129	289	188	235	1016	4021	3321	2448	4201	24341
Gender											
	Female	3988 (49)	133	75	101	479	1630	1704	1048	1742	12267
	Male	4141 (51)	156	113	134	537	2391	1617	1400	2459	12074
Race											
	Black	2803 (34)	211	121	143	763	2495	2169	1461	1923	5793
	White	2748 (34)	45	42	44	154	1196	810	690	1859	14831
	Others	2578 (32)	33	25	48	99	330	342	297	419	3717
Age group (yrs)											
	0 to 4	2385 (30)	109	48	118	391	1139	1485	865	936	10564
	5 to 9	2233 (28)	83	55	38	319	1082	901	787	1180	7801
	10 to 14	1945 (24)	46	47	37	200	1195	608	609	1486	4432
	15 to 18	1411 (18)	48	34	36	101	568	299	168	586	1485

Table S3- 5. Single source models - Associations between exposures to pollutants identified as 5 source classes and ED visits for injury.

Otherwise as Table 3-3.

Exposures	Photochemical RR (95%CI)	Fuel Combustion RR (95%CI)	Combined industrial RR (95%CI)	Gasoline exhaust RR (95%CI)	Industrial RR (95%CI)
4 km buffer					
Current day					
4th quartile	0.87 (0.67- 1.13)	1.04 (0.75- 1.46)	0.86 (0.60- 1.23)	1.00 (0.76- 1.32)	1.29 (0.86- 1.94)
3rd quartile	0.99 (0.78- 1.27)	0.86 (0.64- 1.15)	**0.70 (0.50- 0.99)**	0.98 (0.75- 1.29)	1.05 (0.72- 1.54)
2nd quartile	0.85 (0.66- 1.10)	0.88 (0.66- 1.17)	0.82 (0.63- 1.06)	0.87 (0.66- 1.15)	1.08 (0.79- 1.47)
1 day lag					
4th quartile	0.90 (0.67- 1.20)	1.06 (0.75- 1.50)	0.90 (0.63- 1.30)	0.91 (0.69- 1.21)	0.75 (0.50- 1.14)
3rd quartile	0.94 (0.71- 1.25)	1.06 (0.79- 1.43)	0.78 (0.56- 1.09)	0.91 (0.69- 1.21)	0.79 (0.55- 1.15)
2nd quartile	1.02 (0.77- 1.34)	0.96 (0.71- 1.29)	0.91 (0.70- 1.18)	0.86 (0.65- 1.14)	0.79 (0.57- 1.08)
2-day-lag average					
4th quartile	0.91 (0.70- 1.19)	0.94 (0.69- 1.27)	0.91 (0.65- 1.27)	0.90 (0.70- 1.16)	1.08 (0.74- 1.57)
3rd quartile	0.91 (0.70- 1.17)	0.89 (0.68- 1.17)	0.89 (0.65- 1.21)	0.83 (0.65- 1.07)	1.02 (0.72- 1.43)
2nd quartile	0.88 (0.69- 1.13)	0.80 (0.62- 1.03)	1.02 (0.81- 1.28)	0.95 (0.75- 1.20)	1.03 (0.77- 1.38)
3-day-lag average					
4th quartile	1.05 (0.80- 1.37)	1.01 (0.74- 1.37)	0.89 (0.61- 1.29)	1.01 (0.78- 1.29)	0.90 (0.61- 1.33)
3rd quartile	0.95 (0.73- 1.24)	0.91 (0.69- 1.20)	0.99 (0.71- 1.37)	0.94 (0.73- 1.21)	1.00 (0.71- 1.42)
2nd quartile	0.98 (0.76- 1.26)	0.81 (0.62- 1.05)	0.92 (0.73- 1.15)	1.03 (0.82- 1.30)	0.86 (0.64- 1.15)
4-day-lag average					
4th quartile	0.96 (0.73- 1.26)	1.02 (0.74- 1.41)	0.82 (0.55- 1.21)	1.05 (0.81- 1.35)	1.11 (0.74- 1.67)
3rd quartile	0.99 (0.77- 1.29)	1.01 (0.76- 1.33)	0.87 (0.62- 1.22)	0.96 (0.74- 1.25)	1.10 (0.76- 1.59)
2nd quartile	1.07 (0.84- 1.38)	0.93 (0.71- 1.20)	0.85 (0.68- 1.07)	0.97 (0.77- 1.23)	0.97 (0.72- 1.32)
10 km buffer					
Current day					
4th quartile	1.06 (0.93- 1.21)	1.15 (0.98- 1.33)	0.87 (0.75- 1.02)	1.01 (0.90- 1.15)	0.95 (0.79- 1.14)
3rd quartile	1.07 (0.94- 1.20)	1.00 (0.88- 1.14)	**0.79 (0.68- 0.91)**	1.11 (0.99- 1.25)	0.96 (0.81- 1.13)
2nd quartile	1.08 (0.95- 1.22)	1.04 (0.91- 1.18)	0.93 (0.83- 1.05)	1.03 (0.91- 1.16)	1.00 (0.87- 1.15)
1 day lag					
4th quartile	0.98 (0.86- 1.11)	0.95 (0.81- 1.10)	0.90 (0.76- 1.05)	1.03 (0.91- 1.16)	0.93 (0.78- 1.12)
3rd quartile	1.01 (0.90- 1.14)	0.94 (0.82- 1.06)	0.90 (0.78- 1.04)	1.00 (0.89- 1.13)	0.93 (0.79- 1.10)
2nd quartile	1.02 (0.90- 1.15)	0.95 (0.84- 1.08)	1.02 (0.91- 1.14)	0.98 (0.87- 1.11)	0.94 (0.82- 1.07)
2-day-lag average					
4th quartile	0.97 (0.86- 1.09)	0.98 (0.86- 1.13)	0.90 (0.78- 1.04)	0.96 (0.86- 1.07)	1.05 (0.89- 1.24)
3rd quartile	0.97 (0.87- 1.08)	0.92 (0.81- 1.03)	0.91 (0.79- 1.04)	0.96 (0.87- 1.07)	1.02 (0.88- 1.19)
2nd quartile	0.91 (0.81- 1.01)	0.90 (0.80- 1.00)	0.98 (0.89- 1.09)	1.01 (0.91- 1.12)	0.94 (0.83- 1.06)
3-day-lag average					
4th quartile	1.01 (0.89- 1.13)	1.04 (0.91- 1.19)	**0.80 (0.68- 0.94)**	1.00 (0.89- 1.11)	1.09 (0.92- 1.29)
3rd quartile	1.00 (0.90- 1.12)	0.94 (0.84- 1.07)	0.89 (0.78- 1.03)	0.99 (0.89- 1.10)	1.09 (0.94- 1.27)
2nd quartile	0.94 (0.84- 1.05)	0.89 (0.80- 1.00)	0.92 (0.84- 1.02)	1.01 (0.91- 1.11)	0.95 (0.83- 1.07)
4-day-lag average					
4th quartile	0.99 (0.88- 1.11)	1.09 (0.94- 1.26)	0.84 (0.71- 1.00)	1.04 (0.93- 1.16)	1.11 (0.93- 1.33)
3rd quartile	0.98 (0.88- 1.10)	0.95 (0.84- 1.07)	0.89 (0.77- 1.03)	0.99 (0.88- 1.10)	1.02 (0.87- 1.20)
2nd quartile	0.99 (0.89- 1.10)	**0.89 (0.79- 0.99)**	**0.89 (0.81- 0.99)**	1.03 (0.93- 1.14)	0.93 (0.81- 1.06)

Table S3- 6. Single pollutant models - Associations between exposures to air pollutants (criteria and air toxics) and ED visits for injury. Otherwise as Table 3-6.

Exposures	PM2.5 RR	(95%CI)	CO RR	(95%CI)	NO2 RR	(95%CI)	SO2 RR	(95%CI)	O3# RR	(95%CI)	O3 (Windsor) RR	(95%CI)	Formaldehyde RR	(95%CI)	Benzene RR	(95%CI)	MEK RR	(95%CI)
4 km buffer																		
Current day																		
4th quartile	1.12	(0.86- 1.45)	**1.42**	**(1.13- 1.80)**	1.16	(0.91- 1.49)	**1.35**	**(1.07- 1.71)**	1.03	(0.68- 1.56)	**1.63**	**(1.06- 2.49)**	1.11	(0.82- 1.49)	1.02	(0.80- 1.32)	0.88	(0.61- 1.27)
3rd quartile	1.16	(0.91- 1.49)	1.21	(0.97- 1.51)	1.15	(0.91- 1.46)	1.10	(0.86- 1.39)	1.19	(0.83- 1.70)	**1.66**	**(1.15- 2.40)**	0.95	(0.72- 1.25)	0.77	(0.59- 1.00)	0.94	(0.70- 1.27)
2nd quartile	0.91	(0.72- 1.16)	1.16	(0.93- 1.44)	0.86	(0.67- 1.10)	1.18	(0.93- 1.50)	1.28	(0.93- 1.78)	1.26	(0.94- 1.69)	0.88	(0.67- 1.15)	0.91	(0.71- 1.16)	0.99	(0.78- 1.26)
1 day lag																		
4th quartile	1.08	(0.83- 1.41)	0.99	(0.78- 1.25)	1.02	(0.79- 1.32)	1.00	(0.79- 1.26)	0.86	(0.58- 1.28)	0.93	(0.64- 1.34)	0.88	(0.65- 1.19)	0.86	(0.67- 1.11)	0.80	(0.56- 1.16)
3rd quartile	1.06	(0.82- 1.37)	1.00	(0.80- 1.25)	1.01	(0.78- 1.29)	0.84	(0.66- 1.05)	0.74	(0.51- 1.06)	1.08	(0.81- 1.43)	0.97	(0.73- 1.27)	0.79	(0.61- 1.02)	0.73	(0.54- 0.99)
2nd quartile	**1.27**	**(1.01- 1.61)**	1.17	(0.95- 1.44)	1.23	(0.97- 1.55)	0.89	(0.71- 1.12)	0.81	(0.59- 1.11)	1.10	(0.84- 1.45)	1.00	(0.76- 1.31)	0.98	(0.77- 1.25)	0.99	(0.78- 1.25)
2-day-lag average																		
4th quartile	0.96	(0.74- 1.25)	0.90	(0.71- 1.15)	1.04	(0.81- 1.34)	0.98	(0.77- 1.26)	0.87	(0.58- 1.30)	0.96	(0.71- 1.31)	0.94	(0.71- 1.25)	0.88	(0.70- 1.12)	0.91	(0.64- 1.29)
3rd quartile	1.11	(0.87- 1.41)	0.99	(0.79- 1.23)	0.94	(0.73- 1.21)	1.01	(0.80- 1.27)	0.78	(0.55- 1.10)	1.09	(0.83- 1.44)	0.90	(0.69- 1.17)	0.79	(0.63- 1.00)	**0.71**	**(0.52- 0.95)**
2nd quartile	1.01	(0.80- 1.27)	0.98	(0.79- 1.22)	1.06	(0.84- 1.35)	0.89	(0.70- 1.12)	0.78	(0.57- 1.06)	0.90	(0.68- 1.20)	0.87	(0.68- 1.12)	**0.77**	**(0.62- 0.97)**	0.89	(0.72- 1.11)
3-day-lag average																		
4th quartile	0.97	(0.75- 1.25)	0.94	(0.73- 1.22)	1.08	(0.83- 1.40)	1.08	(0.85- 1.39)	1.01	(0.64- 1.59)	1.10	(0.83- 1.44)	0.91	(0.68- 1.21)	0.90	(0.70- 1.15)	0.89	(0.61- 1.30)
3rd quartile	1.15	(0.90- 1.45)	0.96	(0.77- 1.20)	1.05	(0.81- 1.36)	1.13	(0.89- 1.42)	0.92	(0.62- 1.34)	0.90	(0.68- 1.20)	0.99	(0.76- 1.30)	0.87	(0.69- 1.09)	0.81	(0.59- 1.10)
2nd quartile	1.03	(0.82- 1.29)	0.89	(0.71- 1.11)	0.89	(0.70- 1.15)	0.94	(0.75- 1.20)	0.98	(0.71- 1.34)	0.82	(0.61- 1.09)	0.92	(0.71- 1.18)	**0.80**	**(0.64- 0.99)**	0.89	(0.72- 1.11)
4-day-lag average																		
4th quartile	0.99	(0.76- 1.27)	1.00	(0.77- 1.29)	1.14	(0.87- 1.49)	1.07	(0.83- 1.38)	1.17	(0.73- 1.87)	0.91	(0.69- 1.20)	0.95	(0.71- 1.27)	0.93	(0.72- 1.20)	1.00	(0.68- 1.47)
3rd quartile	1.00	(0.79- 1.28)	0.93	(0.74- 1.17)	1.05	(0.80- 1.37)	0.98	(0.78- 1.25)	1.26	(0.86- 1.85)	0.83	(0.62- 1.11)	0.92	(0.70- 1.23)	0.89	(0.71- 1.13)	0.81	(0.59- 1.12)
2nd quartile	1.01	(0.80- 1.28)	1.04	(0.84- 1.29)	1.12	(0.88- 1.43)	0.99	(0.79- 1.25)	0.92	(0.66- 1.29)	0.86	(0.65- 1.14)	1.07	(0.84- 1.37)	0.83	(0.66- 1.03)	0.93	(0.74- 1.16)
10 km buffer																		
Current day																		
4th quartile	0.99	(0.88- 1.11)	**1.13**	**(1.02- 1.25)**	1.00	(0.90- 1.12)	**1.12**	**(1.01- 1.24)**	1.00	(0.84- 1.19)	1.16	(0.97- 1.40)	1.03	(0.90- 1.18)	1.06	(0.95- 1.19)	0.94	(0.80- 1.12)
3rd quartile	1.03	(0.92- 1.15)	1.03	(0.93- 1.13)	1.00	(0.90- 1.11)	1.07	(0.97- 1.19)	0.98	(0.84- 1.14)	**1.20**	**(1.03- 1.40)**	1.04	(0.92- 1.18)	0.99	(0.88- 1.11)	0.92	(0.79- 1.07)
2nd quartile	0.95	(0.85- 1.05)	1.06	(0.96- 1.16)	0.97	(0.87- 1.07)	1.10	(0.99- 1.22)	1.07	(0.94- 1.23)	**1.15**	**(1.01- 1.29)**	1.02	(0.90- 1.15)	1.11	(1.00- 1.24)	0.95	(0.83- 1.09)
1 day lag																		
4th quartile	0.95	(0.84- 1.06)	1.04	(0.94- 1.15)	1.00	(0.90- 1.12)	1.04	(0.93- 1.15)	1.04	(0.87- 1.24)	1.00	(0.86- 1.17)	0.99	(0.86- 1.13)	0.97	(0.87- 1.09)	0.95	(0.80- 1.12)
3rd quartile	0.96	(0.86- 1.08)	1.04	(0.94- 1.14)	0.99	(0.89- 1.10)	0.97	(0.87- 1.07)	1.14	(0.98- 1.33)	0.96	(0.85- 1.09)	0.99	(0.88- 1.12)	0.94	(0.83- 1.05)	0.99	(0.86- 1.15)
2nd quartile	0.98	(0.89- 1.09)	1.06	(0.97- 1.17)	1.02	(0.92- 1.13)	1.03	(0.93- 1.14)	1.05	(0.91- 1.21)	1.01	(0.89- 1.14)	1.03	(0.91- 1.16)	1.03	(0.92- 1.14)	0.97	(0.85- 1.11)
2-day-lag average																		
4th quartile	0.90	(0.80- 1.01)	0.96	(0.87- 1.07)	1.02	(0.91- 1.13)	1.01	(0.90- 1.12)	0.96	(0.80- 1.14)	0.92	(0.80- 1.05)	0.97	(0.85- 1.09)	0.94	(0.84- 1.05)	1.06	(0.90- 1.24)
3rd quartile	0.95	(0.85- 1.05)	1.03	(0.94- 1.14)	0.97	(0.87- 1.09)	1.01	(0.92- 1.12)	1.07	(0.92- 1.25)	1.02	(0.90- 1.16)	0.95	(0.84- 1.06)	**0.89**	**(0.81- 0.99)**	1.08	(0.94- 1.25)
2nd quartile	0.99	(0.90- 1.10)	1.05	(0.96- 1.16)	1.03	(0.93- 1.14)	1.00	(0.91- 1.11)	1.04	(0.90- 1.19)	1.04	(0.92- 1.18)	0.96	(0.86- 1.07)	0.95	(0.86- 1.05)	0.99	(0.87- 1.11)
3-day-lag average																		
4th quartile	0.95	(0.85- 1.06)	0.97	(0.86- 1.09)	1.04	(0.92- 1.16)	1.02	(0.91- 1.14)	0.93	(0.76- 1.13)	1.04	(0.92- 1.18)	0.99	(0.87- 1.12)	0.99	(0.89- 1.10)	0.99	(0.84- 1.18)
3rd quartile	0.99	(0.89- 1.10)	0.99	(0.90- 1.09)	1.00	(0.89- 1.11)	1.02	(0.92- 1.13)	1.01	(0.85- 1.19)	1.07	(0.94- 1.21)	0.96	(0.85- 1.08)	0.91	(0.82- 1.01)	1.00	(0.86- 1.16)
2nd quartile	1.01	(0.92- 1.11)	0.97	(0.89- 1.07)	0.95	(0.85- 1.05)	0.97	(0.87- 1.07)	1.06	(0.92- 1.21)	1.02	(0.90- 1.15)	0.95	(0.85- 1.06)	0.94	(0.86- 1.04)	0.96	(0.85- 1.08)
4-day-lag average																		
4th quartile	0.94	(0.84- 1.05)	0.93	(0.83- 1.05)	1.04	(0.93- 1.17)	1.05	(0.94- 1.17)	0.98	(0.80- 1.21)	1.06	(0.94- 1.20)	0.96	(0.85- 1.09)	1.01	(0.90- 1.13)	1.08	(0.91- 1.28)
3rd quartile	0.98	(0.89- 1.09)	0.97	(0.87- 1.07)	0.99	(0.89- 1.11)	1.04	(0.93- 1.15)	1.12	(0.95- 1.32)	1.02	(0.90- 1.15)	**0.85**	**(0.75- 0.97)**	0.95	(0.85- 1.05)	1.01	(0.87- 1.17)
2nd quartile	1.00	(0.91- 1.11)	0.99	(0.90- 1.08)	1.02	(0.92- 1.13)	1.08	(0.97- 1.19)	1.01	(0.88- 1.17)	0.99	(0.87- 1.11)	0.98	(0.88- 1.09)	0.94	(0.86- 1.04)	0.97	(0.86- 1.11)

Table S3- 7. Multiple pollutant models - Associations between exposures to criteria air pollutants and ED visits for injury.

Otherwise as Table 3-6.

Exposures	CO		NO2		SO2		O3 (Windsor)		PM2.5	
	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)	RR	(95%CI)
4 km buffer										
Current day										
4th quartile	**1.53**	**(1.10- 2.14)**	0.92	(0.66- 1.29)	-	- -	-	- -	-	- -
3rd quartile	1.26	(0.94- 1.69)	0.98	(0.73- 1.30)	-	- -	-	- -	-	- -
2nd quartile	1.16	(0.90- 1.49)	0.79	(0.61- 1.04)	-	- -	-	- -	-	- -
1 day lag										
4th quartile	0.99	(0.71- 1.39)	1.02	(0.72- 1.44)	-	- -	-	- -	-	- -
3rd quartile	0.97	(0.72- 1.29)	0.98	(0.73- 1.31)	-	- -	-	- -	-	- -
2nd quartile	1.10	(0.87- 1.40)	1.19	(0.93- 1.53)	-	- -	-	- -	-	- -
2-day-lag average										
4th quartile	0.88	(0.63- 1.22)	1.07	(0.78- 1.47)	-	- -	-	- -	-	- -
3rd quartile	0.97	(0.74- 1.27)	0.95	(0.72- 1.27)	-	- -	-	- -	-	- -
2nd quartile	1.02	(0.80- 1.29)	1.07	(0.83- 1.38)	-	- -	-	- -	-	- -
3-day-lag average										
4th quartile	0.83	(0.59- 1.17)	1.13	(0.82- 1.56)	-	- -	-	- -	-	- -
3rd quartile	0.94	(0.72- 1.23)	1.11	(0.83- 1.48)	-	- -	-	- -	-	- -
2nd quartile	0.86	(0.67- 1.10)	0.92	(0.70- 1.19)	-	- -	-	- -	-	- -
4-day-lag average										
4th quartile	0.91	(0.64- 1.28)	1.16	(0.84- 1.59)	-	- -	-	- -	-	- -
3rd quartile	0.92	(0.70- 1.21)	1.04	(0.79- 1.39)	-	- -	-	- -	-	- -
2nd quartile	0.99	(0.78- 1.26)	1.11	(0.87- 1.43)	-	- -	-	- -	-	- -
10 km buffer										
Current day										
4th quartile	**1.23**	**(1.04- 1.46)**	0.88	(0.71- 1.08)	1.06	(0.90- 1.25)	1.08	(0.86- 1.35)	0.96	(0.79- 1.17)
3rd quartile	1.08	(0.93- 1.25)	0.87	(0.74- 1.02)	1.06	(0.92- 1.22)	1.17	(0.96- 1.42)	1.07	(0.91- 1.26)
2nd quartile	1.11	(0.98- 1.26)	0.91	(0.80- 1.04)	1.04	(0.91- 1.19)	1.13	(0.96- 1.32)	0.94	(0.82- 1.08)
1 day lag										
4th quartile	1.16	(0.98- 1.39)	0.88	(0.71- 1.09)	1.08	(0.92- 1.27)	0.91	(0.72- 1.14)	0.95	(0.78- 1.16)
3rd quartile	1.13	(0.97- 1.31)	0.91	(0.77- 1.07)	0.99	(0.86- 1.14)	0.94	(0.78- 1.14)	0.97	(0.82- 1.14)
2nd quartile	1.13	(0.99- 1.28)	0.93	(0.82- 1.07)	1.01	(0.88- 1.16)	0.88	(0.76- 1.03)	0.97	(0.85- 1.11)
2-day-lag average										
4th quartile	0.87	(0.74- 1.03)	1.12	(0.94- 1.33)	1.06	(0.89- 1.26)	1.15	(0.89- 1.49)	0.84	(0.70- 1.00)
3rd quartile	0.99	(0.86- 1.13)	0.98	(0.85- 1.13)	1.05	(0.91- 1.21)	1.05	(0.84- 1.31)	0.90	(0.78- 1.04)
2nd quartile	1.00	(0.88- 1.13)	1.04	(0.92- 1.18)	1.04	(0.91- 1.18)	0.96	(0.81- 1.13)	0.94	(0.82- 1.07)
3-day-lag average										
4th quartile	0.91	(0.77- 1.08)	1.07	(0.90- 1.28)	1.02	(0.87- 1.19)	0.98	(0.75- 1.28)	0.92	(0.78- 1.10)
3rd quartile	0.92	(0.81- 1.06)	1.01	(0.87- 1.18)	1.04	(0.90- 1.20)	0.96	(0.76- 1.20)	0.97	(0.83- 1.13)
2nd quartile	0.93	(0.82- 1.05)	0.95	(0.84- 1.08)	0.98	(0.87- 1.11)	0.91	(0.77- 1.08)	1.04	(0.92- 1.17)
4-day-lag average										
4th quartile	**0.84**	**(0.71- 0.99)**	1.09	(0.90- 1.33)	1.00	(0.85- 1.18)	1.32	(0.98- 1.78)	0.98	(0.82- 1.17)
3rd quartile	**0.86**	**(0.76- 0.99)**	1.01	(0.87- 1.18)	1.03	(0.89- 1.19)	1.21	(0.94- 1.56)	1.01	(0.87- 1.18)
2nd quartile	0.95	(0.84- 1.07)	1.02	(0.90- 1.15)	1.05	(0.93- 1.19)	1.08	(0.88- 1.32)	1.00	(0.87- 1.14)

Table S3- 8. Single source models using single imputation data - Associations between exposures to pollutants identified as 5 source classes and ED visits for respiratory problems using imputed data.

Otherwise as Table 3-3.

Exposures	Petrochemical RR (95%CI)		Fuel Combustion RR (95%CI)		Combined industrial RR (95%CI)		Gasoline exhaust RR (95%CI)		Industrial solvent RR (95%CI)	
4 km buffer										
Current day										
4th quartile	0.94	(0.75- 1.19)	0.83	(0.60- 1.14)	1.26	(0.95- 1.67)	1.08	(0.85- 1.37)	0.95	(0.75- 1.21)
3rd quartile	1.01	(0.81- 1.25)	0.85	(0.68- 1.07)	**1.39**	**(1.08- 1.80)**	1.02	(0.81- 1.27)	0.93	(0.73- 1.18)
2nd quartile	1.00	(0.81- 1.24)	0.98	(0.81- 1.19)	1.06	(0.81- 1.38)	1.01	(0.82- 1.23)	0.90	(0.74- 1.11)
1 day lag										
4th quartile	0.80	(0.63- 1.00)	**1.40**	**(1.02- 1.91)**	1.02	(0.78- 1.33)	1.14	(0.90- 1.45)	**0.73**	**(0.57- 0.94)**
3rd quartile	0.95	(0.76- 1.18)	1.18	(0.94- 1.49)	0.97	(0.76- 1.25)	**1.28**	**(1.03- 1.59)**	0.81	(0.64- 1.03)
2nd quartile	0.99	(0.80- 1.22)	1.21	(1.00- 1.47)	1.04	(0.82- 1.34)	1.00	(0.81- 1.23)	0.90	(0.74- 1.10)
2-day-lag average										
4th quartile	**0.76**	**(0.60- 0.97)**	1.39	(0.99- 1.95)	0.96	(0.71- 1.30)	1.25	(0.98- 1.61)	0.93	(0.69- 1.24)
3rd quartile	0.99	(0.80- 1.22)	1.21	(0.93- 1.58)	1.01	(0.77- 1.32)	**1.30**	**(1.04- 1.63)**	**0.72**	**(0.56- 0.93)**
2nd quartile	0.93	(0.75- 1.15)	1.19	(0.98- 1.44)	0.98	(0.77- 1.27)	1.04	(0.85- 1.28)	0.90	(0.75- 1.10)
3-day-lag average										
4th quartile	0.82	(0.64- 1.05)	**1.86**	**(1.28- 2.70)**	0.88	(0.63- 1.23)	1.26	(0.97- 1.64)	0.78	(0.57- 1.07)
3rd quartile	1.00	(0.80- 1.24)	**1.43**	**(1.08- 1.90)**	0.79	(0.59- 1.06)	**1.32**	**(1.04- 1.67)**	0.77	(0.60- 1.01)
2nd quartile	1.15	(0.93- 1.41)	1.10	(0.91- 1.34)	0.91	(0.71- 1.18)	1.03	(0.84- 1.28)	0.82	(0.67- 1.02)
4-day-lag average										
4th quartile	0.92	(0.71- 1.18)	**2.11**	**(1.39- 3.19)**	0.88	(0.59- 1.30)	1.28	(0.98- 1.68)	1.11	(0.79- 1.56)
3rd quartile	1.04	(0.83- 1.31)	1.26	(0.92- 1.73)	0.78	(0.55- 1.09)	**1.38**	**(1.07- 1.77)**	0.79	(0.60- 1.04)
2nd quartile	**1.23**	**(1.01- 1.51)**	**1.24**	**(1.01- 1.52)**	**0.76**	**(0.58- 0.98)**	1.14	(0.92- 1.42)	0.91	(0.73- 1.12)
10 km buffer										
Current day										
4th quartile	1.05	(0.96- 1.16)	0.94	(0.82- 1.07)	1.04	(0.93- 1.17)	1.05	(0.95- 1.17)	0.95	(0.86- 1.06)
3rd quartile	1.04	(0.95- 1.15)	0.93	(0.84- 1.03)	1.07	(0.96- 1.20)	1.10	(1.00- 1.21)	0.93	(0.84- 1.03)
2nd quartile	1.00	(0.91- 1.10)	0.99	(0.92- 1.08)	0.98	(0.88- 1.10)	1.06	(0.97- 1.15)	0.98	(0.90- 1.07)
1 day lag										
4th quartile	1.04	(0.94- 1.14)	**1.15**	**(1.01- 1.32)**	0.96	(0.86- 1.08)	0.98	(0.89- 1.09)	0.99	(0.89- 1.09)
3rd quartile	1.03	(0.94- 1.14)	1.04	(0.95- 1.15)	0.97	(0.87- 1.08)	**1.10**	**(1.01- 1.21)**	0.96	(0.87- 1.07)
2nd quartile	1.03	(0.94- 1.12)	1.06	(0.98- 1.15)	1.00	(0.90- 1.11)	0.98	(0.90- 1.06)	0.98	(0.90- 1.07)
2-day-lag average										
4th quartile	1.07	(0.97- 1.19)	**1.17**	**(1.02- 1.35)**	0.97	(0.85- 1.10)	1.00	(0.89- 1.11)	0.91	(0.80- 1.03)
3rd quartile	1.07	(0.98- 1.17)	1.02	(0.91- 1.14)	0.96	(0.85- 1.08)	1.06	(0.96- 1.16)	1.00	(0.90- 1.11)
2nd quartile	1.03	(0.94- 1.13)	1.06	(0.98- 1.15)	1.03	(0.92- 1.14)	0.97	(0.89- 1.06)	0.98	(0.90- 1.07)
3-day-lag average										
4th quartile	1.06	(0.96- 1.18)	**1.21**	**(1.04- 1.42)**	0.94	(0.81- 1.09)	1.02	(0.91- 1.14)	0.80	(0.70- 0.92)
3rd quartile	**1.13**	**(1.03- 1.24)**	1.11	(0.99- 1.26)	0.92	(0.81- 1.04)	1.09	(0.98- 1.20)	**0.88**	**(0.78- 0.98)**
2nd quartile	1.06	(0.97- 1.16)	1.03	(0.95- 1.12)	0.91	(0.81- 1.02)	1.05	(0.96- 1.14)	0.92	(0.84- 1.00)
4-day-lag average										
4th quartile	**1.15**	**(1.04- 1.28)**	**1.23**	**(1.03- 1.48)**	1.00	(0.85- 1.19)	1.01	(0.90- 1.14)	0.86	(0.74- 1.00)
3rd quartile	**1.12**	**(1.01- 1.23)**	1.00	(0.87- 1.14)	0.96	(0.83- 1.11)	1.10	(0.99- 1.22)	**0.85**	**(0.76- 0.95)**
2nd quartile	**1.16**	**(1.06- 1.27)**	1.07	(0.98- 1.16)	0.92	(0.82- 1.03)	1.09	(0.99- 1.19)	**0.89**	**(0.81- 0.97)**

Table S3- 9. Single source models - Associations between exposures to pollutants

identified as 5 source classes and ED visits for respiratory problems (observed data)

using negative binomial regression.

Otherwise as Table 3-3.

Exposures	Photochemical RR (95%CI)	Fuel Combustion RR (95%CI)	Combined industrial RR (95%CI)	Gasoline exhaust RR (95%CI)	Industrial solvent RR (95%CI)
4 km radius					
Current day					
4th quartile	0.85 (0.63- 1.15)	0.77 (0.52- 1.15)	1.17 (0.81- 1.70)	0.88 (0.66- 1.19)	1.12 (0.75- 1.69)
3rd quartile	0.85 (0.65- 1.11)	1.07 (0.80- 1.42)	1.21 (0.84- 1.75)	1.05 (0.81- 1.36)	1.07 (0.75- 1.52)
2nd quartile	1.01 (0.78- 1.30)	1.00 (0.78- 1.30)	1.26 (0.92- 1.72)	**0.74 (0.57- 0.97)**	1.11 (0.85- 1.43)
1 day lag					
4th quartile	**1.40 (1.06- 1.85)**	1.18 (0.80- 1.73)	0.88 (0.61- 1.25)	1.09 (0.81- 1.45)	0.69 (0.46- 1.03)
3rd quartile	0.95 (0.74- 1.24)	**1.34 (1.03- 1.75)**	1.17 (0.83- 1.65)	1.08 (0.83- 1.41)	**0.70 (0.50- 0.99)**
2nd quartile	1.05 (0.82- 1.34)	0.92 (0.72- 1.18)	1.24 (0.92- 1.69)	0.89 (0.69- 1.15)	0.95 (0.74- 1.21)
2-day-lag average					
4th quartile	**1.39 (1.07- 1.81)**	1.33 (0.94- 1.88)	0.76 (0.55- 1.06)	1.16 (0.90- 1.49)	0.91 (0.63- 1.33)
3rd quartile	1.19 (0.94- 1.50)	1.28 (0.99- 1.65)	0.89 (0.66- 1.22)	1.19 (0.94- 1.51)	0.75 (0.55- 1.03)
2nd quartile	1.02 (0.81- 1.28)	1.10 (0.88- 1.38)	0.81 (0.61- 1.06)	0.92 (0.73- 1.15)	0.93 (0.74- 1.17)
3-day-lag average					
4th quartile	**1.48 (1.14- 1.92)**	**1.43 (1.01- 2.02)**	0.85 (0.59- 1.23)	1.28 (0.98- 1.66)	0.74 (0.50- 1.10)
3rd quartile	**1.32 (1.03- 1.68)**	**1.42 (1.07- 1.87)**	0.90 (0.64- 1.27)	**1.44 (1.13- 1.84)**	**0.69 (0.50- 0.96)**
2nd quartile	1.16 (0.92- 1.46)	**1.36 (1.09- 1.70)**	1.01 (0.77- 1.34)	1.11 (0.89- 1.39)	0.94 (0.75- 1.18)
4-day-lag average					
4th quartile	**1.33 (1.03- 1.72)**	**1.73 (1.17- 2.54)**	0.73 (0.50- 1.08)	**1.35 (1.04- 1.76)**	0.83 (0.54- 1.26)
3rd quartile	1.09 (0.85- 1.39)	1.27 (0.96- 1.69)	0.90 (0.63- 1.28)	1.29 (0.99- 1.67)	0.75 (0.53- 1.05)
2nd quartile	1.14 (0.91- 1.43)	1.15 (0.92- 1.43)	0.95 (0.72- 1.26)	1.07 (0.85- 1.34)	0.82 (0.64- 1.05)
10 km radius					
Current day					
4th quartile	1.02 (0.89- 1.16)	1.03 (0.86- 1.23)	0.98 (0.83- 1.16)	1.02 (0.89- 1.17)	1.08 (0.90- 1.30)
3rd quartile	0.93 (0.82- 1.04)	1.13 (0.99- 1.28)	1.01 (0.86- 1.20)	**1.16 (1.03- 1.31)**	1.02 (0.87- 1.19)
2nd quartile	1.02 (0.91- 1.15)	1.04 (0.92- 1.17)	0.99 (0.86- 1.15)	1.00 (0.89- 1.13)	1.07 (0.96- 1.20)
1 day lag					
4th quartile	**1.19 (1.05- 1.34)**	1.07 (0.91- 1.27)	1.00 (0.86- 1.18)	1.03 (0.90- 1.17)	0.99 (0.83- 1.18)
3rd quartile	1.06 (0.94- 1.18)	1.13 (1.00- 1.27)	1.03 (0.88- 1.20)	0.99 (0.88- 1.12)	0.94 (0.81- 1.09)
2nd quartile	**1.13 (1.01- 1.26)**	1.07 (0.96- 1.20)	1.05 (0.92- 1.21)	0.96 (0.85- 1.07)	1.03 (0.92- 1.14)
2-day-lag average					
4th quartile	1.10 (0.98- 1.23)	1.12 (0.97- 1.30)	0.92 (0.79- 1.06)	1.00 (0.90- 1.12)	0.91 (0.77- 1.07)
3rd quartile	**1.11 (1.01- 1.23)**	1.08 (0.97- 1.22)	0.98 (0.86- 1.13)	1.06 (0.95- 1.18)	0.93 (0.82- 1.07)
2nd quartile	1.00 (0.91- 1.10)	1.08 (0.98- 1.19)	0.98 (0.87- 1.10)	0.97 (0.88- 1.07)	0.95 (0.86- 1.05)
3-day-lag average					
4th quartile	1.08 (0.96- 1.21)	1.14 (0.98- 1.33)	1.04 (0.88- 1.22)	0.99 (0.88- 1.12)	0.84 (0.70- 1.00)
3rd quartile	**1.12 (1.01- 1.25)**	1.08 (0.96- 1.22)	1.05 (0.90- 1.22)	1.03 (0.92- 1.15)	0.86 (0.75- 1.00)
2nd quartile	1.06 (0.96- 1.18)	**1.11 (1.01- 1.22)**	1.00 (0.89- 1.14)	0.99 (0.90- 1.09)	0.95 (0.86- 1.05)
4-day-lag average					
4th quartile	1.07 (0.96- 1.21)	1.18 (0.99- 1.39)	1.00 (0.84- 1.19)	1.03 (0.92- 1.16)	**0.82 (0.68- 0.99)**
3rd quartile	1.06 (0.95- 1.18)	1.04 (0.92- 1.17)	1.02 (0.87- 1.20)	1.02 (0.91- 1.14)	**0.81 (0.70- 0.94)**
2nd quartile	1.01 (0.91- 1.11)	1.09 (0.99- 1.20)	1.03 (0.91- 1.17)	1.04 (0.94- 1.15)	**0.88 (0.79- 0.98)**

Table S3- 10. Single source models - Associations between exposures to pollutants

identified as 5 source classes and ED visits for asthma (observed data) among children

living within 10 km radius using negative binomial regression.

Otherwise as Table 3-3.

Exposures	Photochemical	Fuel Combustion	Combined industrial	Gasoline exhaust	Industrial solvent
	RR (95%CI)	RR (95%CI)	RR (95%CI)	RR (95%CI)	RR (95%CI)
Current day					
4th quartile	1.09 (0.87- 1.36)	0.89 (0.67- 1.19)	1.31 (0.99- 1.74)	0.92 (0.75- 1.14)	0.98 (0.72- 1.34)
3rd quartile	1.06 (0.87- 1.29)	0.98 (0.79- 1.22)	1.15 (0.88- 1.51)	**0.78 (0.63- 0.96)**	1.12 (0.86- 1.46)
2nd quartile	0.93 (0.76- 1.14)	1.02 (0.83- 1.24)	1.19 (0.95- 1.49)	0.97 (0.80- 1.17)	1.06 (0.87- 1.29)
1 day lag					
4th quartile	1.15 (0.91- 1.45)	0.98 (0.74- 1.31)	1.00 (0.75- 1.34)	1.13 (0.90- 1.41)	0.99 (0.72- 1.36)
3rd quartile	1.12 (0.90- 1.38)	1.12 (0.89- 1.40)	0.94 (0.72- 1.23)	0.98 (0.78- 1.23)	1.01 (0.77- 1.34)
2nd quartile	1.12 (0.91- 1.39)	**1.26 (1.01- 1.56)**	1.07 (0.86- 1.35)	**1.28 (1.04- 1.57)**	1.00 (0.80- 1.24)
2-day-lag average					
4th quartile	0.84 (0.68- 1.05)	0.90 (0.70- 1.17)	1.01 (0.77- 1.32)	1.11 (0.91- 1.36)	0.97 (0.72- 1.32)
3rd quartile	0.95 (0.78- 1.16)	0.93 (0.75- 1.16)	1.03 (0.81- 1.32)	1.04 (0.85- 1.27)	0.87 (0.67- 1.12)
2nd quartile	0.85 (0.70- 1.03)	0.95 (0.79- 1.15)	0.98 (0.80- 1.20)	1.16 (0.97- 1.40)	0.92 (0.74- 1.12)
3-day-lag average					
4th quartile	0.84 (0.68- 1.05)	0.81 (0.62- 1.05)	1.16 (0.87- 1.55)	0.94 (0.76- 1.15)	1.01 (0.74- 1.39)
3rd quartile	1.06 (0.86- 1.29)	0.89 (0.71- 1.12)	1.02 (0.78- 1.32)	0.96 (0.78- 1.17)	0.99 (0.76- 1.29)
2nd quartile	0.96 (0.79- 1.17)	0.92 (0.76- 1.12)	1.11 (0.90- 1.36)	1.02 (0.85- 1.22)	0.87 (0.70- 1.07)
4-day-lag average					
4th quartile	0.82 (0.66- 1.02)	0.76 (0.58- 1.01)	1.32 (0.96- 1.80)	0.82 (0.67- 1.01)	1.00 (0.72- 1.39)
3rd quartile	0.97 (0.79- 1.18)	0.84 (0.67- 1.05)	1.17 (0.90- 1.54)	0.95 (0.78- 1.17)	1.00 (0.76- 1.32)
2nd quartile	0.87 (0.72- 1.05)	0.85 (0.70- 1.03)	**1.24 (1.01- 1.53)**	0.87 (0.72- 1.04)	0.91 (0.73- 1.13)

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Chapter 4
Reproducibility and Imputation of Air Toxics Data

4.1 Abstract

Ambient air quality datasets include missing data, values below method detection limits and outliers, and the precision and accuracy of the measurements themselves are often unknown. At the same time, many analyses require continuous data sequences and assume that measurements are error-free. While a variety of data imputation and cleaning techniques are available, the evaluation of such techniques remains limited. This study evaluates the performance of these techniques for ambient air toxics measurements, a particularly challenging application, and includes the analysis of intra- and inter-laboratory precision.

The analysis uses an unusually complete data set, consisting of daily measurements of over 70 species carbonyls and volatile organic compounds (VOCs) collected over a one year period in Dearborn, Michigan, including 122 pairs of replicates. Analysis was restricted to compounds found above detection limits in ≥20% of the samples. Outliers were detected using the Gumbell extreme value distribution. Error models for inter- and intra-laboratory reproducibility were derived from replicate samples. Imputation variables were selected using a generalized additive model, and the performance of two techniques, multiple imputation and optimal linear estimation, was evaluated for three missingness patterns (random, random block and row-wise).

Many species were rarely detected or had very poor reproducibility. Error models developed for seven carbonyls showed median intra- and inter-laboratory errors of 22% and 25%, respectively. Better reproducibility was seen for the 16 VOCs meeting detection and reproducibility criteria. Imputation performance depended on the compound and missingness pattern. Data missing at random could be adequately

imputed but imputations for row-wise deletions (measurements for all compounds were missing on the same day), the most common type of missingness pattern encountered, were not informative. The analysis shows that air toxics data require significant efforts to identify and mitigate errors, outliers and missing observations, and that these quality assurance steps are essential and should be performed prior to using these data in receptor, exposure, health and other applications.

4.2 Introduction

Most air quality data have been collected for regulatory purposes, such as determining compliance with ambient air quality standards. The use of the same data for other purposes, including epidemiological studies, while convenient and inexpensive, can place different and often more stringent demands on data quality and completeness since most statistical methods assume that observations are error-free and complete, i.e., data sets are fully populated. Data quality is an important and often unappreciated issue, especially for toxic air pollutants where measurement uncertainties can be large. In general, monitoring methods for toxics have been only partially automated, samples must be transported from the monitoring site to the laboratory for analysis, and analyses tend to be complex and intensive. These steps increase the likelihood of errors from a variety of sources, e.g., sample contamination. Further, logistical and cost issues generally prohibit air toxics sampling programs from incorporating many duplicate measurements and other analyses that are necessary to quantify accuracy and precision.

Missing air quality data, another common problem, results from both random and planned events. Random events include power and equipment failures, lost samples or logs, other quality assurance problems, measurement and calibration errors, and faults in data acquisition[1]. Planned events include quality assurance checks (instrument flow, zero and span checks) and calibrations that require that the monitoring instruments be taken off-line. In some cases, pollutants are monitored intermittently, i.e., particulate matter measurements often are collected only every third or sixth day, while ozone may be measured only during the summer "ozone" season. Evaluations of the several approaches that have been used to address problems of missing data have been very limited.

Problems of both missingness and quality assurance must be addressed to obtain complete and reliable datasets.

This chapter evaluates the performance of two imputation methods, optimal linear estimation and multiple imputation, for handling missing air quality data. Performance is tested using an unusually complete urban air toxics dataset containing ambient measurements of volatile organic compounds (VOCs) and carbonyl species. As described below, the imputation of toxics data is particularly challenging, but at the same time highly relevant for epidemiology, source apportionment, risk assessment and other applications that use ambient air quality data. We also demonstrate several quality assurance (QA) filters and reproducibility/uncertainty models that may be generalizable to other measurements.

4.3   Background

4.3.1   Quality assurance issues

Several problems are frequently encountered in ambient air quality datasets, which are grouped together here as QA issues. These issues tend to be especially important for urban air toxics (UATs), more so than for conventional air pollutants for several reasons. First, toxic measurements of trace metals, VOCs, carbonyls, semi-volatiles and other pollutants may reflect low concentrations that fall below method detection limits (MDLs). For some species, concentrations may rarely, if ever, exceed MDLs. Such 'sparse' data patterns can occur because a specific toxic pollutant simply may not be present, or because the MDL is too high to allow frequent detection. This situation rarely occurs for conventional pollutants, both because these pollutants are ubiquitous due to emissions from numerous sources, and because monitoring instruments have been highly refined and are very sensitive.

Second, high concentration values may be encountered on occasion, even for rarely detected pollutants. These detections (or "hits") may be real and significant, or they may be false positives due to contamination, chemical reactions forming artifacts on the sampling adsorbent, interferences, chromatographic shifts, laboratory errors, or some other reason. Without duplicate samples or additional information, it is difficult or

impossible to determine whether a rarely detected compound is a true detection and thus meaningful. High values can be characterized as statistical outliers, e.g., using the Gumbell extreme value distribution originally developed for hydrologic systems[2-4] and applied to air quality data,[5,6] and which we later demonstrate in this paper. However, the designation of a measurement as a statistical outlier does not indicate whether or not the concentration was actually experienced.

Third, it is difficult to characterize the measurement precision and accuracy for commonly-detected toxic pollutants, and exceedingly difficult for rarely detected pollutants. Compared to conventional (so-called criteria) pollutants where relative precisions and accuracies are well-characterized and in the 10% range (or lower), the few available estimates suggest much greater variability[7]. In the (unusually complete) Dearborn study described later, for example, duplicate samples were available on 120 days, and a compound detected on say 5% of days would be expected to have only ~6 duplicate pairs available, too small a sample to construct meaningful statistics. Due to the lack of reference methods and standards, co-located replicate samples and intra- and inter-laboratory comparisons are used to indicate agreement, but in practice such exercises are infrequent and are limited to largely analytical uncertainties, and thus would not necessarily indicate contamination or improper sampling techniques.

4.3.2 Data imputation methods

Missing data have been characterized into three general patterns: missing completely at random (MCAR); missing at random (MAR); and not missing at random (NMAR)[8]. For MCAR, the missing data mechanism is independent from the values of any variables, whether missing or observed.[1] On the other hand, MAR means the missing data mechanism is independent with reference to the values of the missing components of the data but may be depend on the values of the observed components.[1] Like most other data sets, missing air quality data can be expected to be neither MCAR nor MNAR, but a mixture of these patterns[1,9].

The most common approaches to deal with missing data are deletion and imputation methods. The former includes case deletion, pair-wise deletion and list-wise deletion, all standard methods in statistical packages such as SAS[10]. Imputation methods

include single imputation (SI) techniques, which replace each missing one with a single value, and multiple imputation (MI) techniques, which impute multiple plausible values. The most common SI method is *ad hoc* replacement with a specific value, which is most frequently seen when measurements below the MDL that are replaced with one-half of the MDL. MI has been shown to yield valid statistical inferences without the disadvantages of SI techniques, namely, the inability to account for uncertainties attached to the missing values[8,11]. In MI, each missing value is replaced with a vector of m≥2 values resulting in m datasets, each of which is analyzed separately using standard complete-data software to yield "complete-data" statistics[12]. The multiple analyses are then combined yielding composite statistics.

The following summarizes two SI and MI methods that are later evaluated (in the Results section). First, as presented by Batterman[13], optimal linear estimation (OLE) is a SI method based on a Bayesian framework in which observations $\mathbf{Z}_t$ are assumed to contain error $\mathbf{V}_t$:

$$\mathbf{Z}_t = \mathbf{X}_t + \mathbf{V}_t \tag{1}$$

where $\mathbf{X}_t$ = true pollutant level. Error covariance matrix $\mathbf{R}_t$ is:

$$\mathbf{R}_t = E[\mathbf{V}_t \mathbf{V}_t'] \tag{2}$$

Errors $\mathbf{V}_t$ and covariance $\mathbf{R}_t$ must be assumed or estimated. For example, errors might be determined empirically using replicate samples. Alternately, Batterman (1992) estimated the total error by propagating component errors, and estimated a relative error of 30% for 24-hr measurements of fine and coarse fraction particulate matter ($PM_{2.5}$, $PM_{2.5-10}$) and hourly measurements of O_3[13]. Assuming unbiased ($E[\mathbf{V}_t]=\mathbf{0}$) and uncorrelated errors ($E[\mathbf{X}_t \mathbf{V}_t']=0$), the best linear, unbiased and minimum variance estimate $\hat{\mathbf{X}}$ of the missing observations is:

$$\hat{\mathbf{X}}_t = \mathbf{M} + \mathbf{P}(\mathbf{P} + \mathbf{R}_t)^{-1}(\mathbf{Z}_t - \mathbf{M}) \tag{3}$$

where $\mathbf{M}$ = mean vector and $\mathbf{P}$ = covariance matrix, both estimated from available data, and T = number of observations used to estimate $\mathbf{M}$ and $\mathbf{P}$:

$$\mathbf{M} = T^{-1}\sum_t \mathbf{X}_t \tag{4}$$

$$\mathbf{P} = T^{-1} \sum_t [(\mathbf{X}_t - \mathbf{M})(\mathbf{X}_t - \mathbf{M})'] \tag{5}$$

Unlike most SI methods, the OLE approach estimates the uncertainty of imputed values. However, the use of imputed datasets derived from OLE, as well as any other SI method, will lead to standard errors that are systematically underestimated, biasing statistical inference tests and giving erroneously small p-values and confidence intervals[8].

The MI procedure, also derived from a Bayesian perspective, uses m independent random draws from the posterior predictive distribution[14]. The theory behind MI is detailed elsewhere (Rubin 1987, 1996)[11,12]. In brief, for a dataset $\mathbf{Y} = (\mathbf{Y}_{obs}, \mathbf{Y}_{mis})$, where $\mathbf{Y}_{obs}$ = observed values and $\mathbf{Y}_{mis}$ = missing values, the basic result is:

$$P(\mathbf{Y}_{est} | \mathbf{Y}_{obs}) = \int P(\mathbf{Y}_{est} | \mathbf{Y}_{obs}, \mathbf{Y}_{mis}) P(\mathbf{Y}_{mis} | \mathbf{Y}_{obs}) d\mathbf{Y}_{mis} \tag{6}$$

where $P(\mathbf{Y}_{est}|\mathbf{Y}_{obs})$ = complete data posterior distribution of $\mathbf{Y}_{est}$, the estimate of the missing data conditioned on the observed data; and $P(\mathbf{Y}_{mis}|\mathbf{Y}_{obs})$ = predicted posterior distribution of the missing data, also conditioned on the observed data. The final estimate is the average of repeated complete-data posterior means of $\mathbf{Y}_{est}$:

$$E(\mathbf{Y}_{est} | \mathbf{Y}_{obs}) = E[E(\mathbf{Y}_{est} | \mathbf{Y}_{obs}, \mathbf{Y}_{mis}) | \mathbf{Y}_{obs}] \tag{7}$$

and the final variance of $\mathbf{Y}_{est}$, $V(\mathbf{Y}_{est}|\mathbf{Y}_{obs})$, is:

$$V(\mathbf{Y}_{est} | \mathbf{Y}_{obs}) = E[V(\mathbf{Y}_{est} | \mathbf{Y}_{obs}, \mathbf{Y}_{mis}) | \mathbf{Y}_{obs}] + V[E(\mathbf{Y}_{est} | \mathbf{Y}_{obs}, \mathbf{Y}_{mis}) | \mathbf{Y}_{obs}] \tag{8}$$

which represents the sum of the average of repeated complete-data variances of $\mathbf{Y}_{est}$ and the variance of repeated complete-data posterior means. Five imputations provide an efficiency of ~94% for MI estimation when up to 30% of the data is missing[15]. The essential features of MI inferences are that predicted distribution of missing values are conditioned on observed values, and that multiple imputations reflect both within- and between-imputation variances[8]. Hopke et al. (2001) suggests that MI in air quality applications may be beneficial since imperfect imputation models make mistakes for only a fraction of missing information, whereas the complete-dataset is being relied upon for the final inference, and since imperfect models yield large within- and between-imputation variability and consequently will lead to conservative inferences[16].

4.4 Experimental

4.4.1 Data acquisition

Toxics data were obtained from the Michigan Department of Environmental Quality (MDEQ) and included daily measurements for the period 4/19/2001 to 4/18/2002 collected at a permanent monitoring site in Dearborn, Michigan. Samples were shipped to and analyzed by laboratories at the Eastern Research Group (ERG, Research Triangle Park, NC) and the MDEQ (Lansing, MI). VOCs were collected in canisters and analyzed by GC-MS following the TO-15 method. The ERG and MDEQ laboratories reported 59 and 53 VOC species, respectively. Carbonyls were collected on DNPH cartridges and analyzed by HPLC following the TO-11A method, with the ERG and MDEQ laboratories reporting 12 and 13 species, respectively. (Tables S4-1 and S4-2 show the VOC and carbonyl species analyzed by each of the laboratories.)

Reproducibility determinations, intra-laboratory and inter-laboratory comparisons were derived from duplicate sample pairs collected on 122 days (every third day). To determine intra-laboratory reproducibility, both duplicates were sent to ERG on 40 days and to MDEQ on 41 days. To determine inter-laboratory reproducibility, duplicates were sent to both ERG and MDEQ on 41 days. There were 282 and 41 days when a single sample was analyzed by ERG and MDEQ, respectively, and the total possible number of days that ERG and MDEQ analyzed samples were 302 and 83 days, respectively. VOC and carbonyl sampling followed the same schedule.

For imputation purposes, daily or hourly measurements of conventional pollutants were obtained from four nearby (within 20 km) MDEQ sites: Dearborn (daily PM_{10}), Allen Park (CO and $PM_{2.5}$), East Seven Mile (NO_2 and SO_2), and Linwood (CO, NO_2, $PM_{2.5}$ and SO_2). In Michigan, O_3 is monitored for only 6 months of the year (April to September); therefore, O_3 was not considered for this study. Daily (24-hr) values were computed from hourly data if $\geq 75\%$ of hourly data (≥ 18 hr) were available and considered valid. These pollutants are collected using federal reference methods.

Hourly and daily meteorological data, obtained from the MDEQ and the National Oceanic and Atmospheric Administration (NOAA), included temperature, dew point,

minimum and maximum relative humidity, precipitation, wind speed, wind direction, barometric pressure and mixing height. Except for wind direction, daily values were computed from hourly data, again if ≥75% of hourly data were considered valid. For wind direction, eight new variables were defined as the number of hours the wind was in each of eight 45° sectors. These variables were also used for imputation purposes.

4.4.2 Data filters

Several filters were used to select pollutant variables for analysis and provide QA checks. First, to include a toxic pollutant in the analysis, ≥20% of the observations were required to exceed the MDL. This detection frequency is conservative with respect to other studies, i.e., Xie et al. (2005)[17] required ≥63% of the data to be present and above MDLs. Second, following convention, measurements below the MDL were set to ½ MDL. Next, potential statistical outliers were identified by pooling all samples (including replicates analyzed by either laboratory), fitting the top decile of detected concentrations to the Gumbell extreme value distribution, and determining those measurements that departed from the fitted distribution. If the potential outlier had a replicate that disagreed (i.e., near the MDL), then the high value was considered to be erroneous and removed. If the replicate was similar (i.e., considerably above the MDL), then the two replicates were averaged. If a replicate was unavailable, then the observation was removed. After completing the MDL, reproducibility and outlier screens, duplicate measurements at a laboratory, if available, were averaged.

4.4.3 Intra- and inter-laboratory reproducibility

Intra-laboratory reproducibility for each pollutant and laboratory was characterized by examining duplicate samples using both statistical measures, e.g., paired-t tests for means, errors, distributions, and correlations (both parametric Pearson and non-parametric Spearman), and graphical analyses, e.g., scatter plots. Intra-laboratory reproducibility was also quantified by the coefficient of variation, COV (%):[7]

$$\%COV = 100 \cdot \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{(p_i - s_i)}{0.5 \cdot (p_i + s_i)}\right]^2}{2 \cdot n}} \qquad (9)$$

where p_i and s_i = primary and secondary replicates, respectively, and n = number of replicate pairs. We identified those species with COVs ≤15%, an acceptability criterion used by US EPA[7]. If intra-laboratory agreement was minimal, e.g., as indicated by r<0.2 or not statistically significant at α=0.05, then that pollutant was removed from further consideration.

Error models for intra-laboratory reproducibility were constructed following an approach used previously for VOCs[18]. Observations from all carbonyl species that met the minimum detection frequency (20%, discussed above) were pooled together. Replicate pairs were averaged, and measurements below MDLs and statistical outliers were excluded. Then, plots were constructed showing decile concentrations (using the decile average) versus the absolute residuals of replicate pairs in each concentration decile. Finally, the 25th, 50th, 75th and 90th percentile errors in each decile were regressed against the 10th to 100th or 10th to 90th decile concentrations, the latter to address additional outliers observed in the top decile of ERG's carbonyl measurements. This analysis was performed separately for EGR and MDEQ laboratories. The identical procedure was used for VOCs. The resulting intra-laboratory error models are used in the OLE estimator (described below).

Inter-laboratory reproducibility was characterized by examining the replicate samples analyzed by the two laboratories using statistical and graphical analyses as described for the intra-laboratory analyses. If the inter-laboratory agreement was poor (r<0.2) or not statistically significant (at α=0.05) and the correlation coefficient from ERG intra-laboratory comparison was also poor, then that pollutant was removed from the analysis. Differences in mean concentrations reported by the two laboratories were examined using paired t–tests and the non-parametric Wilcoxon signed rank (WSR) tests for two related samples, considering only cases where both laboratories made measurements above MDLs, thus avoid possible biases since MDLs differed.

4.4.4   Optimal linear estimation

The OLE method was implemented in Excel using the XNUMBERS[19] for high precision matrix operations (e.g., inversion in eq. 3), necessary for imputations using a large number of predictor variables. Error covariance matrix $\mathbf{R}_t$ and covariance matrix $\mathbf{P}$

(eqs. 1 and 2) utilized the median intra-laboratory error model (described above). Errors were assumed to be independent and time invariant. Four OLE models were constructed for each pollutant that differed with respect to the treatment of autocorrelation: (1) use of only contemporaneous observations (lag0); (2) contemporaneous plus 1-day lagging observations (lag1); (3) contemporaneous plus 1-day leading observations (lead1); and (4) contemporaneous plus lag and lead (LL1). The inclusion of leading and/or lagging observations incorporates autocorrelation information.

A very large number of possible predictor variables were available. Variables for each imputation model were selected using GLMSELECT, a new procedure utilizing the general linear model framework and available as a test trial in SAS 9.1[10,20]. A forward step-wise procedure was used along with several selection criteria, including the general information criterion[21,22], the corrected Akaike information criterion[23], the Schwarz Bayesian information criterion[21,24], the average square error (ASE), and the average residual sum of squares. The predictor variables identified using GLMSELECT were introduced into the model simultaneously. Each model was examined individually with the goal of developing powerful but parsimonious and robust models. We examined the performance of the OLE estimator using both nominal and log-transformed concentrations, in part to account for the expected log-normal distribution of pollutant concentrations.

4.4.5   Multiple imputation

MI models were constructed using the same data and predictor selection procedures described above and the MI procedure in SAS, a Markov chain Monte Carlo (MCMC) implementation with the multiple chain option[10]. A separate MC chain was used for each imputation. This implementation assumes multivariate normality. As with OLE, we evaluated performance of the same estimator using both the nominal and the log-transformed data. As described for the OLE method, four MI models were constructed for each pollutant using different combinations of leading and lagging observations. Five imputed data sets (m=5) were generated for each pollutant.

4.4.6 Performance evaluation

Imputations from OLE and MI methods were evaluated using the same approach and the same datasets. Initially, performance was evaluated by random deletions, imputing the deleted data, and then comparing actual and imputed measurements using several indicators, e.g., Willmott's index of agreement (d_2), coefficient of determination (R^2), mean absolute error (MAE), distribution analyses (percentiles and box plots), and scatter plots of imputed versus observed values. Among these indicators, d_2 addresses outliers and is a robust measure with a similar interpretation as R^2, e.g., 0 and 1 denote random and perfect fits, respectively[25]. The MI scatter plots used the average of 5 imputed values.

To test different causes of missing values in air pollution data sets, three deletion patterns were used: random deletion, random block deletions of 5, and random row-wise deletions. For each deletion pattern, ~25% of the data were removed following Junninen et al. (2004)[26] and to give a sufficient sample size for imputations (about 79) for robust statistics. Each deletion pattern represents a different situation. Random deletions portray missing data due to data entry problems, outlier removal, and other events that affect single observations. Random block deletions most commonly arise from equipment failures which are not fixed for a period of time (e.g., 5 days in our simulation). Row-rise deletions, which tested model performance using exclusively lag and lead measurements of toxics (but contemporaneous measurements of conventional and meteorology variables were permitted) often reflect missingness pattern for air toxics since multiple pollutants are measured in a single sample, and any day that sample is unavailable results in missing values for all of the toxics in the group. In practice, missingness patterns for air toxics data represent a mixture of these three missing patterns, though row-wise deletions are the most common. Missing at random and random block patterns are dominant in other types of air quality data, e.g., conventional pollutants. The separate analyses of each of these three missingness patterns provide a sensitivity analysis that gives insight regarding how the imputation methods will perform for different types of air quality data. Also, it should be noted that the performance is largely independent of the amount of data that is removed and then imputed, as long as

the sample size is sufficient to give valid statistics. This was verified with 10 and 25% deletions, which gave comparable results.

The evaluation used the ERG dataset, which was the most complete. Replicates, if available, were averaged. Predictor variables were selected after data were deleted, simulating an actual dataset. The present paper presents evaluations for three carbonyl and three VOC species. The selected compounds had different detection frequencies and/or represented different and important types or compounds. For carbonyls, detection frequencies did not differ, so the selection included both very volatile and aromatic carbonyls (acetaldehyde, benzaldehyde and formaldehyde). For VOCs, aromatic and chlorinated VOCs were selected (benzene and tetrachloroethylene); butadiene was also included due to its low detection frequency. (Evaluations for other species are provided in Tables S4-9 and S4-10.)

4.5   Results

4.5.1   Detection frequency, outliers, precision and accuracy

The original data set contained 12 carbonyls (n=266) and 59 VOCs (n=282) measured by the ERG laboratory, and 13 carbonyls (n=54) and 53 VOCs (n=57) measured by the MDEQ laboratory. (Tables S4-1 and S4-2 give statistics of all measured toxics.) Considering the sampling design, missing observations in one year of air monitor data comprised ~6.4% and ~35% of the possible ERG and MDEQ data points, respectively. Data were processed using four QA screens, discussed below.

First, over half of the air toxics species were rarely detected above MDLs. With the 20% (minimum) detection frequency criterion, the first screen eliminated 38 of 59 VOC species and 1 of 12 carbonyl species measured by ERG, and 35 of 53 VOCs and 3 of 13 carbonyls measured by MDEQ. The eliminated compounds, which included many chlorinated VOCs, are not discussed further. Table 4-1 identifies the remaining 13 carbonyls and 24 VOCs.

The second data screen identified outliers. Probability distribution plots for the top decile concentrations of all compounds approximated straight lines, indicating that the Gumbell distribution was appropriate. After reviewing replicates, we considered that

11 compounds had outliers: formaldehyde (n=1), hexaldehyde (n=1), tolualdehyde (n=1), propylene (n=2), *n*-octane (n=1), methylene chloride (n=5), *m,p*-xylene (n=2), ethylbenzene (n=2), *o*-xylene (n=1), 1,3,5-trimethylbenzene (n=1) and toluene (n=2). Several outliers occurred on the same dates, i.e., *n*-octane, *m,p*-xylene, and ethylbenzene on 3/11/2002. (Table S4-3 gives information on the outliers; Figures S4-1 and S4-2 show log-normal distribution plots). Methylene chloride had the largest number of outliers and reached very high concentrations, e.g., MDEQ showed 199 ppb on 7/17/2001, and ERG showed 148 ppb on 3/3/2002. This compound is frequently used as a laboratory solvent and thus these outliers might be a result of inadvertent contamination. These 19 points were removed from the dataset and were considered missing. These outliers represent a very small percentage of the measurements.

Intra-laboratory reproducibility. Intra-laboratory agreement depended on the species and, to a lesser extent, on the laboratory. In many cases, non-parametric statistics (e.g., Spearman rank correlation coefficients) and parametric (e.g., Pearson correlation coefficients) gave similar results (Table 4-2), but the former is emphasized since concentrations of many toxics were not normally distributed and the Pearson statistic is sensitive to extreme values. For the ERG laboratory, dimethylbenzaldehyde and acetone had nil reproducibility ($r \leq 0.2$); crotonaldehyde, valeraldehyde, and carbon tetrachloride showed marginal reproducibility ($0.2 < r < 0.3$), as did acetone measurements by MDEQ. For the 10 carbonyls measured by the ERG surviving this screen, the average correlation between replicate samples was 0.43 ± 0.15; the 20 VOCs obtained higher correlation, 0.62 ± 0.14. The MDEQ laboratory obtained marginally higher performance for carbonyls (average $r = 0.51 \pm 0.10$) and comparable performance for VOCs (average $r = 0.65 \pm 0.18$). Both laboratories had high detection frequencies but poor reproducibilities for acetone and methylene chloride, suggesting possible contamination problems for these widely-used solvents.

Intra-laboratory agreement as indicated by COVs often but not always followed results given by correlations. Reasonably low COVs (<50%) were attained by most VOCs but only one carbonyl (tolualdehyde). For the ERG measurements (limited to compounds with $r > 0.2$), COVs averaged $62 \pm 16\%$ for the carbonyls and $35 \pm 23\%$ for the VOCs. Contrary to results using the intra-laboratory correlations, the ERG laboratory

attained slightly higher reproducibility for carbonyls than MDEQ laboratory (79±13%); for VOCs, the MDEQ laboratory was again comparable (38±18%). The strict 15% COV limit used by US EPA was met by only four compounds measured by ERG (chloromethane, dichlorodifluoromethane, trichlorofluoromethane and trichlorotrifluroethane), and none from MDEQ. In contrast to most other toxic species, these four compounds show a very limited concentration range (Table 4-1). Such constant measurements can "reward" the COV indicator but will "penalize" correlations, e.g., chloromethane's good COV (12%) is not matched by its fair intra-laboratory correlation (r=0.45).

Inter-laboratory reproducibility. Six of the 23 compounds where comparisons were possible showed negligible inter-laboratory correlation (Spearman r<0.2), specifically, crotonaldehyde, iso-valeraldehyde, valeraldehyde, acetone, acetonitrile and carbon tetrachloride (Table 4-2). Inter-laboratory agreement was only marginally better (0.2<r<0.32) for propionaldehyde, chloromethane, and methylene chloride. These nine compounds previously had shown negligible-to-fair intra-laboratory agreement (0.0<r<0.5).

Higher mean concentrations were reported by the ERG laboratory compared to the DEQ laboratory for 8 VOCs (1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, carbon tetrachloride, dichlorodifluoromethane, ethylbenzene, *m,p*-xylene, *o*-xylene, trichlorofluoromethane), based on paired t-tests (Table 4-2). The same VOCs were identified by the non-parametric Wilcoxon signed rank test, along with toluene and two carbonyls (benzaldehyde and acetonitrile). However, only ethylbenzene, *m,p*-xylene and *o*-xylene showed sizable concentration differences (nearly factor of two), differences that were maintained across the measured concentration range. Other compounds showed much smaller differences. These results cannot be explained by MDLs, but appear to result from calibration discrepancies.

Final dataset. Carbonyls and VOC species were selected for further analysis by considering data availability, detection frequency, outliers, intra-laboratory reproducibility, and inter-laboratory agreement. Five compounds measured only by the MDEQ laboratory (*m,p*-tolualdehyde, *n*-butyraldehyde, 1,1,2-trichlor*o*- 1,2,2-

trifluoroethane, 2,2,4-trimethylpentane and hexane) were excluded to avoid having to impute an excessive fraction (>65%) of missing data. The 39 species with low detection frequencies (<20%) were omitted, as were the 19 outliers detected using the Gumbell distribution in the second data screen. Pollutants with poor intra- and inter-laboratory agreement were considered on a case-by-case basis. Crotonaldehyde, valeraldehyde, acetone and carbon tetrachloride were eliminated as they showed little agreement in both intra- and intra-laboratory comparisons. Iso-valeraldehyde and acetonitrile showed fair intra-laboratory agreement (r=0.49 and 0.42, respectively) but nil inter-laboratory agreement (r=-0.38 and -0.20, respectively) and high COVs (both were 102%), so these compounds were eliminated. For 2,5-dimethylbenzaldehyde, only ERG measurements were available, but these showed little reproducibility (r=0.19, COV=96%), thus this compound was eliminated. Methylene chloride showed fair intra-and inter-laboratory agreement (r=0.44 and 0.31, respectively), a poor COV (71%), a number of outliers or erroneous observations apparent in scatter plots, and low Pearson correlations (after removing 5 observations in the second QA screen). Even when restricted to low concentrations, both intra- and inter-laboratory scatter plots showed little evidence of trend. Because of the strong possibility of laboratory contamination and the mediocre reproducibility, methylene chloride was eliminated. Finally, chloromethane also showed fair intra-and inter-laboratory agreement (r=0.45 and 0.32, respectively), but a very good COV (12%). Scatter plots displaying intra- and inter-laboratory comparisons showed a number of outlying points not detected in the second QA data screen (e.g., 1.43 ppb measured on 4/22/01 by MDEQ, and 1.19 ppb on 1/29/02 measured by ERG). Other than such points, chloromethane concentrations appeared nearly constant, e.g., the inter-quartile range was only 0.56 – 0.64 ppb and the 5th to 95th percentile range was only 0.50 - 0.74 ppb. Because these concentration changes seem attributable largely to laboratory errors rather than to local sources, we omitted chloromethane.

The final data set contained 23 compounds (7 carbonyls, 16 VOCs) measured by the ERG laboratory and 15 compounds (5 carbonyls and 10 VOCs) measured by the DEQ laboratory (Table 4-2). For the ERG measurements, intra-laboratory reproducibility measured as the (Spearman rank) correlation coefficient averaged 0.49±0.12 across the carbonyls and 0.67±0.08 across the VOCs, while COVs averaged 55±8% for carbonyls

and 31±15% for VOCs. Inter-laboratory performance was slightly worse, e.g., the correlation was 0.46±0.12 for carbonyls and 0.62±0.08 for VOCs. Benzene was the only species for which both intra- and inter-laboratory correlations exceeded 0.7. Eight other VOCs demonstrated fair-to-good performance (intra- and inter-laboratory correlations exceeding 0.6). Overall, the precision and inferred accuracy (based on inter-laboratory comparisons) for many VOC and most aldehyde measurements appear mixed at best and often poor. This is surprising given that the samples were measured in an urban/industrial setting where concentrations were not particularly low, sample collection procedures followed rigorous protocols and QA procedures, and analyses were conducted by experienced personnel and respected laboratories utilizing similar methods. Measurement performance might be acceptable for a slightly larger number of the toxics using more relaxed criteria, e.g., means within a factor of two.

4.5.2   Uncertainty models

Models showing intra-laboratory precisions based on the final data set show that differences between replicates increase with concentration (Figure 4-1, a-d). For example, carbonyl measurements from the ERG laboratory have median absolute errors that increase to 0.9 ppb as concentrations increase to 6.0 ppb (Figure 4-1a), and the corresponding regression model incorporates both constant and proportional terms: absolute error (ppb) = 0.07 + 0.15 x concentration (ppb). Relative errors tend to be higher for carbonyls as compared to VOCs, and somewhat higher for the MDEQ laboratory compared to the ERG laboratory. While the 50th percentile error model show good fits ($0.76 \leq R^2 \leq 0.88$), additional observations and perhaps wider bins (e.g., quintiles compared to deciles) might improve fits. Models for errors at higher percentiles give much larger errors, but attain comparable fits.

Models for inter-laboratory differences (Figure 4-1, e-f) are similar to the intra-laboratory differences, but predicted errors are generally larger. Using the ERG carbonyl measurements as an example (Figure 4-1e): the median absolute error (ppb) = 0.11 + 0.13 x concentration (ppb). As seen earlier, the carbonyls had higher relative errors than the VOCs. All of the inter-laboratory error models showed good fits ($0.73 \leq R^2 \leq 0.85$).

4.5.3 Predictor variable selection for OLE and MI models

For the random deletions, selected predictor variables for carbonyls included other carbonyl species (current, lead and lag observations), pollutants CO and $PM_{2.5}$, and several meteorological variables (temperature, pressure, precipitation, wind speed, wind sectors and mixing height). Predictors varied by species and models, i.e., the LL1 model for acetaldehyde included current and lead observations of other carbonyls as well as wind sectors, while the LL1 model for benzaldehyde only included current, lag and lead observations of other carbonyls as well as its own lag and lead values. These results follow from the correlations seen between the variables (Tables S4-4 to S4-6). Predictor variables for VOCs were similar with the addition of pollutant SO_2. The most frequently selected meteorological variables were resultant wind speed and SE and NW wind sectors. Similar predictor variables were obtained for the random block deletions.

For row-wise deletions, predictor variables for the three carbonyls included lead and lag observations of other carbonyl species, meteorological variables (most commonly temperature, precipitation and wind speed and occasionally E and SE wind sectors and relative humidity), and criteria air pollutants (CO but only for the LL1 acetaldehyde model). The predictor variables for the three VOCs included lead and lag observations of other VOCs, pollutants CO, $PM_{2.5}$ and SO_2 (but only for benzene and 1,3-butadiene), and meteorological variables in a few instances. Predictors for tetrachloroethylene included only one VOC (leading dichlorodifluoromethane) for the LL1 model and a few meteorological variables for the other tetrachloroethylene models. The GLMSELECT procedure did not select any predictors for the lead1 tetrachloroethylene model because the corrected information criterion was not met. Lag0 models for both carbonyls and VOCs included only meteorological variables.

4.5.4 Evaluation of OLE

Summary statistics describing the OLE performance for the three carbonyls and three VOCs are shown in Table 4-3. Because random block and random deletions obtained similar performance, only the former is shown. (Performance statistics for all carbonyls and VOCs and the three data patterns are shown in Tables S4-7 and S4-8.) Also, because nominal concentrations gave comparable or slightly better performance

than log-transformed data, performance statistics show results for only the former. (Table S4-9 gives results for log-transformed data.) Performance indicators d_2, R^2 and mean absolute error (MAE) yielded similar rankings. Performance depended strongly on the deletion pattern, as discussed below.

The OLE imputations for random deletions, which utilized both contemporaneous co-pollutant and autocorrelative information, were quite successful for carbonyls. Acetaldehyde, benzaldehyde and formaldehyde obtained d_2 values of 0.89, 0.88 and 0.86 (corresponding R^2 values of 0.72, 0.62 and 0.63), respectively, using lag1 and lag0 OLE estimates. Scatter plots of imputed versus measured values showed linear trends, but a tendency to under-predict the highest values (Figure 4-2, a-c). OLE performance for VOCs was mixed: benzene had high agreement ($0.79 \leq d_2 \leq 0.89$, $0.52 \leq R^2 \leq 0.71$, Figure 4-2g); 1,3-butadiene showed lower performance ($0.63 \leq d_2 \leq 0.78$, $0.52 \leq R^2 \leq 0.68$), a strong tendency to underestimate concentrations, and a large fraction of measurements below MDLs (Figure 4-2h); while tetrachloroethylene imputations had little correspondence to observations ($0.23 \leq d_2 \leq 0.27$, $0.00 \leq R^2 \leq 0.03$; Figure 4-2i). Occasionally, the OLE imputations yielded small negative estimates.

OLE imputations for the row-wise deletions of the three carbonyls showed at best modest performance. Imputation values were compressed towards the mean (Figure 4-2, d-f), suggesting that the estimated errors ($\mathbf{R}_t$) may have been too large. For row-wise deletions of VOCs, performance was poor, especially for 1,3-butadiene and tetrachloroethylene (Figure 4-2, k-l). Performance was essentially unchanged for tetrachloroethane, but this VOC had essentially nil agreement for all deletion patterns.

OLE performance was considered good if $d_2 \geq 0.9$ or $R^2 \geq 0.7$; fair if either $0.7 \leq d_2 < 0.9$ or $0.5 \leq R^2 < 0.7$; and poor if either $d_2 < 0.7$ or $R^2 < 0.5$. With these guidelines and considering random and random block deletions: performance was good for acetaldehyde, isobutyraldehyde, propionaldehyde, benzene, ethylbenzene, *m,p*-xylene, *o*-xylene, 1,2,4-trimethylbenzene, and toluene; fair for benzaldehyde, formaldehyde, hexaldehyde, acetylene, 1,3-butadiene, methyl ethyl ketone and 1,3,5-trimethylbenzene; and poor for tolualdehyde, dichlorodifluoromethane, *n*-octane, propylene, tetrachloroethylene, trichlorofluoromethane and trichlorotrifluoromethane. Row-wise

deletions resulted in poor performance for all 23 toxic compounds (Tables S4-7 and S4-8).

These results clearly demonstrate the importance of the missingness pattern. All estimates depended strongly on contemporaneous co-pollutant information. If this information was unavailable (as simulated using row-wise deletions) then performance was significantly degraded. This also explains why random and random block deletions obtained comparable performance: leading and lagging measurements provided relatively little information, and essentially only contemporaneous measurements were utilized in the imputations.

4.5.5 Evaluation of MI

The performance attained by MI was similar to that of OLE. For random deletions, d_2 values ranged from 0.83 to 0.95 ($0.54 \leq R^2 \leq 0.83$) for the three carbonyls, and from 0.33 to 0.89 ($0.01 \leq R^2 \leq 0.65$) for the three VOCs (Table 4-3). Again, performance for tetrachloroethylene was particularly poor. With the exception of tetrachloroethylene, the MI scatter plots showed linear relationships, somewhat less tendency to underestimate high concentrations, slightly better performance for acetaldehyde and 1,3-butadiene, but greater scatter (Figure 4-3, a-c, g-i). In all cases, the MI estimates had higher mean absolute errors (MAE), reflecting the increased scatter, a result of the variance contributed by the 5 imputations. Like OLE, MI occasionally yielded small negative estimates. Row-wise deletions again yielded substantially poorer performance (Table 4-3) and nonlinearities for formaldehyde, 1,3-butadiene and tetrachloroethylene (Figures 4-3, f, k, l). The highest observations were often under-predicted.

Results obtained using log-transformed data (Table S4-10) showed slightly poorer performance and larger standard deviations than imputations obtained using untransformed data. Some of this is a result of evaluating performance using the untransformed data, which tended to emphasize higher values. When log-transformed, imputations were more constrained, and often did not reflect the higher values that are of most interest and significance. Examination of scatter plots using untransformed data (e.g., Figure 4-3) do not show strong evidence of distributional problems, and in fact suggest largely normally-distributed residuals, which was seen in residual plots. Thus,

for the toxics dataset (as well as a better-behaved ozone dataset using 24-hr averages), MI (and OLE) performance was largely insensitive to log transformations. An advantage of using log-transformed data in the imputation model is negative estimates can be avoided.

Overall, MI performance for random and random block deletions was considered good for most aromatic compounds, fair-to-good for all carbonyl compounds, and poor for all chlorinated and fluorinated compounds. Like OLE, MI performance was poor for row-wise deletions for all of the toxics (Tables S4-7 and S4-8).

4.6 Discussion

4.6.1 Quality assurance and reproducibility of toxics data

Fewer than a third of the measured VOC and carbonyl species in the Dearborn data set had detection frequencies above 20% and was felt to provide useful information for time series-types of investigations. Further, the reproducibility of the 23 compounds remaining in the final data set varied considerably. Only benzene was considered highly reproducible, based on intra- and inter-laboratory comparisons, though several other aromatic VOCs (e.g., trimethylbenzenes and xylenes) came close. Several VOCs showed little or no reproducibility, e.g., acetone and methylene chloride, although nearly all observations exceeded MDLs. For carbonyls, reproducibility was only fair. As anticipated, between-laboratory variability exceeded within-laboratory variability, although the difference was not dramatic. While these findings are based on a dataset that is considerably more complete than those available in most air toxic measurement campaigns, the analysis depends upon data collected at only one monitoring site and analytical work performed by only two laboratories. However, both laboratories are known for their adherence to strict QA/QC protocols, and they likely attain performance that is typical of current analyses.

The most recent national study shows that the reproducibility of carbonyl and VOC measurements varies widely[7]. Across the National Air Toxics Trends Stations (NATTS) reporting precision data for 2004, COVs ranged from 0 to 126%, but most (73%) sites and pollutants were reported to meet the 15% COV criterion. In an assessment of the RIOPA study, indoor, outdoor and personal sampling using a large

number (86-171) of replicate passive samples yielded COVs from 19 to 30% for carbonyl compounds and from 6 to 42% for VOCs; active carbonyl measurements had lower COVs (9-19%, excepting glyoxyl not measured here)[27]. While these studies suggest better reproducibility than obtained for most of the toxic species measured at Dearborn, we believe that reproducibility determinations at Dearborn are typical of ambient monitoring, and in particular, routine contract monitoring for several reasons. First, the NATTS sample is very limited and unbalanced, e.g., benzene, which had the largest number of replicate measurements available, showed COVs from 0% (Mayville WI, 1 sample pair) to 59% (Northbrook IL, 59 sample pairs). Our benzene statistics (e.g., COV=19% for ERG) are in the center of this range. Second, contract monitoring is at several disadvantages in comparison to research studies (like RIOPA) where sample storage/hold times are minimized, a larger number of QA/QC measures (e.g., blanks, spiked samples, replicates) are utilized, and there is generally more flexibility to undertake corrective measures if problems are noted. In our research studies, for example, we typically obtain VOC precisions better than 10% (at concentrations exceeding ~0.5 μg m^{-3})[18]. Third, the Dearborn dataset contained up to 122 replicate sample pairs taken across a full year, and the reproducibility estimates obtained from this large sample likely represent the a full range of ambient sampling conditions, e.g., very hot and humid weather, when performance may suffer.

Reproducibility of toxic measurements is determined by many factors, e.g., system cleanliness, sampling/uptake stability, adsorbent breakthrough, loss/artifacts in sample storage, sample recovery, and analytical performance. Some problems can affect only certain toxic species, e.g., crotonaldehyde is known to disappear much more rapidly on DNPH cartridges/extracts than most other aldehydes, and recovery of polar VOCs in canisters may be problematic[28]. Other problems can affect the entire sample, e.g., a poorly cleaned canister or miscalibrated pump. While a full discussion is beyond the present scope, we note that QA/QC programs should be structured to identify (and ultimately rectify) such problems.

This study also shows differences among reproducibility indicators. Often, but not always, indicators such as correlations, COVs, and slopes will yield similar inferences. Both parametric and non-parametric measures should be used since outliers

can be difficult to detect and can strongly influence parametric measures. Multiple measures are needed as examination of a slope (and confidence interval) alone, for example, may miss a possible intercept. The distribution of concentrations will affect the indicators, e.g., COVs may be misleading for compounds that show little variation, which include stable and globally-distributed pollutants such as chloromethane, dichlorodifluoromethane, trichlorofluoromethane, carbon tetrachloride, trichlorotrifluroethane, and tetrachloroethylene[29]. Relative errors are likely to increase for measurements near MDLs. These statistics may also perform poorly for pollutants with low detection frequencies (e.g., 1,3-butadiene). Finally, while cost and logistic issues are recognized, probably at least 15 or 20 replicate samples per site and pollutant are needed to determine performance with a reasonable degree of confidence. If temperature or humidity extremes can influence measurements, then replicates should be taken under the widest possible range of weather conditions.

Uncertainty models. Many of the issues with the reproducibility indicators are addressed by the semi-parametric uncertainty models that incorporate both constant and proportional terms, and that show range of likely errors, e.g., by percentiles. These models provided stable estimates using residuals pooled across the carbonyl and VOC groups. Had sample size permitted, better performance and more insight would be attained using separate models for each compound. Within-laboratory analyses showed median absolute errors from 5 to 15% for VOCs, and about 20% for carbonyls. However, much larger errors were not uncommon, e.g., 90th percentile errors were 40 to 60% for both groups of toxics.

4.6.2 Performance of imputation methods

In most respects, OLE and MI methods gave comparable results. For random and random block deletion patterns, both methods achieved good performance. The OLE method utilized an exogenous estimate of measurement uncertainty for observed results, and as this value was increased, the OLE predictions became more conservative and approached the mean, which was especially noticeable at high concentrations of carbonyls. As expected, MI imputations provided greater dispersion.

Imputations are more accurate for pollutants that are strongly correlated to other pollutants or other measured variables. For random missingness patterns, imputations depended largely on contemporaneous measurements of other toxics. Thus, the best performance was seen for traffic-related VOCs (e.g., BTEX) and for certain combustion-related carbonyls (e.g., acetaldehyde, isobutyraldehyde, propionaldehyde), both of which form highly correlated groups of compounds. Potentially, the inclusion of other predictor variables can help to represent the influence of local sources (e.g., conventional pollutants as surrogates, and wind direction for nearby sources), reactions with other pollutants (temperature and O_3), rainout or washout mechanisms (precipitation), and general atmospheric ventilation (possibly conventional pollutants like CO, mixing height, and atmospheric stability). Interestingly, imputation performance did not suffer for 1,3-butadiene, which had only 26% of its values above MDL but which is also traffic-related; however, performance was poor for tetrachloroethylene, with a similar detection frequency of 33%. Imputations tend to be poor for compounds that are emitted alone or formed independently, e.g., chlorinated solvents and formaldehyde, although inclusion of meteorological information may improve performance. Pollutants that are globally distributed and present at relatively constant levels generally are not highly correlated with other pollutants or meteorological variables, and thus are imputed poorly (in terms of correlations, though COVs may be very small). Such pollutants will provide little information in time-series studies.

Imputation performance was very poor for row-wise deletions, indicating that the serial correlation in the data was insufficient to provide informative estimates. The row-wise imputations also utilized (contemporaneous, leading and lagging) conventional air pollutants and meteorological variables. In comparison to very high contemporaneous inter-pollutant correlations (e.g., $0.6 < r < 0.9$ for BTEX), correlations between toxics and contemporaneous daily measurements of conventional pollutants were lower ($0.0 < r < 0.5$), as were correlations with contemporaneous daily measurements of meteorological variables ($-0.6 < r < 0.7$). Thus, imputations for row-wise deletions did not obtain the performance of the random deletions. In the Dearborn dataset, the dominant missingness pattern was row-wise, thus further attention to this class of problems is warranted.

4.6.3   Other imputation studies of air quality data

There are few evaluations of SI and MI procedures for air quality purposes. The OLE method was used to simultaneously estimate missing data, predict extrema, and check the validity of observations for particulate matter (PM) concentrations in Philadelphia and St. Louis, and missing O_3 data in Houston[13]. The method performed well based on correlation coefficients and bias statistics comparing predicted and observed values. Another SI method, called the site-dependent effect method (SDEM), imputed missing hourly PM_{10} in Italy using additive terms for site, day-of-week, and week-of-year[30]. This method outperformed other SI methods tested (e.g., hourly mean) as well as a model-based MI method. Several SI and MI methods were tested using NO_x, NO_2, O_3, PM_{10}, SO_2 and CO measurements in Helsinki and Belfast[26]. This evaluation showed that performance decreased with increasing complexity of the missing data patterns, SI methods underestimated the error variance of missing data, and MI methods improved accuracy substantially. Self-organizing map and multi-layer back-propagation nets performed well especially when incorporated into a hybrid approach that used linear interpolations for short missing gaps and multivariate methods for longer gaps, however, this study was limited by the short study period. In another study, three MI models that accounted for between-variable correlations, between- and within-variable autocorrelations over time, and random seasonal effects, were used to impute pollutant measurements in the Arctic that were missing or below MDLs[16]. The most complete models produced the most realistic imputations, and MI models outperformed *ad hoc* SI methods that ignored both the autocorrelation and seasonal structure of the data.

There are two notable differences in comparing our results for urban air toxics with the studies mentioned above. First, data quality and reproducibility are very significant issues for air toxics, and even a perfect imputation model would not yield perfect performance scores since the underlying measurements contain errors. That said, we obtained at least comparable performance for most carbonyls and VOCs as obtained for conventional pollutants by Junninen et al. (2004)[26], and better performance than the single imputations of PM_{10} by Plaia and Bondi (2006)[30]. Second, the temporal and spatial concentration patterns for urban pollutants can be more complex and dynamic (variable) than the long-lived species monitored at remote sites, which likely show much

stronger autocorrelation. For this reason, our results are not directly comparable to the imputations at Arctic sites[16].

4.6.4 Applications and limitations

This study highlights the importance of characterizing the reproducibility of ambient air toxics data prior to its use. It is important to identify variables that are informative and thus useful for applications such as regulatory determinations of risk, receptor modeling studies of source apportionments, and epidemiological assessments of health impacts[31,32]. The uncertainty models and quality assurance steps presented here can help to describe and validate ambient data, as well as provide uncertainty estimates for OLE imputations and receptor modeling.

This QA assessment examined only a single monitoring site, only two laboratories, and what must be considered a modest sample size. Thus, generalizations should be made cautiously. Further, the intra-laboratory comparisons focused on analytical uncertainties, which may not dominate actual uncertainties[33]. Many other factors can influence sampling and analysis performance, and there is a clear need to increase the amount of precision and accuracy data for air toxics to better understand these factors.

Many methods are available for imputing missing data and obtaining complete datasets, and for estimating uncertain values[13,16]. For the Dearborn data, OLE and MI attained good performance for random deletions but poor performance for the row-wise deletion pattern that dominated observations at Dearborn. Imputations for especially row-wise missingness patterns might be improved in several ways. First, the variable selection criteria may have been too stringent, i.e., only very parsimonious models were generated by GLMSELECT, a procedure which assumes linear models and which does not incorporate *a priori* information. Imputations might be improved by relaxing these criteria and using more complex models. At times, however, we found that very large (and possibly over-determined) models deteriorated performance. Second, imputations might use many other variables (e.g., season, day-of-week, traffic counts) and other model structures (e.g., auto-regressive integrated moving average models). A third possibility is to derive predictor variables from a combination of meteorological

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parameters that reflect dispersion potential or local source impacts better than additive models. Fourth, models might be constructed that account for long term trends and seasonality. Fifth, uncertainty models might be further refined and potentially can improve performance of OLE estimates.

Finally, this study did not examine the performance of imputation methods in health effect studies, or the performance of other imputation methods. The MI method is designed to recover as much missing information as possible without biases results. Missing air quality data is an important problem in air pollution epidemiology, and a proper imputation scheme can help to remedy the situation. The limited evaluation exercises conducted in this study were primarily intended as an exploration of statistical approaches for exposure assessment purposes.

4.7 Conclusions

A total 323 daily air toxics samples were collected at Dearborn, MI, including 122 pairs of replicate samples. Samples were analyzed by two laboratories for 71 carbonyls and volatile organic compounds (VOCs). Data cleaning including eliminating species with low detection frequency (<20%) and detecting outliers using the Gumbell extreme value distribution. Of the 23 toxics remaining in the final dataset, intra- and inter-laboratory comparisons showed good agreement for only one compound (benzene), moderate agreement for several other VOCs (e.g., trimethylbenzenes, xylenes, ethylbenzene, dichlorodifluoromethane, tetrachloroethylene, and toluene), and poor-to-fair agreement for the remaining VOCs and all carbonyls. Error models, constructed by pooling residuals across the intra- and intra-laboratory analyses, provided a comprehensive description of errors. These results show the need to evaluate air toxics data prior to use in apportionment, exposure, and health studies.

Two methods were tested for their ability to impute missing data for the 23 toxics and for three missingness patterns. Optimal linear estimation (OLE) and multiple imputation (MI) methods obtained comparable performance for random deletions, with results depending on the compound, concentration distribution, and other factors. For the dominant row-wise deletion pattern observed in the air toxics dataset, the performance of

both methods deteriorated. A number of steps are suggested to recover information and improve these imputations.

Figure 4- 1. Absolute relative error models for carbonyls (left) and VOCs (right) from intra-laboratory and inter-laboratory comparisons.
Only concentrations above MDLs were included. Maximum decile concentrations were excluded for VOCs (figures b, d and f).
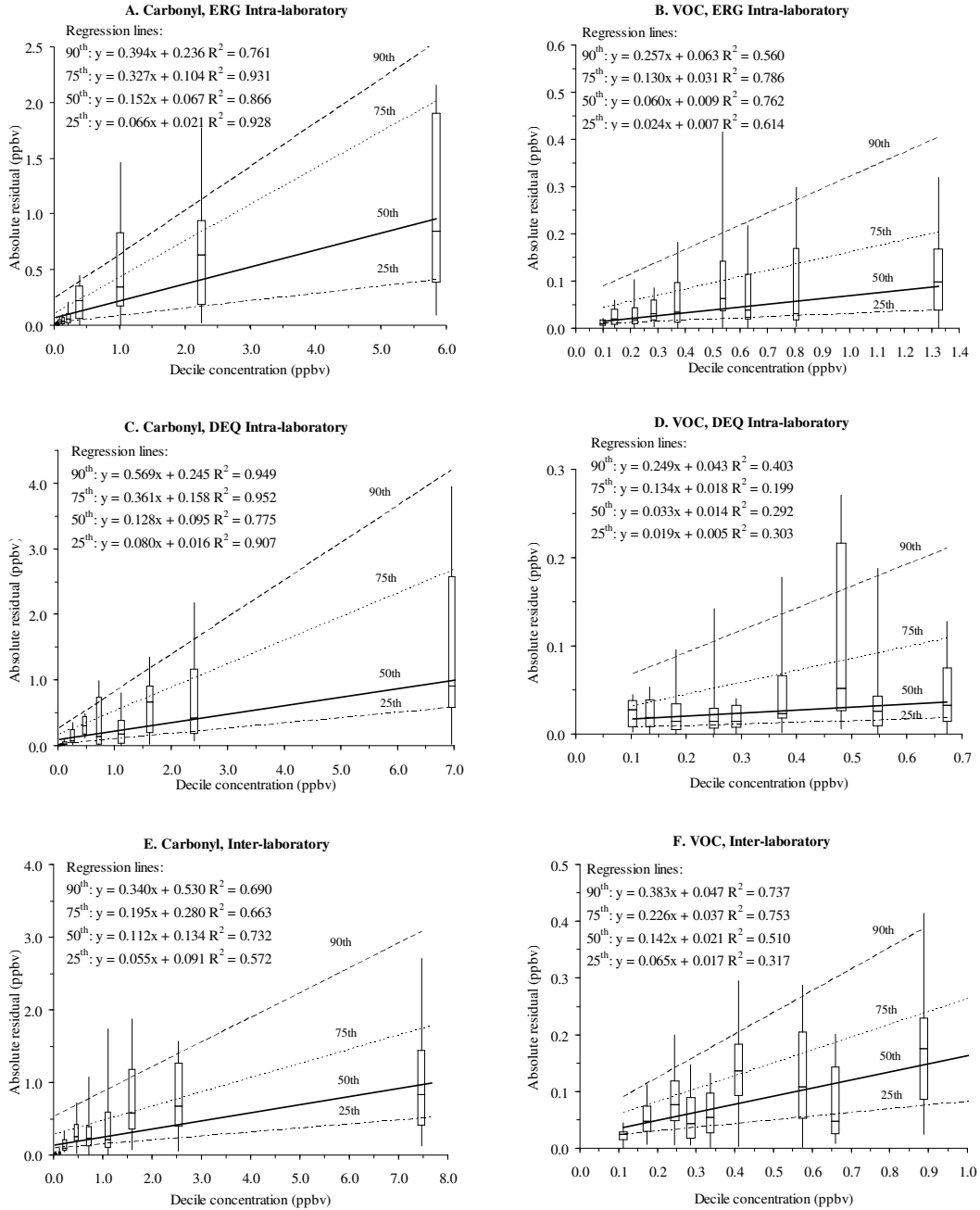
Figure 4- 2. Scatter plots for observed versus imputed data using OLE method for random and row-wise deletions of six toxics.

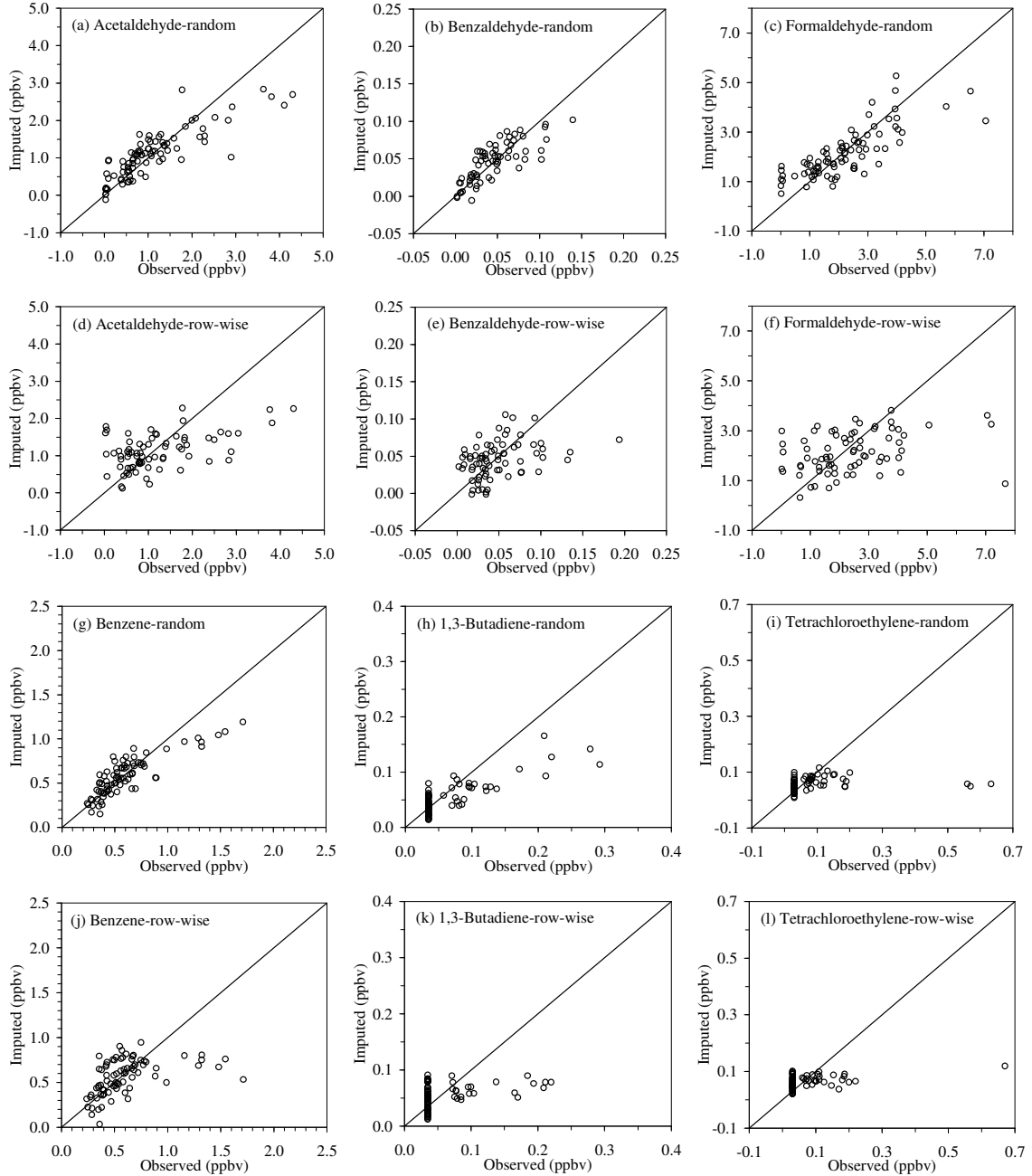Only best models of each group are plotted for each compound.

Figure 4- 3. Scatter plots for observed versus imputed data using MI method.
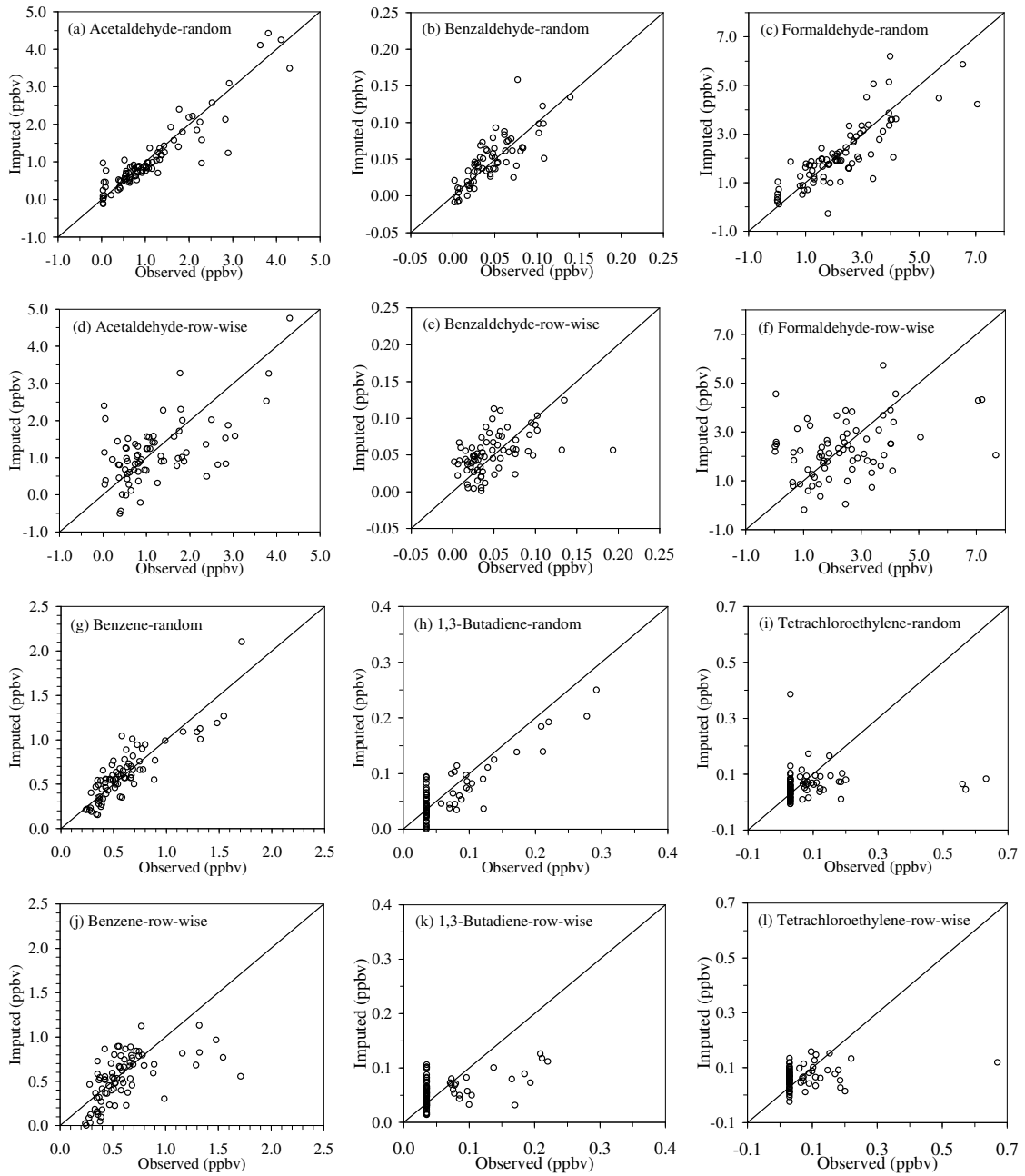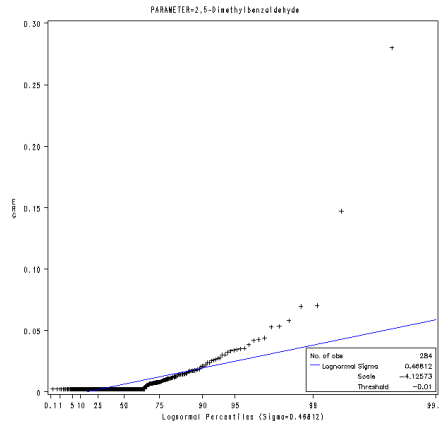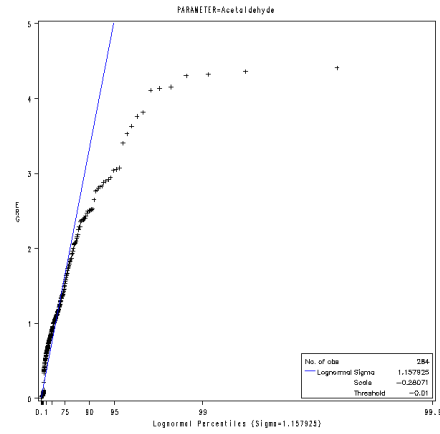Otherwise as Figure 4-2.

Figure S4- 1. Log-normal distribution plots for carbonyls and VOCs concentrations with detection frequencies above 20% from Eastern Research Group laboratory. Duplicates were averaged; Outliers were excluded.

2,5-Dimethylbenzaldehyde

Acetaldehyde

Benzaldehyde
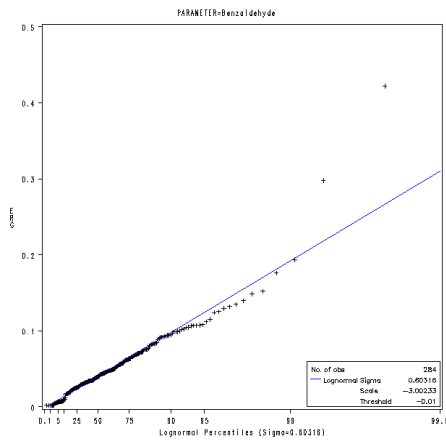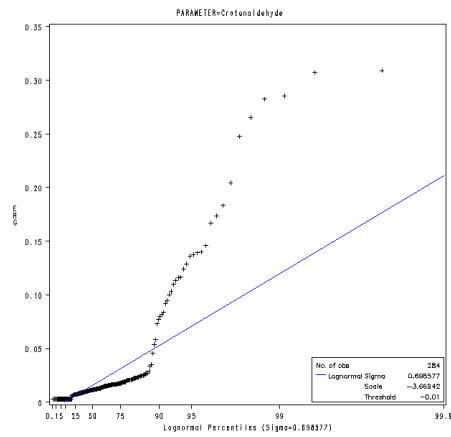
Crotonaldehyde

Formaldehyde
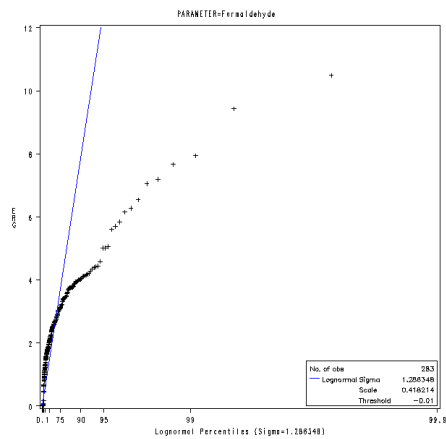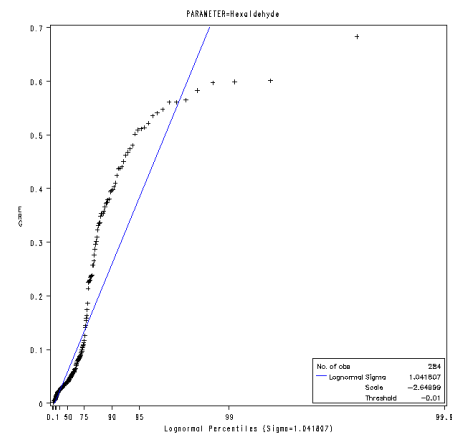
Hexaldehyde

Figure S4-1 (Cont.)

iso-Butyraldehyde

iso-Valeraldehyde
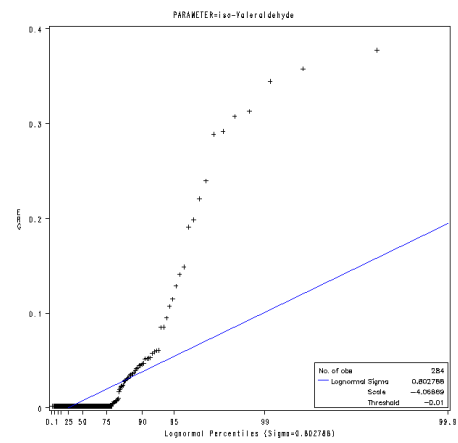
Propionaldehyde
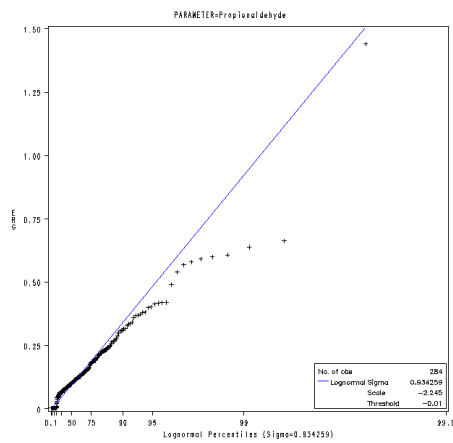
Tolualdehyde

Valeraldehyde

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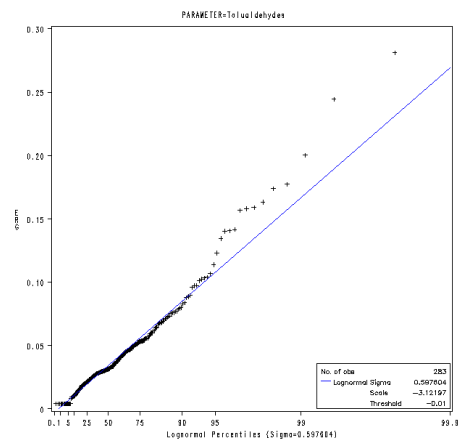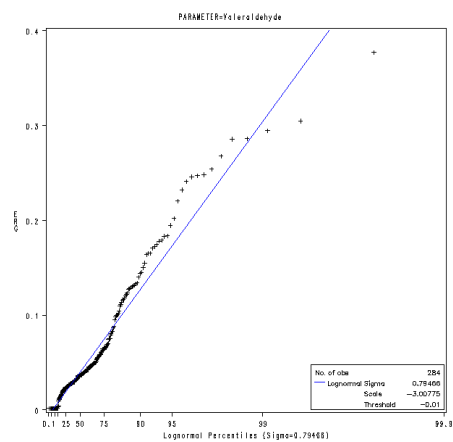
Figure S4-1 (Cont.)

1,2,4-Trimethylbenzene
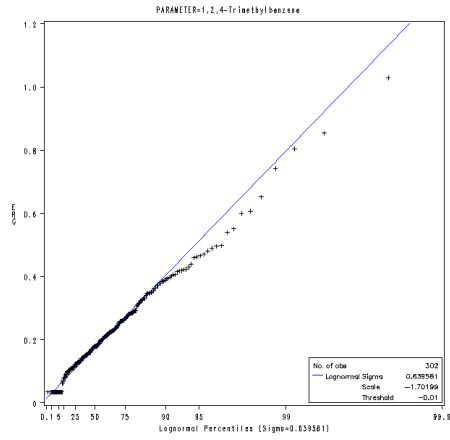
1,3,5-Trimethylbenzene
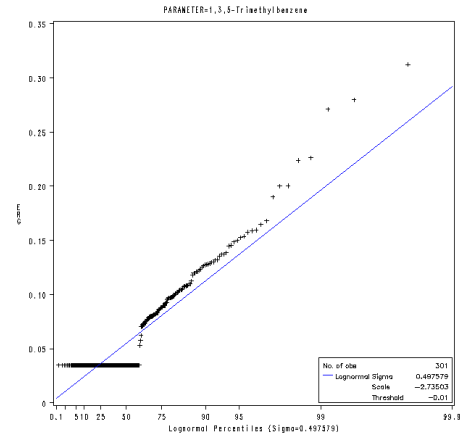
1,3-Butadiene
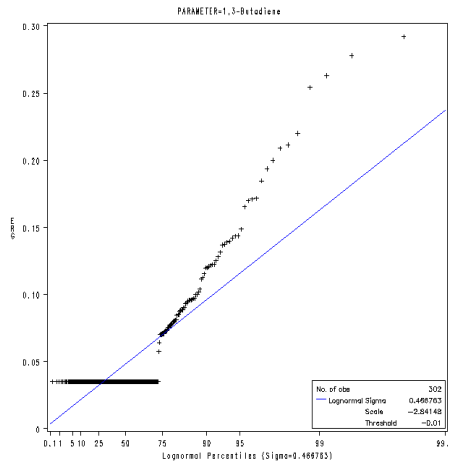
Acetone
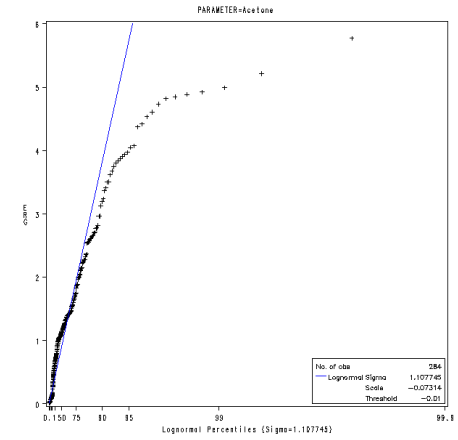
Acetonitrile

Acetylene

154
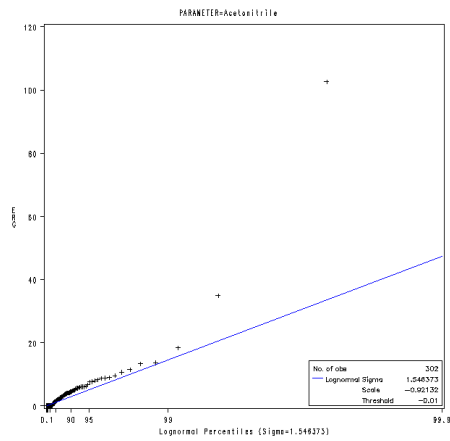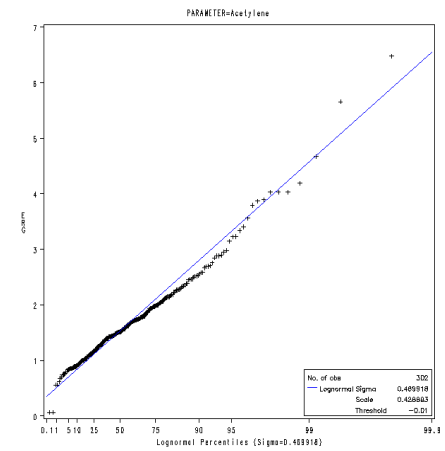
Figure S4-1 (Cont.)

Benzene
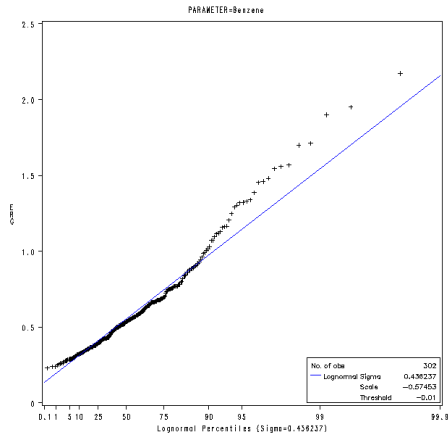
Carbon tetrachloride

Chloromethane

Dichlorodifluoromethane

Ethylbenzene

m,p-Xylene

155
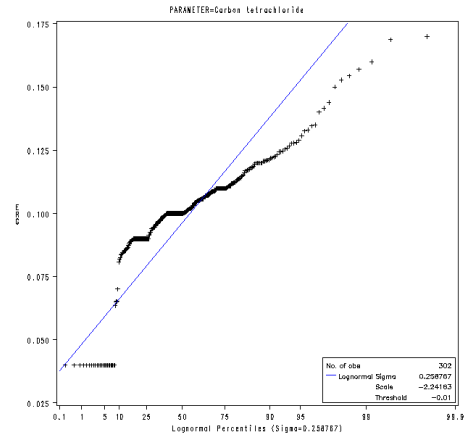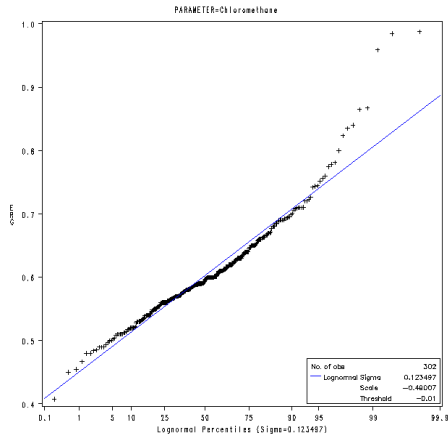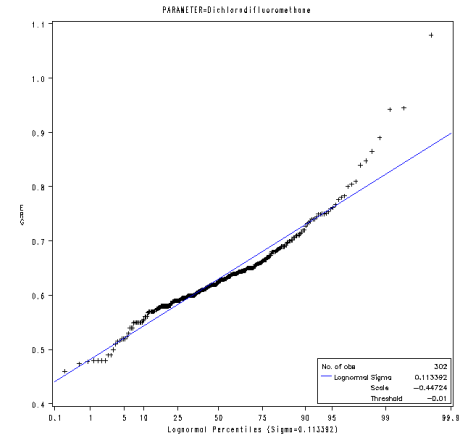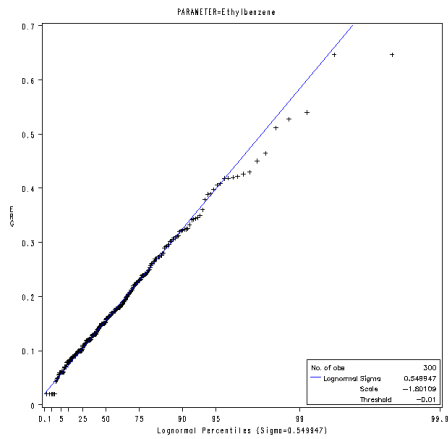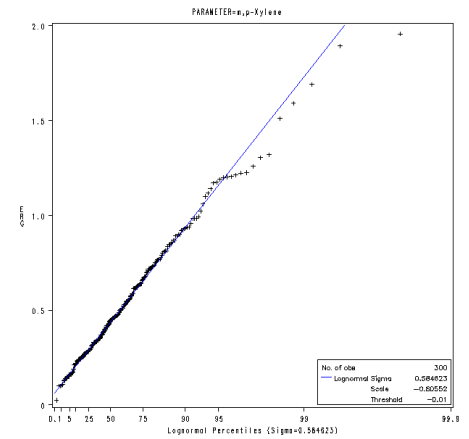
Figure S4-1 (Cont.)

Methyl ethyl ketone
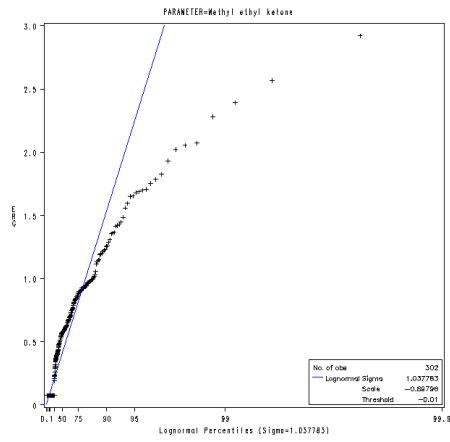
Methylene chloride
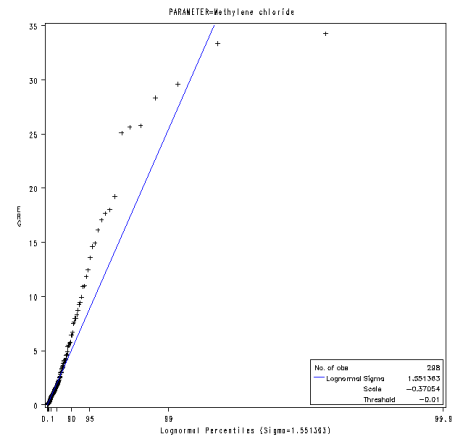
n-Octane
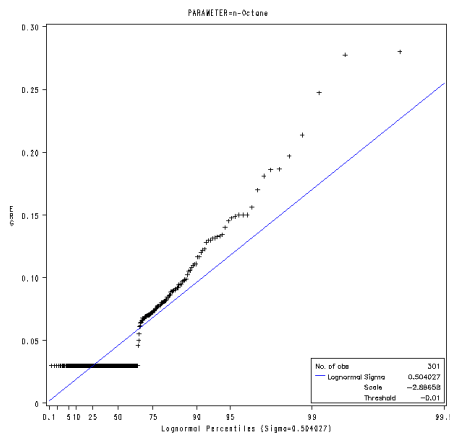
o-Xylene
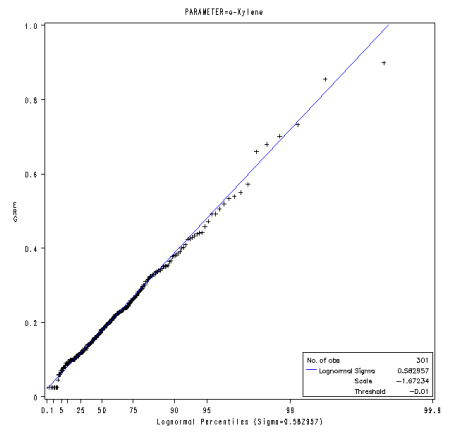
Propylene
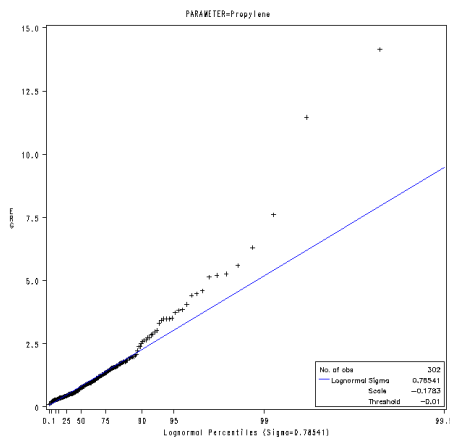
Tetrachloroethylene
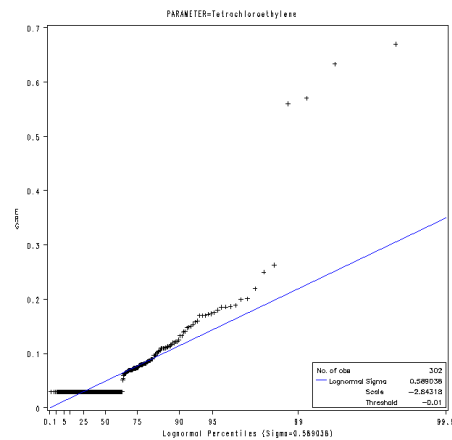
Figure S4-1 (Cont.)

Toluene
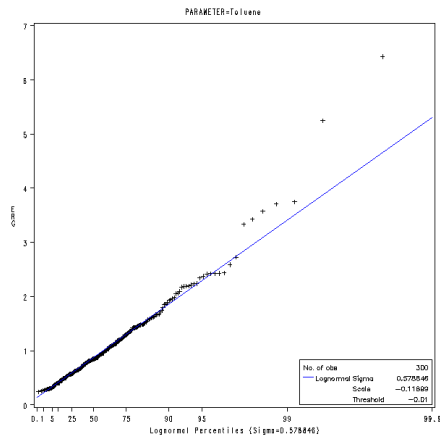
Trichlorofluoromethane
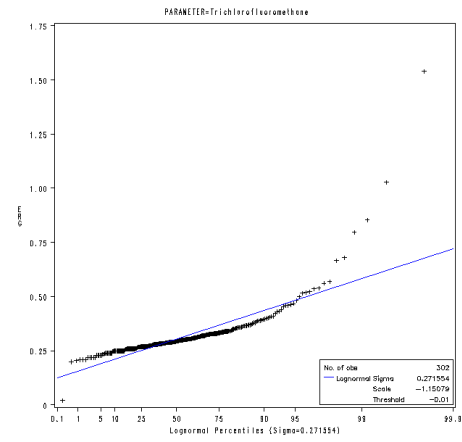
Trichlorotrifluroethene
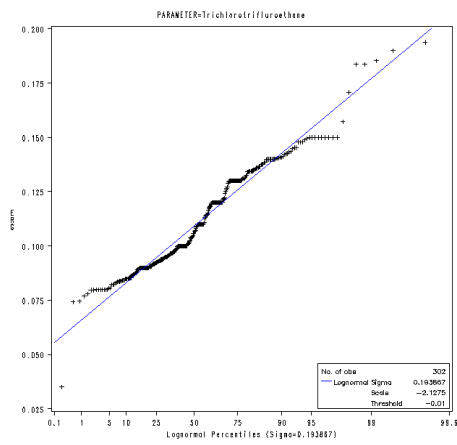
Figure S4- 2. Log-normal distribution plots for carbonyls and VOCs concentrations with detection frequencies above 20% from Michigan Department of Environmental Quality laboratory.

Duplicates were averaged; Outliers were excluded.

Acetaldehyde
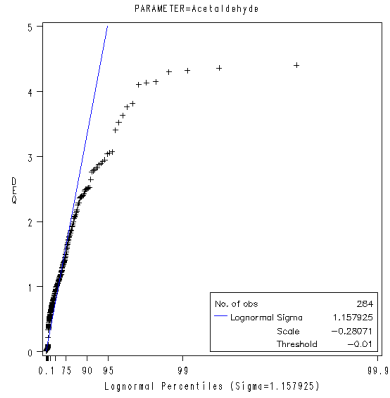
Benzaldehyde
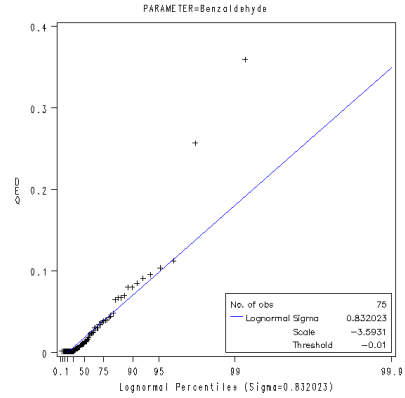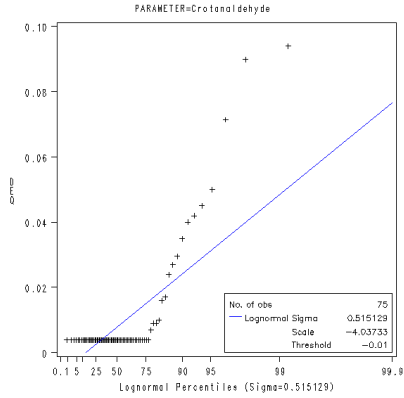
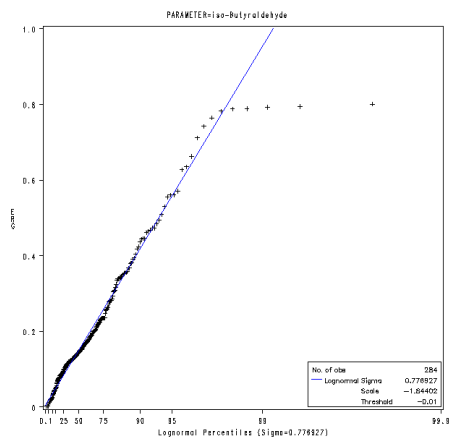Crotonaldehyde

Formaldehyde
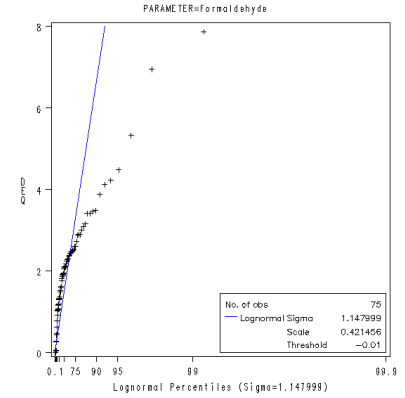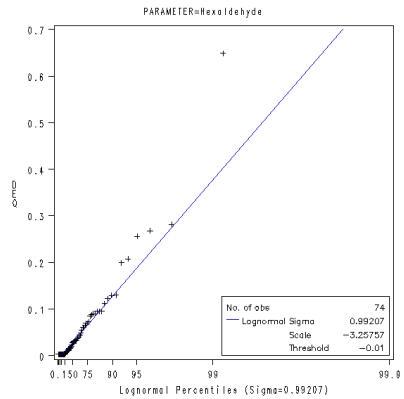
Hexaldehyde

iso-Valeraldehyde
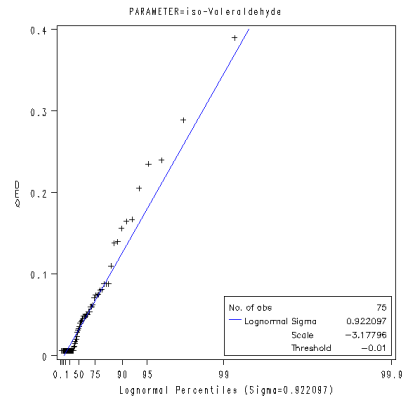
Figure S4-2 (Cont.)

m,p-Tolualdehyde
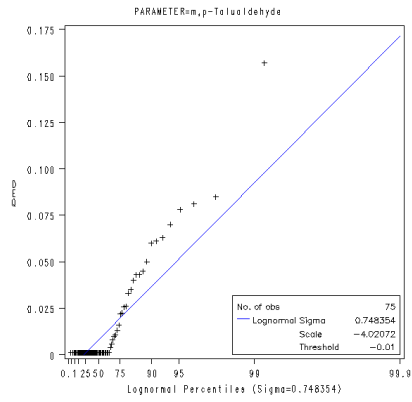
n-Butyraldehyde
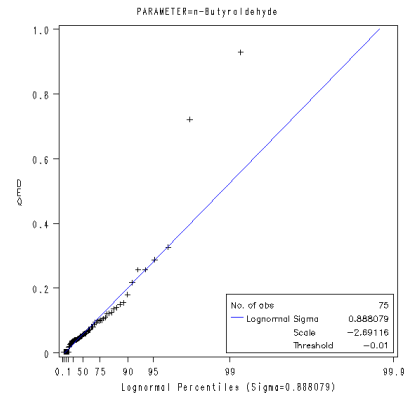
Propionaldehyde
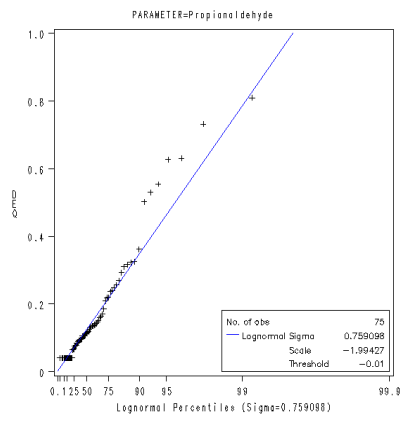
Valeraldehyde
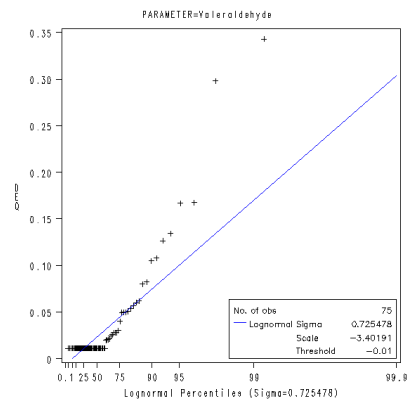
Figure S4-2 (Cont.)

1,1,2-Trichloro-1,2,2-trifluoroethane
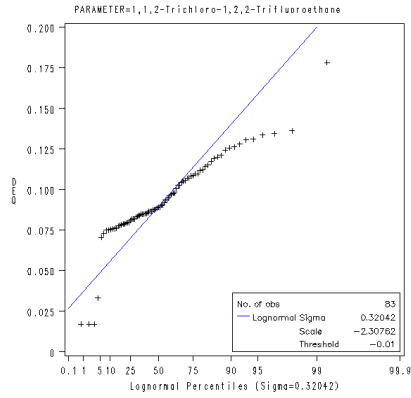
1,2,4-Trimethylbenzene
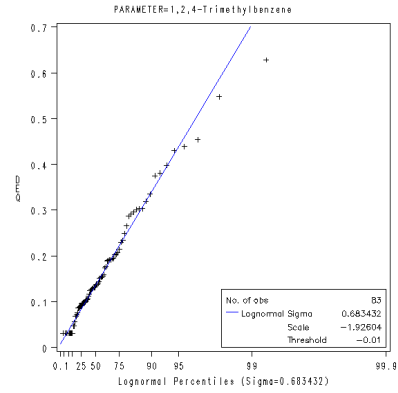
1,3,5-Trimethylbenzene
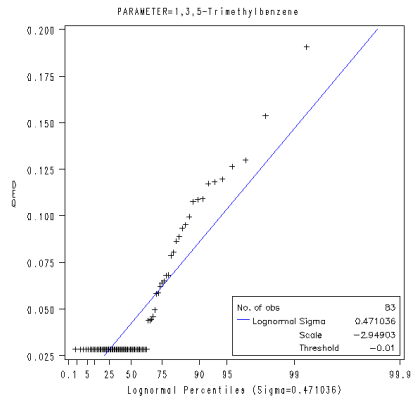
2,2,4-Trimethylpentane

Acetone

Acetonitrile

160
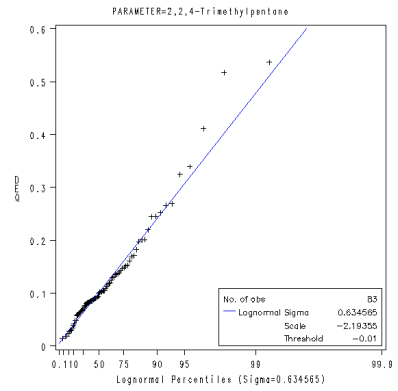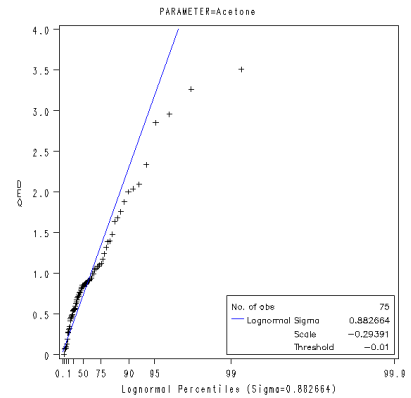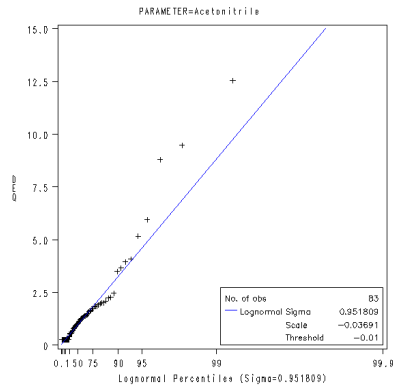
Figure S4-2 (Cont.)

Benzene
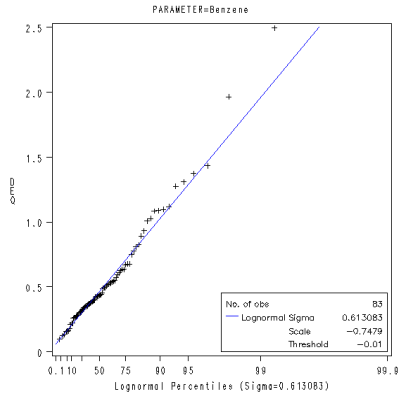
Carbon tetrachloride
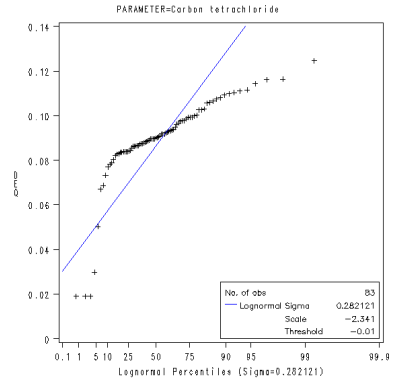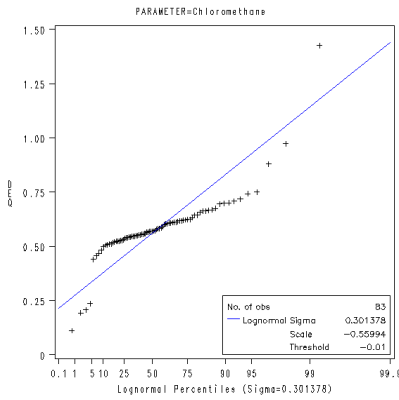
Chloromethane

Dichlorodifluoromethane
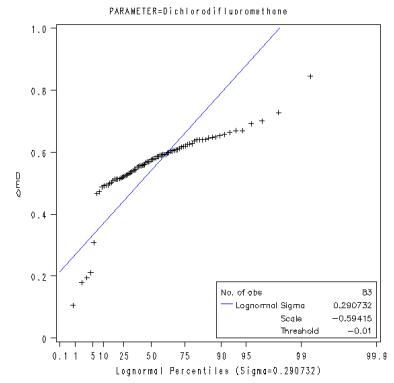
Ethylbenzene
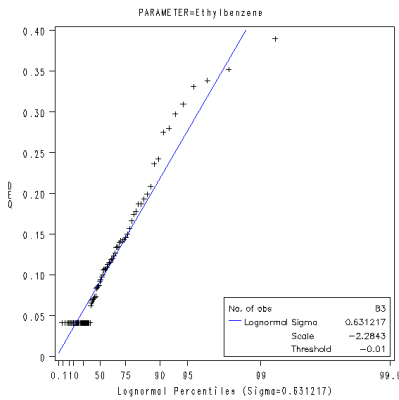
Hexane
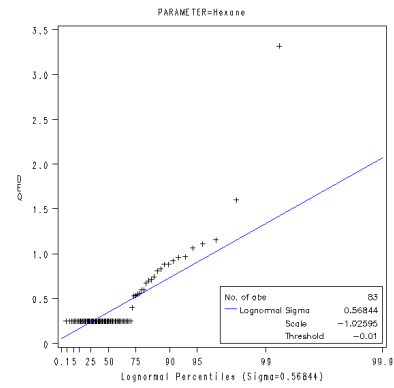
Figure S4-2 (Cont.)

m,p-Xylene
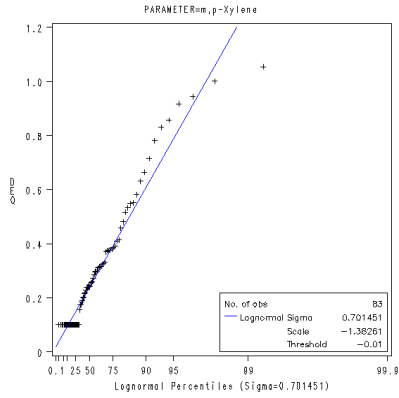
Methylene chloride
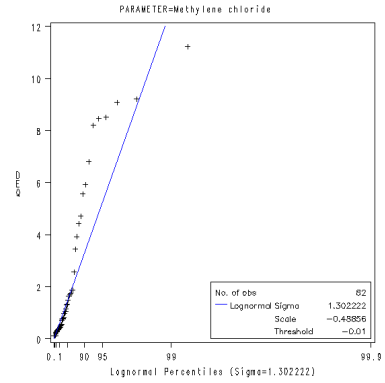
o-Xylene
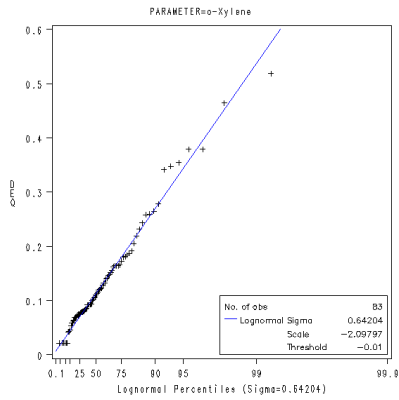
Tetrachloroethylene
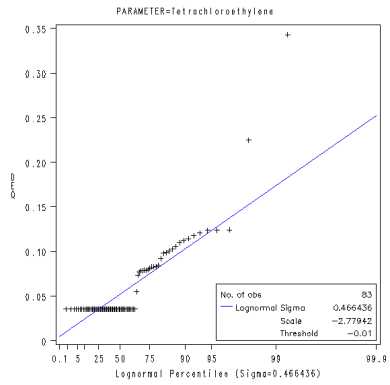
Toluene
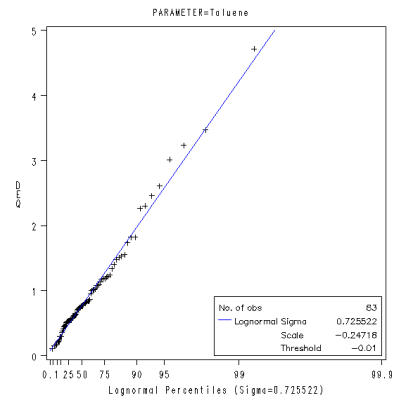
Trichlorofluoromethane
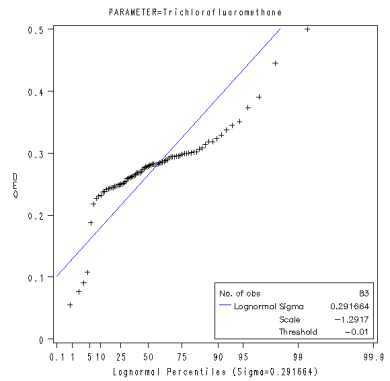
Table 4- 1. Statistics of toxic concentrations measured at Dearborn, Michigan for those VOCs and carbonyls with detection frequencies above 20%.
Duplicates were averaged and outliers excluded. TFE=trifluoroethane; DF=detection frequency; MDL=method detection limit; "-" is not measured or DF<20%.

| Compound	ERG laboratory							MDEQ laboratory						
	N	DF	Mean	50th	75th	Max	MDL	N	DF	Mean	50th	75th	Max	MDL
		(%)	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)		(%)	(ppbv)	(ppbv)	(ppbv)	(ppbv)	(ppbv)
Carbonyls														
2,5-Dimethylbenzaldehyde	284	32	0.009	0.003	0.008	0.280	0.005	-	-	-	-	-	-	-
Acetaldehyde	284	100	1.166	0.914	1.519	4.406	0.014	74	97	0.860	0.760	1.030	5.085	0.009
Benzaldehyde	284	98	0.050	0.040	0.063	0.422	0.004	75	69	0.032	0.012	0.038	0.360	0.004
Crotonaldehyde	284	81	0.027	0.012	0.018	0.309	0.006	75	21	0.011	0.004	0.004	0.094	0.008
Formaldehyde	283	100	2.317	2.089	3.094	10.486	0.016	75	97	2.139	2.055	2.603	7.873	0.008
Hexaldehyde	284	99	0.119	0.041	0.110	0.683	0.004	75	75	0.065	0.027	0.072	0.653	0.005
iso-Butyraldehyde	284	99	0.199	0.144	0.235	0.801	0.005	-	-	-	-	-	-	-
iso-Valeraldehyde	284	21	0.020	0.002	0.002	0.377	0.004	75	60	0.055	0.033	0.073	0.390	0.012
m,p-Tolualdehyde	-	-	-	-	-	-	-	75	35	0.016	0.001	0.019	0.157	0.002
n-Butyraldehyde	-	-	-	-	-	-	-	75	88	0.094	0.058	0.100	0.929	0.007
Propionaldehyde	284	90	0.143	0.103	0.180	1.440	0.007	75	69	0.175	0.115	0.220	0.810	0.083
Tolualdehydes	283	93	0.043	0.031	0.053	0.281	0.008	-	-	-	-	-	-	-
Valeraldehyde	284	91	0.058	0.037	0.065	0.377	0.003	75	33	0.038	0.011	0.035	0.343	0.022
VOCs														
1,1,2-Trichloro-1,2,2-TFE	-	-	-	-	-	-	-	83	95	0.094	0.089	0.109	0.178	0.034
1,2,4-Trimethylbenzene	302	90	0.210	0.179	0.267	1.029	0.070	83	86	0.171	0.135	0.210	0.629	0.062
1,3,5-Trimethylbenzene	301	38	0.065	0.035	0.088	0.312	0.070	83	29	0.050	0.029	0.063	0.191	0.057
1,3-Butadiene	302	26	0.057	0.035	0.071	0.292	0.070	-	-	-	-	-	-	-
2,2,4-Trimethylpentane	-	-	-	-	-	-	-	83	99	0.126	0.099	0.148	0.537	0.017
Acetone	284	100	1.422	1.138	1.771	5.770	0.008	75	99	0.982	0.856	1.115	3.513	0.011
Acetonitrile	302	36	1.804	0.125	1.642	102.600	0.250	83	73	1.561	0.991	1.711	12.552	0.520
Acetylene	302	99	1.684	1.520	1.983	6.480	0.130	-	-	-	-	-	-	-
Benzene	302	100	0.614	0.537	0.697	2.173	0.040	83	100	0.564	0.434	0.654	2.494	0.070
Carbon tetrachloride	302	90	0.099	0.100	0.110	0.170	0.080	83	95	0.089	0.090	0.099	0.125	0.038
Chloromethane	302	100	0.607	0.594	0.644	0.988	0.060	83	100	0.583	0.570	0.623	1.426	0.062
Dichlorodifluoromethane	302	100	0.634	0.625	0.663	1.079	0.040	83	100	0.560	0.576	0.620	0.846	0.048
Ethylbenzene	300	98	0.181	0.155	0.230	0.647	0.040	83	55	0.115	0.092	0.144	0.390	0.083
Hexane	-	-	-	-	-	-	-	83	27	0.435	0.250	0.531	3.318	0.500
m,p-Xylene	300	100	0.517	0.445	0.661	1.957	0.050	83	61	0.311	0.240	0.383	1.055	0.200
Methyl ethyl ketone	302	74	0.613	0.570	0.878	2.920	0.150	-	-	-	-	-	-	-
Methylene chloride	298	96	2.468	0.647	1.731	34.270	0.060	81	79	1.480	0.401	1.302	11.222	0.230
n-Octane	301	33	0.055	0.030	0.072	0.280	0.060	-	-	-	-	-	-	-
o-Xylene	301	97	0.211	0.180	0.262	0.899	0.050	83	90	0.140	0.110	0.169	0.519	0.043
Propylene	300	100	1.116	0.761	1.339	7.599	0.050	-	-	-	-	-	-	-
Tetrachloroethylene	302	33	0.064	0.030	0.074	0.670	0.060	83	34	0.061	0.036	0.080	0.343	0.071
Toluene	300	100	1.049	0.850	1.293	6.431	0.060	83	100	0.998	0.763	1.185	4.718	0.070
Trichlorofluoromethane	302	100	0.319	0.295	0.333	1.540	0.040	83	100	0.274	0.279	0.297	0.500	0.048
Trichlorotrifluroethane	302	100	0.111	0.106	0.130	0.194	0.070	-	-	-	-	-	-	-

Table 4- 2. Intra- and inter-laboratory reproducibility. Based on only detected values. Significant values (p-value<0.05) indicated in bold.

Correl coeff=correlation coefficient; COV=coefficient of variation; WSR=Wilcoxon signed rank; TFE=trifluoroethane; "-" is not measured or detection frequency<20%.

| Compound | Intra-laboratory reproducibility | | | | | | Inter-laboratory reproducibility | | | | Retained (y=yes) |
| | Correl coeff-ERG | | Correl coeff-MDEQ | | % COV | | Correl coeff | | Paired t-test (p-value) | WSR test (p-value) | |
	Pearson	Spearman	Pearson	Spearman	ERG	MDEQ	Pearson	Spearman			
Carbonyls											
2,5-Dimethylbenzaldehyde	0.02	0.19	-	-	96	-	-	-	-	-	
Acetaldehyde	**0.38**	**0.39**	**0.45**	**0.45**	61	70	**0.37**	**0.52**	0.33	0.07	y
Benzaldehyde	**0.54**	**0.61**	0.23	**0.65**	51	78	0.28	**0.46**	1.00	**0.04**	y
Crotonaldehyde	0.32	0.22	0.31	0.48	61	97	-0.06	-0.07	0.83	-	
Formaldehyde	**0.45**	**0.48**	**0.51**	**0.58**	58	64	**0.73**	**0.61**	0.95	0.93	y
Hexaldehyde	**0.50**	**0.64**	0.32	**0.51**	62	83	**0.40**	**0.44**	0.41	0.29	y
iso-Butyraldehyde	0.19	**0.40**	-	-	52	-	-	-	-	-	y
iso-Valeraldehyde	-0.05	**0.49**	**0.52**	**0.34**	102	93	-0.18	-0.28	-	-	
m,p-Tolualdehyde	-	-	0.26	**0.64**	-	85	-	-	-	-	
n-Butyraldehyde	-	-	**0.40**	**0.45**	-	71	-	-	-	-	
Propionaldehyde	**0.34**	0.33	**0.87**	**0.49**	61	59	0.25	0.28	0.07	0.11	y
Tolualdehydes	**0.71**	**0.56**	-	-	42	-	-	-	-	-	y
Valeraldehyde	0.06	0.22	0.55	**0.56**	69	88	0.04	0.13	0.86	0.91	
VOCs											
1,1,2-Trichloro-1,2,2-TFE	-	-	0.30	0.38	-	29	-	-	-	**-**	
1,2,4-Trimethylbenzene	**0.68**	**0.67**	**0.91**	**0.79**	39	35	**0.71**	**0.63**	**<0.01**	**<0.01**	y
1,3,5-Trimethylbenzene	**0.71**	**0.70**	**0.89**	**0.64**	31	16	**0.71**	**0.59**	**<0.01**	**<0.01**	y
1,3-Butadiene	**0.60**	**0.59**	-	-	49	-	-	-	-	-	y
2,2,4-Trimethylpentane	-	-	**0.89**	**0.66**	-	37	-	-	-	-	
Acetone	0.04	-0.01	0.15	0.26	67	73	-0.06	0.14	-	0.17	
Acetonitrile	0.01	**0.42**	**0.40**	**0.49**	102	65	-0.17	-0.20	0.23	**0.01**	
Acetylene	**0.54**	**0.63**	-	-	26	-	-	-	-	**-**	y
Benzene	**0.83**	**0.73**	**0.82**	**0.66**	19	36	**0.81**	**0.71**	0.07	**<0.01**	y
Carbon tetrachloride	0.02	0.27	**0.78**	**0.84**	23	19	0.23	0.17	**0.01**	**<0.01**	
Chloromethane	-0.02	**0.45**	0.44	0.42	12	27	0.32	0.32	0.98	0.47	
Dichlorodifluoromethane	**0.75**	**0.75**	**0.70**	**0.68**	4	29	**0.47**	**0.61**	**<0.01**	**<0.01**	y
Ethylbenzene	**0.69**	**0.65**	**0.92**	**0.88**	44	16	**0.78**	**0.66**	**<0.01**	**<0.01**	y
Hexane	-	-	**0.48**	**0.60**	-	63	-	-	-	-	
m,p-Xylene	**0.60**	**0.71**	**0.92**	**0.88**	35	24	**0.80**	**0.67**	**<0.01**	**<0.01**	y
Methyl ethyl ketone	**0.66**	**0.65**	-	-	50	-	-	-	-	-	y
Methylene chloride	0.05	**0.44**	0.10	**0.71**	71	62	0.14	0.31	0.14	0.36	
n-Octane	0.28	**0.56**	-	-	53	-	-	-	-	-	y
o-Xylene	**0.63**	**0.79**	**0.93**	**0.83**	39	30	**0.79**	**0.67**	**<0.01**	**<0.01**	y
Propylene	**0.90**	**0.70**	-	-	33	-	-	-	-	-	y
Tetrachloroethylene	**0.82**	**0.77**	**0.39**	**0.53**	28	63	**0.64**	**0.61**	0.65	0.73	y
Toluene	**0.82**	**0.73**	**0.93**	**0.82**	28	37	**0.50**	**0.62**	1.00	**0.04**	y
Trichlorofluoromethane	**0.66**	**0.57**	**0.57**	**0.60**	10	28	**0.33**	**0.42**	**0.04**	**0.02**	y
Trichlorotrifluroethane	**0.76**	**0.52**	-	-	10	-	-	-	-	-	y

Table 4- 3. Performance indicators for MI and OLE estimates.
Bold values show highest performing model in group. Abbreviations: lag0=current day observation; lag1=current and previous day observations; lead1=current and next day observations; LL1=current, previous and next day observations; SD=standard deviation; d2=Willmot's index of agreement; R2=coefficient of determination; MAE=mean absolute error.

Performance indicators		Multiple imputation				Optimal estimation			
		lag0(SD)	lag1(SD)	lead1(SD)	LL1(SD)	lag0	lag1	lead1	LL1
Acetaldehyde									
Random	d_2	0.95 (0.01)	0.95 (0.01)	0.95 (0.01)	**0.95 (0.00)**	0.86	**0.89**	0.74	0.88
	R^2	0.83 (0.02)	0.80 (0.02)	0.83 (0.02)	**0.83 (0.01)**	0.69	**0.72**	0.51	0.70
	MAE	0.29 (0.03)	0.30 (0.03)	0.30 (0.02)	**0.30 (0.01)**	0.30	**0.26**	0.46	0.28
Row-wise	d_2	0.58 (0.05)	**0.67 (0.04)**	0.51 (0.05)	0.63 (0.06)	**0.67**	0.63	0.47	0.46
	R^2	0.11 (0.05)	**0.20 (0.06)**	0.04 (0.02)	0.14 (0.08)	**0.32**	0.26	0.09	0.11
	MAE	0.87 (0.08)	**0.85 (0.12)**	0.91 (0.04)	0.87 (0.06)	**0.62**	0.66	0.83	0.79
Benzaldehyde									
Random	d_2	0.80 (0.03)	**0.83 (0.02)**	0.76 (0.05)	0.76 (0.01)	**0.88**	0.82	0.77	0.83
	R^2	0.46 (0.07)	**0.55 (0.03)**	0.38 (0.10)	0.38 (0.03)	**0.62**	0.48	0.44	0.51
	MAE	0.02 (0.00)	**0.02 (0.00)**	0.03 (0.00)	0.03 (0.00)	**0.00**	0.00	0.00	0.00
Row-wise	d_2	0.48 (0.06)	**0.54 (0.03)**	0.35 (0.05)	0.38 (0.05)	0.50	**0.57**	0.25	0.31
	R^2	0.05 (0.05)	**0.09 (0.02)**	0.01 (0.01)	0.00 (0.01)	0.07	**0.13**	0.02	0.00
	MAE	0.04 (0.00)	**0.04 (0.00)**	0.05 (0.00)	0.05 (0.00)	0.00	**0.00**	0.00	0.00
Formaldehyde									
Random	d_2	0.84 (0.02)	0.80 (0.04)	**0.85 (0.01)**	0.81 (0.04)	**0.86**	0.82	0.84	0.83
	R^2	0.53 (0.05)	0.44 (0.07)	**0.54 (0.03)**	0.45 (0.09)	**0.63**	0.62	0.69	0.63
	MAE	0.80 (0.03)	0.90 (0.10)	**0.81 (0.03)**	0.86 (0.05)	**0.72**	0.78	0.69	0.77
Row-wise	d_2	0.51 (0.06)	**0.53 (0.03)**	0.40 (0.06)	0.40 (0.06)	0.52	**0.54**	0.33	0.33
	R^2	0.05 (0.04)	**0.06 (0.03)**	0.01 (0.01)	0.01 (0.01)	0.09	**0.11**	0.00	0.00
	MAE	1.49 (0.14)	**1.58 (0.12)**	1.79 (0.14)	1.79 (0.14)	2.37	**2.31**	2.65	2.65
Benzene									
Random	d_2	**0.87 (0.03)**	0.84 (0.01)	0.87 (0.02)	0.84 (0.02)	**0.89**	0.85	0.84	0.79
	R^2	**0.61 (0.08)**	0.52 (0.03)	0.59 (0.06)	0.52 (0.05)	**0.71**	0.63	0.63	0.52
	MAE	**0.17 (0.02)**	0.18 (0.01)	0.17 (0.01)	0.18 (0.01)	**0.03**	0.04	0.04	0.04
Row-wise	d_2	**0.64 (0.04)**	0.63 (0.03)	0.58 (0.06)	0.57 (0.06)	0.63	**0.65**	0.64	0.53
	R^2	**0.20 (0.05)**	0.18 (0.03)	0.13 (0.05)	0.12 (0.05)	0.22	**0.25**	0.24	0.17
	MAE	**0.26 (0.02)**	0.28 (0.02)	0.28 (0.03)	0.27 (0.01)	0.07	**0.07**	0.07	0.08
1,3-Butadiene									
Random	d_2	0.89 (0.02)	**0.89 (0.01)**	0.87 (0.01)	0.87 (0.02)	**0.78**	0.74	0.62	0.63
	R^2	0.65 (0.06)	**0.65 (0.03)**	0.58 (0.03)	0.58 (0.04)	**0.68**	0.67	0.52	0.52
	MAE	0.03 (0.00)	**0.03 (0.00)**	0.03 (0.00)	0.03 (0.00)	**0.00**	0.00	0.00	0.00
Row-wise	d_2	**0.58 (0.04)**	0.50 (0.03)	0.52 (0.08)	0.46 (0.05)	**0.49**	0.43	0.41	0.30
	R^2	**0.09 (0.03)**	0.05 (0.03)	0.07 (0.05)	0.03 (0.03)	**0.13**	0.08	0.07	0.03
	MAE	**0.04 (0.00)**	0.04 (0.00)	0.05 (0.00)	0.04 (0.00)	**0.00**	0.00	0.00	0.00
Tetrachloroethylene									
Random	d_2	0.30 (0.07)	0.27 (0.03)	0.31 (0.06)	**0.33 (0.06)**	0.22	**0.27**	0.26	0.23
	R^2	0.02 (0.02)	0.01 (0.01)	0.01 (0.01)	**0.01 (0.02)**	0.01	**0.03**	0.03	0.00
	MAE	0.08 (0.01)	0.08 (0.00)	0.08 (0.00)	**0.07 (0.00)**	0.01	**0.01**	0.01	0.01
Row-wise	d_2	**0.41 (0.11)**	0.38 (0.10)	-	0.32 (0.06)	**0.37**	0.30	-	0.27
	R^2	**0.03 (0.02)**	0.02 (0.01)	-	0.01 (0.00)	**0.15**	0.09	-	0.08
	MAE	**0.07 (0.01)**	0.08 (0.01)	-	0.07 (0.01)	**0.01**	0.01	-	0.01

Table S4- 1. Statistics of concentrations at Dearborn, Michigan for VOCs and carbonyls analyzed by Eastern Research Group (ERG) laboratory.
DF=detection frequency; MDL=method detection limit.

| Compound | ERG laboratory-Sample 1 | | | | | | ERG laboratory-Sample 2 | | | | | | |
	N	DF (%)	Min (ppbv)	Mean (ppbv)	SD (ppbv)	Max (ppbv)	N	DF (%)	Min (ppbv)	Mean (ppbv)	SD (ppbv)	Max (ppbv)	MDL (ppbv)
Carbonyls													
2,5-Dimethylbenzaldehyde	266	31	0.003	0.009	0.020	0.280	54	31	0.003	0.010	0.022	0.147	0.005
Acetaldehyde	266	100	0.007	1.203	0.998	4.406	54	100	0.024	0.972	0.604	3.056	0.014
Acetone	266	100	0.017	1.474	1.247	5.770	54	100	0.025	1.198	0.875	4.611	0.008
Benzaldehyde	266	98	0.002	0.050	0.043	0.422	54	98	0.002	0.048	0.035	0.152	0.004
Crotonaldehyde	266	79	0.003	0.027	0.051	0.309	54	80	0.003	0.021	0.044	0.307	0.006
Formaldehyde	266	100	0.008	2.406	1.972	20.980	54	100	0.019	2.373	1.512	7.061	0.016
Hexaldehyde	266	100	0.002	0.123	0.167	0.722	54	96	0.002	0.091	0.123	0.583	0.004
iso-Butyraldehyde	266	99	0.003	0.206	0.175	0.801	54	98	0.003	0.158	0.099	0.601	0.005
iso-Valeraldehyde	266	22	0.002	0.020	0.058	0.377	54	17	0.002	0.024	0.076	0.380	0.004
Propionaldehyde	266	89	0.004	0.147	0.153	1.440	54	93	0.004	0.124	0.082	0.377	0.007
Tolualdehydes	266	92	0.004	0.045	0.051	0.591	54	96	0.004	0.045	0.038	0.193	0.008
Valeraldehyde	266	90	0.002	0.061	0.067	0.377	54	94	0.002	0.040	0.034	0.213	0.003
VOCs													
1,1,1-Trichloroethane	282	5	0.030	0.033	0.014	0.167	52	4	0.030	0.032	0.008	0.072	0.060
1,1,2,2-Tetrachloroethane	282	0	0.030	0.030	0.000	0.030	52	0	0.030	0.030	0.000	0.030	0.060
1,1,2-Trichloroethane	282	0	0.030	0.030	0.000	0.030	52	0	0.030	0.030	0.000	0.030	0.060
1,1-Dichloroethane	282	0	0.040	0.040	0.000	0.040	52	0	0.040	0.040	0.000	0.040	0.080
1,1-Dichloroethene	282	0	0.050	0.050	0.000	0.050	52	0	0.050	0.050	0.000	0.050	0.100
1,2,4-Trichlorobenzene	282	0	0.030	0.030	0.000	0.030	52	0	0.030	0.030	0.000	0.030	0.060
1,2,4-Trimethylbenzene	282	91	0.035	0.212	0.138	1.029	52	85	0.035	0.195	0.146	0.854	0.070
1,2-Dibromoethane	282	0	0.040	0.040	0.000	0.040	52	0	0.040	0.040	0.000	0.040	0.080
1,2-Dichlorobenzene	282	0	0.030	0.030	0.000	0.030	52	0	0.030	0.030	0.000	0.030	0.060
1,2-Dichloroethane	282	0	0.030	0.030	0.000	0.030	52	0	0.030	0.030	0.000	0.030	0.060
1,2-Dichloropropane	282	0	0.035	0.035	0.000	0.035	52	0	0.035	0.035	0.000	0.035	0.070
1,3,5-Trimethylbenzene	282	39	0.035	0.065	0.046	0.312	52	38	0.035	0.081	0.125	0.900	0.070
1,3-Butadiene	282	26	0.035	0.057	0.045	0.292	52	27	0.035	0.060	0.045	0.209	0.070
1,3-Dichlorobenzene	282	0	0.025	0.025	0.000	0.025	52	0	0.025	0.025	0.000	0.025	0.050
1,4-Dichlorobenzene	282	1	0.045	0.046	0.008	0.142	52	6	0.045	0.049	0.016	0.130	0.090
2-Chloro-1,3-Butadiene	282	0	0.050	0.050	0.000	0.050	52	0	0.050	0.050	0.000	0.050	0.100
Acetonitrile	282	35	0.125	1.790	6.893	102.600	52	38	0.125	2.093	3.671	14.080	0.250
Acetylene	282	99	0.065	1.675	0.781	6.480	52	100	0.690	1.767	0.892	4.460	0.130
Acrylonitrile	282	0	0.105	0.105	0.000	0.105	52	0	0.105	0.105	0.000	0.105	0.210
Benzene	282	100	0.231	0.615	0.316	2.173	52	100	0.240	0.600	0.306	1.713	0.040
Benzyl chloride	282	0	0.035	0.035	0.000	0.035	52	0	0.035	0.035	0.000	0.035	0.070
Bromochloromethane	282	0	0.060	0.060	0.000	0.060	52	0	0.060	0.060	0.000	0.060	0.120
Bromodichloromethane	282	0	0.030	0.030	0.000	0.030	52	0	0.030	0.030	0.000	0.030	0.060
Bromoform	282	0	0.040	0.040	0.000	0.040	52	2	0.040	0.054	0.101	0.770	0.080
Bromomethane	282	0	0.045	0.045	0.000	0.045	52	0	0.045	0.045	0.000	0.045	0.090
Carbon tetrachloride	282	91	0.040	0.100	0.024	0.170	52	88	0.040	0.096	0.024	0.140	0.080
Chlorobenzene	282	0	0.030	0.030	0.000	0.030	52	0	0.030	0.030	0.000	0.030	0.060
Chloroethane	282	1	0.040	0.044	0.041	0.626	52	6	0.040	0.044	0.017	0.120	0.080

Table S4-1. (Cont.)

Compound	N	DF (%)	Min (ppbv)	Mean (ppbv)	SD (ppbv)	Max (ppbv)	N	DF (%)	Min (ppbv)	Mean (ppbv)	SD (ppbv)	Max (ppbv)	MDL (ppbv)
			ERG laboratory-Sample 1						ERG laboratory-Sample 2				
Chloroform	282	2	0.025	0.026	0.004	0.065	52	0	0.025	0.025	0.000	0.025	0.050
Chloromethane	282	100	0.408	0.608	0.082	0.988	52	100	0.480	0.600	0.098	1.190	0.060
2-Chloro-1,3-Butadiene	282	0	0.050	0.050	0.000	0.050	52	0	0.050	0.050	0.000	0.050	0.100
cis-1,2-Dichloroethylene	282	0	0.050	0.051	0.019	0.370	52	0	0.050	0.050	0.000	0.050	0.100
cis-1,3-Dichloroprene	282	0	0.050	0.050	0.000	0.050	52	0	0.050	0.050	0.000	0.050	0.100
Dibromochloromethane	282	0	0.040	0.040	0.000	0.040	52	0	0.040	0.040	0.000	0.040	0.080
Dichlorodifluoromethane	282	100	0.460	0.634	0.079	1.079	52	100	0.520	0.619	0.043	0.712	0.040
Dichlorotetrafluoroethane	282	0	0.025	0.025	0.000	0.025	52	0	0.025	0.025	0.000	0.025	0.050
Ethyl acrylate	282	0	0.080	0.080	0.000	0.080	52	0	0.080	0.080	0.000	0.080	0.160
Ethylbenzene	282	98	0.020	0.192	0.157	1.894	52	90	0.020	0.168	0.122	0.647	0.040
Ethyl-tert-butyl-ether	282	0	0.075	0.075	0.000	0.075	52	0	0.075	0.075	0.000	0.075	0.150
Hexachloro-1,3-Butadiene	282	0	0.030	0.030	0.000	0.030	52	0	0.030	0.030	0.000	0.030	0.060
m,p-Xylene	282	100	0.100	0.551	0.482	6.082	52	98	0.025	0.489	0.375	1.893	0.050
Methyl ethyl ketone	282	72	0.075	0.604	0.510	2.920	52	73	0.075	0.601	0.446	1.761	0.150
Methyl isobutyl ketone	282	9	0.075	0.102	0.098	0.736	52	12	0.075	0.102	0.086	0.585	0.150
Methyl methacrylate	282	0	0.090	0.090	0.000	0.090	52	0	0.090	0.090	0.000	0.090	0.180
Methylene chloride	282	96	0.030	3.720	11.711	147.770	52	98	0.030	1.488	3.006	16.990	0.060
Methyl-tert-butyl-ether	282	6	0.090	0.102	0.056	0.585	52	8	0.090	0.109	0.073	0.484	0.180
n-Octane	282	32	0.030	0.055	0.058	0.750	52	46	0.030	0.072	0.064	0.310	0.060
o-Xylene	282	98	0.025	0.220	0.188	2.502	52	90	0.025	0.204	0.166	0.899	0.050
Propylene	282	100	0.110	1.210	1.474	14.137	52	100	0.180	1.248	1.842	11.490	0.050
Styrene	282	7	0.035	0.039	0.017	0.173	52	4	0.035	0.037	0.011	0.093	0.070
Tert-amyl-methyl-ether	282	0	0.060	0.060	0.000	0.060	52	0	0.060	0.060	0.000	0.060	0.120
Tertrachloroethylene	282	34	0.030	0.064	0.080	0.670	52	35	0.030	0.053	0.037	0.160	0.060
Toluene	282	100	0.250	1.112	1.099	13.428	52	100	0.210	1.057	0.929	6.431	0.060
trans-1,2-Dichloroethylene	282	0	0.030	0.030	0.004	0.090	52	0	0.030	0.030	0.000	0.030	0.060
trans-1,3-Dichloropropene	282	0	0.055	0.055	0.000	0.055	52	0	0.055	0.055	0.000	0.055	0.110
Trichloroethylene	282	1	0.035	0.043	0.085	1.268	52	4	0.035	0.329	2.099	15.172	0.070
Trichlorofluoromethane	282	100	0.020	0.321	0.120	1.540	52	100	0.190	0.299	0.052	0.497	0.040
Trichlorotrifluroethane	282	100	0.035	0.111	0.024	0.194	52	100	0.080	0.108	0.021	0.150	0.070
Vinyl chloride	282	0	0.030	0.030	0.000	0.030	52	0	0.030	0.030	0.000	0.030	0.060

Table S4- 2. Statistics of concentrations at Dearborn, Michigan for VOCs and carbonyls analyzed by Michigan Department of Environmental Quality (MDEQ) laboratory. TFE=trifluoroethane; TTFE=tetrafluoroethane; DF=detection frequency; MDL=method detection limit.

Compound	N	DF (%)	Min (ppbv)	Mean (ppbv)	SD (ppbv)	Max (ppbv)	N	DF (%)	Min (ppbv)	Mean (ppbv)	SD (ppbv)	Max (ppbv)	MDL (ppbv)
			MDEQ laboratory-Sample 1						MDEQ laboratory-Sample 2				
Carbonyls													
2,5-Dimethylbenzaldehyde	54	2	0.002	0.005	0.028	0.210	59	2	0.002	0.005	0.028	0.210	0.003
Acetaldehyde	54	89	0.005	1.005	1.207	6.721	59	98	0.005	1.005	1.207	6.721	0.009
Acetone	54	94	0.005	1.150	1.164	5.204	59	98	0.005	1.150	1.164	5.204	0.011
Benzaldehyde	54	72	0.002	0.042	0.085	0.509	59	56	0.002	0.042	0.085	0.509	0.004
Crotonaldehyde	54	24	0.004	0.016	0.030	0.139	59	14	0.004	0.016	0.030	0.139	0.008
Formaldehyde	54	91	0.004	2.046	1.689	8.735	59	97	0.004	2.046	1.689	8.735	0.008
Hexaldehyde	54	69	0.003	0.098	0.205	1.191	59	71	0.003	0.098	0.205	1.191	0.005
iso-Valeraldehyde	54	46	0.006	0.064	0.105	0.525	59	61	0.006	0.064	0.105	0.525	0.012
m,p-Tolualdehyde	54	31	0.001	0.017	0.033	0.161	59	29	0.001	0.017	0.033	0.161	0.002
n-Butyraldehyde	54	81	0.003	0.127	0.228	1.274	59	88	0.003	0.127	0.228	1.274	0.007
o-Tolualdehyde	54	4	0.001	0.002	0.003	0.020	59	0	0.001	0.002	0.003	0.020	0.002
Propionaldehyde	54	63	0.041	0.207	0.246	1.056	59	75	0.041	0.207	0.246	1.056	0.083
Valeraldehyde	54	31	0.011	0.053	0.096	0.519	59	34	0.011	0.053	0.096	0.519	0.022
VOCs													
1,1,1-Trichloroethane	57	5	0.024	0.026	0.007	0.057	58	2	0.024	0.026	0.007	0.057	0.048
1,1,2,2-Tetrachloroethane	57	0	0.041	0.041	0.000	0.041	58	0	0.041	0.041	0.000	0.041	0.081
1,1,2-Trichloro-1,2,2-TFE	57	95	0.017	0.083	0.023	0.178	58	95	0.017	0.083	0.023	0.178	0.034
1,1,2-Trichloroethane	57	0	0.024	0.024	0.000	0.024	58	0	0.024	0.024	0.000	0.024	0.048
1,1-Dichloroethane	57	0	0.045	0.045	0.000	0.045	58	0	0.045	0.045	0.000	0.045	0.089
1,1-Dichloroethene	57	0	0.023	0.023	0.000	0.023	58	2	0.023	0.023	0.000	0.023	0.046
1,2,4-Trichlorobenzene	57	2	0.041	0.042	0.009	0.110	58	0	0.041	0.042	0.009	0.110	0.081
1,2,4-Trimethylbenzene	57	86	0.031	0.174	0.122	0.589	58	83	0.031	0.174	0.122	0.589	0.062
1,2-Dibromoethane	57	0	0.027	0.027	0.000	0.027	58	0	0.027	0.027	0.000	0.027	0.054
1,2-Dichloro-1,1,2,2-TTFE	57	0	0.021	0.021	0.000	0.021	58	0	0.021	0.021	0.000	0.021	0.042
1,2-Dichlorobenzene	57	2	0.033	0.034	0.007	0.085	58	0	0.033	0.034	0.007	0.085	0.066
1,2-Dichloroethane	57	0	0.043	0.043	0.000	0.043	58	0	0.043	0.043	0.000	0.043	0.086
1,2-Dichloropropane	57	0	0.030	0.030	0.000	0.030	58	0	0.030	0.030	0.000	0.030	0.059
1,3,5-Trimethylbenzene	57	30	0.029	0.047	0.034	0.161	58	28	0.029	0.047	0.034	0.161	0.057
1,3-Butadiene	57	0	0.020	0.020	0.000	0.020	58	2	0.020	0.020	0.000	0.020	0.040
1,3-Dichlorobenzene	57	2	0.027	0.027	0.007	0.079	58	0	0.027	0.027	0.007	0.079	0.053
1,4-Dichlorobenzene	57	7	0.027	0.030	0.015	0.106	58	7	0.027	0.030	0.015	0.106	0.053
2,2,4-Trimethylpentane	57	96	0.009	0.118	0.085	0.523	58	98	0.009	0.118	0.085	0.523	0.017
2-Chloro-1,3-Butadiene	57	0	0.015	0.015	0.000	0.015	58	0	0.015	0.015	0.000	0.015	0.030
Acetonitrile	57	70	0.260	1.563	2.773	15.530	58	74	0.260	1.563	2.773	15.530	0.520
Acrylonitrile	57	0	0.195	0.195	0.000	0.195	58	0	0.195	0.195	0.000	0.195	0.390
Benzene	57	96	0.035	0.546	0.397	2.494	58	100	0.035	0.546	0.397	2.494	0.070
Benzyl chloride	57	0	0.038	0.038	0.000	0.038	58	0	0.038	0.038	0.000	0.038	0.076
Bromodichloromethane	57	0	0.037	0.037	0.000	0.037	58	0	0.037	0.037	0.000	0.037	0.073
Bromoform	57	0	0.030	0.030	0.000	0.030	58	0	0.030	0.030	0.000	0.030	0.059
Bromomethane	57	4	0.020	0.022	0.010	0.092	58	0	0.020	0.022	0.010	0.092	0.040

Table S4-2. (Cont.)

| Compound | MDEQ laboratory-Sample 1 | | | | | | MDEQ laboratory-Sample 2 | | | | | | |
	N	DF (%)	Min (ppbv)	Mean (ppbv)	SD (ppbv)	Max (ppbv)	N	DF (%)	Min (ppbv)	Mean (ppbv)	SD (ppbv)	Max (ppbv)	MDL (ppbv)
Carbon tetrachloride	57	95	0.019	0.090	0.020	0.125	58	95	0.019	0.090	0.020	0.125	0.038
Chlorobenzene	57	2	0.020	0.021	0.004	0.049	58	2	0.020	0.021	0.004	0.049	0.040
Chloroethane	57	0	0.020	0.020	0.000	0.020	58	17	0.020	0.020	0.000	0.020	0.040
Chloroform	57	0	0.034	0.034	0.000	0.034	58	0	0.034	0.034	0.000	0.034	0.068
Chloromethane	57	98	0.031	0.568	0.169	1.426	58	100	0.031	0.568	0.169	1.426	0.062
2-Chloro-1,3-Butadiene	57	0	0.015	0.015	0.000	0.015	58	0	0.015	0.015	0.000	0.015	0.030
cis-1,2-Dichloroethylene	57	0	0.029	0.029	0.000	0.029	58	0	0.029	0.029	0.000	0.029	0.057
cis-1,3-Dichloroprene	57	0	0.027	0.027	0.000	0.027	58	0	0.027	0.027	0.000	0.027	0.054
Dibromochloromethane	57	0	0.030	0.030	0.000	0.030	58	0	0.030	0.030	0.000	0.030	0.059
Dichlorodifluoromethane	57	98	0.024	0.554	0.129	0.846	58	100	0.024	0.554	0.129	0.846	0.048
Ethylbenzene	57	68	0.042	0.118	0.086	0.413	58	48	0.042	0.118	0.086	0.413	0.083
Hexachloro-1,3-Butadiene	57	0	0.032	0.032	0.000	0.032	58	0	0.032	0.032	0.000	0.032	0.063
Hexane	57	21	0.250	0.427	0.482	3.318	58	22	0.250	0.427	0.482	3.318	0.500
m,p-Xylene	57	70	0.100	0.319	0.244	1.198	58	53	0.100	0.319	0.244	1.198	0.200
Methyl ethyl ketone	57	0	0.850	0.850	0.000	0.850	58	0	0.850	0.850	0.000	0.850	1.700
Methyl isobutyl ketone	57	0	0.420	0.420	0.000	0.420	58	0	0.420	0.420	0.000	0.420	0.840
Methylene chloride	57	82	0.115	1.621	3.545	22.196	58	81	0.115	1.621	3.545	22.196	0.230
Methyl-tert-butyl-ether	57	5	0.031	0.040	0.044	0.292	58	3	0.031	0.040	0.044	0.292	0.061
o-Xylene	57	89	0.022	0.139	0.098	0.487	58	88	0.022	0.139	0.098	0.487	0.043
Styrene	57	7	0.027	0.031	0.016	0.132	58	5	0.027	0.031	0.016	0.132	0.054
Tertrachloroethylene	57	33	0.036	0.064	0.053	0.343	58	22	0.036	0.064	0.053	0.343	0.071
Toluene	57	98	0.035	0.932	0.685	3.473	58	100	0.035	0.932	0.685	3.473	0.070
trans-1,2-Dichloroethylene	57	0	0.043	0.043	0.000	0.043	58	0	0.043	0.043	0.000	0.043	0.087
trans-1,3-Dichloropropene	57	0	0.031	0.031	0.000	0.031	58	0	0.031	0.031	0.000	0.031	0.062
Trichloroethylene	57	7	0.019	0.022	0.012	0.084	58	3	0.019	0.022	0.012	0.084	0.038
Trichlorofluoromethane	57	96	0.024	0.273	0.073	0.500	58	100	0.024	0.273	0.073	0.500	0.048
Vinyl chloride	57	0	0.022	0.022	0.000	0.022	58	0	0.022	0.022	0.000	0.022	0.044

Table S4- 3. Outlier analysis using Gumbel distribution (type I).

ERG= Eastern Research Group; MDEQ= Michigan Department of Environmental Quality.

Compound	Date	Concentration (ppbv)	Laboratory	Sample
Carbonyls				
Formaldehyde	4/12/2002	20.98	ERG	1
Hexaldehyde	8/5/2001	1.19	MDEQ	1
Tolualdehyde	7/29/2001	0.59	ERG	1
VOCs				
Propylene	10/10/2001	14.14	ERG	1
	10/31/2001	11.49	ERG	1
n-Octane	3/11/2002	0.75	ERG	1
Methylene chloride	7/2/2001	61.71	ERG	1
	7/13/2001	61.41	ERG	1
	7/18/2001	199.27	MDEQ	2
	2/25/2002	51.19	ERG	1
	3/3/2002	147.77	ERG	1
m,p-Xylene	9/17/2001	6.08	ERG	1
	3/11/2002	3.49	ERG	1
Ethylbenzene	9/17/2001	1.89	ERG	1
	3/11/2002	1.26	ERG	1
o-Xylene	9/17/2001	2.50	ERG	1
1,3,5-Trimethylbenzene	8/20/2001	0.90	ERG	2
Toluene	5/20/2001	13.43	ERG	1
	9/17/2001	8.70	ERG	1

Table S4- 4. Spearman rank correlation coefficients between air toxics and criteria pollutants and meteorological variables. Variable dictionary is shown in Table S4-8.

VARIABLES	ACETALD	BNZALD	FORMALD	HEXALD	IBUTYRAL	PROPIONALD	TOLUALD	ACETYL	BNZ	BUTADNE	DCDFM	EBNZ	MEK	MPX	NOCTANE	OXY	PROPYL	TCEL	TCFM	TCTFE	TMBNZ_124	TMBNZ_135	TOLUENE
Criteria pollutants																							
APCO_24HR	0.30	0.25	0.30	0.11	0.21	0.26	0.12	0.60	0.57	0.43	0.15	0.49	0.18	0.48	0.21	0.50	0.48	0.20	0.12	-0.01	0.49	0.46	0.53
AP_PM25	0.41	0.43	0.39	0.40	0.31	0.38	0.34	0.25	0.45	0.12	0.17	0.39	0.56	0.39	0.22	0.41	0.38	0.16	0.28	-0.05	0.41	0.36	0.47
DB_pm10	0.19	0.22	0.15	0.06	0.09	0.18	0.15	0.09	0.10	-0.03	0.02	0.07	0.26	0.06	0.09	0.05	0.20	-0.09	-0.02	-0.06	0.03	0.08	0.05
E7MNO2_24HR	0.19	0.14	0.19	-0.03	0.15	0.17	-0.01	0.54	0.38	0.29	0.08	0.30	0.10	0.28	0.16	0.28	0.52	0.05	-0.02	0.10	0.27	0.20	0.28
E7MSO2_24HR	0.21	0.18	0.14	0.17	0.13	0.22	0.11	0.23	0.31	0.06	0.05	0.06	0.28	0.05	0.09	0.11	0.38	0.07	-0.02	-0.02	0.10	0.08	0.21
LWCO_24HR	0.30	0.30	0.31	0.09	0.21	0.27	0.16	0.54	0.49	0.38	0.09	0.47	0.22	0.46	0.21	0.47	0.58	0.13	0.11	0.04	0.42	0.39	0.47
LWNO2_24HR	0.27	0.30	0.30	0.15	0.23	0.24	0.18	0.47	0.48	0.19	0.03	0.35	0.20	0.33	0.16	0.35	0.48	0.09	-0.07	0.03	0.31	0.24	0.36
LWSO2_24HR	0.17	0.17	0.14	0.12	0.08	0.16	0.11	0.33	0.38	0.09	-0.05	0.15	0.21	0.15	0.15	0.20	0.47	0.09	-0.01	-0.02	0.18	0.13	0.26
LW_PM25	0.23	0.21	0.18	0.14	0.09	0.21	0.15	0.27	0.37	-0.03	0.00	0.19	0.33	0.17	0.11	0.19	0.35	0.06	0.03	-0.05	0.18	0.13	0.27
Meteorology																							
DPTP_DTW	0.54	0.61	0.51	0.70	0.45	0.53	0.54	-0.10	0.24	0.05	0.36	0.36	0.71	0.39	0.18	0.40	0.21	0.16	0.43	-0.11	0.39	0.31	0.45
MIX_HT	0.12	0.25	0.16	0.31	0.09	0.17	0.24	-0.30	-0.20	-0.18	0.14	-0.09	0.16	-0.08	-0.02	-0.09	-0.19	-0.06	0.00	-0.11	-0.09	-0.09	-0.10
MNRH_DTW	-0.12	-0.17	-0.12	-0.18	-0.14	-0.15	-0.14	0.05	0.03	0.00	-0.12	-0.01	-0.11	-0.01	-0.05	-0.01	0.14	0.05	0.03	0.13	-0.04	-0.01	-0.06
MNTP_DTW	0.54	0.62	0.51	0.71	0.46	0.54	0.54	-0.12	0.20	0.02	0.37	0.34	0.72	0.37	0.18	0.38	0.16	0.13	0.41	-0.16	0.38	0.29	0.44
MXRH_DTW	0.19	0.13	0.17	0.17	0.15	0.13	0.12	0.10	0.19	0.16	0.04	0.23	0.17	0.23	0.06	0.22	0.25	0.13	0.18	0.09	0.21	0.16	0.21
PRCP_DTW	-0.08	-0.10	-0.07	-0.01	-0.07	-0.10	-0.11	-0.14	-0.07	-0.14	-0.12	-0.08	-0.04	-0.08	-0.14	-0.09	0.04	-0.04	-0.09	0.05	-0.08	-0.13	-0.11
PRES_DTW	0.03	0.04	0.05	0.00	0.10	0.02	-0.03	0.23	0.21	0.24	0.05	0.18	0.01	0.17	0.10	0.21	0.05	0.04	0.06	-0.01	0.21	0.15	0.24
RWND_DTW	-0.37	-0.44	-0.36	-0.43	-0.32	-0.34	-0.29	-0.38	-0.59	-0.41	-0.26	-0.52	-0.44	-0.53	-0.24	-0.57	-0.25	-0.36	-0.28	0.17	-0.60	-0.54	-0.65
SLVP_DTW	0.00	0.00	0.01	-0.05	0.07	-0.01	-0.07	0.24	0.19	0.24	0.03	0.15	-0.04	0.14	0.09	0.18	0.04	0.02	0.04	0.01	0.18	0.13	0.20
WDIR_S1	0.14	0.16	0.16	0.23	0.16	0.15	0.11	0.18	0.22	0.25	0.24	0.26	0.15	0.28	0.14	0.32	-0.03	0.09	0.27	-0.06	0.36	0.31	0.37
WDIR_S2	0.12	0.09	0.15	0.17	0.15	0.08	0.08	0.13	0.28	0.11	0.08	0.15	0.13	0.15	0.09	0.19	0.02	0.14	0.08	-0.09	0.21	0.13	0.27
WDIR_S3	0.13	0.13	0.11	0.20	0.12	0.09	0.08	0.09	0.42	0.12	0.10	0.14	0.27	0.13	0.09	0.17	0.07	0.21	0.09	-0.09	0.20	0.14	0.27
WDIR_S4	0.23	0.21	0.17	0.20	0.18	0.19	0.09	0.13	0.36	0.07	0.09	0.11	0.32	0.10	0.17	0.15	0.42	0.06	0.11	0.03	0.11	0.08	0.21
WDIR_S5	0.07	-0.02	-0.02	-0.12	-0.01	0.05	-0.08	0.03	-0.08	-0.10	-0.16	-0.12	-0.03	-0.13	0.03	-0.14	0.30	-0.30	-0.11	0.11	-0.18	-0.15	-0.15
WDIR_S6	-0.16	-0.12	-0.12	-0.21	-0.16	-0.14	-0.10	-0.19	-0.35	-0.20	-0.16	-0.13	-0.21	-0.13	-0.18	-0.22	-0.26	-0.19	-0.16	-0.04	-0.23	-0.14	-0.33
WDIR_S7	-0.15	-0.06	-0.07	-0.07	-0.09	-0.11	0.03	-0.14	-0.24	-0.01	0.03	0.09	-0.14	0.10	-0.13	0.03	-0.23	0.14	-0.04	-0.15	0.05	0.07	-0.08
WDIR_S8	-0.01	0.03	0.00	0.11	0.10	0.01	0.08	-0.02	-0.05	0.16	0.10	0.07	-0.03	0.08	0.01	0.11	-0.19	0.16	0.06	-0.08	0.15	0.13	0.14

Table S4- 5. Spearman rank correlation coefficients between selected carbonyls and VOCs.

Variable dictionary is shown in Table S4-8.

VARIABLES	ACETALD	BNZALD	FORMALD	HEXALD	IBUTYRAL	PROPIONALD	TOLUALD	ACETYL	BNZ	BUTADNE	DCDFM	EBNZ	MEK	MPX	NOCTANE	OXY	PROPYL	TCEL	TCFM	TCTFE	TMBNZ_124	TMBNZ_135	TOLUENE
Carbonyls																							
ACETALD	1.00																						
BNZALD	0.80	1.00																					
FORMALD	0.90	0.79	1.00																				
HEXALD	0.77	0.87	0.75	1.00																			
IBUTYRAL	0.85	0.69	0.80	0.72	1.00																		
PROPIONALD	0.95	0.80	0.87	0.79	0.80	1.00																	
TOLUALD	0.66	0.71	0.63	0.76	0.57	0.69	1.00																
VOCs																							
ACETYL	0.30	0.24	0.30	0.11	0.20	0.28	0.14	1.00															
BNZ	0.41	0.41	0.38	0.31	0.29	0.37	0.27	0.69	1.00														
BUTADNE	0.40	0.36	0.41	0.24	0.35	0.36	0.21	0.54	0.52	1.00													
DCDFM	0.38	0.33	0.36	0.40	0.39	0.39	0.31	0.22	0.24	0.26	1.00												
EBNZ	0.44	0.44	0.45	0.34	0.37	0.38	0.32	0.51	0.67	0.55	0.37	1.00											
MEK	0.51	0.59	0.48	0.58	0.47	0.50	0.42	0.16	0.45	0.25	0.40	0.47	1.00										
MPX	0.45	0.46	0.47	0.38	0.39	0.40	0.36	0.49	0.66	0.55	0.39	0.99	0.48	1.00									
NOCTANE	0.36	0.30	0.31	0.26	0.27	0.34	0.26	0.32	0.44	0.52	0.24	0.44	0.32	0.43	1.00								
OXY	0.49	0.50	0.49	0.42	0.40	0.44	0.38	0.53	0.72	0.57	0.40	0.97	0.51	0.97	0.47	1.00							
PROPYL	0.47	0.34	0.42	0.24	0.35	0.42	0.25	0.58	0.57	0.47	0.24	0.47	0.27	0.47	0.39	0.50	1.00						
TCEL	0.10	0.19	0.15	0.15	0.05	0.08	0.12	0.33	0.43	0.35	0.11	0.40	0.27	0.40	0.30	0.43	0.17	1.00					
TCFM	0.42	0.34	0.39	0.42	0.37	0.41	0.35	0.16	0.24	0.28	0.69	0.39	0.35	0.42	0.28	0.43	0.31	0.06	1.00				
TCTFE	0.12	-0.12	0.08	-0.04	0.15	0.07	-0.04	0.05	0.01	0.17	0.09	0.02	-0.01	0.00	0.16	-0.02	0.17	-0.11	0.06	1.00			
TMBNZ_124	0.46	0.47	0.47	0.40	0.38	0.40	0.35	0.53	0.70	0.59	0.40	0.94	0.52	0.94	0.45	0.94	0.44	0.44	0.41	-0.03	1.00		
TMBNZ_135	0.40	0.45	0.40	0.35	0.31	0.36	0.36	0.52	0.63	0.60	0.35	0.81	0.43	0.81	0.45	0.82	0.40	0.45	0.38	-0.04	0.86	1.00	
TOLUENE	0.52	0.55	0.52	0.48	0.43	0.47	0.36	0.57	0.80	0.55	0.37	0.84	0.56	0.84	0.43	0.88	0.51	0.45	0.42	-0.06	0.86	0.75	1.00

Table S4- 6. Variable dictionary

Variables	Descriptions
Carbonyls	
ACETALD	Acetaldehyde
BNZALD	Benzaldehyde
FORMALD	Formaldehyde
HEXALD	Hexaldehyde
IBUTYRAL	iso-Butyraldehyde
PROPIONALD	Propionaldehyde
TOLUALD	Tolualdehyde
VOCs	
ACETYL	Acetylene
BNZ	Benzene
BUTADNE	1,3-Butadiene
CHLOMET	Chloromethane
DCDFM	Dichlorodifluoromethane
EBNZ	Ethylbenzene
MEK	Methyl ethyl ketone
MPX	m,p-Xylene
NOCTANE	n-Octane
OXY	o-Xylene
PROPYL	Propylene
TCEL	Tetrachloroethylene
TCFM	Trichlorofluoromethane
TCTFE	Trichlorotrifluoroethane
TMBNZ_124	1,2,4-Trimethylbenzene
TMBNZ_135	1,3,5-Trimethylbenzene
TOLUENE	Toluene
Criteria pollutants	
APCO_24HR	Allen Park-24H CO
AP_PM25	Allen Park-PM2.5
DB_pm10	PM10 at Dearborn
E7MNO2_24HR	East Seven Mile-24H NO2
E7MSO2_24HR	East Seven Mile-24H SO2
LWCO_24HR	Linwood-24H CO
LWNO2_24HR	Linwood-24H NO2
LWSO2_24HR	Linwood-24H SO2
LW_PM25	Linwood-PM2.5
Meteorology	
AWND_DTW	Detroit metro airport avg wind speed
DPTP_DTW	Detroit metro airport dewpoint
MIX_HT	Mixing height
MNRH_DTW	Detroit metro airport min relative humidity
MNTP_DTW	Detroit metro airport temperature
MXRH_DTW	Detroit metro airport max relative humidity
PRCP_DTW	Detroit metro airport precipitation
PRES_DTW	Detroit metro airport pressure
RDIR_DTW	Detroit metro airport resultant wind direction
RWND_DTW	Detroit metro airport resultant wind speed
SLVP_DTW	Detroit metro airport sea level pressure

Table S4- 7. Performance indicators for MI and OLE estimates for carbonyls. Bold values show highest performing model in group. Abbreviations: lag0=current day observation; lag1=current and previous day observations; lead1=current and next day observations; LL1=current, previous and next day observations; SD=standard deviation; d_2=Willmot's index of agreement; R^2=coefficient of determination; MAE=mean absolute error.

Performance indicators		Multiple imputation				Optimal estimation			
		lag0(SD)	lag1(SD)	lead1(SD)	LL1(SD)	lag0	lag1	lead1	LL1
Acetaldehyde									
Random	d_2	**0.95 (0.01)**	0.95 (0.01)	0.95 (0.01)	0.95 (0.00)	0.86	**0.89**	0.74	0.88
	R^2	**0.83 (0.02)**	0.80 (0.02)	0.83 (0.02)	0.83 (0.01)	0.69	**0.72**	0.51	0.70
	MAE	**0.29 (0.03)**	0.30 (0.03)	0.30 (0.02)	0.30 (0.01)	0.30	**0.26**	0.46	0.28
Block 5	d_2	**0.95 (0.01)**	0.95 (0.01)	0.95 (0.01)	0.94 (0.00)	0.79	0.81	0.71	**0.86**
	R^2	**0.84 (0.03)**	0.83 (0.02)	0.84 (0.03)	0.82 (0.01)	0.73	0.73	0.69	**0.79**
	MAE	**0.30 (0.03)**	0.31 (0.01)	0.30 (0.04)	0.31 (0.01)	0.43	0.42	0.57	**0.32**
Row-wise	d_2	0.58 (0.05)	**0.67 (0.04)**	0.51 (0.05)	0.63 (0.06)	**0.67**	0.63	0.47	0.46
	R^2	0.11 (0.05)	**0.20 (0.06)**	0.04 (0.02)	0.14 (0.08)	**0.32**	0.26	0.09	0.11
	MAE	0.87 (0.08)	**0.85 (0.12)**	0.91 (0.04)	0.87 (0.06)	**0.62**	0.66	0.83	0.79
Benzaldehyde									
Random	d_2	0.80 (0.03)	**0.83 (0.02)**	0.76 (0.05)	0.76 (0.01)	**0.88**	0.82	0.77	0.83
	R^2	0.46 (0.07)	**0.55 (0.03)**	0.38 (0.10)	0.38 (0.03)	**0.62**	0.48	0.44	0.51
	MAE	0.02 (0.00)	**0.02 (0.00)**	0.03 (0.00)	0.03 (0.00)	**0.00**	0.00	0.00	0.00
Block 5	d_2	**0.77 (0.03)**	0.72 (0.01)	0.63 (0.07)	0.73 (0.03)	**0.55**	0.50	0.36	0.51
	R^2	**0.49 (0.06)**	0.43 (0.06)	0.29 (0.11)	0.46 (0.07)	**0.41**	0.30	0.09	0.32
	MAE	**0.02 (0.00)**	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	**0.00**	0.00	0.00	0.00
Row-wise	d_2	0.48 (0.06)	**0.54 (0.03)**	0.35 (0.05)	0.38 (0.05)	0.50	**0.57**	0.25	0.31
	R^2	0.05 (0.05)	**0.09 (0.02)**	0.01 (0.01)	0.00 (0.01)	0.07	**0.13**	0.02	0.00
	MAE	0.04 (0.00)	**0.04 (0.00)**	0.05 (0.00)	0.05 (0.00)	0.00	**0.00**	0.00	0.00
Formaldehyde									
Random	d_2	0.84 (0.02)	0.80 (0.04)	**0.85 (0.01)**	0.81 (0.04)	**0.86**	0.82	0.84	0.83
	R^2	0.53 (0.05)	0.44 (0.07)	**0.54 (0.03)**	0.45 (0.09)	**0.63**	0.62	0.69	0.63
	MAE	0.80 (0.03)	0.90 (0.10)	**0.81 (0.03)**	0.86 (0.05)	**0.72**	0.78	0.69	0.77
Block 5	d_2	**0.88 (0.03)**	0.85 (0.03)	0.86 (0.01)	0.87 (0.04)	0.78	0.79	0.79	**0.80**
	R^2	**0.63 (0.09)**	0.56 (0.08)	0.58 (0.04)	0.60 (0.10)	0.55	0.65	0.66	**0.66**
	MAE	**0.84 (0.11)**	0.84 (0.11)	0.87 (0.04)	0.83 (0.12)	1.12	0.99	1.00	**0.97**
Row-wise	d_2	0.51 (0.06)	**0.53 (0.03)**	0.40 (0.06)	0.40 (0.06)	0.52	**0.54**	0.33	0.33
	R^2	0.05 (0.04)	**0.06 (0.03)**	0.01 (0.01)	0.01 (0.01)	0.09	**0.11**	0.00	0.00
	MAE	1.49 (0.14)	**1.58 (0.12)**	1.79 (0.14)	1.79 (0.14)	2.37	**2.31**	2.65	2.65

Table S4-7. (Cont.)

Performance indicators		Multiple imputation				Optimal estimation			
		lag0(SD)	lag1(SD)	lead1(SD)	LL1(SD)	lag0	lag1	lead1	LL1
Hexaldehyde									
Random	d_2	0.70 (0.04)	0.82 (0.03)	0.83 (0.02)	**0.85 (0.04)**	0.69	0.69	0.52	**0.81**
	R^2	0.26 (0.05)	0.46 (0.07)	0.50 (0.04)	**0.55 (0.09)**	0.29	0.41	0.13	**0.54**
	MAE	0.12 (0.01)	0.09 (0.00)	0.10 (0.01)	**0.07 (0.00)**	0.02	0.01	0.02	**0.01**
Block 5	d_2	0.71 (0.04)	0.68 (0.03)	0.70 (0.03)	**0.76 (0.03)**	0.62	0.54	0.56	**0.66**
	R^2	0.32 (0.07)	0.23 (0.07)	0.29 (0.05)	**0.37 (0.05)**	0.39	0.22	0.24	**0.44**
	MAE	0.12 (0.01)	0.13 (0.01)	0.12 (0.01)	**0.12 (0.01)**	0.02	0.03	0.03	**0.02**
Row-wise	d_2	0.64 (0.03)	**0.76 (0.05)**	0.64 (0.04)	0.75 (0.03)	0.71	0.74	0.73	**0.73**
	R^2	0.18 (0.04)	**0.34 (0.09)**	0.17 (0.05)	0.33 (0.06)	0.39	0.45	0.43	**0.42**
	MAE	0.14 (0.01)	**0.12 (0.01)**	0.14 (0.00)	0.12 (0.01)	0.02	0.02	0.02	**0.02**
iso-Butyraldehyde									
Random	d_2	**0.90 (0.01)**	0.90 (0.01)	0.90 (0.01)	0.89 (0.03)	**0.79**	0.79	0.79	0.79
	R^2	**0.68 (0.03)**	0.68 (0.03)	0.68 (0.03)	0.65 (0.09)	**0.74**	0.74	0.74	0.67
	MAE	**0.08 (0.00)**	0.08 (0.00)	0.08 (0.00)	0.09 (0.01)	**0.02**	0.02	0.02	0.02
Block 5	d_2	0.83 (0.02)	0.83 (0.02)	0.83 (0.02)	**0.85 (0.02)**	0.74	0.74	0.74	**0.81**
	R^2	0.52 (0.03)	0.52 (0.03)	0.52 (0.03)	**0.58 (0.05)**	0.47	0.47	0.47	**0.53**
	MAE	0.10 (0.01)	0.10 (0.01)	0.10 (0.01)	**0.09 (0.01)**	0.02	0.02	0.02	**0.01**
Row-wise	d_2	0.56 (0.10)	0.56 (0.03)	0.37 (0.05)	**0.58 (0.08)**	0.64	0.44	0.27	0.40
	R^2	0.12 (0.08)	0.09 (0.04)	0.01 (0.01)	**0.11 (0.05)**	0.24	0.06	0.01	0.05
	MAE	0.15 (0.02)	0.17 (0.01)	0.18 (0.00)	**0.15 (0.01)**	**0.02**	0.02	0.02	0.02
Propionaldehyde									
Random	d_2	**0.93 (0.01)**	0.93 (0.01)	0.93 (0.00)	0.93 (0.01)	0.84	0.86	0.86	**0.87**
	R^2	**0.77 (0.04)**	0.78 (0.02)	0.75 (0.02)	0.77 (0.04)	0.72	0.75	0.75	**0.76**
	MAE	**0.05 (0.00)**	0.05 (0.00)	0.05 (0.00)	0.05 (0.01)	0.01	0.01	0.01	**0.01**
Block 5	d_2	**0.93 (0.01)**	0.93 (0.01)	0.92 (0.01)	0.93 (0.01)	0.75	0.79	0.77	**0.83**
	R^2	**0.78 (0.03)**	0.76 (0.02)	0.74 (0.04)	0.76 (0.02)	0.65	0.71	0.67	**0.76**
	MAE	**0.05 (0.00)**	0.05 (0.00)	0.05 (0.00)	0.05 (0.00)	0.01	0.01	0.01	**0.01**
Row-wise	d_2	-	-	0.62 (0.04)	0.56 (0.16)	**0.68 (0.02)**	0.59	0.41	0.27	0.32
	R^2	-	-	0.16 (0.06)	0.13 (0.14)	**0.22 (0.04)**	0.22	0.06	0.00	0.01
	MAE	-	-	0.11 (0.01)	0.05 (0.01)	**0.11 (0.01)**	**0.01**	0.02	0.02	0.02
Tolualdehyde									
Random	d_2	**0.72 (0.04)**	0.60 (0.07)	0.54 (0.09)	0.54 (0.09)	**0.58**	0.54	0.36	0.36
	R^2	**0.30 (0.07)**	0.15 (0.08)	0.10 (0.05)	0.10 (0.05)	**0.25**	0.23	0.05	0.05
	MAE	**0.03 (0.00)**	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	**0.00**	0.00	0.00	0.00
Block 5	d_2	**0.66 (0.05)**	0.59 (0.06)	0.50 (0.03)	0.50 (0.03)	**0.55**	0.50	0.39	0.39
	R^2	**0.22 (0.06)**	0.13 (0.06)	0.06 (0.03)	0.06 (0.03)	**0.20**	0.15	0.05	0.05
	MAE	**0.03 (0.00)**	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	**0.00**	0.00	0.00	0.00
Row-wise	d_2	**0.56 (0.08)**	0.51 (0.11)	0.46 (0.13)	0.53 (0.09)	**0.64**	0.52	0.45	0.52
	R^2	**0.10 (0.07)**	0.06 (0.05)	0.05 (0.09)	0.08 (0.07)	**0.26**	0.12	0.07	0.12
	MAE	**0.04 (0.00)**	0.04 (0.00)	0.04 (0.01)	0.03 (0.00)	**0.00**	0.00	0.00	0.00

Table S4- 8. Performance indicators for MI and OLE estimates for VOCs.
Otherwise as Table S4-9.

Performance indicators		Multiple imputation				Optimal estimation			
		lag0(SD)	lag1(SD)	lead1(SD)	LL1(SD)	lag0	lag1	lead1	LL1
Acetylene									
Random	d_2	**0.84 (0.04)**	0.72 (0.02)	0.76 (0.04)	0.66 (0.03)	**0.73**	0.65	0.59	0.46
	R^2	**0.52 (0.08)**	0.30 (0.04)	0.37 (0.08)	0.19 (0.04)	**0.57**	0.44	0.39	0.23
	MAE	**0.51 (0.05)**	0.66 (0.04)	0.60 (0.06)	0.71 (0.02)	**0.46**	0.55	0.60	0.68
Block 5	d_2	**0.86 (0.02)**	0.76 (0.03)	0.81 (0.04)	0.70 (0.03)	**0.69**	0.60	0.58	0.52
	R^2	**0.57 (0.05)**	0.37 (0.04)	0.44 (0.08)	0.28 (0.04)	**0.46**	0.36	0.35	0.21
	MAE	**0.46 (0.02)**	0.57 (0.03)	0.59 (0.02)	0.62 (0.03)	**0.47**	0.55	0.56	0.66
Row-wise	d_2	**0.65 (0.06)**	0.65 (0.03)	0.63 (0.07)	0.62 (0.05)	0.45	0.38	**0.46**	0.37
	R^2	**0.19 (0.08)**	0.18 (0.04)	0.16 (0.08)	0.15 (0.05)	0.09	0.06	**0.11**	0.04
	MAE	**0.63 (0.05)**	0.67 (0.06)	0.69 (0.06)	0.72 (0.05)	0.60	0.61	**0.58**	0.63
Benzene									
Random	d_2	**0.87 (0.03)**	0.84 (0.01)	0.87 (0.02)	0.84 (0.02)	**0.89**	0.85	0.84	0.79
	R^2	**0.61 (0.08)**	0.52 (0.03)	0.59 (0.06)	0.52 (0.05)	**0.71**	0.63	0.63	0.52
	MAE	**0.17 (0.02)**	0.18 (0.01)	0.17 (0.01)	0.18 (0.01)	**0.03**	0.04	0.04	0.04
Block 5	d_2	0.85 (0.02)	**0.85 (0.04)**	0.84 (0.04)	0.83 (0.02)	**0.88**	0.85	0.84	0.88
	R^2	0.55 (0.05)	**0.56 (0.09)**	0.54 (0.10)	0.49 (0.03)	**0.68**	0.62	0.60	0.65
	MAE	0.19 (0.02)	**0.19 (0.02)**	0.19 (0.02)	0.20 (0.02)	**0.03**	0.04	0.04	0.04
Row-wise	d_2	**0.64 (0.04)**	0.63 (0.03)	0.58 (0.06)	0.57 (0.06)	0.63	**0.65**	0.64	0.53
	R^2	**0.20 (0.05)**	0.18 (0.03)	0.13 (0.05)	0.12 (0.05)	0.22	**0.25**	0.24	0.17
	MAE	**0.26 (0.02)**	0.28 (0.02)	0.28 (0.03)	0.27 (0.01)	0.07	**0.07**	0.07	0.08
1,3-Butadiene									
Random	d_2	**0.89 (0.02)**	0.89 (0.01)	0.87 (0.01)	0.87 (0.02)	**0.78**	0.74	0.62	0.63
	R^2	**0.65 (0.06)**	0.65 (0.03)	0.58 (0.03)	0.58 (0.04)	**0.68**	0.67	0.52	0.52
	MAE	**0.03 (0.00)**	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	**0.00**	0.00	0.00	0.00
Block 5	d_2	0.88 (0.02)	0.86 (0.03)	0.88 (0.02)	**0.88 (0.01)**	0.76	0.75	0.77	**0.78**
	R^2	0.61 (0.06)	0.56 (0.08)	0.59 (0.05)	**0.61 (0.04)**	0.50	0.49	0.53	**0.56**
	MAE	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	**0.03 (0.00)**	0.00	0.00	0.00	**0.00**
Row-wise	d_2	**0.58 (0.04)**	0.50 (0.03)	0.52 (0.08)	0.46 (0.05)	**0.49**	0.43	0.41	0.30
	R^2	**0.09 (0.03)**	0.05 (0.03)	0.07 (0.05)	0.03 (0.03)	**0.13**	0.08	0.07	0.03
	MAE	**0.04 (0.00)**	0.04 (0.00)	0.05 (0.00)	0.04 (0.00)	**0.00**	0.00	0.00	0.00
Dichlorodifluoromethane									
Random	d_2	0.62 (0.06)	0.58 (0.07)	0.63 (0.05)	**0.64 (0.04)**	0.52	0.33	0.41	**0.52**
	R^2	0.15 (0.06)	0.12 (0.07)	0.17 (0.04)	**0.18 (0.06)**	0.12	0.04	0.12	**0.25**
	MAE	0.06 (0.01)	0.06 (0.01)	0.06 (0.00)	**0.06 (0.01)**	0.01	0.01	0.00	**0.00**
Block 5	d_2	0.59 (0.03)	0.57 (0.06)	**0.59 (0.02)**	0.58 (0.07)	0.35	0.34	0.37	**0.44**
	R^2	0.16 (0.02)	0.14 (0.07)	**0.17 (0.03)**	0.15 (0.07)	0.09	0.03	0.11	**0.18**
	MAE	0.06 (0.00)	0.07 (0.00)	**0.07 (0.01)**	0.07 (0.01)	0.01	0.01	0.01	**0.01**
Row-wise	d_2	0.44 (0.12)	0.44 (0.07)	**0.45 (0.05)**	0.38 (0.09)	0.29	**0.46**	0.22	0.29
	R^2	0.04 (0.05)	0.03 (0.04)	**0.03 (0.03)**	0.02 (0.02)	0.03	**0.16**	0.00	0.03
	MAE	0.08 (0.01)	0.08 (0.00)	**0.09 (0.01)**	0.09 (0.01)	0.01	**0.01**	0.01	0.01

Table S4-8. (Cont.)

Performance indicators		Multiple imputation								Optimal estimation			
		lag0(SD)		lag1(SD)		lead1(SD)		LL1(SD)		lag0	lag1	lead1	LL1
Ethylbenzene													
Random	d_2	0.99	(0.00)	**0.99**	**(0.00)**	0.99	(0.00)	0.99	(0.00)	0.88	**0.89**	0.88	0.87
	R^2	0.96	(0.01)	**0.96**	**(0.00)**	0.95	(0.01)	0.96	(0.01)	0.76	**0.76**	0.75	0.74
	MAE	0.02	(0.00)	**0.01**	**(0.00)**	0.02	(0.00)	0.02	(0.00)	0.00	**0.00**	0.00	0.00
Block 5	d_2	0.99	(0.00)	0.99	(0.00)	**0.99**	**(0.00)**	0.99	(0.00)	**0.90**	0.89	0.85	0.79
	R^2	0.97	(0.00)	0.97	(0.00)	**0.97**	**(0.00)**	0.97	(0.00)	**0.90**	0.87	0.86	0.71
	MAE	0.02	(0.00)	0.02	(0.00)	**0.01**	**(0.00)**	0.02	(0.00)	**0.00**	0.00	0.00	0.01
Row-wise	d_2	0.58	(0.09)	0.58	(0.05)	0.54	(0.10)	**0.60**	**(0.08)**	0.51	**0.62**	0.51	0.61
	R^2	0.12	(0.07)	0.10	(0.05)	0.08	(0.07)	**0.13**	**(0.08)**	0.06	**0.18**	0.07	0.15
	MAE	0.10	(0.01)	0.10	(0.01)	0.10	(0.01)	**0.10**	**(0.01)**	0.01	**0.01**	0.01	0.01
Methyl ethyl ketone													
Random	d_2	0.74	(0.04)	0.75	(0.05)	0.71	(0.02)	0.75	(0.05)	0.70	0.70	0.57	**0.70**
	R^2	0.32	(0.06)	0.34	(0.08)	0.25	(0.04)	0.33	(0.08)	0.36	0.38	0.18	**0.40**
	MAE	0.38	(0.04)	0.38	(0.02)	0.40	(0.02)	0.39	(0.02)	0.18	0.18	0.23	**0.17**
Block 5	d_2	**0.65**	**(0.05)**	0.64	(0.06)	0.63	(0.05)	0.62	(0.07)	0.74	**0.75**	0.73	0.73
	R^2	**0.20**	**(0.06)**	0.18	(0.07)	0.19	(0.06)	0.16	(0.07)	0.36	**0.38**	0.34	0.35
	MAE	**0.40**	**(0.03)**	0.40	(0.03)	0.45	(0.05)	0.41	(0.03)	0.12	**0.12**	0.14	0.12
Row-wise	d_2	**0.71**	**(0.02)**	0.69	(0.06)	0.65	(0.03)	0.68	(0.07)	**0.82**	0.80	0.81	0.80
	R^2	**0.28**	**(0.03)**	0.25	(0.10)	0.18	(0.05)	0.25	(0.10)	**0.49**	0.46	0.48	0.45
	MAE	**0.37**	**(0.02)**	0.38	(0.03)	0.38	(0.04)	0.39	(0.03)	**0.10**	0.10	0.10	0.11
m,p-Xylene													
Random	d_2	0.99	(0.00)	0.99	(0.00)	**0.99**	**(0.00)**	0.99	(0.00)	0.88	**0.88**	0.88	0.88
	R^2	0.97	(0.01)	0.97	(0.00)	**0.97**	**(0.00)**	0.97	(0.00)	0.77	**0.78**	0.78	0.78
	MAE	0.04	(0.01)	0.04	(0.01)	**0.04**	**(0.00)**	0.04	(0.01)	0.03	**0.03**	0.03	0.03
Block 5	d_2	0.99	(0.00)	**0.99**	**(0.00)**	0.99	(0.00)	0.99	(0.00)	0.87	0.87	0.86	**0.87**
	R^2	0.97	(0.01)	**0.97**	**(0.00)**	0.97	(0.00)	0.97	(0.01)	0.74	0.74	0.74	**0.75**
	MAE	0.04	(0.01)	**0.04**	**(0.00)**	0.04	(0.00)	0.04	(0.00)	0.03	0.03	0.03	**0.03**
Row-wise	d_2	0.50	(0.05)	0.56	(0.05)	0.52	(0.05)	**0.60**	**(0.04)**	0.50	**0.55**	0.52	0.45
	R^2	0.05	(0.03)	0.08	(0.03)	0.06	(0.03)	**0.13**	**(0.04)**	0.06	**0.12**	0.08	0.06
	MAE	0.31	(0.02)	0.32	(0.03)	0.31	(0.02)	**0.28**	**(0.02)**	0.11	**0.10**	0.10	0.10
n-Octane													
Random	d_2	**0.52**	**(0.04)**	0.52	(0.04)	0.53	(0.09)	0.47	(0.06)	0.32	0.32	0.42	**0.48**
	R^2	**0.06**	**(0.03)**	0.06	(0.03)	0.07	(0.07)	0.04	(0.05)	0.01	0.01	0.01	**0.04**
	MAE	**0.04**	**(0.00)**	0.04	(0.00)	0.04	(0.01)	0.04	(0.00)	0.00	0.00	0.00	**0.00**
Block 5	d_2	0.53	(0.05)	0.53	(0.05)	**0.57**	**(0.05)**	0.44	(0.06)	0.34	0.34	0.38	**0.39**
	R^2	0.06	(0.05)	0.06	(0.05)	**0.10**	**(0.05)**	0.02	(0.01)	0.01	0.01	0.02	**0.01**
	MAE	0.04	(0.00)	0.04	(0.00)	**0.04**	**(0.00)**	0.05	(0.00)	0.00	0.00	0.00	**0.00**
Row-wise	d_2	0.40	(0.06)	**0.38**	**(0.08)**	0.35	(0.10)	0.37	(0.12)	0.26	**0.31**	0.26	0.26
	R^2	0.01	(0.01)	**0.01**	**(0.02)**	0.01	(0.01)	0.03	(0.03)	0.01	**0.00**	0.01	0.01
	MAE	0.05	(0.00)	**0.05**	**(0.00)**	0.02	(0.00)	0.04	(0.00)	0.00	**0.00**	0.00	0.00

Table S4-8. (Cont.)

Performance indicators		Multiple imputation								Optimal estimation			
		lag0(SD)		lag1(SD)		lead1(SD)		LL1(SD)		lag0	lag1	lead1	LL1
o-Xylene													
Random	d_2	**0.98**	**(0.00)**	0.98	(0.00)	0.98	(0.00)	0.98	(0.00)	0.86	0.86	0.83	**0.94**
	R^2	**0.94**	**(0.01)**	0.94	(0.01)	0.92	(0.01)	0.93	(0.01)	0.89	0.89	0.85	**0.92**
	MAE	**0.03**	**(0.00)**	0.03	(0.00)	0.03	(0.00)	0.03	(0.00)	0.01	0.01	0.01	**0.00**
Block 5	d_2	**0.98**	**(0.00)**	0.98	(0.00)	0.98	(0.00)	0.98	(0.00)	0.87	0.88	0.84	**0.93**
	R^2	**0.94**	**(0.02)**	0.93	(0.01)	0.93	(0.01)	0.92	(0.01)	0.90	0.90	0.87	**0.89**
	MAE	**0.03**	**(0.00)**	0.03	(0.00)	0.03	(0.00)	0.03	(0.00)	0.01	0.01	0.01	**0.00**
Row-wise	d_2	0.60	(0.08)	**0.63**	**(0.05)**	0.59	(0.06)	0.63	(0.08)	0.60	0.63	0.55	**0.64**
	R^2	0.15	(0.08)	**0.17**	**(0.06)**	0.12	(0.06)	0.17	(0.09)	0.22	0.21	0.13	**0.24**
	MAE	0.13	(0.01)	**0.12**	**(0.01)**	0.12	(0.01)	0.12	(0.01)	0.02	0.02	0.02	**0.02**
Propylene													
Random	d_2	0.45	(0.04)	0.41	(0.11)	0.42	(0.06)	**0.45**	**(0.06)**	**0.66**	0.56	0.61	0.65
	R^2	0.07	(0.03)	0.06	(0.08)	0.04	(0.04)	**0.07**	**(0.05)**	**0.23**	0.10	0.15	0.19
	MAE	1.28	(0.15)	1.30	(0.10)	1.30	(0.15)	**1.24**	**(0.16)**	**0.76**	0.86	0.65	0.59
Block 5	d_2	**0.47**	**(0.11)**	0.44	(0.11)	0.29	(0.05)	0.32	(0.04)	**0.49**	0.36	0.28	0.27
	R^2	**0.09**	**(0.06)**	0.07	(0.05)	0.01	(0.01)	0.01	(0.01)	**0.24**	0.12	0.05	0.04
	MAE	**1.14**	**(0.07)**	1.21	(0.05)	1.33	(0.10)	1.27	(0.11)	**2.48**	2.79	3.04	3.09
Row-wise	d_2	**0.58**	**(0.05)**	0.51	(0.02)	0.54	(0.05)	0.44	(0.06)	0.65	0.53	**0.66**	0.57
	R^2	**0.14**	**(0.05)**	0.07	(0.02)	0.10	(0.04)	0.02	(0.02)	0.25	0.14	**0.27**	0.19
	MAE	**1.26**	**(0.15)**	1.30	(0.11)	1.23	(0.13)	1.30	(0.05)	1.08	1.25	**1.04**	1.15
Tetrachloroethylene													
Random	d_2	0.30	(0.07)	0.27	(0.03)	0.31	(0.06)	**0.33**	**(0.06)**	0.22	**0.27**	0.26	0.23
	R^2	0.02	(0.02)	0.01	(0.01)	0.01	(0.01)	**0.01**	**(0.02)**	0.01	**0.03**	0.03	0.00
	MAE	0.08	(0.01)	0.08	(0.00)	0.08	(0.00)	**0.07**	**(0.00)**	0.01	**0.01**	0.01	0.01
Block 5	d_2	0.39	(0.04)	**0.41**	**(0.12)**	0.34	(0.04)	0.32	(0.09)	0.27	0.33	**0.39**	0.26
	R^2	0.01	(0.02)	**0.04**	**(0.06)**	0.01	(0.00)	0.02	(0.02)	0.02	0.05	**0.11**	0.05
	MAE	0.07	(0.01)	**0.08**	**(0.01)**	0.07	(0.01)	0.08	(0.00)	0.01	0.01	**0.01**	0.01
Row-wise	d_2	**0.41**	**(0.11)**	0.38	(0.10)	-	-	0.32	(0.06)	**0.37**	0.30	-	0.27
	R^2	**0.03**	**(0.02)**	0.02	(0.01)	-	-	0.01	(0.00)	**0.15**	0.09	-	0.08
	MAE	**0.07**	**(0.01)**	0.08	(0.01)	-	-	0.07	(0.01)	**0.01**	0.01	-	0.01
Trichlorofluoromethane													
Random	d_2	0.61	(0.08)	**0.62**	**(0.08)**	0.61	(0.08)	0.57	(0.05)	0.23	0.31	0.23	**0.51**
	R^2	0.17	(0.10)	**0.17**	**(0.09)**	0.17	(0.10)	0.12	(0.05)	0.02	0.01	0.02	**0.17**
	MAE	0.10	(0.01)	**0.10**	**(0.01)**	0.10	(0.01)	0.11	(0.01)	0.01	0.01	0.01	**0.01**
Block 5	d_2	0.47	(0.11)	**0.51**	**(0.05)**	0.47	(0.11)	0.29	(0.09)	0.39	**0.47**	0.39	0.43
	R^2	0.10	(0.07)	**0.10**	**(0.04)**	0.10	(0.07)	0.03	(0.04)	0.04	**0.10**	0.04	0.08
	MAE	0.10	(0.02)	**0.09**	**(0.01)**	0.10	(0.02)	0.12	(0.02)	0.00	**0.00**	0.00	0.00
Row-wise	d_2	-	-	0.30	(0.08)	-	-	**0.34**	**(0.10)**	-	0.34	-	**0.38**
	R^2	-	-	0.01	(0.01)	-	-	**0.03**	**(0.04)**	-	0.00	-	**0.01**
	MAE	-	-	0.12	(0.02)	-	-	**0.12**	**(0.01)**	-	0.01	-	**0.01**

Table S4-8. (Cont.)

Performance indicators		Multiple imputation								Optimal estimation			
		lag0	(SD)	lag1	(SD)	lead1	(SD)	LL1	(SD)	lag0	lag1	lead1	LL1
Trichlorotrifluoromethane													
Random	d_2	0.42	(0.09)	0.58	(0.02)	0.49	(0.06)	**0.67**	**(0.04)**	0.19	**0.20**	0.18	0.18
	R^2	0.02	(0.04)	0.09	(0.02)	0.03	(0.04)	**0.19**	**(0.07)**	0.01	**0.01**	0.02	0.01
	MAE	0.03	(0.00)	0.02	(0.00)	0.02	(0.00)	**0.02**	**(0.00)**	0.00	**0.00**	0.00	0.00
Block 5	d_2	0.44	(0.05)	0.39	(0.04)	0.39	(0.06)	**0.45**	**(0.04)**	0.21	0.18	0.20	**0.20**
	R^2	0.01	(0.02)	0.00	(0.01)	0.01	(0.01)	**0.01**	**(0.01)**	0.01	0.03	0.01	**0.01**
	MAE	0.03	(0.00)	0.03	(0.00)	0.03	(0.00)	**0.03**	**(0.00)**	0.00	0.00	0.00	**0.00**
Row-wise	d_2	0.42	(0.07)	0.56	(0.03)	0.49	(0.03)	**0.59**	**(0.03)**	0.18	0.18	**0.20**	0.19
	R^2	0.01	(0.01)	0.07	(0.02)	0.02	(0.01)	**0.10**	**(0.03)**	0.07	0.06	**0.03**	0.04
	MAE	0.03	(0.00)	0.02	(0.00)	0.03	(0.00)	**0.02**	**(0.00)**	0.00	0.00	**0.00**	0.00
1,2,4-Trimethylbenzene													
Random	d_2	**0.98**	**(0.00)**	0.98	(0.00)	0.98	(0.00)	0.98	(0.00)	0.65	**0.86**	0.60	0.63
	R^2	**0.92**	**(0.01)**	0.92	(0.02)	0.91	(0.02)	0.91	(0.02)	0.52	**0.69**	0.44	0.47
	MAE	**0.04**	**(0.00)**	0.04	(0.00)	0.04	(0.00)	0.04	(0.00)	0.02	**0.01**	0.02	0.02
Block 5	d_2	0.98	(0.00)	**0.98**	**(0.00)**	0.98	(0.00)	0.98	(0.00)	0.63	**0.88**	0.72	0.62
	R^2	0.92	(0.01)	**0.93**	**(0.01)**	0.93	(0.01)	0.92	(0.01)	0.42	**0.79**	0.54	0.41
	MAE	0.04	(0.00)	**0.04**	**(0.00)**	0.04	(0.00)	0.04	(0.00)	0.02	**0.01**	0.02	0.02
Row-wise	d_2	0.66	(0.07)	0.66	(0.03)	0.54	(0.04)	**0.69**	**(0.04)**	0.63	**0.70**	0.58	0.67
	R^2	0.21	(0.07)	0.20	(0.03)	0.07	(0.03)	**0.25**	**(0.06)**	0.24	**0.33**	0.17	0.26
	MAE	0.12	(0.01)	0.12	(0.01)	0.14	(0.01)	**0.12**	**(0.01)**	0.02	**0.02**	0.02	0.02
1,3,5-Trimethylbenzene													
Random	d_2	0.90	(0.01)	**0.91**	**(0.01)**	0.90	(0.02)	0.90	(0.01)	0.81	0.81	0.80	**0.85**
	R^2	0.66	(0.03)	**0.68**	**(0.03)**	0.68	(0.06)	0.65	(0.03)	0.51	0.51	0.48	**0.55**
	MAE	0.02	(0.00)	**0.02**	**(0.00)**	0.02	(0.00)	0.02	(0.00)	0.00	0.00	0.00	**0.00**
Block 5	d_2	0.90	(0.01)	**0.92**	**(0.01)**	0.91	(0.01)	0.92	(0.01)	0.85	0.84	0.84	**0.88**
	R^2	0.67	(0.02)	**0.73**	**(0.03)**	0.70	(0.04)	0.72	(0.02)	0.65	0.63	0.63	**0.61**
	MAE	0.02	(0.00)	**0.02**	**(0.00)**	0.02	(0.00)	0.02	(0.00)	0.00	0.00	0.00	**0.00**
Row-wise	d_2	0.58	(0.08)	0.57	(0.07)	**0.59**	**(0.12)**	0.56	(0.03)	0.46	0.48	**0.65**	0.58
	R^2	0.10	(0.06)	0.10	(0.07)	**0.14**	**(0.12)**	0.09	(0.03)	0.07	0.09	**0.24**	0.17
	MAE	0.04	(0.00)	0.04	(0.00)	**0.04**	**(0.00)**	0.04	(0.00)	0.00	0.00	**0.00**	0.00
Toluene													
Random	d_2	0.90	(0.02)	0.88	(0.02)	0.89	(0.02)	**0.91**	**(0.01)**	0.84	0.75	0.90	**0.95**
	R^2	0.68	(0.06)	0.64	(0.05)	0.67	(0.05)	**0.72**	**(0.04)**	0.61	0.44	0.74	**0.83**
	MAE	0.35	(0.04)	0.38	(0.04)	0.38	(0.04)	**0.36**	**(0.03)**	0.19	0.26	0.13	**0.08**
Block 5	d_2	**0.91**	**(0.01)**	0.87	(0.01)	0.90	(0.02)	0.89	(0.03)	0.60	0.51	**0.81**	0.81
	R^2	**0.70**	**(0.03)**	0.60	(0.04)	0.67	(0.05)	0.66	(0.07)	0.38	0.19	**0.63**	0.59
	MAE	**0.38**	**(0.02)**	0.40	(0.03)	0.36	(0.01)	0.36	(0.05)	0.56	0.69	**0.35**	0.36
Row-wise	d_2	**0.56**	**(0.05)**	0.52	(0.11)	0.55	(0.10)	0.51	(0.06)	0.50	0.46	0.50	**0.50**
	R^2	**0.11**	**(0.04)**	0.08	(0.09)	0.10	(0.09)	0.08	(0.04)	0.09	0.07	0.12	**0.12**
	MAE	**0.61**	**(0.04)**	0.69	(0.09)	0.68	(0.07)	0.67	(0.04)	0.68	0.69	0.64	**0.64**

Table S4- 9. Performance indicators for OLE using both un-transformed and log-transformed data.

Otherwise as Table S4-7.

Performance indicators		Untransformed				Log-transformed			
		lag0	lag1	lead1	LL1	lag0	lag1	lead1	LL1
Acetaldehyde									
Random	d2	0.86	**0.89**	0.74	0.88	0.78	0.80	0.78	**0.83**
	R2	0.69	**0.72**	0.51	0.70	0.62	0.66	0.62	**0.69**
	MAE	0.30	**0.26**	0.46	0.28	0.01	0.00	0.00	**0.00**
Row-wise	d2	**0.67**	0.63	0.47	0.46	**0.42**	0.35	0.35	0.36
	R2	**0.32**	0.26	0.09	0.11	**0.06**	0.02	0.01	0.03
	MAE	**0.62**	0.66	0.83	0.79	**0.00**	0.00	0.00	0.00
Benzaldehyde									
Random	d2	**0.88**	0.82	0.77	0.83	**0.65**	0.55	0.76	0.59
	R2	**0.62**	0.48	0.44	0.51	**0.34**	0.19	0.42	0.35
	MAE	**0.00**	0.00	0.00	0.00	**0.00**	0.00	0.00	0.00
Row-wise	d2	0.50	**0.57**	0.25	0.31	**0.55**	0.53	0.29	0.32
	R2	0.07	**0.13**	0.02	0.00	**0.14**	0.12	0.00	0.00
	MAE	0.00	**0.00**	0.00	0.00	**0.00**	0.00	0.00	0.00
Formaldehyde									
Random	d2	**0.86**	0.82	0.84	0.83	0.69	0.57	0.65	**0.70**
	R2	**0.63**	0.62	0.69	0.63	0.48	0.30	0.45	**0.37**
	MAE	**0.72**	0.78	0.69	0.77	0.00	0.00	0.00	**0.00**
Row-wise	d2	0.52	**0.54**	0.33	0.33	**0.41**	0.36	0.19	0.19
	R2	0.09	**0.11**	0.00	0.00	**0.09**	0.02	0.02	0.02
	MAE	2.37	**2.31**	2.65	2.65	**0.58**	0.00	0.00	0.00
Benzene									
Random	d2	**0.89**	0.85	0.84	0.79	**0.61**	0.43	0.45	0.41
	R2	**0.71**	0.63	0.63	0.52	**0.22**	0.08	0.10	0.07
	MAE	**0.03**	0.04	0.04	0.04	**0.00**	0.00	0.00	0.00
Row-wise	d2	0.63	**0.65**	0.64	0.53	0.70	**0.71**	0.70	0.69
	R2	0.22	**0.25**	0.24	0.17	0.30	**0.32**	0.30	0.29
	MAE	0.07	**0.07**	0.07	0.08	0.00	**0.00**	0.00	0.00
1,3-Butadiene									
Random	d2	**0.78**	0.74	0.62	0.63	**0.53**	0.30	0.29	0.29
	R2	**0.68**	0.67	0.52	0.52	**0.16**	0.03	0.02	0.02
	MAE	**0.00**	0.00	0.00	0.00	**0.00**	0.00	0.00	0.00
Row-wise	d2	**0.49**	0.43	0.41	0.30	**0.56**	0.49	0.48	0.45
	R2	**0.13**	0.08	0.07	0.03	**0.16**	0.13	0.09	0.06
	MAE	**0.00**	0.00	0.00	0.00	**0.00**	0.00	0.00	0.00
Tetrachloroethylene									
Random	d2	0.22	**0.27**	0.26	0.23	0.32	0.38	**0.55**	0.34
	R2	0.01	**0.03**	0.03	0.00	0.04	0.17	**0.30**	0.09
	MAE	0.01	**0.01**	0.01	0.01	0.00	0.00	**0.00**	0.00
Row-wise	d2	**0.37**	0.30	-	0.27	**0.48**	0.37	-	0.37
	R2	**0.15**	0.09	-	0.08	**0.17**	0.07	-	0.08
	MAE	**0.01**	0.01	-	0.01	**0.00**	0.00	-	0.00

Table S4- 10. Performance indicators for MI using both untransformed and log-transformed data.

Otherwise as Table S4-7.

Performance indicators		Un-transformed				Log-transformed			
		lag0(SD)	lag1(SD)	lead1(SD)	LL1(SD)	lag0(SD)	lag1(SD)	lead1(SD)	LL1(SD)
Acetaldehyde									
Random	d_2	0.95 (0.01)	0.95 (0.01)	0.95 (0.01)	**0.95 (0.00)**	**0.93 (0.01)**	0.92 (0.02)	0.92 (0.03)	0.93 (0.01)
	R^2	0.83 (0.02)	0.80 (0.02)	0.83 (0.02)	**0.83 (0.01)**	**0.79 (0.04)**	0.75 (0.06)	0.76 (0.07)	0.77 (0.03)
	MAE	0.29 (0.03)	0.30 (0.03)	0.30 (0.02)	**0.30 (0.01)**	**0.31 (0.03)**	0.31 (0.04)	0.32 (0.05)	0.30 (0.02)
Row-wise	d_2	0.58 (0.05)	**0.67 (0.04)**	0.51 (0.05)	0.63 (0.06)	0.29 (0.19)	**0.31 (0.17)**	0.33 (0.13)	0.34 (0.09)
	R^2	0.11 (0.05)	**0.20 (0.06)**	0.04 (0.02)	0.14 (0.08)	0.04 (0.06)	**0.10 (0.08)**	0.02 (0.03)	0.04 (0.03)
	MAE	0.87 (0.08)	**0.85 (0.12)**	0.91 (0.04)	0.87 (0.06)	1.56 (0.48)	**1.53 (0.51)**	1.32 (0.25)	1.34 (0.15)
Benzaldehyde									
Random	d_2	0.80 (0.03)	**0.83 (0.02)**	0.76 (0.05)	0.76 (0.01)	**0.85 (0.05)**	0.78 (0.04)	0.67 (0.08)	0.69 (0.12)
	R^2	0.46 (0.07)	**0.55 (0.03)**	0.38 (0.10)	0.38 (0.03)	**0.57 (0.10)**	0.41 (0.07)	0.27 (0.08)	0.28 (0.11)
	MAE	0.02 (0.00)	**0.02 (0.00)**	0.03 (0.00)	0.03 (0.00)	**0.02 (0.00)**	0.02 (0.00)	0.02 (0.00)	0.02 (0.00)
Row-wise	d_2	0.48 (0.06)	**0.54 (0.03)**	0.35 (0.05)	0.38 (0.05)	0.41 (0.09)	**0.43 (0.12)**	0.26 (0.06)	0.33 (0.06)
	R^2	0.05 (0.05)	**0.09 (0.02)**	0.01 (0.01)	0.00 (0.01)	0.04 (0.05)	**0.08 (0.04)**	0.01 (0.01)	0.00 (0.00)
	MAE	0.04 (0.00)	**0.04 (0.00)**	0.05 (0.00)	0.05 (0.00)	0.04 (0.00)	**0.04 (0.02)**	0.05 (0.00)	0.04 (0.01)
Formaldehyde									
Random	d_2	0.84 (0.02)	0.80 (0.04)	**0.85 (0.01)**	0.81 (0.04)	0.74 (0.05)	0.66 (0.08)	**0.76 (0.03)**	0.75 (0.04)
	R^2	0.53 (0.05)	0.44 (0.07)	**0.54 (0.03)**	0.45 (0.09)	0.48 (0.05)	0.39 (0.08)	**0.52 (0.08)**	0.45 (0.09)
	MAE	0.80 (0.03)	0.90 (0.10)	**0.81 (0.03)**	0.86 (0.05)	1.13 (0.10)	1.27 (0.22)	**1.05 (0.04)**	1.09 (0.11)
Row-wise	d_2	0.51 (0.06)	**0.53 (0.03)**	0.40 (0.06)	0.40 (0.06)	0.16 (0.12)	**0.23 (0.14)**	0.16 (0.10)	0.16 (0.10)
	R^2	0.05 (0.04)	**0.06 (0.03)**	0.01 (0.01)	0.01 (0.01)	0.02 (0.02)	**0.03 (0.02)**	0.02 (0.02)	0.02 (0.02)
	MAE	1.49 (0.14)	**1.58 (0.12)**	1.79 (0.14)	1.79 (0.14)	3.92 (1.37)	**3.98 (1.84)**	3.79 (0.95)	3.79 (0.95)
Benzene									
Random	d_2	**0.87 (0.03)**	0.84 (0.01)	0.87 (0.02)	0.84 (0.02)	**0.88 (0.04)**	0.78 (0.03)	0.83 (0.05)	0.81 (0.02)
	R^2	**0.61 (0.08)**	0.52 (0.03)	0.59 (0.06)	0.52 (0.05)	**0.62 (0.11)**	0.41 (0.06)	0.51 (0.11)	0.46 (0.05)
	MAE	**0.17 (0.02)**	0.18 (0.01)	0.17 (0.01)	0.18 (0.01)	**0.14 (0.02)**	0.17 (0.02)	0.17 (0.01)	0.17 (0.01)
Row-wise	d_2	**0.64 (0.04)**	0.63 (0.03)	0.58 (0.06)	0.57 (0.06)	**0.64 (0.07)**	0.63 (0.04)	0.59 (0.07)	0.58 (0.07)
	R^2	**0.20 (0.05)**	0.18 (0.03)	0.13 (0.05)	0.12 (0.05)	**0.20 (0.07)**	0.18 (0.04)	0.14 (0.08)	0.13 (0.06)
	MAE	**0.26 (0.02)**	0.28 (0.02)	0.28 (0.03)	0.27 (0.01)	**0.21 (0.02)**	0.22 (0.02)	0.22 (0.02)	0.23 (0.01)
1,3-Butadiene									
Random	d_2	0.89 (0.02)	**0.89 (0.01)**	0.87 (0.01)	0.87 (0.02)	**0.81 (0.07)**	0.79 (0.04)	0.78 (0.05)	0.76 (0.07)
	R^2	0.65 (0.06)	**0.65 (0.03)**	0.58 (0.03)	0.58 (0.04)	**0.54 (0.11)**	0.52 (0.05)	0.44 (0.09)	0.42 (0.13)
	MAE	0.03 (0.00)	**0.03 (0.00)**	0.03 (0.00)	0.03 (0.00)	**0.03 (0.00)**	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)
Row-wise	d_2	**0.58 (0.04)**	0.50 (0.03)	0.52 (0.08)	0.46 (0.05)	**0.57 (0.07)**	0.48 (0.04)	0.51 (0.10)	0.42 (0.03)
	R^2	**0.09 (0.03)**	0.05 (0.03)	0.07 (0.05)	0.03 (0.03)	**0.14 (0.07)**	0.05 (0.03)	0.10 (0.07)	0.02 (0.01)
	MAE	**0.04 (0.00)**	0.04 (0.00)	0.05 (0.00)	0.04 (0.00)	**0.03 (0.00)**	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)
Tetrachloroethylene									
Random	d_2	0.30 (0.07)	0.27 (0.03)	0.31 (0.06)	**0.33 (0.06)**	**0.29 (0.06)**	0.21 (0.04)	0.28 (0.04)	0.27 (0.04)
	R^2	0.02 (0.02)	0.01 (0.01)	0.01 (0.01)	**0.01 (0.02)**	**0.02 (0.02)**	0.00 (0.00)	0.01 (0.01)	0.02 (0.03)
	MAE	0.08 (0.01)	0.08 (0.00)	0.08 (0.00)	**0.07 (0.00)**	**0.06 (0.00)**	0.06 (0.00)	0.06 (0.00)	0.06 (0.00)
Row-wise	d_2	**0.41 (0.11)**	0.38 (0.10)	-	0.32 (0.06)	**0.40 (0.14)**	0.33 (0.11)	0.31 (0.12)	0.25 (0.05)
	R^2	**0.03 (0.02)**	0.02 (0.01)	-	0.01 (0.00)	**0.07 (0.07)**	0.03 (0.04)	0.02 (0.04)	0.01 (0.01)
	MAE	**0.07 (0.01)**	0.08 (0.01)	-	0.07 (0.01)	**0.05 (0.00)**	0.05 (0.00)	0.05 (0.00)	0.05 (0.01)

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Chapter 5
Conclusions

In this dissertation, both acute and long-term health effects of ambient air pollutants were investigated. Chapter 3 focused on adverse birth outcomes, while Chapter 4 examined childhood respiratory-related illness in the Detroit, Michigan metropolitan area. The research also evaluated statistical approaches to handle missing air quality data and used multivariate receptor models to derive source apportionments from an air toxics dataset. Exposure scores obtained from the multivariate receptor models were used as exposure measures in health models to examine associations with acute respiratory-related illness in children.

This concluding chapter highlights the key findings, implications and significance of this research. The study's strength and limitations are summarized, and recommendations for further research are suggested.

5.1   Key findings

5.1.1   Air pollution and adverse birth outcomes

Chapter 2 investigated whether ambient air pollutants, including CO, NO_2, PM_{10} and SO_2, were associated with low birth weight (LBW), small for gestational age (SGA) and preterm birth (PTB) outcomes in a cohort of 155,000 singleton births in Detroit, Michigan between 1990 and 2001. These outcomes were based on birth certificate data of mothers living within a 4 km radius of three air quality monitors located in Allen Park, East 7 Mile, and Linwood. Using logistic regression models with control of key covariates, including infant sex, gestational age, maternal age, education levels, smoking status, prenatal care, birth season and site of residency, CO,

NO$_2$ and PM$_{10}$ exposures were associated with increased risk of SGA births, and SO$_2$ exposure was associated with increased risk of LBW and PTB births. In testing various time windows of exposure, the early pregnancy period was most important for the CO-SGA, NO$_2$-SGA and SO$_2$-LBW associations, and the late pregnancy period for SO$_2$-PTB and PM$_{10}$-SGA associations. Except for PM$_{10}$, exposures to other pollutants appear to have stronger effects on infants of Black mothers for all three adverse birth outcomes, as compared with infants of White mothers. Additionally, the analysis highlights the importance of accounting for long-term trends and maternal smoking status in evaluating relationships between pollutant exposures and adverse birth outcomes.

This study is one of the few studies in the U.S. that had a large African American population and allowed examination of effects due to race/ethnicity. This study also permitted investigation into the effects of maternal smoking status, which, while a well-recognized risk factor for adverse birth outcomes, has often not been available in other adverse birth outcome studies. In addition, most of the recent U.S. studies have come mainly from southern California and the East Coast, areas that are generally less industrialized than Detroit. Furthermore, portions of Detroit are considered air pollution "hot spots" by U.S. EPA for failing to meet National Ambient Air Quality Standards (NAAQS) for PM$_{2.5}$[1], and the Detroit area has distinct summer and winter climates that may affect how individuals are exposed to various air pollutants.[2] Due primarily to local and regional emissions from industrial sources, the concentrations, composition and toxicity of ambient air pollutants in the study area may differ from those in the earlier studies. Thus, the present study informs the birth outcome literature by explicitly examining effects of race/ethnicity, smoking status, and geographic location.

5.1.2 Air pollution and acute childhood respiratory-related illness

Chapter 3 had the objective of determining whether exposure to ambient air toxic pollutants, broken down into different source classes that emitted these pollutants, was associated with respiratory-related illness among children. This chapter described an epidemiological investigation of children enrolled in Medicaid and living in Dearborn, Michigan within 4 and 10 km of the Dearborn air quality monitor during a one year study period (April 2001 to April 2002). During this period, these children made a total of

1,166 and 4,617 emergency department (ED) visits for asthma and respiratory problems, respectively. As part of the Detroit Pilot Project, daily measurements of urban air toxics (UAT), including carbonyls and volatile organic compounds (VOCs), were made, including a large number of duplicate samples. Using positive matrix factorization (PMF) receptor modeling, the air toxics dataset was reduced to a set of five source classes which explained from 44 to 100% and 74 to 92% of the variation in the carbonyl and aromatic VOC data, respectively. Exposures to three source classes, identified as fuel combustion, photochemical pollutants, and gasoline exhaust/evaporated gasoline increased the odds of ED visits for respiratory problems. Although the sample size was smaller, effects were stronger for subjects living within 4 km of the monitor, as compared to a 10 km distance. No statistically significant associations were found between injury, the control case, and the air pollutant measures.

The analysis described above represents one of the first studies to use source-apportioned exposure measures in order to link toxic pollutant exposures and respiratory-related illness. Perhaps the most significant feature of this approach is that it inherently accounts for exposure to mixtures of multiple pollutants and multiple emission sources, an important limitation of most of the current air pollution epidemiological studies.

5.1.3 Reproducibility and imputation of air toxics data

Chapter 4 described analyses of the air toxics data used in the epidemiological investigation reported in Chapter 3. It evaluated whether imputation offered a useful approach for recovering missing values of ambient air pollutant data, and investigated several quality assurance issues. The study used a total of 323 daily air toxics samples collected at the Dearborn monitoring site, which included 122 pairs of replicate samples. These samples were analyzed by two laboratories for 12 carbonyl and 59 VOC species. After data cleaning, including eliminating species with low detection frequency (<20%) and detecting outliers using the Gumbell extreme value distribution, 23 compounds were selected for the final dataset. Of these, intra- and inter-laboratory comparisons showed good agreement for only one compound (benzene), moderate agreement for several other VOCs (e.g., trimethylbenzenes, xylenes, ethylbenzene, dichlorodifluoromethane, tetrachloroethylene, and toluene), and poor-to-fair agreement for the remaining VOCs

and all carbonyls. Uncertainty models, which were constructed by pooling residuals across the intra- and intra-laboratory analyses, provided a comprehensive description of analytical uncertainties, and the median intra- and inter-laboratory relative uncertainties were 22% and 25%, respectively, across the final 23 compounds (7 carbonyls and 16 VOCs).

Two methods were evaluated for their ability to impute missing data for the 23 selected compounds and for three missingness patterns. Optimal linear estimation (OLE) and multiple imputation (MI) methods obtained comparable performance for random deletions, with results depending on the compound, concentration distribution, and other factors. For the dominant row-wise deletion pattern observed in the air toxics dataset, however, the performance of both methods deteriorated.

The analysis highlighted the critical importance of characterizing the reproducibility of ambient air toxics dataset prior to its use. It is essential to identify variables that are informative and thus useful in applications such as regulatory determinations of risk, receptor modeling studies of source apportionments, and epidemiological assessments of health impacts. The uncertainty models and quality assurance steps presented in Chapter 4 can help to describe and validate ambient data, as well as provide uncertainty estimates useful in imputation and other applications.

5.1.4   Receptor modeling

Appendix 1 provides a detailed description of the receptor modeling used in Chapter 3. The principal approach used, positive matrix factorization (PMF), indicated that concentrations of ambient air toxics measured at the Dearborn site in the Detroit Air Toxics Initiative Project could be explained by five source classes: (1) gasoline exhaust/evaporated gasoline, (2) fuel combustion, (3) combined industrial sources, (4) photochemical pollutants, and (5) industrial solvents. The results indicate that even in the highly industrialized study area, concentrations were dominated by vehicular emission sources. PMF yield "cleaner" and more realistic source profiles than those obtained from principal component analysis.

The distinction between the receptor models used in this study and those in earlier studies is the incorporation of different compound groups of UATs, including carbonyls,

VOCs and metals, in the same model, thereby providing a more comprehensive assessment. In addition, the analysis incorporated site-specific uncertainty estimates, based on replicate samples as described in Chapter 4, thus reflecting a more realistic situation than the fixed uncertainty values commonly used in PMF analyses.

5.2 Study strengths and limitations

5.2.1 Air pollution and adverse birth outcomes

The specific strengths of the analyses in Chapter 2 included a large sample size (n=155,094), a long study duration (7-12 years), and good representation of individual-level information on residence location, race, smoking status, pregnancy and educational attainment. Temporal trends in pollutant concentrations, which affected SO_2 and CO results, and multiple pollutant models were examined. A large African American population in the study sample allowed us to examine possible heterogeneity by race. Finally, restricting births to mothers residing quite close (≤ 4 km) to air monitors in the analysis potentially minimized exposure measurement error.[3]

There are several weaknesses of the study. Geocoding of individual residences was unavailable, thus residences (and subjects) were selected if their ZIP code area was within 4 km of an air quality monitor. Pollutant levels in Detroit generally fell below those in other studies, and lower exposures may have been subject to greater exposure measurement error. Exposure misclassification was possible for subjects living near major traffic routes (more likely near Linwood and East Seven Mile sites), which could have increased exposures above levels measured at the monitoring sites. By comparison, monitoring sites were located in residential areas at least several blocks from major roads. However, limiting participants to a relatively small radius around the monitor should have minimized such errors. Missing pollutant data may have influenced results, although results using a single monitor (Linwood) were consistent with those using all three sites, suggesting that any bias was minimal. Additional information on potential covariates and confounders not available in the birth certificate database may have been helpful, e.g., alcohol consumption, although the effects of any such factors are suspected to be likely correlated with other individual-level risk factors that were available, thus

minimizing confounding. Finally, measurements of personal or indoor exposures were unavailable, a limitation of all studies that rely on ambient measures of exposure.[4-6]

5.2.2   Acute childhood respiratory-related illness

The major strength of the study lies in its exposure assessment. The use of receptor models to derive source-apportioned exposure measures is attractive in that such measures may be more strongly associated with health impacts, improving statistical power. Other strengths include the use of source-apportioned exposures derived from measurements of VOCs and carbonyls together, and sensitivity analyses that incorporated metals measurements. In contrast, the current receptor modeling literature analyses these groups separately, and mainly focuses on VOCs. The stronger associations were found between source-apportioned exposure measures, with carbonyls as key species, and ED visits for respiratory problems. In addition, by examining only children enrolled in Medicaid, confounding by social economic status (SES), a known indicator of utilization of urgent care for asthma,[7] is minimized.

There are several limitations. First of all, the sample size was not large enough to adequately assess certain relationships between exposures and health outcomes, specifically ED visits for asthma. Also, by examining only the Medicaid population and a single site, results are not generalizable to the general population. The study's duration was only one year which, of course, affected sample size and missing exposure data might have influenced the results. Some exposure misclassification was inherent in the study design, which could be seen in results for the 10 km radius where risk ratios were forced toward the null. Finally, personal exposure data were unavailable, and indoor sources of toxics, especially VOCs,[8] might have affected results.

5.2.3   Reproducibility and imputation of air toxics data

This study enjoyed the advantage of a relatively large dataset with daily measurements of several types of air toxics for a full year. Due to expense and logistical issues, air toxics generally are measured only every 3rd or 6th day. Also, because carbonyls, VOCs and other toxic pollutants require different sampling and analytical methods, simultaneous measurement of different classes of air toxics is relatively uncommon. In addition, this study was able to examine the reproducibility of air toxics

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measurements, including both within and between laboratories variability, due to the availability of replicate samples. The uncertainty models developed in Chapter 4 (developed for each decile of concentrations) provide analytical uncertainties over a wide range of concentrations, and should be generally applicable to air pollution research.

Several limitations are recognized in Chapter 4's analysis. Only a single monitoring site was analyzed, and only two laboratories were involved. While the sample size was relatively large for air toxics monitoring programs, the analysis used what must be considered a modest sample size in statistical terms. The intra-laboratory comparisons focused on analytical uncertainties, which may not dominate actual uncertainties.[9] Many factors can influence sampling and analysis performance, and the true accuracy of the data was not established. Due to these factors, generalizations should be made cautiously, although the data and results are believed to be generally representative of current monitoring practice. The analysis investigated only a subset of the many methods that can be used to impute missing data and estimate uncertainties.[10,11]

Finally, this study did not evaluate the performance of imputation methods as applied to health effect studies. The MI approach was developed to minimize the bias caused by the missing information in health effect studies. Therefore, performance evaluations should examine risk estimates with and without imputed data. In the early stage of this research, MI was used to investigate associations between O_3 exposures and low birth weight (data not shown) because O_3 data were not available for six months of the year. However, due to concerns that half of the data required imputation, O_3 was excluded from the analysis. Air toxics posed different issues. Due to the low reproducibility of the data and the novelty of using the receptor modeling approach, constructing the health models and interpreting the results using imputed data was beyond the scope of this research.

5.2.4 Receptor modeling

There are a number of strengths in the receptor modeling study. First, VOCs and carbonyls were simultaneously modeled, and carbonyls showed comparable or stronger indicators of vehicular emission sources than VOCs alone, suggesting that groupings of VOCs alone in the previous studies[12,13] might not have adequately described this source

class. Second, this study was able to examine seasonal effects. Other studies have used shorter study periods, e.g., a single summer (ozone) season.[14-16] Third, measurement uncertainty was estimated using site-specific uncertainty models, instead of a fixed value, thereby increasing the realism of the source classes and the other receptor model results.

The receptor modeling analysis has several limitations. Ideally, each PMF factor represents a single source category, confirmed by a unique and known chemical profile, and uncorrelated with other source categories. More realistically, in complicated systems a PMF factor consists of features from several sources,[16] especially when longer averaging periods (e.g., 24 hr at Dearborn) are used, emissions from several or many source classes have similar compositions, compounds are chemically reactive (which includes several of the aldehyde and VOC species used), and local estimates of source compositions are not available. These reasons advise caution in the interpretation of the results.

5.3   Recommendations for future studies

The topics investigated in this dissertation have spanned a wide range of areas in the epidemiological and exposure analysis fields. This section makes several recommendations for future studies in the major areas covered, namely: (1) exposure assessment; (2) statistical treatment and imputation of air quality data; and (3) adverse birth outcomes and acute respiratory effect-related studies.

5.3.1   Exposure assessment

In the area of exposure assessment, there is a need for complete, continuous, and high resolution (i.e., daily or perhaps hourly) air quality data, especially in areas that are considered to be pollution "hot spots." With the growth of the environmental epidemiology field, air quality data increasingly is being used for many applications besides compliance purposes, therefore, there is a demand for complete datasets, especially for air toxics, O_3, PM_{10} and $PM_{2.5}$.

Additional research is needed to improve receptor modeling for air toxics, especially with the emphasis on health effects studies. Models using additional information, potentially meteorology, criteria air pollutants, and traffic data, might help

to obtain "cleaner" source contributions with minimal collinearity between sources. This would also help to improve the robustness of exposure measures used in health studies.

5.3.2 Statistical treatment and imputation of air quality data

Regarding statistical treatment and imputation of air quality data, research is needed to improve imputations, especially for row-wise missingness patterns. The variable selection criteria used in Chapter 4 may have been too stringent and *a priori* information was not incorporated. A sensitivity analysis of these criteria and more complex models using other variables (e.g., season, day-of-week, traffic counts) and other model structures (e.g., auto-regressive integrated moving average models) could be evaluated. Predictor variables might also be derived that combine meteorological parameters that reflect dispersion potential and local source impacts, and models might be used to account for long term trends and seasonality. There is also a need to refine the uncertainty models that may improve OLE estimates. The performance of other imputation methods should be examined, and other datasets should be used to ensure that results are representative. Finally, the performance of imputation methods should be evaluated in health effects studies of air pollution.

5.3.3 Health effects studies

Further research using individual-level exposure monitoring would help to quantify the relative contribution of ambient versus localized exposures to the occurrence of adverse birth outcomes and respiratory-related illness in children. In addition, incorporating information regarding the proximity of residences to major traffic routes and human activity patterns in health models would help to minimize exposure misclassification.

For adverse birth outcome studies, few studies have used $PM_{2.5}$ and O_3, in part because $PM_{2.5}$ has only been measured relatively recently and often intermittently. Although ozone has been measured for many years, however, in Michigan, O_3 measurements are conducted only in the high O_3 season (April to September); therefore, this pollutant has not been investigated extensively, especially in longitudinal study designs where continuous and all year round measurements are required. In addition, associations between exposures to air toxics (i.e. carbonyls, VOCs and metals) and birth

outcomes have not been investigated. There is a need to include these pollutants in future research. The biological pathways linking air pollutant exposures to adverse birth outcomes are not well understood, future studies using additional biomonitoring indicators such as biomarkers of traffic-related pollutants that can reflect the actual exposures and the toxicity pathways targeting the reproductive system would help to support the plausibility of the associations. The utilization of birth certificate data is common in birth outcome studies; however, this type of data does not capture information regarding other factors that may affect pregnant women and their fetus, e.g., genetic make-up, bacterial infections, or exposures to other waterborne or food-borne pollutants that could lead to the likelihood of having adverse birth outcomes. Modification in the study designs of future studies to incorporate this additional information (i.e., two-levels logistic models)[17] would help to clarify the associations.

For acute respiratory-related illness among children, studies using larger sample sizes, longer durations, and multiple monitoring sites would help to investigate health outcomes that involve ED visits and would likely strengthen associations. Expanding the study population beyond those enrolled in Medicaid, would also help to generalize study results.

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Appendix 1
Receptor Modeling of Ambient Air Toxics and Metals at Dearborn, Michigan

Table of Contents

List of Supplemental Tables

1.1   Abstract

Ambient air toxics data from the Detroit Air Toxics Initiative Pilot Project, including daily measurements of 12 carbonyls and 59 volatile organic compounds (VOCs) measured from April 2001 through April 2002 at Dearborn, Michigan, were analyzed using positive matrix factorization (PMF) to identify and apportion emission sources contributing to the ambient measurements. The monitoring site, located at an elementary school, was near residential and industrial facilities in an area of historically high toxics emissions. Based on detection frequency, reproducibility and quality assurance criteria, the original data set was reduced to 23 compounds. On an annual basis, PMF apportioned the toxics measurements into five source categories: gasoline exhaust/evaporated gasoline, 28% contribution; fuel combustion, 24%; combined industrial sources, 22%; photochemical pollutants, 13%; and industrial solvents, 13%. These results suggest that vehicle source contributions exceeded industrial emissions in the study area. The paper discusses these findings and the implications of using receptor modeling results as exposure measures in health effects studies.

1.2   Introduction

Receptor models (RM) utilize ambient pollutant data to identify and quantify contributions of the emission sources, or classes of emission sources, that are responsible for observed pollutant levels monitored at a "receptor," i.e., a monitoring location. Receptor models have been widely used for particulate matter, but relatively few applications have been reported for VOCs and carbonyls.[1-9] A recent expert panel has concluded that source apportionment results obtained using RMs are sufficiently robust for application to particulate matter with aerodynamic less than 2.5 microns ($PM_{2.5}$) and health effects assessment.[10-12] To date, however, there are very few examples of exposure indicators derived from source apportionments that have been used in epidemiological studies. There are several advantages of such indicators in epidemiological investigations. First, because source contributions are derived in a manner to be mutually orthogonal, health models can simultaneously incorporate multiple sources (and pollutants) with fewer of the complications that arise from

collinearity as seen in other multi-pollutant models. Second, because RM utilizes essentially all the data, it may yield results that are more robust.

This appendix describes the application of two receptor modeling methods, positive matrix factorization (PMF) and principal component analysis (PCA), that are employed to apportion daily carbonyl and VOC measurements at the Dearborn, Michigan monitoring site for the period from April 2001 to April 2002. The identified source classes are then used to derive daily exposure scores for the health effects study described in Chapter 3 of this dissertation (entitled "Ambient air toxics source apportionment and daily emergency department visits for respiratory-related illness among pediatric Medicaid population in Dearborn, Michigan").

This appendix is written as a stand alone manuscript with the anticipation of submission for publication.

1.3   Background

1.3.1   Receptor modeling

The fundamental principle underlying receptor modeling is that a chemical mass balance analysis can be used to identify and apportion sources of ambient air pollutants.[13] Only the general framework of receptor modeling will be discussed here. Details can be found elsewhere.[13-19] The mass balance can be written as:

$$X_{i,j} = \sum_{k=1}^{p} f_{i,k} g_{k,j} \qquad (1)$$

where $X_{i,j}$ is the concentration of the ith component (i.e., chemical species) measured in the jth sample, i.e., the "measurement" (ppb); $f_{i,k}$ is the fractional composition of the ith component in emissions from the kth source, i.e., the "source profile"; and $g_{k,j}$ is the airborne concentration of the chemical species from the kth source contributing to the jth sample (ppb).

To obtain valid results, RMs must meet several fundamental constraints: (1) the original data must be reproduced by the model, thus the model must explain the observation; (2) the predicted source compositions $f_{i,k}$ must be non-negative; (3) the predicted source contributions $g_{j,k}$ to the aerosol must all be non-negative (a source

cannot emit negative mass); (4) the sum of the predicted contributions of each source must be less than or equal to total measured mass for each chemical species.[20]

To solve equation (1), k sources must be identified and compositions measured or estimated. In most cases, however, sources are unknown and compositions of the local sources have not been measured.[18] Thus, compositions of sources measured elsewhere are typically used.

There are several different RM approaches. Chemical mass balance (CMB) models utilize regression approaches to solve eq. (1) and require *a priori* estimates of source profiles for all contributing source types.   This need for accurate profiles is a key limitation associated with CMB models.[21] According to Watson et al. (2001), CMB models complement rather than replace other data analysis and modeling methods.[15] In addition, CMB models do not account for physical and chemical processes in the atmosphere that may alter compositions as pollutants travel from source to receptor.

Multivariate RMs estimate the number and compositions of the sources, as well as their contributions to measured concentrations. These models utilize factor analysis, eigenvector analysis, principal component analysis (PCA), and related methods. For example, in PCA, the most commonly-used method, the new variables necessary to reproduce the measured concentrations are determined using an eigenvector analysis of the correlation matrix.[13] There are several problems with multivariate approaches: (1) a large number of measurements are needed; (2) interpretation of results can be problematic and although the results are statistically sound, they may be physically invalid;[21-23] (3) PCA often requires a transformation or rotation to produce factors that appear to resemble physically meaningful source profiles; however, "true" profiles cannot be fully determined without additional information;[18] (4) scaling of the data by column or by row in PCA will lead to distortions in the analysis;[16] and (5) results are not unique, but dependent on the number of source profiles, rotations and other parameters.

In view of PCA limitations, positive matrix factorization (PMF) was developed with the advantage that results are guaranteed to be non-negative. PMF has used in many PM and VOC source apportionment studies.[1,3-5,8,10,24] Studies by Zhao et al. (2004) and Xie et al. (2005) demonstrated the feasibility of PMF models in identifying sources of

VOCs in Houston, Texas which involved meteorological measurements and other factors (e.g. wind speed, wind direction, temperature, and weekend/weekday).[3,8]

An alternative to PMF, which provides more flexibility as well as additional constraints, is called the multilinear engine (ME). ME has not been widely used.[25] Another receptor method that has the closest performance to PMF is UNMIX, a linear mixture multivariate receptor models developed by Henry.[22] However, the current version of UNMIX software only reports the minimum R^2 and signal to noise ratio (S/N) values for the worst-fit compound included in the model whereas PMF provides values for all compounds.[4] In addition, Jorquera et al.(2004) reported that source profile for VOCs obtained from PMF method were more credible than of that UNMIX.[1] Using simulated personal exposure data for VOCs, Miller et al.(2002) reported that source profiles from PMF more closely resembled the original sources than CMB, PCA and UNMIX results.[9] For $PM_{2.5}$, a recent inter-comparison of different multivariate RMs found that $PM_{2.5}$ apportionment results were consistent across users and methods.[10]

RMs have several disadvantages. The estimated source class contributions contain errors. The classifications into source types may be uncertain. The numbers of source profiles and contributing sources are unknown. Measurement errors may be unknown. Finally, the physical meaning of results differs from that typically reported in as exposure measures in epidemiological analyses. While the use of RM-based apportionments as exposure indicators in environmental epidemiology holds great promise, the current application of such indicators must be viewed as experimental.

Among the various RM approaches available, we selected PMF due to several advantages, specifically, because profiles are guaranteed be non-negative (required for physical interpretation), and because weights (uncertainties) can be incorporated for individual data points. The mathematical basis of PMF is described below. Detailed information can be found elsewhere.[16,17]

1.3.2 Positive matrix factorization (PMF)

The **X** matrix in equation (1) can be decomposed as:

$$\mathbf{X} = \mathbf{USV}^{'} = \overline{\mathbf{US}}\,\overline{\mathbf{V}}^{'} + \mathbf{E} \tag{2}$$

where **U** and **V** matrices are calculated from eigenvalue-eigenvector analyses of the **X X'** and **X' X** matrices, respectively; $\overline{\mathbf{U}}$ and $\overline{\mathbf{V}}$ are the first p columns of the **U** and **V** matrices; and the "residual matrix" **E** is defined as:

$$\sum_{i=1}^{m}\sum_{j=1}^{n} e_{i,j}^2 = \sum_{i=1}^{m}\sum_{j=1}^{n}\left(x_{i,j} - \sum_{p=1}^{p} g_{i,p} f_{p,j} \right)^2 \qquad (3)$$

Different from PCA, which is an *implicit* least-squares analysis in that it minimizes the sum of squared residuals for the models (eq. 3), PMF takes the approach of an *explicit* least-squares approach in which minimizes the objective function Q:[26]

$$Q(E) = \sum_{j=1}^{n}\sum_{i=1}^{m}\left(\frac{x_{i,j} - \sum_{p=1}^{p} g_{i,p} f_{p,j}}{s_{i,j}} \right)^2 \qquad (4)$$

where $s_{i,j}$ is an estimate of the uncertainty in the jth variable measured in the ith sample. The objective function Q is to be minimized with respect to G and F with the constraint that each of the elements of G and F are non-negative through the use of a penalty function. Details of penalty function are presented elsewhere.[16-18,26]

As mentioned, one advantages of PMF is that the uncertainty of each observation or missing value can be incorporated into the analysis by weights. [27] PMF shares the same disadvantages as other multivariate RM approaches, including the difficulty of determining the correct number of factors or sources that should be used.[18]

1.4   Methods

1.4.1   Data acquisition and cleaning

This study used a dataset that has been previously evaluated for quality assurance and reproducibility, as described in Chapter 4.[28] In brief, daily air samples were collected from 4/19/2001 to 4/18/2002 at Dearborn, Michigan (Figure A1-1) and analyzed by Eastern Research Group (ERG) for 12 carbonyl and 59 VOC species. This dataset included duplicate sampling on 122 days, with analyses by the same ERG laboratory on 40 days, and the same Michigan Department of Environmental Quality (MDEQ) laboratory on 41 days, permitting intra-laboratory analyses, as well as both laboratories

on 41 days, permitting inter-laboratory comparisons. Duplicate samples were averaged and outliers were excluded. Measurements that fell below the compound-specific method detection limit (MDL) were set to ½ MDL. Carbonyl and VOC species were selected after excluding compounds with detection frequencies below 20% and correlation between duplicate measurements below 0.2. The final cleaned dataset included 16 VOC and 7 carbonyl species, and a total of 302 and 283 observations (days of measurements), respectively.

Uncertainties associated with each measurement were estimated using uncertainty models derived from an analysis of duplicate measurements (intra-laboratory comparison), which were pooled together (VOCs and carbonyls separately).[28] Uncertainties for VOCs and carbonyls were estimated as:

$$\sigma_{VOC} = 0.060 \; C_{VOC} + 0.009 \qquad\qquad (R^2 = 0.76) \qquad\qquad (5)$$

$$\sigma_{CAR} = 0.152 \; C_{CAR} + 0.067 \qquad\qquad (R^2 = 0.87) \qquad\qquad (6)$$

where σ_{VOC} and σ_{CAR} are the median absolute errors; C_{VOC} and C_{CAR} are concentrations for VOCs and carbonyls, respectively (ppbv); and the coefficients are the results of regression analyses using the medians in each decile of the aggregated VOC and carbonyl data. For example, eq. (2) shows that carbonyl measurements have a median absolute error of 0.22 ppbv at a concentration of 1 ppb. For values below the MDL, uncertainties were set to 5/6 MDL.[27] Due to the sampling design, observations (all species) were missing on roughly 6.4% of the possible sampling days. These missing values were replaced using the geometric mean (GM), and the corresponding uncertainty was set to 4 GM.[27]

Additional data were obtained from the Michigan Department of Environmental Quality (MDEQ) to investigate the sensitivity of the PMF results, specifically, the identification of sources. MDEQ collected particulate samples every 6th day at the Dearborn site which were analyzed for arsenic, beryllium, cadmium, chromium, lead, manganese and nickel. A total 60 observations were available for the study period. Replicate samples for these metals measurements were unavailable at Dearborn; therefore, replicate samples from a nearby site (Southwest High School) were used to estimate uncertainties.   (MDEQ uses the same data to estimate the precision of the metal measurements for the Detroit area.) Uncertainty models were constructed following the

approach described previously (results shown later).

1.4.2   Positive Matrix Factorization

EPA's PMF version 1.1 software package was used for this study.[29]   Initially, the number of sources was based on a principal component analysis (PCA) using varimax rotation and selected on the basis of the number of eigenvalues exceeding one. However, we also selected other cut-offs to gauge the sensitivity of PMF results to a larger number of source factors. In the PMF analysis, a species was considered as uninformative (bad), modestly informative (weak) and good if its signal/noise (S/N) ratio <0.2, $0.2 \leq S/N < 2$, and $S/N \geq 2$, respectively, cut-offs that have been successfully applied in PM apportionments.[30-33] Bad species were excluded from further analyses, and weak species were down-weighted by increasing their associated uncertainties by a factor of three prior to modeling.

The PMF analysis used 20 random starting points to determine the global minimum. The optimum random run was selected by examining the robust Q value of all the random run output. Robust Q value is preferred over true Q value because no observation is allowed to have extreme influence in the fitting of the model, thereby preventing over-fitting of these extreme values. As shown in eq. (4), the Q value is the sum of square measures that is used to quantify model fit.

PCA analyses were also conducted and results compared to those from PMF. PMF and PCA models were run on both annual and seasonal levels. (Spring was defined as March to May, summer as June to August, fall as September to November, and winter as December to February.) Models were tested using observed data only, as well as imputed data. Models incorporating the metals data used only observed data and were conducted at only the annual level due to sample size limitations in the metals data.

1.5   Results

1.5.1   Overview of the data set

The quality assurance and filtering procedures, described previously,[28] showed good agreement in intra- and inter-laboratory comparisons for only one compound (benzene), moderate agreement for several other VOCs (e.g., trimethylbenzene, xylenes,

ethylbenzene, dichlorodifluoromethane, tetrachloroethylene, and toluene), and poor-to-fair agreement for the remaining VOCs and all carbonyls (Table SA1-1). The final data set used in the RM analyses included 7 carbonyls and 16 VOCs (Table A1-1). Daily measurements were missing for 17% of the VOCs measurements (n=300) and 22% of the carbonyl measurements (n=283). Together, measurements of all 23 compounds were available on 265 days (of a possible 365). With the exception of chlorinated and fluorinated VOCs, most species had moderate-to-high correlation with other species, e.g., aromatic VOCs were highly correlated ($0.66 \leq r \leq 0.99$), as were most carbonyls ($0.55 \leq r \leq 0.86$) (Table SA1-2).

With the exception of cadmium and nickel, the metals measurements had moderate correlation with each other ($0.19 \leq r \leq 0.74$; Table A1-1), and with PM_{10} ($0.35 \leq r \leq 0.68$) and $PM_{2.5}$ ($0.39 \leq r \leq 0.62$; Table SA1-2). These high correlation coefficients suggest that most metals occur in fine fraction particulate matter. Measurements of both air toxics and metals were available for only 35 days. Overall, the correlation between air toxics and metals was low to fair. Among the seven metals, manganese and nickel showed significant correlation with air toxics ($r \leq 0.38$). For example, 1,2,4-trimethylbenzene was negatively correlated with manganese ($r = -0.30$) and positively correlated with nickel ($r = -0.38$).

Differences between replicate metals measurements increased with concentration (Figure SA1-1), and the uncertainty model of decile concentration incorporated both constant and proportional terms,

$$\sigma_{metal} = 0.07\ C_{metal} + 0.09 \qquad\qquad (R^2 = 0.95) \qquad\qquad (7)$$

where σ_{metal} is estimated median absolute error (ng/m^3), and C_{metal} is the measured metals concentration (ng/m^3). For example, metal measurements have a median absolute error of 0.16 ng/m^3 at a concentration of 1 ng/m^3. Most of the uncertainty models for other percentiles also showed good fits ($0.94 \leq R^2 \leq 0.98$). As expected, models for the higher percentiles gave larger uncertainties.

1.5.2   PMF analyses

For the observed data, trichlorotrifluoroethane was identified as an uninformative species, while 1,3-butadiene, n-octane, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene,

benzaldehyde, tolualdehyde, beryllium were considered only modestly informative. Since the inclusion of these species only slightly affected results, these species were neither removed nor down-weighted (Figures SA1-2 and SA1-3).

Five source classes were identified, as described below and in Figure A1-2:

1) *The fuel combustion source class* included key species of acetaldehyde, hexaldehyde, iso-butyraldehyde, propionaldehyde and tolualdehyde. Fuel combustion is a well-known direct source of these carbonyls, a result of incomplete combustion.[34] Acetaldehyde is emitted by vehicles as a primary emission. It is also a secondary pollutant, also related to combustion. The carbonyls have relatively short half-lives in the atmosphere. There are some indications that diesel vehicles may have high emissions of selected carbonyls (i.e. acetaldehyde, formaldehyde), but improvement in diesel fuel and in diesel engines over the years have reduced diesel emissions and many of its components.[35,36]

2) *Photochemical pollutants* are indicated by formaldehyde, most of which is formed by reactions with isoprene and other pollutants (as opposed to emissions from road traffic and other sources.[37]) However, formaldehyde also has been strongly associated with traffic emissions and acetaldehyde in a number of studies.

3) *Gasoline exhaust/evaporated gasoline* is indicated by 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,3-butadiene, benzene, ethylbenzene, m,p-xylene, o-xylene and toluene. The VOCs comprising this source class remain quite stable across seasons. These also tend to be the VOCs measured at the higher concentrations.

4) *Combined industrial sources* are suggested by acetylene, propylene, dichlorodifluoromethane, n-octane, tetrachloroethylene, trichlorofluoromethane, and trichlorotrifluoroethane. Tetrachloroethylene releases are known to occur at airports and waste handling facilities, although the estimated releases total only several hundreds of lbs/yr, based on U.S. EPA toxic inventory report (TRI) for Wayne County which contains Dearborn (382 lbs and 633 lbs for 2001 and 2002, respectively).[38] Much larger emissions (23,000 lb/yr) occur in Midland, Michigan, but this is too distant to affect monitoring observations at the Dearborn site. As noted above, acetylene also is a constituent of vehicle exhaust.

5) *Industrial solvents* are suggested by methyl ethyl ketone (MEK). Annually,

95% of the MEK was assigned to this profile. No other compound was associated with this source class. Known sources of air releases (from the TRI inventory) for MEK include GM's assembly facilities in Detroit, Visteon in Ypsilanti, among others, although 2002 releases are relatively modest (<20,000 lbs/yr per facility). MEK is also a common laboratory solvent and could represent an artifact.

Except for n-octane and propylene, other constituents had >40% of their mass apportioned to each of the identified source classes. Contributions of n-octane and propylene were approximately equally split (>30% each) to the fuel combustion and combined industrial source classes. Sources of n-octane may come from fuel evaporation as well as emissions from industry, solvents and paints. Propylene is often a marker of petrochemical sources,[39] although the single refinery in Detroit (Marathon) is some distance from the Dearborn monitoring site. Propylene is also a product of incomplete combustion.

Diagnostic statistics for the PMF models indicated that most of the variation in the VOC and carbonyl concentrations was explained by the five source classes (Table A1-2). This applied to the aromatic VOCs ($0.74 \leq R^2 \leq 0.92$), MEK ($R^2 = 1.00$), acetylene ($R^2 = 0.80$), 1,3-butadiene ($R^2 = 0.62$), and most of the carbonyls including acetaldehyde, benzaldehyde, formaldehyde, hexaldehyde, isobutylaldehyde, proprionaldehyde and tolualdehyde ($0.44 \leq R^2 \leq 1.00$). However, it did not apply to other chlorinated and fluorinated VOCs ($0.03 \leq R^2 \leq 0.21$), n-octane ($R^2 = 0.10$), and propylene ($R^2 = 0.08$). While the low R^2 values for these VOCs may be due to several reasons, the most likely explanations are reproducibility problems and the generally small amount of variation observed in concentrations of these VOCs, as noted previously.[28]

Figure A1-3 shows the annual contributions of the five source classes. Vehicle-related source classes dominated these results. The annual source apportionments were: gasoline exhaust and evaporated gasoline, 28%; fuel combustion, 24%; combined industrial sources, 22%; photochemical pollutants (13%); and industrial solvents, 13%.

The seasonal models using five source classes obtained similar results (Figures SA1-6 to SA1-8). Source classes for spring and winter seasons were unchanged. For the summer models (Figure SA1-7), MEK and few VOCs (1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,3-butadiene, benzene, m,p-xylene and o-xylene) were assigned

together with constituents identified as combined industrial sources, and hexaldehyde had 97% of its mass apportioned to a new source class. Automobile assembly facilities in the Detroit area are often shutdown during the summer time, which might reduce MEK emissions. In addition, somewhat different patterns of traffic during the summer season and higher rates of photochemical reactions and the consumption of reactive compounds and production of secondary species might contribute to the variability in some of the VOCs and hexaldehyde. For the fall models (Figure SA1-8), propylene had 96% of its mass apportioned to a new source class (petroleum pollutants), while chlorinated and fluorinated VOCs were assigned together with formaldehyde in the photochemical pollutant source class. These results suggest that variability due to seasonality affects only a few of the source classes and only during summer and fall seasons.

Analyses using six source classes did not significantly change results (Figure SA1-4). The 6th source class had hexaldehyde as the main constituent with 81% of its mass assigned to this source; the five other source classes were almost unchanged. In addition, the R^2 value did not improve as compared to the 5-source class models (Figure SA1-5); therefore, the 5-source models appear to be adequate.

Source classes and annual apportionments obtained using imputed data were similar to those obtained using observed data (Figures SA1-10 to SA1-12). Similar estimated annual source apportionments were also obtained: gasoline exhaust and evaporated gasoline, 27%; fuel combustion, 25%; combined industrial sources, 22%; industrial solvents, 14%; and photochemical pollutants, 12%.

1.5.3 Source classes with additional metals information

Results obtained using five source classes along with additional metals information are shown in Figure A1-4. The additional information provided by the metals data did not change the source classes identified previously. The metals resolved in their own source class included cadmium, arsenic, lead, chromium and manganese, and likely represented diesel and industrial sources. Formaldehyde, previously identified as a photochemical pollutants source class, merged with the rest of the carbonyls of the fuel combustion source class and distributed a small part of its mass among other source classes. Beryllium was apportioned to the industrial solvent source class along with

MEK, however, this might be an artifact since the variance explained by this element is only 0.06 ng/m^3 (Table A1-2). Among the seven metals, only chromium (R^2=0.72) and manganese (R^2=0.92) explained most of the variability of the models that contained metals (Table A1-2). Due to small sample size (n=35), the interpretation of the models that included metals must be limited.

1.5.4 PCA analyses

Results from the principal component analyses for annual and seasonal models are shown in Figures SA1-13 to SA1-S20. Using an eigenvalue of approximately one as a minimal cut-off, we identified five or six source classes (Table SA1-3). Overall, the PCA models yielded similar patterns of source profiles as those obtained from PMF. However, the PCA factor loadings included negative values, which limit their physical interpretation. In addition, source profiles obtained from PCA were more mixed in composition, i.e., in the six source class models, two profiles resembled a combined industrial source, and two others resembled industrial solvents.

Compared to PMF analyses, the PCA models explained a slightly higher fraction of variance of each species ($0.48 \leq R^2 \leq 0.96$), especially for the chlorinated VOCs, possibly a result of not using weights in the PCA modeling that account for measurement uncertainties. There were no significantly differences in results obtained using observed and imputed data (Figures SA1-21 to SA1-23), and the PCA models with metals data gave similar results as those obtained from the PMF models (Figure SA1-24).

1.6 Discussion

The PMF models using combined VOC and carbonyl measurements identified five source classes identified as gasoline exhaust/evaporated gasoline, fuel combustion, combined industrial sources, photochemical pollutants, and industrial solvents. Ideally, each PMF factor represents a single identified source category that is uncorrelated with other source categories. However, in complicated systems, a PMF factor may consist of features from several sources.[3] Combined source factors are also more likely in longer samples, e.g., 24-hr samples collected at Dearborn (as compared to 1-hr samples collected in Houston, for example[3]) since winds from a number of directions are likely and may bring contaminants from several source types to the monitor site, and thus

separate sources in effect become correlated. A further complication arises as several aldehydes (e.g., formaldehyde, acetaldehyde) and VOCs (e.g., 1,3-butadiene) in the dataset are chemically reactive, and their concentration and lifetime will be affected by photochemistry, temperature, sunlight, and other reactive species and precursors (e.g., isoprene) that may be present. Such effects will likely vary seasonally. Thus, measurements of these compounds will reflect both primary emissions (directly from the source) and secondary production. Moreover, measured levels from primary emissions will reflect the portion remaining after any consumption from atmospheric reactions. All of these effects will tend to "blur" profiles for sources that include reactive components, and may create new profiles that primarily reflect secondary pollutants. In comparison, this is not a problem for $PM_{2.5}$ or PM_{10} apportionments that utilize elemental composition.

While the breakdown into factors using receptor models may not isolate single sources or source types, the use of source factors remains a valid way to represent the pattern of concentrations to which individuals are exposed, and its use in health models can thus identify those pollutants and pollutant mixtures that are associated with adverse health effects.

1.6.1   Other receptor modeling studies of air toxics

Overall, results from this study are consistent with the source apportionment analyses by Hafner et al. (2004) which also used air toxics data collected at Dearborn in 2001 and the PMF model.[40] This study identified a total of 7 factors representing aldehydes/secondary, unknown, three types of industrial, motor vehicle and combined diesel and industrial sources using carbonyls, VOCs, semi VOCs, metals and PAHs data. The key species for the unknown source factor is propene (also known as propylene). In this study, propylene was apportioned to both fuel combustion and photochemical pollutant sources.

Results from this study also resemble a recent Dearborn study in which factor analysis was used to identify sources of ambient VOCs collected outside 85 residence homes during fall and spring seasons.[41] Carbonyls were not measured in this study, but a wider range of VOCs were successfully quantified. This study identified four factors: (1)

gasoline-related composite (key species: aromatic and aliphatic VOCs); (2) biogenic emissions (solvents, cleaners and fragrances related VOCs); (3) industrial sources (styrene and chlorinated VOCs); and (4) gasoline evaporation (alkanes). These results together with those from the current study suggest that community ambient air toxics monitoring is representative in identifying the sources of the community exposures to ambient air.

A wider range of measured species will generally help to resolve sources. In comparison to recent work using urban air toxics, this study retained a relatively small number (23) of compounds, specifically the compounds that met minimum detection frequencies and that showed at least fair reproducibility among replicates. In comparison, Xie and Berkowitz (2005) in apportioning VOCs used 55 compounds (all VOCs).[3] Many of the common VOCs, for example, are emitted by many source categories. For example, Baldosano (1998) showed that benzene, toluene, ethybenzene, xylenes and other compounds are all emitted from traffic (diesel and gasoline combined), gasoline vapor, architectural coatings, waste water treatment, graphic arts, automotive painting, solvent use, and wood combustion. Additional compounds can help resolve such sources.[42]

1.6.2   Contributions of carbonyls

To our knowledge, the current study is one of the few studies that utilized both carbonyls and VOCs in receptor modeling, probably due to the cost of sampling and analysis (these classes of pollutants require different sampling and analytical approaches). Source identification has focused on VOCs, possibly because these constitute well known tracers of many sources, and because carbonyl sources lack unique tracers. Carbonyls are emitted by many mobile and stationary sources, and they are also stable intermediate products of the photochemical oxidation of virtually all hydrocarbons and precursors to free radicals, ozone and peroxyacyl nitrates.[43-45]

Consistent with previous studies, this study found that acetaldehyde and formaldehyde are the most abundant carbonyls in the ambient air with geometric mean concentrations of 0.73 and 1.47 ppbv, respectively (Table A1-1).[46-48]   The PMF analysis indicates that formaldehyde is a key species for photochemical pollutants sources, while

acetaldehyde together with other carbonyls are key species for fuel combustion sources. Studies from Rio de Janeiro (Brazil) and Santiago (Chile) also reported photochemical oxidations are the main sources of formaldehyde.[46,47,49] Similar to formaldehyde, acetaldehyde is also responsible for O_3 formation[46] and is detected in automobile exhaust.[49,50]

Although results from this study indicated that the presence of carbonyls in the models did not greatly influence other sources profiles revolved by VOCs, the inclusion of carbonyls in receptor modeling can help derive exposure scores for health effects studies. Carbonyls also are important because of their irritant and toxic properties, mutagenicity and carcinogenicity.[51,52] Finally, with the growth of biofuels, it is important to quantify both emissions and health risks of fuel-related emissions. In particular, a recent study predicted an increase in carbonyl concentrations (with the exception of benzaldehyde) in Brazil where 4.5 million m^3 of ethanol were consumed in 2005 (compared with 22.5 millions m^3 of gasoline in the same period).[53] The combustion of ethanol produces acetaldehyde as a major product, and ethanol-gasoline blends produce more acetaldehyde than gasoline alone.[46]

1.6.3   Contributions of metals

Generally, RM results were insensitive to the addition of metals on the subset of days when these data were available (n=35). Due to the small sample size, however, the metals data did not provide much information regarding the identification of sources or the reliability of the apportionment.

1.6.4   Utilization of uncertainty models in receptor modeling

This study utilized uncertainty models to obtain daily uncertainties for several groups of air toxics and metals, rather than the error estimates recommended by Polissar et al. (1998). Often, uncertainties are estimated empirically using trial and error or other methods.[3,27] Commonly, uncertainties are estimated as:[3,18]

$$\sigma_{i,j}^{k} = u_{i,j}^{k} + d_{i,j}^{k}/3$$

where $\sigma_{i,j}^{k}$, $u_{i,j}^{k}$ and $d_{i,j}^{k}$ are the error estimate, analytical uncertainty and method detection limit, respectively. This approach was not used in part because the analytical

uncertainty was not readily available, and because an alternate, site-specific method was available. Since analytical methods are not independent (i.e. the analytical calibration and hardware are shared), the analyses represent random errors (or method precisions) rather than fixed errors.[54] The uncertainty models used here have the advantages of capturing the precision measures from replicated samples, thereby reflecting random error component. In addition, the uncertainty models also capture a wide range of concentrations, which is common in air toxics concentrations. The approach used may not be conservative since higher percentile absolute relative error models (i.e. 75th or 90th percentiles models) might well represent the actual errors.

1.6.5   Recommendations for future studies

Future analyses might utilize additional meteorological variables, e.g., wind direction and wind speed, which affect the transport path and which may lead to variations observed at the receptor. This study was limited to 24-hr samples, however, Paatero et al. (2002) demonstrated that high-resolution weather data (1-hr) may enhance the usefulness of 24-hr concentration data.[55] For example, variations in wind speed cause variations in the transport path which lead to variation at the receptor. Wind speed is also influenced by seasonal factors, therefore, incorporating wind speed in the receptor models can help to explain seasonal variation of source strength. Utilizing meteorological data such as wind speed in receptor model required more advanced and flexible software, e.g., the multilinear engine, which is beyond the scope of this study.

Most of the issues discussed above regarding the derivation and identification of PMF profiles are broadly applicable, i.e., not limited to the Dearborn dataset. Similarly, other recommendations are also generalizable. In particular, PMF results might be enhanced by the use of shorter sampling periods (possibly separate day and night measurements to separate photochemistry), improved sensitivity of the measurements, better reproducibility, routine use of replicates (allowing better detection of outliers), and the measurement of a wider set of pollutant species. There may also be some gain in exploring the effects of different error models, further evaluating outliers in the dataset, and utilizing a smaller set of profiles in the health models.

1.6.6   Implication for epidemiological studies

To date, very few studies have used source apportionments in epidemiological studies.[30,56] Guo et al. (1999)[57] separated traffic and fossil fuel sources in examining asthma prevalence, Laden et al. (2000)[58] found that mobile and coal combustion sources explained a portion of daily mortality, and Mar et al. (2006)[12] found that combustion-related pollutants and secondary aerosols (sulfates) were associated with daily changes in cardiovascular mortality. The current investigators (and others) have used wind-direction specific exposure metrics to examine daily fluctuations in asthma aggravations.[59] A comparison across multiple apportionment approaches gave consistent results in explaining daily cardiovascular and total mortality, suggesting that these methods provide reliable insights into those source components that contribute to health effects.[11,12,24]

Epidemiologic studies using source-apportioned exposure measures are potentially attractive for several reasons: (1) increased statistical power since the exposure measures may be more strongly associated with health impacts; (2) the correlation in the larger data set is used to derive a smaller number of robust exposure measures; and (3) the enhanced biological plausibility and relevance of the exposure measure. In essence, the derived source contributions or composite scores from the receptor models are used as exposure measures in the same or similar statistical framework used to associate conventional exposure measures, e.g., PM, with health outcomes.

1.7   Conclusion

The receptor model apportionments suggest that ambient air toxics measured at Dearborn, Michigan arise largely due to five sources: gasoline exhaust/evaporated gasoline, fuel combustion, combined industrial sources, photochemical pollutants and industrial solvents. Vehicular emissions account for the dominant contribution, larger than the many industrial sources that are present in the area. In this study, PMF yield "cleaner" and more realistic source profiles than those obtained from PCA. Finally, the RM results can be used in health models to assess the effects of mixtures and health impacts, especially the high incidence of asthma among children in the area.

Table A1- 1. Summary of VOC, carbonyl and metals concentrations with detection frequencies above 20%.
Duplicates were averaged, and outliers were excluded. Ms = missing measurements; BDL = below detection limit measurements; S/N = ratio of signal to noise; GM = geometric mean.

Compounds	Ms (%)	BDL (%)	S/N	GM
Carbonyls (ppbv)				
Acetaldehyde	22	0	44.7	0.73
Benzaldehyde	22	2	0.4	0.04
Formaldehyde	22	0	46.8	1.47
Hexaldehyde	22	1	2.0	0.05
iso-Butyraldehyde	22	1	2.9	0.14
Propionaldehyde	22	10	3.2	0.08
Tolualdehyde	22	7	0.3	0.03
VOCs (ppbv)				
Acetylene	17	1	7.7	1.52
Benzene	17	0	4.1	0.55
1,3-Butadiene	17	73	0.7	0.05
Dichlorodifluoromethane	17	0	3.7	0.63
Ethylbenzene	18	2	2.5	0.15
Methyl ethyl ketone	17	26	7.7	0.39
m,p-Xylene	18	0	3.1	0.43
n-Octane	18	66	0.5	0.04
o-Xylene	18	3	5.2	0.18
Propylene	17	0	3.5	0.82
Tetrachloroethylene	17	66	2.5	0.05
Trichlorofluoromethane	17	0	3.6	0.31
Trichlorotrifluoroethane	17	0	0.1	0.11
1,2,4-Trimethylbenzene	17	9	1.0	0.17
1,3,5-Trimethylbenzene	18	61	0.5	0.05
Toluene	18	0	14.7	0.88
Metals (ng/m^3)				
Arsenic	84	0	5.6	2.15
Beryllium	84	18	0.6	0.06
Cadmium	84	0	2.4	0.55
Chromium	84	2	6.6	5.27
Lead	84	0	7.9	150.14
Manganese	84	0	8.3	2.75
Nickel	84	0	5.6	22.06

Table A1- 2. Diagnostic statistics for 5 source class models for observed carbonyls, VOCs and metals.

VOC, volatile organic compounds; ppbv, part per billion volume; RMSE, root mean square error; R^2, coefficients of determinant.

Pollutants	Air toxics (N=265)		Air toxics and metals (N=35)	
	RMSE	R^2	RMSE	R^2
Carbonyls (ppbv)				
Acetaldehyde	0.01	1.00	0.01	1.00
Formaldehyde	0.01	1.00	0.01	1.00
Propionaldehyde	0.04	0.89	0.02	0.94
iso-Butyraldehyde	0.06	0.78	0.06	0.49
Benzaldehyde	0.02	0.62	0.01	0.67
Hexaldehyde	0.07	0.52	0.04	0.63
Tolualdehyde	0.02	0.44	0.01	0.65
VOCs (ppbv)				
Methyl ethyl ketone	0.02	1.00	0.24	0.81
Toluene	0.19	0.92	0.09	0.99
o-Xylene	0.04	0.91	0.04	0.92
1,2,4-Trimethylbenzene	0.05	0.85	0.04	0.90
m,p-Xylene	0.12	0.84	0.15	0.80
Ethylbenzene	0.04	0.83	0.05	0.78
Acetylene	0.24	0.80	0.34	0.80
1,3,5-Trimethylbenzene	0.02	0.78	0.02	0.84
Benzene	0.13	0.74	0.16	0.77
1,3-Butadiene	0.02	0.62	0.02	0.70
Dichlorodifluoromethane	0.14	0.21	0.15	0.26
n-Octane	0.02	0.10	0.02	0.42
Propylene	0.36	0.08	0.42	0.01
Trichlorofluoromethane	0.08	0.05	0.07	0.37
Tetrachloroethylene	0.02	0.04	0.03	0.41
Trichlorotrifluoroethane	0.03	0.03	0.05	0.00
Metals (ng/m^3)				
Manganese	-	-	37.47	0.92
Chromium	-	-	1.42	0.72
Lead	-	-	5.95	0.61
Arsenic	-	-	0.67	0.20
Nickel	-	-	0.78	0.09
Beryllium	-	-	0.02	0.01
Cadmium	-	-	0.16	0.00

Table SA1- 1. Intra- and inter-laboratory reproducibility.

COV=coefficient of variation; WSR=Wilcoxon signed rank; All analyses used only detected values; Significant values (p <0.05) indicated in bold.

Compound	Intra-laboratory reproducibility						Inter-laboratory reproducibility				Retained (y=yes)
	Correl coeff-ERG		Correl coeff-MDEQ		% COV		Correl coeff		Paired t-test (p-value)	WSR test (p-value)	
	Pearson	Spearman	Pearson	Spearman	ERG	MDEQ	Pearson	Spearman			
Carbonyls											
Acetaldehyde	**0.38**	**0.39**	**0.45**	**0.45**	61	70	**0.37**	**0.52**	0.33	0.07	y
Benzaldehyde	**0.54**	**0.61**	0.23	**0.65**	51	78	0.28	**0.46**	1.00	**0.04**	y
Formaldehyde	**0.45**	**0.48**	**0.51**	**0.58**	58	64	**0.73**	**0.61**	0.95	0.93	y
Hexaldehyde	**0.50**	**0.64**	0.32	**0.51**	62	83	**0.40**	**0.44**	0.41	0.29	y
iso-Butyraldehyde	0.19	**0.40**	-	-	52	-	-	-	-	-	y
Propionaldehyde	**0.34**	0.33	**0.87**	**0.49**	61	59	0.25	0.28	0.07	0.11	y
Tolualdehydes	**0.71**	**0.56**	-	-	42	-	-	-	-	-	y
VOCs											
1,2,4-Trimethylbenzene	**0.68**	**0.67**	**0.91**	**0.79**	39	35	**0.71**	**0.63**	**<0.01**	**<0.01**	y
1,3,5-Trimethylbenzene	**0.71**	**0.70**	**0.89**	**0.64**	31	16	**0.71**	**0.59**	**<0.01**	**<0.01**	y
1,3-Butadiene	**0.60**	**0.59**	-	-	49	-	-	-	-	-	y
Acetylene	**0.54**	**0.63**	-	-	26	-	-	-	-	**-**	y
Benzene	**0.83**	**0.73**	**0.82**	**0.66**	19	36	**0.81**	**0.71**	0.07	**<0.01**	y
Chloromethane	-0.02	**0.45**	**0.44**	**0.42**	12	27	**0.32**	**0.32**	0.98	0.47	y
Dichlorodifluoromethane	**0.75**	**0.75**	**0.70**	**0.68**	4	29	**0.47**	**0.61**	**<0.01**	**<0.01**	y
Ethylbenzene	**0.69**	**0.65**	**0.92**	**0.88**	44	16	**0.78**	**0.66**	**<0.01**	**<0.01**	y
m,p-Xylene	**0.60**	**0.71**	**0.92**	**0.88**	35	24	**0.80**	**0.67**	**<0.01**	**<0.01**	y
Methyl ethyl ketone	**0.66**	**0.65**	-	-	50	-	-	-	-	-	y
n-Octane	0.28	**0.56**	-	-	53	-	-	-	-	-	y
o-Xylene	**0.63**	**0.79**	**0.93**	**0.83**	39	30	**0.79**	**0.67**	**<0.01**	**<0.01**	y
Propylene	**0.90**	**0.70**	-	-	33	-	-	-	-	-	y
Tetrachloroethylene	**0.82**	**0.77**	**0.39**	**0.53**	28	63	**0.64**	**0.61**	0.65	0.73	y
Toluene	**0.82**	**0.73**	**0.93**	**0.82**	28	37	**0.50**	**0.62**	1.00	**0.04**	y
Trichlorofluoromethane	**0.66**	**0.57**	**0.57**	**0.60**	10	28	**0.33**	**0.42**	**0.04**	**0.02**	y
Trichlorotrifluroethane	**0.76**	**0.52**	-	-	10	-	-	-	-	-	y

Table SA1- 2. Pearson correlation coefficient for carbonyls, volatile organic compounds, metals and particulate matters

Pollutants	Propylene	Acetylene	1,3-Butadiene	n-Octane	Methyl ethyl ketone	Trichlorofluoromethane	Tetrachloroethylene	Trichlorotrifluoroethane	Dichlorodifluoromethane	m,p-Xylene	Benzene	Toluene	Ethylbenzene	o-Xylene	1,3,5-Trimethylbenzene	1,2,4-Trimethylbenzene	iso-Butyraldehyde	Formaldehyde	Acetaldehyde	Propionaldehyde	Hexaldehyde	Benzaldehyde	Tolualdehyde	PM10	PM2.5	Arsenic	Beryllium	Cadmium	Chromium	Lead	Manganese	Nickel
N	300	302	345	301	345	345	345	302	345	343	345	343	343	344	344	345	284	329	330	330	329	330	283	361	114	60	60	60	60	60	59	60
Propylene	1.00																															
Acetylene	0.32	1.00																														
1,3-Butadiene	0.32	0.68	1.00																													
n-Octane	0.22	0.34	0.47	1.00																												
Methyl ethyl ketone	0.17	0.22	0.21	0.31	1.00																											
Trichlorofluoromethane	0.08	0.11	0.21	0.15	0.10	1.00																										
Tetrachloroethylene	-0.01	0.18	0.18	0.10	0.15	-0.01	1.00																									
Trichlorotrifluoroethane	0.20	0.04	0.15	0.17	-0.05	0.00	-0.06	1.00																								
Dichlorodifluoromethane	0.16	0.27	0.35	0.24	0.22	0.57	0.06	0.13	1.00																							
m,p-Xylene	0.23	0.61	0.69	0.35	0.37	0.26	0.22	0.01	0.44	1.00																						
Benzene	0.26	0.68	0.54	0.37	0.42	0.18	0.27	-0.02	0.35	0.66	1.00																					
Toluene	0.20	0.61	0.56	0.34	0.45	0.18	0.23	-0.06	0.33	0.80	0.76	1.00																				
Ethylbenzene	0.23	0.62	0.68	0.36	0.37	0.24	0.22	0.03	0.43	0.99	0.67	0.81	1.00																			
o-Xylene	0.24	0.65	0.71	0.40	0.37	0.29	0.22	0.00	0.44	0.97	0.71	0.83	0.96	1.00																		
1,3,5-Trimethylbenzene	0.22	0.66	0.74	0.41	0.39	0.24	0.27	0.00	0.40	0.89	0.70	0.82	0.89	0.90	1.00																	
1,2,4-Trimethylbenzene	0.25	0.67	0.73	0.42	0.43	0.28	0.26	0.02	0.45	0.94	0.74	0.85	0.94	0.93	0.95	1.00																
iso-Butyraldehyde	0.21	0.19	0.24	0.20	0.38	0.23	0.08	0.16	0.36	0.31	0.30	0.27	0.30	0.29	0.31	0.35	1.00															
Formaldehyde	0.21	0.28	0.28	0.24	0.31	0.15	0.08	0.03	0.30	0.38	0.34	0.34	0.37	0.39	0.35	0.39	0.67	1.00														
Acetaldehyde	0.26	0.30	0.33	0.29	0.37	0.27	0.10	0.13	0.41	0.45	0.45	0.42	0.45	0.45	0.45	0.49	0.86	0.82	1.00													
Propionaldehyde	0.16	0.20	0.17	0.18	0.32	0.16	0.06	0.06	0.26	0.26	0.29	0.26	0.25	0.27	0.28	0.32	0.75	0.77	0.79	1.00												
Hexaldehyde	0.10	0.07	0.16	0.18	0.40	0.25	0.11	-0.02	0.35	0.33	0.28	0.31	0.32	0.32	0.32	0.36	0.65	0.55	0.70	0.61	1.00											
Benzaldehyde	0.10	0.22	0.24	0.16	0.35	0.11	0.05	-0.11	0.25	0.33	0.36	0.35	0.33	0.35	0.32	0.35	0.57	0.70	0.59	0.70	0.59	1.00										
Tolualdehyde	0.11	0.16	0.18	0.20	0.38	0.14	0.12	0.01	0.26	0.32	0.28	0.30	0.31	0.33	0.37	0.38	0.61	0.65	0.72	0.70	0.64	0.64	1.00									
PM10	0.15	0.03	-0.06	0.08	0.23	-0.03	-0.08	-0.03	0.01	0.04	0.07	0.03	0.05	0.01	0.04	0.02	0.09	0.19	0.14	0.14	0.10	0.11	0.16	1.00								
PM2.5	0.24	0.14	-0.04	-0.10	0.11	-0.02	-0.08	-0.13	-0.04	-0.01	0.16	0.02	0.01	-0.03	-0.02	-0.03	-0.08	0.03	0.01	0.13	0.02	0.12	0.04	0.66	1.00							
Arsenic	0.14	0.19	0.11	0.00	-0.12	0.22	-0.06	0.03	0.09	0.14	0.15	0.13	0.16	0.15	0.10	0.08	0.20	-0.03	0.08	0.24	0.03	0.05	0.06	0.35	0.54	1.00						
Beryllium	0.25	0.19	0.07	0.12	-0.12	-0.09	0.01	0.01	-0.03	0.02	0.09	0.15	0.03	0.03	0.11	0.04	-0.33	0.09	0.07	-0.11	-0.06	-0.03	-0.10	0.50	0.39	0.19	1.00					
Cadmium	-0.12	0.09	-0.01	0.06	0.01	-0.12	0.20	0.08	-0.13	0.01	0.11	0.01	0.02	0.02	0.09	0.03	-0.11	0.01	0.03	-0.03	-0.02	-0.05	-0.16	0.07	0.21	0.25	0.02	1.00				
Chromium	0.07	0.00	-0.09	0.04	-0.15	0.00	-0.06	0.12	-0.02	-0.01	-0.08	-0.06	-0.08	-0.12	-0.05	-0.10	-0.44	-0.15	-0.14	-0.16	-0.12	-0.17	-0.11	0.63	0.41	0.29	0.30	0.14	1.00			
Lead	-0.13	0.13	-0.09	0.11	-0.19	-0.10	-0.03	-0.06	-0.06	-0.13	0.02	0.03	-0.12	-0.12	0.01	-0.11	-0.31	-0.17	-0.09	-0.11	-0.13	-0.09	-0.19	0.62	0.62	0.50	0.51	0.35	0.59	1.00		
Manganese	0.00	-0.14	-0.19	-0.01	-0.25	-0.21	-0.30	0.06	-0.20	-0.25	-0.25	-0.17	-0.24	-0.30	-0.23	-0.30	-0.44	-0.26	-0.25	-0.30	-0.25	-0.31	-0.34	0.68	0.48	0.22	0.58	0.02	0.74	0.68	1.00	
Nickel	-0.11	0.09	0.01	0.01	0.23	0.25	0.24	-0.31	0.32	0.31	0.21	0.33	0.30	0.34	0.33	0.38	-0.12	0.28	0.29	0.19	0.06	0.23	0.28	0.13	-0.04	0.06	0.11	0.17	0.19	0.14	-0.07	1.00

Table SA1- 3. Eigenvalues explained by each factor from PCA.

Replicates were averaged from both laboratories for observed and single imputation.

Factor	Observed					Imputed (SI)				
	All	Spring	Summer	Fall	Winter	All	Spring	Summer	Fall	Winter
1	10.13	12.82	8.95	10.45	9.54	9.46	11.06	8.41	10.64	8.84
2	3.47	2.62	3.79	4.70	5.03	3.46	3.49	3.60	4.20	4.87
3	1.65	1.75	2.28	1.82	2.05	1.63	1.71	2.24	1.80	2.24
4	1.29	1.19	1.47	1.29	1.49	1.35	1.11	1.33	1.29	1.32
5	1.07	1.04	1.10	1.11	0.95	1.00	1.06	1.19	1.03	1.08
6	0.88	0.74	1.03	0.99	0.91	0.88	0.98	1.03	0.94	0.96

Figure A1- 1. Map showing the Dearborn air monitoring site
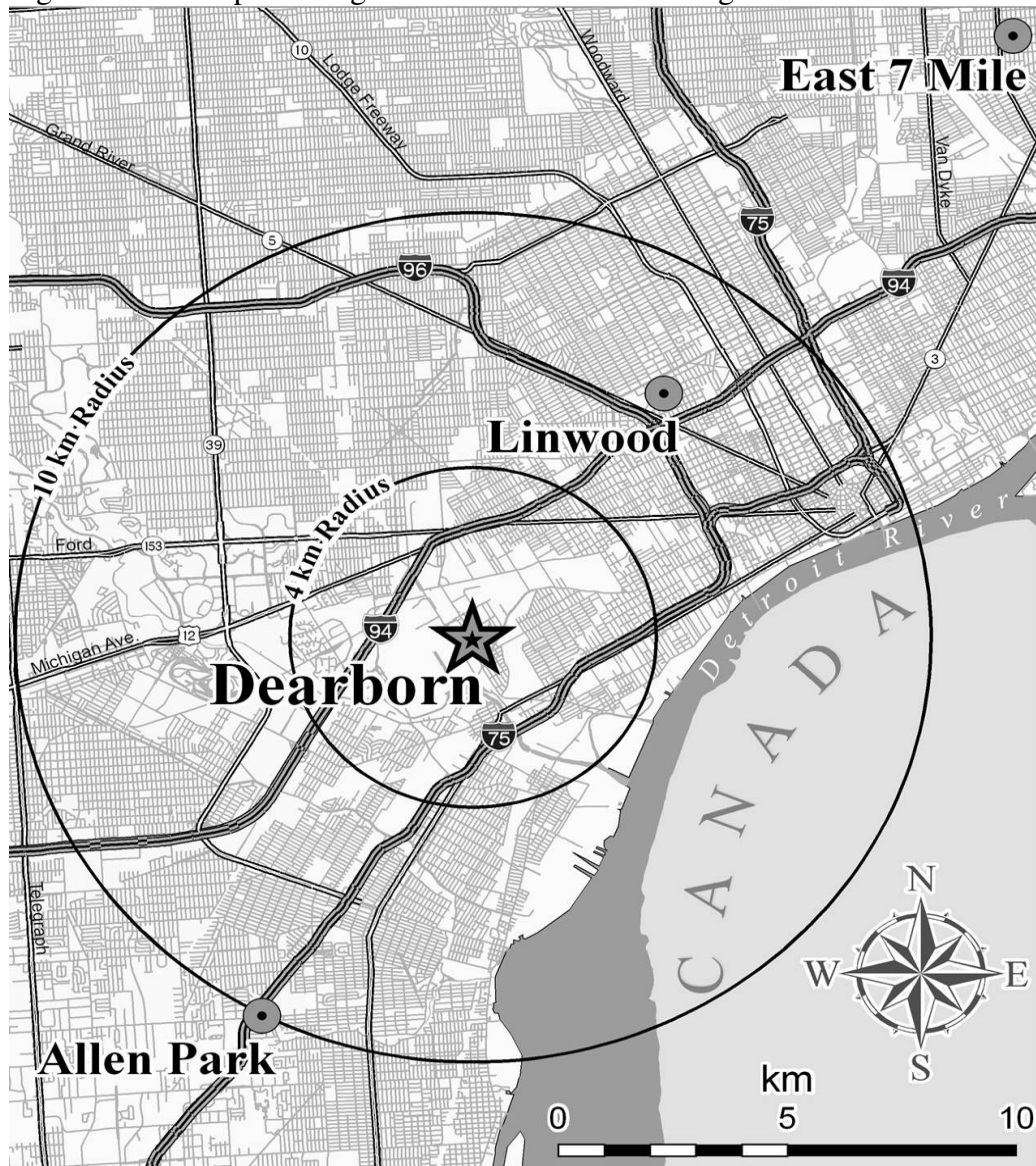
Figure A1 - 2. Concentration of species apportioned to sources for observed UATs
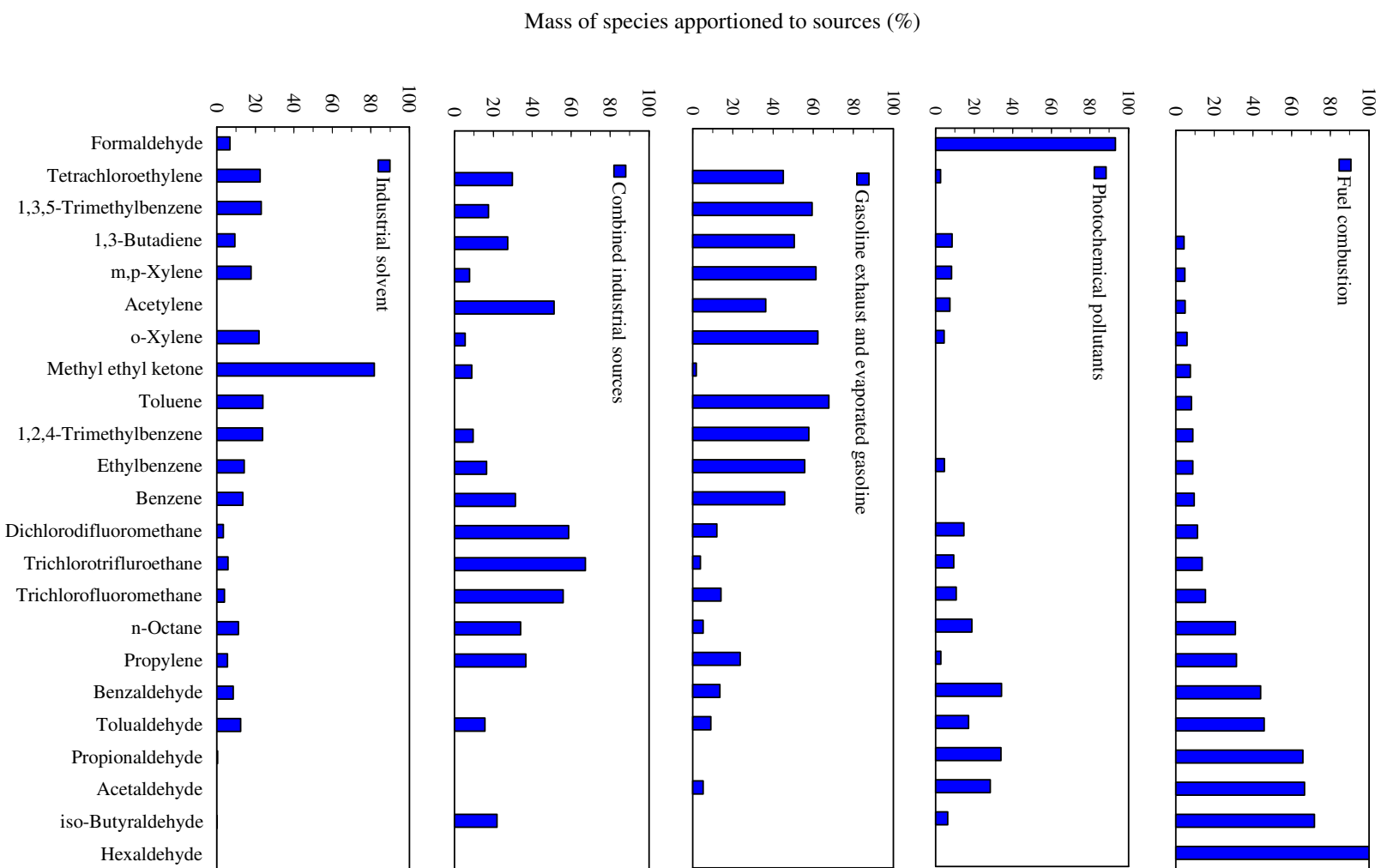
Figure A1- 3. Annual PMF factor contributions for total mass concentrations of observed carbonyls and VOCs
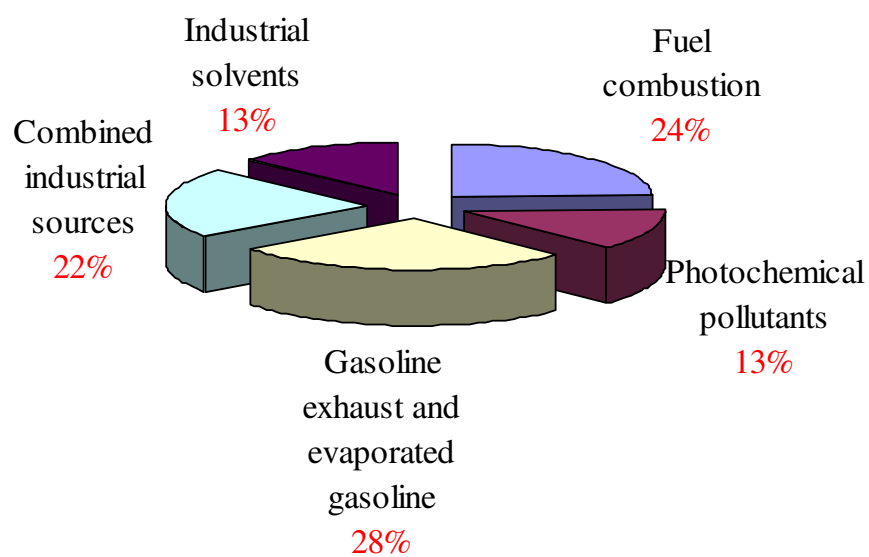
Figure A1 - 4. Concentration of species apportioned to sources for observed UATs and metals
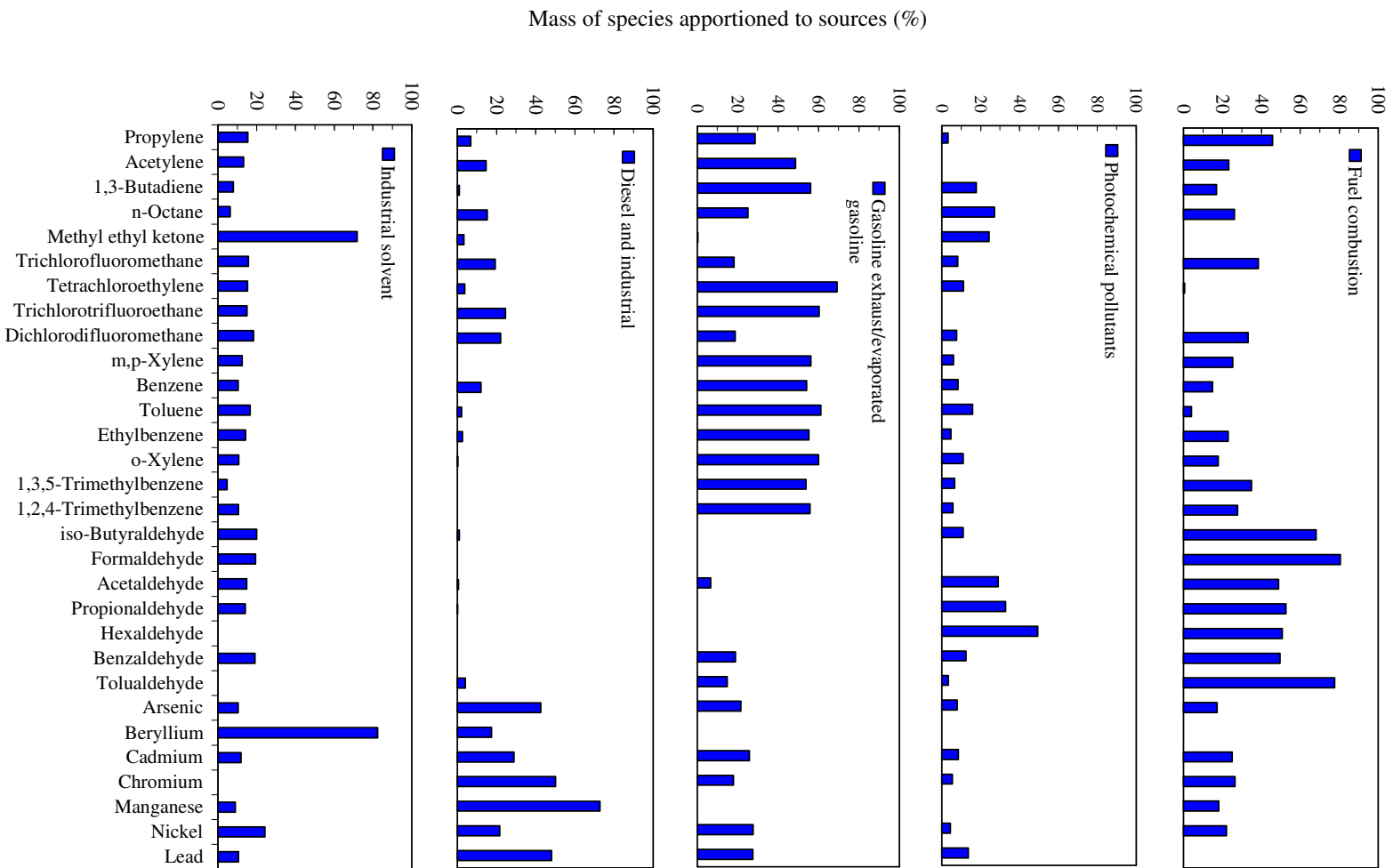
Figure SA1- 1. Absolute relative error models for metals from inter-laboratory comparison.
Only concentrations above MDLs were included. Maximum decile concentrations were excluded.

Regression lines:

90th: $y = 0.21x + 0.23$ $R^2 = 0.94$

75th: $y = 0.11x + 0.14$ $R^2 = 0.98$

50th: $y = 0.07x + 0.09$ $R^2 = 0.95$

25th: $y = 0.03x + 0.07$ $R^2 = 0.94$
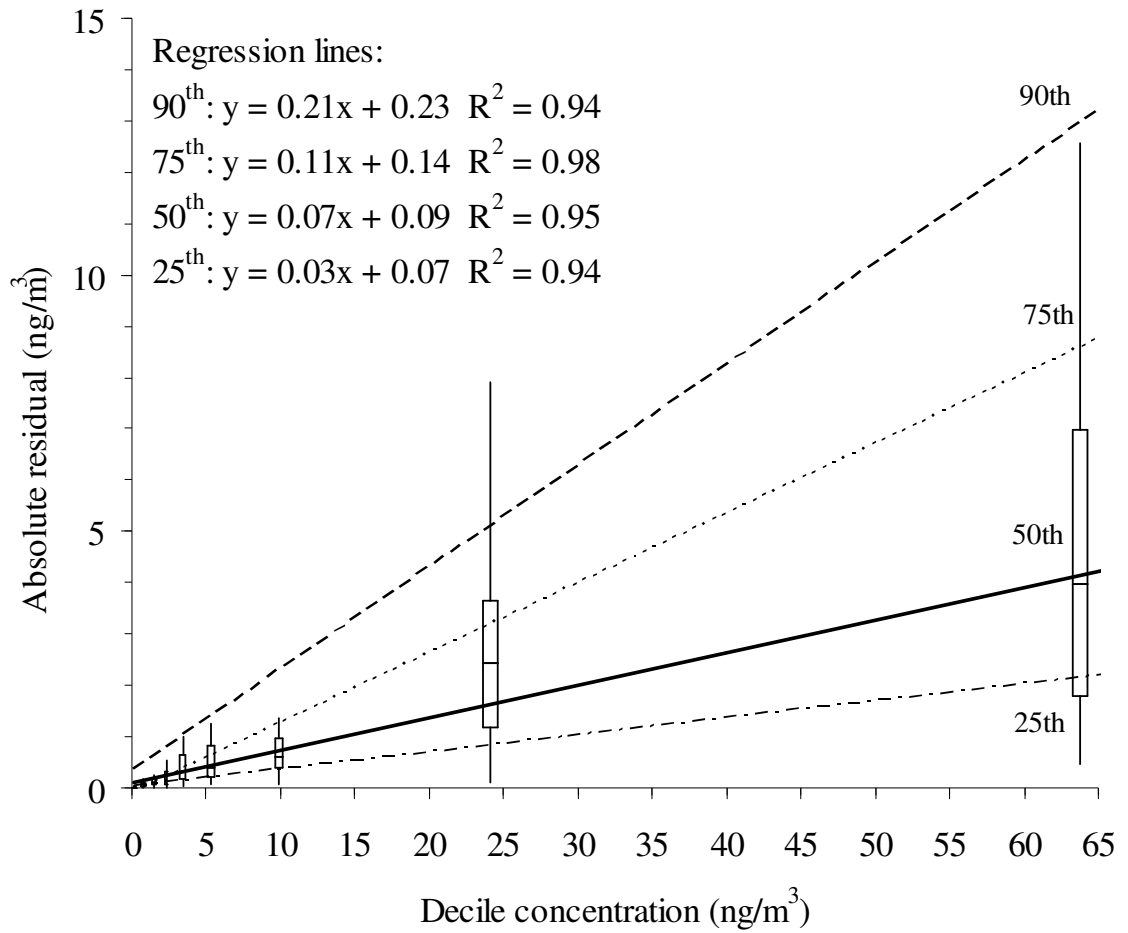
Figure SA1- 2. Annual percentage concentration of each species apportioned to 5 source classes using observed urban air toxics (UATs). Weak species were down-weighted and bad species were excluded.
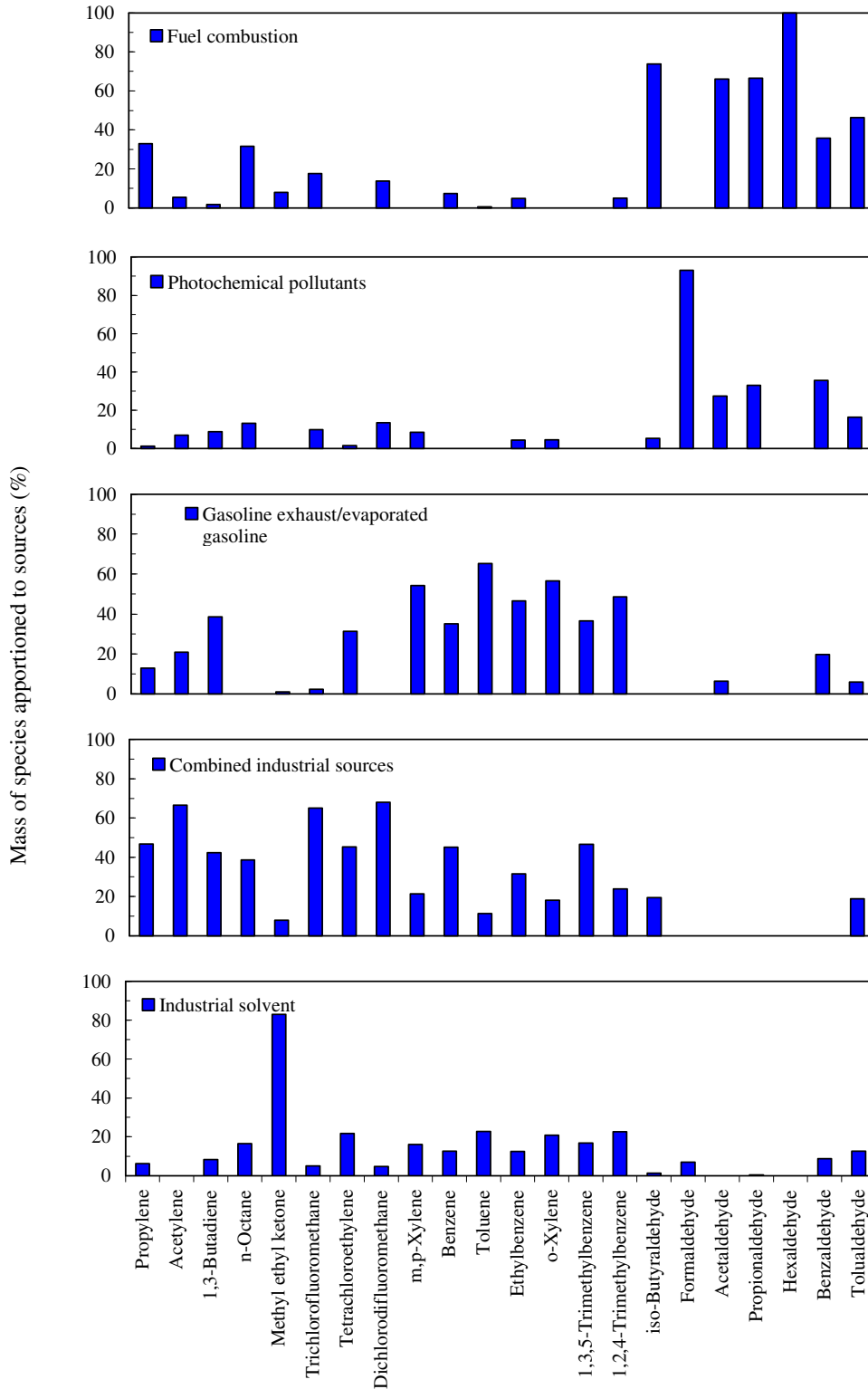
Figure SA1 - 3. Annual percentage of concentration of each species apportioned to 5 source classes using observed urban air toxics (UATs). Weak and bad species were down-weighted
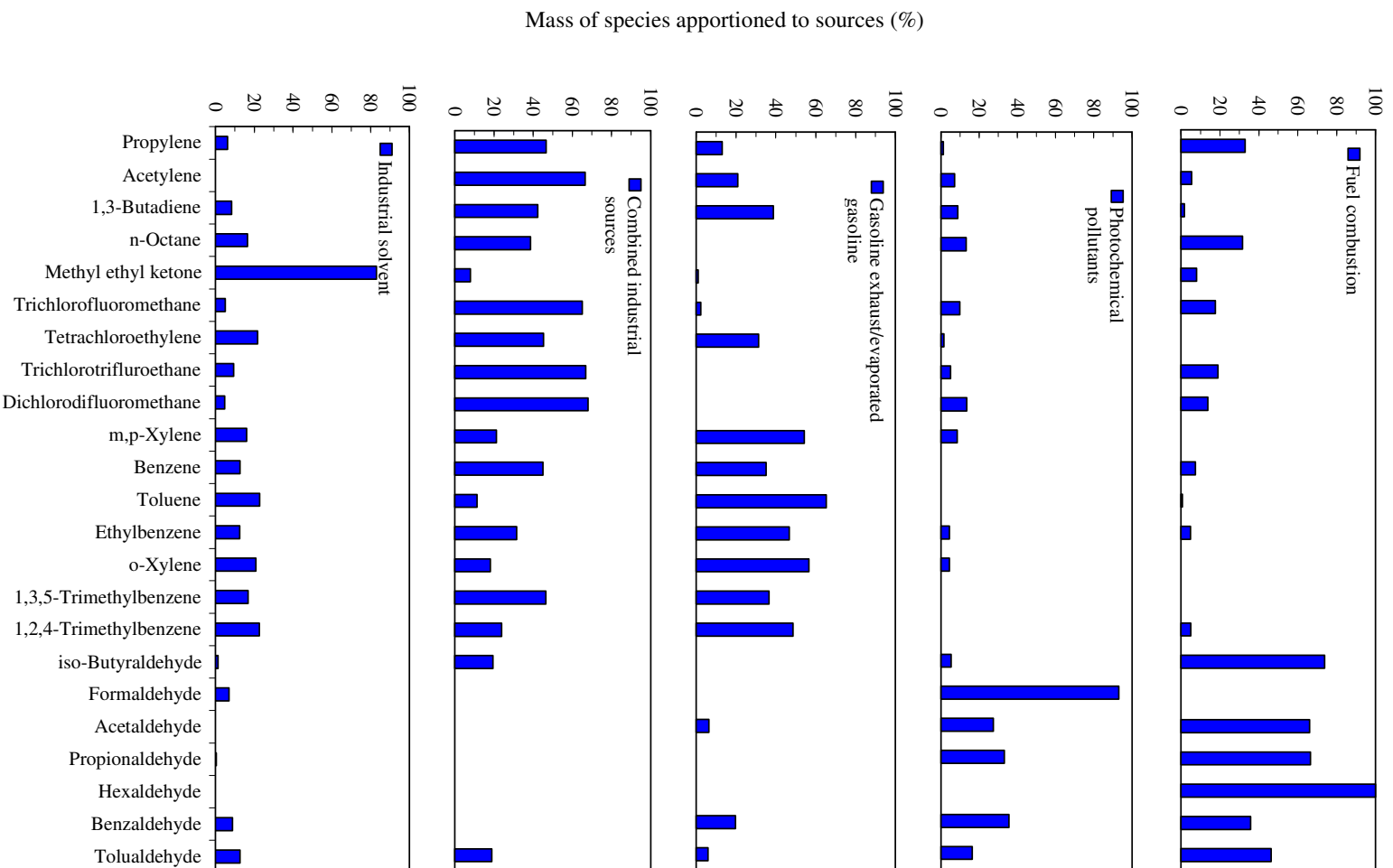
Figure SA1- 4. Annual percentage of concentration of each species apportioned to 6 sources classes using observed urban air toxics (UATs). Weak and bad species were neither down-weighted nor excluded.
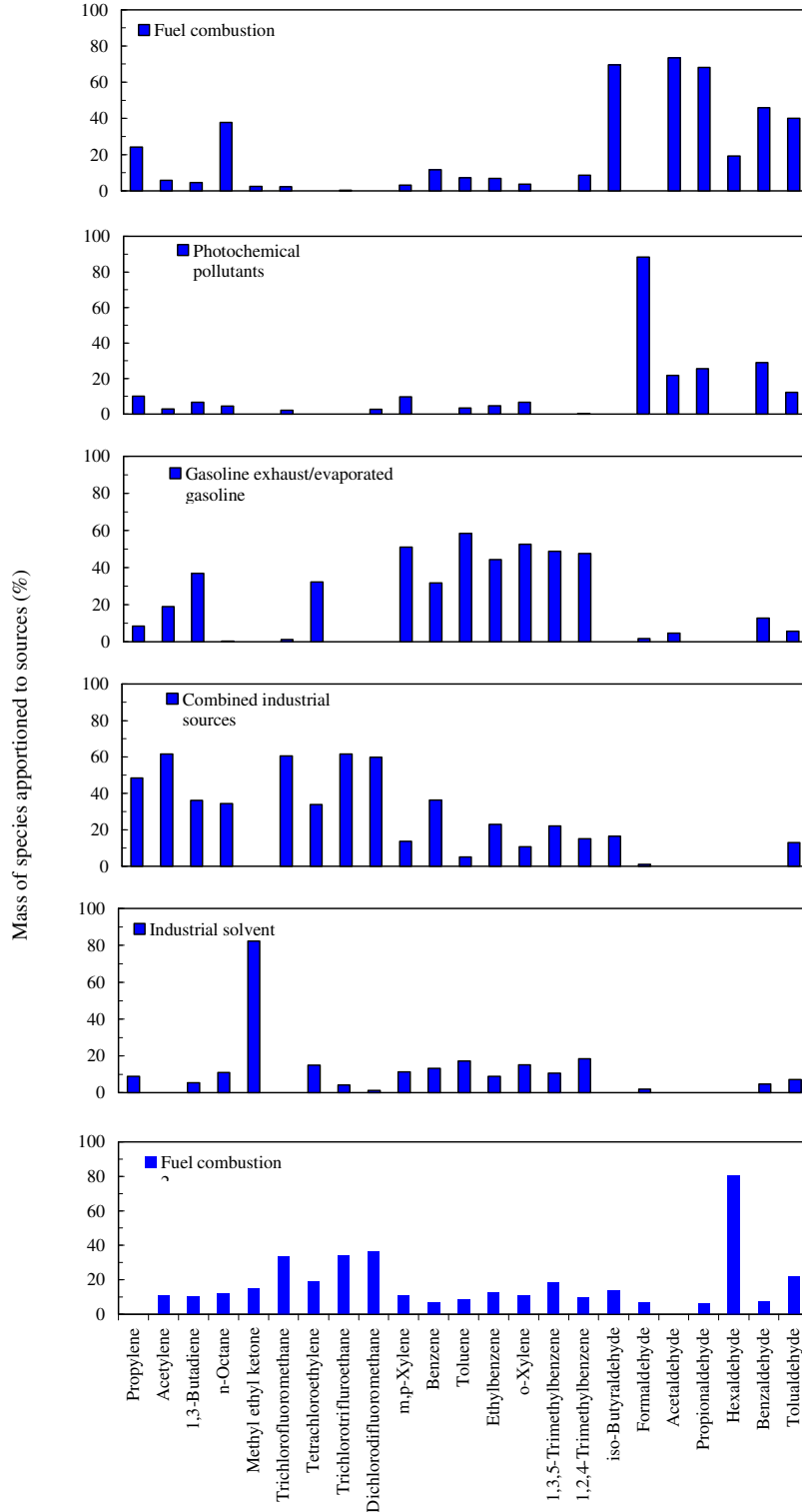
Figure SA1- 5. Coefficients of determinant for 6 source classes using observed UATs. Weak and bad species were neither down-weighted nor excluded.
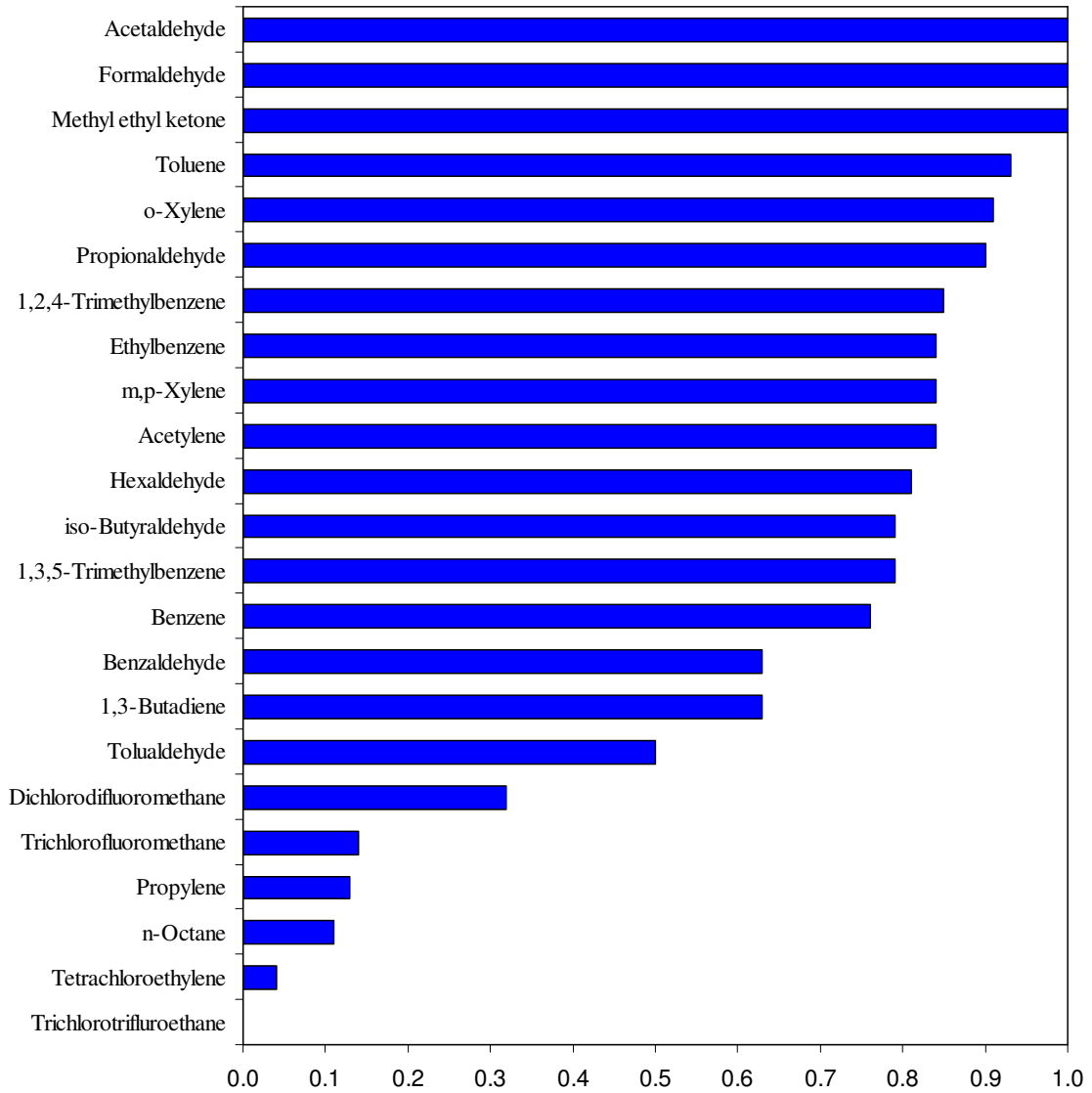
Figure SA1- 6. Percentage of concentration of each species apportioned to 5 source classes using observed urban air toxics (UATs) for spring season. Weak and bad species were neither down-weighted nor excluded.
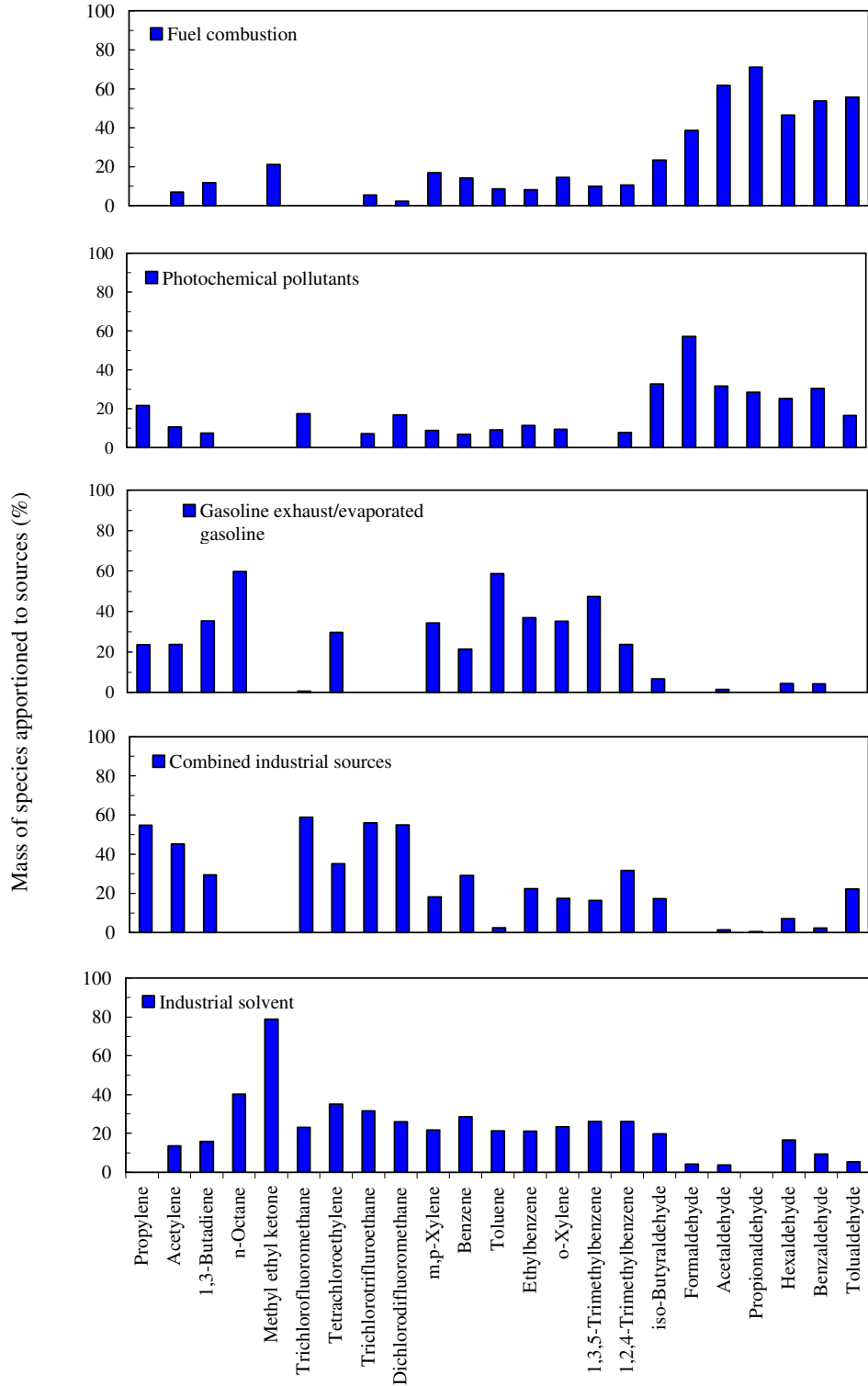
Figure SA1- 7. Percent of concentration of each species apportioned to 5 source classes using observed urban air toxics (UATs) for summer season. Weak and bad species were neither down-weighted nor excluded.
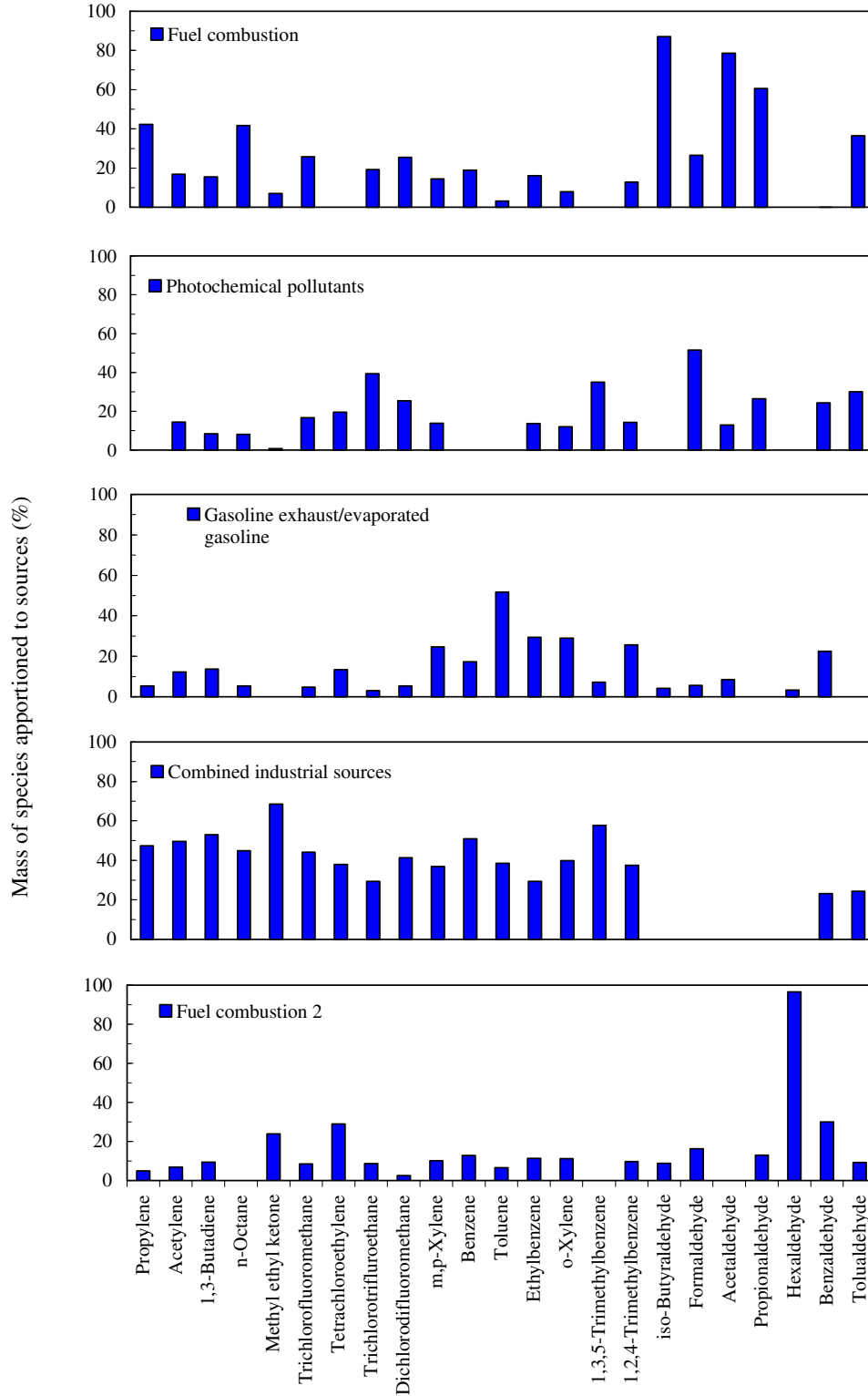
Figure SA1- 8. Percentage of concentration of each species apportioned to 5 source classes using observed urban air toxics (UATs) for fall season. Weak and bad species were neither down-weighted nor excluded.
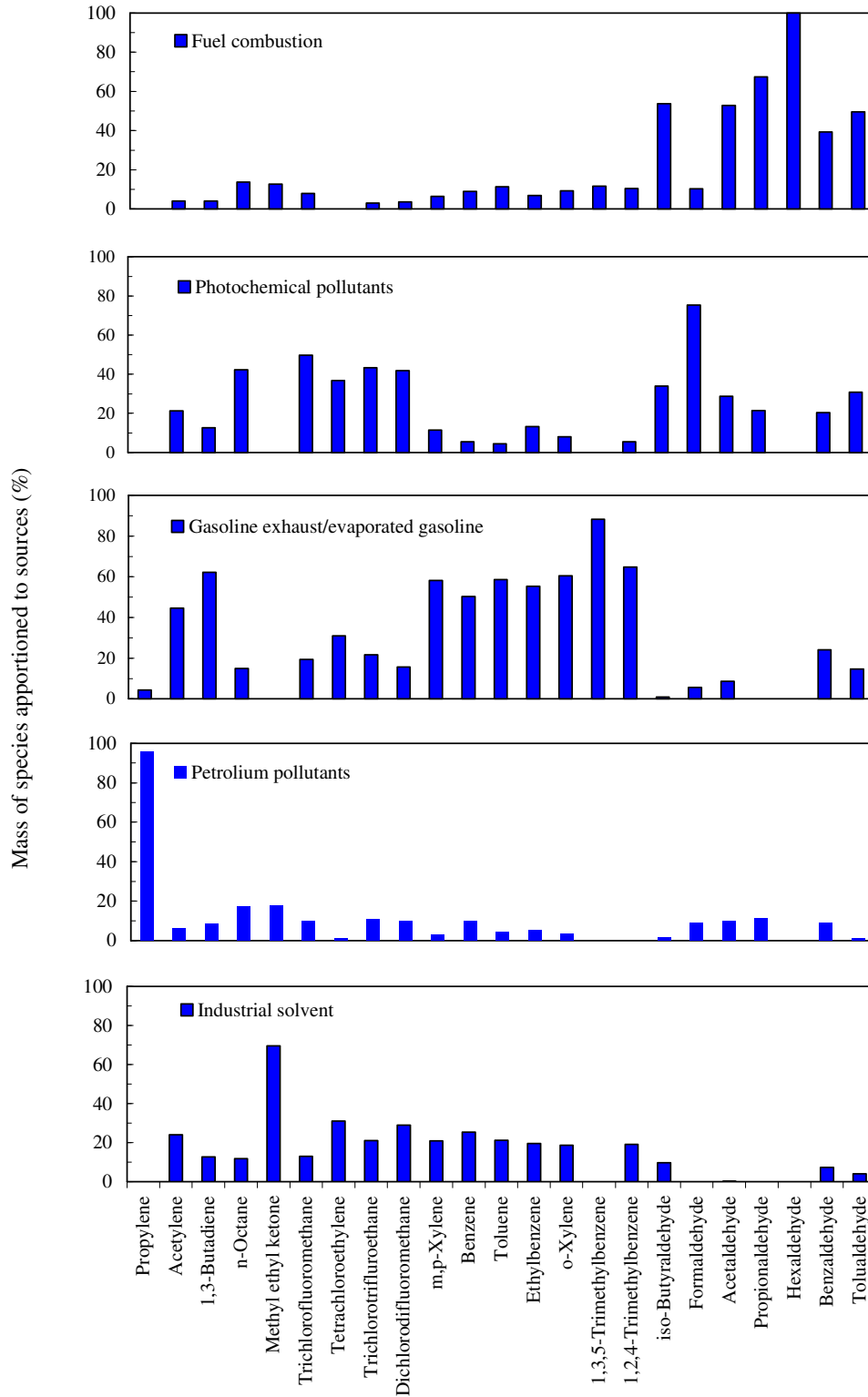
Figure SA1- 9. Percentage of concentration of each species apportioned to 5 source classes using observed urban air toxics (UATs) for winter season. Weak and bad species were neither down-weighted nor excluded.
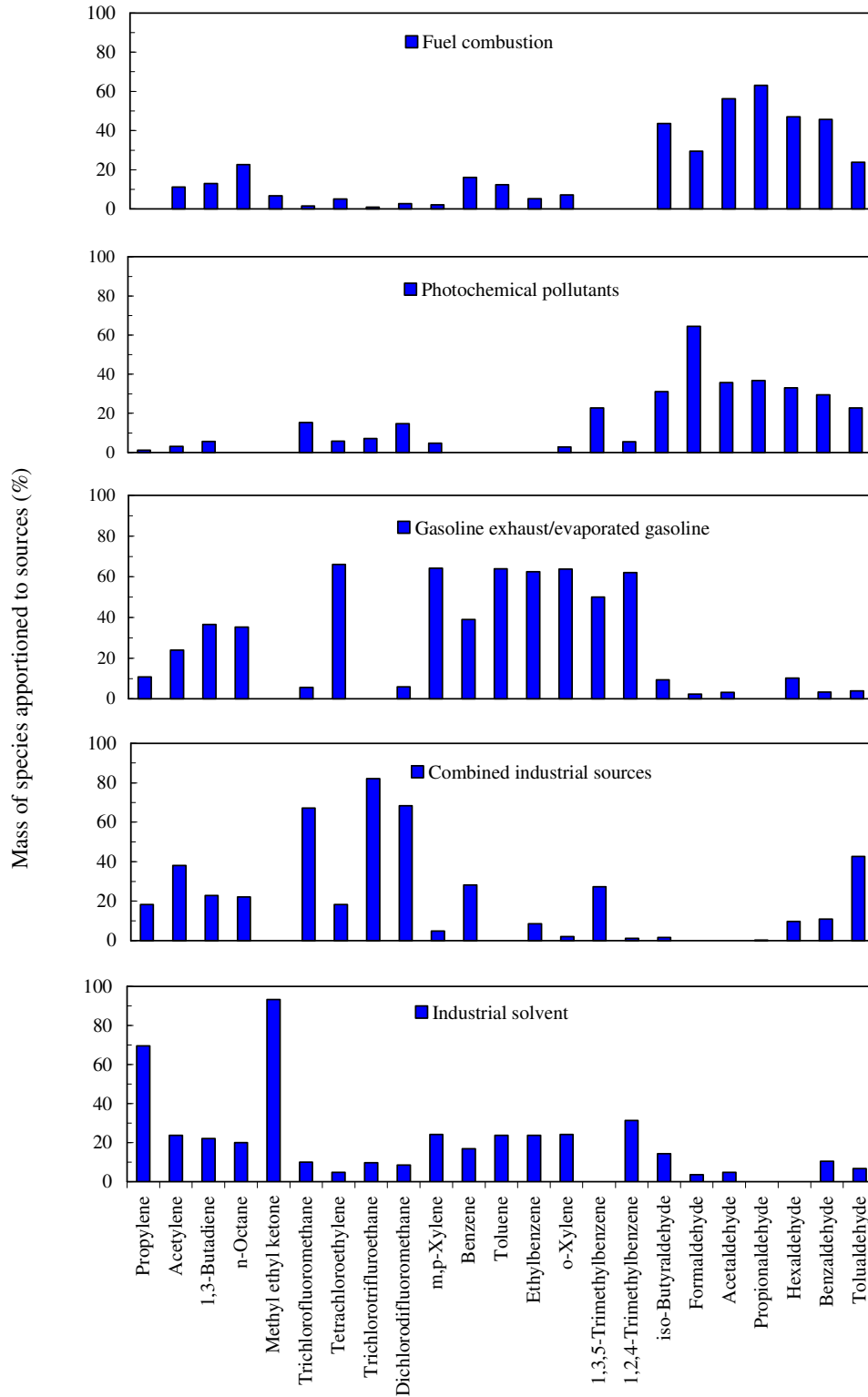
Figure SA1- 10. Annual percentage of concentration of each species apportioned to 5 source classes using imputed urban air toxics (UATs). Weak and bad species were neither down-weighted nor excluded.
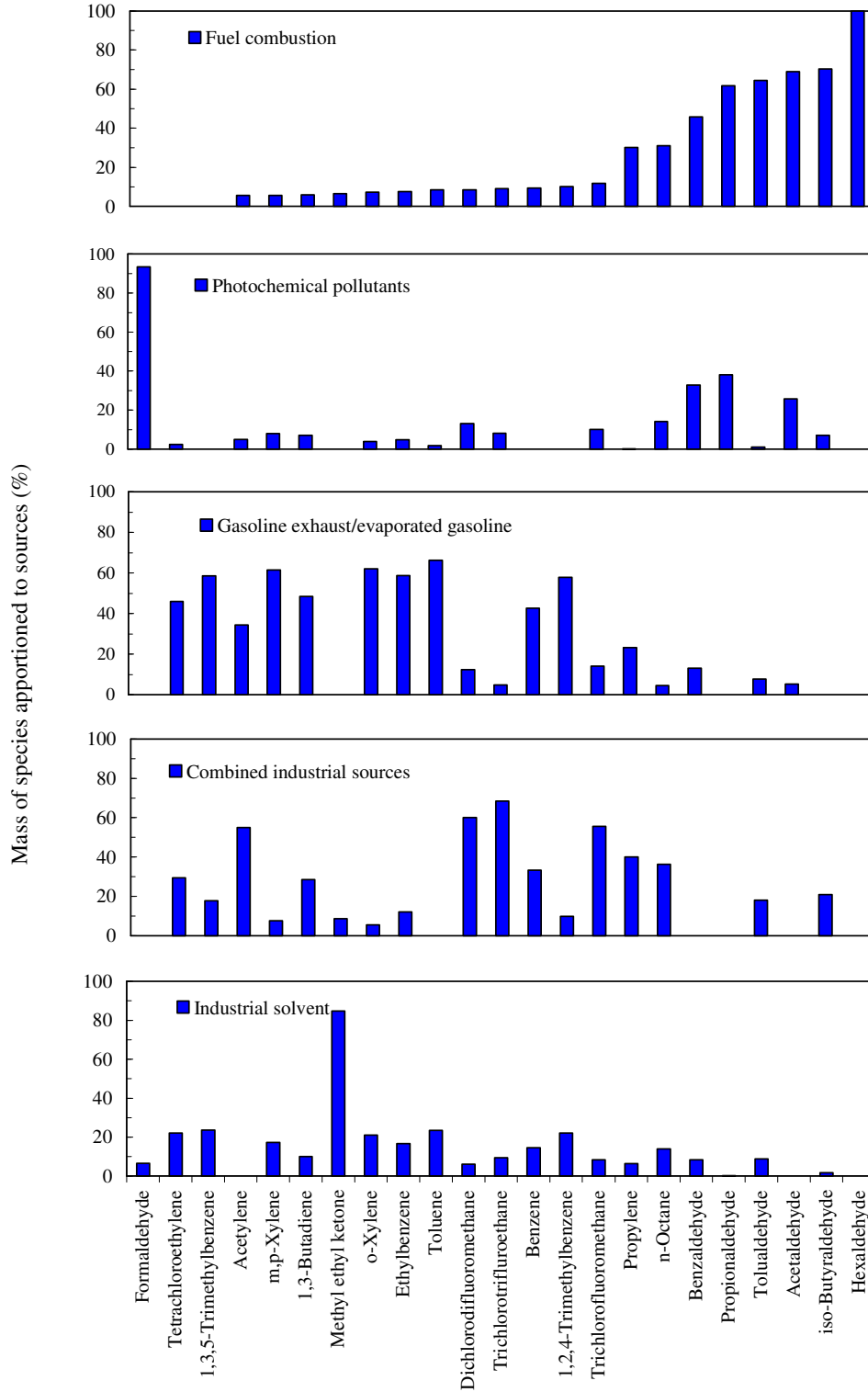
Figure SA1- 11. Coefficients of determination for 5 source class models using imputed data (SI)
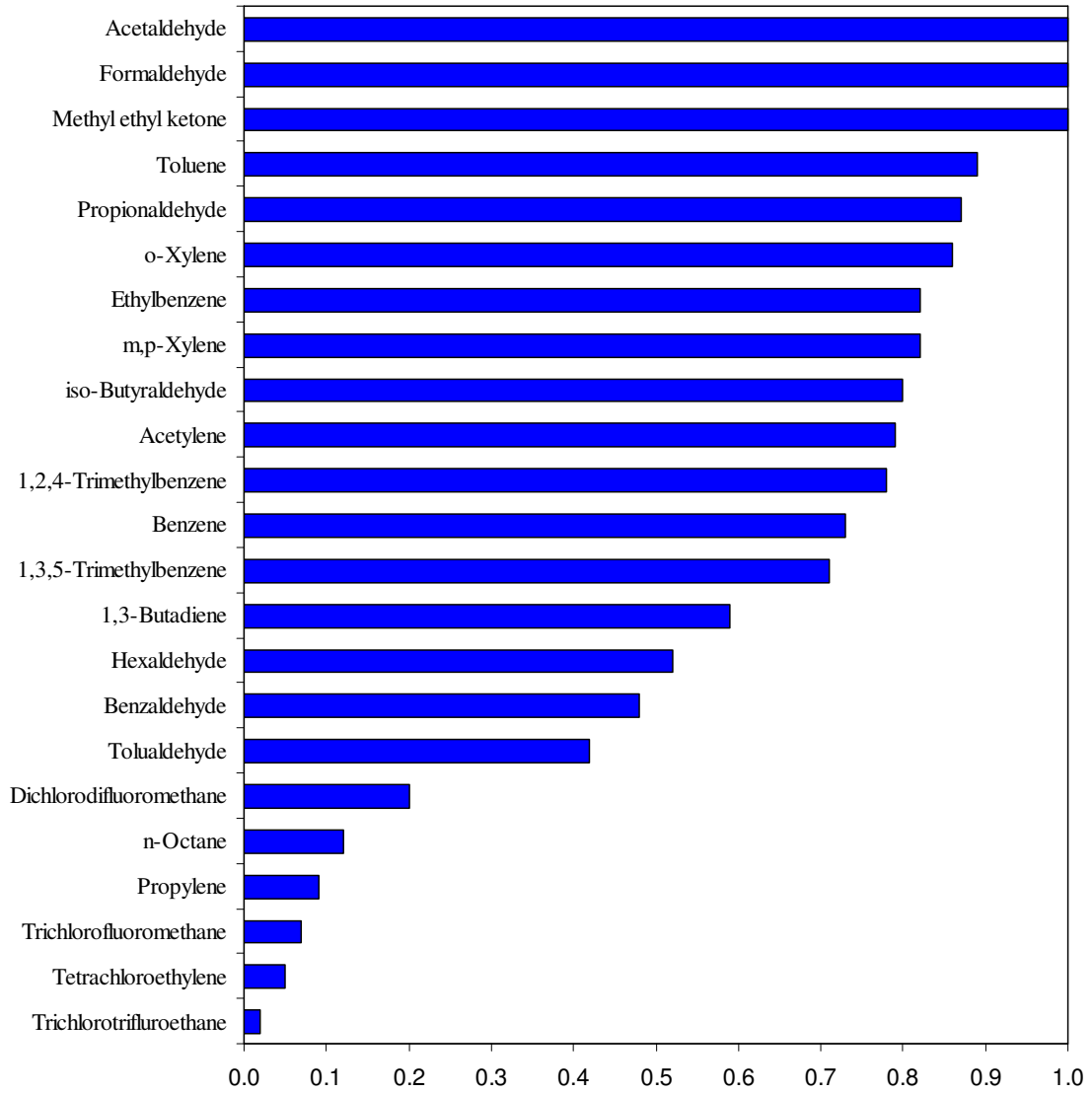
Figure SA1- 12. Annual PMF factor contributions for total concentrations of carbonyls and VOCs using both observed and imputed data
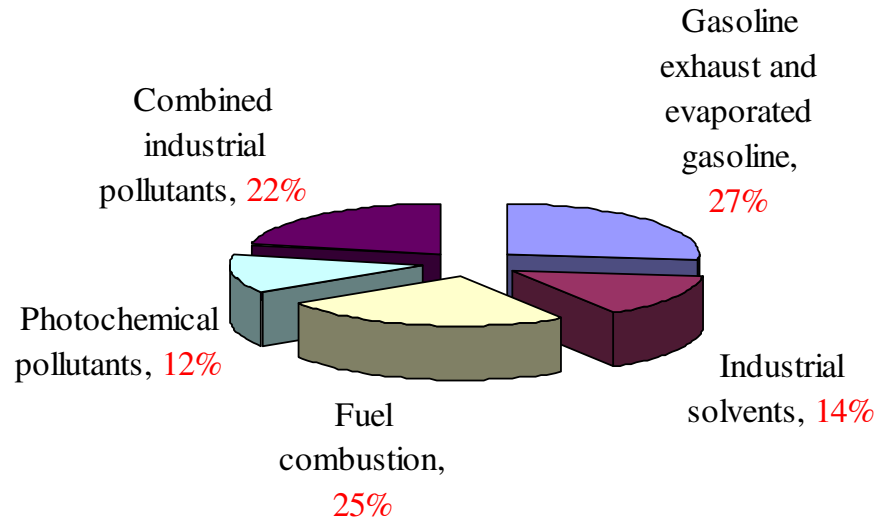
Figure SA1- 13. Principal component analysis (PCA) – Annual factor loadings for 5 source class model using observed UATs
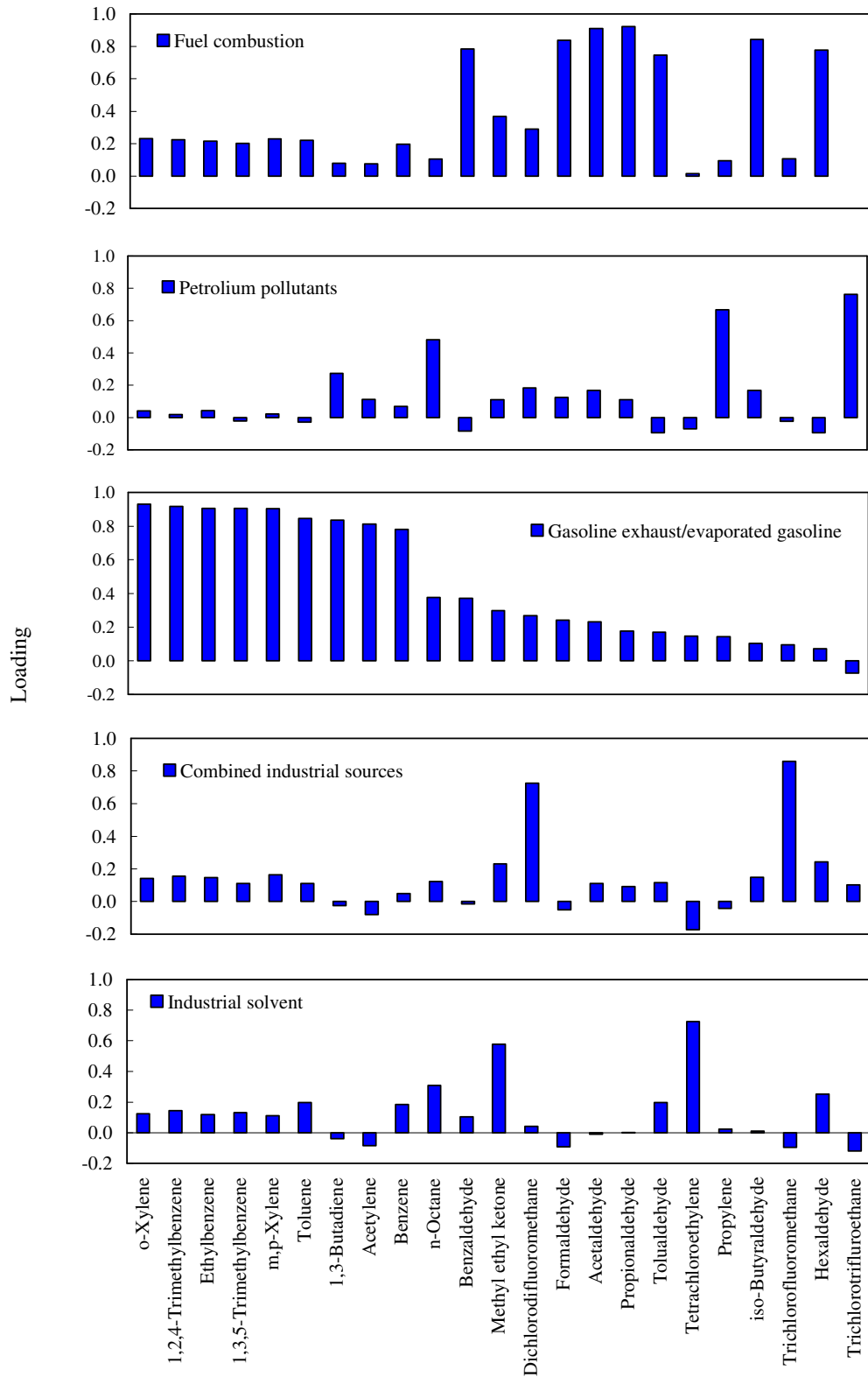
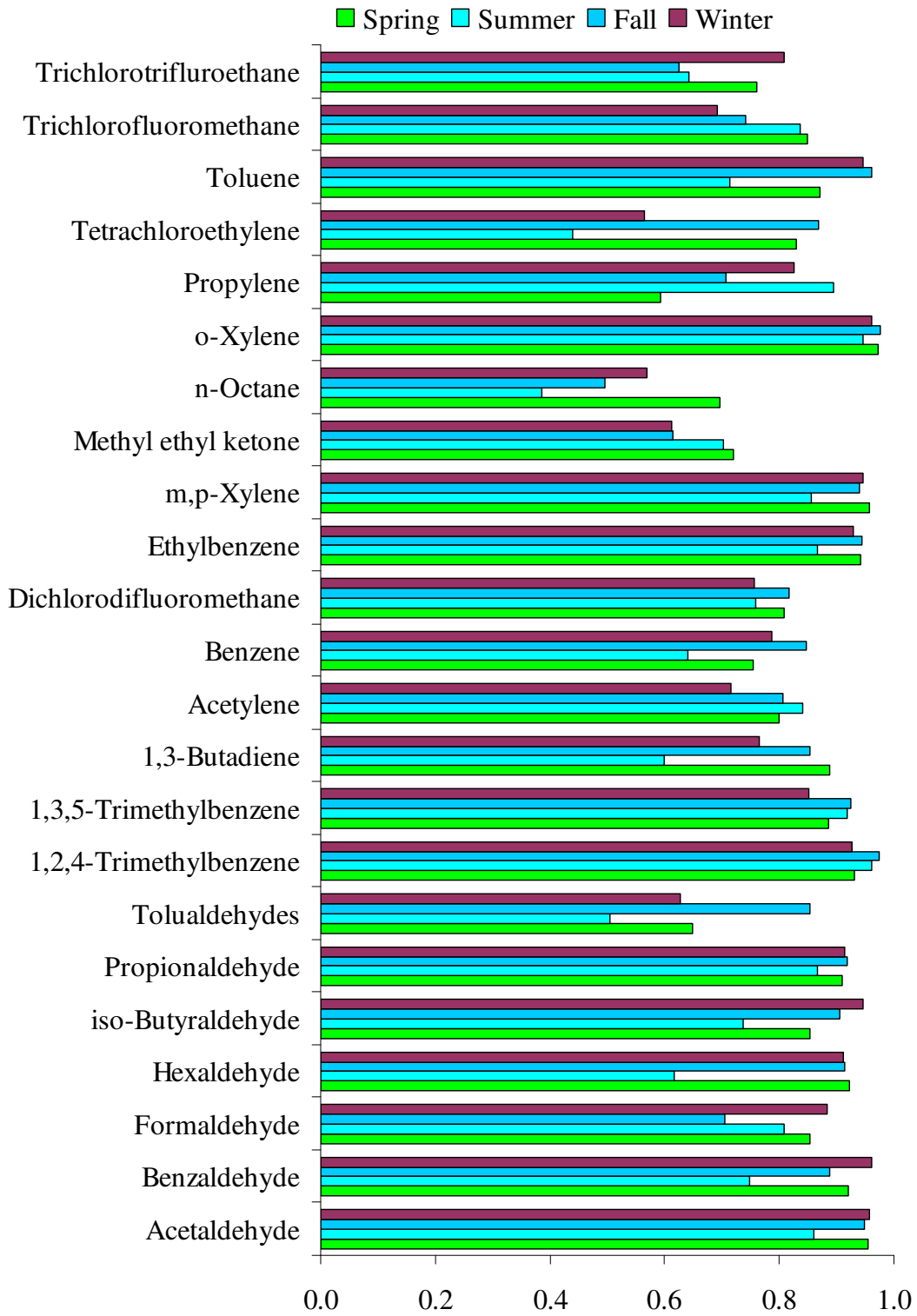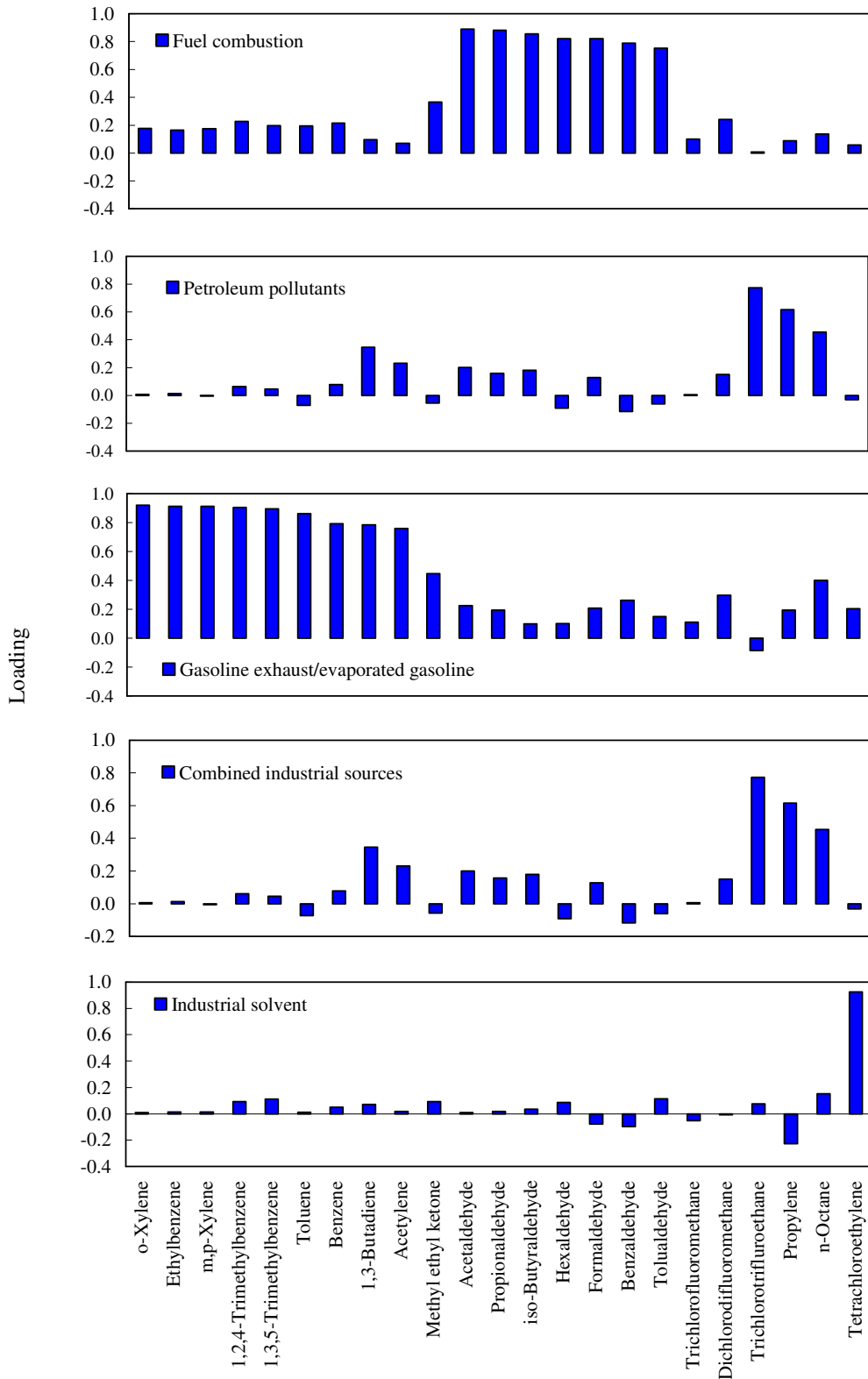Figure SA1- 14. PCA – Annual factor loadings for 6 source class models using observed UATs
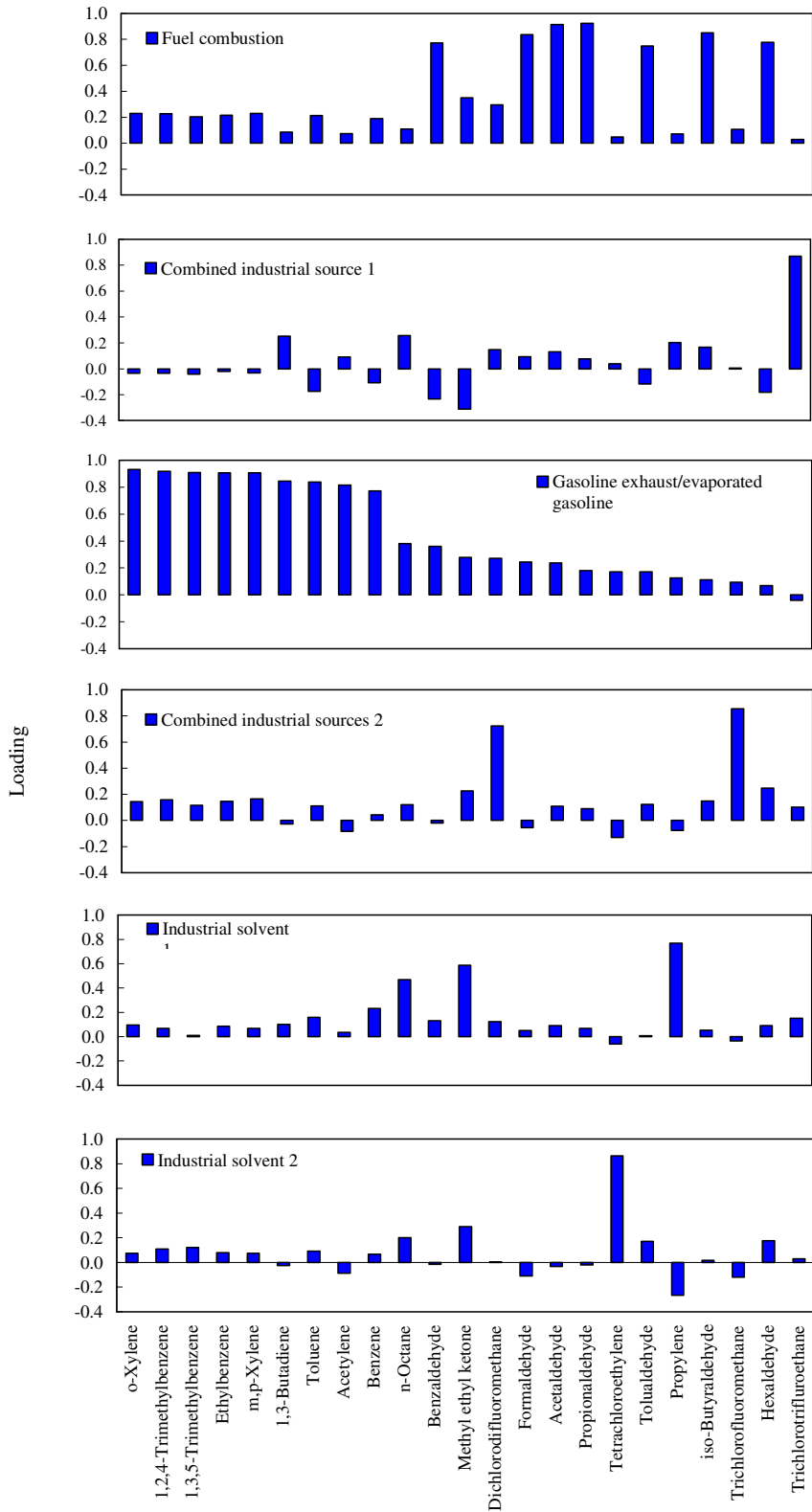
Figure SA1- 15. PCA -Variance explained for 5 and 6 source class models using observed UATs
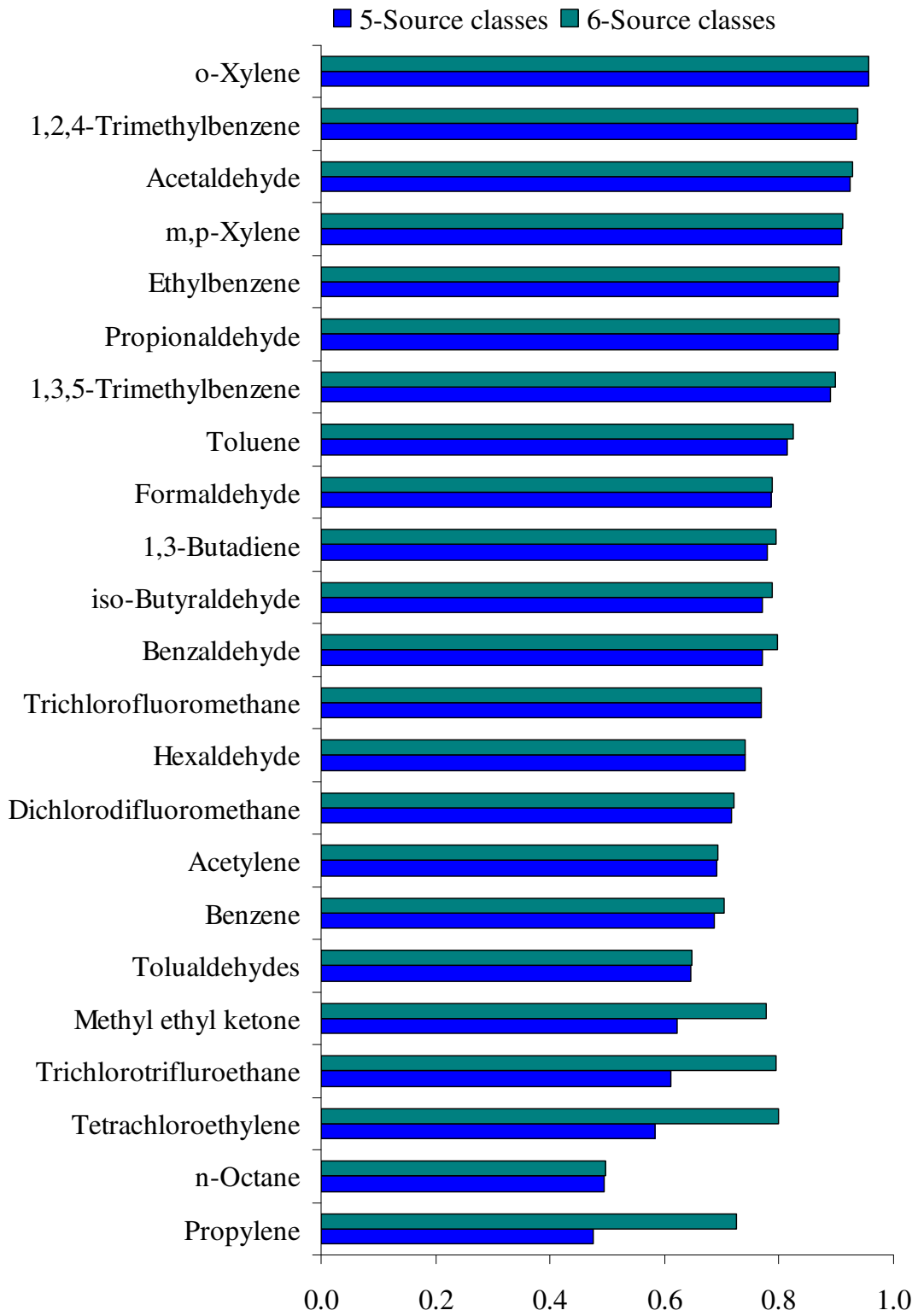
Figure SA1- 16. PCA – Factor loadings for 5 source classes using observed UATs for spring season
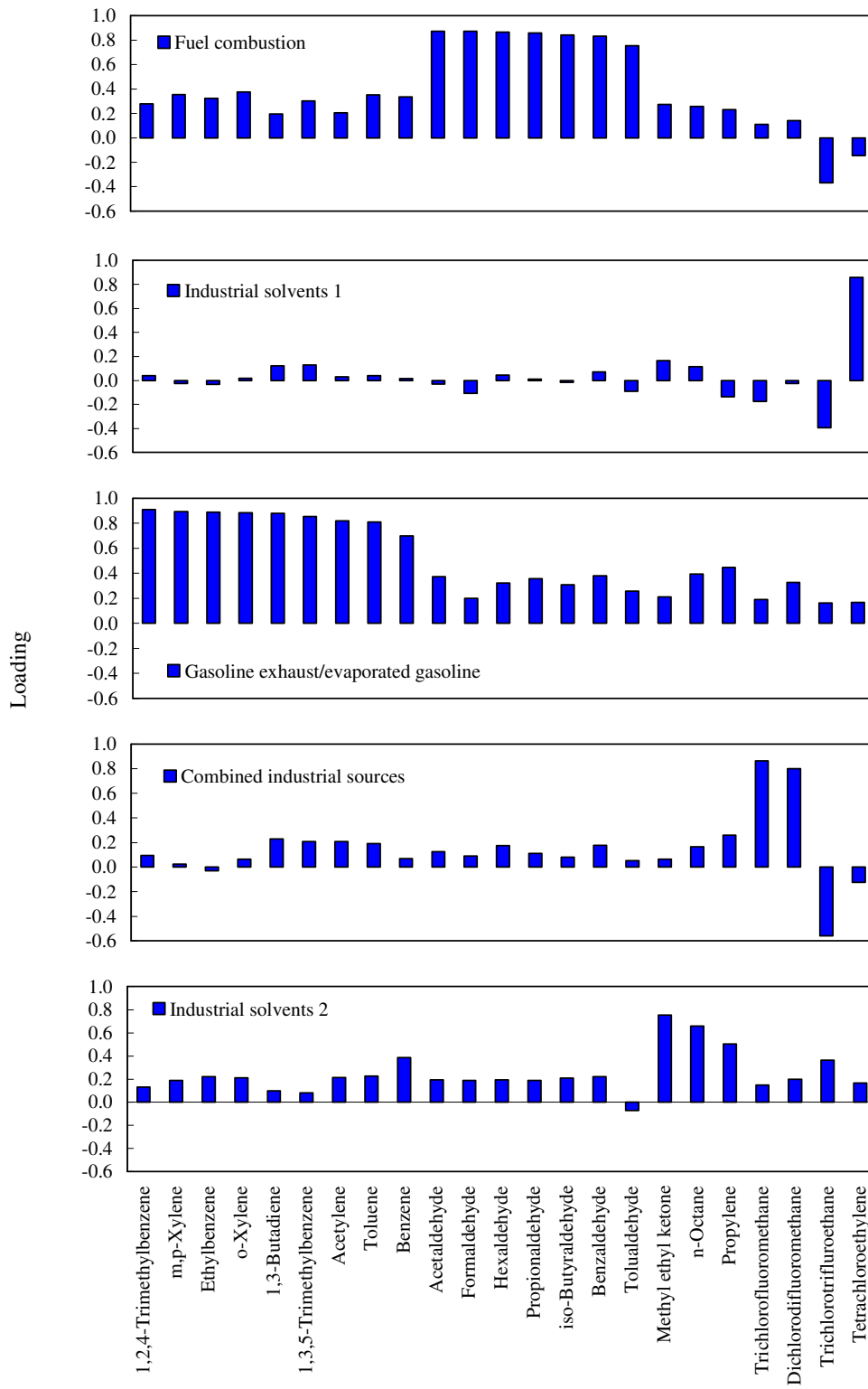
Figure SA1- 17. PCA – Factor loadings for 5 source classes using observed UATs for summer season
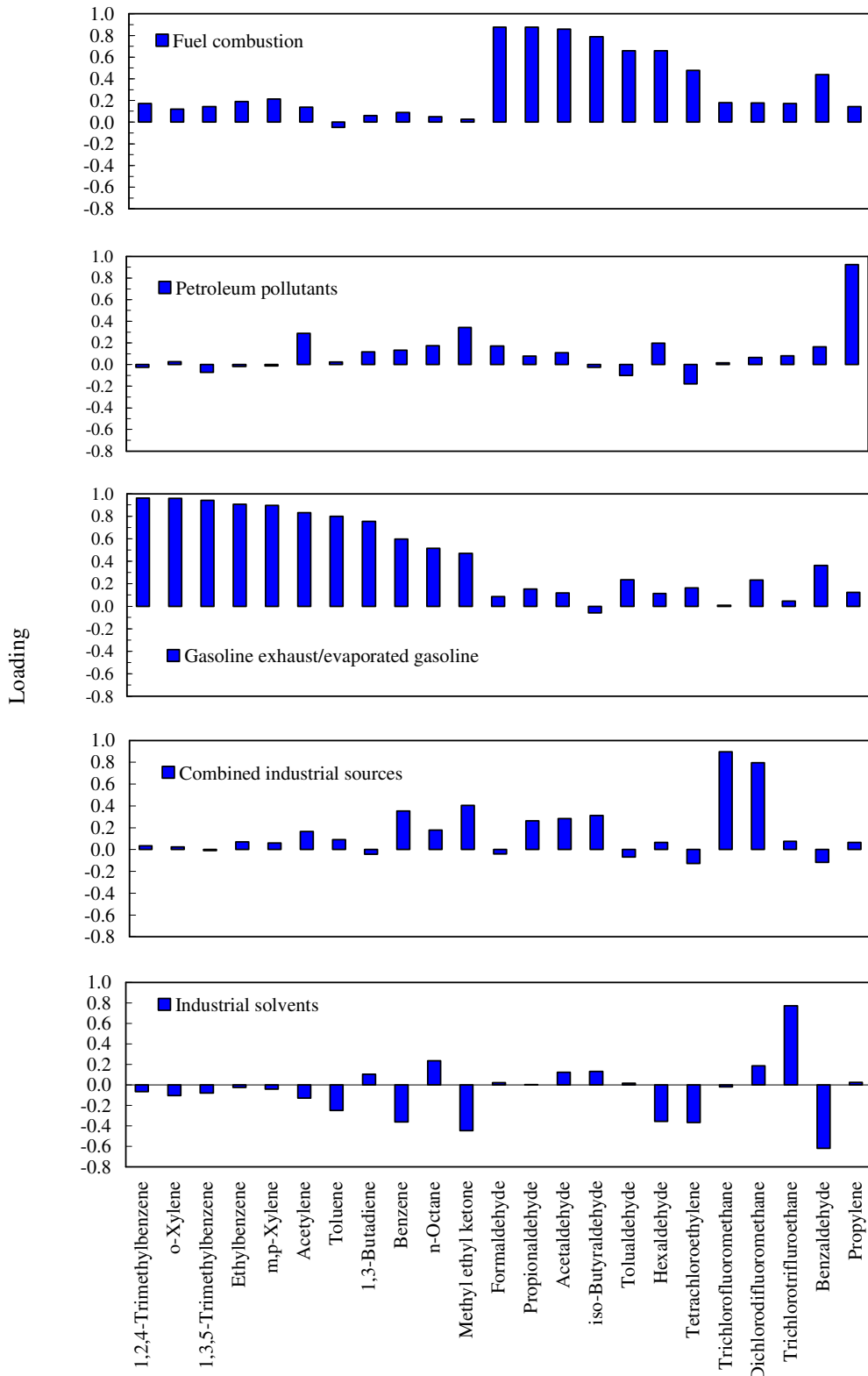
Figure SA1- 18. PCA – Factor loadings for 5 source classes using observed UATs for fall season
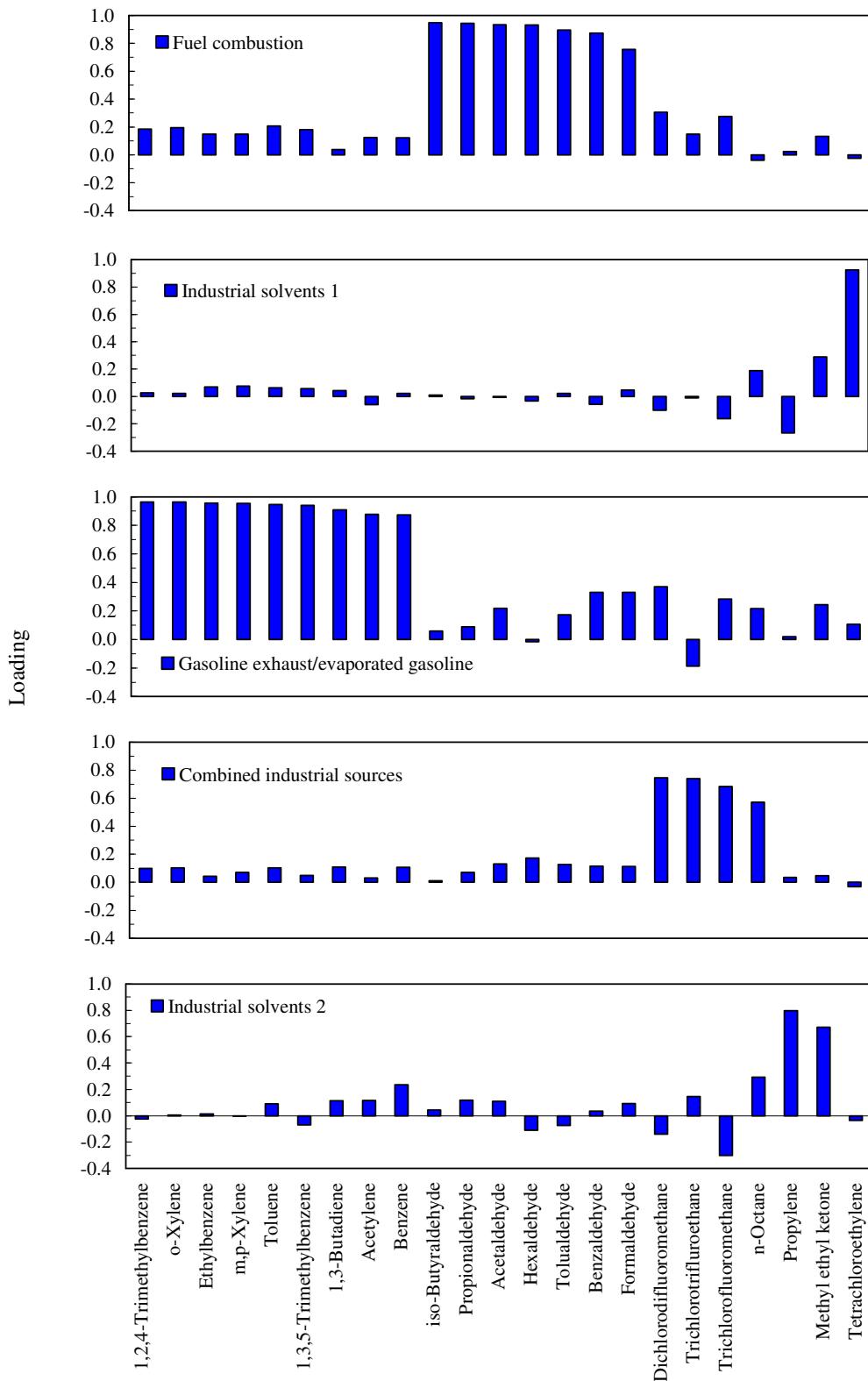
Figure SA1- 19. PCA – Factor loadings for 5 source classes using observed UATs for winter season
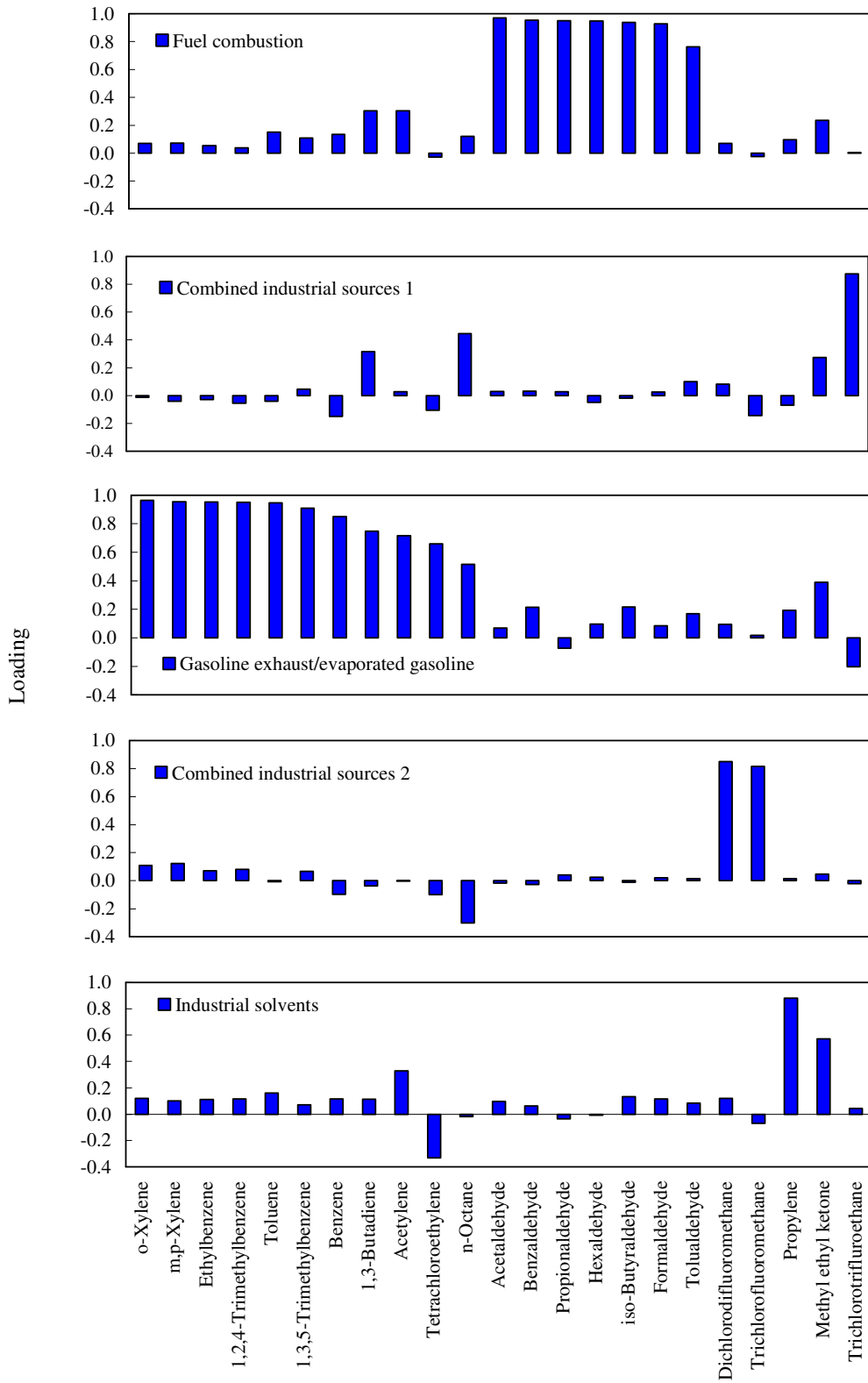
Figure SA1- 20. PCA -Variance explained for 5 source classes of observed UATs by seasons

Figure SA1- 21. Principal component analysis (PCA) – Annual factor loadings for 5 source classes using imputed UATs data

Figure SA1- 22. Principal component analysis (PCA) – Annual factor loadings for 6 source classes using imputed UATs data
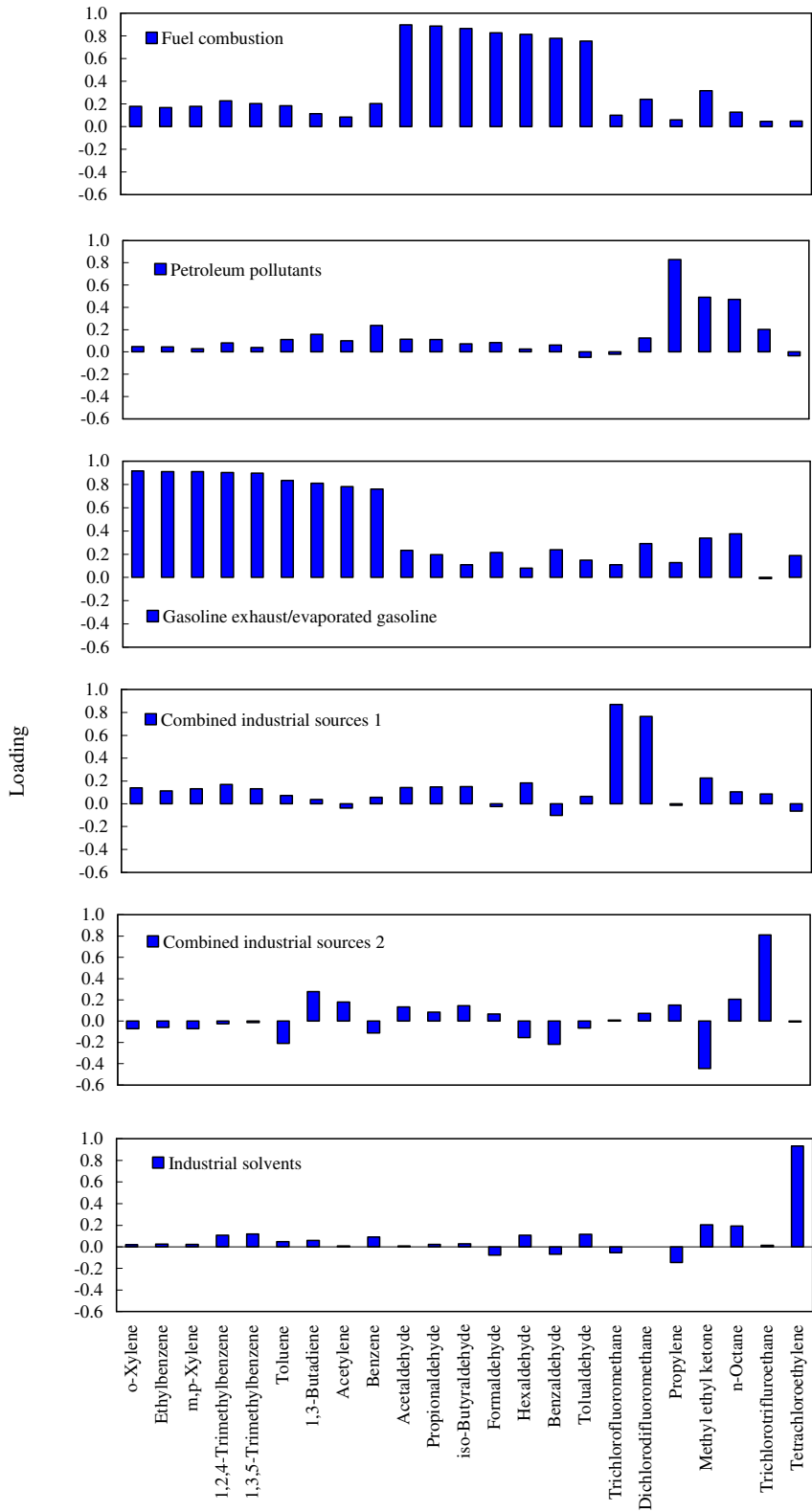
Figure SA1- 23. PCA -Variance explained for 5 and 6 source classes of imputed UATs data
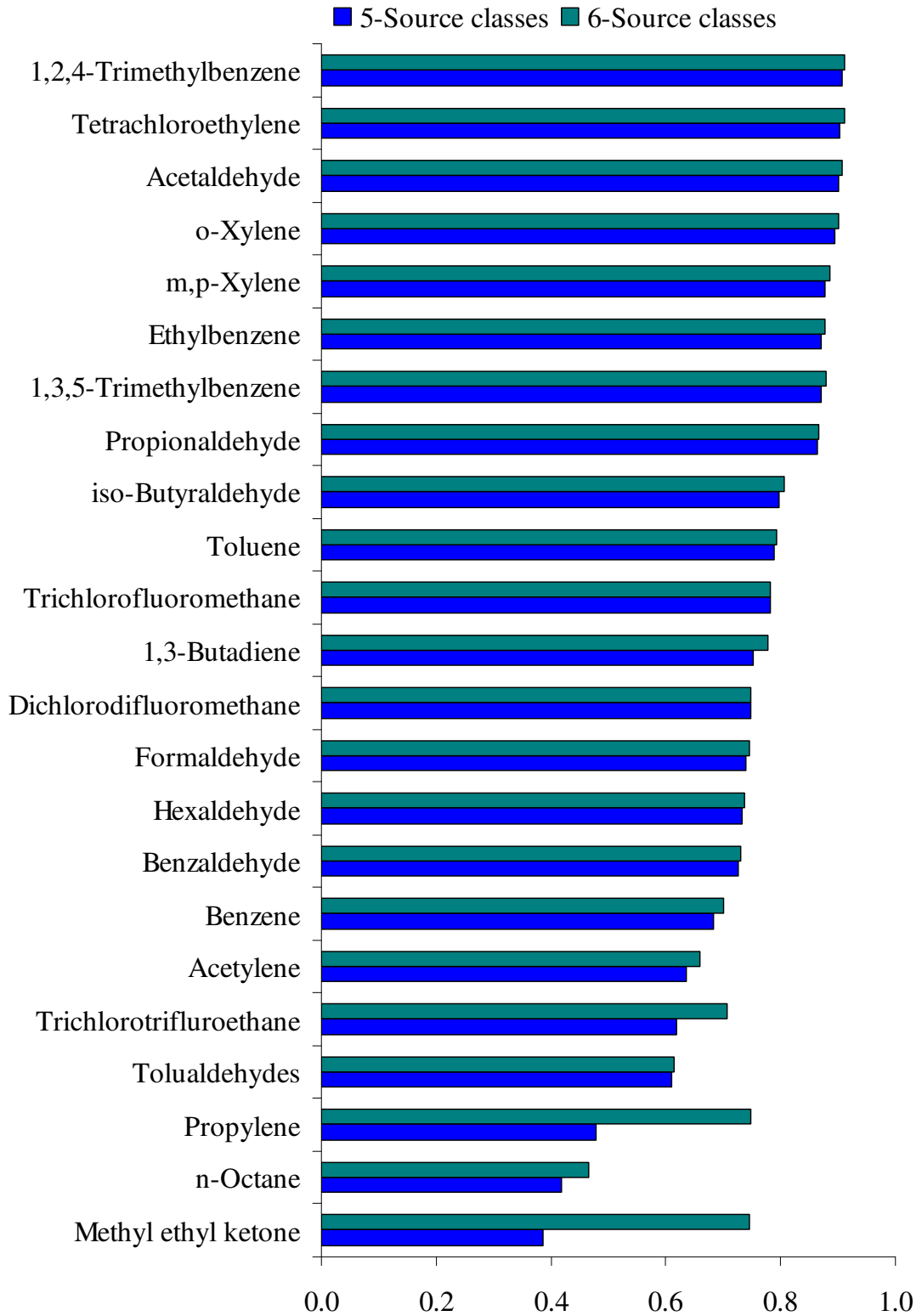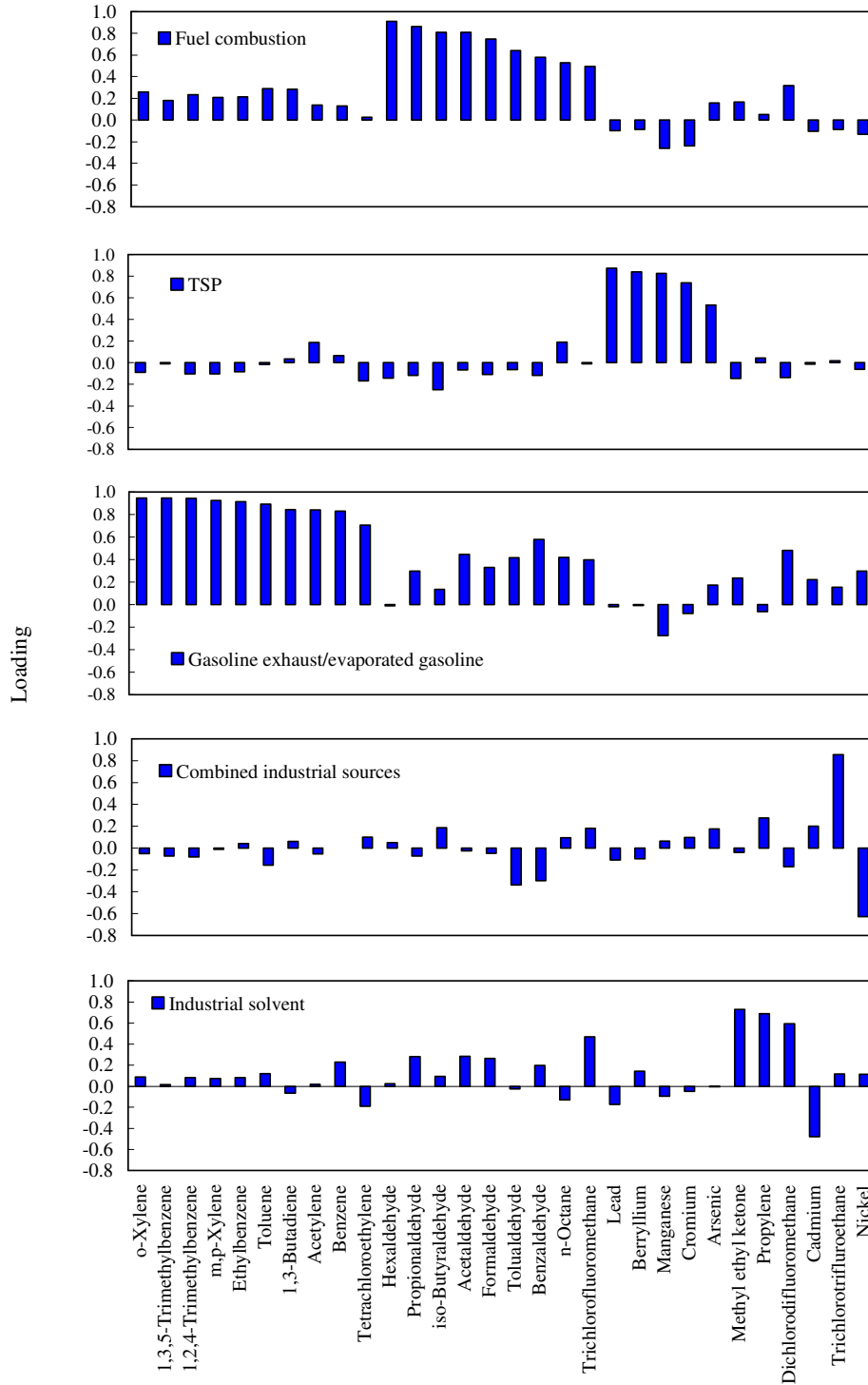
Figure SA1- 24. Principal component analysis (PCA) – Annual factor loadings for 5 source classes using observed UATs and metals data

Loading

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Appendix 2

Journal paper: Le, HQ; Batterman, SA; Wahl, RL. Reproducibility and Imputation of Air Toxics Data. J. Environ. Monit., 2007, 9, 1358-1372.

Reproducibility and imputation of air toxics data†

Hien Q. Le,[a] Stuart A. Batterman*[a] and Robert L. Wahl[b]

Ambient air quality datasets include missing data, values below method detection limits and outliers, and the precision and accuracy of the measurements themselves are often unknown. At the same time, many analyses require continuous data sequences and assume that measurements are error-free. While a variety of data imputation and cleaning techniques are available, the evaluation of such techniques remains limited. This study evaluates the performance of these techniques for ambient air toxics measurements, a particularly challenging application, and includes the analysis of intra- and inter-laboratory precision. The analysis uses an unusually complete-dataset, consisting of daily measurements of over 70 species of carbonyls and volatile organic compounds (VOCs) collected over a one year period in Dearborn, Michigan, including 122 pairs of replicates. Analysis was restricted to compounds found above detection limits in $\geq 20\%$ of the samples. Outliers were detected using the Gumbell extreme value distribution. Error models for inter- and intra-laboratory reproducibility were derived from replicate samples. Imputation variables were selected using a generalized additive model, and the performance of two techniques, multiple imputation and optimal linear estimation, was evaluated for three missingness patterns. Many species were rarely detected or had very poor reproducibility. Error models developed for seven carbonyls showed median intra- and inter-laboratory errors of 22% and 25%, respectively. Better reproducibility was seen for the 16 VOCs meeting detection and reproducibility criteria. Imputation performance depended on the compound and missingness pattern. Data missing at random could be adequately imputed, but imputations for row-wise deletions, the most common type of missingness pattern encountered, were not informative. The analysis shows that air toxics data require significant efforts to identify and mitigate errors, outliers and missing observations, and that these steps are essential and should be performed prior to using these data in receptor, exposure, health and other applications.

1. Introduction

Most air quality data have been collected for regulatory purposes, such as determining compliance with ambient air quality standards. The use of the same data for other purposes, including epidemiological studies, while convenient and inexpensive, can place different and often more stringent demands on data quality and completeness, since most statistical methods assume that observations are error-free and complete, *i.e.*, datasets are fully populated. Data quality is an important and often unappreciated issue, especially for toxic air pollutants where measurement uncertainties can be large. In general, monitoring methods for toxics have been only partially automated, samples must be transported from the monitoring site to the laboratory for analysis, and analyses tend to be complex and intensive. These steps increase the likelihood of errors from a variety of sources, *e.g.*, sample contamination. Further, logistical and cost issues generally prohibit air toxics sampling programs from incorporating

many duplicate measurements and other analyses that are necessary to quantify accuracy and precision.

Missing air quality data, another common problem, results from both random and planned events. Random events include power and equipment failures, lost samples or logs, other quality assurance problems, measurement and calibration errors, and faults in data acquisition.[1] Planned events include quality assurance checks (instrument flow, zero and span checks) and calibrations that require that the monitoring instruments be taken off-line. In some cases, pollutants are monitored intermittently, *i.e.*, particulate matter measurements often are collected only every third or sixth day, while ozone may be measured only during the summer "ozone" season. Evaluations of the several approaches that have been used to address problems of missing data have been very limited. Problems of both missingness and quality assurance must be addressed to obtain complete and reliable datasets.

This study evaluates the performance of two imputation methods, optimal linear estimation and multiple imputation, for handling missing air quality data. Performance is tested using an unusually complete urban air toxics dataset containing ambient measurements of volatile organic compounds (VOCs) and carbonyl species. As described below, the imputation of toxics data is particularly challenging, but at the same time highly relevant for epidemiology, source apportionment,

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† Electronic supplementary information (ESI) available: Supplements 1–12, additional materials, figures and tables. See DOI: 10.1039/b709816b

risk assessment and other applications that use ambient air quality data. We also demonstrate several quality assurance (QA) filters and reproducibility/uncertainty models that may be generalizable to other measurements.

2. Background

2.1 Quality assurance issues

Several problems are frequently encountered in ambient air quality datasets, which are grouped together here as QA issues. These issues tend to be especially important for urban air toxics (UATs), more so than for conventional air pollutants, for several reasons. First, toxic measurements of trace metals, VOCs, carbonyls, semi-volatiles and other pollutants may reflect low concentrations that fall below method detection limits (MDLs). For some species, concentrations may rarely, if ever, exceed MDLs. Such 'sparse' data patterns can occur because a specific toxic pollutant simply may not be present, or because the MDL is too high to allow frequent detection. This situation rarely occurs for conventional pollutants, both because these pollutants are ubiquitous due to emissions from numerous sources, and because monitoring instruments have been highly refined and are very sensitive.

Second, high concentration values may be encountered on occasion, even for rarely detected pollutants. These detections (or "hits") may be real and significant, or they may be false positives due to contamination, chemical reactions forming artifacts on the sampling adsorbent, interferences, chromatographic shifts, laboratory errors, or some other reason. Without duplicate samples or additional information, it is difficult or impossible to determine whether a rarely detected compound is a true detection and thus meaningful. High values can be characterized as statistical outliers, e.g., using the Gumbell extreme value distribution originally developed for hydrologic systems[2][4] and applied to air quality data,[5,6] and which we later demonstrate in this paper. However, the designation of a measurement as a statistical outlier does not indicate whether or not the concentration was actually experienced.

Third, it is difficult to characterize the measurement precision and accuracy for commonly-detected toxic pollutants, and exceedingly difficult for rarely detected pollutants. Compared to conventional (so-called criteria) pollutants, where relative precisions and accuracies are well-characterized and in the 10% range (or lower), the few available estimates suggest much greater variability.[7] In the (unusually complete) Dearborn study described later, for example, duplicate samples were available on 120 days, and a compound detected on say 5% of days would be expected to have only ~6 duplicate pairs available, too small a sample to construct meaningful statistics. Due to the lack of reference methods and standards, co-located replicate samples and intra- and inter-laboratory comparisons are used to indicate agreement, but in practice, such exercises are infrequent and are limited to largely analytical uncertainties, and thus would not necessarily indicate contamination or improper sampling techniques.

2.2 Data imputation methods

Missing data have been characterized into three general patterns: missing completely at random (MCAR); missing at random (MAR); and not missing at random (NMAR).[8] Like most other datasets, missing air quality data can be expected to be neither MCAR nor MNAR, but a mixture of these patterns.[1,9]

The most common approaches to deal with missing data are deletion and imputation methods. The former includes case deletion, pair-wise deletion and list-wise deletion, all standard methods in statistical packages such as SAS.[10] Imputation methods include single imputation (SI) techniques, which replace each missing one with a single value, and multiple imputation (MI) techniques, which impute multiple plausible values. The most common SI method is *ad hoc* replacement with a specific value, which is most frequently seen when measurements below the MDL that are replaced with one-half of the MDL. MI has been shown to yield valid statistical inferences without the disadvantages of SI techniques, namely, the inability to account for uncertainties attached to the missing values.[8,11] In MI, each missing value is replaced with a vector of $m \geq 2$ values resulting in m datasets, each of which is analyzed separately using standard complete-data software to yield "complete-data" statistics.[12] The multiple analyses are then combined, yielding composite statistics.

The following summarizes two SI and MI methods that are later evaluated (in the Results section). First, as presented by Batterman,[13] optimal linear estimation (OLE) is a SI method based on a Bayesian framework in which observations Z_t are assumed to contain error V_t:

$$Z_t = X_t + V_t \qquad (1)$$

where X_t = true pollutant level. Error covariance matrix R_t is:

$$R_t = E[V_t \, V'_t] \qquad (2)$$

Errors V_t and covariance R_t must be assumed or estimated. For example, errors might be determined empirically using replicate samples. Alternately, Batterman estimated the total error by propagating component errors, and estimated a relative error of 30% for 24 h measurements of fine and coarse fraction particulate matter ($PM_{2.5}$, $PM_{2.5 \, 10}$) and hourly measurements of O_3.[13] Assuming unbiased ($E[V_t] = 0$) and uncorrelated errors ($E[X_t \, V'_t] = 0$), the best linear, unbiased and minimum variance estimate $\hat{X}$ of the missing observations is:

$$\hat{X}_t = M + P(P + R_t)^{-1} (Z_t - M) \qquad (3)$$

where M = mean vector and P = covariance matrix, both estimated from available data, and T = number of observations used to estimate M and P:

$$M = T^{-1} \Sigma_t \, X_t \qquad (4)$$

$$P = T^{-1} \Sigma_t \, [(X_t - M)(X_t - M)'] \qquad (5)$$

Unlike most SI methods, the OLE approach estimates the uncertainty of imputed values. However, the use of imputed datasets derived from OLE, as well as any other SI method, will lead to standard errors that are systematically

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underestimated, biasing statistical inference tests and giving erroneously small *p*-values and confidence intervals.[8]

The MI procedure, also derived from a Bayesian perspective, uses *m* independent random draws from the posterior predictive distribution.[14] The theory behind MI is detailed elsewhere (Rubin 1987, 1996).[11,12] In brief, for a dataset $\mathbf{Y} = (\mathbf{Y}_{obs}, \mathbf{Y}_{mis})$, where $\mathbf{Y}_{obs}$ = observed values and $\mathbf{Y}_{mis}$ = missing values, the basic result is:

$$P(\mathbf{Y}_{est}|\mathbf{Y}_{obs}) = \int P(\mathbf{Y}_{est}|\mathbf{Y}_{obs}, \mathbf{Y}_{mis})P(\mathbf{Y}_{mis}|\mathbf{Y}_{obs})d\mathbf{Y}_{mis} \quad (6)$$

where $P(\mathbf{Y}_{est}|\mathbf{Y}_{obs})$ = complete-data posterior distribution of $\mathbf{Y}_{est}$, the estimate of the missing data conditioned on the observed data; and $P(\mathbf{Y}_{mis}|\mathbf{Y}_{obs})$ = predicted posterior distribution of the missing data, also conditioned on the observed data. The final estimate is the average of repeated complete-data posterior means of $\mathbf{Y}_{est}$:

$$E(\mathbf{Y}_{est}|\mathbf{Y}_{obs}) = E[E(\mathbf{Y}_{est}|\mathbf{Y}_{obs}, \mathbf{Y}_{mis})|\mathbf{Y}_{obs}] \quad (7)$$

and the final variance of $\mathbf{Y}_{est}$, $V(\mathbf{Y}_{est}|\mathbf{Y}_{obs})$, is:

$$V(\mathbf{Y}_{est}|\mathbf{Y}_{obs}) = E[V(\mathbf{Y}_{est}|\mathbf{Y}_{obs}, \mathbf{Y}_{mis})|\mathbf{Y}_{obs}] \\ + V[E(\mathbf{Y}_{est}|\mathbf{Y}_{obs}, \mathbf{Y}_{mis})|\mathbf{Y}_{obs}] \quad (8)$$

which represents the sum of the average of repeated complete-data variances of $\mathbf{Y}_{est}$ and the variance of repeated complete-data posterior means. Five imputations provide an efficiency of ~94% for MI estimation when up to 30% of the data is missing.[15] The essential features of MI inferences are that predicted distribution of missing values are conditioned on observed values, and that multiple imputations reflect both within- and between-imputation variances.[8] Hopke *et al.* suggests that MI in air quality applications may be beneficial, since imperfect imputation models make mistakes for only a fraction of missing information, whereas the complete-dataset is being relied upon for the final inference, and since imperfect models yield large within- and between-imputation variability and consequently will lead to conservative inferences.[16]

3. Experimental

3.1 Data acquisition

Toxics data were obtained from the Michigan Department of Environmental Quality (MDEQ) and included daily measurements for the period 4/19/2001 to 4/18/2002, collected at a permanent monitoring site in Dearborn, Michigan. Samples were shipped to and analyzed by laboratories at the Eastern Research Group (ERG, Research Triangle Park, NC, USA) and the MDEQ (Lansing, MI, USA). VOCs were collected in canisters and analyzed by GC-MS following the TO-15 method. The ERG and MDEQ laboratories reported 59 and 53 VOC species, respectively. Carbonyls were collected on DNPH cartridges and analyzed by HPLC following the TO-11A method, with the ERG and MDEQ laboratories reporting 12 and 13 species, respectively. (Supplements 1 and 2 in the ESI† show the VOC and carbonyl species analyzed by each of the laboratories.)

Reproducibility determinations, intra-laboratory and inter-laboratory comparisons were derived from duplicate sample pairs collected on 122 days (every third day). To determine intra-laboratory reproducibility, both duplicates were sent to ERG on 40 days and to MDEQ on 41 days. To determine inter-laboratory reproducibility, duplicates were sent to both ERG and MDEQ on 41 days. There were 282 and 41 days when a single sample was analyzed by ERG and MDEQ, respectively, and the total possible number of days that ERG and MDEQ analyzed samples were 302 and 83 days, respectively. VOC and carbonyl sampling followed the same schedule.

For imputation purposes, daily or hourly measurements of conventional pollutants were obtained from four nearby (within 20 km) MDEQ sites: Dearborn (daily PM_{10}), Allen Park (CO and $PM_{2.5}$), East Seven Mile (NO_2 and SO_2), and Linwood (CO, NO_2, $PM_{2.5}$ and SO_2). In Michigan, O_3 is monitored for only 6 months of the year (April to September); therefore, O_3 was not considered for this study. Daily (24 h) values were computed from hourly data if $\geq 75\%$ of hourly data (≥ 18 h) were available and considered valid. These pollutants are collected using federal reference methods.

Hourly and daily meteorological data, obtained from the MDEQ and the National Oceanic and Atmospheric Administration (NOAA), included temperature, dew point, minimum and maximum relative humidity, precipitation, wind speed, wind direction, barometric pressure and mixing height. Except for wind direction, daily values were computed from hourly data, again if $\geq 75\%$ of hourly data were considered valid. For wind direction, eight new variables were defined as the number of hours the wind was in each of eight 45° sectors. These variables were also used for imputation purposes.

3.2 Data filters

Several filters were used to select pollutant variables for analysis and provide QA checks. First, to include a toxic pollutant in the analysis, $\geq 20\%$ of the observations were required to exceed the MDL. This detection frequency is conservative with respect to other studies, *i.e.*, Xie *et al.* required $\geq 63\%$ of the data to be present and above MDLs.[17] Second, following convention, measurements below the MDL were set to 1/2 MDL. Next, potential statistical outliers were identified by pooling all samples (including replicates analyzed by either laboratory), fitting the top decile of detected concentrations to the Gumbell extreme value distribution, and determining those measurements that departed from the fitted distribution. If the potential outlier had a replicate that disagreed (*i.e.*, near the MDL), then the high value was considered to be erroneous and removed. If the replicate was similar (*i.e.*, considerably above the MDL), then the two replicates were averaged. If a replicate was unavailable, then the observation was removed. After completing the MDL, reproducibility and outlier screens, duplicate measurements at a laboratory, if available, were averaged.

3.3. Intra- and inter-laboratory reproducibility

Intra-laboratory reproducibility for each pollutant and laboratory was characterized by examining duplicate samples using both statistical measures, *e.g.*, paired *t*-tests for means, errors, distributions, and correlations (both parametric Pearson and non-parametric Spearman), and graphical

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analyses, *e.g.*, scatter plots. Intra-laboratory reproducibility was also quantified by the coefficient of variation, COV (%):[7]

$$\%COV = 100 \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{(p_i - s_i)}{0.5(p_i + s_i)}\right]^2}{2n}} \quad (9)$$

where p_i and s_i = primary and secondary replicates, respectively, and n = number of replicate pairs. We identified those species with COVs $\leq 15\%$, an acceptability criterion used by US EPA.[7] If intra-laboratory agreement was minimal, *e.g.*, as indicated by $r < 0.2$ or not statistically significant at $\alpha = 0.05$, then that pollutant was removed from further consideration.

Error models for intra-laboratory reproducibility were constructed following an approach used previously for VOCs.[18] Observations from all carbonyl species that met the minimum detection frequency (20%, discussed above) were pooled together. Replicate pairs were averaged, and measurements below MDLs and statistical outliers were excluded. Then, plots were constructed showing decile concentrations (using the decile average) *versus* the absolute residuals of replicate pairs in each concentration decile. Finally, the 25th, 50th, 75th and 90th percentile errors in each decile were regressed against the 10th to 100th or 10th to 90th decile concentrations, the latter to address additional outliers observed in the top decile of ERG's carbonyl measurements. This analysis was performed separately for ERG and MDEQ laboratories. The identical procedure was used for VOCs. The resulting intra-laboratory error models are used in the OLE estimator (described below).

Inter-laboratory reproducibility was characterized by examining the replicate samples analyzed by the two laboratories using statistical and graphical analyses as described for the intra-laboratory analyses. If the inter-laboratory agreement was poor ($r < 0.2$) or not statistically significant (at $\alpha = 0.05$) and the correlation coefficient from ERG intra-laboratory comparison was also poor, then that pollutant was removed from the analysis. Differences in mean concentrations reported by the two laboratories were examined using paired *t*-tests and the non-parametric Wilcoxon signed rank (WSR) tests for two related samples, considering only cases where both laboratories made measurements above MDLs, thus avoiding possible biases since MDLs differed.

3.4 Optimal linear estimation

The OLE method was implemented in Excel using the XNUMBERS[19] add-in for high precision matrix operations (*e.g.*, inversion in eqn (3)), necessary for imputations using a large number of predictor variables. Error covariance matrix $\mathbf{R}_t$ and covariance matrix $\mathbf{P}$ (eqns (1) and (2)) utilized the median intra-laboratory error model (described above). Errors were assumed to be independent and time invariant. Four OLE models were constructed for each pollutant that differed with respect to the treatment of autocorrelation: (1) use of only contemporaneous observations (lag0); (2) contemporaneous plus 1 day lagging observations (lag1); (3) contemporaneous plus 1 day leading observations (lead1); and (4) contemporaneous plus lag and lead (LL1). The inclusion of leading and/or lagging observations incorporates autocorrelation information.

A very large number of possible predictor variables were available. Variables for each imputation model were selected using GLMSELECT, a new procedure utilizing the general linear model framework and available as a test trial in SAS 9.1.[10,20] A forward step-wise procedure was used along with several selection criteria, including the general information criterion,[21,22] the corrected Akaike information criterion,[23] the Schwarz Bayesian information criterion,[22,24] the average square error (ASE), and the average residual sum of squares. The predictor variables identified using GLMSELECT were introduced into the model simultaneously. Each model was examined individually, with the goal of developing powerful but parsimonious and robust models. We examined the performance of the OLE estimator, using both nominal and log-transformed concentrations, in part to account for the expected log-normal distribution of pollutant concentrations.

3.5 Multiple imputation

MI models were constructed using the same data and predictor selection procedures described above and the MI procedure in SAS, a Markov chain Monte Carlo (MCMC) implementation with the multiple chain option.[10] A separate MC chain was used for each imputation. This implementation assumes multivariate normality. As with OLE, we evaluated performance of the same estimator using both the nominal and the log-transformed data. As described for the OLE method, four MI models were constructed for each pollutant using different combinations of leading and lagging observations. Five imputed datasets ($m = 5$) were generated for each pollutant.

3.6 Performance evaluation

Imputations from OLE and MI methods were evaluated using the same approach and the same datasets. Initially, performance was evaluated by random deletions, imputing the deleted data, and then comparing actual and imputed measurements using several indicators, *e.g.*, Willmott's index of agreement (d_2), coefficient of determination (R^2), mean absolute error (MAE), distribution analyses (percentiles and box plots), and scatter plots of imputed *versus* observed values. Among these indicators, d_2 addresses outliers and is a robust measure with a similar interpretation as R^2, *e.g.*, 0 and 1 denote random and perfect fits, respectively.[25] The MI scatter plots used the average of 5 imputed values.

To test different causes of missing values in air pollution datasets, three deletion patterns were used: random deletion, random block deletions of 5, and random row-wise deletions. For each deletion pattern, $\sim 25\%$ of the data were removed following Junninen *et al.* (2004) and to give a sufficient sample size for imputations (about 79) for robust statistics. Each deletion pattern represents a different situation. Random deletions portray missing data due to data entry problems, outlier removal, and other events that affect single observations. Random block deletions most commonly arise from equipment failures, which are not fixed for a period of time (*e.g.*, 5 days in our simulation). Row-rise deletions, which tested model performance using exclusively lag and lead

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measurements of toxics (but contemporaneous measurements of conventional and meteorology variables were permitted) often reflect a missingness pattern for air toxics, since multiple pollutants are measured in a single sample, and any day that sample is unavailable results in missing values for all of the toxics in the group. In practice, missingness patterns for air toxics data represent a mixture of these three missing patterns, though row-wise deletions are the most common. Missing at random and random block patterns are dominant in other types of air quality data, *e.g.*, conventional pollutants. The separate analyses of each of these three missingness patterns provide a sensitivity analysis that gives insight regarding how the imputation methods will perform for different types of air quality data. Also, it should be noted that the performance is largely independent of the amount of data that is removed and then imputed, as long as the sample size is sufficient to give valid statistics. This was verified with 10 and 25% deletions, which gave comparable results.

The evaluation used the ERG dataset, which was the most complete. Replicates, if available, were averaged. Predictor variables were selected after data were deleted, simulating an actual dataset. The present paper presents evaluations for three carbonyl and three VOC species. The selected compounds had different detection frequencies and/or represented different and important types of compounds. For carbonyls, detection frequencies did not differ, so the selection included both very volatile and aromatic carbonyls (acetaldehyde, benzaldehyde and formaldehyde). For VOCs, aromatic and chlorinated VOCs were selected (benzene and tetrachloroethylene); butadiene was also included due to its low detection frequency. (Evaluations for other species are provided in Supplements 9 and 10 of the ESI†.)

4. Results

4.1 Detection frequency, outliers, precision and accuracy

The original dataset contained 12 carbonyls ($n = 266$) and 59 VOCs ($n = 282$) measured by the ERG laboratory, and 13 carbonyls ($n = 54$) and 53 VOCs ($n = 57$) measured by the MDEQ laboratory. (Supplements 1 and 2 in the ESI† give statistics of all measured toxics.) Considering the sampling design, missing observations in one year of air monitoring data comprised ~6.4% and ~35% of the possible ERG and MDEQ data points, respectively. Data were processed using four QA screens, discussed below.

First, over half of the air toxics species were rarely detected above MDLs. With the 20% (minimum) detection frequency criterion, the first screen eliminated 38 of 59 VOC species and 1 of 12 carbonyl species measured by ERG, and 35 of 53 VOCs and 3 of 13 carbonyls measured by MDEQ. The eliminated compounds, which included many chlorinated VOCs, are not discussed further. Table 1 identifies the remaining 13 carbonyls and 24 VOCs.

The second data screen identified outliers. Probability distribution plots for the top decile concentrations of all compounds approximated straight lines, indicating that the Gumbell distribution was appropriate. After reviewing replicates, we considered that 11 compounds had outliers: formal-

dehyde ($n = 1$), hexaldehyde ($n = 1$), tolualdehyde ($n = 1$), propylene ($n = 2$), *n*-octane ($n = 1$), methylene chloride ($n = 5$), *m,p*-xylene ($n = 2$), ethylbenzene ($n = 2$), *o*-xylene ($n = 1$), 1,3,5-trimethylbenzene ($n = 1$) and toluene ($n = 2$). Several outliers occurred on the same dates, *i.e.*, *n*-octane, *m,p*-xylene, and ethylbenzene on 3/11/2002. (Supplement 3 of the ESI† gives information on the outliers; Supplements 4 and 5 of the ESI† show log-normal distribution plots). Methylene chloride had the largest number of outliers and reached very high concentrations, *e.g.*, MDEQ showed 199 ppb on 7/17/2001, and ERG showed 148 ppb on 3/3/2002. This compound is frequently used as a laboratory solvent and thus these outliers might be a result of inadvertent contamination. These 19 points were removed from the dataset and were considered missing. These outliers represent a very small percentage of the measurements.

Intra-laboratory reproducibility. Intra-laboratory agreement depended on the species and, to a lesser extent, on the laboratory. In many cases, non-parametric statistics (*e.g.*, Spearman rank correlation coefficients) and parametric (*e.g.*, Pearson correlation coefficients) gave similar results (Table 2), but the former is emphasized since concentrations of many toxics were not normally distributed and the Pearson statistic is sensitive to extreme values. For the ERG laboratory, dimethylbenzaldehyde and acetone had nil reproducibility ($r \leq 0.2$); crotonaldehyde, valeraldehyde, and carbon tetrachloride showed marginal reproducibility ($0.2 < r < 0.3$), as did acetone measurements by MDEQ. For the 10 carbonyls measured by the ERG surviving this screen, the average correlation between replicate samples was 0.43 ± 0.15; the 20 VOCs obtained higher correlation, 0.62 ± 0.14. The MDEQ laboratory obtained marginally higher performance for carbonyls (average $r = 0.51 \pm 0.10$) and comparable performance for VOCs (average $r = 0.65 \pm 0.18$). Both laboratories had high detection frequencies but poor reproducibilities for acetone and methylene chloride, suggesting possible contamination problems for these widely-used solvents.

Intra-laboratory agreement, as indicated by COVs, often but not always followed results given by correlations. Reasonably low COVs ($< 50\%$) were attained by most VOCs but only one carbonyl (tolualdehyde). For the ERG measurements (limited to compounds with $r > 0.2$), COVs averaged $62 \pm 16\%$ for the carbonyls and $35 \pm 23\%$ for the VOCs. Contrary to results using the intra-laboratory correlations, the ERG laboratory attained slightly higher reproducibility for carbonyls than the MDEQ laboratory (79 $\pm 13\%$); for VOCs, the MDEQ laboratory was again comparable (38 $\pm$ 18%). The strict 15% COV limit used by US EPA was met by only four compounds measured by ERG (chloromethane, dichlorodifluoromethane, trichlorofluoromethane and trichlorotrifluoroethane), and none from MDEQ. In contrast to most other toxic species, these four compounds show a very limited concentration range (Table 1). Such constant measurements can "reward" the COV indicator but will "penalize" correlations, *e.g.*, chloromethane's good COV (12%) is not matched by its fair intra-laboratory correlation ($r = 0.45$).

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Table 1 Statistics of toxic concentrations measured at Dearborn, Michigan for those VOCs and carbonyls with detection frequencies above 20%. Duplicates were averaged and outliers excluded. TFE = trifluoroethane; DF = detection frequency; MDL = method detection limit; — = is not measured or DF <20%.

	ERG laboratory							MDEQ laboratory						
Compound	N	DF (%)	Mean (ppbv)	50th (ppbv)	75th (ppbv)	Max (ppbv)	MDL (ppbv)	N	DF (%)	Mean (ppbv)	50th (ppbv)	75th (ppbv)	Max (ppbv)	MDL (ppbv)
Carbonyls														
2,5-Dimethylbenzaldehyde	284	32	0.009	0.003	0.008	0.280	0.005	—	—	—	—	—	—	—
Acetaldehyde	284	100	1.166	0.914	1.510	4.406	0.014	74	97	0.860	0.760	1.030	5.085	0.009
Benzaldehyde	284	98	0.050	0.040	0.063	0.422	0.004	75	69	0.032	0.012	0.038	0.360	0.004
Crotonaldehyde	284	81	0.027	0.012	0.018	0.309	0.006	75	21	0.011	0.004	0.004	0.094	0.008
Formaldehyde	283	100	2.317	2.089	3.094	10.486	0.016	75	97	2.139	2.055	2.603	7.873	0.008
Hexaldehyde	284	99	0.119	0.041	0.110	0.683	0.004	75	75	0.065	0.027	0.072	0.653	0.005
iso-Butyraldehyde	284	99	0.199	0.144	0.235	0.801	0.005	—	—	—	—	—	—	—
iso-Valeraldehyde	284	21	0.020	0.002	0.002	0.377	0.004	75	60	0.055	0.033	0.073	0.390	0.012
m,p-Tolualdehyde	—	—	—	—	—	—	—	75	35	0.016	0.001	0.019	0.157	0.002
n-Butyraldehyde	—	—	—	—	—	—	—	75	88	0.094	0.058	0.100	0.929	0.007
Propionaldehyde	284	90	0.143	0.103	0.180	1.440	0.007	75	69	0.175	0.115	0.220	0.810	0.083
Tolualdehydes	283	93	0.043	0.031	0.053	0.281	0.008	—	—	—	—	—	—	—
Valeraldehyde	284	91	0.058	0.037	0.065	0.377	0.003	75	33	0.038	0.011	0.035	0.343	0.022
VOCs														
1,1,2-Trichloro-1,2,2-TFE	—	—	—	—	—	—	—	83	95	0.094	0.089	0.109	0.178	0.034
1,2,4-Trimethylbenzene	302	90	0.210	0.179	0.267	1.029	0.070	83	86	0.171	0.135	0.210	0.629	0.062
1,3,5-Trimethylbenzene	301	38	0.065	0.035	0.088	0.312	0.070	83	29	0.050	0.029	0.063	0.191	0.057
1,3-Butadiene	302	26	0.057	0.035	0.071	0.292	0.070	—	—	—	—	—	—	—
2,2,4-Trimethylpentane	—	—	—	—	—	—	—	83	99	0.126	0.099	0.148	0.537	0.017
Acetone	284	100	1.422	1.138	1.771	5.770	0.008	75	99	0.982	0.856	1.115	3.513	0.011
Acetonitrile	302	36	1.804	0.125	1.642	102.600	0.250	83	73	1.561	0.991	1.711	12.552	0.520
Acetylene	302	99	1.684	1.520	1.983	6.480	0.130	—	—	—	—	—	—	—
Benzene	302	100	0.614	0.537	0.697	2.173	0.040	83	100	0.564	0.434	0.654	2.494	0.070
Carbon tetrachloride	302	90	0.099	0.100	0.110	0.170	0.080	83	95	0.089	0.090	0.099	0.125	0.038
Chloromethane	302	100	0.607	0.594	0.644	0.988	0.060	83	100	0.583	0.570	0.623	1.426	0.062
Dichlorodifluoromethane	302	100	\cos4	0.625	0.663	1.079	0.040	83	100	0.560	0.576	0.620	0.846	0.048
Ethylbenzene	300	98	0.181	0.155	0.230	0.647	0.040	83	55	0.115	0.092	0.144	0.390	0.083
Hexane	—	—	—	—	—	—	—	83	27	0.435	0.250	0.531	3.318	0.500
m,p-Xylene	300	100	0.517	0.445	0.661	1.957	0.050	83	61	0.311	0.240	0.383	1.055	0.200
Methyl ethyl ketone	302	74	0.613	0.570	0.878	2.920	0.150	—	—	—	—	—	—	—
Methylene chloride	298	96	2.468	0.647	1.731	34.270	0.060	81	79	1.480	0.401	1.302	11.222	0.230
n-Octane	301	33	0.055	0.030	0.072	0.280	0.060	—	—	—	—	—	—	—
o-Xylene	301	97	0.211	0.180	0.262	0.899	0.050	83	90	0.140	0.110	0.169	0.519	0.043
Propylene	302	100	1.193	0.764	1.354	14.137	0.050	—	—	—	—	—	—	—
Tetrachloroethylene	302	33	0.064	0.030	0.074	0.670	0.040	83	34	0.061	0.036	0.080	0.343	0.071
Toluene	300	100	1.049	0.850	1.293	6.431	0.060	83	100	0.998	0.763	1.185	4.718	0.070
Trichlorofluoromethane	302	100	0.319	0.295	0.333	1.540	0.040	83	100	0.274	0.279	0.297	0.500	0.048
Trichlorotrifluoroethane	302	100	0.111	0.106	0.130	0.194	0.070	—	—	—	—	—	—	—

Inter-laboratory reproducibility. Six of the 23 compounds where comparisons were possible showed negligible inter-laboratory correlation (Spearman $r < 0.20$), specifically, crotonaldehyde, iso-valeraldehyde, valeraldehyde, acetone, acetonitrile and carbon tetrachloride (Table 2). Inter-laboratory agreement was only marginally better ($0.20 < r < 0.32$) for propionaldehyde, chloromethane, and methylene chloride. These nine compounds previously had shown negligible-to-fair intra-laboratory agreement ($r < 0.50$).

Higher mean concentrations were reported by the ERG laboratory compared to the DEQ laboratory for 8 VOCs (1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, carbon tetrachloride, dichlorodifluoromethane, ethylbenzene, m,p-xylene, o-xylene, trichlorofluoromethane), based on paired t-tests (Table 2). The same VOCs were identified by the non-parametric Wilcoxon signed rank test, along with toluene and two carbonyls (benzaldehyde and acetonitrile). However, only ethylbenzene, m,p-xylene and o-xylene showed sizable concentration differences (nearly factor of two), differences that were maintained across the measured concentration range. Other compounds showed much smaller differences. These results cannot be explained by MDLs, but appear to result from calibration discrepancies.

Final dataset. Carbonyls and VOC species were selected for further analysis by considering data availability, detection frequency, outliers, intra-laboratory reproducibility, and inter-laboratory agreement. Five compounds measured only by the MDEQ laboratory (m,p-tolualdehyde, n-butyraldehyde, 1,1,2-trichloro- 1,2,2-trifluoroethane, 2,2,4-trimethylpentane and hexane) were excluded to avoid having to impute an excessive fraction ($>65\%$) of missing data. The 39 species with low detection frequencies ($<20\%$) were omitted, as were the 19 outliers detected using the Gumbell distribution in the second data screen. Pollutants with poor intra- and inter-laboratory agreement were considered on a case-by-case basis. Crotonaldehyde, valeraldehyde, acetone and carbon tetrachloride were eliminated, as they showed little agreement in both intra- and intra-laboratory comparisons. Iso-valeraldehyde and acetonitrile showed fair intra-laboratory agreement

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Table 2 Intra- and inter-laboratory reproducibility. Based on only detected values. Significant values (p-value < 0.05) indicated in bold. WSR = Wilcoxon signed rank; TFE = trifluoroethane; — = is not measured or detection frequency $<20\%$

| Compound | Intra-laboratory reproducibility | | | | | | Inter-laboratory reproducibility | | | | Retained in final dataset (y = yes) |
| | Coefficient of variance | | Correlation coefficient—ERG | | Correlation coefficient—MDEQ | | Correlation coefficient | | Paired t-test (p-value) | WSR test (p-value) | |
	ERG (%)	MDEQ (%)	Pearson	Spearman	Pearson	Spearman	Pearson	Spearman			
Carbonyls											
2,5-Dimethylbenzaldehyde	96	—	0.02	0.19	—	—	—	—	—	—	
Acetaldehyde	61	70	**0.38**	**0.39**	0.31	**0.41**	**0.37**	**0.52**	0.37	—	y
Benzaldehyde	51	78	**0.54**	**0.61**	0.23	**0.65**	0.28	**0.46**	1.00	**0.04**	y
Crotonaldehyde	61	97	0.32	0.22	0.31	**0.48**	−0.06	−0.07	0.83	—	
Formaldehyde	58	64	**0.45**	**0.48**	**0.51**	**0.58**	**0.73**	**0.61**	0.95	0.93	y
Hexaldehyde	62	83	**0.50**	**0.64**	0.32	**0.51**	**0.40**	**0.44**	0.41	0.29	y
iso-Butyraldehyde	52	—	0.19	**0.40**	—	—	—	—	—	—	y
iso-Valeraldehyde	102	93	−0.05	**0.49**	**0.52**	**0.34**	−0.18	−0.28	—	—	
m,p-Tolualdehyde	—	85	—	—	0.26	**0.64**	—	—	—	—	
n-Butyraldehyde	—	71	—	—	**0.40**	**0.45**	—	—	—	—	
Propionaldehyde	61	59	**0.34**	**0.33**	**0.87**	**0.49**	0.25	0.28	0.07	0.11	y
Tolualdehydes	42	—	**0.71**	**0.56**	—	—	—	—	—	—	y
Valeraldehyde	69	88	0.06	0.22	**0.55**	**0.56**	0.04	0.13	0.86	0.91	
VOCs											
1,1,2-Trichloro-1,2,2-TFE	—	29	—	—	0.30	0.38	—	—	—	—	
1,2,4-Trimethylbenzene	39	35	**0.68**	**0.67**	**0.91**	**0.79**	**0.71**	**0.63**	**<0.01**	**<0.01**	y
1,3,5-Trimethylbenzene	31	16	**0.71**	**0.70**	**0.89**	**0.64**	**0.71**	**0.59**	**<0.01**	**<0.01**	y
1,3-Butadiene	49	—	**0.60**	**0.59**	—	—	—	—	—	—	y
2,2,4-Trimethylpentane	—	37	—	—	**0.89**	**0.66**	—	—	—	—	
Acetone	67	73	0.04	−0.01	0.15	0.26	−0.06	0.14	—	0.17	
Acetonitrile	102	65	0.01	0.42	0.40	0.49	−0.17	−0.20	0.23	**0.01**	
Acetylene	26	—	**0.54**	**0.63**	—	—	—	—	—	—	y
Benzene	19	36	**0.83**	**0.73**	**0.82**	**0.66**	**0.81**	**0.71**	0.07	**<0.01**	y
Carbon tetrachloride	23	19	0.02	0.27	**0.78**	**0.84**	0.23	0.17	**0.01**	**<0.01**	
Chloromethane	12	27	−0.02	**0.45**	0.44	0.42	0.32	0.32	0.98	0.47	
Dichlorodifluoromethane	4	29	**0.75**	**0.75**	**0.70**	**0.68**	**0.47**	**0.61**	**<0.01**	**<0.01**	y
Ethylbenzene	44	16	**0.69**	**0.65**	**0.92**	**0.88**	**0.78**	**0.66**	**<0.01**	**<0.01**	y
Hexane	—	63	—	—	**0.48**	**0.60**	—	—	—	—	
m,p-Xylene	35	24	**0.60**	**0.71**	**0.92**	**0.88**	**0.80**	**0.67**	**<0.01**	**<0.01**	y
Methyl ethyl ketone	50	—	**0.66**	**0.65**	—	—	—	—	—	—	y
Methylene chloride	71	62	0.05	**0.44**	0.10	**0.71**	0.14	0.31	0.14	0.36	
n-Octane	53	—	0.28	**0.56**	—	—	—	—	—	—	y
o-Xylene	39	30	**0.63**	**0.79**	**0.93**	**0.83**	**0.79**	**0.67**	**<0.01**	**<0.01**	y
Propylene	32	—	**0.97**	**0.73**	—	—	—	—	—	—	y
Tetrachloroethylene	28	63	**0.82**	**0.77**	**0.39**	**0.53**	**0.64**	**0.61**	0.65	0.73	y
Toluene	28	37	**0.82**	**0.73**	**0.93**	**0.82**	**0.50**	**0.62**	1.00	**0.04**	y
Trichlorofluoromethane	10	28	**0.66**	**0.57**	**0.57**	**0.60**	0.33	0.42	**0.04**	**0.02**	y
Trichlorotrifluroethane	10	—	**0.76**	**0.52**	—	—	—	—	—	—	y

($r = 0.49$ and 0.42, respectively) but nil inter-laboratory agreement ($r = -0.38$ and -0.20, respectively) and high COVs (both were 102%), so these compounds were eliminated. For 2,5-dimethylbenzaldehyde, only ERG measurements were available, but these showed little reproducibility ($r = 0.19$, COV = 96%), thus this compound was eliminated. Methylene chloride showed fair intra- and inter-laboratory agreement ($r = 0.44$ and 0.31, respectively), a poor COV (71%), a number of outliers or erroneous observations apparent in scatter plots, and low Pearson correlations (after removing 5 observations in the second QA screen). Even when restricted to low concentrations, both intra- and inter-laboratory scatter plots showed little evidence of a trend. Because of the strong possibility of laboratory contamination and the mediocre reproducibility, methylene chloride was eliminated. Finally, chloromethane also showed fair intra- and inter-laboratory agreement ($r = 0.45$ and 0.32, respectively), but a very good

COV (12%). Scatter plots displaying intra- and inter-laboratory comparisons showed a number of outlying points not detected in the second QA data screen (*e.g.*, 1.43 ppb measured on 4/22/01 by MDEQ, and 1.19 ppb on 1/29/02 measured by ERG). Other than such points, chloromethane concentrations appeared nearly constant, *e.g.*, the inter-quartile range was only 0.56–0.64 ppb and the 5th to 95th percentile range was only 0.50–0.74 ppb. Because these concentration changes seem attributable largely to laboratory errors rather than to local sources, we omitted chloromethane.

The final dataset contained 23 compounds (7 carbonyls, 16 VOCs) measured by the ERG laboratory and 15 compounds (5 carbonyls and 10 VOCs) measured by the MDEQ laboratory (Table 2). For the ERG measurements, intra-laboratory reproducibility measured as the (Spearman rank) correlation coefficient averaged 0.49 ± 0.12 across the carbonyls and 0.67 ± 0.08 across the VOCs, while COVs averaged

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55 ±÷8% for carbonyls and 31 ±÷15% for VOCs. Inter-laboratory performance was slightly worse, *e.g.*, the correlation was 0.46 ± 0.12 for carbonyls and 0.62 ± 0.08 for VOCs. Benzene was the only species for which both intra- and inter-laboratory correlations exceeded 0.7. Eight other VOCs demonstrated fair-to-good performance (intra- and inter-laboratory correlations exceeding 0.6). Overall, the precision and inferred accuracy (based on inter-laboratory comparisons) for many VOCs and most aldehyde measurements appear mixed at best and often poor. This is surprising given that the samples were measured in an urban/industrial setting where concentrations were not particularly low, sample collection procedures followed rigorous protocols and QA procedures, and analyses were conducted by experienced personnel and respected laboratories utilizing similar methods. Measurement

performance might be acceptable for a slightly larger number of the toxics using more relaxed criteria, *e.g.*, means within a factor of two.

4.2 Error models

Models showing intra-laboratory precisions based on the final dataset show that differences between replicates increase with concentration (Fig. 1a–d). For example, carbonyl measurements from the ERG laboratory have median absolute errors that increase to 0.9 ppb as concentrations increase to 6.0 ppb (Fig. 1a), and the corresponding regression model incorporates both constant and proportional terms: absolute error (ppb) = 0.07 + 0.15 X concentration (ppb). Relative errors tend to be higher for carbonyls as compared to VOCs, and somewhat higher for the MDEQ laboratory compared to the
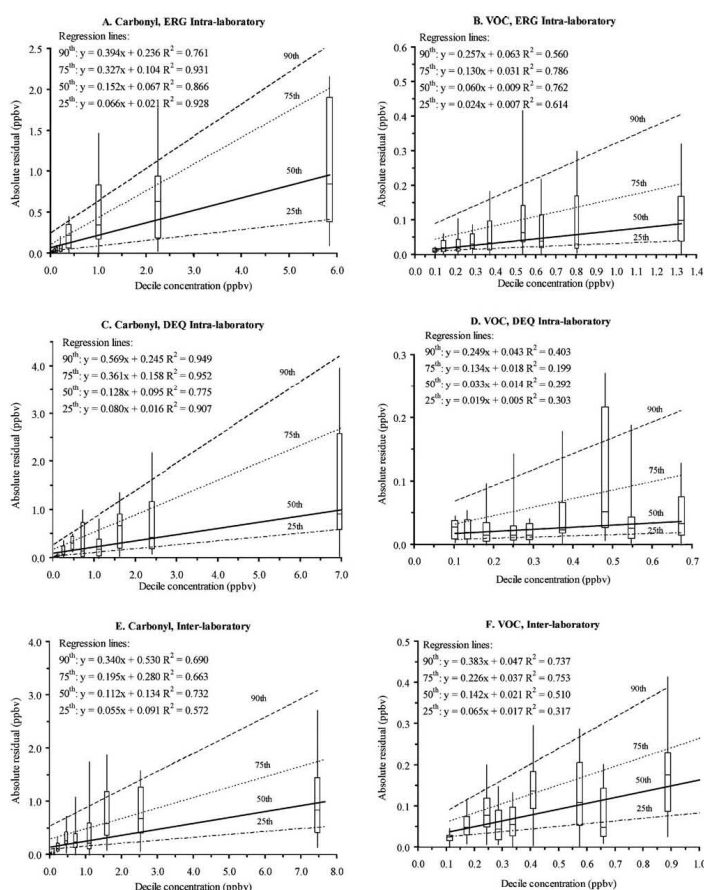

Fig. 1 Absolute relative error models for carbonyls (left) and VOCs (right) from intra-laboratory and inter-laboratory comparisons. Only concentrations above MDLs were included. Maximum decile concentrations were excluded for VOCs (b, d and f).

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ERG laboratory. While the 50th percentile error model show good fits ($0.76 \leq R^2 \leq 0.88$), additional observations and perhaps wider bins (*e.g.*, quintiles compared to deciles) might improve fits. Models for errors at higher percentiles give much larger errors, but attain comparable fits.

Models for inter-laboratory differences (Fig. 1e and f) are similar to the intra-laboratory differences, but predicted errors are generally larger. Using the ERG carbonyl measurements as an example (Fig. 1e): the median absolute error (ppb) = $0.11 + 0.13\ X$ concentration (ppb). As seen earlier, the carbonyls had higher relative errors than the VOCs. All of the inter-laboratory error models showed good fits ($0.73 \leq R^2 \leq 0.85$).

4.3 Predictor variable selection for OLE and MI models

For the random deletions, selected predictor variables for carbonyls included other carbonyl species (current, lead and lag observations), pollutants CO and $PM_{2.5}$, and several meteorological variables (temperature, pressure, precipitation, wind speed, wind sectors and mixing height). Predictors varied by species and models, *i.e.*, the LL1 model for acetaldehyde included current and lead observations of other carbonyls, as well as wind sectors, while the LL1 model for benzaldehyde only included current, lag and lead observations of other carbonyls, as well as its own lag and lead values. These results follow from the correlations seen between the variables (Supplements 6-8 of the ESI†). Predictor variables for VOCs were similar with the addition of pollutant SO_2. The most frequently selected meteorological variables were resultant wind speed and SE and NW wind sectors. Similar predictor variables were obtained for the random block deletions.

For row-wise deletions, predictor variables for the three carbonyls included lead and lag observations of other carbonyl species, meteorological variables (most commonly temperature, precipitation and wind speed and occasionally E and SE wind sectors and relative humidity), and criteria air pollutants (CO but only for the LL1 acetaldehyde model). The predictor variables for the three VOCs included lead and lag observations of other VOCs, pollutants CO, $PM_{2.5}$ and SO_2 (but only for benzene and 1,3-butadiene), and meteorological variables in a few instances. Predictors for tetrachloroethylene included only one VOC (leading dichlorodifluoromethane) for the LL1 model and a few meteorological variables for the other tetrachloroethylene models. The GLMSELECT procedure did not select any predictors for the lead1 tetrachloroethylene model because the corrected information criterion was not met. Lag0 models for both carbonyls and VOCs included only meteorological variables.

4.4 Evaluation of OLE

Summary statistics describing the OLE performance for the three carbonyls and three VOCs are shown in Table 3. Because random block and random deletions obtained similar performance, only the former is shown. (Performance statistics for all carbonyls and VOCs and the three data patterns are shown in Supplements 9 and 10 of the ESI†.) Also, because nominal concentrations gave comparable or slightly better performance than log-transformed data, performance statistics show results

for only the former. (Supplement 11 of the ESI† gives results for log-transformed data.) Performance indicators d_2, R^2 and mean absolute error (MAE) yielded similar rankings. Performance depended strongly on the deletion pattern, as discussed below.

The OLE imputations for random deletions, which utilized both contemporaneous co-pollutant and autocorrelative information, were quite successful for carbonyls. Acetaldehyde, benzaldehyde and formaldehyde obtained d_2 values of 0.89, 0.88 and 0.86 (corresponding R^2 values of 0.72, 0.62 and 0.63), respectively, using lag1 and lag0 OLE estimates. Scatter plots of imputed *versus* measured values showed linear trends, but a tendency to under-predict the highest values (Fig. 2a–c). OLE performance for VOCs was mixed: benzene had high agreement ($0.79 \leq d_2 \leq 0.89$, $0.52 \leq R^2 \leq 0.71$, Fig. 2g); 1,3-butadiene showed lower performance ($0.63 \leq d_2 \leq 0.78$, $0.52 \leq R^2 \leq 0.68$), a strong tendency to underestimate concentrations, and a large fraction of measurements below MDLs (Fig. 2h); while tetrachloroethylene imputations had little correspondence to observations ($0.23 \leq d_2 \leq 0.27$, $0.00 \leq R^2 \leq 0.03$; Fig. 2i). Occasionally, the OLE imputations yielded small negative estimates.

OLE imputations for the row-wise deletions of the three carbonyls showed at best modest performance. Imputation values were compressed towards the mean (Fig. 2d–f), suggesting that the estimated errors (R_t) may have been too large. For row-wise deletions of VOCs, performance was poor, especially for 1,3-butadiene and tetrachloroethylene (Fig. 2k and l). Performance was essentially unchanged for tetrachloroethane, but this VOC had essentially nil agreement for all deletion patterns.

OLE performance was considered good if $d_2 \geq 0.9$ or $R^2 \geq 0.7$; fair if either $0.7 \leq d_2 < 0.9$ or $0.5 \leq R^2 < 0.7$; and poor if either $d_2 < 0.7$ or $R^2 < 0.5$. With these guidelines and considering random and random block deletions: performance was good for acetaldehyde, isobutyraldehyde, propionaldehyde, benzene, ethylbenzene, *m,p*-xylene, *o*-xylene, 1,2,4-trimethylbenzene, and toluene; fair for benzaldehyde, formaldehyde, hexaldehyde, acetylene, 1,3-butadiene, methyl ethyl ketone and 1,3,5-trimethylbenzene; and poor for tolualdehyde, dichlorodifluoromethane, *n*-octane, propylene, tetrachloroethylene, trichlorofluoromethane and trichlorotrifluoromethane. Row-wise deletions resulted in poor performance for all 23 toxic compounds (Supplements 9 and 10 of the ESI†).

These results clearly demonstrate the importance of the missingness pattern. All estimates depended strongly on contemporaneous co-pollutant information. If this information was unavailable (as simulated using row-wise deletions) then performance was significantly degraded. This also explains why random and random block deletions obtained comparable performance: leading and lagging measurements provided relatively little information, and essentially only contemporaneous measurements were utilized in the imputations.

4.5 Evaluation of MI

The performance attained by MI was similar to that of OLE. For random deletions, d_2 values ranged from 0.83 to 0.95

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Table 3 Performance indicators for MI and OLE estimates. Bold values show highest performing model in group. Abbreviations: lag0 = current day observation; lag1 = current and previous day observations; lead1 = current and next day observations; LL1 = current, previous and next day observations; SD = standard deviation; d_2 = Willmot's index of agreement; R^2 = coefficient of determination; MAE = mean absolute error

Performance indicators		Multiple imputation				Optimal estimation			
		lag0 (SD)	lag1 (SD)	lead1 (SD)	LL1 (SD)	lag0	lag1	lead1	LL1
Acetaldehyde									
Random	d_2	0.95 (0.01)	0.95 (0.01)	0.95 (0.01)	**0.95 (0.00)**	0.86	**0.89**	0.74	0.88
	R^2	0.83 (0.02)	0.80 (0.02)	0.83 (0.02)	**0.83 (0.01)**	0.69	**0.72**	0.51	0.70
	MAE	0.29 (0.03)	0.30 (0.03)	0.30 (0.02)	**0.30 (0.01)**	0.30	**0.26**	0.46	0.28
Row-wise	d_2	0.58 (0.05)	**0.67 (0.04)**	0.51 (0.05)	0.63 (0.06)	**0.67**	0.63	0.47	0.46
	R^2	0.11 (0.05)	**0.20 (0.06)**	0.04 (0.02)	0.14 (0.08)	**0.32**	0.26	0.09	0.11
	MAE	0.87 (0.08)	**0.85 (0.12)**	0.91 (0.04)	0.87 (0.06)	**0.62**	0.66	0.83	0.79
Benzaldehyde									
Random	d_2	0.80 (0.03)	**0.83 (0.02)**	0.76 (0.05)	0.76 (0.01)	**0.88**	0.82	0.77	0.83
	R^2	0.46 (0.07)	**0.55 (0.03)**	0.38 (0.10)	0.38 (0.03)	**0.62**	0.48	0.44	0.51
	MAE	0.02 (0.00)	**0.02 (0.00)**	0.03 (0.00)	0.03 (0.00)	**0.00**	0.00	0.00	0.00
Row-wise	d_2	0.48 (0.06)	**0.54 (0.03)**	0.35 (0.05)	0.38 (0.05)	0.50	**0.57**	0.25	0.31
	R^2	0.05 (0.05)	**0.09 (0.02)**	0.01 (0.01)	0.00 (0.01)	0.07	**0.13**	0.02	0.00
	MAE	0.04 (0.00)	**0.04 (0.00)**	0.05 (0.00)	0.05 (0.00)	0.00	**0.00**	0.00	0.00
Formaldehyde									
Random	d_2	0.84 (0.02)	0.80 (0.04)	**0.85 (0.01)**	0.81 (0.04)	**0.86**	0.82	0.84	0.83
	R^2	0.53 (0.05)	0.44 (0.07)	**0.54 (0.03)**	0.45 (0.09)	**0.63**	0.62	0.69	0.63
	MAE	0.80 (0.03)	0.90 (0.10)	**0.81 (0.03)**	0.86 (0.05)	**0.72**	0.78	0.69	0.77
Row-wise	d_2	0.51 (0.06)	**0.53 (0.03)**	0.40 (0.06)	0.40 (0.06)	0.52	**0.54**	0.33	0.33
	R^2	0.05 (0.04)	**0.06 (0.03)**	0.01 (0.01)	0.01 (0.01)	0.09	**0.11**	0.00	0.00
	MAE	1.49 (0.14)	**1.58 (0.12)**	1.79 (0.14)	1.79 (0.14)	2.37	**2.31**	2.65	2.65
Benzene									
Random	d_2	**0.87 (0.03)**	0.84 (0.01)	0.87 (0.02)	0.84 (0.02)	**0.89**	0.85	0.84	0.79
	R^2	**0.61 (0.08)**	0.52 (0.03)	0.59 (0.06)	0.52 (0.05)	**0.71**	0.63	0.63	0.52
	MAE	**0.17 (0.02)**	0.18 (0.01)	0.17 (0.01)	0.18 (0.01)	**0.03**	0.04	0.04	0.04
Row-wise	d_2	**0.64 (0.04)**	0.63 (0.03)	0.58 (0.06)	0.57 (0.06)	0.63	**0.65**	0.64	0.53
	R^2	**0.20 (0.05)**	0.18 (0.03)	0.13 (0.05)	0.12 (0.05)	0.22	**0.25**	0.24	0.17
	MAE	**0.26 (0.02)**	0.28 (0.02)	0.28 (0.03)	0.27 (0.01)	0.07	**0.07**	0.07	0.08
1,3-Butadiene									
Random	d_2	0.89 (0.02)	**0.89 (0.01)**	0.87 (0.01)	0.87 (0.02)	**0.78**	0.74	0.62	0.63
	R^2	0.65 (0.06)	**0.65 (0.03)**	0.58 (0.04)	0.58 (0.04)	**0.68**	0.67	0.52	0.52
	MAE	0.03 (0.00)	**0.03 (0.00)**	0.03 (0.00)	0.03 (0.00)	**0.00**	0.00	0.00	0.00
Row-wise	d_2	**0.58 (0.04)**	0.50 (0.03)	0.52 (0.08)	0.46 (0.05)	**0.49**	0.43	0.41	0.30
	R^2	**0.09 (0.03)**	0.05 (0.03)	0.07 (0.05)	0.03 (0.03)	**0.13**	0.08	0.07	0.03
	MAE	**0.04 (0.00)**	0.04 (0.00)	0.05 (0.00)	0.04 (0.00)	**0.00**	0.00	0.00	0.00
Tetrachloroethylene									
Random	d_2	0.30 (0.07)	0.27 (0.03)	0.31 (0.06)	**0.33 (0.06)**	0.22	**0.27**	0.26	0.23
	R^2	0.02 (0.02)	0.01 (0.01)	0.01 (0.01)	**0.01 (0.02)**	0.01	**0.03**	0.03	0.00
	MAE	0.08 (0.01)	0.08 (0.00)	0.08 (0.00)	**0.07 (0.00)**	0.01	**0.01**	0.01	0.01
Row-wise	d_2	**0.41 (0.11)**	0.38 (0.10)	—	0.32 (0.06)	0.37	0.30	—	0.27
	R^2	**0.03 (0.02)**	0.02 (0.01)	—	0.01 (0.00)	0.15	0.09	—	0.08
	MAE	**0.07 (0.01)**	0.08 (0.01)	—	0.07 (0.01)	0.01	0.01	—	0.01

($0.54 \leq R^2 \leq 0.83$) for the three carbonyls, and from 0.33 to 0.89 ($0.01 \leq R^2 \leq 0.65$) for the three VOCs (Table 3). Again, performance for tetrachloroethylene was particularly poor. With the exception of tetrachloroethylene, the MI scatter plots showed linear relationships, somewhat less tendency to underestimate high concentrations, slightly better performance for acetaldehyde and 1,3-butadiene, but greater scatter (Fig. 3a–c and g–i). In all cases, the MI estimates had higher MAE, reflecting the increased scatter, a result of the variance contributed by the 5 imputations. Like OLE, MI occasionally yielded small negative estimates. Row-wise deletions again yielded substantially poorer performances (Table 3) and non-linearities for formaldehyde, 1,3-butadiene and tetrachloroethylene (Fig. 3f, k and l). The highest observations were often under-predicted.

Results obtained using log-transformed data (Supplement 12 of the ESI†) showed slightly poorer performance and larger standard deviations than imputations obtained using untransformed data. Some of this is a result of evaluating performance using the untransformed data, which tended to emphasize higher values. When log-transformed, imputations were more constrained, and often did not reflect the higher values that are of most interest and significance. Examination of scatter plots using untransformed data (e.g., Fig. 3) do not show strong evidence of distributional problems, and in fact suggest largely normally-distributed residuals, which was seen in residual plots. Thus, for the toxics dataset (as well as a better-behaved ozone dataset using 24 h averages), MI (and OLE) performance was largely insensitive to log-transformations. An advantage of using log-
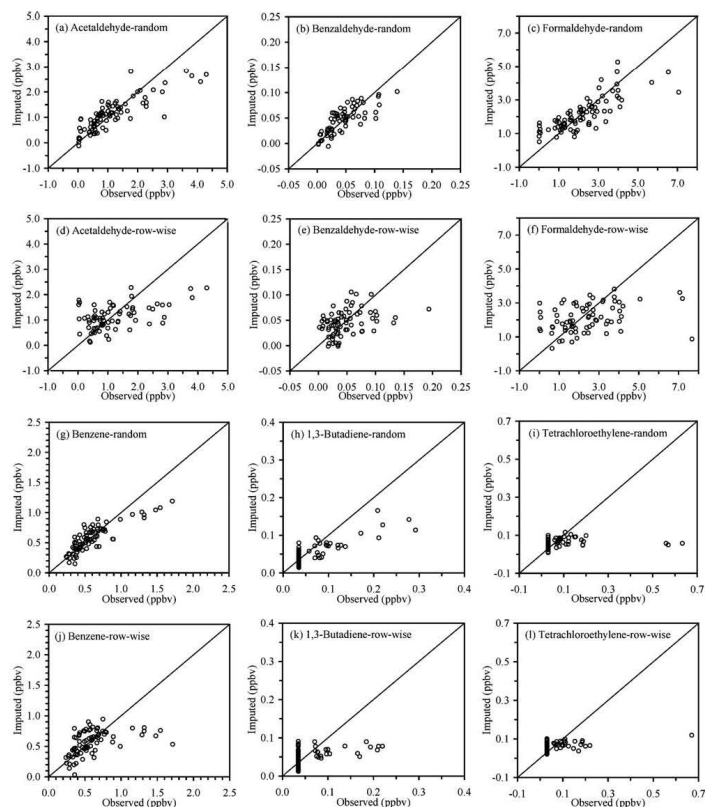
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Fig. 2 Scatter plots for observed *versus* imputed data using OLE method for random and row-wise deletions of six toxics. Only best models of each group are plotted for each compound.

transformed data in the imputation model is negative estimates can be avoided.

Overall, MI performance for random and random block deletions was considered good for most aromatic compounds, fair-to-good for all carbonyl compounds, and poor for all chlorinated and fluorinated compounds. Like OLE, MI performance was poor for row-wise deletions for all of the toxics (Supplements 9 and 10 of the ESI†).

5. Discussion

5.1 Quality assurance and reproducibility of toxics data

Fewer than a third of the measured VOC and carbonyl species in the Dearborn dataset had detection frequencies above 20% and was felt to provide useful information for time series-types of investigations. Further, the reproducibility of the 23 compounds remaining in the final dataset varied considerably. Only benzene was considered highly reproducible, based on

intra- and inter-laboratory comparisons, though several other aromatic VOCs (*e.g.*, trimethylbenzenes and xylenes) came close. Several VOCs showed little or no reproducibility, *e.g.*, acetone and methylene chloride, although nearly all observations exceeded MDLs. For carbonyls, reproducibility was only fair. As anticipated, between-laboratory variability exceeded within-laboratory variability, although the difference was not dramatic. While these findings are based on a dataset that is considerably more complete than those available in most air toxic measurement campaigns, the analysis depends upon data collected at only one monitoring site and analytical work performed by only two laboratories. However, both laboratories are known for their adherence to strict QA/QC protocols, and they likely attain performance that is typical of current analyses.

The most recent national study shows that the reproducibility of carbonyl and VOC measurements varies widely.[7] Across the National Air Toxics Trends Stations (NATTS) reporting precision data for 2004, COVs ranged from 0 to
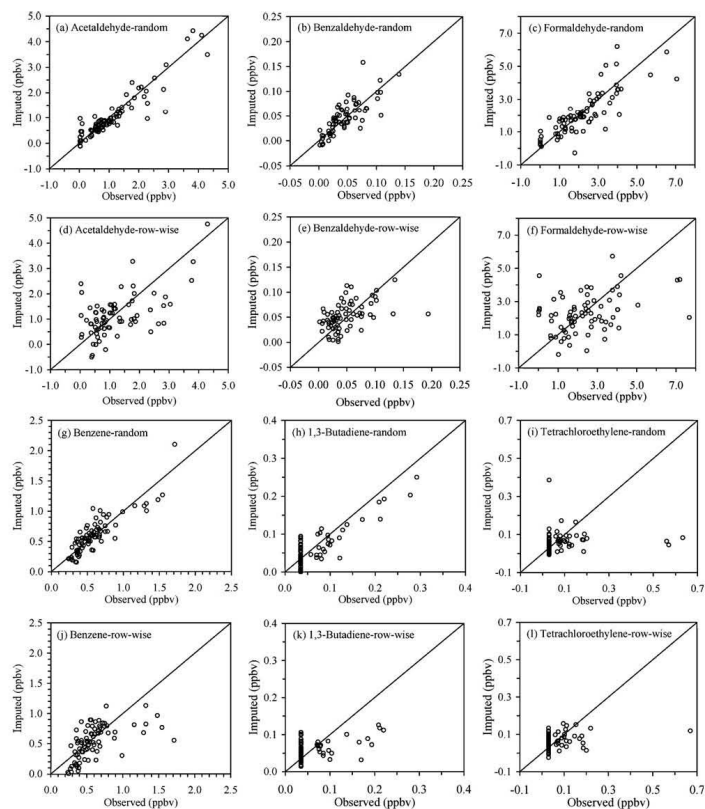
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Fig. 3 Scatter plots for observed *versus* imputed data using MI method. Otherwise as Fig. 2.

126%, but most (73%) sites and pollutants were reported to meet the 15% COV criterion. In an assessment of the RIOPA study, indoor, outdoor and personal sampling using a large number (86–171) of replicate passive samples yielded COVs from 19 to 30% for carbonyl compounds and from 6 to 42% for VOCs; active carbonyl measurements had lower COVs (9–19%, excepting glyoxyl not measured here).[26] While these studies suggest better reproducibility than obtained for most of the toxic species measured at Dearborn, we believe that reproducibility determinations at Dearborn are typical of ambient monitoring, and in particular, routine contract monitoring for several reasons. First, the NATTS sample is very limited and unbalanced, *e.g.*, benzene, which had the largest number of replicate measurements available, showed COVs from 0% (Mayville WI USA, 1 sample pair) to 59% (Northbrook IL USA, 59 sample pairs). Our benzene statistics (*e.g.*, COV = 19% for ERG) are in the center of this range. Second, contract monitoring is at several disadvantages in comparison to research studies

(like RIOPA) where sample storage/hold times are minimized, a larger number of QA/QC measures (*e.g.*, blanks, spiked samples, replicates) are utilized, and there is generally more flexibility to undertake corrective measures if problems are noted. In our research studies, for example, we typically obtain VOC precisions better than 10% (at concentrations exceeding ~0.5 μg m^{-3}).[18] Third, the Dearborn dataset contained up to 122 replicate sample pairs taken across a full year, and the reproducibility estimates obtained from this large sample likely represent the a full range of ambient sampling conditions, *e.g.*, very hot and humid weather, when performance may suffer.

Reproducibility of toxic measurements is determined by many factors, *e.g.*, system cleanliness, sampling/uptake stability, adsorbent breakthrough, loss/artifacts in sample storage, sample recovery, and analytical performance. Some problems can affect only certain toxic species, *e.g.*, crotonaldehyde is known to disappear much more rapidly on DNPH cartridges/extracts than most other aldehydes, and recovery of

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polar VOCs in canisters may be problematic.[27] Other problems can affect the entire sample, *e.g.*, a poorly cleaned canister or miscalibrated pump. While a full discussion is beyond the present scope, we note that QA/QC programs should be structured to identify (and ultimately rectify) such problems.

This study also shows differences among reproducibility indicators. Often, but not always, indicators such as correlations, COVs, and slopes will yield similar inferences. Both parametric and non-parametric measures should be used, since outliers can be difficult to detect and can strongly influence parametric measures. Multiple measures are needed as examination of a slope (and confidence interval) alone, for example, may miss a possible intercept. The distribution of concentrations will affect the indicators, *e.g.*, COVs may be misleading for compounds that show little variation, which include stable and globally-distributed pollutants, such as chloromethane, dichlorodifluoromethane, trichlorofluoromethane, carbon tetrachloride, trichlorotrifluoroethane, and tetrachloroethylene.[28] Relative errors are likely to increase for measurements near MDLs. These statistics may also perform poorly for pollutants with low detection frequencies (*e.g.*, 1,3-butadiene). Finally, while cost and logistic issues are recognized, probably at least 15 or 20 replicate samples per site and pollutant are needed to determine performance with a reasonable degree of confidence. If temperature or humidity extremes can influence measurements, then replicates should be taken under the widest possible range of weather conditions.

Error models. Many of the issues with the reproducibility indicators are addressed by the semi-parametric error models that incorporate both constant and proportional terms, and that show a range of likely errors, *e.g.*, by percentiles. These models provided stable estimates using residuals pooled across the carbonyl and VOC groups. Had sample size permitted, better performance and more insight would be attained using separate models for each compound. Within-laboratory analyses showed median absolute errors from 5 to 15% for VOCs, and about 20% for carbonyls. However, much larger errors were not uncommon, *e.g.*, 90th percentile errors were 40 to 60% for both groups of toxics.

5.2 Performance of imputation methods

In most respects, OLE and MI methods gave comparable results. For random and random block deletion patterns, both methods achieved good performance. The OLE method utilized an exogenous estimate of measurement uncertainty for observed results, and as this value was increased, the OLE predictions became more conservative and approached the mean, which was especially noticeable at high concentrations of carbonyls. As expected, MI imputations provided greater dispersion.

Imputations are more accurate for pollutants that are strongly correlated to other pollutants or other measured variables. For random missingness patterns, imputations depended largely on contemporaneous measurements of other toxics. Thus, the best performance was seen for traffic-related VOCs (*e.g.*, BTEX) and for certain combustion-related carbonyls (*e.g.*, acetaldehyde, isobutyraldehyde, propionaldehyde),

both of which form highly correlated groups of compounds. Potentially, the inclusion of other predictor variables can help to represent the influence of local sources (*e.g.*, conventional pollutants as surrogates, and wind direction for nearby sources), reactions with other pollutants (temperature and O_3), rainout or washout mechanisms (precipitation), and general atmospheric ventilation (possibly conventional pollutants like CO, mixing height, and atmospheric stability). Interestingly, imputation performance did not suffer for 1,3-butadiene, which had only 26% of its values above MDL but which is also traffic-related; however, performance was poor for tetrachloroethylene, with a similar detection frequency of 33%. Imputations tend to be poor for compounds that are emitted alone or formed independently, *e.g.*, chlorinated solvents and formaldehyde, although inclusion of meteorological information may improve performance. Pollutants that are globally distributed and present at relatively constant levels generally are not highly correlated with other pollutants or meteorological variables, and thus are imputed poorly (in terms of correlations, though COVs may be very small). Such pollutants will provide little information in time-series studies.

Imputation performance was very poor for row-wise deletions, indicating that the serial correlation in the data was insufficient to provide informative estimates. The row-wise imputations also utilized (contemporaneous, leading and lagging) conventional air pollutants and meteorological variables. In comparison to very high contemporaneous inter-pollutant correlations (*e.g.*, $0.6 < r < 0.9$ for BTEX), correlations between toxics and contemporaneous daily measurements of conventional pollutants were lower ($0.0 < r < 0.5$), as were correlations with contemporaneous daily measurements of meteorological variables ($-0.6 < r < 0.7$). Thus, imputations for row-wise deletions did not obtain the performance of the random deletions. In the Dearborn dataset, the dominant missingness pattern was row-wise, thus further attention to this class of problems is warranted.

5.3 Other imputation studies of air quality data

There are few evaluations of SI and MI procedures for air quality purposes. The OLE method was used to simultaneously estimate missing data, predict extrema, and check the validity of observations for particulate matter concentrations in Philadelphia and St. Louis, and missing O_3 data in Houston.[13] The method performed well based on correlation coefficients and bias statistics comparing predicted and observed values. Another SI method, called the site-dependent effect method (SDEM), imputed missing hourly PM_{10} in Italy using additive terms for site, day-of-week, and week-of-year.[29] This method outperformed other SI methods tested (*e.g.*, hourly mean) as well as a model-based MI method. Several SI and MI methods were tested using NO_x, NO_2, O_3, PM_{10}, SO_2 and CO measurements in Helsinki and Belfast.[30] This evaluation showed that performance decreased with increasing complexity of the missing data patterns, SI methods underestimated the error variance of missing data, and MI methods improved accuracy substantially. Self-organizing map and multi-layer back-propagation nets performed well, especially

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when incorporated into a hybrid approach that used linear interpolations for short missing gaps and multivariate methods for longer gaps; however, this study was limited by the short study period. In another study, three MI models that accounted for between-variable correlations, between- and within-variable autocorrelations over time, and random seasonal effects, were used to impute pollutant measurements in the Arctic that were missing or below MDLs.[16] The most complete models produced the most realistic imputations, and MI models outperformed *ad hoc* SI methods that ignored both the autocorrelation and seasonal structure of the data.

There are two notable differences in comparing our results for urban air toxics with the studies mentioned above. First, data quality and reproducibility are very significant issues for air toxics, and even a perfect imputation model would not yield perfect performance scores, since the underlying measurements contain errors. That said, we obtained at least comparable performance for most carbonyls and VOCs as obtained for conventional pollutants by Junninen *et al.* (2004),[30] and better performance than the single imputations of PM_{10} by Plaia and Bondi (2006).[29] Second, the temporal and spatial concentration patterns for urban pollutants can be more complex and dynamic (variable) than the long-lived species monitored at remote sites, which likely show much stronger autocorrelation. For this reason, our results are not directly comparable to the imputations at Arctic sites.[16]

5.4 Applications and limitations

This study highlights the importance of characterizing the reproducibility of ambient air toxics data prior to its use. It is important to identify variables that are informative and thus useful for applications, such as regulatory determinations of risk, receptor modeling studies of source apportionments, and epidemiological assessments of health impacts.[31,32] The error models and quality assurance steps presented here can help to describe and validate ambient data, as well as provide uncertainty estimates for OLE imputations.

This QA assessment examined only a single monitoring site, only two laboratories, and what must be considered a modest sample size. Thus, generalizations should be made cautiously. Further, the intra-laboratory comparisons focused on analytical uncertainties, which may not dominate actual errors.[33] Many other factors can influence sampling and analysis performance, and there is a clear need to increase the amount of precision and accuracy data for air toxics to better understand these factors.

Many methods are available for imputing missing data and obtaining complete-datasets, and for estimating uncertain values.[13,16] For the Dearborn data, OLE and MI attained good performance for random deletions but poor performance for the row-wise deletion pattern that dominated observations at Dearborn. Imputations for especially row-wise missingness patterns might be improved in several ways. First, the variable selection criteria may have been too stringent, *i.e.*, only very parsimonious models were generated by GLMSELECT, a procedure which assumes linear models and which does not incorporate *a priori* information. Imputations might be improved by relaxing these criteria and using more complex

models. At times, however, we found that very large (and possibly over-determined) models deteriorated performance. Second, imputations might use many other variables (*e.g.*, season, day-of-week, traffic counts) and other model structures (*e.g.*, auto-regressive integrated moving average models). A third possibility is to derive predictor variables from a combination of meteorological parameters that reflect dispersion potential or local source impacts better than additive models. Fourth, models might be constructed that account for long term trends and seasonality. Fifth, error models might be further refined and can potentially improve performance of OLE estimates. Finally, we did not examine the performance of other imputation methods.

6. Conclusions

A total 323 daily air toxics samples were collected at Dearborn, MI, USA, including 122 pairs of replicate samples. Samples were analyzed by two laboratories for 71 carbonyls and VOCs. Data cleaning included eliminating species with a low detection frequency ($<20\%$) and detecting outliers using the Gumbell extreme value distribution. Of the 23 toxics remaining in the final dataset, intra- and inter-laboratory comparisons showed good agreement for only one compound (benzene), moderate agreement for several other VOCs (*e.g.*, trimethylbenzenes, xylenes, ethylbenzene, dichlorodifluoromethane, tetrachloroethylene, and toluene), and poor-to-fair agreement for the remaining VOCs and all carbonyls. Error models, constructed by pooling residuals across the intra- and inter-laboratory analyses, provided a comprehensive description of errors. These results show the need to evaluate air toxics data prior to use in apportionment, exposure, and health studies.

Two methods were tested for their ability to impute missing data for the 23 toxics and for three missingness patterns. Optimal linear estimation (OLE) and multiple imputation (MI) methods obtained comparable performances for random deletions, with results depending on the compound, concentration distribution, and other factors. For the dominant row-wise deletion pattern observed in the air toxics dataset, the performance of both methods deteriorated. A number of steps are suggested to recover information and improve these imputations.

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