

AIR POLLUTION SOURCE APPORTIONMENT BEFORE, DURING, AND AFTER
THE 2008 BEIJING OLYMPICS AND ASSOCIATION OF SOURCES TO
ALDEHYDES AND BIOMARKERS OF BLOOD COAGULATION, PULMONARY
AND SYSTEMIC INFLAMMATION, AND OXIDATIVE STRESS IN HEALTHY
YOUNG ADULTS

By BRENT A. ALTEMOSE

A dissertation submitted to the

School of Public Health

and the

Graduate School-New Brunswick

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

written under the direction of

Mark G. Robson, Ph.D., MPH, DrPH

and approved by

New Brunswick, New Jersey

May, 2014

ABSTRACT OF THE DISSERTATION

Air Pollution Source Apportionment Before, During, and After the 2008 Beijing Olympics and Association of Sources to Aldehydes and Biomarkers of Blood Coagulation, Pulmonary and Systemic Inflammation, and Oxidative Stress in Healthy Young Adults

By

Brent A. Altemose

Dissertation Director: Mark G. Robson, Ph.D., MPH, DrPH

Based on principal component analysis (PCA) of air pollution data collected during the Summer Olympic Games held in Beijing, China during 2008, the five source types of air pollution identified – natural soil/road dust, vehicle and industrial combustion, vegetative burning, oil combustion, and secondary formation, were all distinctly lower during the Olympics. This was particularly true for vehicle and industrial combustion and oil combustion, and during the main games period between the opening and closing ceremonies. The reduction in secondary formation was reflective of a reduction in nitrogen oxides, but this also contributed to increased ozone concentrations during the Olympic period.

Among three toxic aldehydes measured in Beijing during the same time period, only acetaldehyde had a reduction in mean concentration during the Olympic air pollution control period compared to the pre-Olympic period. Accordingly, acetaldehyde was significantly correlated with primary emission sources including vegetative burning and oil combustion, and with several pollutants emitted mainly from primary sources. In contrast, formaldehyde and acrolein increased during the Olympic air pollution control

period; accordingly both were significantly correlated with ozone and with the secondary formation source type. These findings indicate primary sources may dominate for acetaldehyde while secondary sources may dominate for formaldehyde and acrolein.

Biomarkers for pulmonary inflammation (exhaled breath condensate (EBC) pH, exhaled nitric oxide, and EBC nitrite) and hemostasis and blood coagulation (vWF and sCD62p) were most consistently associated with vehicle and industrial combustion, oil combustion, and vegetative burning. The systemic inflammation biomarker 8-OHdG was most consistently associated with vehicle and industrial combustion. In contrast, the associations between the biomarkers and the aldehydes were generally not significant or in the hypothesized direction, although EBC nitrite was associated with both acrolein and acetaldehyde, and sCD62p was associated with acetaldehyde. Notably, the biomarker sCD40L showed few significant associations with any of the air pollution source types or aldehydes.

The findings indicate that implementing controls for combustion sources may have a positive impact on cardiorespiratory health, even in healthy young adults. More aggressive control of vegetative burning and further reduction of nitrogen oxide concentrations would likely have an even more positive impact.

ACKNOWLEDGEMENTS

I thank Dr. Robson for his wise advice and guidance throughout my pursuit of this degree, and Dr. Zhang for his invaluable input and guidance on the technical aspects of this dissertation. Without them, I could not have completed this long journey. I also thank Drs. Kipen, Ohman-Strickland, and Meng for their time and input into this dissertation. In addition, I thank Jicheng Gong for the time he spent on the aldehyde and biomarker analyses that preceded my work, as well as his careful review and input on what consist of the second and third chapters of this dissertation.

I also thank all the students and staff from Dr. Tong Zhu and Dr. Min Hu's labs for their assistance on aldehydes sample collection and air pollution monitoring. This research was funded in part by a grant from HEI (#4760-RPFA05-3) and a grant from NIEHS (#1R01 ES0158640). Dr. Zhang was in part supported by two NIEHS Center grants (#P30 ES05022, and #5P30ES007048). Dr. Zhu was partly funded by Beijing EPA (OITC-G08026056). However, the opinions expressed in this manuscript are solely of the authors and do not necessarily reflects those of the funding agencies.

TABLE OF CONTENTS

Abstract.....	ii
Acknowledgements.....	iv
List of Tables.....	vi
List of Figures.....	viii
Introduction	1
Chapter 1. Air Pollution Source Apportionment Before, During, and After the 2008 Beijing Olympics	5
Chapter 2. Ambient Concentrations of Aldehydes in Relation to Air Pollution Sources Before, During, and After the 2008 Beijing Olympics.....	33
Chapter 3. Association Between Air Pollution Sources and Biomarkers of Blood Coagulation, Pulmonary and Systemic Inflammation, and Oxidative Stress in Healthy Young Adults	67
Overall Conclusions and Recommendations.....	106
Appendix A – R Scripts.....	111
Appendix B – Quartile Plots.....	118
Appendix C – Time Series Plots for Pollutants.....	130
Appendix D – Descriptive Statistics for Pollutants.....	136
Appendix E – Correlation Matrix for Principal Component Analysis.....	137
Appendix F – Regression of Air Pollution Source Types with Weather Data.....	138
Appendix G – Potential Impact of Ozone on Aldehyde Measurements.....	143
Appendix H – Regression of Aldehydes with Air Pollution Source Types.....	145
Appendix I – Association of Biomarkers with Source Types and Aldehydes (Fall Data Omitted).....	148
References.....	162

LIST OF TABLES

Chapter 1

Table 1. Summary of pollutant species, measurement time resolution, and measurement techniques	24
Table 2. Summary of PM _{2.5} constituents from 4-channel sampler.....	25
Table 3. Limits of detection of PM _{2.5} constituents from 4-channel sampler.....	26
Table 4. Key to variable names.....	27
Table 5. VARIMAX rotated factor loading matrix for Beijing air pollution data..	28
Table 6. Descriptive statistics for air pollution source type factor scores, Beijing, China, June – October 2008.....	29
Table 7. Statistical comparison of air pollution source type factor scores during August 2008 and the rest of the study.....	30
Table 8. Statistical comparison of air pollution source type factor scores during the 2008 main Olympic period and the rest of the study.....	31
Table 9. Significance of regression coefficients for air pollution source type factor scores with weather variables, Beijing, China, June – October 2008.....	32

Chapter 2

Table 1. Concentration of aldehydes in pre-, during, and post-Olympic periods...	59
Table 2. Mean, median, and standard deviation of air pollutants and meteorological parameters in three periods (Rich et al. 2012).....	60
Table 3. Spearman correlation coefficients among aldehydes, other pollutants, and meteorological parameters.....	61
Table 4. VARIMAX rotated factor loading matrix for Beijing air pollution data (without aldehydes).....	62
Table 5. VARIMAX rotated factor loading matrix for Beijing air pollution data (with aldehydes).....	63
Table 6. Linear regression coefficients, relative contributions of air pollution source types to aldehyde concentrations.....	64
Table 7. Concentrations of aldehydes in ambient air in different cities.....	65

Table 8. Linear regression coefficients, relative contributions of background, primary source and secondary source to formaldehyde and acetaldehyde in three Olympic periods.....	66
---	----

Chapter 3

Table 1. Summary of the biomarker collection and analysis Beijing, China, June – October 2008.....	102
--	-----

Table 2. Descriptive statistics for biomarkers Beijing, China, June – October 2008..	103
--	-----

Table 3. Summary of significant associations between biomarkers and air pollution source types.....	104
---	-----

Table 4. Summary of significant associations between biomarkers and aldehydes...	105
--	-----

Appendices

Table A1. R script for principal component analyses.....	111
--	-----

Table A2. R script for regression of factor scores with weather data.....	113
---	-----

Table A3. R script for regression of aldehydes with factor scores.....	114
--	-----

Table A4. R script for linear mixed effects model.....	115
--	-----

Table D1. Descriptive statistics for pollutants.....	136
--	-----

Table E1. Correlation matrix for principal component analysis.....	137
--	-----

Table F1. Regression of factor 1 with weather data.....	138
---	-----

Table F2. Regression of factor 2 with weather data.....	139
---	-----

Table F3. Regression of factor 3 with weather data.....	140
---	-----

Table F4. Regression of factor 4 with weather data.....	141
---	-----

Table F5. Regression of factor 5 with weather data.....	142
---	-----

Table G1. Measured concentrations for three aldehydes with different ozone concentrations and the recovery for two different methods.....	143
---	-----

Table H1. Regression of formaldehyde with air pollution source types.....,.....	145
---	-----

Table H2. Regression of acetaldehyde with air pollution source types	146
--	-----

Table H3. Regression of acrolein with air pollution source types.....	147
---	-----

LIST OF FIGURES

Chapter 1

Figure 1. Factor scores for principal component analysis of Beijing air pollution data, June 2 – July 6, 2008.....	21
Figure 2. Factor scores for principal component analysis of Beijing air pollution data, August 1 – August 29, 2008.....	22
Figure 3. Factor scores for principal component analysis of Beijing air pollution data, September 30 – October 30, 2008.....	23

Chapter 2

Figure 1. Time scheme of the pre-, the during-, and the post-Olympic periods, two sub periods, and the periods when aldehyde measurements were conducted (indicated by dotted lines with double-headed arrows).....	55
Figure 2. Rose plots of wind measurements at Peking University in the (A) pre- and (B) during- Olympic periods in 2008.....	56
Figure 3. Period-specific means of ambient aldehydes and meteorological parameters, e.g. temperature, relative humidity, wind speed, and precipitation in three sampling periods.....	57
Figure 4. Ozone and formaldehyde concentrations as a function of nitrogen oxide concentration, Beijing, China, June to October 2008.....	58

Chapter 3

Figure 1. Percent change in pH associated with one interquartile increase in factor score, controlling for temperature (ns=1), relative humidity (ns=1), 6 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements.....	88
Figure 2. Percent change in EBC Nitrite associated with one interquartile increase in factor score, controlling for temperature (ns=2), relative humidity (ns=1), 7 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.....	89
Figure 3. Percent change in eNO associated with one interquartile increase in factor score, controlling for temperature (ns=2), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 7 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.....	90

Figure 4. Percent change in vWF associated with one interquartile increase in factor score, controlling for temperature (ns=3), relative humidity (ns=3), 7 day moving average of temperature (ns=3), 6 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.....	91
Figure 5. Percent change in sCD62p associated with one interquartile increase in factor score, controlling for temperature (ns=1), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 4 day moving average of relative humidity (ns= 2), gender, and day of week for biomarker measurements.....	92
Figure 6. Percent change in sCD40L associated with one interquartile increase in factor score, controlling for temperature (ns=1), relative humidity (ns=1), 5 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements.....	93
Figure 7. Percent change in log(8-OHdG) associated with one interquartile increase in factor score, controlling for temperature (ns=1), relative humidity (ns=1), 7 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.....	94
Figure 8. Percent change in pH associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=1), relative humidity (ns=1), 6 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements.....	95
Figure 9. Percent change in EBC Nitrite associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=2), relative humidity (ns=1), 7 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.....	96
Figure 10. Percent change in eNO associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=2), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 7 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.....	97
Figure 11. Percent change in vWF associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=3), relative humidity (ns=3), 7 day moving average of temperature (ns=3), 6 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.....	98
Figure 12. Percent change in sCD62p associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=1), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 4 day moving average of relative humidity (ns= 2), gender, and day of week for biomarker measurements.....	99

Figure 13. Percent change in sCD40L associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=1), relative humidity (ns=1), 5 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements.....	100
--	-----

Figure 14. Percent change in log(8-OHdG) associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=1), relative humidity (ns=1), 7 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements....	101
--	-----

Appendices

Figure B1. Pollutant quartile plots, non-log transformed data.....	118
--	-----

Figure B2. Pollutant quartile plots, log transformed data.....	124
--	-----

Figure C1. Time series plots for pollutants.....	130
--	-----

Figure I1. Percent change in pH associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 6 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements.....	148
---	-----

Figure I2. Percent change in EBC Nitrite associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=2), relative humidity (ns=1), 7 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.....	149
--	-----

Figure I3. Percent change in eNO associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=2), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 7 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.....	150
--	-----

Figure I4. Percent change in vWF associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=3), relative humidity (ns=3), 7 day moving average of temperature (ns=3), 6 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.....	151
--	-----

Figure I5. Percent change in sCD62p associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 4 day moving average of relative humidity (ns= 2), gender, and day of week for biomarker measurement.....	152
--	-----

Figure I6. Percent change in sCD40L associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 5 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurement..... 153

Figure I7. Percent change in log(8-OHdG) associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 7 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements..... 154

Figure I8. Percent change in pH associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 6 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements..... 155

Figure I9. Percent change in EBC Nitrite associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=2), relative humidity (ns=1), 7 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements... 156

Figure I10. Percent change in eNO associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=2), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 7 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements... 157

Figure I11. Percent change in vWF associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=3), relative humidity (ns=3), 7 day moving average of temperature (ns=3), 6 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements... 158

Figure I12. Percent change in sCD62p associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 4 day moving average of relative humidity (ns= 2), gender, and day of week for biomarker measurements... 159

Figure I13. Percent change in sCD40L associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 5 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements.... 160

Figure I14. Percent change in log(8-OHdG) associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 7 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.... 161

Introduction

The Summer Olympic Games held in Beijing, China during 2008 afforded a unique opportunity to evaluate the sources of and health effects resulting from air pollutants, as a result of the Chinese government's mandatory control actions on certain pollutant emissions during the games. This study examines the changes in air pollution composition and concentration using principal component analysis (PCA), applies the PCA to identify predominant sources of the air pollution and the impact of those source types on aldehyde concentrations, and examines the relationship between the source types and aldehydes with biomarkers of blood coagulation, pulmonary and systemic inflammation, and oxidative stress in healthy young adults.

Based on the intensity of the air pollution control measures (Wang et al., 2009a), our study used three periods defined as follows: the pre-Olympic period (June 4th - July 19th) when some light controls were implemented, the during-Olympic period (July 20th - September 19th) when the full-scale control measures were implemented, and the post-Olympic period (September 20th - October 30th) when the control measures were relaxed. In addition, extra control measures were adopted during the Olympic period (August 8th - August 24th) and the Paralympic period (September 6th - September 17th). Therefore, the during-Olympic period can be further divided into two sub-periods: sub-period 1 with full-scale control measures (July 20th - August 7th and August 24th - September 5th) and sub-period 2 with the full-scale control measures and the extra actions (August 8th - August 23rd and September 6th - September 17th).

Although the control measures clearly resulted in significant reductions in concentrations of primary emitted pollutants (e.g., PM_{2.5}, SO₂, NO_x) as reported in

previous publications (Huang et al., 2010; Li et al., 2010a; Li et al., 2010b; Wang et al., 2009a; Wang et al., 2010a; Wang et al., 2010b; Wang et al., 2010c; Wang and Xie, 2009; Wang et al., 2009b; Wang et al., 2009d; Xin et al., 2010; Zhou et al., 2010), it is less clear whether there were reductions for pollutants, such as ozone and aldehydes, that had both primary and secondary sources, and other studies have not fully examined which sources contributed most to the changes observed.

This study examines the impact of air pollution sources on ambient concentrations of three aldehydes – formaldehyde, acetaldehyde, and acrolein. These three aldehydes are considered Hazardous Air Pollutants by the United States Environmental Protection Agency because of their toxicity, and it is important to identify dominant sources in order to set up more effective control strategies. Although important sources of aldehydes include vehicles, power plants, and residential wood burning (Stahl 1969; Lipari 1984) as well as secondary sources (Altshuller, 1993; Chan and Yao, 2008; Feng et al., 2005), compared to many other air pollutants (e.g., hydrocarbons, PM mass and certain species), aldehydes have been understudied in characterizing relative contributions of primary and secondary sources in metropolitan centers.

Recent studies have focused on biological mechanisms for the health effects observed from air pollution, including cardiorespiratory effects. A prominent mechanistic hypothesis is that fine and ultrafine particles increase lung oxidative stress and provoke alveolar inflammation (Seaton et al. 1995, Kipen et al. 2011), and that this leads to increased blood coagulability within hours or days (Seaton et al. 1995, Jacobs et al. 2010, Huang et al. 2012a).

Several biomarkers have shown promise as indicators of cardiorespiratory effects and oxidative stress. For instance, a recent study of the effects of diesel exhaust exposure showed several biomarker changes, including exhaled breath condensate (EBC) pH, and exhaled nitric oxide (eNO), associated with exposure to ultra-fine particles and elemental carbon (Zhang et al. 2009). Based on the HEART study from which the data for this analysis is being obtained (Rich et al. 2012, Huang et al. 2012a, Zhang et al. 2013), biomarkers showing strong effects associated with PM include: exhaled nitric oxide (eNO), exhaled breath condensate (EBC) nitrite, sCD62P, EBC pH, and plasma fibrinogen.

The four primary hypotheses to be tested in each of three papers are as follows.

Hypothesis #1: The first hypothesis to be tested is that the relative contributions of factors representing vehicle and industrial sources of air pollution in Beijing were different during the Olympic Games compared to the time period before and after the mandatory control actions were put in place. The expected result is that the relative contribution of the factors associated with vehicle and industrial source types will be greater before and after the Olympic period, compared to during the Olympics.

Hypothesis #2: The second hypothesis to be tested is that aldehyde concentrations are influenced by both primary and secondary air pollution sources. The expected result is that the three aldehydes measured will have statistically significant linear regression coefficients for both primary and secondary factors identified through the PCA. The primary factors associated with the aldehydes will be combustion sources (vehicle, industrial, and biomass).

Hypothesis #3: The third hypothesis to be tested is that biomarkers of blood coagulation, pulmonary and systemic inflammation, and oxidative

stress are associated with combustion sources. The expected result is that the multiple regression analyses for the selected biomarkers with the factors derived from the PCA will result in statistically significant regression coefficients for the factors representing combustion sources. Hypothesis #4: The fourth and final hypothesis to be tested is that the biomarkers, particularly those for pulmonary inflammation, are associated with the aldehyde concentrations. The expected result is that the multiple regression analyses for the biomarkers will result in statistically significant regression coefficients for all three aldehydes.

Chapter 1

Air Pollution Source Apportionment Before, During, and After the 2008 Beijing Olympics

Brent Altemose^{a*}, Mark G. Robson^b, Howard M. Kipen^c, Pamela Ohman Strickland^a, Qingyu Meng^a, Min Hu, Tong Zhu, and Junfeng Zhang^d

^aSchool of Public Health, Rutgers University, Piscataway, NJ; ^bSchool of Environmental and Biological Sciences, Rutgers University, New Brunswick, NJ; ^cEnvironmental and Occupational Sciences Institute (EOHSI), Rutgers University, Piscataway, NJ; ^dNicholas School of the Environment & Duke Global Health Institute, Duke University, Durham, North Carolina

*Corresponding author. Tel: (908)500-4784; Fax: (908)320-7999; E-mail: brent@sabresafety.net

Abstract. Using air pollution data collected before, during, and after the Summer Olympic Games in Beijing in August 2008, this study examines sources and trends in air pollution utilizing principal component analysis (PCA). Due to mandatory controls implemented by the Chinese government during the Olympics, many sources of air pollution, including vehicle and industrial sources, power plants, construction work, and road dust were intentionally curtailed and suppressed. Based on the factors scores from the PCA, the five primary sources of air pollution identified – natural soil/road dust, vehicle and industrial combustion, vegetative burning, oil combustion, and secondary formation, were all distinctly lower during the Olympics. This was particularly true for vehicle and industrial combustion and oil combustion, and during the main games period between the opening and closing ceremonies, when the factors scores for all five source types were lower compared to before and after ($p < 0.03$). The reduction in secondary formation was reflective of a reduction in nitrogen oxides, but this also contributed to increased ozone concentrations during the Olympic period. These findings indicate that

the restrictions implemented by the Chinese government during the Olympic period significantly decreased the contribution of all major sources of air pollution in Beijing.

1. Introduction

1.1. Unique opportunity to collect air pollution data.

The Summer Olympic Games held in Beijing, China during 2008 afforded a unique opportunity to evaluate the sources of and health effects resulting from air pollution, as a result of the Chinese government's mandatory control actions on certain pollutant emission sources during the games. Vehicle and industrial sources were significantly restricted during the games, and consequently both the concentration and composition of air pollution in Beijing was expected to change. This study examined the changes in air pollution composition and concentration using principal component analysis. The control actions were implemented using a tiered series of actions. Tier 1 actions were implemented from July 20 through September 17 (starting 2 weeks before the Olympic opening ceremony and ending after the Paralympics) and included:

1. Keeping approximately 1 million high-emission vehicles, out of an expected 3.5 million motor vehicles
2. Suspending the operation of the coke, sinter, and metal smelting plants of Capital Steel Company, the largest steel manufacturer in the region
3. Restraining the operation of other high-emission factories and power plants
4. Ceasing construction work on almost all of the city's >3,000 building sites
5. Ceasing all exterior spray painting and welding work in the city
6. Spraying the roads several times a day to reduce re-suspension of road dust
7. Seeding clouds to induce rain to further reduce ambient PM levels

Tier 2 actions were implemented from August 8 through August 24 (the main games period), including restricting the use of another 0.96 million motor vehicles and closing the operation of additional factories. In addition, regional air pollution control strategies were implemented as a part of the Campaigns of Air Quality Research in Beijing and Surrounding Regions (CAREBEIJING) project.

1.2. Principal component analysis and source apportionment

Principal component analysis (PCA) is a common technique to define new variables from linear combinations of initial variables (Jolliffe 2002). It has been applied many times to evaluate the apportionment of air pollution sources (Artaxo et al. 1999, Henry et al. 1994, Manoli et al. 2002, Ozkaynak and Thurston 1987, Statheropoulos et al. 1998). PCA was applied in this study in order to examine the predominance of air pollution sources throughout the duration of the study, to evaluate how the magnitude of these sources may have been impacted by the air pollution controls put in place during the Olympics.

Song et al. previously utilized PCA for source apportionment of $PM_{2.5}$ in Beijing (Song et al. (1) 2006). Based on data they collected for 6 days during each season (January, April, July, and October) in 2000, the primary sources of $PM_{2.5}$ in Beijing were secondary sulfate and nitrate, mixed coal/biomass burning, industrial emissions, motor vehicle exhaust, and road dust. Cao et al. also previously conducted source apportionment based on airborne particulate matter data collected just outside of Beijing (to the northwest, in an area of heavy motor vehicle traffic) from December 1998 to September 2000 (Cao et al. 2002). The four most predominant sources identified

included soil and fly ash, a mixture of refuse incineration and limestone from construction activities, motor vehicle and coal burning sources, and sea spray.

Liu et al. utilized the United States Environmental Protection Agency (USEPA) Community Multiscale Air Quality (CMAQ) modeling system to study seasonal variations and formation mechanisms of major air pollutants in China (Liu et al. (1) 2010, Liu et al (2) 2010). They found higher surface concentrations of sulfur dioxide, nitrogen dioxide, PM₁₀, and carbon monoxide in winter and fall compared to spring and summer. Ozone, on the other hand, was higher in spring and summer.

2. Methods

2.1. Air sample collection, storage, and analysis

Sample collection, storage, and analysis were performed in conjunction with the Health Effects of an Air pollution Reduction Trial (HEART) study (Zhang et al. 2013). The HEART study included a comprehensive characterization of air pollution before, during, and after the games. All the air samplers and monitors were collocated at a secured spot on the Peking University 1st Hospital campus that served as the clinical base for the health outcome measurements of the HEART study. The hospital is located in the center of Beijing, within the 2nd ring road, 3 kilometers northwest of Tiananmen Square, surrounded by busy streets of local motor vehicle traffic, cyclists, and pedestrians.

The real-time monitors were operated continuously throughout the entire measurement period (~6 months). The integrated measurements of PM_{2.5} mass concentrations as well as PM_{2.5} constituents were collected for approximately 24 hours each day (from 10 am to 10 am the next day) within the following three periods: from

6/2/08-7/6/08 (pre-Olympic period), 8/1/08-8/29/08 (Olympic period) and 9/30/08-10/30/08 (post-Olympic period). Pollutant species and their measurement time resolution are summarized in Table 1.

Additional data was collected simultaneously during the HEART study, including particle counts, PM_{10} concentration (real-time and integrated), and several gases (O_3 , SO_2 , NO_2 , and CO). A β -radiation attenuation device, BAM 1020 (Met One, Inc., USA), was used to carry out the continuous monitoring of $PM_{2.5}$ mass concentration. The monitor was calibrated with collocated gravimetric $PM_{2.5}$ measurements. The gravimetric measurements were collected daily for approximately 24 hours using a 4-channel sampler (TH16A) coupled with cyclone size-selective inlets and sampled at 16.7 liters per minute (L/min). The four channels were split onto four different filters. Teflon filters and pre-fired quartz fiber filters (with organic impurities removed) were used as sampling media for subsequent $PM_{2.5}$ component analyses (see Table 2). Some additional $PM_{2.5}$ components were analyzed, however, only those used in the PCA are shown in Table 2.

The pre- and post-sampling weights of filters were determined, using a CAHN C-30 microbalance with a sensitivity of 0.1 milligrams (mg) and with an anti-static device, after 24-hour equilibration in the weighing room, which was maintained at a constant temperature and humidity. The limits of detection for the $PM_{2.5}$ constituents are shown in Table 3.

Concurrent data for barometric pressure, wind speed and direction, and ambient temperature and relative humidity were also collected. However, the data for wind speed and direction could not be used as they were affected by the location of a building near

the monitoring station. Therefore, an alternate set of weather data from another nearby source were obtained and used, and also included ultraviolet radiation (both near UV-A and actinic UV-B) and rain measurements. Complete data were available for most of the study dates in June, July, and August, but not in October.

Statistical analysis of the data and the principal component analysis were conducted using R version 2.14.2 (Platform: i386-pc-mingw32/i386 (32-bit), copyright 2012 by The R Foundation for Statistical Computing). Some additional descriptive statistics, data manipulation, and charts were completed using Microsoft Excel 2010 (copyright 2010 Microsoft Corporation).

The following descriptive statistics and charts were generated to understand the data set and its appropriateness for the principal component analysis (see Supplemental Materials for more information):

1. Quartile plots were generated for each pollutant, as well as the log transformed data for each pollutant, in order to assess the normality and log normality of the data
2. Each pollutant was plotted as a function of time for the entire study duration
3. The average concentration of each pollutant before, during and after the Olympics was calculated

There were 94 days of data available from the HEART study. Among the 35 variables included in this analysis, 33 had two or fewer missing days of data. The two exceptions are sulfur dioxide (SO₂), which is missing 7 days of data during the middle period, and nickel, which is missing 16 days of data mostly during the middle period.

2.2. Source apportionment by principal component analysis

A principal component analysis (PCA) was conducted using the daily average concentrations of the PM_{2.5} constituents, as shown in Tables 1 and 2, as well as PM₁₀ concentrations and the daily average concentrations of several gases measured (O₃, SO₂, NO₂, and CO). To support the PCA, statistical analysis was completed in R. The principal() function in R from the 'psych' package was used. This function utilizes a correlation matrix.

Certain pollutant data from the HEART study was omitted from this analysis. Organic matter (OM) data were omitted as they were well represented by elemental carbon (EC) plus organic carbon (OC). Nitrogen oxides (NO_x) data were omitted as they were well represented by nitrogen oxide (NO) plus nitrogen dioxide (NO₂).

There were a large number of elements (24) and polycyclic aromatic hydrocarbons (PAHs, 14) in the HEART study data. The abbreviations/variable names used for the elements and PAHs, as well as other variables used in the study model, are provided in Table 4. In order to keep a reasonable ratio between the number of days and the number of pollutant variables, 14 elements and 4 PAHs were chosen for PCA.

The elements were chosen based on two criteria – the average concentration observed and their expected utility as a tracer for particular sources. All elements whose average concentrations were below 0.003 micrograms per cubic meter (µg/m³) were excluded (Cd, Co, Tl, Mo, Th, and U). Four elements whose average concentration was between 0.003 to 0.05 µg/m³ were omitted (P, Ba, As, and Cr), while six elements in this range were included due to their potential utility as source indicators (Mn, Ti, Cu, Se, V,

and Ni). All other elements included had an average concentration above $0.1 \mu\text{g}/\text{m}^3$, up to $1.35 \mu\text{g}/\text{m}^3$. These included Pb, Mg, Zn, Al, Na, Fe, Ca, and K.

PAHs were chosen for inclusion in the PCA based on their molecular weight. Lower molecular weight PAHs are not as useful for source apportionment since they are converted in the atmosphere (Park et al. 2002, Schauer et al. 1996). PAHs with molecular weights greater than 252 have, however, been shown to be stable in atmospheric pollution mass balance equations. Based on this, four PAHs were included in the PCA – benzo(b)fluoranthene (BbF, MW=252.3), benzo(e)pyrene (BeP, MW=252.3), indeno(1,2,3-cd)pyrene (IcP, MW=276.3), and benzo(ghi)-perylene (BghiP, MW=276.3).

Since the principal component analysis ignores rows with missing data, replacement was made for missing data with the arithmetic average value for the pollutant. As mentioned previously, 33 of 35 pollutants had 2 or less days missing from the 94 days of data, and the greatest number missing was 16 (for nickel), so the impact of replacement was expected to be minimal. To test the sensitivity of the model, however, a PCA was also run without data replacement (i.e. for the 61 days with complete data for all pollutants). The resultant factors were similar, although ordered differently in terms of the percent variance for which each accounted.

A similar sensitivity analysis was also carried out by comparing log-transformed data to non-log transformed data. This was done because pollutant data often follows a log-normal distribution, and one of the underlying assumptions of the principal component analysis is normally distributed variables. However, the quartile plots for this data show that while many of the pollutants appear to be log-normally distributed, many

also appear to be normally distributed. Comparison of the PCA with and without log transformation resulted in similar factors, although they were ordered differently in terms of percent variance.

By inspection of the loadings for each factor, comparison to the existing literature, and consultation with co-authors on PM_{2.5} source compositions, assessments were made regarding the most likely source type of each factor. This analysis, along with the information provided by the PCA regarding the percent of variance in the data explained by each factor, was used to surmise the relative contribution of each major, underlying source type for air pollution in Beijing.

In order to test the sensitivity of the PCA to the number of factors included, the VARIMAX rotations were compared with the number of factors decreased incrementally from 10 to 5. While six factors were found to have eigenvalues greater than one, the sixth factor was very sensitive to the number of factors included. Based on the sensitivity of this factor, the fact that its eigenvalue was barely over one (1.1), the source apportionment was limited to five factors. All five factors that were included had eigenvalues greater than 1.4, and each accounted for at least 7.9% of the variability in the data. The five factors in total accounted for 85% of the variability in the data.

3. Results and Discussion

3.1. Descriptive statistics

The Supplemental Materials (Appendix C) contain the time-series plots generated for the concentration of each pollutant in the study as a function of time and provides the descriptive statistics for each pollutant. As expected, most of the pollutants had average concentrations that were lower during the Olympic period compared to the

periods both before and after. The exceptions are several species that are associated with secondary formation in the atmosphere and the polycyclic aromatic hydrocarbons (PAHs). As expected, secondary formation of sulfate (SO_4^{2-}), ozone (O_3), and ammonium (NH_4^+) were lowest during the cooler, fall month after the Olympic period.

The PAHs were also lowest during October. PAHs are typically highest in the winter as they are heavily influenced by increased fuel usage for heating (Park et al. 2002, Prevedouros et al. 2004). A study in South Korea in 1999 also showed that PAHs were lowest in the fall, specifically September in that study (Park et al. 2002). This is likely due to the mild weather conditions associated with decreased fuel use during this time of year, since indoor fuel use is the primary source of biomass burning emissions in this region of the world (Yan et al. 2006).

3.2. Source apportionment by principal component analysis

The results of the principal component analysis are shown in Table 5. Five factors are included, all with meaningful interpretations with respect to sources contributing to the air pollution in Beijing during this study. Factor 1 appears to be a mixed vehicle and industrial combustion source, based on the contribution of OC, EC, Cu, NO_2^- , Se, Na, $\text{PM}_{2.5}$, Zn, Pb, NO_3^- , and Mn to the factor. Factor 2 is predominated by elements including Ca, Ti, Al, Mg, Fe, Na, Mn, and Ni, as well as the ions Ca^{2+} , F^- , Mg^{2+} , and Na^+ . This source is consistent with natural soil and road dust. Factor 4 is primarily V, Ni, Zn, and Mn, which is indicative of an oil combustion source.

Factor 3 has a strong positive correlation to NO and NO_2 , and a strong negative correlation to ozone, that is, it is strongly related to the titration reaction between ozone and the nitrogen oxides. Notably, once the Olympic controls were put in place, the

concentrations of ozone actually were increased due increased incident sunlight as well as a significant reduction in nitrogen oxides, which normally act to reduce ozone concentrations near the city center. The average ozone concentration was 31.8 ppb before the Olympic controls and 42.2 ppb with the Olympic controls in place. Even during the main games period from August 8 to August 24, when most pollutants were even further repressed by additional control measures, the average ozone concentration was still 41.0 ppb.

Factor 5 is primarily associated with the four PAHs included in the model, although NH_4^+ , SO_4^{2-} , Cl^- , CO , Pb , $\text{PM}_{2.5}$, K^+ , and K are also significant components. This factor appears to be associated with vegetative burning, based on the presence of the PAHs along with CO and K . The reason for the heavy loading for the PAHs with the vegetative burning source type and negligible loadings for the other combustion source types does not necessarily indicate that PAHs were not emitted by the other sources, but does imply that the variation of PAHs during this study followed the trend for vegetative burning sources more closely than the other combustion sources.

The five sources identified – vehicle and industrial combustion, natural soil/road dust, secondary formation, oil combustion, and vegetative burning- are consistent with past source apportionment studies in Beijing (Song et al. (1) 2006, Song et al. (2) 2006, Song et al. 2007, Wang et al. 2008, Zheng et al. 2005). However, either motor vehicles or industrial sources, or both, were separate factors in all of these previous studies, whereas in this study these were accounted for jointly by Factor 1 (vehicle and industrial combustion). This may be due to the fact that these two sources were both specifically

targeted for control during the Olympic period, and therefore the sources were highly correlated during the study period.

The only other major differences between the source apportionment in this study and previous studies is the addition of an oil combustion source and the lesser impact of secondary formation in the variance of the data. The lack of an oil combustion source in past studies may be simply that in previous studies this was included with other combustion sources such as motor vehicles or industrial sources. The greater contribution of secondary formation in the previous studies is easily explained, since each of these studies included winter and spring months that were not included in this study, and seasonal differences in secondary formation would therefore be more evident with the more dramatic changes in atmospheric and weather conditions.

It is also worth noting that even though the spring Asian dust storms that impact Beijing did not occur during the time frame of this study, Factor 2 (natural soil/road dust) still accounted for a significant proportion of the variance in the principal component analysis (23.5%).

3.3. Principal component analysis factor score trends

Table 6 shows the descriptive statistics calculated for the five factors from the PCA. Figures 1 through 3 show the factors scores plotted as function of time for the periods before, during, and after the Olympics, respectively. Three of the factors – those associated with vehicle and industrial combustion, secondary formation, and oil combustion – were all lowest during August, when the Olympics occurred.

As shown in Table 7, for these three factors the difference between the average factor scores during August and the rest of the study were all statistically significant

with $p < 0.001$. The p-values were determined using a two sample t-test for populations with unequal variances. Notably, the lower scores for Factor 3 (secondary formation) were enhanced by its inverse relationship with ozone concentrations, which were highest during August, when nitrogen oxides were lowest.

Factor 5 (vegetative burning) was lowest on average during October, well after the Olympic period, and its average factor scores during August were not statistically different than the rest of the study period. As previously discussed, vegetative burning was likely lowest in October due to the mild weather conditions, with decreased fuel and energy use for heating and cooling. Furthermore, vegetative burning was not specifically controlled by the Chinese government during the Olympic period.

Factor 2 (natural soil/road dust) was lowest during June, prior to the Olympic period, and highest in October, after the Olympic period. The reason for this trend is not clear, although it is worth noting that the Asian dust storms that would be expected to most strongly influence this factor did not occur during this study. Furthermore, the difference between the factor scores in August and the rest of the study was not statistically significant. It is also worth noting that during October, Factor 2 showed three significant peaks which all occurred one day after a significant peak for Factor 1 (vehicle and industrial combustion). The reason for this is also not clear, but may be due to activity or weather patterns on one day leading to increased vehicle and industrial combustion, and then on the following day leading to increased natural soil and road dust component concentrations.

Despite the seasonal trends for Factors 2 and 5, their factor scores were still lowest during the main Olympic Games period (August 8 to 24). Figure 2 clearly shows

very few positive values for all five factors during the time period between the opening and closing ceremonies. Notably, there is a significant peak for Factor 5 (vegetative burning) shortly before and after the opening and closing ceremonies. This may correspond with a flourish of activity before and after the opening and closing ceremonies, and may also indicate that while vegetative burning was not directly controlled by the Chinese government, during the main games period vegetative burning was nonetheless decreased.

Table 8 shows the statistical analysis comparing the factor scores during the core Olympic period to the rest of the study period. The factors scores were lower during the core Olympic period compared to the combined data before (in June and the first week of August) and after (in the last week of August and October) the Olympics ($p < 0.03$ in all cases).

To evaluate the effect of weather, the available weather data was regressed with each factor. As shown in Table 9, although most of the weather variables were not significant in a regression model with each factor score, each factor was significantly associated with certain weather variables.

Ambient temperature had significant, positive associations with Factor 1 (vehicle and industrial combustion, $p = 0.007$) and a significant, negative association with Factor 3 (secondary formation, $p = 0.008$) and Factor 4 (oil combustion, $p = 0.025$). Ambient relative humidity had significant, negative associations with Factor 2 (natural soil/road dust, $p = 0.02$) and Factor 4 ($p = 0.007$). Barometric pressure had a significant, negative association with Factor 3 ($p = 0.01$). Actinic ultraviolet radiation (UVB, wavelength 280 to 320 nanometers) had negative associations of possible significance with Factor 1

($p=0.048$), Factor 4 ($p=0.056$), and Factor 5 (vegetative burning, $p=0.083$). Rain, wind velocity, and wind direction were not significantly associated with any of the factors, with the exception of a negative association between Factor 1 and winds out of the north ($p=0.044$).

The negative association for vehicle and industrial combustion sources with northerly winds may be due to the fact that the monitoring location was north of the city center. Therefore, concentrations of the pollutants from vehicle and industrial combustion sources would be lowest at the monitoring station when winds carried emissions near the city center in the opposite direction. The reason for the negative association for vehicle and industrial combustion sources with UVB and the positive association with temperature is unclear.

The negative association between natural soil/road dust and ambient relative humidity is likely due to the fact that during the study period, relative humidity was highest during the Olympic, when roads were wetted and traffic was restricted, leading to lower emissions of natural soil or road dust.

The negative association for secondary formation with temperature is easily explained, since this factor was negatively associated with ozone concentrations. Ozone was increased during the Olympic period when the average ambient temperature and incident sunlight (including UVB) were highest. Furthermore, as discussed previously, the higher temperature and incident sunlight during the Olympics occurred concurrently with a significant reduction in the emission of nitrogen oxides, which normally act to reduce ozone concentrations. The reason for the negative association with barometric pressure is unclear.

The negative association between oil combustion and ambient temperature, relative humidity, and UVB is likely explained by increased use of oil for heating during colder outdoor temperatures (and corresponding lower outdoor humidity and incident sunlight).

Finally, the relatively weak negative association between UVB and vegetative burning may be due to the fact that the seasonal trends for vegetative burning are such that emissions would be highest during colder months when UVB is lowest.

4. Conclusions

Based on the factors scores from the PCA, the five predominant sources of air pollution identified were vehicle and industrial combustion, natural soil/road dust, secondary formation, oil combustion, and vegetative burning. These sources were generally consistent with past source apportionment studies in Beijing, with slight differences that may be explained by the lack of spring and winter data in this study, as well as by the mandatory control actions put in place during the Olympics.

All five sources of air pollution were lower during the main Olympic period than during the rest of the study. This was particularly true for vehicle and industrial combustion and oil combustion, which were both significantly lower during the entire August Olympic period. Secondary formation was also lowest during August but is reflective of decreased nitrogen oxides concentrations and increased ozone concentrations. These findings indicate that the restrictions implemented by the Chinese government during the Olympic period significantly decreased the contribution of all major sources of air pollution in Beijing.

Figure 1. Factor scores for principal component analysis of Beijing air pollution data, June 2 – July 6, 2008

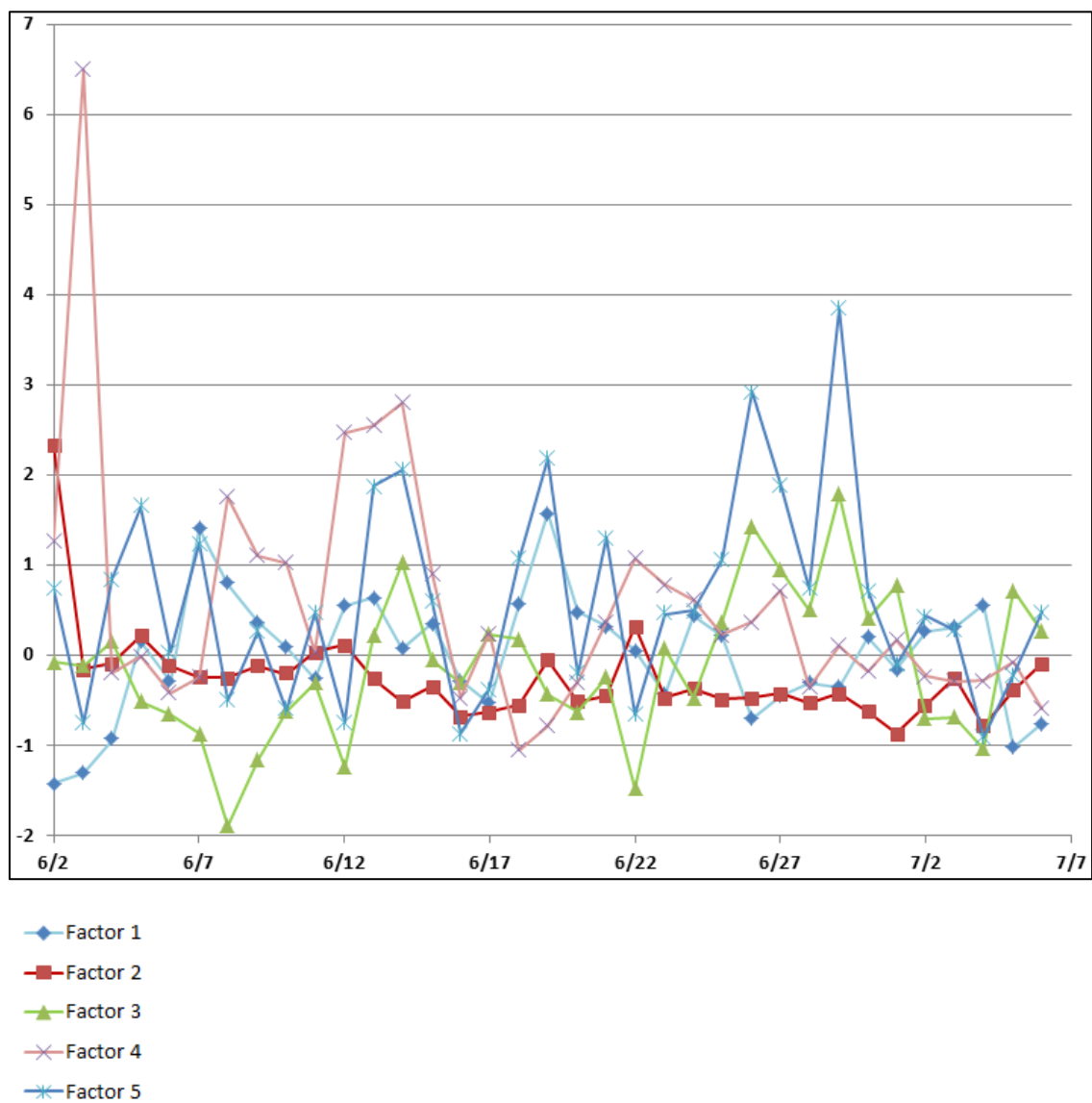


Figure 2. Factor scores for principal component analysis of Beijing air pollution data, August 1 – August 29, 2008

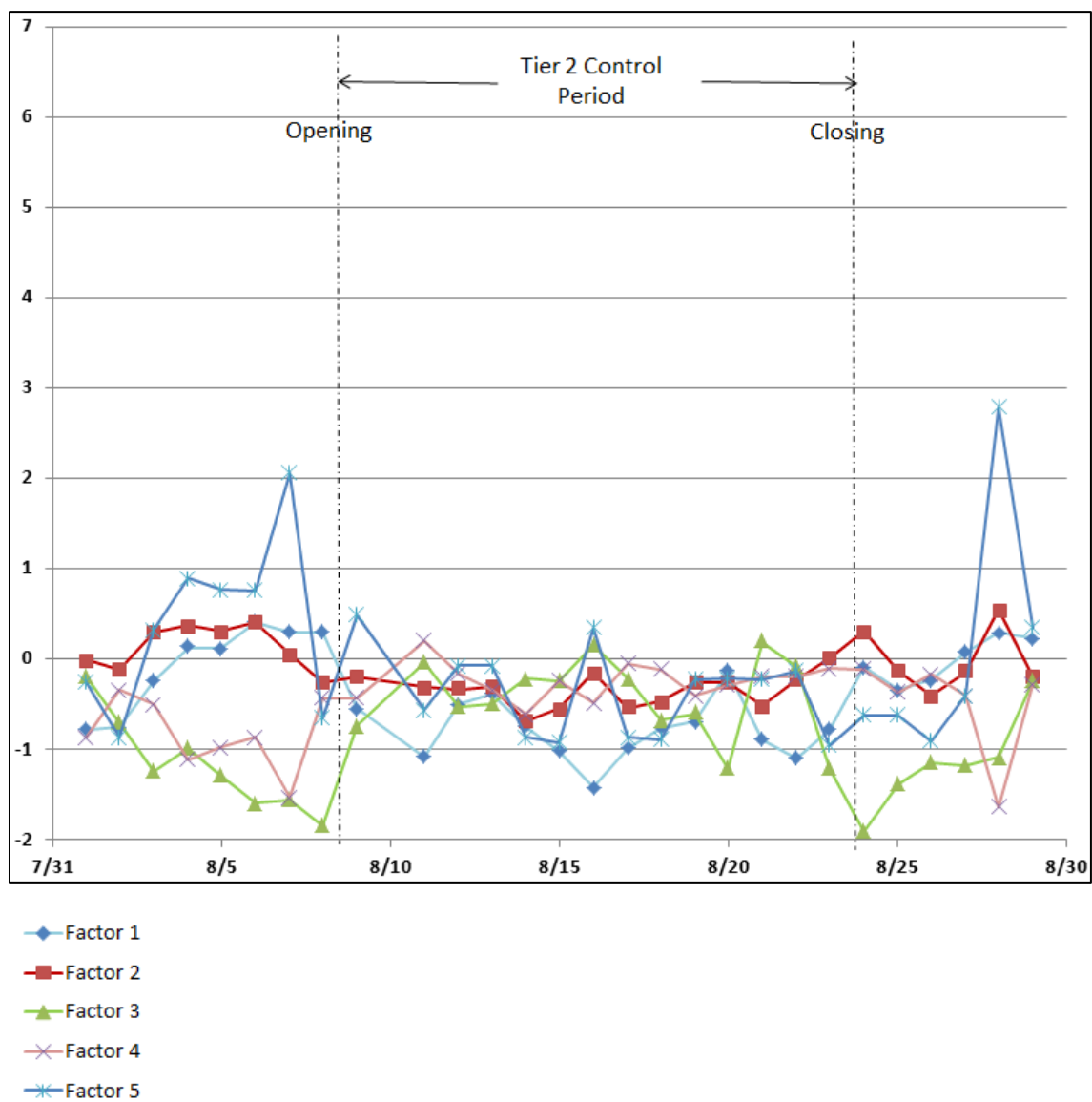


Figure 3. Factor scores for principal component analysis of Beijing air pollution data, September 30 – October 30, 2008

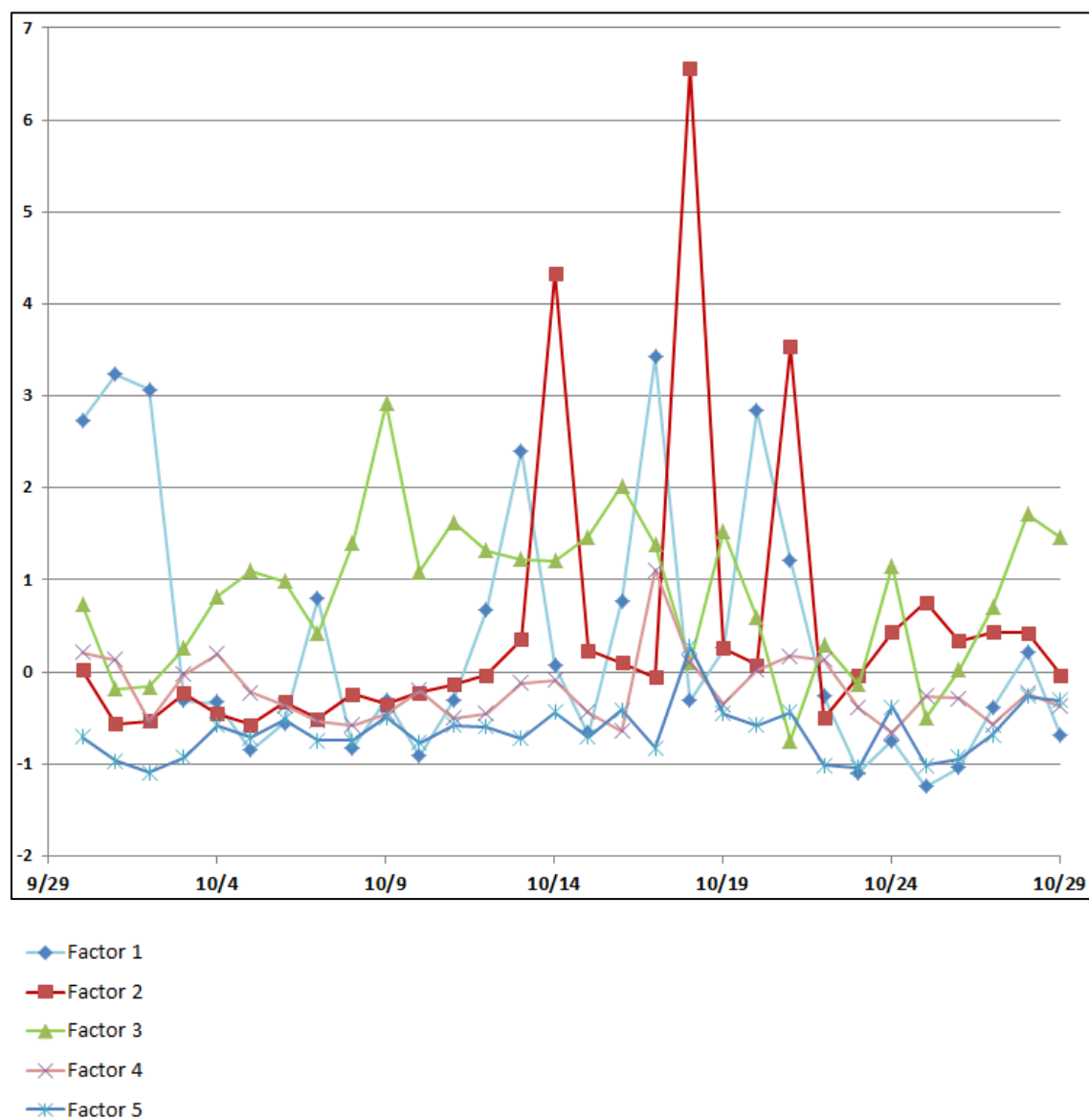


Table 1. Summary of pollutant species, measurement time resolution and measurement techniques

Species	Sampling/Monitoring equipment	Time resolution	Principle/equipment of measurement
PM _{2.5} mass	MetOne/BAM 1020	Continuous	β -radiation attenuation
PM _{2.5} mass	Cyclone/quartz fiber filter/ Teflon filter	24 hours	Gravimetric
Black Carbon in PM _{2.5}	Cyclone/MAAP	0.5 hr (semi-continuous)	Multi-Angle-Absorption- Photometer
EC/OC in PM _{2.5}	Cyclone/quartz fiber filter	24 hours	Thermal optical reflectance (TOR) Analyzer
PAHs in PM _{2.5}	Cyclone/Teflon filter	24 hours	GC/MS
Ions in PM _{2.5}	Cyclone/Teflon filter	24 hours	IC
Metals in PM _{2.5}	Cyclone/Teflon filter	24 hours	ICP/MS

Table 2. Summary of PM_{2.5} constituents from 4-channel sampler*

Channel Number	Filter Type	Analytes
1	Quartz	ECOC: Elemental carbon (EC) and Organic carbon (OC)
2	Teflon	Ions: Na ⁺ , NH ₄ ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , F ⁻ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻
3	Teflon	Elements: Na, Mg, Al, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Se, Pb
4	Quartz	Polycyclic Aromatic Hydrocarbons (PAHs): benzo(b)fluoranthene (BbF), Benzo(e)pyrene (BeP, benzo(ghi)perylene (Bghi), indeno(123-cd)pyrene (IcP)

*Additional PM_{2.5} constituents were analyzed; only those included in the PCA are shown in Table 2 and 3.

Table 3. Limits of detection of PM_{2.5} constituents from 4-channel sampler

ICP-MS: elements detection [units: nanograms (ng)]

Elements	LOD	elements	LOD
Na	0.0152	Mn	0.0153
Mg	0.0007	Fe	0.0831
Al	0.1910	Ni	0.0225
K	0.0644	Cu	0.0187
Ca	0.2936	Zn	0.0920
Ti	0.1446	Se	0.0953
V	0.0250	Pb	0.0009

PAHs detection [units: nanograms per microliter (ng/μL)]

PAHs	LOD	recovery
Benzo(b)fluoranthene (BbF)	0.020	69.16%
Benzo(e)pyrene (BeP)	0.010	72.45%
Indeno(1,2,3-cd)pyrene (IcP)	0.040	51.21%
Benzo(g,h,i)perylene (BgHi)	0.020	63.72%

IC: Ions detection [units: milligrams per liter (mg/L)]

Ions	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
MDL	0.03	0.06	0.1	0.1	0.05	0.03	0.03	0.01	0.01

Table 4. Key to variable names

SO2	Sulfur dioxide, 24 hour average
NO	Nitrous oxide, 24 hour average
NO2	Nitrogen dioxide, 24 hour average
O3	ozone, 24 hour average
CO	Carbon monoxide, 24 hour average
PM25	Particulate matter aerodynamic diameter < 2.5 microns
OC	Organic carbon
EC	Elemental carbon
Na	Sodium
Mg	Magnesium
Al	Aluminum
K	Potassium
Ca	Calcium
Ti	Titanium
Mn	Manganese
Fe	Iron
Cu	Copper
Zn	Zinc
Pb	Lead
Ni	Nickel
V	Vanadium
Se	Selenium
Na1	Sodium ion
NH41	Ammonium ion
K1	Potassium ion
Mg2	Magnesium ion
Ca2	Calcium ion
F_	Fluorine ion
Cl_	Chlorine ion
NO3_	Nitrate ion
SO42_	Sulfate ion
BbF	Benzo(b)fluoranthene
BeP	Benzo(e)pyrene
IcP	Indeno(1,2,3-cd)pyrene
BghiP	Benzo(ghi)perylene
Tavg	24 hour average temperature
RHavg	24 hour average relative humidity
Baroavg	24 hour average barometric pressure
UVAavg	24 hour average near ultraviolet radiation, 320 to 400 nanometers
UVBavg	24 hour average actinic ultraviolet radiation, 280 to 320 nanometers
WindVavg	24 hour average wind velocity
Rain	24 hour total precipitation
N,S,E,W	Fractional predominance of wind direction – north, south, east, and west

Table 5. VARIMAX rotated factor loading matrix for Beijing air pollution data

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
	Vehicle/industrial combustion	Natural soil / road dust	Secondary formation	Oil Combustion	Vegetative burning
SO ₂	0.655	0.143	-0.060	0.372	0.181
NO	0.195	0.315	0.756	-0.092	-0.222
NO ₂	0.679	0.319	0.605	0.091	-0.047
O ₃	-0.026	-0.070	-0.850	-0.122	0.033
CO	0.490	0.050	0.255	0.432	0.492
PM _{2.5}	0.794	0.254	-0.114	0.085	0.474
OC	0.827	0.304	0.330	-0.021	0.013
EC	0.780	0.352	0.363	-0.023	0.084
Na	0.720	0.512	0.077	0.173	0.301
Mg	0.138	0.903	-0.042	0.218	0.076
Al	0.239	0.897	0.195	0.173	-0.031
K	0.600	0.245	0.095	0.441	0.439
Ca	0.131	0.957	0.085	0.115	0.022
Ti	0.196	0.924	0.046	0.165	0.006
Mn	0.503	0.504	0.221	0.542	0.150
Fe	0.376	0.749	0.206	0.239	0.180
Cu	0.772	0.161	-0.075	0.038	0.179
Zn	0.584	0.164	0.225	0.648	0.241
Pb	0.717	0.127	0.030	0.382	0.467
Ni	0.200	0.438	0.137	0.732	-0.036
V	0.055	0.162	-0.152	0.866	0.232
Se	0.761	0.151	0.258	0.374	0.245
Na ⁺	0.641	0.445	0.017	0.238	0.398
NH ₄ ⁺	0.617	-0.040	-0.318	0.014	0.635
K ⁺	0.568	0.136	-0.015	0.385	0.525
Mg ²⁺	0.239	0.904	0.058	0.063	-0.013
Ca ²⁺	0.109	0.950	0.039	0.027	-0.017
F ⁻	0.105	0.936	0.157	0.004	-0.043
Cl ⁻	0.359	0.126	0.211	0.137	0.628
NO ₃ ⁻	0.752	0.174	0.061	0.089	0.405
SO ₄ ²⁻	0.584	0.028	-0.468	0.008	0.563
BbF	0.181	-0.040	-0.107	0.129	0.946
BeP	0.033	-0.091	-0.225	0.124	0.945
IcP	0.326	0.040	0.011	0.056	0.906
BghiP	0.245	-0.019	-0.046	0.064	0.934
Eigenvalue	16.79	6.92	1.41	1.87	2.84
% Var.	25.7%	23.5%	7.9%	9.5%	18.6%
Cum% var.	25.7%	49.2%	57.1%	66.6%	85.2%

Table 6. Descriptive statistics for air pollution source type factor scores, Beijing, China, June – October 2008

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
	Vehicle/industrial combustion	Natural soil / road dust	Secondary formation	Oil Combustion	Vegetative burning
arith avg	0.000	0.000	0.000	0.000	0.000
SD	1.00	1.00	1.00	1.00	1.00
N	94	94	94	94	94
Max	3.4	6.6	2.9	6.5	3.8
Min	-1.4	-0.9	-1.9	-1.6	-1.1
6/2-7/6	0.004	-0.255	-0.128	0.560	0.620
8/1-8/29	-0.419	-0.137	-0.798	-0.467	-0.058
9/30-10/30	0.374	0.412	0.866	-0.210	-0.648

Table 7. Statistical comparison of air pollution source type factor scores during August 2008 and the rest of the study

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
	Vehicle/industrial combustion	Natural soil / road dust	Secondary formation	Oil Combustion	Vegetative burning
During (8/1-8/29)	-0.42	-0.14	-0.80	-0.47	-0.06
SD	0.52	0.32	0.61	0.43	0.90
N	28	28	28	28	28
Before & After (6/2-7/6, 9/30-10/30)	0.18	0.06	0.34	0.20	0.02
SD	1.10	1.17	0.94	1.10	1.04
n	66	66	66	66	66
t test statistic	-3.58	-1.25	-6.98	-4.20	-0.39
v - deg of freedom	90.96	83.81	77.01	91.62	58.53
p	0.0006	0.203	<0.0005	<0.0005	0.710

Table 8. Statistical comparison of air pollution source type factor scores during the 2008 main Olympic period and the rest of the study

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
	Vehicle/industrial combustion	Natural soil / road dust	Secondary formation	Oil Combustion	Vegetative burning
8/8-8/24 average	-0.68	-0.30	-0.61	-0.25	-0.40
8/8-8/24 St. Dev.	0.44	0.24	0.65	0.20	0.46
8/8-8/24 n	16	16	16	16	16
All other data average	0.14	0.06	0.12	0.05	0.08
All other data St. Dev.	1.03	1.08	1.02	1.09	1.06
All other data n	78	78	78	78	78
t test statistic	-5.14	-2.64	-3.69	-2.27	-2.94
v - deg. of freedom	54.26	91.41	32.50	91.69	53.83
P	<0.0005	0.009	0.0005	0.026	0.006

Table 9. Significance of regression coefficients for air pollution source type factor scores with weather variables, Beijing, China, June – October 2008

Weather variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Tavg	0.007	>0.1	0.008	0.025	>0.1
RHavg	>0.1	0.02	>0.1	0.007	>0.1
Baroavg	>0.1	>0.1	0.010	>0.1	>0.1
UVAavg	>0.1	>0.1	>0.1	>0.1	>0.1
UVBavg	0.048	>0.1	>0.1	0.056	0.083
WindVavg	> 0.1	>0.1	>0.1	>0.1	>0.1
Rain	> 0.1	>0.1	>0.1	>0.1	>0.1
N winds	0.044	>0.1	>0.1	>0.1	>0.1
W winds	>0.1	>0.1	>0.1	>0.1	>0.1
S winds	>0.1	>0.1	>0.1	>0.1	>0.1
E winds	>0.1	>0.1	>0.1	>0.1	>0.1

Chapter 2

Ambient Concentrations of Aldehydes in Relation to Air Pollution Sources Before, During, and After the 2008 Beijing Olympics

Brent Altemose^{a*}, Jicheng Gong^b, Tong Zhu^c, Min Hu^c, Liwen Zhang^c, Hong Cheng^c, Lin Zhang^a, Jian Tong^a, Mark G. Robson^d, and Junfeng Zhang^b

^aSchool of Public Health, Rutgers University, Piscataway, NJ; ^bNicholas School of the Environment & Duke Global Health Institute, Duke University, Durham, North Carolina; ^cState Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China; ^dSchool of Environmental and Biological Sciences, Rutgers University, New Brunswick, NJ

*Corresponding author Tel: (908)500-4784; Fax: (908)320-7999; E-mail: brent@sabresafety.net

Abstract. This study was carried out to characterize three aldehydes of health concern (formaldehyde, acetaldehyde, and acrolein) at a central Beijing site in the summer and early fall of 2008 (from June to October). Aldehydes in polluted atmospheres come from both primary and secondary sources, which could complicate the control strategy for these reactive compounds. Measurements were made before, during, and after the Beijing Olympics to examine whether the air pollution control measures implemented during the Olympics had an impact on concentrations of the three aldehydes. Average concentrations of formaldehyde, acetaldehyde and acrolein were $29.3 \pm 15.1 \mu\text{g}/\text{m}^3$, $27.1 \pm 15.7 \mu\text{g}/\text{m}^3$ and $2.3 \pm 1.0 \mu\text{g}/\text{m}^3$, respectively, for the entire period of measurements; all being at the high end of concentration ranges measured in cities around the world in photochemical smog seasons. Among the three measured aldehydes, only acetaldehyde had a reduction in mean concentration during the Olympic air pollution control period compared to the pre-Olympic period. Formaldehyde and acrolein increased during this period; both followed the changing pattern of temperature

and were each significantly correlated with ozone (a secondary product of photochemical reactions) and with a secondary formation factor identified by principal component analysis (PCA). In contrast, acetaldehyde was reduced during the Olympic period and was significantly correlated with several pollutants emitted mainly from local emission sources (e.g., NO_2 , CO, and $\text{PM}_{2.5}$). Acetaldehyde was also more strongly associated with primary emission sources including vegetative burning and oil combustion factors identified through the PCA. Our findings point to the complexity of source control strategies for secondary pollutants. Keywords: aldehydes, air pollution, acrolein, primary source, secondary source, principal component analysis.

1. Introduction

1.1 Unique opportunity to collect air pollution data

Beijing is one of the mega cities in the world with a population of over 17 million. The rapid economic growth in China places a high demand on energy consumption, resulting in massive fossil fuel emissions of pollutants, e.g. nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), sulfur dioxide (SO_2), carbon monoxide (CO), volatile organic carbons (VOCs) and particulate matter (Tang, 2004). In recent years, the number of automobiles in Beijing increased rapidly at a rate of approximately 15% annually (Chan and Yao, 2008; Hao et al., 2006). The car stock in Beijing grew to 4 million by the end of 2009 and reached 5 million in 2012.

The Chinese government implemented a series of aggressive air pollution control measures to improve the air quality during the Beijing Olympics and Paralympics. Control measures included the reduction of pollutant emission from factories and industrial facilities and reducing the number of private cars by half through an odd/even

plate number rule. Additionally, all construction projects were suspended during the Olympic period (Wang et al., 2009a). Although these control measures clearly resulted in significant reductions in concentrations of primarily emitted pollutants (e.g., $\text{PM}_{2.5}$, SO_2 , NO_x) as reported in previous publications (Huang et al., 2010; Li et al., 2010a; Li et al., 2010b; Wang et al., 2009a; Wang et al., 2010a; Wang et al., 2010b; Wang et al., 2010c; Wang and Xie, 2009; Wang et al., 2009b; Wang et al., 2009d; Xin et al., 2010; Zhou et al., 2010), it is less straight forward as to whether there were reductions for pollutants, such as ozone and aldehydes, that had both primary and secondary sources.

Based on the intensity of the air pollution control measures (Wang et al., 2009a), our study used three periods defined as follows: the pre-Olympic period (June 4th - July 19th) when some light controls were implemented, the during-Olympic period (July 20th - September 19th) when the full-scale control measures were implemented, and the post-Olympic period (September 20th - October 30th) when the control measures were relaxed. In addition, extra control measures were adopted during the Olympic period (August 8th - August 24th) and the Paralympic period (September 6th - September 17th). These extra controls included barring of additional 20% government-owned cars from traveling on the road, suspending outdoor construction work, and temporarily closing some gas stations.

Therefore, the during-Olympic period can be further divided into two sub-periods: sub-period 1 with full-scale control measures (July 20th - August 7th and August 24th - September 5th) and sub-period 2 with the full-scale control measures and the extra actions described above (August 8th - August 23rd and September 6th - September 17th).

1.2 Ambient concentrations and sources of aldehydes

Aldehydes are reactive compounds that can produce adverse health effects in humans and experimental animals (Akbar-Khanzadeh and Mlynek, 1997; Benjebria et al., 1994; Cassee et al., 1996a; Cassee et al., 1996b). Although a number of papers have been published assessing air quality impacts of emission controls during the Beijing Olympics (Huang et al., 2010; Li et al., 2010a; Wang et al., 2009a; Wang and Xie, 2009; Wang et al., 2009d), only one paper was on formaldehyde and acetaldehyde measured at one quasi-suburban Beijing site, and none on acrolein. (In fact, our overall knowledge about ambient acrolein exposure is extremely limited despite high toxicity of this compound). Aldehydes can be directly emitted into the atmosphere from the incomplete combustion of biomass and fossil fuels (Schauer et al., 2001; Zhang and Smith, 1999), and formed in the atmosphere as a result of photochemical oxidation of reactive hydrocarbons (Altshuller, 1993; Possanzini et al., 2002). Important combustion sources of aldehydes include vehicles, power plants, and residential wood burning (Stahl 1969; Lipari 1984). Hence it is important to identify dominant sources in order to set up more effective control strategies. Compared to many other air pollutants (e.g., hydrocarbons, PM mass and certain species), aldehydes have been understudied in characterizing relative contributions of primary and secondary sources in metropolitan centers (Altshuller, 1993; Chan and Yao, 2008; Feng et al., 2005).

In order to examine whether aldehyde concentrations were reduced during the air pollution control period, we measured formaldehyde, acetaldehyde, and acrolein within a 1-month time window for each of the pre-Olympic, during-Olympic, and post-Olympic periods. The measurement scheme is shown in Figure 1. Note that in the

during-Olympic period, aldehydes were measured in both sub-periods 1 and 2. Furthermore, in order to better understand the impact of the Beijing Olympic control measures on concentrations of these aldehydes, we also measured other air pollutants (PM, CO, SO₂, NO, NO₂, NO_x and ozone) at the same monitoring site, collected meteorological data (temperature, relative humidity, wind speed, and wind direction), and analyzed their relationships with the aldehydes.

1.3 Influence of weather and meteorology on pollution in Beijing

Another important factor resulting in high concentrations of ambient aldehydes could be meteorological conditions affecting air quality during the summer months in Beijing (Streets et al., 2007). Beijing is located at 39°56'N and 116°20'E on the northwest border of the Great North China Plain. It is located in a warm temperate zone and has a typical continental monsoon climate (Chan and Yao, 2008). The air quality of Beijing in the summer is largely determined by the meteorology (Streets et al., 2007), as, for example, temperature as well as solar radiation are key factors that control the photochemistry processes (Wang et al., 2009d). Wind direction is associated with the origin of air masses transported from the surrounding areas of Beijing and wind speed controls the dispersion of air pollution. In summer months, Beijing typically has a high temperature (mean: 27 °C) and high RH (mean: 64%), both of which favor the photochemical reactions. In the summer, Beijing also has few windy days, which is unfavorable for atmospheric dispersion of air pollutants.

1.4 Principal component analysis and source apportionment

Using air pollution data collected before, during, and after the Summer Olympic Games in Beijing in August 2008, the authors previously examined sources and trends in

air pollution utilizing principal component analysis (PCA) (see Chapter 1). Based on the PCA, five predominant sources of air pollution were identified – natural soil/road dust, vehicle and industrial combustion, vegetative burning, oil combustion, and secondary formation. In this paper we examined the relationship of these sources with aldehyde concentrations.

2. Methods

2.1 Air sample collection, storage, and analysis

Sample collection, storage, and analysis were performed in conjunction with the Health Effects of an Air pollution Reduction Trial (HEART) study (Zhang et al. 2013). The HEART study included a comprehensive characterization of air pollution before, during, and after the games. All the air samplers and monitors were collocated at a secured spot on the Peking University 1st Hospital campus that served as the clinical base for the health outcome measurements of the HEART study. The hospital is located in the center of Beijing, within the 2nd ring road, 3 kilometers northwest of Tiananmen Square, surrounded by busy streets of local motor vehicle traffic, cyclists, and pedestrians. Further detail regarding the collection of the air samples and the subsequent principal component analysis are described in the author's previous paper.

2.2 Aldehyde measurement methods

We used a passive sampling technique to collect aldehydes on a 24-hour integrated basis and then used an HPLC-fluorescence technique to analyze aldehydes. This method was developed to overcome the shortcomings of the “conventional” DNPH-based method, as described in previous publications (Herrington et al., 2005; Zhang et al., 2000). Our method used a C18 cartridge (LC-18, 0.5g/4.5mL, Supelco, Inc.

US) coated with dansylhydrazine (DNSH) (as opposed to the use of a C18 cartridge coated with DNPH in the conventional method) to collect and derivatize aldehydes. The aldehydes-DNSH derivatives were analyzed using a fluorescence detector (as opposed to the use of a UV detector in the conventional method and thus improving the sensitivity). We used the DNSH-based method instead of the DNPH-based method for the following reasons: (1) This method is not affected by ozone at concentrations up to 300 ppb, as previously reported by Rodler et al. (1993). This finding was also reproduced in a set of experiments we have conducted to test the effects of ozone on the aldehydes recovery, as shown in Appendix G. (2) This method is more reliable for acrolein. The DNSH-based method has proven to substantially improve the collection efficiency and precision for acrolein and crotonaldehyde (Herrington et al., 2005; Weisel et al, 2005). (3) This method uses passive sampling thus offering convenience in the field.

Samples and field controls were eluted with acetonitrile and aliquots of extracts were analyzed using an HPLC system with fluorescent detection. A Nova-Pak C18 column was used. The methods are described further in the Supplementary Materials.

Throughout the entire sampling period, 78 aldehyde samples were collected in total, including 28, 26, and 24 samples for the pre-, during-, and post-Olympic periods, respectively. One field control and one duplicate sample were collected every 3 to 5 days for quality control purposes. Sample concentrations were corrected with the average field blank concentrations. All the samples had detectable concentrations of aldehydes.

2.3 Other pollutants and meteorological data measurement methods

Other pollutants, including O₃, CO, SO₂, NO, NO₂, NO_x and fine particles (PM_{2.5}), were measured simultaneously with the aldehydes (i.e. at the same site and on the same dates). Meteorological data (temperature, relative humidity, wind speed, and wind direction) were collected at a nearby meteorological station (within 5 km). These methods are detailed in previous papers (Zhang et al. 2013).

2.4 Statistical analysis

Statistical analyses of the data were conducted using R version 2.14.2 (Platform: i386-pc-mingw32/i386 (32-bit), copyright 2012 by The R Foundation for Statistical Computing). Some additional descriptive statistics, data manipulation, and charts were completed using Microsoft Excel 2010 (copyright 2010 Microsoft Corporation). P-values for comparison of aldehyde concentrations between periods was calculated using a two-tailed t test.

2.5 Principal component analysis

Our previous principal component analysis (PCA) and source apportionment identified the following five air pollution source types during the time period of this study (see Chapter 1): Factor 1 – Vehicle and industrial combustion; Factor 2 – Natural soil / road dust; Factor 3 – Secondary formation; Factor 4 – Oil combustion; Factor 5 – Vegetative burning.

To evaluate how the aldehydes affected the PCA, our analysis was performed with and without the aldehydes in the models. The addition of the aldehydes did not change the interpretation of the source apportionment or the ordering of the factors in terms of eigenvalues or percent variance explained by each factor. Each aldehyde was

regressed with the daily scores for the five factors in order to evaluate the strength of the associations. The factors determined without the aldehydes in the PCA were used for this regression.

3. Results

3.1 Concentrations of atmospheric aldehydes

Mean, standard deviation, minimum and maximum concentrations of aldehydes concentrations throughout the entire period and in the three specific periods are given in Table 1. The average concentrations of all three aldehydes were lowest during the post-Olympic period. Furthermore, despite the controls put in place during the Olympics, the average concentrations of both formaldehyde and acrolein were highest in this period, although the difference for formaldehyde from the pre- to the during-Olympic period was not statistically significant. The concentration of formaldehyde increased by 1.6 $\mu\text{g}/\text{m}^3$ (4%, $p=0.576$) from the pre- to the during-Olympic period and decreased by 23.4 $\mu\text{g}/\text{m}^3$ (63%, $p<0.0001$) from the during- to the post-Olympic period. The concentration of acrolein increased by 0.5 $\mu\text{g}/\text{m}^3$ (20%, $p=0.038$) from the pre- to the during-Olympic period and decreased by 1.5 $\mu\text{g}/\text{m}^3$ (52%, $p<0.0001$) from the during- to the post-Olympic period.

For acetaldehyde, on the other hand, the average concentrations were highest before the Olympics. Period-specific mean concentration of acetaldehyde decreased by 11.5 $\mu\text{g}/\text{m}^3$ (33%, $p=0.0074$) from the pre- to the during-Olympic period and continued to decrease by 3.1 $\mu\text{g}/\text{m}^3$ (13%, $p=0.483$) from the during- to the post-Olympic period.

Sixteen and ten samples were collected in the sub-period 1 (with full scale controls) and 2 (with full scale and extra controls), respectively. Average concentrations

of aldehydes were higher in sub-period 1 than in the sub-period 2 in all three cases. The average concentrations were $37.7 \pm 10.7 \mu\text{g}/\text{m}^3$ (28.2 ± 8.0 ppb) and $36.5 \pm 12.4 \mu\text{g}/\text{m}^3$ (27.2 ± 9.3 ppb) for formaldehyde, $26.3 \pm 15.9 \mu\text{g}/\text{m}^3$ (13.4 ± 8.1 ppb) and $19.9 \pm 12.3 \mu\text{g}/\text{m}^3$ (10.1 ± 6.3 ppb) for acetaldehyde, and $3.0 \pm 0.8 \mu\text{g}/\text{m}^3$ (1.2 ± 0.3 ppb) and $2.7 \pm 0.8 \mu\text{g}/\text{m}^3$ (1.1 ± 0.3 ppb) for acrolein during sub-period 1 and 2, respectively. The reduction in aldehydes concentrations in sub-period 2 compared to sub-period 1 was 3%, 24%, and 10% for formaldehyde, acetaldehyde and acrolein, respectively.

3.2 Meteorological conditions

Figure 2 depicts the prevailing wind direction in summertime of Beijing's urban area as S-SSE-SE and was consistent before and during the Olympics. The daily average temperature, relative humidity, precipitation, and wind speed in the three sampling periods are summarized in Table 2. The average temperature increased by 2.6°C (10.1%, $p=0.0733$) from the pre-Olympic period to the during-Olympic period, but decreased by about 11.7°C (41.8%, $p<0.0001$) from the during-Olympic period to the post-Olympic period. Daily average relative humidity (RH) increased by about 0.7% (1.2%, $p=0.904$) from the pre- to the during-Olympic period and decreased by 12.2% (18.9%, $p=0.0560$) from the during- to the post-Olympic period. Daily average precipitation increased by 3.0 mm (99.4%, $p=0.167$) from the pre- to the during-Olympic period, and decreased by 5.7 mm (93.3%, $p=0.012$) from the during- to the post-Olympic period. Wind speed increased by 0.16 m/s (14.8%, $p=0.599$) from the pre- to the during-Olympic period and increased by 0.07 m/s (5.6%, $p=0.822$) from the during- to the post-Olympic period. There was no significant change in temperature, RH, or wind speed between the pre- and the during-Olympic period. The precipitation in

the during-Olympic period was about twice as much as that in the pre-Olympic period. In contrast, the change between the during- and the post-Olympic periods was much larger for all three parameters.

3.3 Correlation of aldehydes with other air pollutants and meteorological conditions

Since some of the air pollutants, e.g. $\text{PM}_{2.5}$, NO and NO_2 , did not satisfy the normality distribution assumption, the Spearman rank correlation test was used to examine the association between pollutants. The Spearman correlation coefficients among aldehydes and other air pollutants are shown in Table 3. The p-value for each coefficient was calculated using permutation test and the significance level of each correlation coefficient is indicated in Table 3 as well. Formaldehyde, acetaldehyde, and acrolein were significantly correlated with each other. The correlation coefficients were 0.59 for formaldehyde and acetaldehyde, 0.63 for formaldehyde and acrolein, and 0.43 for acetaldehyde and acrolein. Formaldehyde was significantly correlated with oxides of nitrogen (NO, NO_2 and NO_x) in the negative direction and the correlation coefficients ranged from -0.31 to -0.53. Formaldehyde was significantly correlated with each of daily average O_3 , daily maximum O_3 , CO and $\text{PM}_{2.5}$ in the positive direction with coefficients of 0.41, 0.38, 0.26, and 0.39, respectively. Acetaldehyde was significantly and positively correlated with SO_2 , NO_2 , CO and $\text{PM}_{2.5}$ with correlation coefficients of 0.51, 0.23, 0.46, and 0.47, respectively. Acrolein was significantly correlated with oxides of nitrogen in the negative direction ($r=-0.53$ with NO and -0.36 with NO_2) and significantly correlated with daily average ozone ($r=0.34$), daily maximum ozone ($r=0.33$), and $\text{PM}_{2.5}$ ($r=0.24$) in the positive direction. No significant correlation was found for any of the three aldehydes with daily average photooxidant. However, daily

maximum photooxidant was significantly correlated with formaldehyde ($r=0.26$, $p=0.023$) and acrolein ($r=0.23$, $p=0.053$), respectively. Both formaldehyde and acrolein were significantly correlated with temperature ($r=0.56$ and 0.59) and RH ($r=0.62$ and 0.38). Acetaldehyde was significantly and positively correlated with RH ($r=0.30$) but not with temperature.

3.4 Association of aldehydes with air pollution sources

As shown in Tables 4 and 5, the principal component analysis (PCA) was performed with and without the aldehydes in the model. Interpretation of the PCA was discussed in Chapter 1. Inclusion of the aldehydes did not significantly change the interpretation of the source apportionment or the ordering of the factors in terms of eigenvalues or percent variance explained by each factor. Formaldehyde and acrolein had component loadings between 0.73 to 0.75 for the secondary formation factor, while acetaldehyde had a component loading of 0.46 for this factor. The only other component loading above 0.4 for any of the aldehydes within the factors was acetaldehyde, which had a component loading of 0.42 for the oil combustion factor. It is worth noting the percent variance explained by the secondary formation factor did increase slightly with the addition of the aldehydes to the model, and that ozone also had a significant, positive loading for this factor (0.70), while nitrogen oxide and nitrogen dioxide had significant, negative loadings for this factor (-0.66 and -0.50, respectively), which were the opposite signs compared to the loadings without the aldehydes in the model.

Each aldehyde was then regressed with the five factors in order to evaluate the strength of the association between them and the identified air pollution sources. The

factors determined without the aldehydes included in the PCA were used for this regression. Table 6 shows the results of the regressions.

The daily concentrations of both formaldehyde and acrolein were most significantly related to the secondary formation factor, both in terms of the magnitude of the regression coefficients as well as the statistical significance of those coefficients ($p < 0.0001$). Both coefficients were negative relative to the secondary formation factor. This is due to a negative component loading for ozone in the secondary formation factor, and a positive component loading for nitrogen oxides in the factor. That is, the secondary formation factor daily score was highest when NO_x concentrations were higher and ozone concentrations were lower. Since formaldehyde and acrolein positively associated with ozone and negatively associated with NO_x , they were negatively associated with the secondary formation factor; their concentration tended to be highest when the secondary formation daily score was lowest.

All three aldehydes were positively associated with the vegetative burning factor. In fact, for acetaldehyde, this was the most significant factor in terms of both magnitude and statistical significance of the regression coefficient ($p = 0.0004$). Formaldehyde and acrolein were also significantly associated, but less significantly than acetaldehyde ($p = 0.0007$ and 0.009 , respectively).

Acetaldehyde and acrolein also had a significant association with the oil combustion factor ($p = 0.005$ and $p = 0.046$, respectively), while formaldehyde also had a significant association with the natural soil/road dust factor ($p = 0.0008$). Unexpectedly, none of the aldehydes had a significant association with the vehicle and industrial combustion factor.

4. Discussion

4.1 Comparison of aldehyde concentrations in this study to other cities

As shown in Table 4, formaldehyde and acetaldehyde concentrations during the summer in Beijing were in the high-end of concentration ranges measured in other cities during photochemical seasons. For example, Milan and Rome in Italy, the downtown area of Savannah, Georgia in the US, Rio de Janeiro in Brazil, and Guangzhou in China, all had lower formaldehyde and acetaldehyde concentrations in the atmosphere as compared to Beijing during the photochemical seasons (Andreini et al., 2000; Baez et al., 1995; Feng et al., 2005; Feng et al., 2004; Grosjean et al., 2002; MacIntosh et al., 2000; Possanzini et al., 1996; Zhang et al., 1994).

4.2 Changes in aldehyde concentrations before, during, and after the Olympic period

As described earlier, the changing patterns for formaldehyde, acetaldehyde, and acrolein between the pre- and the during-Olympics periods were different; formaldehyde and acrolein increased from the pre- to the during-Olympic period, whereas acetaldehyde decreased. In terms of the sub periods, because of the extra air pollution control measures implemented in sub-period 2, a greater reduction in aldehydes concentrations were expected in sub-period 2 as opposed to sub-period 1. Data showed that the reduction in acetaldehyde concentration (15.3 $\mu\text{g}/\text{m}^3$, 44%) from the pre-Olympics to sub-period 2 was markedly larger than the reduction from the pre-Olympics to sub-period 1 (8.9 $\mu\text{g}/\text{m}^3$, 25%). However, the standard deviation in the two sub-periods was large (SD=14.7 $\mu\text{g}/\text{m}^3$), leading to a marginal significance ($p=0.079$). Because the observation did not follow a normal distribution, we also calculated the median of acetaldehyde as 25.1 $\mu\text{g}/\text{m}^3$ and 17.7 $\mu\text{g}/\text{m}^3$ in sub-periods 1 and 2,

respectively. Therefore, these findings only provide weak evidence suggesting an association between the Beijing Olympic air pollution control measures and the reduction in ambient concentration of acetaldehyde.

4.3 Sources of aldehydes in Beijing

Aldehydes in the atmosphere are generated primarily from direct emissions from industrial and/or traffic sources and secondarily from photochemical reactions. Both of these sources might have contributed to the high concentration of atmospheric aldehydes in Beijing during the summer of 2008 when the present study was conducted. Our monitoring site was located in central Beijing and was surrounded by streets with high densities of motor vehicles. Hence, we think the mobile source was an important contributor to the high aldehyde concentrations we measured. In addition to directly emitting aldehydes, the mobile source emits NO_x and VOCs, both of which are precursors of photochemical smog products including aldehydes.

As previously discussed, the results of our regression of the concentration of aldehydes with the five air pollution source types are shown in Table 6. As shown in the table, all three aldehydes are negatively correlated with the secondary formation factor, since this factor has positive coefficients for NO_x and a negative coefficient for ozone (see Table 4), and the aldehydes are negatively correlated with NO_x and positively correlated with ozone. Formaldehyde and acrolein in particular have highly significant, negative regression coefficients for the secondary formation factor.

This relationship helps explain why the concentrations of formaldehyde and acrolein were higher during the Olympic period, when most air pollution sources and individual pollutant concentrations were significantly decreased. However, ozone

concentrations were higher during the Olympic period, both due to high incident sunlight as well as due to decreased NO_x and a corresponding decreased titration reaction with NO_x to decrease ozone. Ozone formation is typically either NO_x limited or VOC limited (Seinfeld and Pandis, 1998). The Beijing urban area was most likely in a VOC-limited regime (Wang et al., 2009c). Therefore a reduction in NO_x would be expected to result in higher ozone production, which might contribute to the higher concentration of formaldehyde in the during-Olympic period.

All three aldehydes are significantly associated in the positive direction with the vegetative burning factor. This relationship may be driven by wood burning for cooking which is known to produce aldehydes (Lipari et al., 1984).

Acetaldehyde and acrolein, but not formaldehyde, are significantly associated in the positive direction with oil combustion. However, none of the aldehydes are significantly associated with the vehicle and industrial combustion factor, which includes motor vehicle and industrial sources. Although these sources, particularly motor vehicles, were expected to contribute to atmospheric aldehyde concentrations, their contribution during this study may be obscured by the strong influence of the secondary formation factor and the fact that as NO_x emissions from motor vehicles decreased, ozone and aldehyde concentrations tended to increase.

The only other significant relationship among the aldehydes and air pollution factors in this study is formaldehyde in the negative direction with the natural soil/road dust factor ($p < 0.001$). This implies that on days when the contribution of natural soil and road dust were higher, formaldehyde concentrations were decreased. It may be that weather or other patterns that lead to higher natural soil and road dust, such as windy

days, are also associated with decreased formaldehyde concentrations. However, as shown in Table 3, the aldehydes did not show an association with wind speed. Furthermore, the other aldehydes did not show a significant relationship with natural soil and road dust.

4.4 Effect of weather on aldehyde concentrations

Average concentrations of aldehydes and the mean values of meteorological parameters in the three periods were plotted together pairwise in Figure 3. We observed that formaldehyde and acrolein followed the changing pattern of temperature between periods. The 10.1% increase of temperature was accompanied by a 4% and 20% increase in formaldehyde and in acrolein from the pre- to the during-Olympic period; and that the 41.8% decrease in temperature was followed by a 63% reduction in formaldehyde and a 52% reduction in acrolein from the during- to the post-Olympic period. Higher relative humidity favors the formation of photochemical smog (Seinfeld and Pandis, 1998); this explains our observation that concentrations of formaldehyde and acrolein tracked the RH levels (see Figure 3). In the post-Olympic period, RH decreased by 18.9% which was accompanied by large reductions in the aldehydes concentrations. These relationships between the aldehydes and temperature and RH suggest that the secondary photochemical sources were a major contributor to atmospheric formaldehyde and acrolein in Beijing. In contrast, temperature and RH had much smaller impact on acetaldehyde concentrations; and the variation in acetaldehyde concentration by period appears to be driven by changes in emission sources. In addition, during the Olympic period, higher precipitation was observed in the current study, and this was favorable to lower concentrations of water soluble pollutants such as aldehydes. Thus, the reduction

in acetaldehyde in the during-Olympic period might be partly due to the higher rainfall intensity (Li et al., 2010a).

4.5 Comparison to other research on aldehydes in Beijing in 2008

In a recent publication, Li et al. (2010a) presents equations for estimating contributions of primary and secondary sources to formaldehyde in Beijing as follows:

$$P_{\text{primary}} = \beta_1 [\text{CO}]_i / (\beta_0 + \beta_1 [\text{CO}]_i + \beta_2 [\text{O}_3]_i) \times 100\%$$

$$P_{\text{secondary}} = \beta_2 [\text{O}_3]_i / (\beta_0 + \beta_1 [\text{CO}]_i + \beta_2 [\text{O}_3]_i) \times 100\%$$

$$P_{\text{background}} = \beta_0 / (\beta_0 + \beta_1 [\text{CO}]_i + \beta_2 [\text{O}_3]_i) \times 100\%$$

P_{primary} , $P_{\text{secondary}}$, and $P_{\text{background}}$ indicate contributions of the primary, secondary, and background sources; β_0 , β_1 , and β_2 are coefficients obtained by multi-linear regression models. We used these equations to further evaluate the relative contribution of primary and secondary sources to formaldehyde and acetaldehyde. As shown in Table 8, we found that the secondary source contributed more than the primary source to formaldehyde, especially in the during-Olympic period (50.3% vs. 15.4%), which is consistent with our findings for the linear regression of formaldehyde with the air pollution sources identified by principal component analysis. As reported in Table 3, a significant correlation between formaldehyde and daily average ozone or daily maximum ozone was observed, however, associations between formaldehyde and primary pollutants, i.e., CO and SO₂ were not significant. Surface ozone and formaldehyde were not reduced in the during-Olympic period.

The primary source was more important to acetaldehyde than the secondary source, particularly in the pre-Olympic period (47.4% vs. 11.4%). This is consistent with the strong association of acetaldehyde with vegetative burning and oil combustion during the study, as well as its strong association with CO and SO₂. This also helps

explain why acetaldehyde had a more noticeable decrease in concentration during the pollution control period, whereas formaldehyde and acrolein did not.

There appears to be an inconsistency between the current study and Li et al. (2010a) on formaldehyde concentrations and the change of formaldehyde among periods. Li et al. (2010a) observed a reduction in formaldehyde in the Olympic period, which was not seen in the current study. We can speculate the following possible reasons for the difference: (1) The sampling sites in the two studies were different. The current study collected air samples on the top of a 7-story building located in central Beijing, within the 2nd ring road. This building was situated in the center of a hospital campus surrounded by streets with high densities of motor vehicles. The Li et al. (2010a) study collected samples on top of a building about 9 km to the northwest of our sampling site. The Li et al. site was more suburban than our site and might have had smaller local traffic contributions to aldehydes. (2) Although efforts were made to avoid potential impact of sources very near to the sampling site (e.g., a combustion facility such as a boiler), these kinds of sources are sometimes hard to detect, especially in a large hospital complex. (3) Aldehydes were not measured on the exact same dates in the two studies. When Li et al reported that formaldehyde mixing ratios (concentrations) were lower during the Olympics than before the Olympics, they did not include measurements made during the Paralympics.

4.6 Effect of VOC and biogenic emissions on aldehyde concentrations

It is interesting to note that with even further controls during sub-period 2 during the Olympics, formaldehyde and acrolein concentrations did begin to decrease, compared to sub-period 1 during the Olympics. This might suggest a transition from a

VOC limited (NO_x saturated) regime during sub-period 1 to a NO_x limited regime during sub-period 2, as evidenced by the fact that both NO_x and ozone decreased from sub-period 1 to 2. However, as shown in Figure 4, a decrease in ozone and formaldehyde concentrations were not observed at the lowest NO_x concentrations during this study. The lowest daily average NO_x concentration measured during this study was 10.5 ppb. Although this may be at the cusp of the transition from a VOC-limited to a NO_x -limited regime, data was not available to determine the concentration at which this transition might occur in Beijing. It is higher than NO_x concentrations at which this transition was observed to occur in the San Joaquin Valley in California, where the transition occurred at approximately 5 to 9 ppb NO_x even at high ambient temperatures (Pusede and Cohen 2012).

VOC emissions were not measured in this study. However, biogenic emissions such as isoprene, might play some role for formaldehyde in the Beijing area, and if it is true then during the Olympic period where there was less vehicle traffic the secondary formation of formaldehyde would be enhanced whereas for acetaldehyde it would not. It is possible that the observed overall behavior was the result of slightly increased temperature in the during-Olympic period causing increased formaldehyde production that compensated for the reduction from vehicular emissions. There may be an indication of the importance in isoprene in Table 1 particularly in the post-Olympic data, because formaldehyde decreased substantially during the post-Olympic period. This would be expected if there was a substantial contribution from atmospheric isoprene oxidation, as both the biogenic production of isoprene and photochemical activity were

substantially reduced in the post-Olympic early fall period compared to the summer months of the pre- and during-Olympic periods.

4.7 Limitations

It is important to note that our observations were made from only one monitoring site in central Beijing, and the results may not necessarily reflect the overall situation for Beijing. Furthermore, only summer and fall seasons were encountered during the study; spring and winter conditions were not included or evaluated.

5. **Conclusions**

In the summer of 2008 when Beijing hosted the Olympics, concentrations of formaldehyde, acetaldehyde, and acrolein were found to be at the high-end of concentration ranges measured in other cities around the globe. Although the aggressive air pollution control measures implemented during the Olympics, especially when coupled with favorable meteorological conditions, led to drastic reductions in pollutants of large primary sources (e.g., PM_{2.5}, CO, SO₂, and NO_x), there was not a reduction in concentrations of formaldehyde and acrolein. Our findings point to the complexity of source control strategies for secondary pollutants, suggesting that the secondary photochemical processes may have dominated the formation of formaldehyde and acrolein. The importance of the photochemical contribution to formaldehyde and acrolein is evident since both had highly significant regression coefficients for the secondary formation factor identified using principal component analysis. Based on the results of this regression, it appears the elevated concentrations of formaldehyde and acrolein during the Beijing Olympics may be due largely to their relationship to elevated ozone concentrations, and coincided with high incident sunlight and decreased NO_x

concentrations during the Olympic period. Concentrations of acetaldehyde, on the other hand, decreased during the Olympic period compared to the period before. Our regression for acetaldehyde indicate that the reduction in primary emissions may have contributed to the reduction in acetaldehyde concentration, since acetaldehyde was more strongly associated with primary emission sources including vegetative burning and oil combustion rather than secondary formation. Higher rainfall intensity during the Olympics may also have contributed to the lower acetaldehyde concentration.

Figure 1. Time scheme of the pre-, the during-, and the post-Olympic periods, two sub periods, and the periods when aldehydes measurement was conducted (indicated by dotted lines with double-headed arrows).

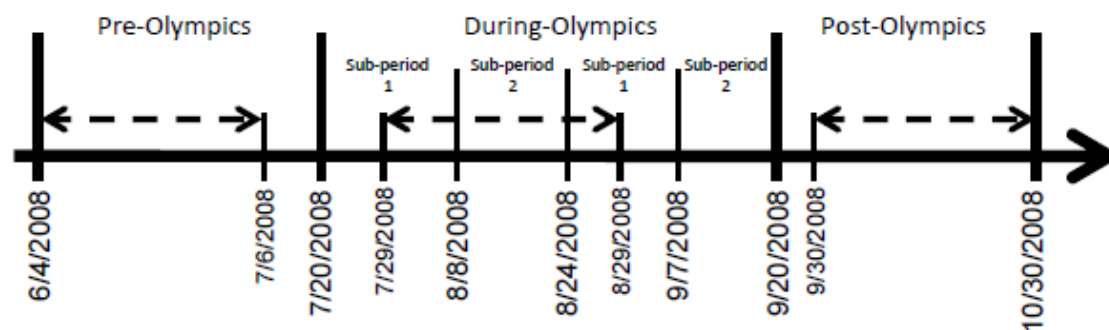


Figure 2. Rose plots of wind measurements at Peking University in the (A) pre- and (B) during-Olympic periods in 2008.

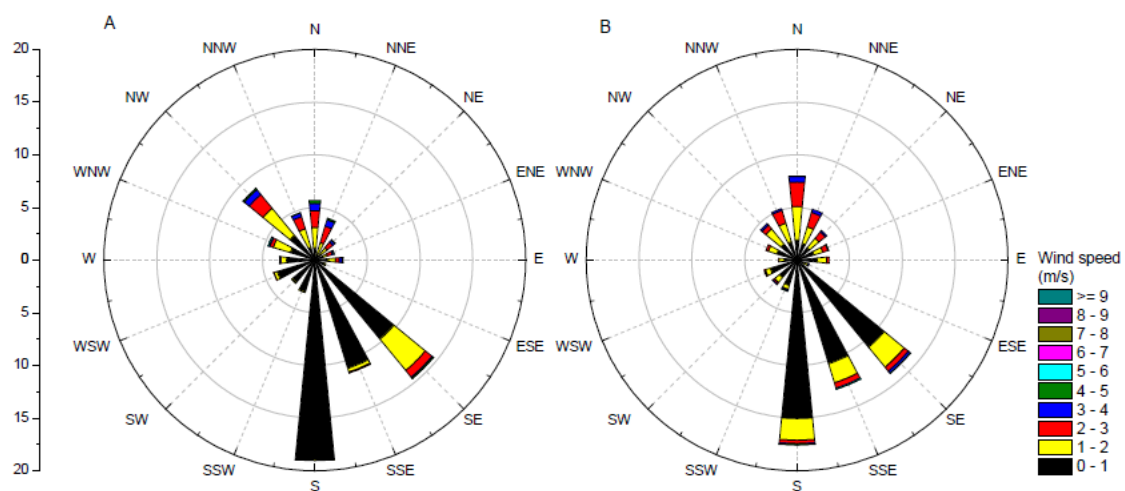


Figure 3. Period-specific means of ambient aldehydes and meteorological parameters, e.g. temperature, relative humidity, wind speed, and precipitation, in three sampling periods.

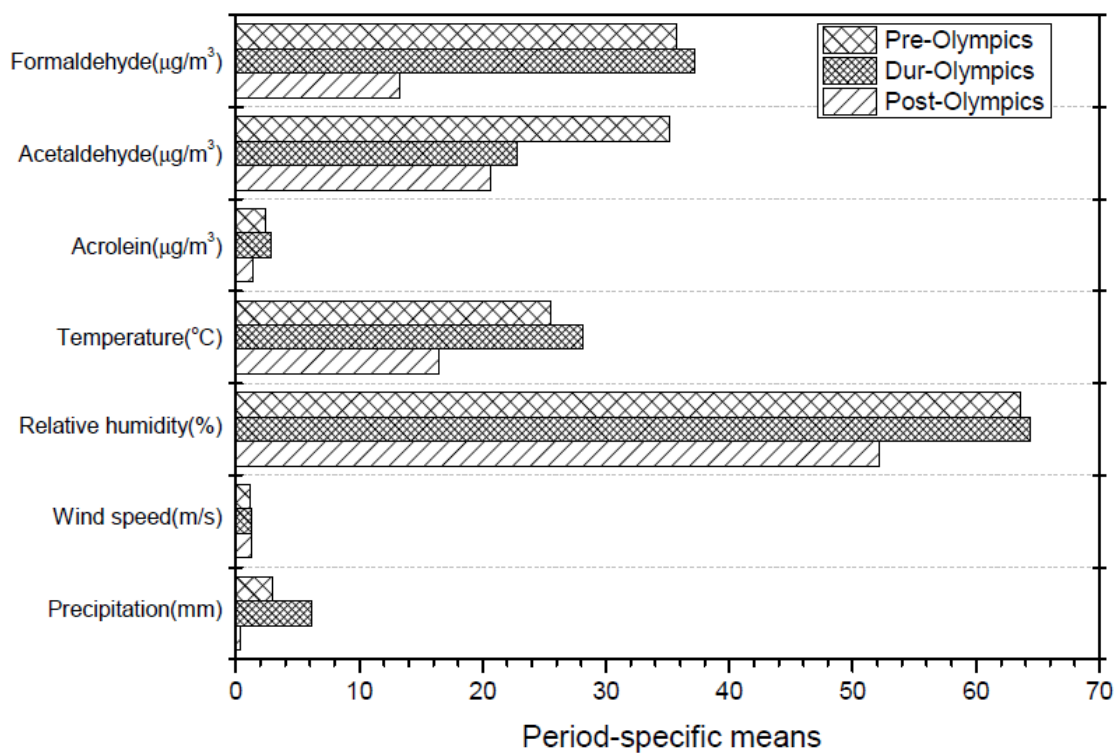


Figure 4. Ozone and formaldehyde concentrations as a function of nitrogen oxide concentration, Beijing, China, June to October 2008

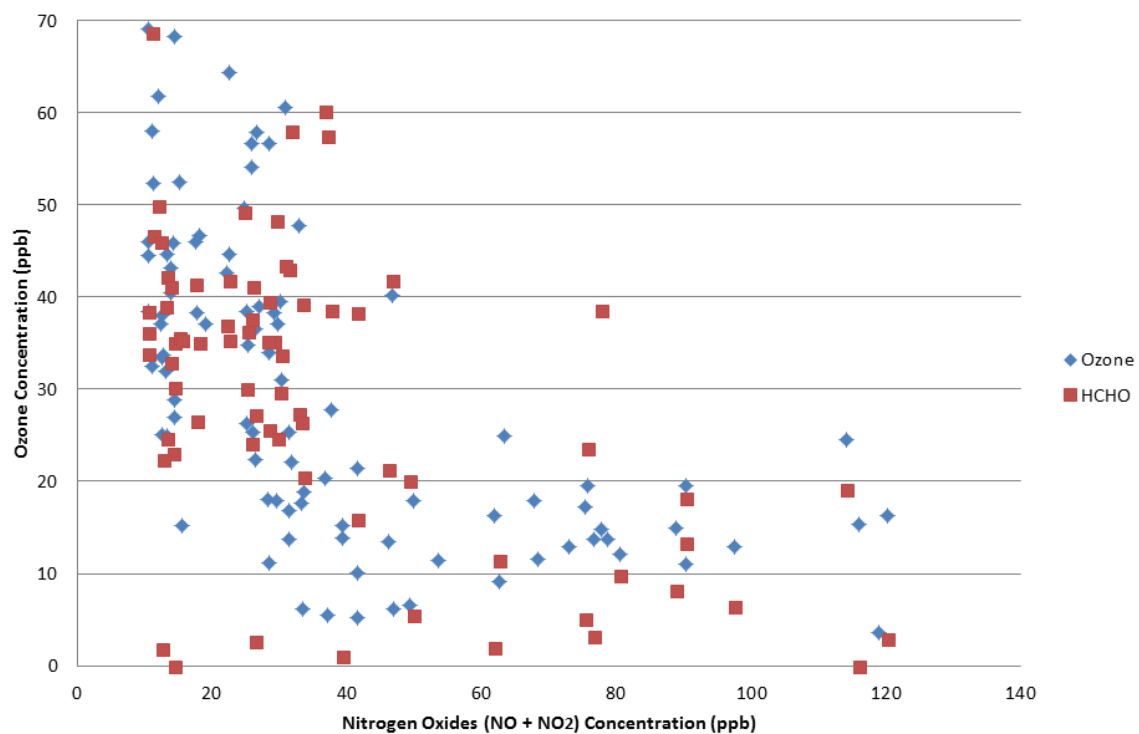


Table 1. Concentrations of aldehydes in pre-, during-, and post-Olympic periods (unit: $\mu\text{g}/\text{m}^3$)*

	Pre-Olympics				During-Olympics				Post-Olympics				Whole period			
	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
Formaldehyde	35.70	9.04	15.83	60.12	37.25	11.18	17.06	68.60	13.88	13.89	1.02	57.50	29.34	15.12	1.02	68.60
Acetaldehyde	35.20	15.12	15.73	67.23	23.75	14.67	2.02	63.87	20.63	13.59	3.31	62.35	27.09	15.74	2.02	67.23
Acrolein	2.41	0.86	1.02	4.51	2.88	0.78	1.79	4.63	1.38	0.49	0.64	2.48	2.32	0.95	0.64	4.63

* Concentrations were field blank corrected; average concentration of aldehydes was calculated if the duplicated samples were collected.

Table 2. Mean, median and standard deviation of air pollutants and meteorological parameters in three periods (Rich et al. 2012)

Air pollutants and meteorological condition	Pre-Olympics (6/2/2008-7/19/2008)			During-Olympics (7/20/2008-9/19/2008)			Post-Olympics (9/20/2008-10/30/2008)		
	Mean	Median	SD	Mean	Median	SD	Mean	Median	SD
SO ₂ (ppb)	7.82	7.28	4.00	4.65	4.45	2.61	5.92	5.51	3.51
NO (ppb)	3.66	2.96	2.09	2.29	1.88	1.92	21.81	20.45	17.43
NO ₂ (ppb)	24.15	23.49	5.55	18.81	15.50	7.94	38.03	32.47	16.85
NO _x (ppb)	28.37	26.79	7.00	21.06	17.63	9.66	60.18	59.30	29.24
O ₃ (daily average, ppb)	33.43	35.21	15.16	39.22	38.26	16.74	14.45	13.88	6.67
O ₃ (daily maximum, ppb)	70.69	72.17	31.60	82.85	82.30	27.56	40.43	38.90	19.92
O ₃ +NO ₂ (daily average, ppb)	57.45	57.21	13.70	57.42	56.77	15.23	52.43	46.21	18.47
O ₃ +NO ₂ (daily maximum, ppb)	92.19	89.81	30.14	97.62	98.00	27.86	71.81	64.39	29.18
CO (ppm)	1.15	1.07	0.40	0.64	0.58	0.22	0.76	0.63	0.57
PM _{2.5} (µg/m ³)	96.7	96.9	38.7	75.6	62.2	41.5	71.8	53.48	58.0
Temperature (°C)	25.5	25.1	1.0	28.1	27.7	1.0	16.4	17.1	1.0
Relative Humidity (%)	63.6	66.4	4.2	64.4	63.7	4.5	52.2	54.0	4.4
Precipitation (mm)	3.0	0.2	108.2*	6.1	0.0	180.2	0.4	0.0	13.2
Wind Speed (m/s)	1.1	1.2	0.2	1.3	1.3	0.2	1.3	1.0	0.2

* For the precipitation data, the third column for each period, i.e. SD column, represents the sum of the precipitation in that period, instead of standard deviation.

Table 3. Spearman correlation coefficients among aldehydes, other air pollutants, and meteorological parameters

	Formaldehyde	Acetaldehyde	Acrolein	SO ₂	NO	NO ₂	NOx	¹ O ₃	² O ₃	¹ O ₃ +NO ₂	² O ₃ +NO ₂	CO	PM _{2.5}	T	RH
Formaldehyde	1														
Acetaldehyde	0.59**	1													
Acrolein	0.63**	0.43**	1												
SO₂	0.13	0.51**	0.005	1											
NO	-0.53**	-0.009	-0.53**	0.096	1										
NO₂	-0.31*	0.23*	-0.36*	-0.40**	0.80**	1									
NOx	-0.41**	0.14	-0.47**	0.31**	0.89**	0.97**	1								
¹O₃	0.41**	0.07	0.34*	0.21*	-0.73**	-0.57**	-0.65**	1							
²O₃	0.38**	0.04	0.33**	0.27**	-0.61**	-0.40**	-0.49**	0.92**	1						
¹O₃+NO₂	0.060	0.14	0.017	0.58**	-0.19*	0.11	0.014	0.68**	0.77**	1					
²O₃+NO₂	0.26*	0.14	0.23	0.46**	-0.39**	-0.10	-0.21	0.79**	0.91**	0.91**	1				
CO	0.26*	0.46**	0.20	0.50**	0.17*	0.35**	0.29**	-0.01	0.08	0.30**	0.25**	1			
PM_{2.5}	0.39**	0.47**	0.24*	0.67**	-0.15	0.20*	0.09	0.31**	0.34**	0.56**	0.49**	0.65**	1		
Temperature	0.56**	0.10	0.59**	0.17*	-0.74**	-0.58**	-0.67**	0.79**	0.76**	0.43**	0.61**	0.08	0.33**	1	
RH	0.62**	0.30*	0.38*	-0.04	-0.17*	-0.02	-0.08	-0.17*	-0.17*	-0.28**	-0.18*	0.29**	0.32**	-0.05	1
Wind speed	-0.03	-0.03	0.08	-0.05	-0.34**	-0.44**	-0.41**	0.31**	0.17*	0	0.033	-0.27*	-0.07	0.18*	-0.31**

Significance of each coefficient is determined by the p-value, * indicates that the coefficient is significant at the significant level of 0.05; ** indicates that the coefficient is significant at the significant level of 0.01; ¹ daily average (24-hour) concentration; ² 1 hour maximum concentration within a day. All data is based on 24-hour average except ²O₃ and ²O₃+NO₂.

Table 4. VARIMAX rotated factor loading matrix for Beijing air pollution data (without aldehydes)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
	Vehicle/industrial combustion	Natural soil / road dust	Secondary formation	Oil Combustion	Vegetative burning
SO ₂	0.655	0.143	-0.060	0.372	0.181
NO	0.195	0.315	0.756	-0.092	-0.222
NO ₂	0.679	0.319	0.605	0.091	-0.047
O ₃	-0.026	-0.070	-0.850	-0.122	0.033
CO	0.490	0.050	0.255	0.432	0.492
PM _{2.5}	0.794	0.254	-0.114	0.085	0.474
OC	0.827	0.304	0.330	-0.021	0.013
EC	0.780	0.352	0.363	-0.023	0.084
Na	0.720	0.512	0.077	0.173	0.301
Mg	0.138	0.903	-0.042	0.218	0.076
Al	0.239	0.897	0.195	0.173	-0.031
K	0.600	0.245	0.095	0.441	0.439
Ca	0.131	0.957	0.085	0.115	0.022
Ti	0.196	0.924	0.046	0.165	0.006
Mn	0.503	0.504	0.221	0.542	0.150
Fe	0.376	0.749	0.206	0.239	0.180
Cu	0.772	0.161	-0.075	0.038	0.179
Zn	0.584	0.164	0.225	0.648	0.241
Pb	0.717	0.127	0.030	0.382	0.467
Ni	0.200	0.438	0.137	0.732	-0.036
V	0.055	0.162	-0.152	0.866	0.232
Se	0.761	0.151	0.258	0.374	0.245
Na ⁺	0.641	0.445	0.017	0.238	0.398
NH ₄ ⁺	0.617	-0.040	-0.318	0.014	0.635
K ⁺	0.568	0.136	-0.015	0.385	0.525
Mg ²⁺	0.239	0.904	0.058	0.063	-0.013
Ca ²⁺	0.109	0.950	0.039	0.027	-0.017
F ⁻	0.105	0.936	0.157	0.004	-0.043
Cl ⁻	0.359	0.126	0.211	0.137	0.628
NO ₃ ⁻	0.752	0.174	0.061	0.089	0.405
SO ₄ ²⁻	0.584	0.028	-0.468	0.008	0.563
BbF ⁻	0.181	-0.040	-0.107	0.129	0.946
BeP	0.033	-0.091	-0.225	0.124	0.945
IcP	0.326	0.040	0.011	0.056	0.906
BghiP	0.245	-0.019	-0.046	0.064	0.934
Eigenvalue	16.79	6.92	1.41	1.87	2.84
% Var.	26%	23%	8%	10%	19%
Cum % var.	26%	49%	57%	66%	85%

Table 5. VARIMAX rotated factor loading matrix for Beijing air pollution data (with aldehydes)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
SO ₂	0.653	0.161	0.176	0.363	0.126
NO	0.286	0.252	-0.664	0.050	-0.248
NO ₂	0.746	0.277	-0.498	0.174	-0.073
O ₃	-0.142	-0.007	0.697	-0.298	0.075
CO	0.550	0.046	-0.027	0.503	0.414
PM _{2.5}	0.793	0.262	0.190	0.047	0.449
OC	0.858	0.280	-0.266	-0.007	0.002
EC	0.819	0.322	-0.304	0.005	0.074
Na	0.742	0.510	0.026	0.169	0.263
Mg	0.140	0.914	0.002	0.171	0.080
Al	0.267	0.886	-0.198	0.170	-0.036
K	0.632	0.253	0.055	0.459	0.380
Ca	0.147	0.953	-0.125	0.093	0.028
Ti	0.205	0.926	-0.078	0.124	0.013
Mn	0.525	0.513	-0.169	0.517	0.149
Fe	0.420	0.738	-0.116	0.273	0.135
Cu	0.748	0.170	0.073	-0.034	0.200
Zn	0.601	0.178	-0.155	0.626	0.244
Pb	0.731	0.138	0.090	0.373	0.430
Ni	0.207	0.466	-0.109	0.675	-0.029
V	0.037	0.214	0.201	0.796	0.225
Se	0.792	0.146	-0.142	0.389	0.216
Na ⁺	0.663	0.448	0.093	0.238	0.350
NH ₄ ⁺	0.600	-0.021	0.393	-0.027	0.604
K ⁺	0.591	0.147	0.163	0.400	0.461
Mg ²⁺	0.257	0.897	-0.064	0.051	-0.030
Ca ²⁺	0.125	0.943	-0.075	0.010	-0.022
F ⁻	0.131	0.918	-0.202	0.005	-0.040
Cl ⁻	0.412	0.108	-0.106	0.192	0.598
NO ₃ ⁻	0.772	0.169	0.033	0.087	0.375
SO ₄ ²⁻	0.547	0.058	0.523	-0.062	0.532
BbF	0.200	-0.035	0.180	0.151	0.931
BeP	0.041	-0.076	0.289	0.133	0.929
IcP	0.358	0.034	0.079	0.094	0.888
BghiP	0.272	-0.021	0.131	0.096	0.916
HCHO	0.065	-0.295	0.755	0.114	0.154
MeCHO	0.178	-0.075	0.464	0.418	0.166
acrolein	0.037	-0.106	0.729	0.213	0.073
Eigenvalue	16.9	7.62	1.95	1.60	3.00
% Var.	26%	22%	9%	9%	16%
Cum % var.	26%	47%	56%	65%	82%

Table 6. Linear regression coefficients, relative contributions of air pollution source types to aldehyde concentrations

P-value significance codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

	Linear regression coefficients					
	β_0 (intercept)	β_1 (mixed combustion)	β_2 (natural soil/ road dust)	β_3 (secondary formation)	β_4 (oil combustion)	β_5 (vegetative burning)
Formaldehyde	28.7***	1.36	-4.46***	-8.63***	2.43	4.98***
Acetaldehyde	26.8***	1.61	-3.57	-2.89	6.15**	6.22***
Acrolein	2.20***	0.01	-0.17	-0.44***	0.24*	0.26**

Table 7. Concentrations of aldehydes in ambient air in different cities

Location	Study season	Average aldehyde concentration ($\mu\text{g}/\text{m}^3$ / ppb)			Measuring interval	References
		Formaldehyde	Acetaldehyde	Acrolein		
Milan, Italy	Summer (August)	8.9 / 6.65	13.7 / 6.97	Non-available	Non-available	Andreini et al., 2000
Rome, Italy	June – July 1994	22.77 / 17.00	18.27 / 9.30	1.75 / 0.70	1 hour	Possanzini et al., 1996
Downtown Savannah, GA, USA	December 1995 through November 1996	2.0 / 1.49	2.3 / 1.17	Non-available	12 hours	MacIntosh et al., 2000
Suburban area in Central New Jersey, USA	June – August 1992	15.37 / 11.48	4.75 / 2.42	Non-available	2.5-3.5 hours	Zhang et al., 1994
Mexico city, Mexico	March-May 1993	43.5 / 32.48	33.8 / 17.21	Non-available	2 hours	Baez et al., 1995
Rio de Janeiro, Brazil	May to November 2000	10.84 / 8.09	10.43 / 5.31	0.82 / 0.33	2-3 hours	Grosjean et al., 2002
Guangzhou, China	June to September 2003	13.68 / 10.21	8.33 / 4.24	1.36 / 0.54	2-3 hours	Feng et al., 2005
Guangzhou, China	August–September 2002	13.29 / 9.92	7.6 / 3.87	Non-available	3.5 hours	Feng et al., 2004
Beijing, China	June to October 2008	29.34 / 21.91	27.09 / 13.79	2.32 / 0.93	24 hours	Current study

Table 8. Linear regression coefficients, relative contributions of background, primary source and secondary source to formaldehyde and acetaldehyde in three Olympic periods

Linear regression coefficients	β_0	β_1	β_2	p-value
Formaldehyde	10.195	7.609	0.403	<.0001
Acetaldehyde	12.924	12.351	0.107	0.0013

Formaldehyde	Background	Primary	Secondary
Pre-Olympics	31.59 %	29.50 %	38.91 %
During-Olympics	34.37 %	15.36 %	50.27 %
Post-Olympics	47.46 %	22.90 %	29.64 %

Acetaldehyde			
Pre-Olympics	41.18 %	47.40 %	11.42 %
During-Olympics	52.92 %	29.80 %	17.29 %
Post-Olympics	58.84 %	33.11 %	8.06 %

Chapter 3

Association Between Air Pollution Sources and Aldehydes with Biomarkers of Blood Coagulation, Pulmonary and Systemic Inflammation, and Oxidative Stress in Healthy Young Adults.

Brent Altemose^{a*}, Mark G. Robson^b, Howard M. Kipen^c, Pamela Ohman Strickland^a, Qingyu Meng^a, Jicheng Gong^d, Wei Huang, Tong Zhu, and Junfeng Zhang^d

^aSchool of Public Health, Rutgers University, Piscataway, NJ; ^bSchool of Environmental and Biological Sciences, Rutgers University, New Brunswick, NJ; ^cEnvironmental and Occupational Sciences Institute (EOHSI), Rutgers University, Piscataway, NJ ;

^dNicholas School of the Environment & Duke Global Health Institute, Duke University, Durham, North Carolina

*Corresponding author. Tel: (908)500-4784; Fax: (908)320-7999; E-mail: brent@sabresafety.net

Abstract. Using data collected before, during, and after the Summer Olympic Games in Beijing in August 2008, this study examines associations between biomarkers of blood coagulation (vWF, sCD62P and sCD40L), pulmonary inflammation (EBC pH, EBC Nitrite, and eNO), and systemic and oxidative stress (8-OHdG) with sources of air pollution previously identified utilizing principal component analysis and with concentrations of three aldehydes of health concern. Association between these seven biomarkers and the five source types of air pollution identified and the aldehydes were examined using a linear mixed effects model, regressing each biomarker and each source type or aldehyde on zero through seven lag days and controlling for ambient temperature, relative humidity, gender, and day of week for the biomarker measurements.

The biomarkers for pulmonary inflammation, particularly pH and eNO, were most consistently associated with vehicle and industrial combustion, oil combustion, and vegetative burning. The biomarkers for hemostasis and blood coagulation, particularly

vWF and sCD62p, were most consistently associated with oil combustion, but also associated with vehicle and industrial combustion and vegetative burning. Systemic inflammation, as indicated by 8-OHdG, was most consistently associated with vehicle and industrial combustion. The associations between the biomarkers and the aldehydes were generally not significant or in the hypothesized direction, although EBC nitrite was associated with both acrolein and acetaldehyde, and sCD62p was associated with acetaldehyde.

These findings indicate that the restrictions implemented by the Chinese government during the Olympic period, which significantly decreased the contribution of all major sources of air pollution in Beijing, also had a beneficial impact on biomarkers of blood coagulation, pulmonary inflammation, and systemic and oxidative stress. Further research is needed to confirm the association of various air pollutants and sources, particularly vehicle and industrial sources, oil combustion, and vegetative burning, with these biomarkers.

1. Introduction

1.1 Principal component analysis and source apportionment

Using air pollution data collected before, during, and after the Summer Olympic Games in Beijing in August 2008, the authors previously examined sources and trends in air pollution utilizing principal component analysis (PCA). Due to mandatory controls implemented by the Chinese government during the Olympics, many sources of air pollution, including vehicle and industrial sources, power plants, construction work, and road dust were intentionally curtailed and suppressed. Based on the PCA, five primary sources of air pollution were identified – natural soil/road dust, vehicle and industrial

combustion, vegetative burning, oil combustion, and secondary formation. Analysis of the data indicated that, as expected, restrictions implemented by the Chinese government during the Olympic period significantly decreased the contribution of all major sources of air pollution in Beijing.

1.2 Effects of air pollution on cardiorespiratory health

Many studies have shown health effects associated with air pollution changes, including associations of health effects with abrupt regulatory changes that affected air pollution. These studies have shown an association between regulatory changes in air pollution and death rates (Mar et al. 2000, Hedley et al. 2002), air pollution and respiratory symptoms and lung function (Friedman et al. 2001, Heinrich et al. 2000, Frye et al. 2003), and air pollution and cardiovascular mortality (Hedley et al. 2002).

Many studies have also shown a relationship between air pollution and cardiovascular effects, including cardiovascular mortality (Schwartz 1993, Schwartz 1994, Ostro 1995, Wordley et al. 1997, Zmirou et al. 1998), congestive heart failure (Wellenius 2006, Wellenius 2005, Symons et al. 2006, Ballester et al. 2001, Metzger et al. 2004) and ischemic stroke (Wordley et al. 1997, Moolgavkar 2000, Linn et al. 2000, Tsai et al. 2003, Wellenius et al. 2005). Cardiovascular mortality and hospital admissions for cardiovascular disease and congestive heart failure have been shown to be related to a number of components of air pollution, including traffic-related sources (Wellenius et al. 2005), carbon monoxide (Mar et al. 2000, Burnett et al. 1999, Schwartz 1997, Wellenius et al. 2005), fine and coarse particles (Mar et al. 2000, Pope et al. 1992, Wellenius et al. 2005, Zanobetti et al. 2000, Goldberg et al. 2001, Jerrett et al. 2005, Son et al. 2012, Huang et al. 2012b, Rich et al. 2008), elemental and organic carbon (Mar et

al. 2000, Tolbert et al. 2000, Henneberger et al. 2005, Ruckerl et al. 2006), nitrogen oxides (Mar et al. 2000, Wellenius et al. 2005, Son et al. 2012), sulfur dioxide (Mar et al. 2000, Zmirou et al. 1998, Wellenius et al. 2005), ozone (Zmirou et al. 1998), potassium from vegetative burning (Mar et al. 2000), sulfate (Burnett et al. 2000, Son et al. 2012), ammonium (Son et al. 2012), and elements including iron, nickel, and zinc (Burnett et al. 2000). Air pollution has been shown to be related to ventricular arrhythmias (Vedal et al. 2004, Rich et al. 2004), including relationships of arrhythmias to particulate matter (Peters et al. 2000, Dockery et al. 2005 (1), Dockery et al. 2005 (2), Rich et al. 2005, Rich et al. 2006) and sulfates (Dockery et al. 2005 (2), Sarnat 2006). Changes in particle exposure have been related to myocardial infarction (Peters et al. 2001, D'Ippoliti et al. 2003, Forastiere et al. 2005, Sharovsky et al. 2004, Peters and Heier 2005, Zanobetti and Schwartz 2005), and in particular $PM_{2.5}$ has been shown to be associated with transmural myocardial infarctions (Rich et al. 2011) and heart rate variability in the elderly (Liso et al. 1999, Sullivan et al. 2005, Liao et al. 1999, Creason et al. 2001, Devlin et al. 2003, Holguin et al. 2003, Schwartz et al. 2005, Magari et al. 2001, Riediker et al. 2004, Luttmann-Gibson et al. 2006, Timonen et al. 2006, Pope et al. 1999, Pope et al. 2004, Gold et al. 2000) while PM_{10} may cause sequestration of red blood cells (Seaton et al. 1999).

1.3 Biomarkers of air pollution health effects

Recent studies have focused on biological mechanisms for the health effects observed from air pollution, including cardiorespiratory effects. A prominent mechanistic hypothesis is that fine and ultrafine particles increase lung oxidative stress and provoke alveolar inflammation (Seaton et al. 1995, Kipen et al. 2011), and that this

leads to increased blood coagulability within hours or days (Seaton et al. 1995, Jacobs et al. 2010, Huang et al. 2012a). Exposure to wood smoke was shown to affect inflammation, coagulation, and lipid peroxidation (Barregard et al. 2006). Exposure to diesel exhaust was shown to increase ischemic burden and to inhibit fibrinolytic capacity (Mills et al. 2007), and in another study exposure to diesel exhaust and secondary organic aerosols were shown to increase oxidative stress and inflammation through decreased proteasome activity in peripheral blood cells (Kipen et al. 2011). Furthermore, increased oxidative DNA damage, and decreased total serum anti-oxidant capacity has been shown to be related to the occurrence and severity of coronary artery disease and cardiorespiratory effects (Demirbag 2005, Vassalle et al. 2004, Botto et al. 2002).

Several biomarkers have shown promise as indicators of cardiorespiratory effects and systemic oxidative stress. For instance, a recent study of the effects of diesel exhaust exposure showed several biomarker changes, including exhaled breath condensate (EBC) pH, and exhaled nitric oxide (eNO), associated with exposure to ultra-fine particles and elemental carbon (Zhang et al. 2009). Based on the HEART study from which the data for this analysis is being obtained (Rich et al. 2012, Huang et al. 2012a, Zhang et al. 2013), biomarkers showing strong effects associated with PM include: exhaled nitric oxide (eNO), exhaled breath condensate (EBC) nitrite, sCD62P, EBC pH, and plasma fibrinogen.

2. Methods

2.1 Air sample collection, storage, and analysis

Sample collection, storage, and analysis were performed in conjunction with the Health Effects of an Air pollution Reduction Trial (HEART) study (Zhang et al. 2013).

The HEART study included a comprehensive characterization of air pollution before, during, and after the games. All the air samplers and monitors were collocated at a secured spot on the Peking University 1st Hospital campus that served as the clinical base for the health outcome measurements of the HEART study. The hospital is located in the center of Beijing, within the 2nd ring road, 3 kilometers northwest of Tiananmen Square, surrounded by busy streets of local motor vehicle traffic, cyclists, and pedestrians. Further detail regarding the collection of the air samples are described in Chapters 1 and 2.

2.2 Biomarker sample collection, preservation, and analysis

Concurrent with the air pollution measurements before, during, and after the 2008 Beijing Olympics, several biomarkers were analyzed from Peking University Hospital students during the HEART study, reflecting blood coagulation, pulmonary and systemic inflammation, endothelial dysfunction, autonomic dysfunction, and oxidative stress. Seven of the biomarkers collected were chosen for this study to examine their association with the air pollution sources. The biomarkers chosen were based on the quality of the data available and the extent of association of the biomarkers with individual pollutants collected during the HEART study. Table 1 shows a summary of the biomarker collection and analytical methods.

A total of 128 subjects were recruited – 64 males and 64 females. Three subjects (two females and one male) dropped out of the study. Two dropped out after the first visit and one dropped out after the second visit. Otherwise, four of the female subjects and seven of the male subjects missed one of six visits. So, 56 males and 58 females attended all six visits.

2.3 Statistical analysis

Statistical analysis of the data were conducted using R version 2.14.2 (Platform: i386-pc-mingw32/i386 (32-bit), copyright 2012 by The R Foundation for Statistical Computing). Some additional descriptive statistics, data manipulation, and charts were completed using Microsoft Excel 2010 (copyright 2010 Microsoft Corporation).

Association between the seven biomarkers with the five air pollution source types and the three aldehydes at zero through seven lag days were examined using a linear mixed effects model. Each biomarker was separately regressed with each source type or aldehyde on a given lag day controlling for ambient temperature, relative humidity, a moving average of temperature, a moving average of relative humidity, gender, and day of week for biomarker measurements. The number of days to use for the moving averages of temperature and relative humidity, and the number of degrees of freedom for the natural splines used in the adjustments, were based on prior analysis for each biomarker in the HEART study. This prior study used Akaike information criterion scores to determine the appropriate values for each.

The air pollution sources used in the analysis were the following five source types determined from our previous principal component analysis and source apportionment: Factor 1 – Vehicle and industrial combustion; Factor 2 – Natural soil / road dust; Factor 3 – Secondary formation; Factor 4 - Oil combustion; Factor 5 – Vegetative burning. The aldehydes included in the analysis were formaldehyde, acrolein, and acetaldehyde. The percent change in each biomarker corresponding with an inter-quartile range increase in each source type or aldehyde on each lag day was evaluated.

3. Results and Discussion

3.1 Descriptive statistics

Table 2 shows the descriptive statistics for the biomarkers. More detail regarding the trends for these biomarkers are described in Zhang et al. In some cases, when a subject made a visit, one or more selected biomarkers may not have been collected. For vWF, eNO, and pH, this occurred only one time for one subject for each, out of 743 total collection opportunities. For sCD40L and sCD62p, a total of ten collection opportunities were missed – and six of these ten were for one male subject who did not have these biomarkers collected during any of his six visits. For 8-OHdG, 18 collection opportunities were missed. Finally, for EBC Nitrite, 50 collection opportunities were missed – and 48 of these were during the sixth visit for the 124 subjects who made a sixth visit.

Notably several very low EBC pH values were observed. Three different subjects had pHs of 4.7, 5.0, and 5.3, respectively, whereas all other data were above 5.8. These low values are likely not due to measurement error but rather due to recent ingestion of acidic beverages or a medical condition such as acid reflux (Paget-Brown et al. 2006). Therefore, these data were not omitted from the analysis, and a sensitivity analysis with the three low values omitted did not show any significant impact on the results.

All of the biomarkers trended in the expected direction during the Olympic period compared to before the Olympics. EBC Nitrite, eNO, sCD62p, sCD40L, and 8-OHdG all decreased during the Olympic period compared to the period before the Olympics, and then increased after the Olympics. vWF decreased during the Olympics compared to before, and continued to decrease after the Olympics. pH increased during

the Olympics, which is the expected direction, and continued to increase after the Olympics.

3.2 Linear mixed effects model results – biomarker trends by source type

The results of the linear mixed effect models are shown in Figures 1 through 7. Table 3 is a summary of the significant associations between the biomarkers and the air pollution factors. There were many significant positive associations, in the expected direction, for the biomarkers with the air pollution source factors. This section describes the trends for each biomarker, while the following section describes the trend for each factor.

The biomarkers for pulmonary inflammation (pH, EBC Nitrite, and eNO) showed significant positive associations most consistently with Factor 1 (vehicle and industrial combustion) and Factor 5 (vegetative burning). In Zhang et al., these biomarkers showed consistent positive associations with several components of Factor 1 – CO, EC, SO₂, and NO₂, and one component of Factor 5, CO. Factors 2 (natural soil/road dust) and 4 (oil combustion) showed some, less consistent, significant positive associations. The primary components for these factors were metals and other elements. As shown in Appendix I, it is also notable that the pulmonary inflammation biomarkers and Factors 1, 4, and 5 had similar trends and associations with and without the fall data included, while their association with Factor 2 was very sensitive to the omission of the fall data.

Of the three pulmonary inflammation biomarkers, only EBC Nitrite shows consistent, significant associations with Factor 3 (secondary formation). These associations were similar with and without the fall data included. This is also consistent

with Zhang et al.'s analysis of the individual pollutants. Although all three pulmonary inflammation biomarkers showed significant positive associations with NO₂, only EBC Nitrite showed consistent negative associations with O₃, which also had a strong loading for Factor 3.

As shown in Figure 1, pH was significantly and negatively associated with Factors 1, 2, 4, and 5, and positively associated with Factor 3. The negative associations are in the hypothesized direction, as they indicate a decreased exhaled breath condensate (EBC) pH (increased airway acidification associated with an increase in a pollution source). For Factor 1 (vehicle and industrial combustion), pH decreased by 0.6 to 1.2% on lag days 0 through 6 ($p < 0.02$); in Zhang et al. pH was significantly associated in the expected direction with many constituents of Factor 1, including PM_{2.5}, SO₄²⁻, CO, EC, SO₂, and NO₂. For Factor 2 (natural soil/road dust), only lag days 5 and 7 showed a significant decrease (0.3 and 0.4%, $p < 0.01$). Factor 3 (secondary formation), showed associations in the opposite (positive) direction. On lag days 3 through 5, pH increased by 0.7 to 1.1% ($p < 0.01$). This may be due to the fact that, as previously discussed, Factor 3 is inversely related to O₃ concentrations, and O₃ may decrease EBC pH. In Zhang et al.'s work, O₃ did not show significant negative or positive associations with EBC pH, nor in general did NO₂. However, it is possible the inverse relationship between these two pollutants were masking the effects in Zhang et al. Factor 4 (oil combustion) showed significant associations with decreased pH on lag days 0 through 3 (0.5 to 1.1%, $p < 0.01$) and lag day 7 (0.4%, $p < 0.001$). Finally, Factor 5 (vegetative burning) showed significant associations with decreased pH on lag days 1 (0.6%, $p = 0.019$) and 5 through 7 (0.5 to 1.1%, $p < 0.01$). Zhang et al. showed significant,

positive associations with $\text{PM}_{2.5}$, SO_4^{2-} , and CO, which are all components of Factor 5. Also note that the trends and association of pH with these factors was similar with and without the fall data included.

As shown in Figure 2, the trends for the associations of EBC nitrite with the air pollution factors tended to follow the same pattern for four of the five factors. The only exception was Factor 2 (natural soil/road dust), which showed no significant positive associations except for lag day 4 (24.0%, $p=0.001$). For the other four factors, there were significant positive associations with EBC Nitrite on lag days 1 through 3, but generally not on lag day 0 or 4 through 7. For Factor 1 (vehicle and industrial combustion), there were significant positive associations on lag days 1 through 3 (11.1 to 13.9%, $p<0.001$). In Zhang et al., EBC nitrite was consistently and significantly associated in the expected direction with CO, SO_2 , EC, OC, and NO_2 , all components of Factor 1. For Factor 3 (secondary formation), there were also significant positive associations on lag days 1 through 3 (18.8 to 33.9%, $p<0.001$). As previously noted, this pattern was not observed for other pulmonary inflammation biomarkers, but is consistent with Zhang et al.'s findings, since EBC nitrite was consistently and positively associated with NO_2 , and consistently and negatively associated with O_3 . For Factor 4 (oil combustion), the significant positive associations with EBC nitrite occurred on lag days 1 through 4 (15.5 to 43.6%, $p<0.001$). Finally, for Factor 5 (vegetative burning), the significant positive associations were on lag days 0 through 3 (7.0 to 32.7%, $p<0.05$), whereas in Zhang et al. the only component of Factor 5 with consistent positive associations with EBC nitrite was CO. In general, the trends and associations of EBC nitrite with the factors were similar with and without the fall data included, although which lag days showed

significant, positive associations with Factor 1 did change when the fall data was removed.

As shown in Figure 3, eNO was positively and significantly associated with Factor 5 (vegetative burning) on all lag days at 14.3 to 36.5% ($p < 0.02$). Based on Zhang et al., eNO was consistently positively associated with three primary components of Factor 5, $\text{PM}_{2.5}$, SO_4^{2-} , and CO. It was also significantly and positively association with Factor 4 (oil combustion) at 14.6 to 31.9% on lag days 0 through 3 ($p < 0.001$), but the associations were not significant at greater lag days, except lag day 7 (6.2%, $p = 0.017$). For Factor 1 (vehicle and industrial combustion), there was a significant positive association on lag days 0 and 2 through 6, with by far the strongest association on lag day 3 (101.0%, $p < 0.001$). Based on Zhang et al., eNO was consistently positively associated with six primary pollutants in Factor 1 – $\text{PM}_{2.5}$, SO_4^{2-} , CO, EC, SO_2 , and NO_2 . The association of eNO with Factors 1, 4, and 5 was similar with and without the fall data included.

There was no consistent trend for the association of eNO with the other two factors, although each factor did have a positive association on certain lag days. For Factor 2 (natural soil/road dust), there were significant positive associations on lag days 1, 4, and 5 (10.3 to 21.2%, $p < 0.02$). For Factor 3 (secondary formation), the significant positive associations occurred on lag days 6 and 7 (26.5 to 37.6%, $p < 0.05$). This is consistent with the findings of Zhang et al., who showed consistent positive association with NO_2 , but no consistent association with O_3 . Notably, the associations of eNO with Factors 2 and 3 were different when the fall data is excluded.

Two of the biomarkers for hemostasis and blood coagulation (vWF and sCD62P) showed significant associations in the expected direction consistently with Factors 1 (vehicle and industrial combustion), 4 (oil combustion), and 5 (vegetative burning). In Zhang et al., these biomarkers showed positive associations with $PM_{2.5}$ and SO_2 , which are both components of Factor 5, and with $PM_{2.5}$, SO_4^{2-} , EC, SO_2 , and CO, which are all components of Factor 1. Furthermore, the association of these two biomarkers with Factors 1, 4, and 5 were similar with and without the fall data included.

None of the three biomarkers for hemostasis and blood coagulation showed consistent, significant associations with Factor 2 (natural soil/road dust) or Factor 3 (secondary formation). The finding for Factor 3 is consistent with Zhang et al.'s analysis of the individual pollutants, since all three biomarkers showed no consistent association with O_3 .

As shown in Figure 4, vWF was positively associated with Factor 4 (oil combustion) on all lag days with a high level of significance ($p < 0.001$), with effect estimates of 2.0 to 6.9%. It was also positively associated with Factor 5 (vegetative burning) on all lag days, with effect estimates of 2.3 to 8.4%, although on lag day 1, the association was not significant ($p = 0.019$ on lag day 0, $p = 0.085$ on lag day 1, $p < 0.001$ on all other lag days). These associations were similar with and without the fall data included. In Zhang et al. vWF was consistently associated with three components of Factor 5, $PM_{2.5}$, SO_4^{2-} , and CO.

The association of vWF with the other three factors was less consistent, although it was positively and significantly associated with both Factor 1 (vehicle and industrial combustion) and Factor 3 (secondary formation) on several lag days, including lag day

0, at 3.6 and 11.3%, respectively. In Zhang et al., vWF was consistently associated with five components of Factor 1 - $\text{PM}_{2.5}$, SO_4^{2-} , EC, SO_2 , and CO. vWF generally showed a negative association with Factor 2 (natural soil/road dust), which is not the expected direction, and there is not an obvious explanation for this result. This relationship was not consistent when the fall data was omitted, and may be spurious.

Interestingly, the association between vWF and Factor 3 (secondary formation) trended from a strong positive association, 11.3%, on lag day 0 ($p < 0.001$) to a strong negative association, -4.0 to -6.3%, on later lag days ($p < 0.02$ on lag days 5 through 7). Since this factor was driven by the titration reaction and increased with nitrogen oxide concentrations but decreased with ozone concentrations, it is possible that the observed trend is due to cyclical trends in the concentrations of these pollutants. Furthermore, previous work by Zhang et al. indicated a similar trend for the association of vWF with nitrogen dioxide, and a similar but opposite trend for the association of vWF with ozone. These results may imply that vWF is increased when nitrogen oxide concentrations are elevated and ozone concentrations are repressed, and is decreased when the opposite is true. However, some of these associations were not significant when the fall data was omitted, and the trend was not as distinct.

As shown in Figure 5, sCD62p showed significant positive associations with Factors 1, 4, and 5. For Factors 4 (oil combustion) and 5 (vegetative burning), the associations were significant on all lag days ($p < 0.001$) and ranged from 3.1 to 8.9% and 5.6 to 11.2%, respectively. These results were similar with and without the fall data included, although the significance of some of the associations disappears when the fall data is omitted. Furthermore, in Zhang et al., sCD62p was consistently associated with

three components of Factor 5 - $\text{PM}_{2.5}$, SO_4^{2-} , and CO. For Factor 1 (vehicle and industrial combustion), the significant positive associations occurred on lag days 0 to 5 (4.1 to 15.3%, $p < 0.005$), which was generally consistent with its association in Zhang et al. with components of Factor 1, including $\text{PM}_{2.5}$, SO_4^{2-} , EC, OC, SO_2 , CO, and NO_2 .

The association between sCD62p and Factor 2 (natural soil/road dust) was significant only on lag day 5, with a positive effect estimate of 2.9% ($p = 0.001$). For Factor 3 (secondary formation), there was a significant positive association on lag day 2 (7.1%, $p = 0.003$), but significant negative associations on lag days 3 and 4 (-4.2 and -3.2%, $p = 0.037$ and 0.047 , respectively). The inconsistency of the associations for this factor may again be due to this factor's inverse relationship with ozone concentrations, although it is worth noting that in Zhang et al.'s work, sCD62p was negatively associated with O_3 on several lag days and positively associated with NO_2 on most lag days. So, if this relationship held, Factor 3 should show a positive association with sCD62p, but, as with several other biomarkers, the relationships may be masked by the inverse relationship between the components of Factor 3.

As shown in Figure 6, sCD40L showed only a few significant, positive associations. This was also true for individual pollutants in Zhang et al.'s work. For Factors 3 (secondary formation) and 4 (oil combustion), there were no significant associations in either direction. For Factor 1 (vehicle and industrial combustion), there was a significant negative association on lag day 1 (3.8%, $p = 0.008$) and significant positive associations on lag days 4 and 5 (3.8 and 3.9%, $p = 0.002$ and 0.001 , respectively). Factor 2 (natural soil/road dust) showed a negative association on lag day

0 (2.1%, $p=0.002$) and a positive association on lag day 6 (1.1%, $p=0.047$). These few significant associations were generally not consistent when the fall data was omitted.

As shown in Figure 7, the biomarker for systemic inflammation and oxidative stress, 8-OHdG, showed the most consistent positive and significant associations with Factor 1 (vehicle and industrial combustion) on lag days 0 through 4 (3.5 to 6.7%, $p<0.01$). The trends in these associations were similar with and without the fall data included, although the significance of several lag days disappears when the fall data is omitted. In Zhang et al.'s work, 8-OHdG also showed consistent, significant positive associations with three components of Factor 1 – $PM_{2.5}$, SO_4^{2-} , and EC.

8-OHdG was not consistently associated with Factor 3 (secondary formation) or Factor 5 (oil combustion), but did have significant positive associations on lag days 2, 4, 6, and 7 (4.6 to 8.7%, $p<0.05$) with Factor 3 and on lag days 1, 3, and 4 (3.2 to 4.9%, $p<0.05$) with Factor 5. The association with these factors was also sensitive to the omission of the fall data. The findings for secondary formation are consistent with Zhang et al.'s findings that showed inconsistent associations of 8-OHdG with NO_2 and O_3 , but generally in the positive and negative directions with these two pollutants, respectively. 8-OHdG showed significant positive associations with Factor 2 (natural soil/road dust) and Factor 4 (oil combustion) on only one lag day each – lag day 1 (1.5%, $p<0.05$) and lag day 5 (1.9%, $p<0.05$), respectively.

3.3 Linear mixed effects model results –source type trends

Table 3 is a summary of the associations between each biomarker and each source type. Factor 1 (vehicle and industrial combustion), consistently had significant associations in the hypothesized direction on multiple lag days with most of the

biomarkers. The exception was sCD40L, which had a significant negative association on lag day 1 and significant positive associations on lag days 4 and 5. The associations of Factor 1 with each biomarker was generally consistent with and without the fall data included.

Factor 2 (natural soil/road dust) had very few significant associations in either direction for any of the biomarkers. Furthermore, in the few cases where a significant association was observed, it was generally in the opposite direction. This trend may be due to the typically, relatively benign composition of natural soil and road dust, and indicates that it does not appear to have short term effects on the biomarkers in this study.

Factor 3 (secondary formation) showed a number of significant positive associations, but also a number of significant negative associations. As discussed previously, the inconsistency of the associations for this factor may be due to the fact that it represents the titration reaction and is positively associated with the oxides of nitrogen and negatively associated with ozone. These associations were also sensitive to the omission of the fall data, as might be expected, due to the seasonal nature of secondary formation.

Factors 4 (oil combustion) and 5 (vegetative burning) consistently had significant associations in the expected direction on multiple lag days for most of the biomarkers. It is worth noting that both of these air pollution factors are influenced significantly by seasonal factors. Both of these factors were observed to be lowest during the post-Olympic test period, in the fall months, compared to the pre-Olympic test period in the summer. However, the associations observed between these two factors and the

biomarkers were generally consistent with and without the fall data included, indicating that while the factors may have a seasonal component, their association with the biomarkers does not appear to be affected by this.

3.4 Linear mixed effects model results –aldehyde trends

Figures 8 through 14 and Table 4 show the associations between each biomarker and the three aldehydes. Formaldehyde had very few significant associations in the hypothesized direction with any of the biomarkers. However, it did have associations in the opposite direction on multiple lags with EBC Nitrite, eNO, and sCD62P, and on lag day 1 with vWF and 8-OHdG. This trend, and the lack of associations in the hypothesized direction, may be due to formaldehyde's strong association with secondary sources described in Chapter 2, i.e. its association with ozone but inverse association with nitrogen oxides. Ozone and formaldehyde showed a similar trend for the biomarkers, while the nitrogen oxides showed an opposite trend. So, the apparent beneficial effect of formaldehyde on the biomarkers may be due rather to the fact that when formaldehyde concentrations were higher, the concentration of nitrogen oxides were lower. Notably, many of the significant, negative associations for formaldehyde with the biomarkers were not significant when the fall data was omitted from the analysis (see Appendix I).

Acrolein was also shown in Chapter 2 to be strongly associated with secondary sources and, like formaldehyde, was positively associated with ozone but negatively associated with nitrogen oxides. However, unlike formaldehyde, acrolein did show some significant associations in the hypothesized direction for lag days 0, 1, and 3 for EBC Nitrite. These results may indicate that acrolein affects EBC Nitrite, and the associations

on lag days 0 and 3 were still significant with the fall data omitted. The association may be spurious, though, since for all of the other biomarkers, including others for pulmonary inflammation, acrolein did not show significant associations in the hypothesized direction, except for a few on later lag days (3 or greater). The inconsistent associations with most of the biomarkers for acrolein may be due to its association with secondary sources and, like formaldehyde, the apparent beneficial impact of acrolein on many of the biomarkers may actually be due to the lower nitrogen oxide concentrations when acrolein concentrations were higher.

Acetaldehyde had a number of significant associations in the hypothesized direction with several of the biomarkers. For EBC Nitrite, it had significant associations on lag days 0, 1, and 3, and these were all still significant with the fall data omitted. It also showed significant associations on all lag days except lag day 6 for sCD62P, with the strongest associations in terms of both magnitude and significance on lag days 0 and 1. Only lag days 1 and 4 were not significant with the fall data omitted. Acetaldehyde also showed significant associations with eNO and sCD40L, but these were only on later lag days (3 or greater), and the associations with eNO were sensitive to the omission of the fall data.

As shown in Tables 2 and 6 in Chapter 2, acetaldehyde was associated with the oil combustion and vegetative burning source types, and with a number of individual combustion pollutants, including nitrogen dioxide, carbon monoxide, PM_{2.5}, and sulfur dioxide. These source types and pollutants followed similar trends to acetaldehyde in their associations with the biomarkers, and it is also possible that the trends observed for acetaldehyde are actually due to the relationship of the biomarkers to the combustion

sources rather than to acetaldehyde itself. It is also worth noting that the magnitude of the percent change of two of the pulmonary inflammation biomarkers, EBC Nitrite and eNO, for one inter-quartile range increase in acetaldehyde were higher than the percent change for the other biomarkers (see Table 4). This may be due to a stronger relationship for acetaldehyde with respiratory effects than for cardiovascular effects.

The biomarkers pH, sCD40L, and 8-OHdG had very few significant associations in the expected direction with any of the aldehydes. This is not surprising for sCD40L, as this biomarker had few significant associations with any air pollution sources in this study or other individual pollutants in Zhang et al. The finding is somewhat surprising for pH and 8-OHdG, though, as these were both associated with primary and secondary air pollution sources and a number of individual pollutants. The lack of associations between the aldehydes and these biomarkers may be due to different biological mechanisms for the aldehydes compared to the other pollutants and sources (i.e. fewer cardiovascular effects), the variability in daily aldehyde concentrations, and the smaller available data set for the aldehydes. Notably, most likely due the daily variability and smaller data sets, the confidence intervals for the percent biomarker change per inter-quartile range increase in aldehyde concentrations were generally higher than for other individual pollutants or the five source types identified.

4. Conclusions

These findings indicate that the restrictions implemented by the Chinese government during the Olympic period, which significantly decreased the contribution of all major sources of air pollution in Beijing, also had a beneficial impact on

biomarkers of blood coagulation, pulmonary and systemic inflammation, and oxidative stress.

Most of the biomarkers included in this study showed significant associations with multiple air pollution factors on many lag days. The most notable exception was sCD40L. The most consistent, significant associations with the biomarkers were with the vehicle and industrial combustion, oil combustion, and vegetative burning factors. The natural soil/road dust factor had very few significant associations in either direction for any of the biomarkers, and the secondary formation factor showed a number of significant positive associations with the biomarkers, but also a number of significant negative associations.

The biomarkers for pulmonary inflammation, particularly pH and eNO, were most consistently associated with the factors for vehicle and industrial combustion, oil combustion, and vegetative burning. The biomarkers for hemostasis and blood coagulation, particularly vWF and sCD62p, were most consistently associated with oil combustion, but also associated with vehicle and industrial combustion and vegetative burning. Systemic inflammation, as indicated by 8-OHdG, was most consistently associated with vehicle and industrial combustion. 8-OHdG also showed a number of associations with secondary formation and vegetative burning, however, these were sensitive to the omission of the fall data. The associations between the biomarkers and the aldehydes were generally not significant or in the hypothesized direction, although EBC nitrite was associated with both acrolein and acetaldehyde, and sCD62p was associated with acetaldehyde. Further research is needed to confirm the positive association of air pollutants and sources with these biomarkers.

Figure 1. Percent change in pH associated with one interquartile increase in factor score, controlling for temperature (ns=1), relative humidity (ns=1), 6 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements.

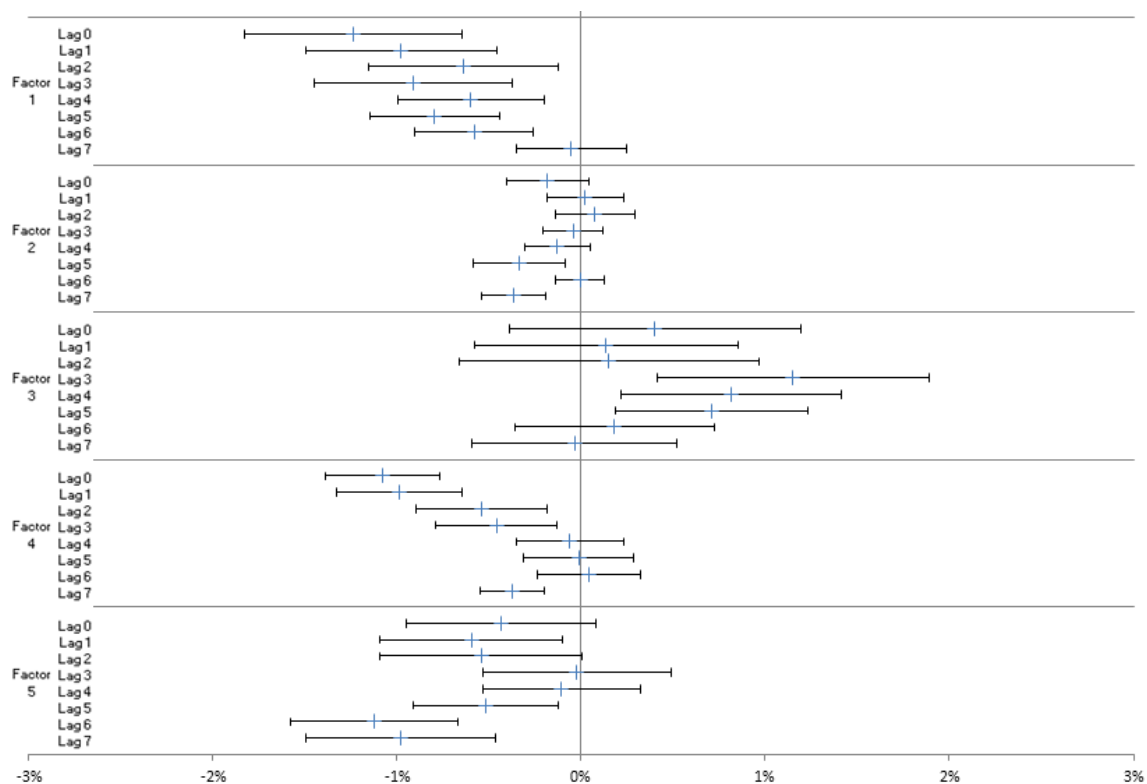


Figure 2. Percent change in EBC Nitrite associated with one interquartile increase in factor score, controlling for temperature (ns=2), relative humidity (ns=1), 7 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

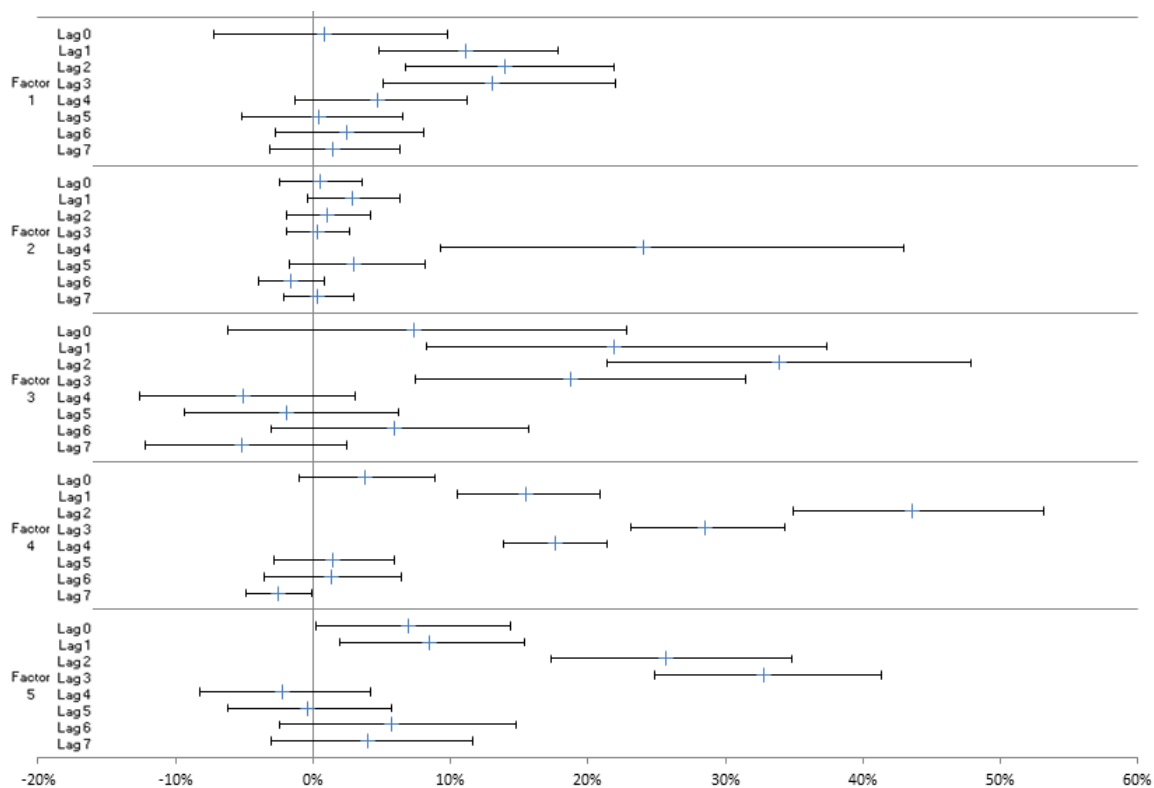


Figure 3. Percent change in eNO associated with one interquartile increase in factor score, controlling for temperature (ns=2), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 7 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

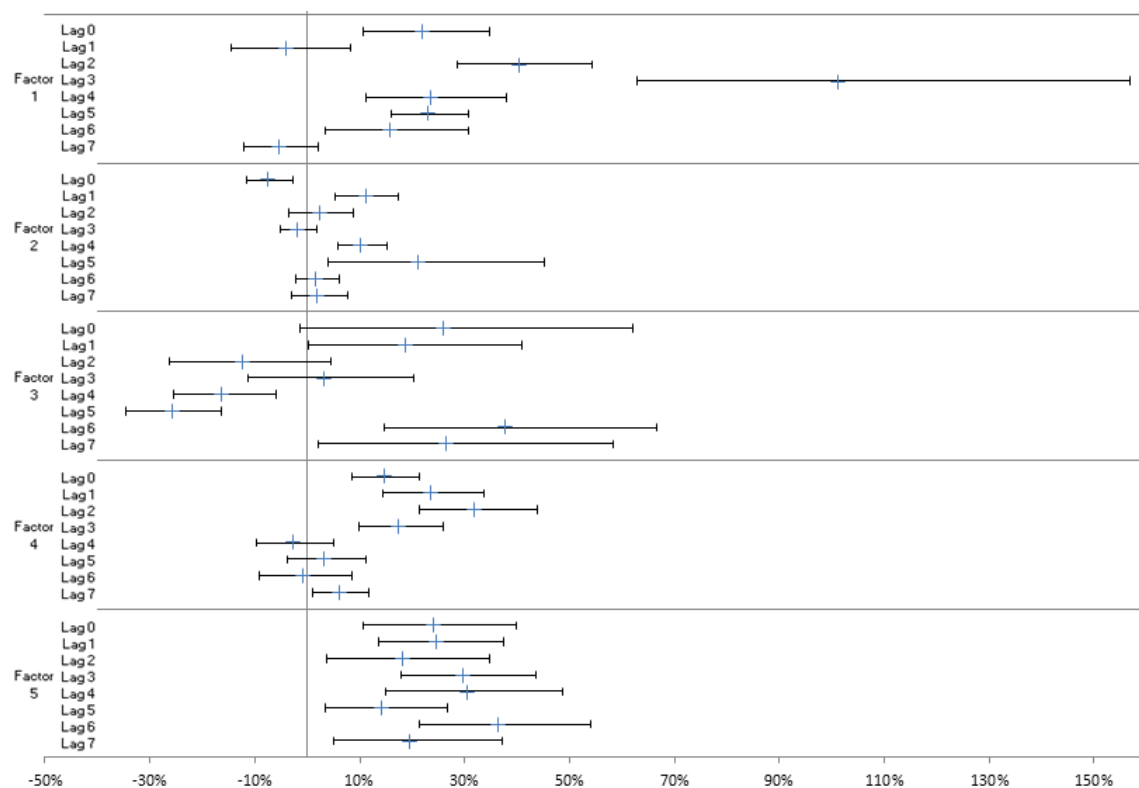


Figure 4. Percent change in vWF associated with one interquartile increase in factor score, controlling for temperature (ns=3), relative humidity (ns=3), 7 day moving average of temperature (ns=3), 6 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

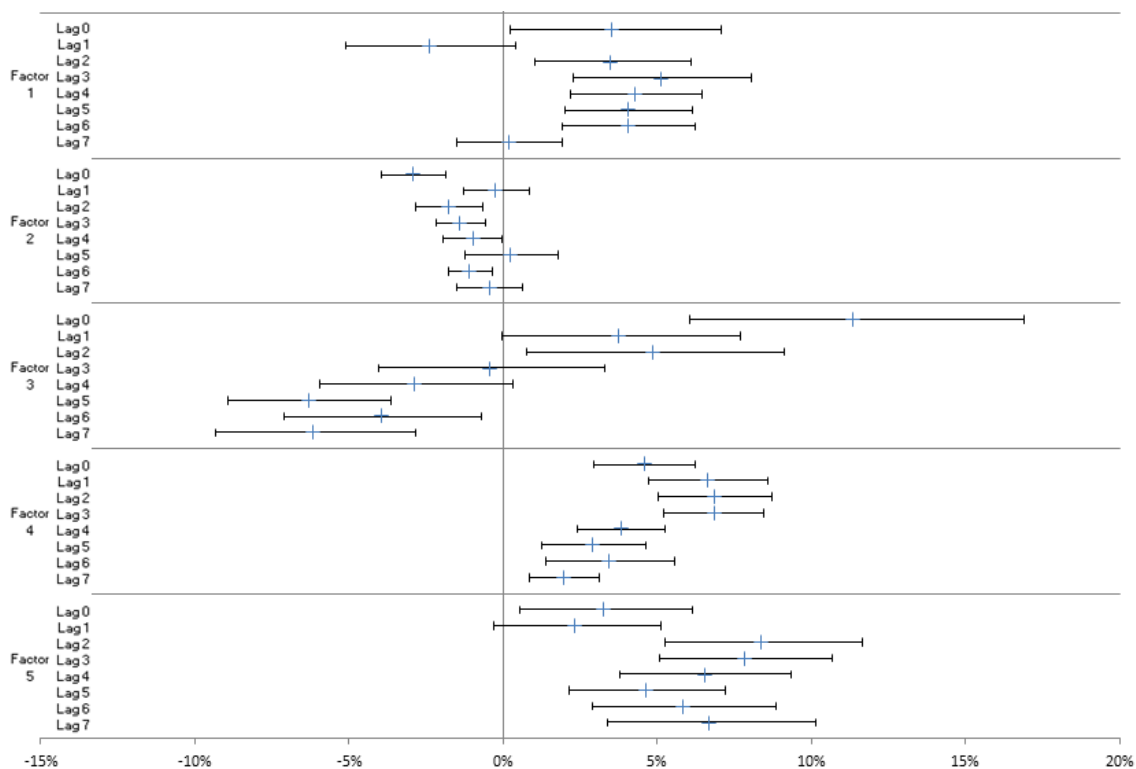


Figure 5. Percent change in sCD62p associated with one interquartile increase in factor score, controlling for temperature (ns=1), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 4 day moving average of relative humidity (ns= 2), gender, and day of week for biomarker measurements.

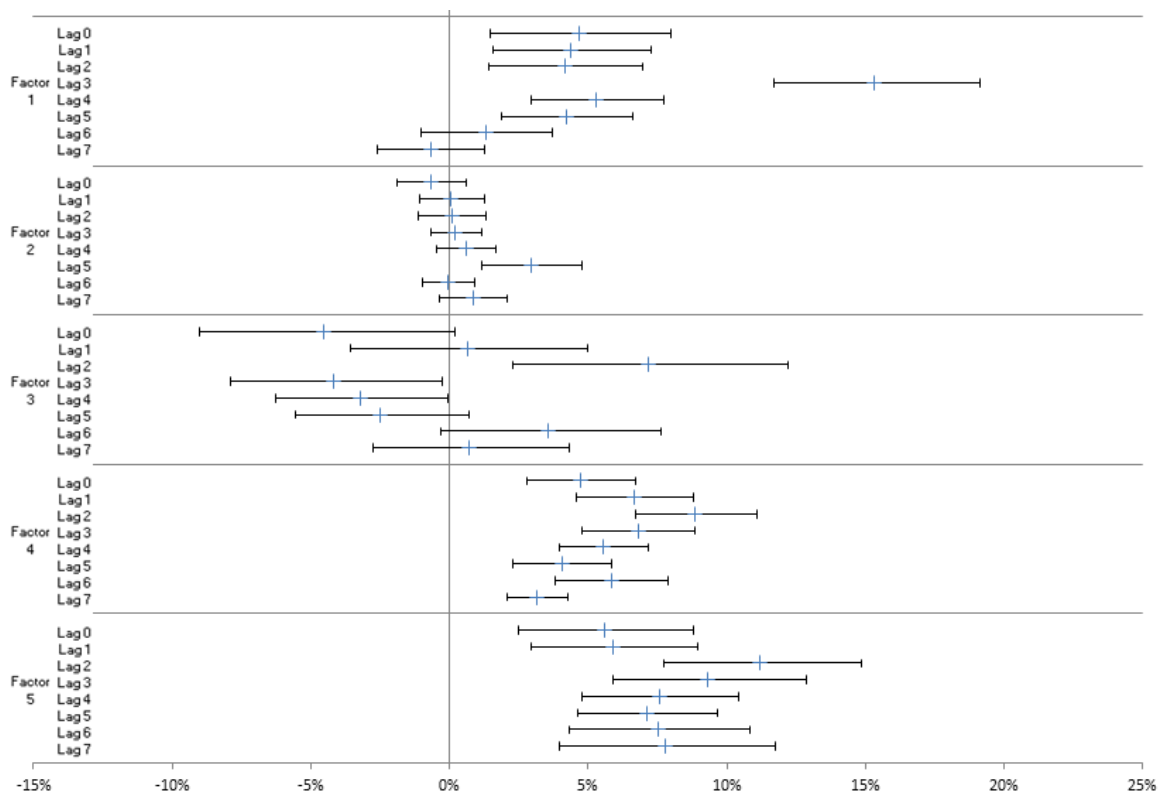


Figure 6. Percent change in sCD40L associated with one interquartile increase in factor score, controlling for temperature (ns=1), relative humidity (ns=1), 5 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements

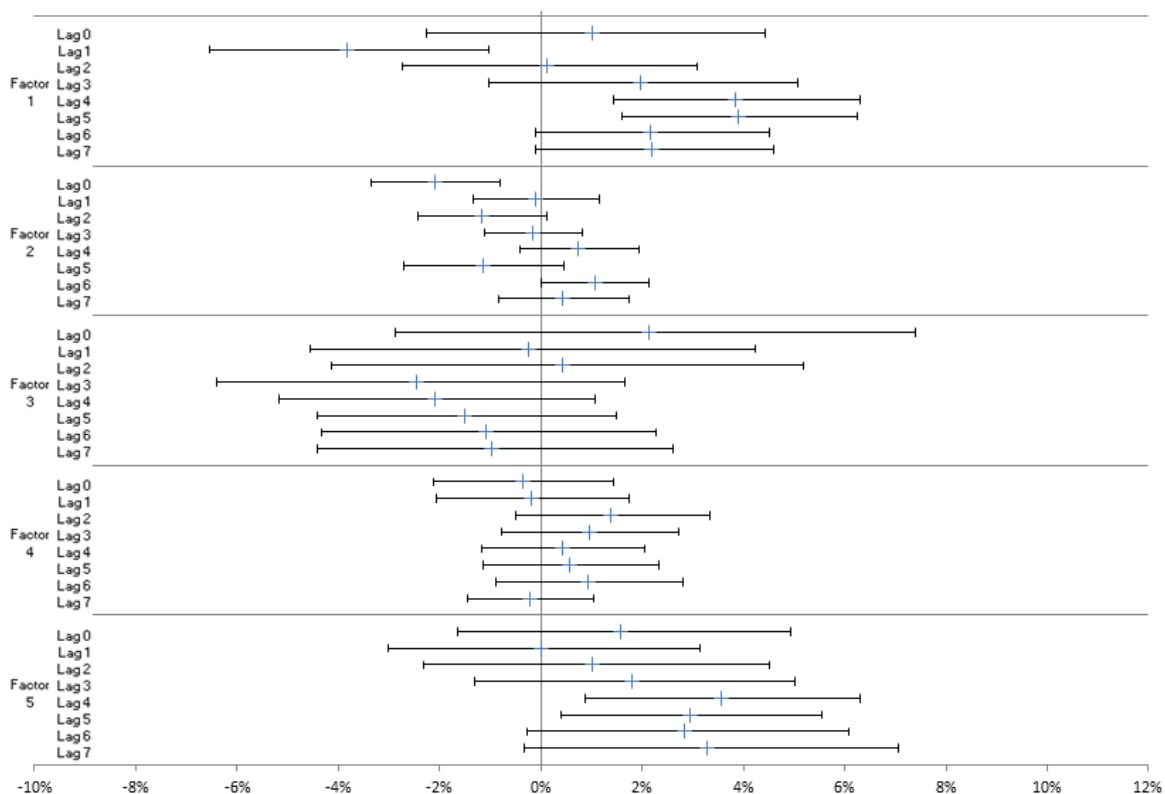


Figure 7. Percent change in log(8-OHdG) associated with one interquartile increase in factor score, controlling for temperature (ns=1), relative humidity (ns=1), 7 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

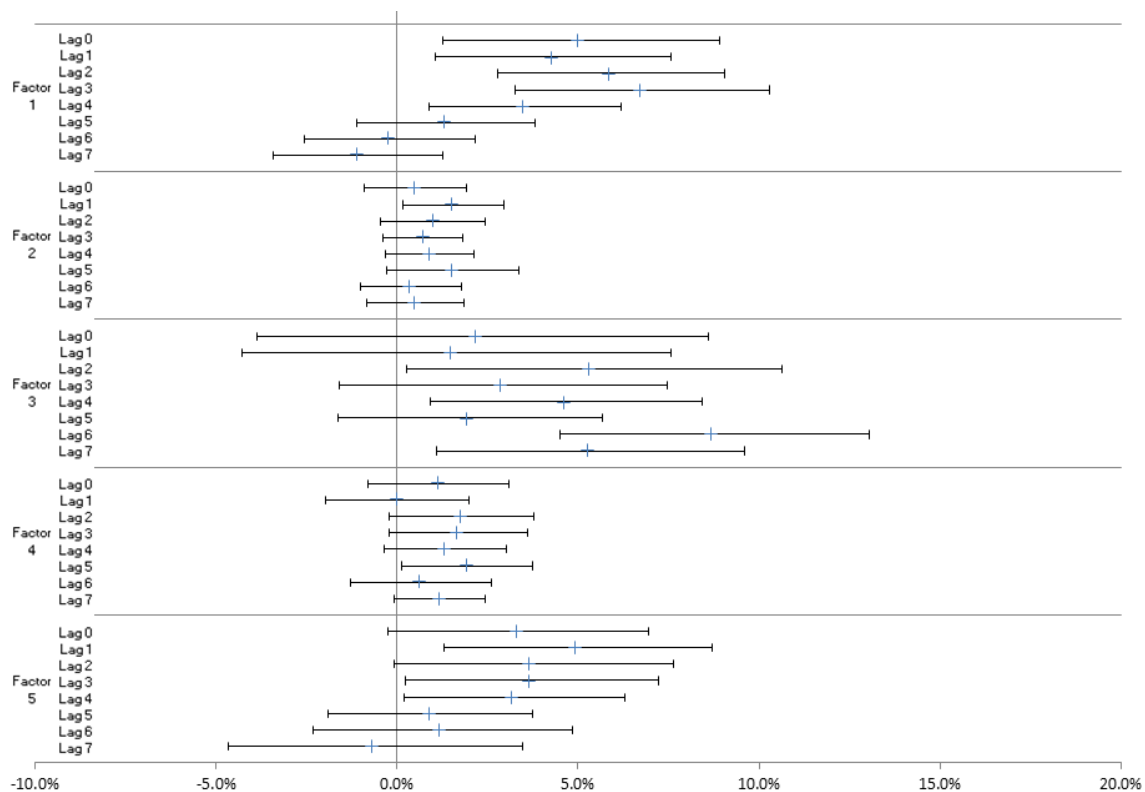
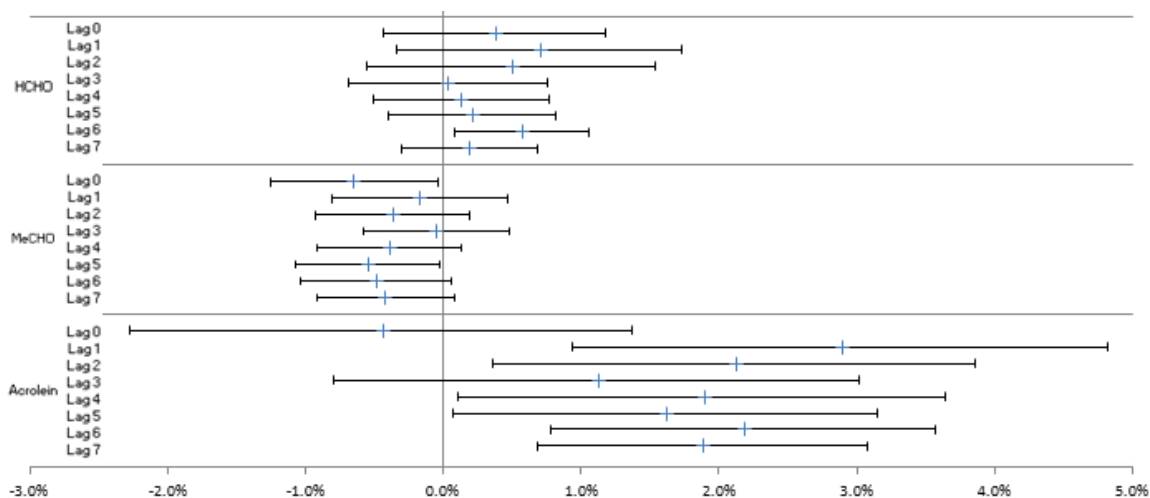
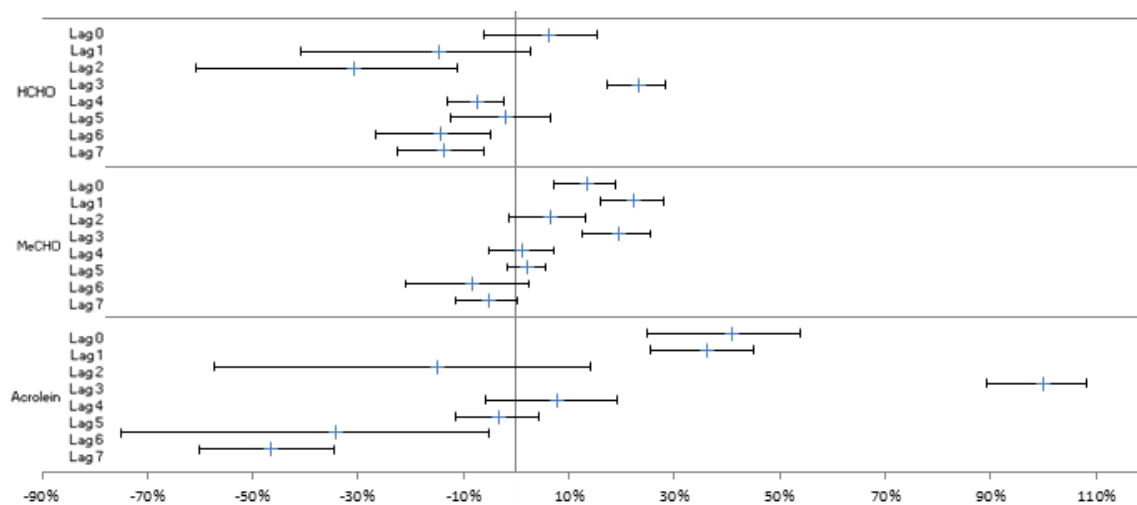


Figure 8. Percent change in pH associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=1), relative humidity (ns=1), 6 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns=1), gender, and day of week for biomarker measurements.



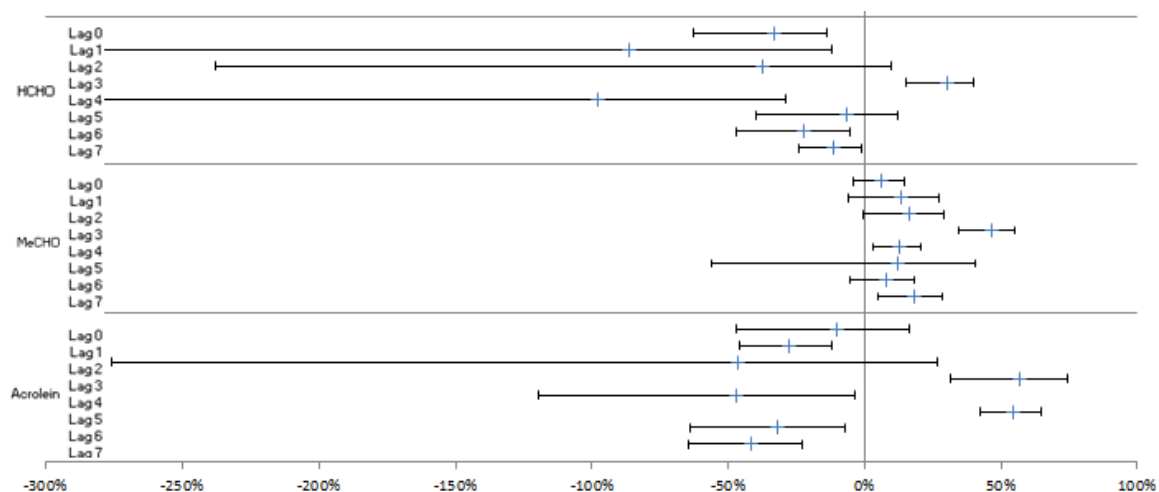
HCHO = Formaldehyde; MeHCO = Acetaldehyde

Figure 9. Percent change in EBC Nitrite associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=2), relative humidity (ns=1), 7 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.



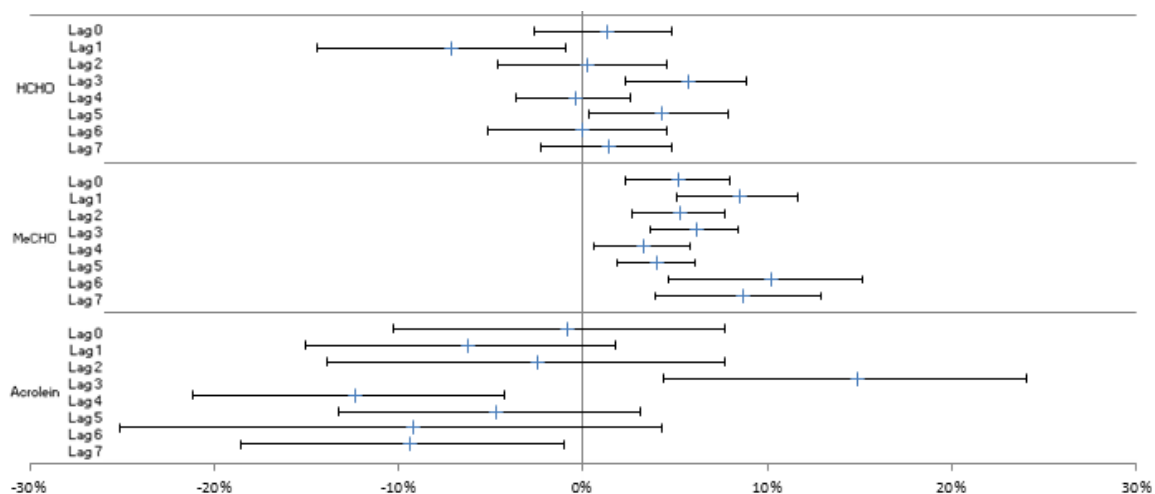
HCHO = Formaldehyde; MeHCO = Acetaldehyde

Figure 10. Percent change in eNO associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=2), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 7 day moving average of relative humidity (ns=3), gender, and day of week for biomarker measurements.



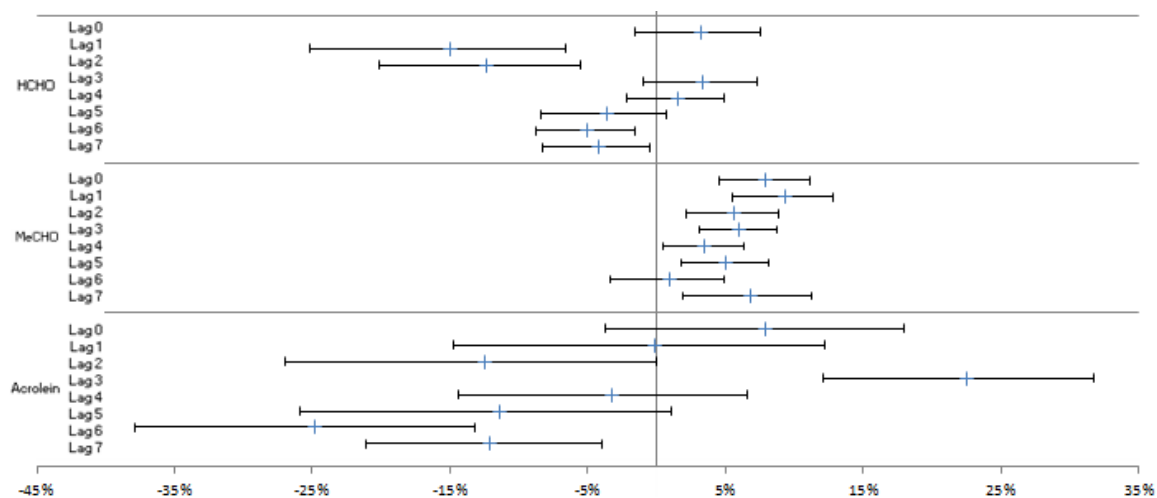
HCHO = Formaldehyde; MeHCO = Acetaldehyde

Figure 11. Percent change in vWF associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=3), relative humidity (ns=3), 7 day moving average of temperature (ns=3), 6 day moving average of relative humidity (ns=3), gender, and day of week for biomarker measurements.



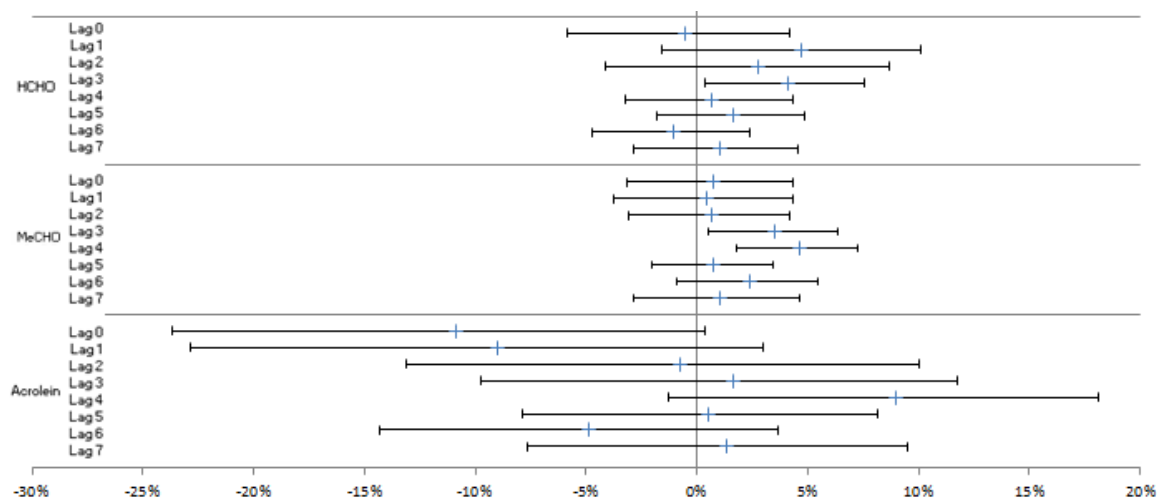
HCHO = Formaldehyde; MeHCO = Acetaldehyde

Figure 12. Percent change in sCD62p associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=1), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 4 day moving average of relative humidity (ns= 2), gender, and day of week for biomarker measurements.



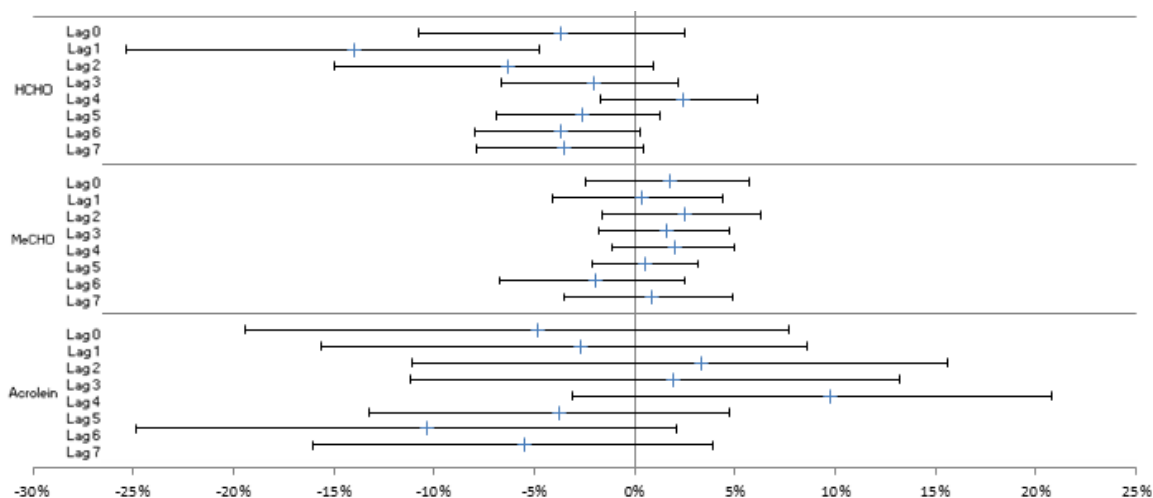
HCHO = Formaldehyde; MeHCO = Acetaldehyde

Figure 13. Percent change in sCD40L associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=1), relative humidity (ns=1), 5 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements



HCHO = Formaldehyde; MeHCO = Acetaldehyde

Figure 14. Percent change in log(8-OHdG) associated with one interquartile increase in aldehyde concentration, controlling for temperature (ns=1), relative humidity (ns=1), 7 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.



HCHO = Formaldehyde; MeHCO = Acetaldehyde

Table 1. Summary of the biomarker collection and analysis, Beijing, China, June – October 2008

Physiological function/pathway/Domain	Specimen type	Collection/measurement duration	Biomarker	Principle/equipment of measurement
Pulmonary inflammation	Exhaled breath condensate	20 min	pH	pH meter
			Nitrite	HPLC-UV
	Exhaled breath	5 min	Exhaled nitric oxide (eNO)	NO _x chemiluminescence analyzer
Hemostasis / blood coagulation	Blood	~2 min	von Willebrand Factor	ELISA based assay
			Soluble CD62P (sCD62P)	
			sCD40L	
Systemic inflammation and oxidative stress	Urine	~1 min	8-Hydroxy-2'-deoxyguanosine (8-OHdG)	HPLC-ECD

Table 2. Descriptive statistics for biomarkers, Beijing, China, June – October 2008

	pH	EBC Nitrite ($\mu\text{mol/L}$)	eNO (ppm)	vWF (% of normal)	sCD62p (ng/mL)	sCD40L (ng/mL)	8-OHdG (mg/mol creatinine)
Mean	7.52	6.46	11.55	92.3	5.79	1.91	8.44
Standard deviation	0.37	4.22	7.33	30.4	1.6	0.56	18.67
Number	742	693	742	742	733	733	725
Before (6/10-7/7)	7.43	8.49	13.09	102.6	6.69	1.93	9.58
During (8/4-8/29)	7.52	5.43	7.27	90.2	5.20	1.80	7.51
After (10/6-10/30)	7.61	5.11	14.22	83.8	5.45	2.00	8.21
Maximum	8.23	36.47	54.8	176.7	11.63	7.54	292.7
Minimum	4.7	0.53	0.17	7.21	2.92	0.61	-3.59

Key: $\mu\text{mol/L}$ =micromoles per liter; ppb=parts per billion; ng/mL=nanograms per milliliter;
mg/mol=milligrams per mole

Table 3. Summary of significant associations between biomarkers and air pollution source types

	Bio-marker	Factor 1 Vehicle/ industrial combustion	Factor 2 Natural soil/ road dust	Factor 3 Secondary formation	Factor 4 Oil combustion	Factor 5 Vegetative burning
Pulmonary inflammation	pH	0-1: 1.0-1.2%*** 2: 0.6%* 3: 0.9%*** 4: 0.6%* 5-6: 0.6-0.8%	5: 0.3%** 7: 0.4%***	3-5: 0.7-1.1%**	0-1: 1.0-1.1%*** 2 to 3: 0.5%** 7: 0.4%***	1: 0.6%* 5: 0.5%** 6-7: 1.0-1.1%***
	EBC Nitrite	1-3: 11.1-13.9%***	4: 24.0%***	1: 21.9%** 2-3: 18.8-33.9%	1-4: 15.5-43.6%***	0-1: 7.0-8.4%* 2-3: 25.6-32.7%***
	eNO	0: 21.9%*** 2-5: 23.1-101.0%*** 6: 15.9%*	0: 7.4%** 1: 11.0%*** 4: 10.3%*** 5: 21.2%*	1: 18.7%* 4: 16.3%** 5: 26.0%*** 6: 37.6%*** 7: 26.5%*	0-3: 14.6-31.9%*** 7: 6.2%*	0-1: 24.1-24.8%*** 2: 17.9%* 3-4: 29.9-30.4%*** 5: 14.3%** 6: 36.5%*** 7: 19.7%**
Hemostasis / blood coagulation	vWF	0: 3.6%* 2: 3.5%** 3-6: 4.0-5.1%***	0: 2.9%*** 2: 1.8%** 3: 1.4%*** 4: 1.0%* 6: 1.1%**	0: 11.3%* 2: 4.8%* 5: 6.3%*** 6: 4.0%* 7: 6.1%***	0-7: 2.0-6.9%***	0: 3.3%* 2-7: 2.3-8.4%***
	sCD62 P	0-2: 4.1-4.7%** 3-5: 4.2-15.3%***	5: 2.9%***	2: 7.1%** 3-4: 3.2-4.2%*	0-7: 3.1-8.9%***	0-7: 5.6-11.2%***
	sCD40L	1: 3.8%** 4: 3.8%** 5: 3.9%***	0: 2.1%** 6: 1.1%*	No significant associations	No significant associations	5: 3.6%** 6: 2.9%*
Systemic inflammation / oxidative stress	8-OHdG	0-1: 4.2-5.0%** 2-3: 5.9-6.7%*** 4: 3.5%**	1: 1.5%*	2: 5.3%* 4: 4.6%* 6: 8.7%*** 7: 5.3%*	5: 1.9%*	1: 4.9%** 3-4: 3.2-3.7%*

Key: Only significant associations are shown. Number of lag days precedes the colon; followed by the percent change or range of percent change (for multiple lag days) in the given biomarker for one interquartile increase in factor score. Sign and highlighting (+ or -) indicates whether association was positive or negative, respectively. Significance of association indicated by asterisks as follows: ***=0 to 0.001; **=0.001 to 0.01; *=0.01 to 0.05.

Table 4. Summary of significant associations between biomarkers and aldehydes

	Biomarker	Formaldehyde (HCHO)	Acetaldehyde (MeCHO)	Acrolein
Pulmonary inflammation	pH	6: +0.6%*	0: 0.6%* 5: 0.5%*	1-2: +2.1-2.9%* 4-7: +1.6-2.2%*
	EBC Nitrite	2: +30.9%*** 3: +23.1%*** 4: 7.4%** 6: +14.5%** 7: -13.7%***	0-1: +13.3-22.3%*** 3: +19.3%***	0-1: +36.1-40.9%*** 3: +100%*** 6: +34.3%* 7: -46.5%***
	eNO	0: +33.4%*** 1: +86.6%*** 3: +30.3%*** 4: +97.5%** 6-7: +11.2-22.3%**	3: +46.5%*** 4: +12.7%* 7: +18.1%**	1: +27.5%*** 3: +56.7%*** 4: +46.9%* 5: +54.4%*** 6-7: +31.9-46.7%***
Hemostasis / blood coagulation	vWF	1: 7.2%* 3: +5.8%** 5: +4.3%**	0-3: +5.2-8.5%*** 4: +3.3%* 5-7: +4.0-10.2%***	3: +14.9%** 4: +12.3%** 7: 9.3%*
	sCD62P	1-2: +12.3-15.0%*** 6-7: +4.2-5.0%*	0-1: +7.9-9.3%*** 2: +5.6%** 3: +6.0%*** 4: +3.5%* 5: +5.1%** 7: +6.8%**	2: +12.5%* 3: +22.5%*** 6-7: +12.1-13.2%**
	sCD40L	3: +4.1%*	3: +3.5%* 4: +4.6%**	No significant associations
Systemic inflammation / oxidative stress	8-OHdG	1: +4.7%***	No significant associations	No significant associations

Key: Only significant associations are shown. Number of lag days precedes the colon; followed by the percent change or range of percent change (for multiple lag days) in the given biomarker for one interquartile increase in aldehyde concentration. Sign and highlighting (+ or -) indicates whether association was positive or negative, respectively. Significance of association indicated by asterisks as follows: ***=0 to 0.001; **=0.001 to 0.01; *=0.01 to 0.05.

Overall Conclusions and Recommendations

Based on the factors scores from the PCA, the five predominant sources of air pollution identified were vehicle and industrial combustion, natural soil/road dust, secondary formation, oil combustion, and vegetative burning. Separate factors for vehicle and industrial sources were expected as output from the PCA. Otherwise, these sources were generally consistent with past source apportionment studies in Beijing, and the slight differences may be explained by the lack of spring and winter data in this study, as well as by the mandatory control actions put in place during the Olympics.

As hypothesized, the factors representing vehicle and industrial combustion and oil combustion were significantly lower ($p < 0.001$) during the Olympic period compared to before and after the Olympics. Somewhat unexpectedly, the factor representing secondary formation was also lower during the Olympics ($p < 0.0005$). This factor was positively correlated with nitrogen oxides, which were indeed lower during the Olympics, and was negatively correlated with ozone, which was actually higher during the Olympics due to decreased titration by the nitrogen oxides.

Also somewhat unexpectedly, all five sources of air pollution – even natural soil/road dust and vegetative burning - were lower during the main Olympic period (sub-period 2, between the opening and closing ceremonies) than during the rest of the study ($p < 0.01$ except oil combustion, $p = 0.026$). These findings indicate that the restrictions implemented by the Chinese government during the Olympic period significantly decreased the contribution of all major sources of air pollution in Beijing.

The hypothesis that the aldehyde concentrations would be associated with both primary and secondary pollutants was confirmed for formaldehyde and acrolein.

Formaldehyde and acrolein were significantly associated with the factors for secondary formation and vegetative burning, and formaldehyde was also significantly associated with natural soil/road dust, although the mechanism for that association is not clear. Furthermore, although the aggressive air pollution control measures implemented during the Olympics, especially when coupled with favorable meteorological conditions, led to drastic reductions in air pollution sources as well as individual pollutants such as PM_{2.5}, CO, SO₂ and NO_x, there was not a reduction in concentrations of formaldehyde or acrolein. These findings point to the complexity of source control strategies for secondary pollutants, suggesting that the secondary photochemical processes may have dominated the formation of formaldehyde and acrolein. It appears the elevated concentrations of formaldehyde and acrolein during the Beijing Olympics may be due largely to their relationship to elevated ozone concentrations, and coincided with high incident sunlight and decreased NO_x concentrations during the Olympic period.

Concentrations of acetaldehyde, on the other hand, decreased during the Olympic period compared to the period before. Furthermore, acetaldehyde was significantly associated with the primary source factors for oil combustion and vegetative burning, but not with the factor for secondary formation. So, although secondary sources did appear to influence acetaldehyde concentrations, the primary sources dominated for this aldehyde.

The restrictions implemented by the Chinese government during the Olympic period, and the corresponding decreases in all major sources of air pollution in Beijing, also had a beneficial impact on biomarkers of blood coagulation, pulmonary and systemic inflammation, and oxidative stress. Most of the biomarkers included in this

study showed significant associations with multiple air pollution factors on many lag days. The most notable exception was sCD40L.

As expected, the biomarkers had consistent, significant associations with combustion sources (vehicle and industrial, oil, and vegetative burning). The natural soil/road dust factor had very few significant associations in either direction for any of the biomarkers. This is not surprising given the more benign composition of natural soil/road dust, which is dominated by low toxicity elements and ions such as calcium, magnesium, titanium, and aluminum. The secondary formation factor showed a number of significant positive associations with the biomarkers, but also a number of significant negative associations. This is also not surprising, since the secondary formation factor score increased with increasing NO_x concentrations but decreased with increasing ozone concentrations. Both of these pollutants are expected to impact cardiorespiratory health, so the complex relationship of these two secondary pollutants to one another may have obscured any observable impact on the biomarkers. Finally, the associations between the biomarkers and the aldehydes were generally not significant or in the hypothesized direction, although EBC nitrite was associated with both acrolein and acetaldehyde, and sCD62p was associated with acetaldehyde.

This research indicates that the mandatory air pollution controls implemented by the Chinese government during the 2008 Beijing Olympics resulted in measurable and statistically significant decreases in all major air pollution sources. They also indicate that both primary and secondary source controls are important for aldehydes, although secondary sources appear to dominate for formaldehyde and acrolein while primary combustion sources appear to dominate for acetaldehyde. Furthermore, the combustion

sources (vehicle, industrial, oil, and vegetative burning) showed consistent, statistically significant relationships to biomarkers of blood coagulation, pulmonary and systemic inflammation, and oxidative stress. The findings indicate that implementing controls for combustion sources may have a positive impact on cardiorespiratory health, even in healthy young adults.

In particular, the aggressive control of vehicle and industrial sources by the Chinese government had clear impact on reducing the concentrations of many important pollutants, and consequently the positive impact on the cardiorespiratory biomarkers. However, the results also indicate that even greater benefits on cardiorespiratory health could be expected if vegetative burning was more aggressively controlled. The Chinese government did not implement any substantial control measures for these sources, but this source showed significant associations with many of the biomarkers. Furthermore, the results also indicate that even greater benefits on cardiorespiratory health could be expected if the vehicle and industrial combustion source controls decreased nitrogen oxide concentrations even further, below at least 10 ppb in this case, so that the secondary formation of ozone transitioned to a nitrogen oxide limited regime and ozone concentrations would thereby be reduced rather than increased.

There are limitations to this study. The study only encompassed two seasons (summer and fall) with air pollution data from only one fixed location outside central Beijing and may not reflect the overall trends in Beijing and may not be generalizable to other geographical regions. Furthermore, the association between the biomarkers and the air pollution sources is limited by the accuracy of the principal component analysis to apportion the individual pollutants into the source types. Finally, the human subjects for

the biomarker data were drawn from a relatively homogeneous population of healthy young Chinese students and the findings may not be generalizable to other populations.

Further research is needed to explore the relationship between sources of air pollution and concentrations of aldehydes and the impact of specific sources on biomarkers of blood coagulation, pulmonary and systemic inflammation, and oxidative stress. The research should cover a longer time period across all seasons, different study populations for the biomarkers, and different geographic regions.

Appendix A – R Scripts

Table A1. R script for principal component analyses

```
# remove all objects
rm(list=ls());
# set the working directory. always use forward slashes
setwd("C:/Users/Owner/My Documents/PhD_Publish/DISSERTATION BEIJING/R/");
# load RODBC package
library("RODBC");
library("timeSeries");
library("stats");
library("GPArotation");
library("psych");
SourceDataSheet1 <- odbcConnectExcel("air pollution merge data sets.xls");
# sqlTables(SourceDataSheet1);
Data_No_Blanks <- sqlFetch(SourceDataSheet1, "data no blanks_4 PAHs");
D1<-as.Date(Data_No_Blanks[[1]])
# command for removing columns
Data_No_Blanks[[1]]<-NULL;
Data_No_Blanks$F37<-NULL;
# start factor analysis
var_list <- paste(names(Data_No_Blanks), sep = "+",collapse="+");
var_list<-paste("~",var_list,sep="",collapse="");
print(var_list);
pdf(file="Principal Components 2.pdf")
# calculate a correlation matrix
cordata <- cor(Data_No_Blanks,use="pairwise.complete.obs",method="pearson")
write.table(cordata,"clipboard",sep="\t",col.names=NA)
#principal values
principal_val<- principal(Data_No_Blanks,rotate="varimax",nfactors=5,scores=TRUE)
summary(principal_val)
# VALUES gives eigen values
eigen <- principal_val$values
#loadings gives the rotated factors matrix
loadings <- principal_val$loadings
weights <- principal_val$weights
scores <- principal_val$scores
write.table(eigen,"clipboard",sep="\t",col.names=NA)
write.table(loadings,"clipboard",sep="\t",col.names=NA)
write.table(weights,"clipboard",sep="\t",col.names=NA)
```

```

write.table(scores,"clipboard",sep="\t",col.names=NA)
# TIME SERIES PLOTS
# no of variables in frame
pdf(file="Time Series Plots.pdf");
for (i in 1:length(Data_No_Blanks))
# for (i in 2:2)
{
z<-timeSeries(Data_No_Blanks[i],D1 );
# png(file=paste("myplot",i,".png"),width=800, height=600 );
# win.graph(width=10.0, height=5.5)
plot(z, main="Plot of Time Series Data",sub="", lwd=2,col.main="blue",
col.sub="blue", col="red", xlab="Time Period" );
}
# close the device else the pdf will be locked
dev.off();
# Q & Q plots
# for (i in 2:2)
pdf(file="QandQ Plots.pdf")
for (i in 1:length(Data_No_Blanks))
{
qqnorm.default(Data_No_Blanks[[i]],col="red",main=names(Data_No_Blanks)[i]) ;
qqline(Data_No_Blanks[[i]]) ;
}
#end of script for project

```

Table A2. R script for regression of air pollution source types with weather data

```

rm(list=ls());
setwd("C:/Users/Owner/My Documents/PhD_Publish/DISSERTATION BEIJING/R/");
# load packages
library("RODBC");
library("car");
SourceDataSheet1 <- odbcConnectExcel("weather data.xls");
Data_No_Blanks <- sqlFetch(SourceDataSheet1, "Weather")
D1<-as.Date(Data_No_Blanks[[1]])
Data_No_Blanks[[1]]<-NULL;
Data_No_Blanks$F14<-NULL;
var_list <- paste(names(Data_No_Blanks), sep = "+",collapse="+");
print(var_list);
Factor1 <- Data_No_Blanks[[1]]
Tavg <- Data_No_Blanks[[2]]
Rhavg <- Data_No_Blanks[[3]]
Baroavg <- Data_No_Blanks[[4]]
UVAavg <- Data_No_Blanks[[5]]
UVBavg <- Data_No_Blanks[[6]]
WindVavg <- Data_No_Blanks[[7]]
Rain <- Data_No_Blanks [[8]]
N <- Data_No_Blanks[[9]]
W <- Data_No_Blanks[[10]]
S <- Data_No_Blanks[[11]]
E <- Data_No_Blanks[[12]]
options(contrasts=c(unordered="contr.sum",ordered="contr.poly"))
fit <- lm(Factor1 ~ Tavg + Rhavg + Baroavg + UVAavg + UVBavg + WindVavg +
Rain + N + W + S + E)
summary(fit) # show results
coeff <- coefficients(fit) # model coefficients
write.table(coeff,"clipboard",sep="\t",col.names=NA)
ci <- confint(fit, level=0.95) # CIs for model parameters
write.table(ci,"clipboard",sep="\t",col.names=NA)
anova <- Anova(fit,type="III") # anova table Type III sum of squares
write.table(anova,"clipboard",sep="\t",col.names=NA)
odbcClose(SourceDataSheet1);

```

Table A3. R script for regression of aldehydes with air pollution source types

```

rm(list=ls());
setwd("C:/Users/Owner/My Documents/DISSERTATION BEIJING/R/");
# load packages
library("RODBC");
library("car");
SourceDataSheet1 <- odbcConnectExcel("aldehydes with factors.xls");
Data_No_Blanks <- sqlFetch(SourceDataSheet1, "Aldehydes")
D1<-as.Date(Data_No_Blanks[[1]])
Data_No_Blanks[[1]]<-NULL;
Data_No_Blanks$F14<-NULL;
var_list <- paste(names(Data_No_Blanks), sep = "+",collapse="+");
print(var_list);
HCHO <- Data_No_Blanks[[1]]
Factor1 <- Data_No_Blanks[[2]]
Factor2 <- Data_No_Blanks[[3]]
Factor3 <- Data_No_Blanks[[4]]
Factor4 <- Data_No_Blanks[[5]]
Factor5 <- Data_No_Blanks[[6]]
options(contrasts=c(unordered="contr.sum",ordered="contr.poly"))
fit <- lm(HCHO ~ Factor1 + Factor2 + Factor3 + Factor4 + Factor5)
summary(fit) # show results
coeff <- coefficients(fit) # model coefficients
write.table(coeff,"clipboard",sep="\t",col.names=NA)
ci <- confint(fit, level=0.95) # CIs for model parameters
write.table(ci,"clipboard",sep="\t",col.names=NA)
anova <- Anova(fit,type="III") # anova table Type III sum of squares
write.table(anova,"clipboard",sep="\t",col.names=NA)
odbcClose(SourceDataSheet1);

```

Table A4. R script for linear mixed effects model

```

# load packages
library("RODBC");
library("nlme");
library("splines");
# delete all the objects
rm(list=ls())
# set working directory
setwd("C:/Users/Owner/My Documents/DISSERTATION BEIJING/R/")
#initialize these variables for storing results
model_var<-NULL
ciu <- NULL
cil <- NULL
z <- NULL
p <- NULL
slope <- NULL
se <- NULL
ai <- NULL
intr<- NULL
# connect to excel
conn <- odbcConnectExcel("STEP1_VERSION2.xls")
# import from excel
main_data <- sqlQuery(conn, "select * from [Sheet1$]")
# rename illegal names
names(main_data) <- make.names(names(main_data))
# attach the main_data, so that we need not use$ we will detach with detach
attach(main_data)
# this vars will be in all datasets
always_var=subset(main_data,select=c("TEMPHR24","RHHR24","wkday","gender","i
d"))
#dvs
# uncomment this line for entire dataset and comment the next line
for (i in 2:8){
#for(i in 7:8){
    for (j in 24:71){
#    for (j in 24:25){
        # add dependent variable biomarker
        reg_data<-main_data[i]
        # add the always needed data

```

```

reg_data<-cbind(reg_data,always_var)
# add the pollutant IV variable
reg_data<-cbind(reg_data,main_data[j])
  #now for selecting the moving average temp and H
  # for dep var vWF
  switch(names(reg_data)[1],"vWF"={reg_data<-
cbind(reg_data,TEMPMA7,RHMA6)},
  "eNO_con_ppb"={reg_data<-cbind(reg_data,TEMPMA7,RHMA7)},
  "nitriteinEBC_uM"={reg_data<-cbind(reg_data,TEMPMA7,RHMA3)},
  "Corrected_OHdG_mgmol"={reg_data<-
cbind(reg_data,TEMPMA7,RHMA2)},
  "PH"={reg_data<-cbind(reg_data,TEMPMA6,RHMA3)},
  "sCD40L_ngml"={reg_data<-cbind(reg_data,TEMPMA5,RHMA2)},
  "sCD62p_ngml"={reg_data<-cbind(reg_data,TEMPMA7,RHMA4)})
# based on dependent variable change the spline ns also
switch(names(reg_data)[1],"vWF"={ns_vec<-c(3,3,3,3)},
  "eNO_con_ppb"={ns_vec<-c(2,3,2,3)},
  "nitriteinEBC_uM"={ns_vec<-c(2,1,3,3)},
  "Corrected_OHdG_mgmol"={ns_vec<-c(1,1,1,3)},
  "PH"={ns_vec<-c(1,1,3,1)},
  "sCD40L_ngml"={ns_vec<-c(1,1,1,1)},
  "sCD62p_ngml"={ns_vec<-c(1,3,2,2)})
#print(head(reg_data))
  # end of loop for each combination of a given dep and IV variable
# print(summary(reg_data))
# Run the regression using the temp data set
old_names=names(reg_data)
names(reg_data)=c("vdep","TEMPHR24","RHHR24","wkday","gender","id","VIV1","
TEMPMA","RHMA")
  TEMP24_ns<-ns(TEMPHR24,ns_vec[1])
  RHR24_ns <-ns(RHHR24,ns_vec[2])
  TEMPMA_ns<- ns(reg_data$TEMPMA,ns_vec[3])
  RHMA_ns<- ns(reg_data$RHMA,ns_vec[4])
  a1 <- lme(vdep ~ VIV1 + TEMP24_ns + RHR24_ns + TEMPMA_ns +
RHMA_ns + factor(gender) + factor(wkday), random=~1|id, data=reg_data,
na.action=na.omit)
  # retrieve the values that need to be saved
model_var1<-paste(old_names,collapse="|")
model_var2<-paste(ns_vec,collapse="|")
# print(model_var2)

```

```

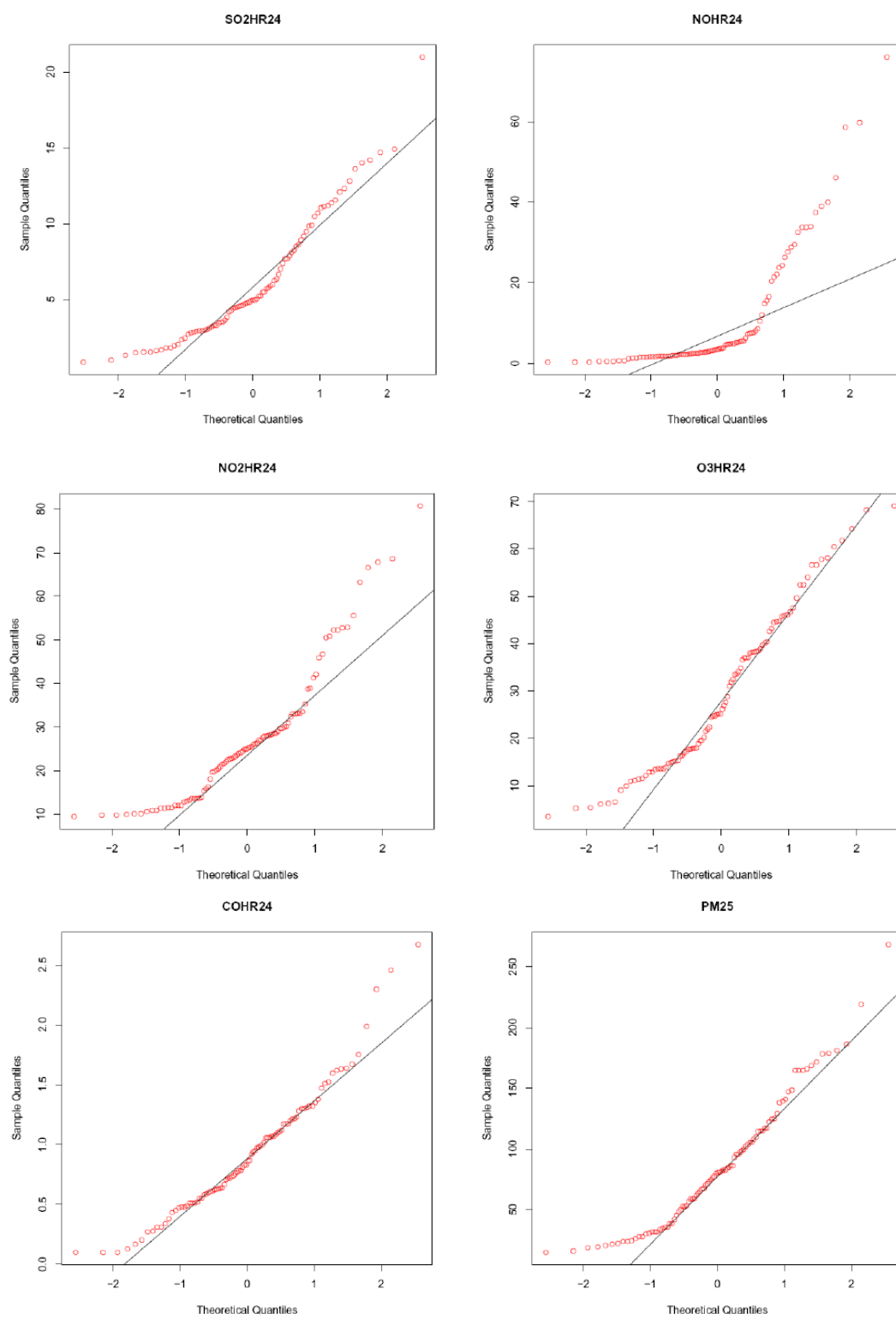
model_var3<-paste(model_var1,"|",model_var2)
model_var<-c(model_var,model_var3)
# print(model_var)
  ciu <-c(ciu,a1$coef$fixed[2]+1.96*sqrt(a1$var[2,2]))
  cil <-c(cil,a1$coef$fixed[2]-1.96*sqrt(a1$var[2,2]))
  z <- c(z,a1$coef$fixed[2]/sqrt(a1$var[2,2]))
  p <- c(p,2*(1-pnorm(abs(a1$coef$fixed[2]/sqrt(a1$var[2,2])))))
  slope <- c(slope,a1$coef$fixed[2])
  se <- c(se,sqrt(a1$var[2,2]))
  ai <- c(ai,AIC(a1))
intr<-c(intr,a1$coef$fixed[1])
# delete the temp data set
rm(reg_data)
ns_vec<-NULL
  }
}
final_output=data.frame(model_var,ciu,cil,z,p,slope,se,ai,intr)
write.table(final_output, "final_output.csv", col.names = NA, sep = ", " )

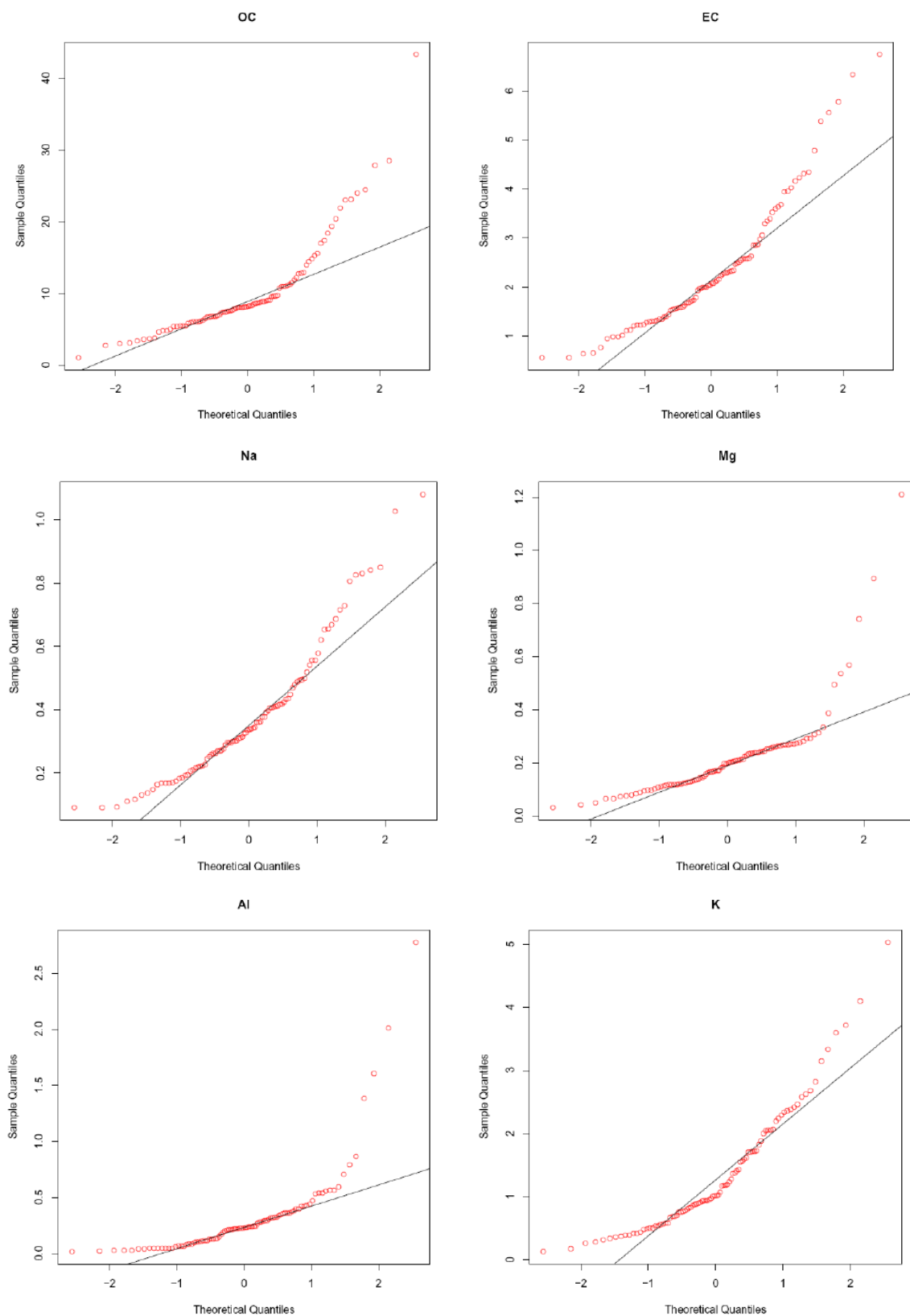
odbcClose(conn);

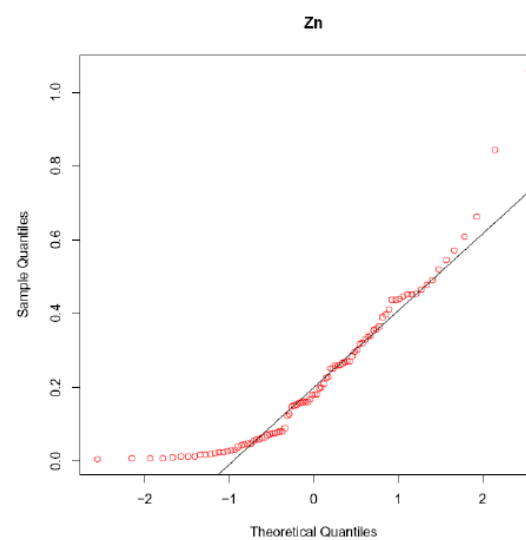
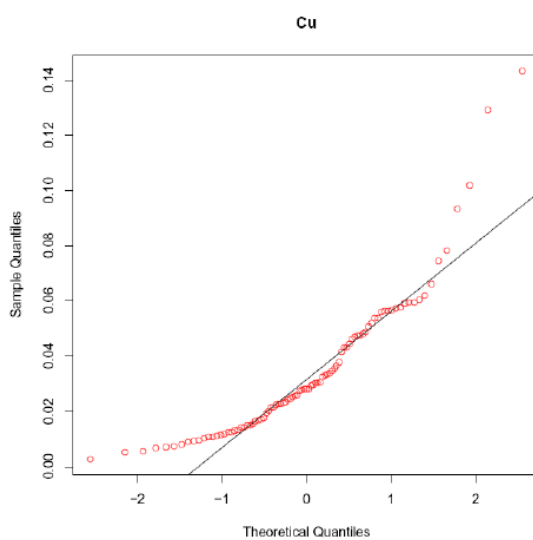
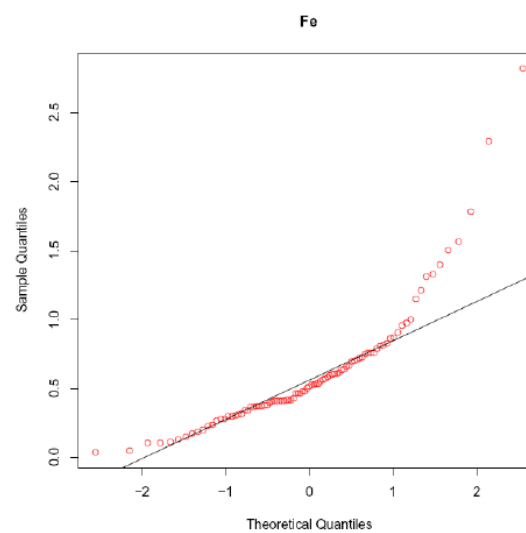
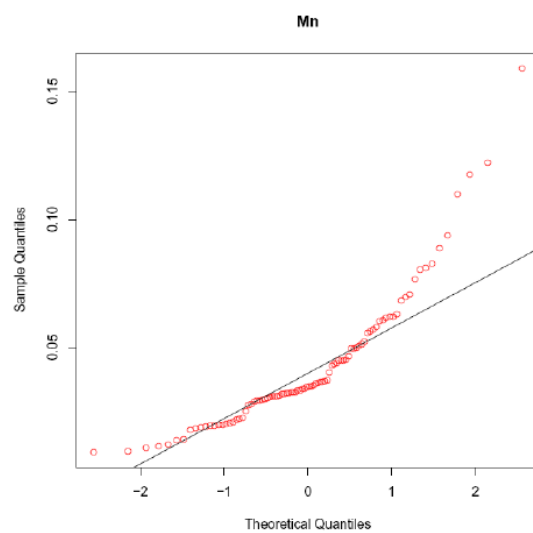
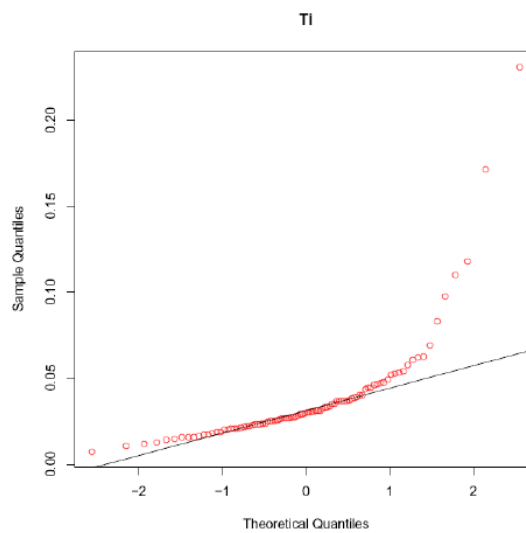
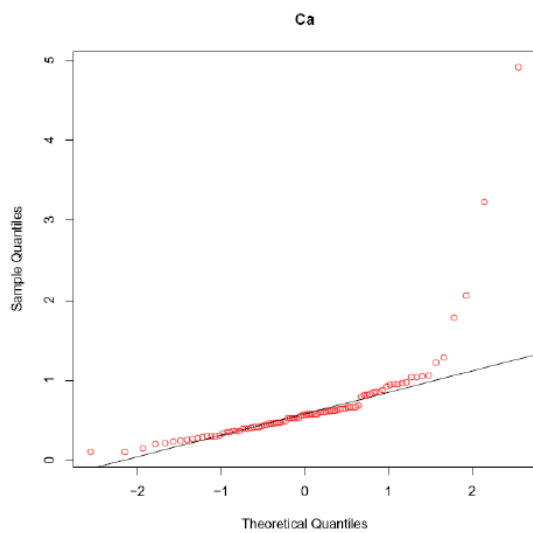
```

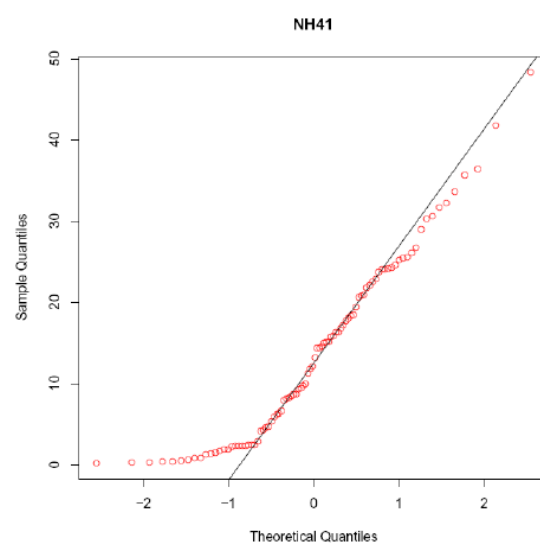
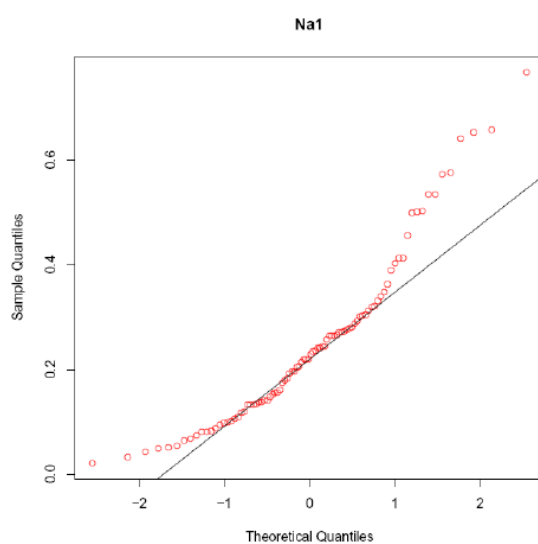
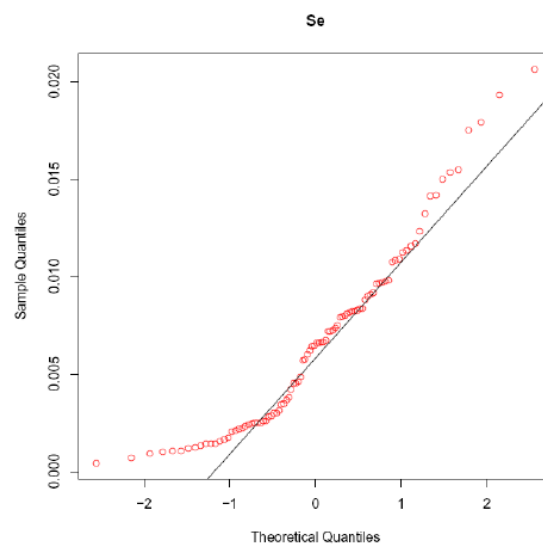
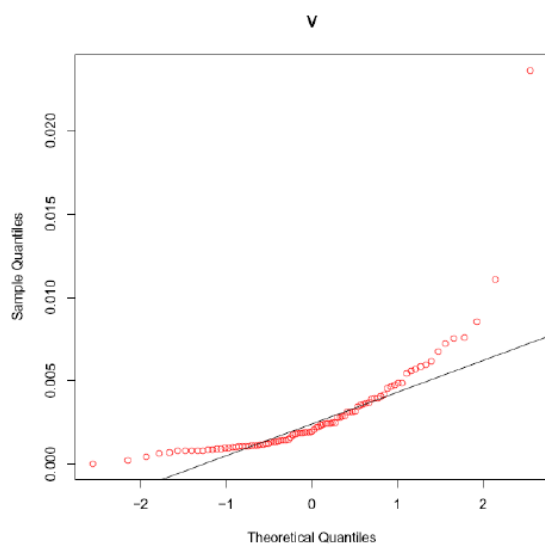
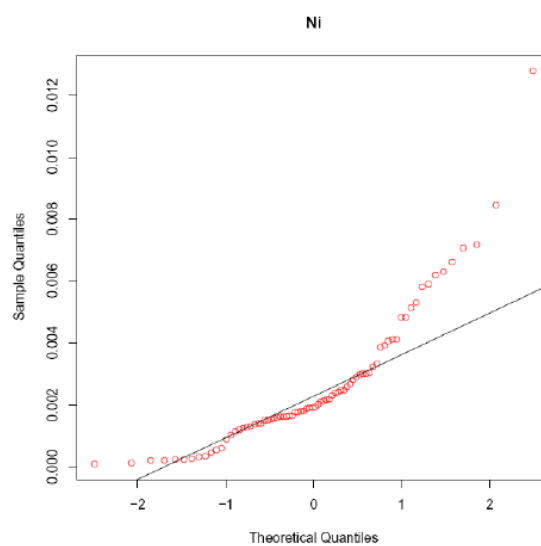
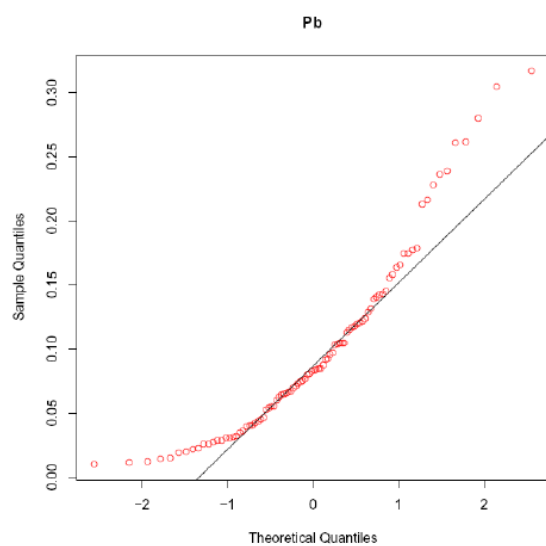

Appendix B – Quartile Plots

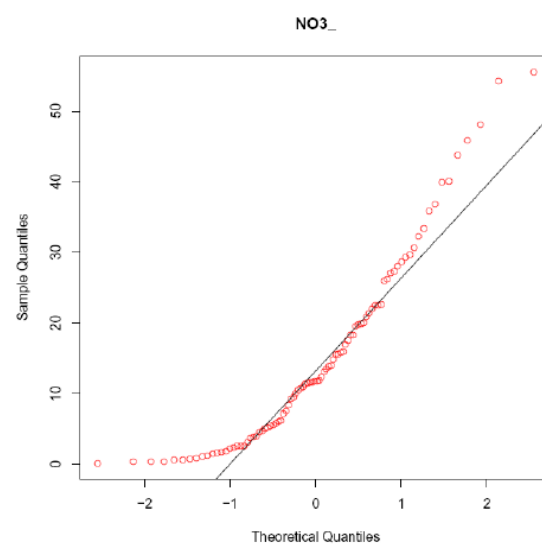
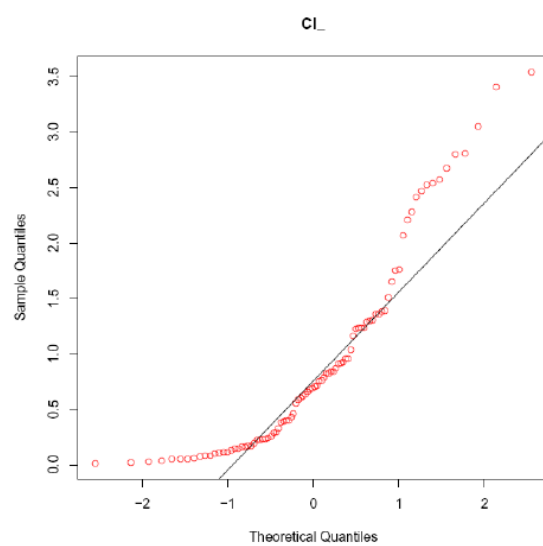
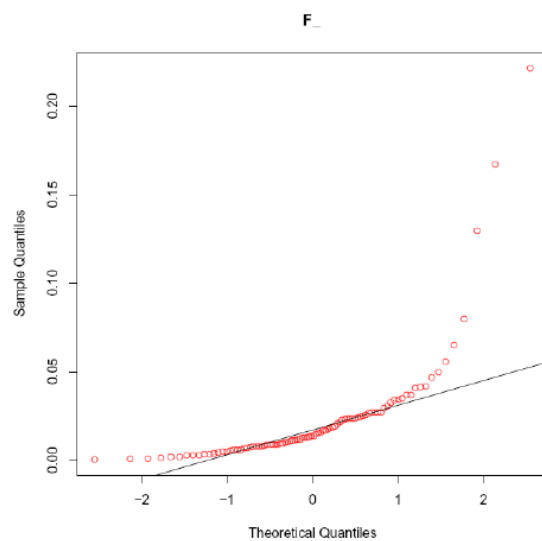
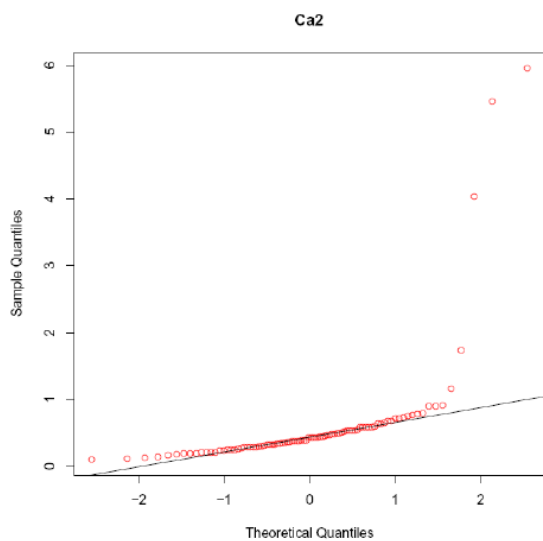
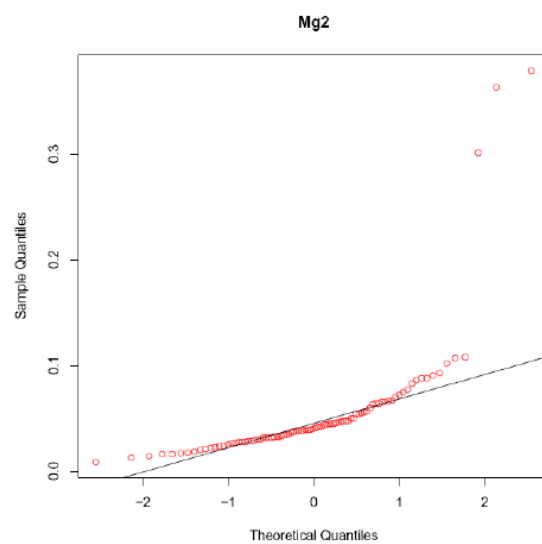
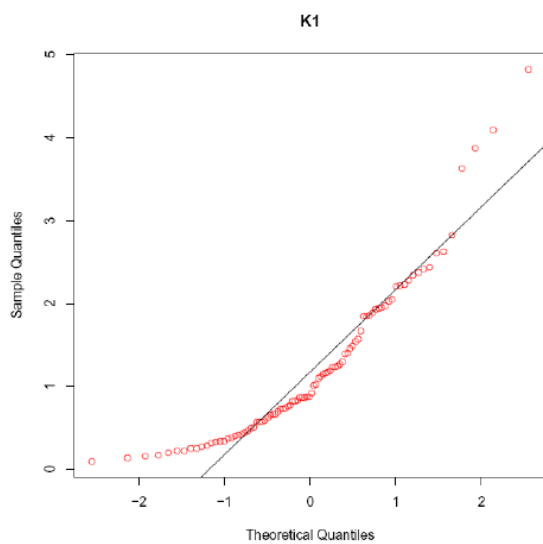
Figure B1. Pollutant quartile plots, non-log transformed data











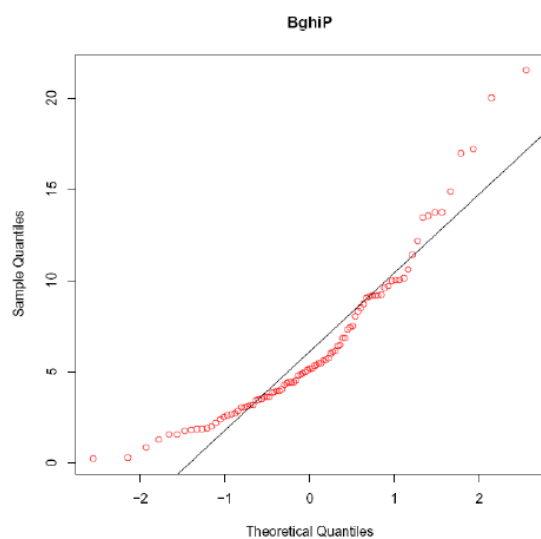
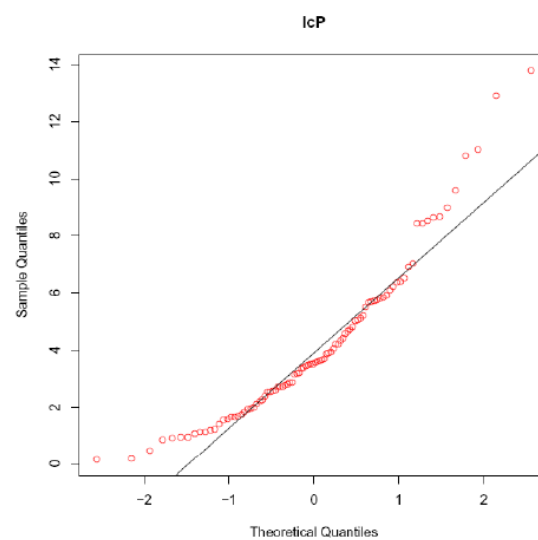
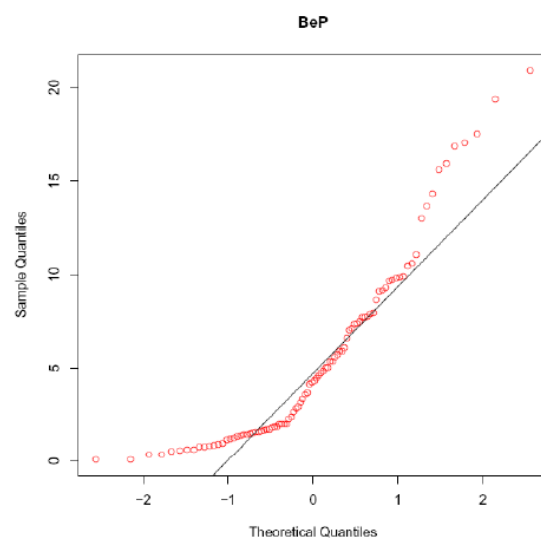
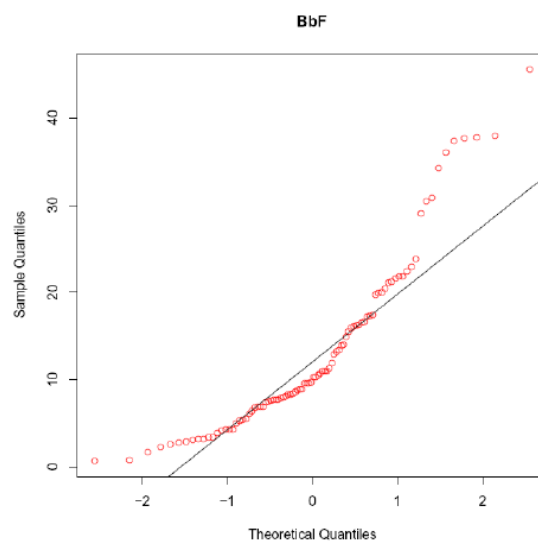
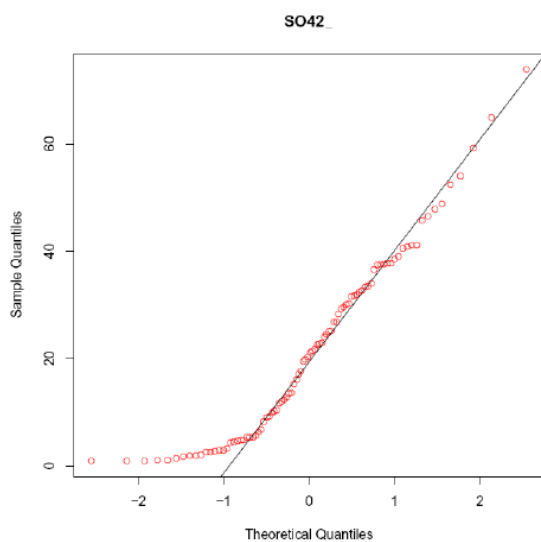
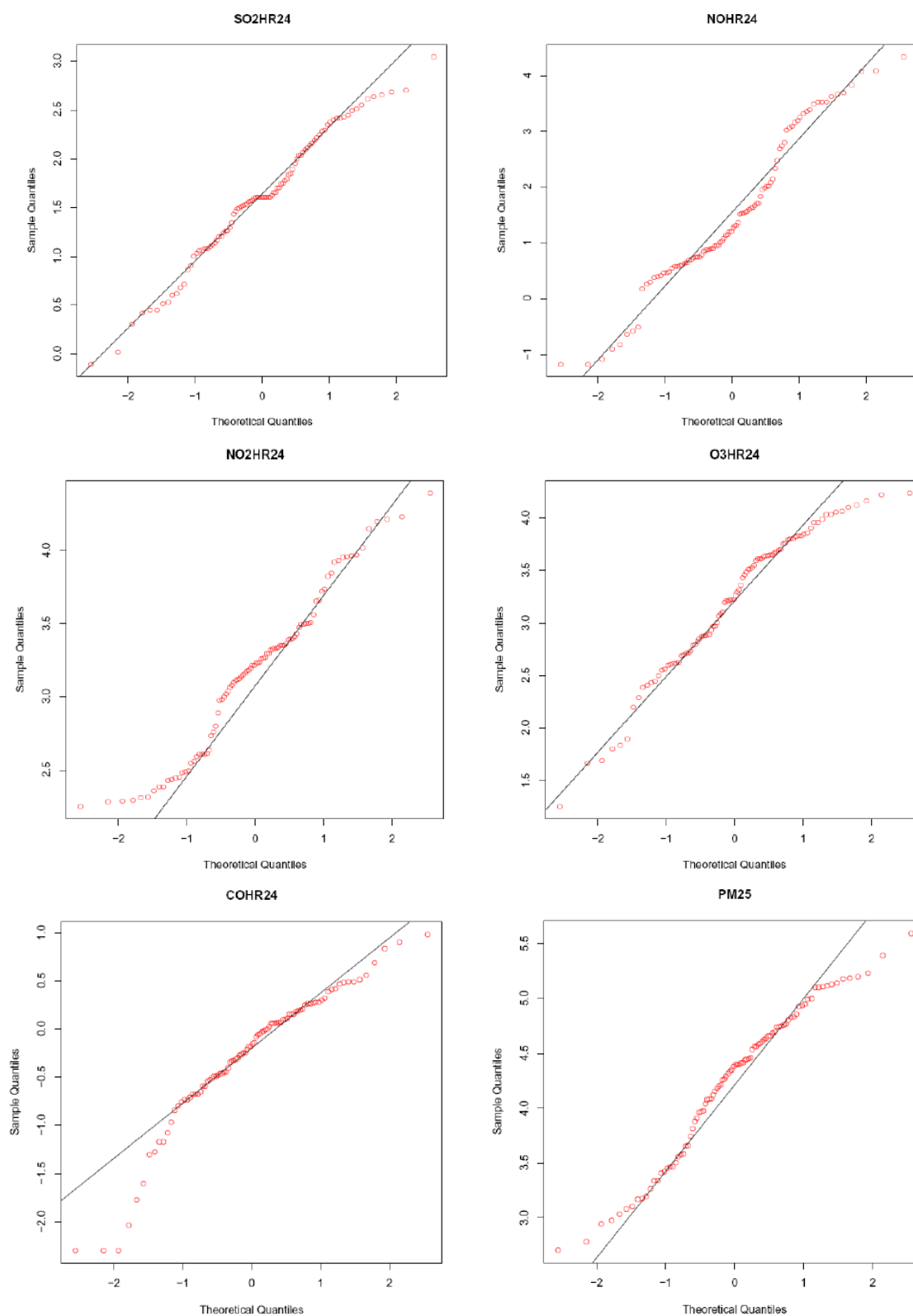
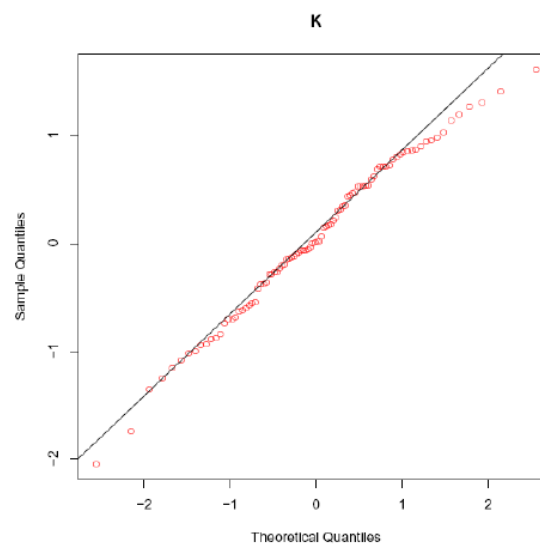
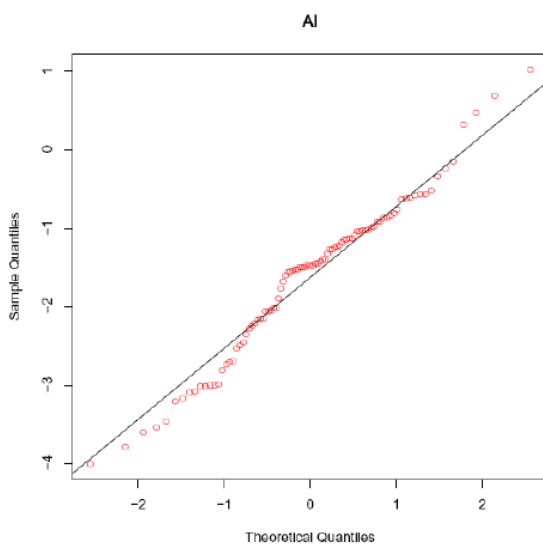
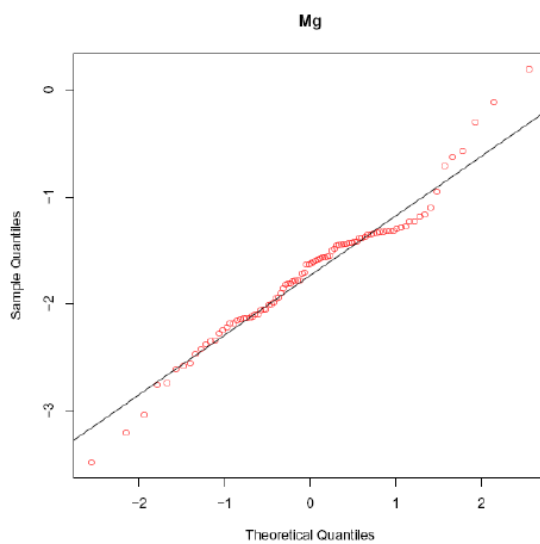
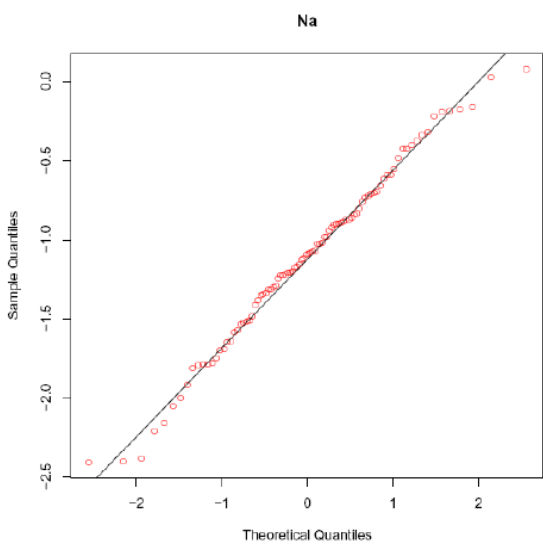
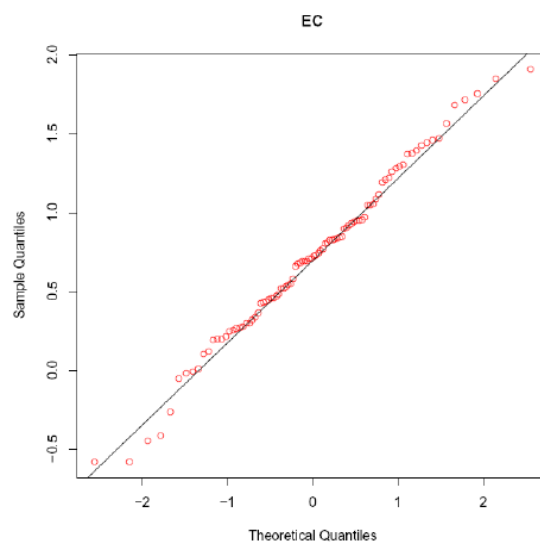
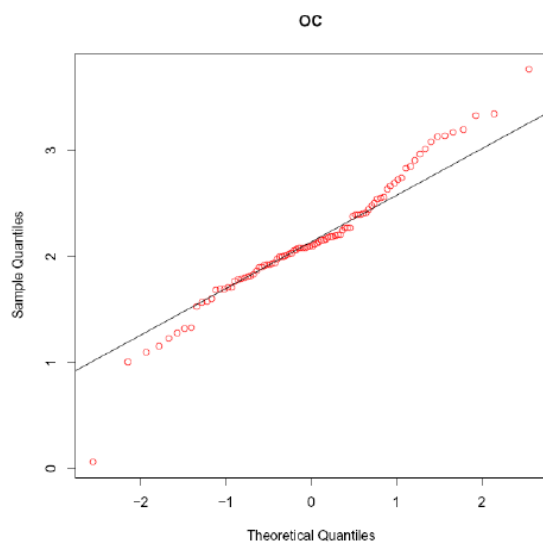
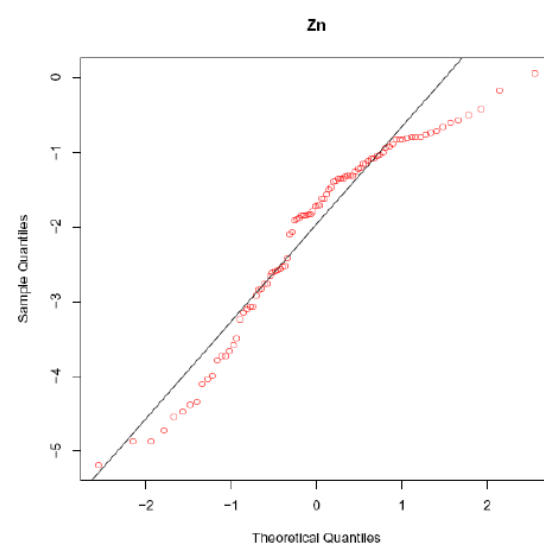
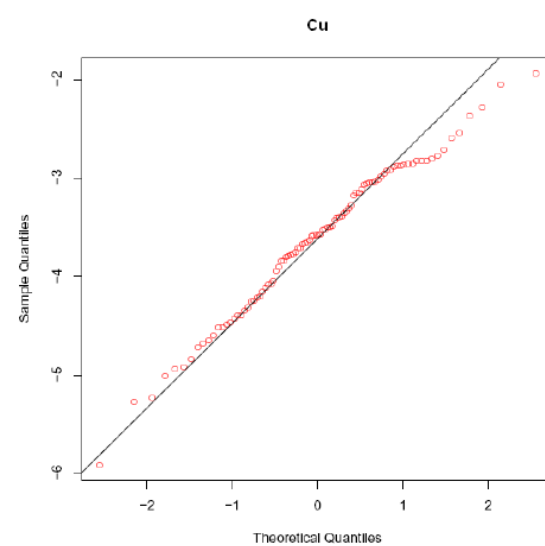
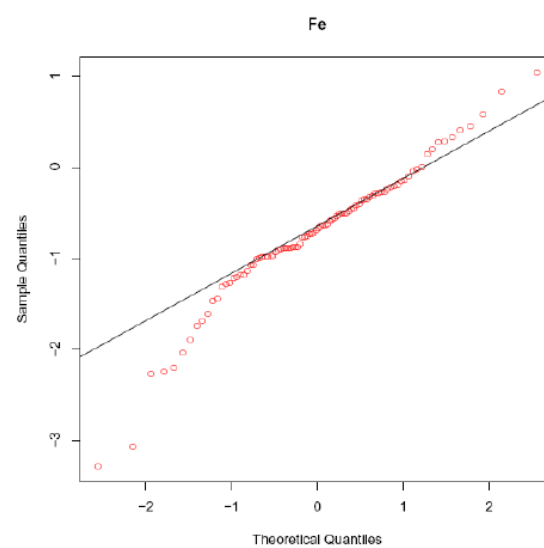
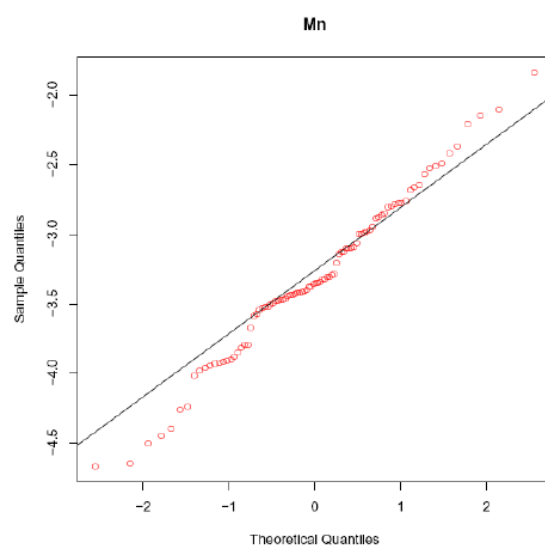
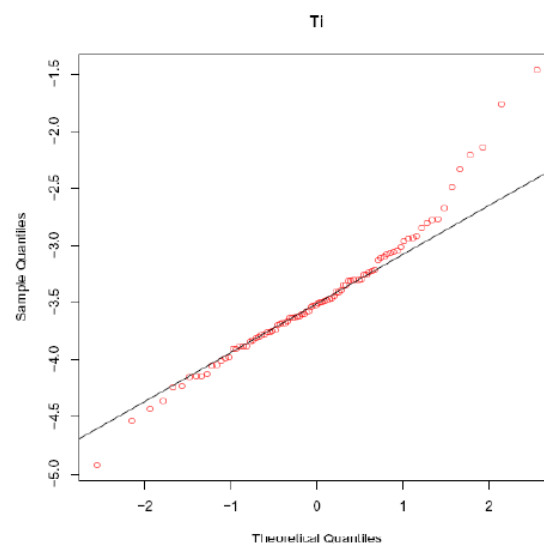
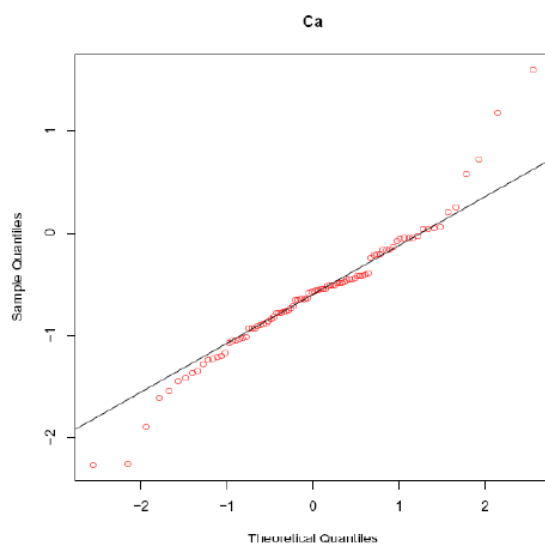
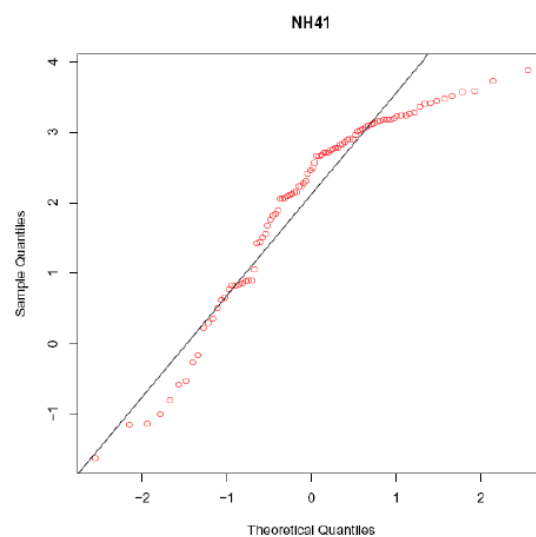
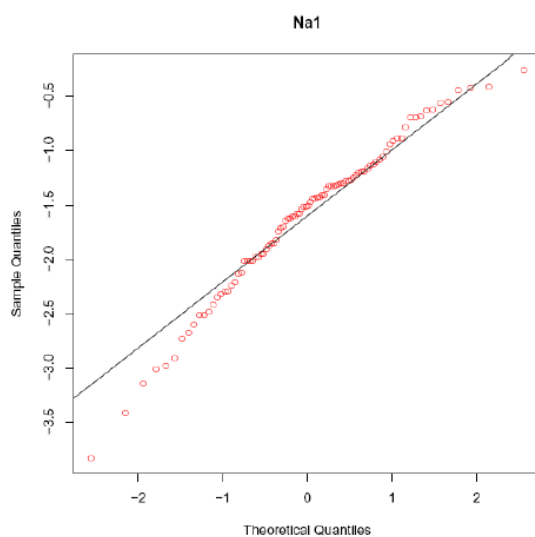
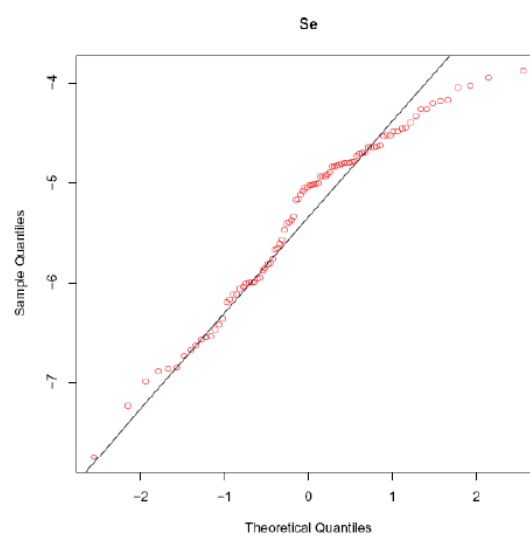
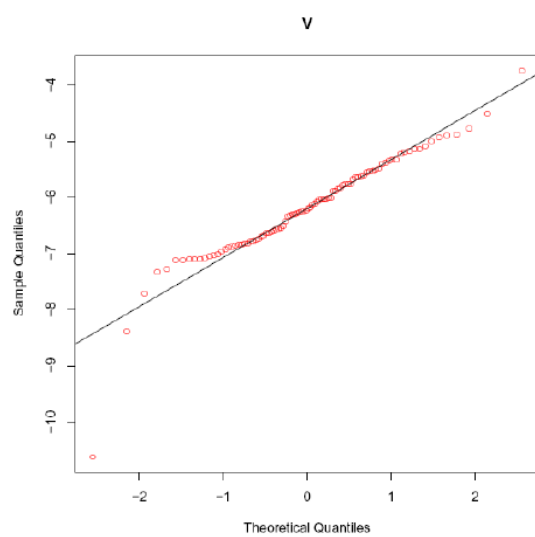
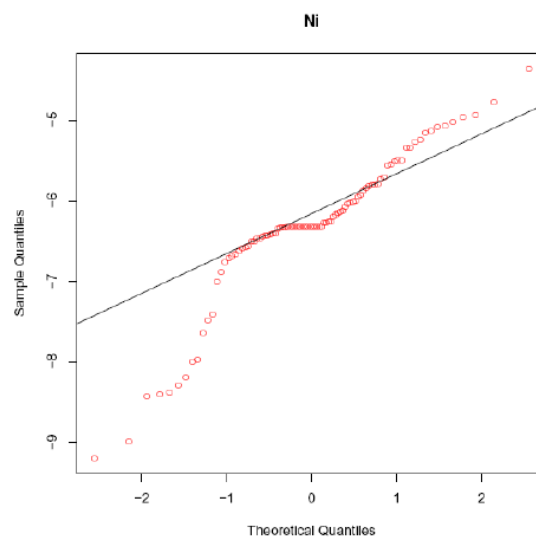
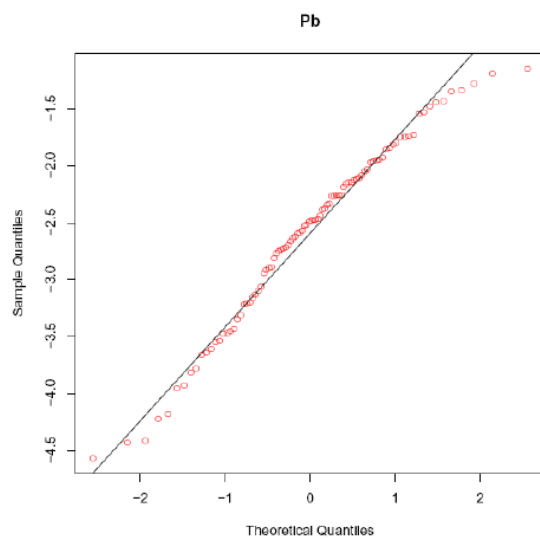
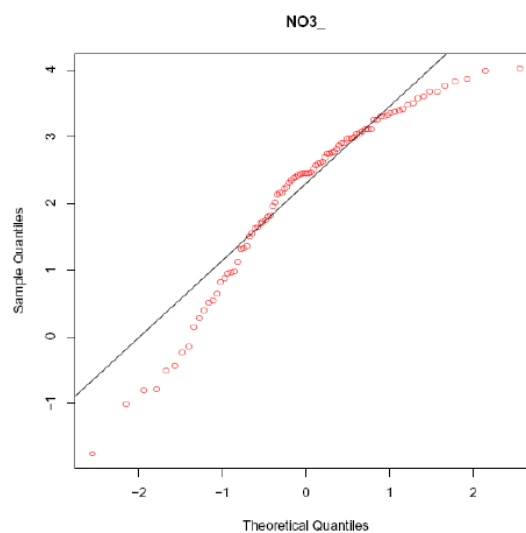
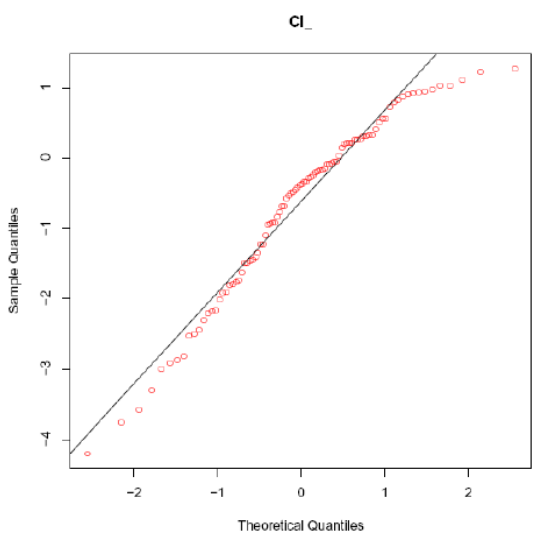
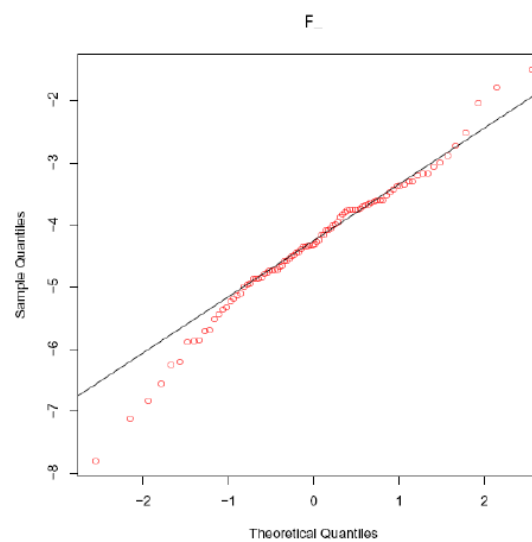
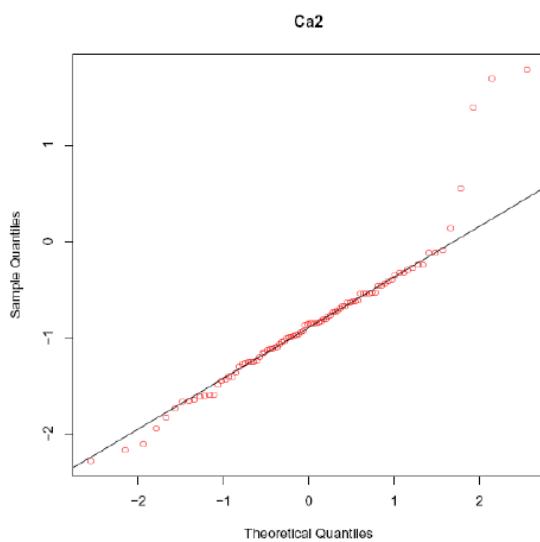
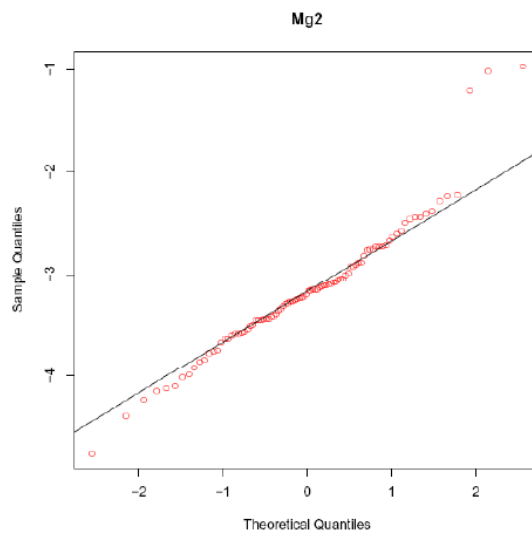
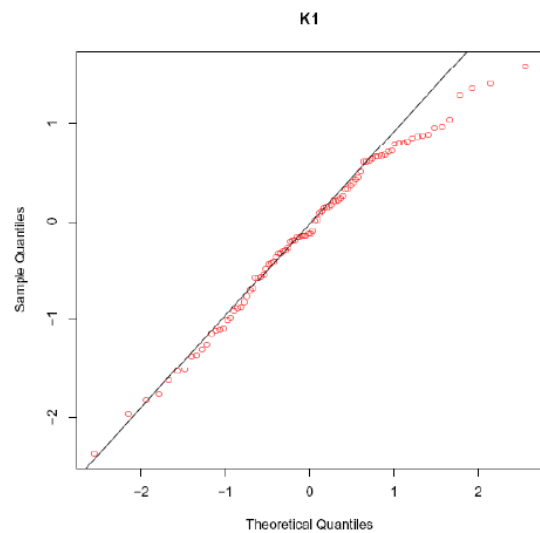


Figure B2. Pollutant quartile plots, log transformed data

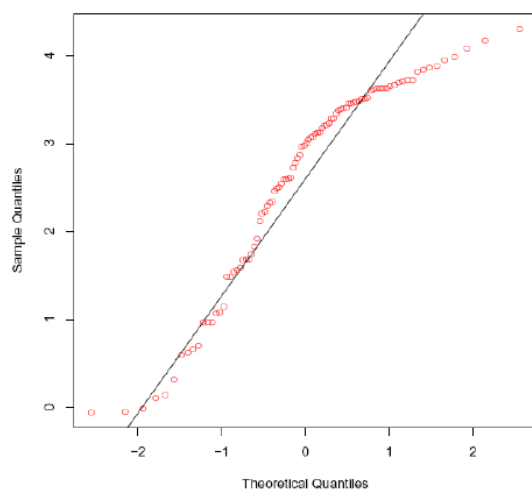




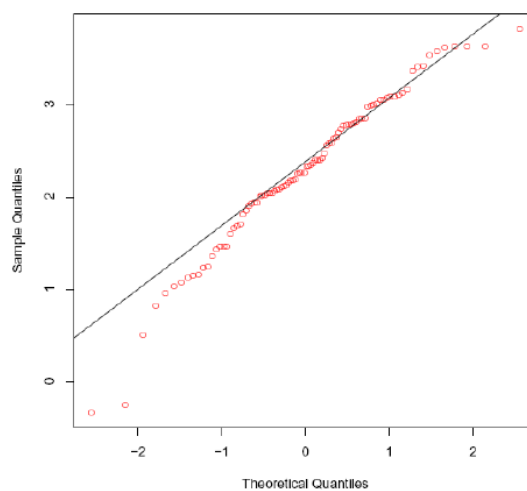




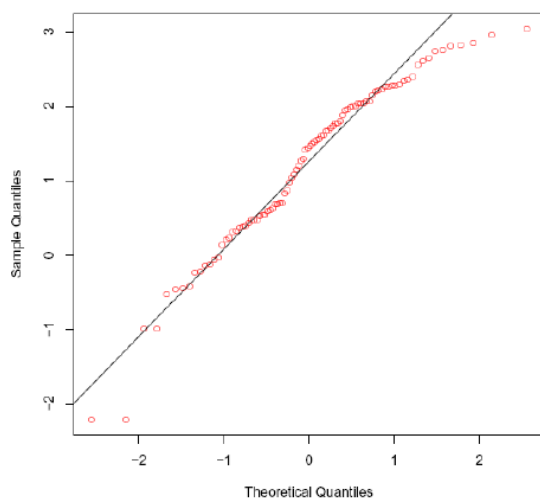
SO42



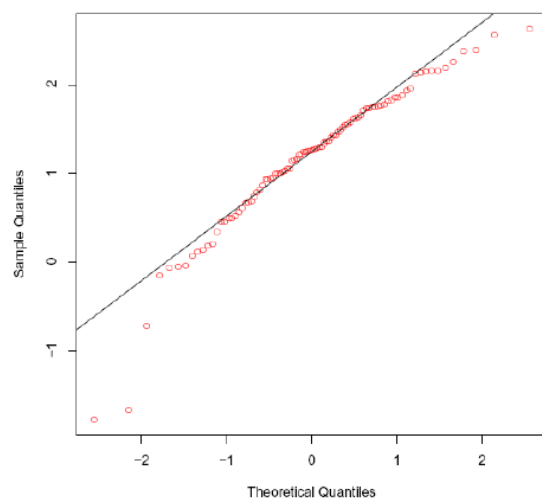
BbF



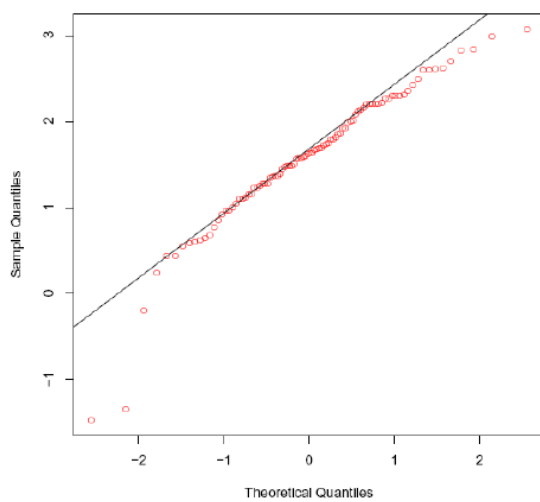
BeP

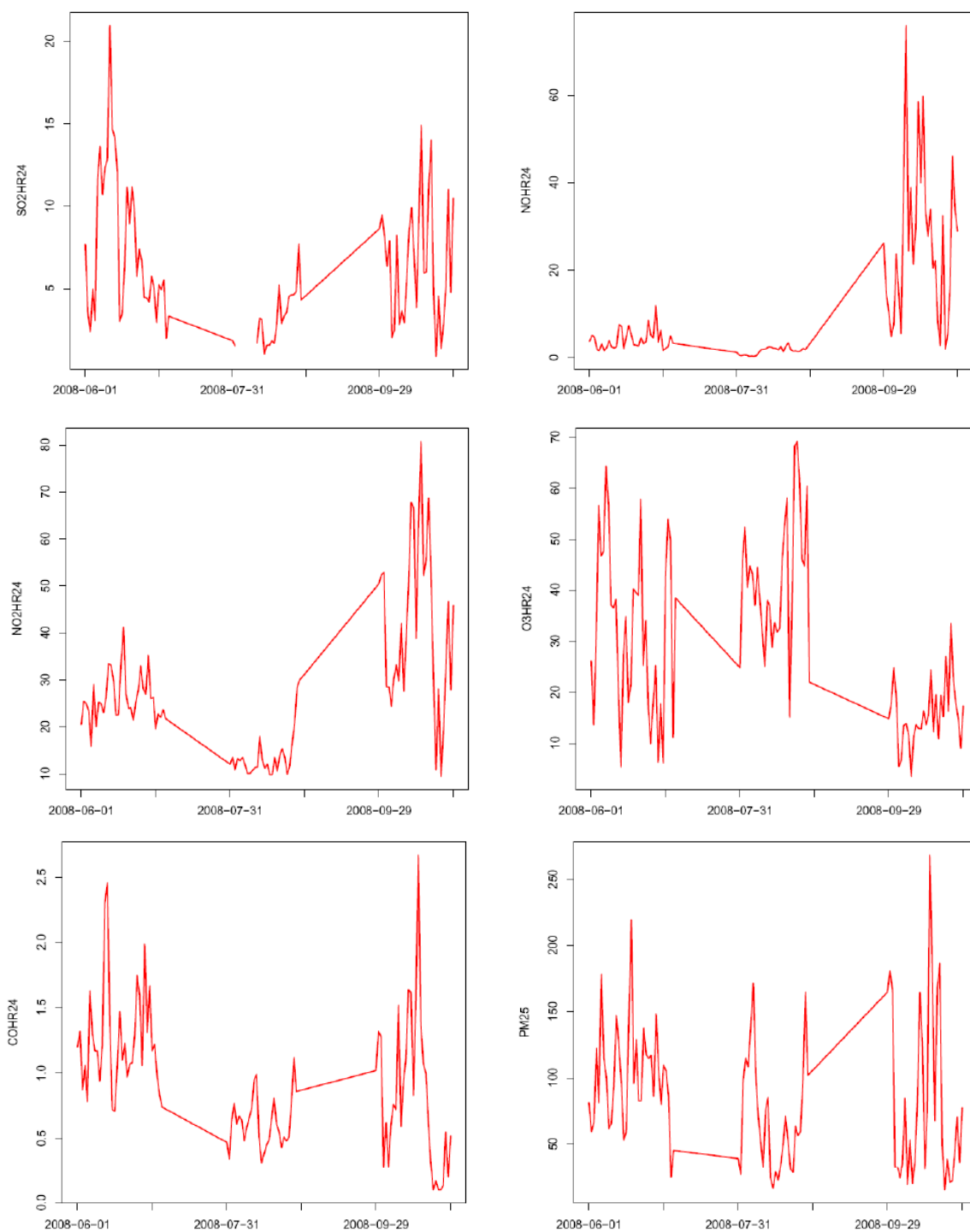


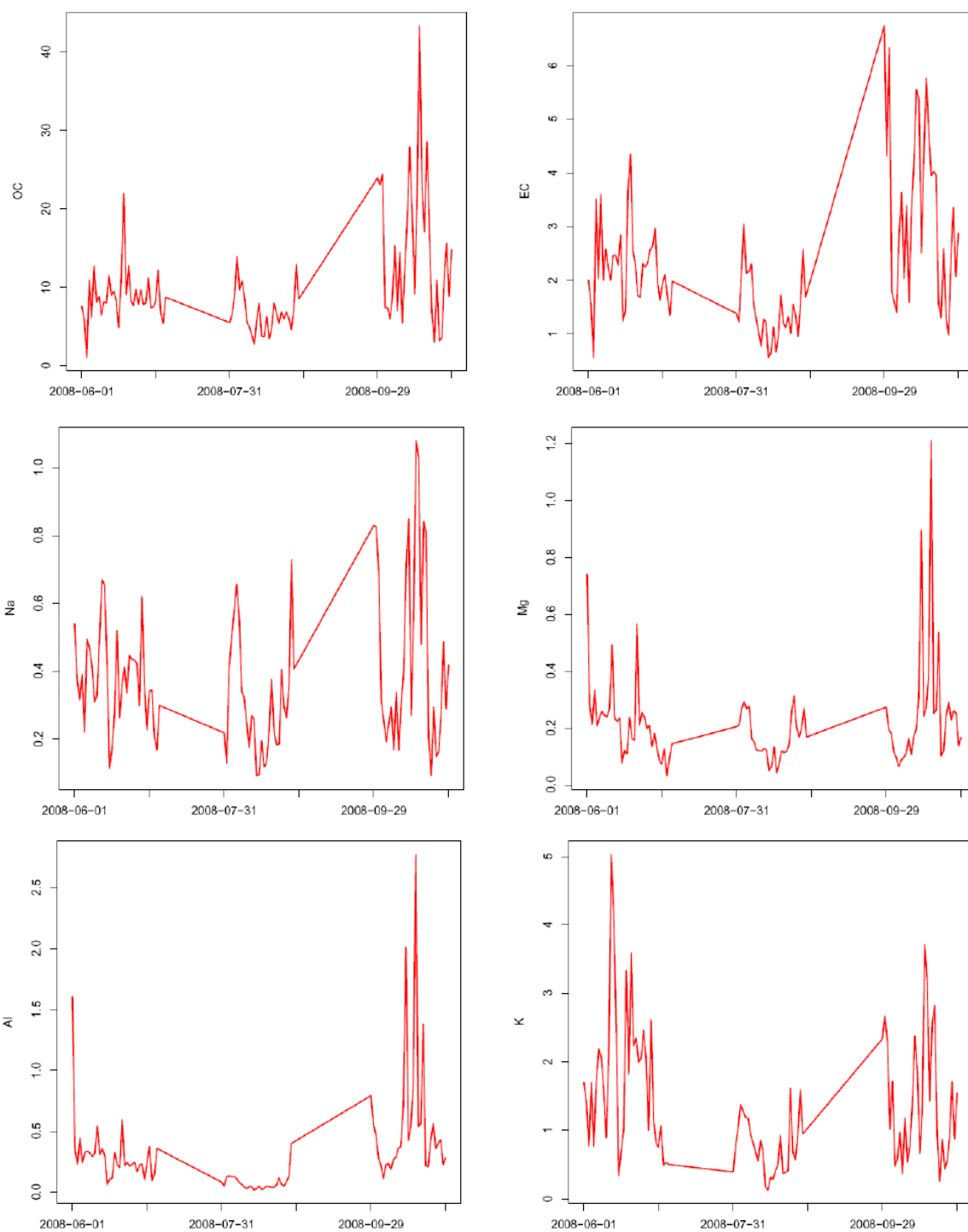
IcP

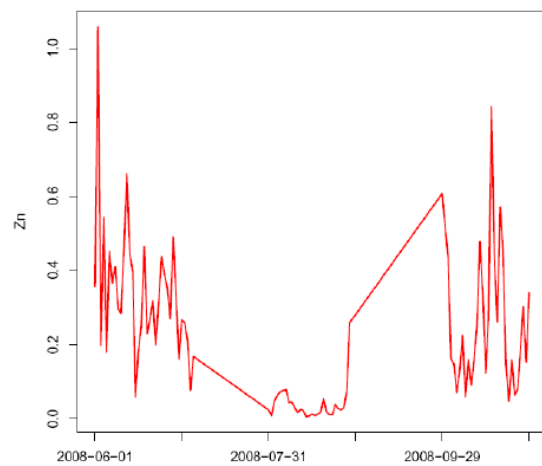
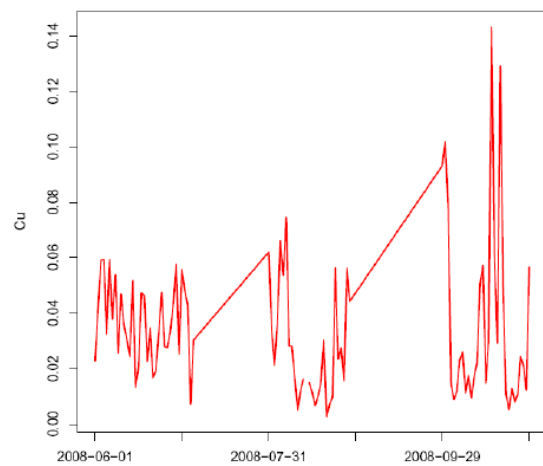
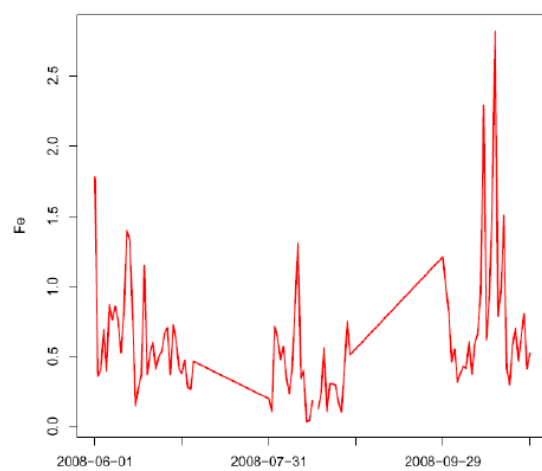
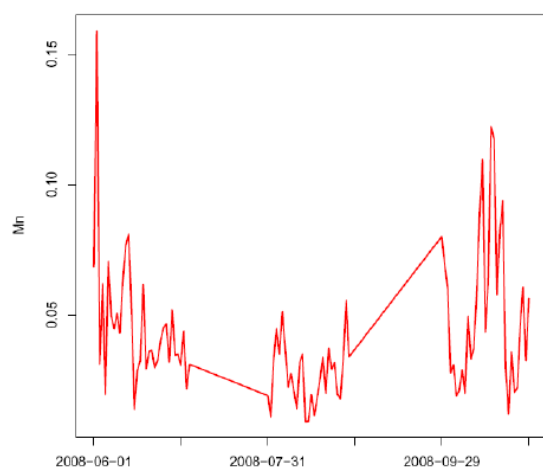
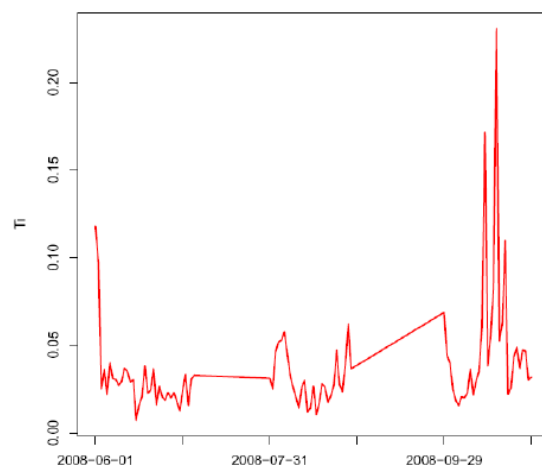
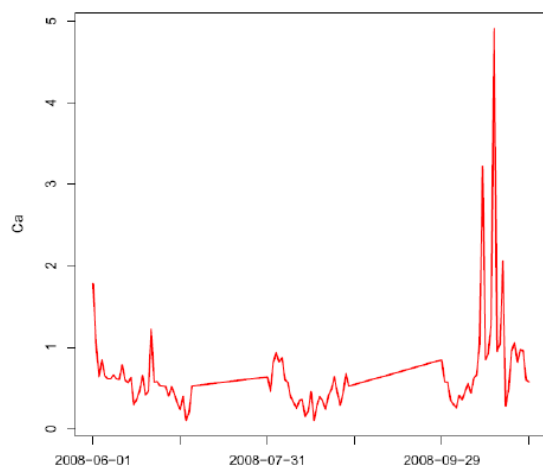


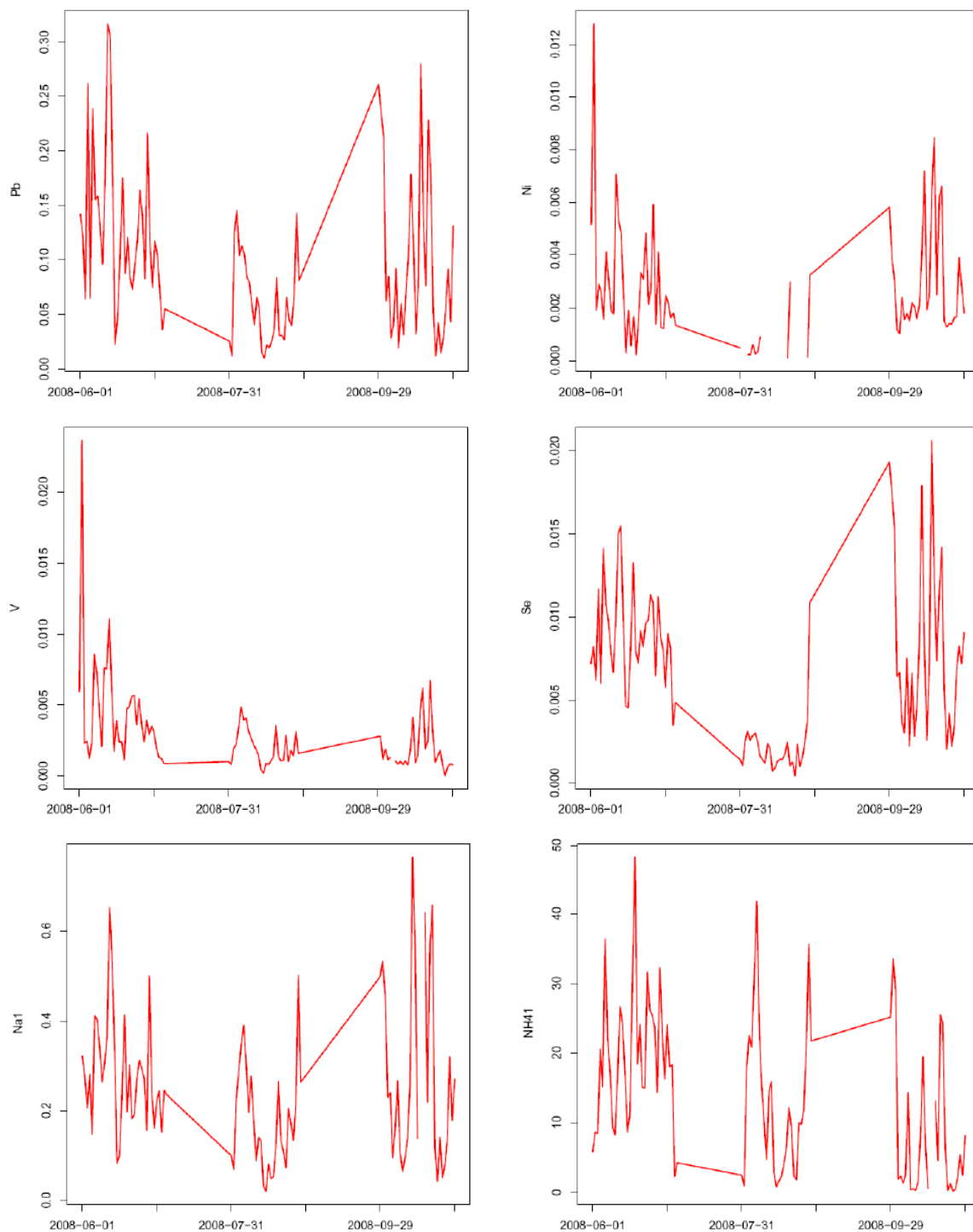
BghiP

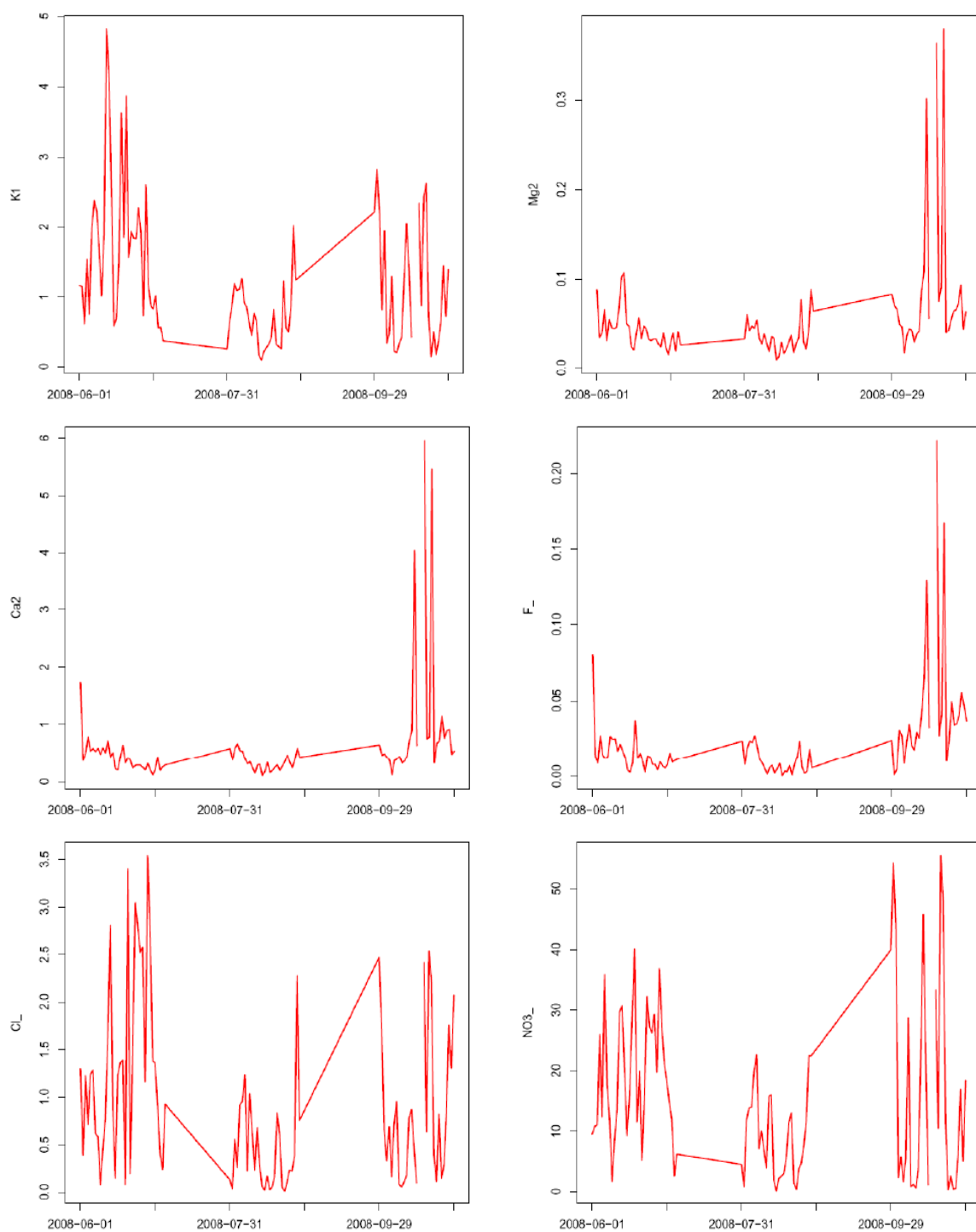


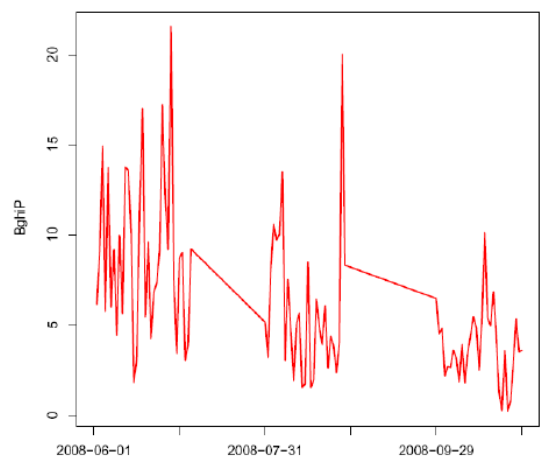
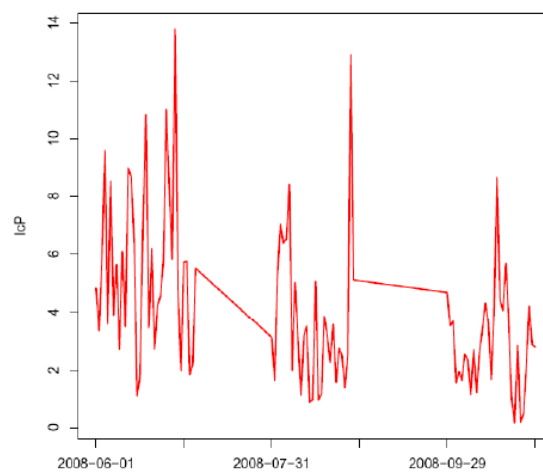
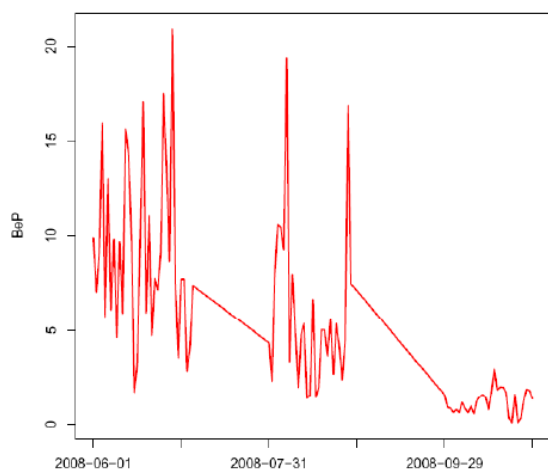
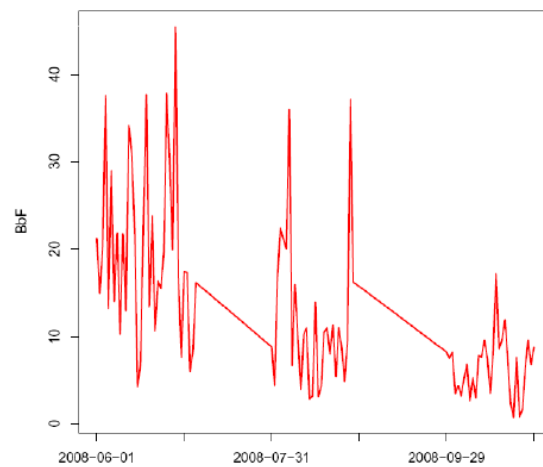
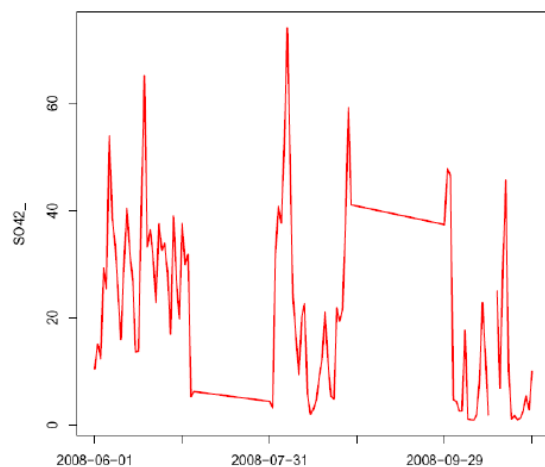
Appendix C – Time Series Plots for Pollutants**Figure C1.** Time series plots for pollutants











Appendix D – Descriptive Statistics for Pollutants

Table D1. Descriptive statistics for pollutants

	SO ₂ HR ₂₄	NO ₂ HR ₂₄	NO ₂ HR ₂₄	O ₃ HR ₂₄	COHR ₂₄	PM _{2.5}	OC	EC	Na	Mg	Al	K	Ca	Ti	Mn	Fe	Cu
	ppb	ppb	ppb	ppb	ppm	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³
arith avg	6.191	10.574	27.542	29.586	0.922	85.791	10.204	2.349	0.381	0.219	0.322	1.349	0.670	0.038	0.043	0.614	0.035
SD	4.03	15.01	15.40	16.67	0.51	52.37	6.62	1.29	0.21	0.17	0.40	0.95	0.61	0.03	0.03	0.45	0.03
n	87	94	94	94	94	94	94	94	94	94	94	94	94	94	94	93	93
max	21.0	75.9	80.7	69.1	2.7	268.2	43.3	6.7	1.1	1.2	2.8	5.0	4.9	0.2	0.2	2.8	0.1
min	0.9	0.3	9.5	3.5	0.1	15.0	1.1	0.6	0.1	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0
GM	5.0	4.5	23.9	24.5	0.8	69.8	8.7	2.0	0.3	0.2	0.2	1.1	0.5	0.0	0.0	0.5	0.0
GSD	1.99	3.75	1.71	1.94	1.97	1.98	1.78	1.71	1.75	1.83	2.73	2.09	1.83	1.76	1.77	2.07	2.15
Before	7.606	4.089	26.018	31.822	1.251	100.915	8.820	2.249	0.375	0.221	0.306	1.750	0.583	0.031	0.046	0.629	0.037
During	3.212	1.523	13.925	42.156	0.618	70.222	6.887	1.446	0.310	0.170	0.081	0.764	0.471	0.031	0.028	0.368	0.029
After	6.610	26.072	41.561	15.708	0.824	82.777	14.761	3.277	0.452	0.259	0.558	1.426	0.949	0.052	0.053	0.811	0.037

	Zn	Pb	Ni	V	Se	Na1	NH ₄ 1	K1	Mg2	Ca2	F ₋	Cl ₋	NO ₃ ₋	SO ₄ 2 ₋	BbF	BeP	IcP	BghiP
	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ug/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³
arith avg	0.226	0.099	0.003	0.003	0.007	0.249	13.859	1.223	0.055	0.603	0.023	0.927	15.238	21.762	13.201	5.495	4.148	6.295
SD	0.20	0.07	0.00	0.00	0.00	0.16	11.16	0.95	0.06	0.89	0.03	0.88	13.31	16.99	9.85	4.92	2.78	4.34
n	94	94	78	93	94	92	92	92	92	92	92	92	92	92	94	94	94	93
max	1.1	0.3	0.0	0.0	0.0	0.8	48.3	4.8	0.4	6.0	0.22	3.5	55.5	73.9	45.6	20.9	13.8	21.6
min	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.0	0.1	0.0	0.0	0.2	1.0	0.7	0.1	0.2	0.2
GM	0.1	0.1	0.0	0.0	0.0	0.2	7.9	0.9	0.0	0.4	0.0	0.5	8.7	13.4	9.9	3.4	3.2	4.9
GSD	3.55	2.23	2.46	2.47	2.37	2.03	3.71	2.32	1.87	1.98	2.96	3.58	3.59	3.17	2.28	3.07	2.22	2.22
Before	0.338	0.129	0.003	0.0046	0.009	0.282	19.053	1.714	0.042	0.431	0.015	1.338	18.802	28.376	19.972	9.017	5.602	8.918
During	0.041	0.061	0.001	0.0020	0.002	0.178	13.085	0.703	0.036	0.352	0.010	0.449	9.115	23.203	12.123	5.840	3.714	5.913
After	0.267	0.099	0.003	0.0019	0.008	0.278	8.336	1.131	0.088	1.055	0.045	0.894	16.849	12.389	6.530	1.208	2.898	3.765

Appendix E – Correlation Matrix for Principal Component Analysis

Table E1. Correlation matrix for principal component analysis

	SO2HR24	NOHR24	NO2HR24	O3HR24	COHR24	PM25	OC	EC	Na	Mg	Al	K	Ca	Ti	Mn	Fe	Cu	
SO2HR24	1.000	0.118	0.497	0.020	0.545	0.620	0.528	0.526	0.640	0.357	0.320	0.754	0.234	0.236	0.562	0.497	0.448	
NOHR24	0.118	1.000	0.706	-0.550	0.184	0.031	0.509	0.545	0.312	0.264	0.427	0.122	0.379	0.368	0.387	0.384	0.086	
NO2HR24	0.497	0.706	1.000	-0.528	0.532	0.534	0.869	0.848	0.694	0.381	0.579	0.550	0.456	0.470	0.698	0.610	0.523	
O3HR24	0.020	-0.550	-0.528	1.000	-0.184	0.043	-0.247	-0.299	-0.125	-0.001	-0.255	-0.143	-0.145	-0.123	-0.258	-0.242	0.035	
COHR24	0.545	0.184	0.532	-0.184	1.000	0.677	0.523	0.519	0.618	0.277	0.306	0.740	0.214	0.237	0.629	0.537	0.448	
PM25	0.620	0.031	0.534	0.043	0.677	1.000	0.726	0.693	0.852	0.390	0.396	0.757	0.368	0.421	0.633	0.566	0.763	
OC	0.528	0.509	0.869	-0.247	0.523	0.726	1.000	0.897	0.803	0.389	0.516	0.601	0.446	0.499	0.687	0.595	0.694	
EC	0.526	0.545	0.848	-0.299	0.519	0.693	0.897	1.000	0.771	0.432	0.570	0.581	0.481	0.511	0.678	0.631	0.612	
Na	0.640	0.312	0.694	-0.125	0.618	0.852	0.803	0.771	1.000	0.633	0.647	0.768	0.621	0.687	0.803	0.772	0.745	
Mg	0.357	0.264	0.381	-0.001	0.277	0.390	0.389	0.432	0.633	1.000	0.902	0.446	0.944	0.901	0.628	0.802	0.288	
Al	0.320	0.427	0.579	-0.255	0.306	0.396	0.516	0.570	0.647	0.902	1.000	0.436	0.936	0.912	0.669	0.867	0.324	
K	0.754	0.122	0.550	-0.143	0.740	0.757	0.601	0.581	0.768	0.446	0.436	1.000	0.380	0.371	0.669	0.655	0.497	
Ca	0.234	0.379	0.456	-0.145	0.214	0.368	0.446	0.481	0.621	0.944	0.936	0.380	1.000	0.952	0.637	0.808	0.291	
Ti	0.236	0.368	0.470	-0.123	0.237	0.421	0.499	0.511	0.687	0.901	0.912	0.371	0.952	1.000	0.732	0.801	0.375	
Mn	0.562	0.387	0.698	-0.258	0.629	0.633	0.687	0.678	0.803	0.628	0.669	0.669	0.637	0.732	1.000	0.727	0.555	
Fe	0.497	0.384	0.610	-0.242	0.537	0.566	0.595	0.631	0.772	0.802	0.867	0.655	0.808	0.801	0.727	1.000	0.391	
Cu	0.448	0.086	0.523	0.035	0.448	0.763	0.694	0.612	0.745	0.288	0.324	0.497	0.291	0.375	0.555	0.391	1.000	
	Zn	Pb	Ni	V	Se	Na1	NH41	K1	Mg2	Ca2	F_	CL_	NO3_	SO42_	BbF	BeP	IcP	BghiP
SO2HR24	0.626	0.740	0.330	0.374	0.679	0.680	0.477	0.740	0.352	0.221	0.241	0.381	0.507	0.491	0.356	0.252	0.406	0.351
NOHR24	0.198	0.045	0.222	-0.131	0.236	0.146	-0.257	-0.035	0.356	0.322	0.415	0.035	0.051	-0.299	-0.255	-0.385	-0.098	-0.180
NO2HR24	0.643	0.525	0.427	0.072	0.730	0.584	0.179	0.419	0.503	0.402	0.458	0.358	0.572	0.097	0.029	-0.166	0.224	0.115
O3HR24	-0.269	-0.075	-0.220	-0.034	-0.291	-0.135	0.186	-0.085	-0.167	-0.154	-0.246	-0.282	-0.207	0.317	0.158	0.244	0.076	0.124
COHR24	0.704	0.755	0.420	0.455	0.724	0.593	0.530	0.667	0.164	0.099	0.064	0.494	0.568	0.451	0.577	0.480	0.632	0.595
PM25	0.652	0.823	0.327	0.310	0.757	0.775	0.852	0.718	0.392	0.323	0.276	0.607	0.838	0.819	0.599	0.484	0.701	0.639
OC	0.602	0.621	0.360	0.035	0.713	0.614	0.358	0.450	0.439	0.351	0.401	0.341	0.630	0.303	0.142	-0.047	0.353	0.239
EC	0.627	0.655	0.346	0.065	0.750	0.669	0.400	0.489	0.497	0.408	0.446	0.365	0.672	0.345	0.194	0.013	0.372	0.276
Na	0.669	0.796	0.516	0.355	0.730	0.866	0.572	0.653	0.613	0.524	0.513	0.547	0.728	0.566	0.408	0.265	0.566	0.471
Mg	0.383	0.332	0.567	0.328	0.338	0.525	0.091	0.302	0.799	0.814	0.801	0.200	0.254	0.146	0.114	0.048	0.175	0.113
Al	0.460	0.349	0.580	0.242	0.474	0.557	0.031	0.294	0.855	0.875	0.879	0.252	0.347	0.052	-0.018	-0.121	0.087	0.004
K	0.747	0.852	0.480	0.488	0.804	0.777	0.582	0.936	0.419	0.320	0.314	0.630	0.671	0.537	0.542	0.428	0.596	0.535
Ca	0.346	0.259	0.533	0.264	0.314	0.507	0.033	0.236	0.862	0.901	0.899	0.207	0.268	0.077	0.018	-0.063	0.114	0.043
Ti	0.395	0.309	0.593	0.337	0.319	0.557	0.081	0.229	0.837	0.858	0.853	0.183	0.298	0.136	0.032	-0.049	0.143	0.069
Mn	0.839	0.702	0.755	0.627	0.703	0.728	0.315	0.539	0.595	0.526	0.537	0.369	0.554	0.296	0.292	0.156	0.403	0.328
Fe	0.553	0.597	0.556	0.308	0.600	0.694	0.235	0.532	0.757	0.740	0.737	0.381	0.480	0.231	0.209	0.092	0.319	0.233
Cu	0.602	0.664	0.282	0.195	0.614	0.577	0.546	0.418	0.269	0.198	0.170	0.412	0.637	0.530	0.349	0.228	0.480	0.411
	Zn	Pb	Ni	V	Se	Na1	NH41	K1	Mg2	Ca2	F_	CL_	NO3_	SO42_	BbF	BeP	IcP	BghiP
SO2HR24	0.626	0.198	0.643	-0.269	0.704	0.652	0.602	0.627	0.669	0.383	0.460	0.747	0.346	0.395	0.839	0.553	0.602	
Pb	0.740	0.045	0.525	-0.075	0.755	0.823	0.621	0.655	0.796	0.332	0.349	0.852	0.259	0.309	0.702	0.597	0.664	
Ni	0.330	0.222	0.427	-0.220	0.420	0.327	0.360	0.346	0.516	0.567	0.580	0.480	0.533	0.593	0.755	0.556	0.282	
V	0.374	-0.131	0.072	-0.034	0.455	0.310	0.035	0.065	0.355	0.328	0.242	0.488	0.264	0.337	0.627	0.308	0.195	
Se	0.679	0.236	0.730	-0.291	0.724	0.757	0.713	0.750	0.730	0.338	0.474	0.804	0.314	0.319	0.703	0.600	0.614	
Na1	0.680	0.146	0.584	-0.135	0.593	0.775	0.614	0.669	0.866	0.525	0.557	0.777	0.507	0.557	0.728	0.694	0.577	
NH41	0.477	-0.257	0.179	0.186	0.530	0.852	0.358	0.400	0.572	0.091	0.031	0.582	0.033	0.081	0.315	0.235	0.546	
K1	0.740	-0.035	0.419	-0.085	0.667	0.718	0.450	0.489	0.853	0.302	0.294	0.936	0.236	0.229	0.539	0.532	0.418	
Mg2	0.352	0.356	0.503	-0.167	0.164	0.392	0.439	0.497	0.613	0.799	0.855	0.419	0.862	0.837	0.595	0.757	0.269	
Ca2	0.221	0.322	0.402	-0.154	0.099	0.323	0.351	0.408	0.524	0.814	0.875	0.320	0.901	0.858	0.526	0.740	0.198	
F_	0.241	0.415	0.458	-0.246	0.064	0.276	0.401	0.446	0.513	0.801	0.879	0.314	0.899	0.853	0.537	0.737	0.170	
CL_	0.381	0.035	0.358	-0.282	0.494	0.607	0.341	0.365	0.547	0.200	0.252	0.630	0.207	0.183	0.369	0.381	0.412	
NO3_	0.507	0.051	0.572	-0.207	0.568	0.838	0.630	0.672	0.728	0.254	0.347	0.671	0.268	0.298	0.554	0.480	0.637	
SO42_	0.491	-0.299	0.097	0.317	0.451	0.819	0.303	0.345	0.566	0.146	0.052	0.537	0.077	0.136	0.296	0.231	0.530	
BbF	0.356	-0.255	0.029	0.158	0.577	0.599	0.142	0.194	0.408	0.114	-0.018	0.542	0.018	0.032	0.292	0.209	0.349	
BeP	0.252	-0.385	-0.166	0.244	0.480	0.484	-0.047	0.013	0.265	0.048	-0.121	0.428	-0.063	-0.049	0.156	0.092	0.228	
IcP	0.406	-0.098	0.224	0.076	0.632	0.701	0.353	0.372	0.566	0.175	0.087	0.596	0.114	0.143	0.403	0.319	0.480	
BghiP	0.351	-0.180	0.115	0.124	0.595	0.639	0.239	0.276	0.471	0.113	0.004	0.535	0.043	0.069	0.328	0.233	0.411	
	Zn	Pb	Ni	V	Se	Na1	NH41	K1	Mg2	Ca2	F_	CL_	NO3_	SO42_	BbF	BeP	IcP	BghiP
Zn	1.000	0.804	0.694	0.638	0.869	0.657	0.436	0.863	0.323	0.245	0.253	0.506	0.637	0.364	0.418	0.280	0.479	0.422
Pb	0.804	1.000	0.436	0.444	0.849	0.809	0.681	0.823	0.309	0.203	0.182	0.581	0.766	0.633	0.625	0.498	0.691	0.634
Ni	0.694	0.436	1.000	0.653	0.493	0.463	0.074	0.355	0.497	0.454	0.422	0.277	0.358	0.050	0.067	-0.006	0.121	0.073
V	0.638	0.444	0.653	1.000	0.352	0.404	0.289	0.466	0.194	0.181	0.135	0.285	0.243	0.310	0.339	0.343	0.278	0.289
Se	0.869	0.849	0.493	0.352	1.000	0.734	0.534	0.742	0.368	0.270	0.277	0.570	0.768	0.455	0.381	0.226	0.481	0.410
Na1	0.657	0.809	0.463	0.404	0.734	1.000	0.628	0.797	0.623	0.506	0.505	0.593	0.810	0.603	0.477	0.364	0.573	0.514
NH41	0.436	0.681	0.074	0.289	0.534	0.628	1.000	0.694	0.091	0.026	-0.042	0.609	0.783	0.965	0.712	0.677	0.718	0.716
K1	0.863	0.823	0.355	0.466	0.742	0.797	0.694	1.000	0.346	0.236	0.218	0.670	0.730	0.645	0.603	0.520	0.617	0.587
Mg2	0.323	0.309	0.497	0.194	0.368	0.623	0.091	0.346	1.000	0.966	0.923	0.242	0.396	0.138	-0.023	-0.107	0.085	0.018
Ca2	0.245	0.203	0.454	0.181	0.270	0.506	0.026	0.236	0.966	1.000	0.954	0.201	0.304	0.079	-0.055	-0.120	0.034	-0.028
F_	0.253	0.182	0.422	0.135	0.277	0.505	-											

Appendix F – Regression of Air pollution Source Types with Weather Data

Significance codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table F1. Regression of factor 1 with weather data

				Coefficients:			
	x	2.50%	97.50%		Estimate	Std. Error	t value Pr(> t)
(Intercept)	-30.8702	-83.0213	21.28087	(Intercept)	-30.870196	25.876703	-1.193 0.23927
Tavg	0.106407	0.030585	0.182229	Tavg	0.106407	0.037622	2.828 0.00702 **
Rhavg	0.00968	-0.0127	0.032059	Rhavg	0.009680	0.011104	0.872 0.38808
Baroavg	0.028292	-0.02221	0.078792	Baroavg	0.028292	0.025057	1.129 0.26498
UVAavg	-0.01553	-0.16987	0.138813	UVAavg	-0.015531	0.076583	-0.203 0.84023
UVBavg	-2.13319	-4.25109	-0.01529	UVBavg	-2.133187	1.050875	-2.030 0.04844 *
WindVavg	0.054719	-0.85899	0.968425	WindVavg	0.054719	0.453370	0.121 0.90448
Rain	-0.00115	-0.01577	0.013464	Rain	-0.001155	0.007254	-0.159 0.87425
N	-0.00992	-0.01956	-0.00027	N	-0.009918	0.004786	-2.072 0.04413 *
W	-0.00993	-0.03036	0.010492	W	-0.009934	0.010135	-0.980 0.33237
S	-0.00774	-0.03846	0.022983	S	-0.007738	0.015243	-0.508 0.61426
E	-0.0021	-0.02481	0.02061	E	-0.002100	0.011268	-0.186 0.85301
	Sum Sq	Df	F value	Pr(>F)			
(Intercept)	0.409076	1	1.423184	0.239274			
Tavg	2.299319	1	7.999386	0.007019			
Rhavg	0.21843	1	0.759924	0.388084			
Baroavg	0.366434	1	1.274834	0.26498			
UVAavg	0.011822	1	0.041128	0.840227			
UVBavg	1.184399	1	4.120551	0.048439			
WindVavg	0.004187	1	0.014567	0.904484			
Rain	0.007283	1	0.025339	0.874253			
N	1.234312	1	4.294201	0.044134			
W	0.276136	1	0.960684	0.332373			
S	0.074065	1	0.257673	0.614259			
E	0.009984	1	0.034734	0.85301			
Residuals	12.64723	44	NA	NA			

Table F2. Regression of factor 2 with weather data

				Coefficients:			
	x	2.50%	97.50%		Estimate	Std. Error	t value Pr(> t)
(Intercept)	-24.7059	-63.2517	13.83994	(Intercept)	-24.705891	19.125957	-1.292 0.2032
Tavg	-0.0105	-0.06654	0.045545	Tavg	-0.010497	0.027807	-0.377 0.7076
Rhavg	-0.01977	-0.03631	-0.00323	Rhavg	-0.019773	0.008207	-2.409 0.0202 *
Baroavg	0.025672	-0.01165	0.062997	Baroavg	0.025672	0.018520	1.386 0.1727
UVAavg	-0.01132	-0.1254	0.102757	UVAavg	-0.011321	0.056604	-0.200 0.8424
UVBavg	-1.04188	-2.60726	0.5235	UVBavg	-1.041880	0.776722	-1.341 0.1867
WindVavg	-0.1245	-0.79984	0.550836	WindVavg	-0.124502	0.335094	-0.372 0.7120
Rain	0.008307	-0.0025	0.019113	Rain	0.008307	0.005361	1.549 0.1284
N	0.005426	-0.0017	0.012555	N	0.005426	0.003538	1.534 0.1322
W	0.009277	-0.00582	0.024374	W	0.009277	0.007491	1.239 0.2221
S	0.009215	-0.01349	0.031921	S	0.009215	0.011266	0.818 0.4178
E	0.009426	-0.00736	0.026212	E	0.009426	0.008329	1.132 0.2638
	Sum Sq	Df	F value	Pr(>F)			
(Intercept)	0.262015	1	1.668609	0.203189			
Tavg	0.022374	1	0.142488	0.707635			
Rhavg	0.911456	1	5.804496	0.020237			
Baroavg	0.301704	1	1.921367	0.172691			
UVAavg	0.006281	1	0.04	0.842401			
UVBavg	0.282537	1	1.799304	0.18668			
WindVavg	0.021677	1	0.138044	0.712016			
Rain	0.376982	1	2.400764	0.12844			
N	0.369397	1	2.352458	0.132245			
W	0.240859	1	1.533883	0.222098			
S	0.105054	1	0.669023	0.4178			
E	0.201152	1	1.281011	0.263842			
Residuals	6.909137	44	NA	NA			

Table F3. Regression of factor 3 with weather data

				Coefficients:			
	x	2.50%	97.50%		Estimate	Std. Error	t value Pr(> t)
(Intercept)	74.80164	18.75225	130.851	(Intercept)	7.480e+01	2.781e+01	2.690 0.01007 *
Tavg	-0.11177	-0.19326	-0.03028	Tavg	-1.118e-01	4.043e-02	-2.764 0.00830 **
Rhavg	0.007633	-0.01642	0.031685	Rhavg	7.633e-03	1.193e-02	0.640 0.52575
Baroavg	-0.07273	-0.12701	-0.01846	Baroavg	-7.273e-02	2.693e-02	-2.701 0.00978 **
UVAavg	0.020547	-0.14533	0.186428	UVAavg	2.055e-02	8.231e-02	0.250 0.80403
UVBavg	-0.89459	-3.1708	1.381625	UVBavg	-8.946e-01	1.129e+00	-0.792 0.43257
WindVavg	-0.20759	-1.18959	0.774421	WindVavg	-2.076e-01	4.873e-01	-0.426 0.67216
Rain	0.003428	-0.01228	0.01914	Rain	3.428e-03	7.796e-03	0.440 0.66232
N	0.001127	-0.00924	0.011493	N	1.126e-03	5.144e-03	0.219 0.82767
W	9.48E-05	-0.02186	0.022047	W	9.485e-05	1.089e-02	0.009 0.99309
S	0.00202	-0.031	0.035036	S	2.020e-03	1.638e-02	0.123 0.90245
E	-0.00988	-0.03429	0.014524	E	-9.883e-03	1.211e-02	-0.816 0.41885
	Sum Sq	Df	F value	Pr(>F)			
(Intercept)	2.401856	1	7.234175	0.010068			
Tavg	2.537062	1	7.641404	0.008301			
Rhavg	0.135821	1	0.409081	0.525753			
Baroavg	2.421722	1	7.29401	0.009785			
UVAavg	0.020691	1	0.062319	0.804029			
UVBavg	0.208299	1	0.627379	0.432568			
WindVavg	0.060261	1	0.1815	0.672165			
Rain	0.064186	1	0.193323	0.662317			
N	0.015923	1	0.047959	0.827666			
W	2.52E-05	1	7.58E-05	0.993092			
S	0.005045	1	0.015196	0.902452			
E	0.221116	1	0.665982	0.418852			
Residuals	14.60867	44	NA	NA			

Table F4. Regression of factor 4 with weather data

				Coefficients:				
	x	2.50%	97.50%		Estimate	Std. Error	t value	Pr(> t)
(Intercept)	7.699861	-85.4353	100.835	(Intercept)	7.699861	46.212490	0.167	0.86843
Tavg	-0.15638	-0.29179	-0.02097	Tavg	-0.156381	0.067188	-2.328	0.02460 *
Rhavg	-0.05624	-0.0962	-0.01627	Rhavg	-0.056238	0.019831	-2.836	0.00688 **
Baroavg	0.001631	-0.08856	0.091817	Baroavg	0.001631	0.044749	0.036	0.97109
UVAavg	-0.11213	-0.38777	0.163508	UVAavg	-0.112131	0.136768	-0.820	0.41672
UVBavg	-3.68071	-7.463	0.101594	UVBavg	-3.680705	1.876729	-1.961	0.05620 .
WindVavg	0.467168	-1.16459	2.098931	WindVavg	0.467168	0.809660	0.577	0.56688
Rain	0.007194	-0.01891	0.033302	Rain	0.007194	0.012954	0.555	0.58150
N	-0.00783	-0.02506	0.009393	N	-0.007834	0.008548	-0.917	0.36440
W	-0.02333	-0.05981	0.013142	W	-0.023335	0.018099	-1.289	0.20405
S	0.009054	-0.04581	0.063917	S	0.009054	0.027222	0.333	0.74101
E	-0.02487	-0.06542	0.01569	E	-0.024866	0.020124	-1.236	0.22314
	Sum Sq	Df	F value	Pr(>F)				
(Intercept)	0.02545	1	0.027762	0.868433				
Tavg	4.966233	1	5.417309	0.024601				
Rhavg	7.37285	1	8.042515	0.00688				
Baroavg	0.001217	1	0.001328	0.971095				
UVAavg	0.6162	1	0.672168	0.416716				
UVBavg	3.526162	1	3.846438	0.056199				
WindVavg	0.3052	1	0.332921	0.566885				
Rain	0.282687	1	0.308363	0.581499				
N	0.770047	1	0.839989	0.364396				
W	1.523778	1	1.662181	0.204046				
S	0.101414	1	0.110626	0.741013				
E	1.399739	1	1.526875	0.223139				
Residuals	40.33631	44	NA	NA				

Table F5. Regression of factor 5 with weather data

				Coefficients:			
	x	2.50%	97.50%		Estimate	Std. Error	t value Pr(> t)
(Intercept)	-2.70736	-100.108	94.69324	(Intercept)	-2.707e+00	4.833e+01	-0.056 0.9556
Tavg	0.004586	-0.13702	0.146196	Tavg	4.586e-03	7.027e-02	0.065 0.9483
Rhavg	0.023903	-0.01789	0.0657	Rhavg	2.390e-02	2.074e-02	1.153 0.2553
Baroavg	0.002381	-0.09194	0.096697	Baroavg	2.381e-03	4.680e-02	0.051 0.9597
UVAavg	0.006688	-0.28157	0.29495	UVAavg	6.688e-03	1.430e-01	0.047 0.9629
UVBavg	-3.47908	-7.4346	0.476447	UVBavg	-3.479e+00	1.963e+00	-1.773 0.0832
WindVavg	-1.30642	-3.01292	0.400071	WindVavg	-1.306e+00	8.467e-01	-1.543 0.1300
Rain	0.006477	-0.02083	0.033781	Rain	6.477e-03	1.355e-02	0.478 0.6349
N	9.92E-05	-0.01792	0.018115	N	9.922e-05	8.939e-03	0.011 0.9912
W	-0.01162	-0.04977	0.026524	W	-1.162e-02	1.893e-02	-0.614 0.5423
S	0.013581	-0.04379	0.070957	S	1.358e-02	2.847e-02	0.477 0.6357
E	0.021724	-0.02069	0.064138	E	2.172e-02	2.105e-02	1.032 0.3076
	Sum Sq	Df	F value	Pr(>F)			
(Intercept)	0.003146	1	0.003138	0.95558			
Tavg	0.004271	1	0.00426	0.948256			
Rhavg	1.331953	1	1.328463	0.255303			
Baroavg	0.002595	1	0.002588	0.959658			
UVAavg	0.002192	1	0.002186	0.962917			
UVBavg	3.150418	1	3.142163	0.083216			
WindVavg	2.386746	1	2.380492	0.130021			
Rain	0.229202	1	0.228602	0.63493			
N	0.000124	1	0.000123	0.991194			
W	0.378089	1	0.377098	0.542323			
S	0.22819	1	0.227592	0.635676			
E	1.068333	1	1.065534	0.307597			
Residuals	44.1156	44	NA	NA			

Appendix G – Potential Impact of Ozone on Aldehyde Measurements

In order to evaluate the possibility of DNSH and DNSH-derivatives oxidation within the sampling cartridges, we used a dynamic dilution system. Aldehydes and ozone were introduced into the dilution system at desired concentrations. A wide range of carbonyls (1-100ppb) and ozone (0-300ppb) were achieved by adjusting the ozone generator output and regulating the total flow rates through the clean dilution air. The test conditions were as the following: (1) sampling duration was 48 hours; (2) chamber temperature was 25°C; (3) face velocity was 0.05 m/s; (4) relative humidity were 32% and 90%; (5) ozone concentrations in the chamber (ppb) were 0, 50, 100, 200, and 300.

Measured concentrations of formaldehyde, acetaldehyde, and acrolein, under different ozone concentrations are shown in Table G1. Results show that the presence of ozone from 50 ppb to 300 ppb caused <10% changes in measured concentrations of formaldehyde and that the presence of ozone from 50 ppb to 200 ppb caused <10% changes in measured concentrations of acetaldehyde and <15% changes in measured concentrations of acrolein.

Table G1. Measured concentrations for three aldehydes with different ozone concentrations and the recovery for two different methods

Ozone (ppb)	Aldehydes concentration: Mean±sd (ppb, n=4)				
	0	50	100	200	300
Formaldehyde	42.39±1.14	37.94±2.55	39.01±2.15	39.02±3.30	38.39±4.18
Acetaldehyde	22.23±0.25	20.12±1.30	20.12±1.07	21.01±1.66	17.89±0.94
Acrolein	17.03±0.39	14.73±0.67	15.31±1.22	14.46±1.06	13.02±0.81

The ratio of measured aldehydes concentrations, with and without the presence of ozone, ranged from 89.5%-92.0% for formaldehyde, 80.5%-94.5% for acetaldehyde, and 76.5%-89.9% for acrolein.

Samples and field controls were eluted with acetonitrile and aliquots of extracts were analyzed using an HPLC system with fluorescent detection. A Nova-Pak C18 column was used, along with a mobile phase program described as follows: mobile phase A was composed of 80% water, 10% acetonitrile, and 10% tetrahydrofuran containing 0.68 g/L of KH_2PO_4 and 3.48 g/L of K_2HPO_4 ; mobile phase B was composed of 30% water, 40% acetonitrile, and 30% tetrahydrofuran containing 0.68 g/L of KH_2PO_4 and 3.48 g/L of K_2HPO_4 . The excitation and emission wavelengths used for detecting aldehyde–DNSH derivatives were 250 nm and 525 nm, respectively. The collection efficiencies for ambient formaldehyde, acetaldehyde and acrolein of this method were $115.5\% \pm 11.0\%$, $105.8\% \pm 9.1\%$, and $87.5\% \pm 4.7\%$ (mean \pm SD, N=30), respectively. The analytical detection limits of the method were 0.98 ng, 0.86 ng and 1.15 ng per cartridge and the analytical precision, determined as relative standard deviations (RSDs) of replicate samples, were 7.72%, 1.84% and 4.56% (N=8) for formaldehyde, acetaldehyde and acrolein, respectively.

Appendix H – Regression of Aldehydes with Air pollution Source Types

P-value significance codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table H1. Regression of formaldehyde with air pollution source types

x	Beta			
(Intercept)	28.73245	***		
Factor1	1.363131			
Factor2	-4.45709	***		
Factor3	-8.62932	***		
Factor4	2.42638			
Factor5	4.985685	***		
	2.50%	97.50%		
(Intercept)	26.01616	31.44873		
Factor1	-1.64708	4.373338		
Factor2	-6.9829	-1.93128		
Factor3	-11.4413	-5.81734		
Factor4	-1.09895	5.95171		
Factor5	2.173796	7.797574		
	Sum Sq	Df	F value	Pr(>F)
(Intercept)	59771.1	1	445.5374	1.44E-31
Factor1	109.5416	1	0.81653	0.369387
Factor2	1663.404	1	12.39912	0.000772
Factor3	5030.665	1	37.49888	5.16E-08
Factor4	253.0551	1	1.886288	0.174133
Factor5	1679.385	1	12.51824	0.000732
Residuals	9122.544	68	NA	NA

Table H2. Regression of acetaldehyde with air pollution source types

x	Beta			
(Intercept)	26.78771	***		
Factor1	1.611338			
Factor2	-3.57009			
Factor3	-2.89021			
Factor4	6.147548	**		
Factor5	6.221243	***		
	2.50%	97.50%		
(Intercept)	23.3637	30.21173		
Factor1	-2.03905	5.261731		
Factor2	-9.58794	2.447767		
Factor3	-6.46996	0.689538		
Factor4	1.921706	10.37339		
Factor5	2.873307	9.569178		
	Sum Sq	Df	F value	Pr(>F)
(Intercept)	44895.09	1	244.4208	2.31E-23
Factor1	142.9203	1	0.778096	0.381077
Factor2	258.1512	1	1.405444	0.240267
Factor3	478.1386	1	2.603114	0.111652
Factor4	1552.305	1	8.451163	0.005031
Factor5	2532.794	1	13.7892	0.000436
Residuals	11571.81	63	NA	NA

Table H3. Regression of acrolein with air pollution source types

x	Beta				
(Intercept)	2.204626	***			
Factor1	0.008989				
Factor2	-0.17058				
Factor3	-0.43983	***			
Factor4	0.243469	*			
Factor5	0.257751	**			
	2.50%	97.50%			
(Intercept)	2.015871	2.393381			
Factor1	-0.19871	0.216692			
Factor2	-0.41521	0.074047			
Factor3	-0.63408	-0.24558			
Factor4	0.005022	0.481917			
Factor5	0.065806	0.449696			
	Sum Sq	Df	F value	Pr(>F)	
(Intercept)	322.2458	1	544.7688	1.04E-32	
Factor1	0.004425	1	0.00748	0.931352	
Factor2	1.148582	1	1.941722	0.168378	
Factor3	12.11039	1	20.47308	2.74E-05	
Factor4	2.462733	1	4.163344	0.045504	
Factor5	4.259533	1	7.200903	0.009297	
Residuals	37.26624	63	NA	NA	

Appendix I – Association of Biomarkers with Source Types and Aldehydes (Fall Data Omitted)

Figure I1. Percent change in pH associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 6 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements.

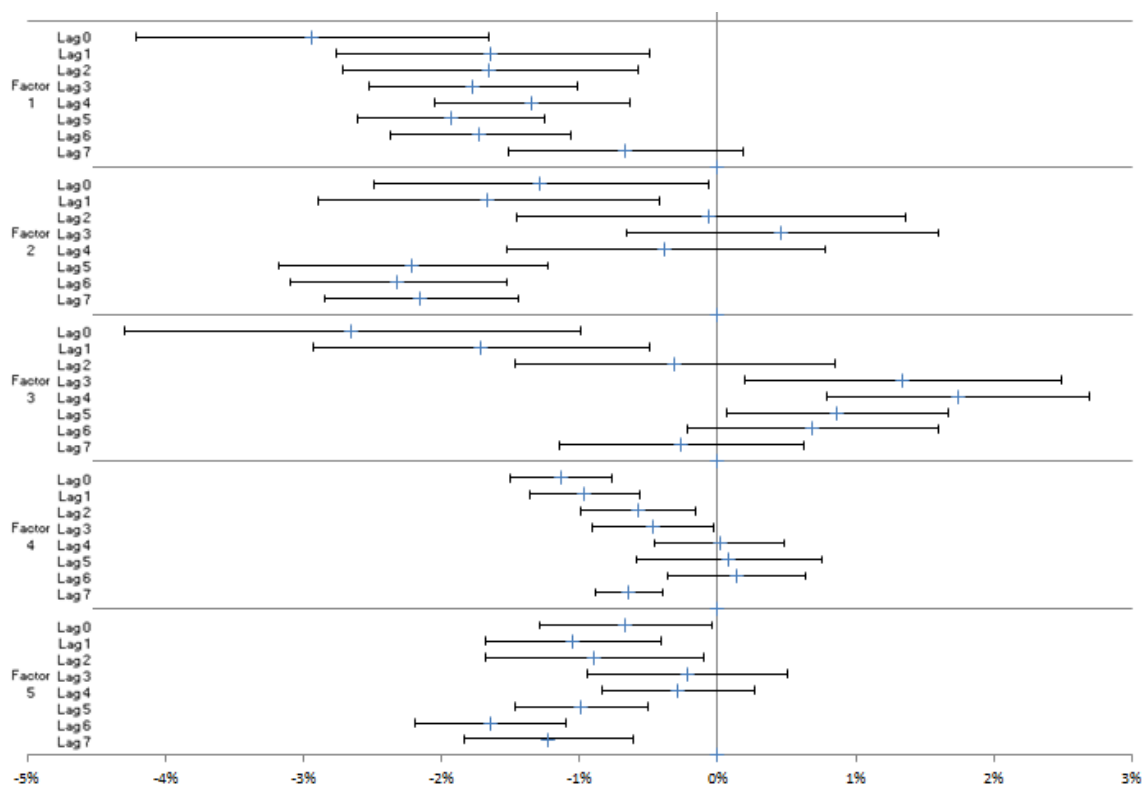


Figure I2. Percent change in EBC Nitrite associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=2), relative humidity (ns=1), 7 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

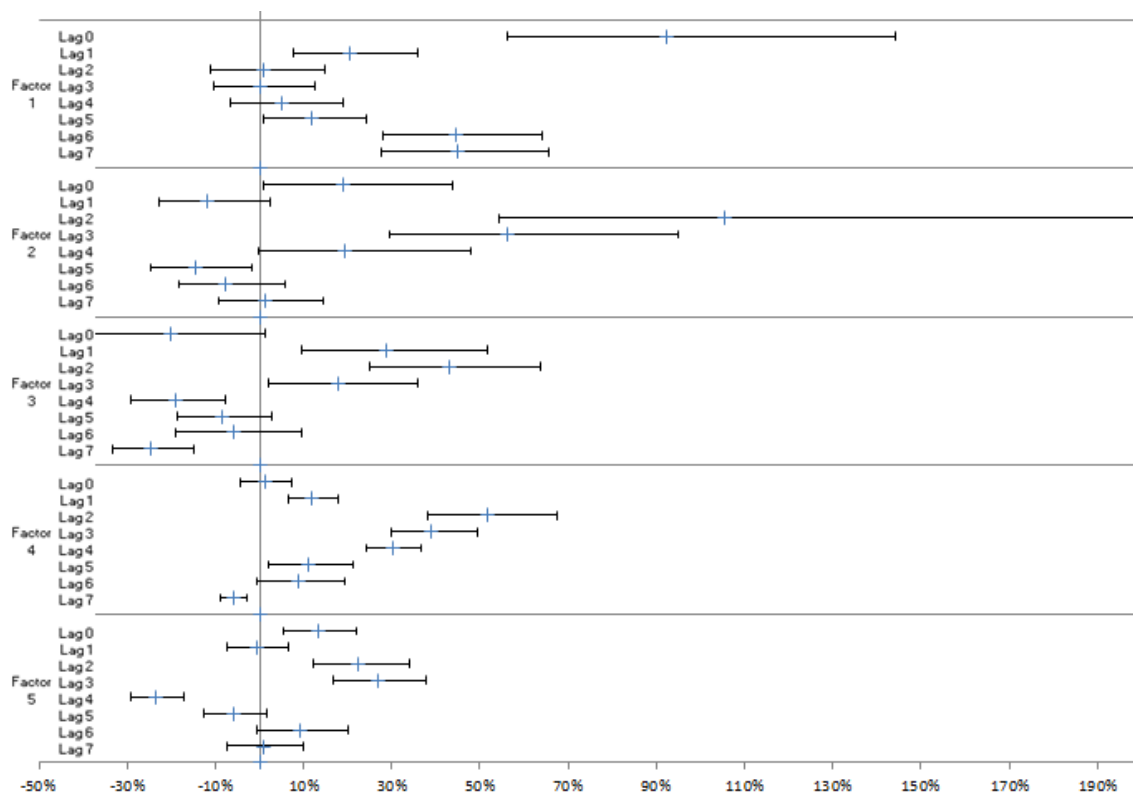


Figure I3. Percent change in eNO associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=2), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 7 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

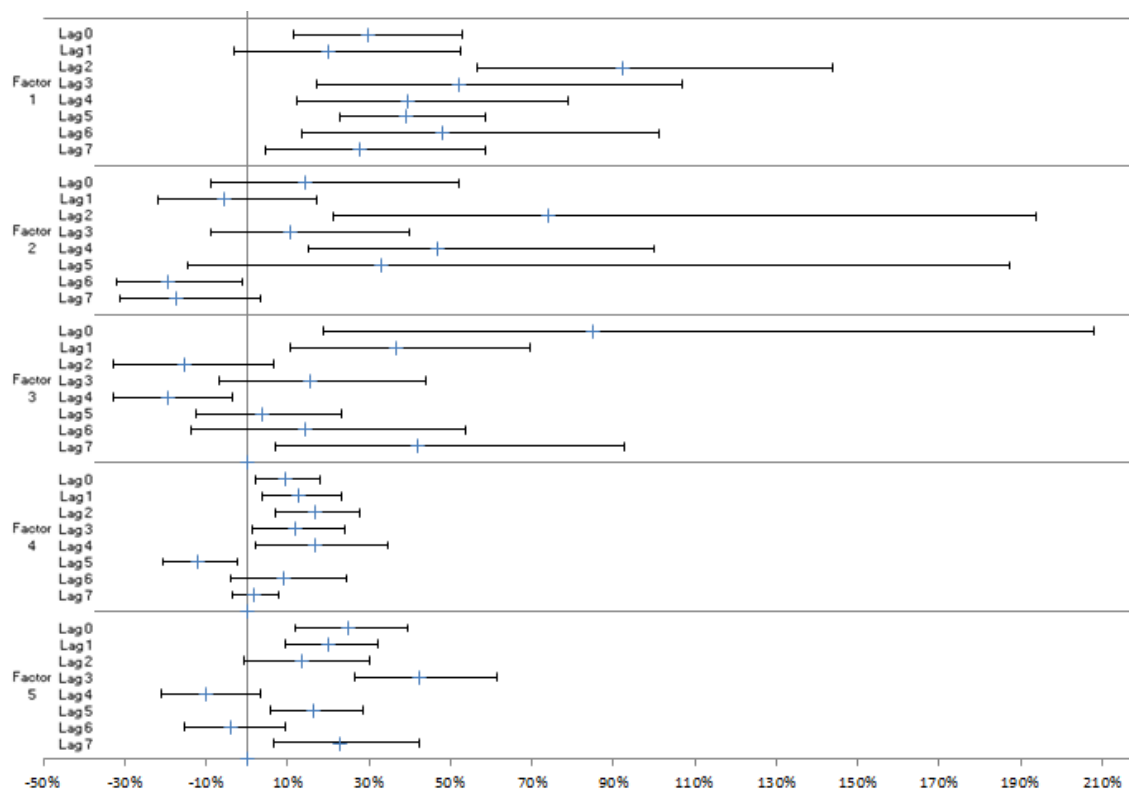


Figure I4. Percent change in vWF associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=3), relative humidity (ns=3), 7 day moving average of temperature (ns=3), 6 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

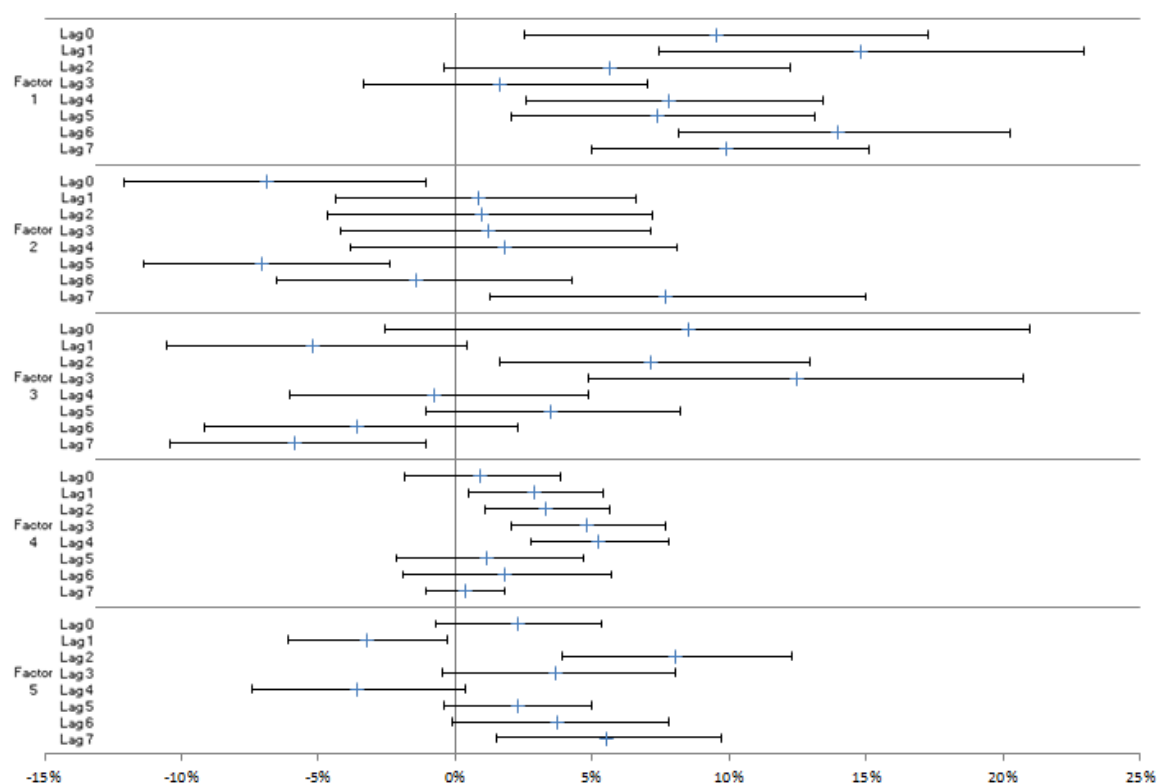


Figure 15. Percent change in sCD62p associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 4 day moving average of relative humidity (ns= 2), gender, and day of week for biomarker measurements.

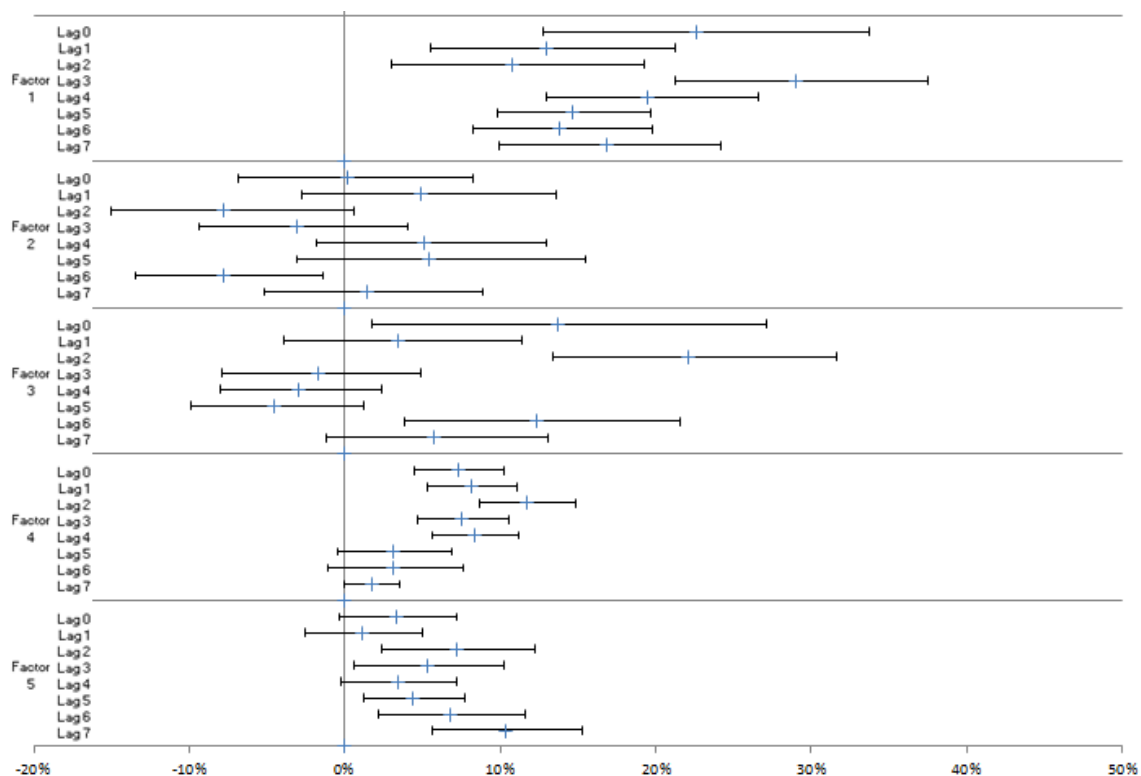


Figure I6. Percent change in sCD40L associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 5 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements

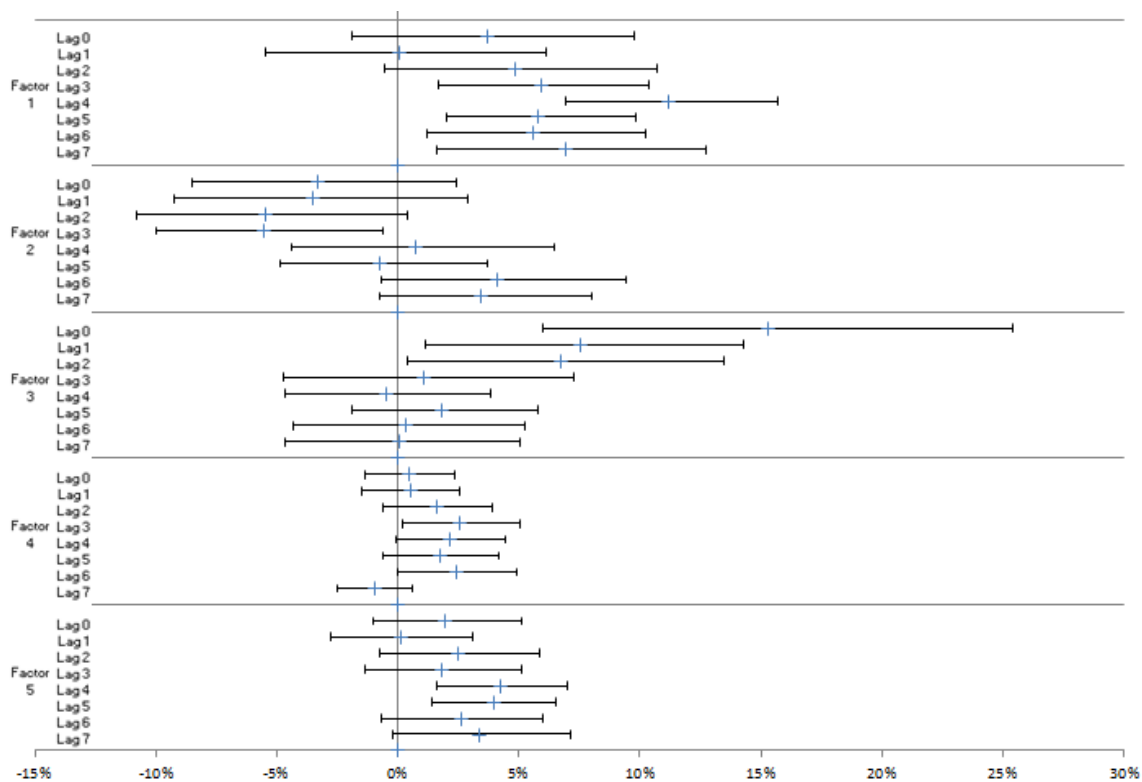


Figure 17. Percent change in log(8-OHdG) associated with one interquartile increase in factor score, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 7 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

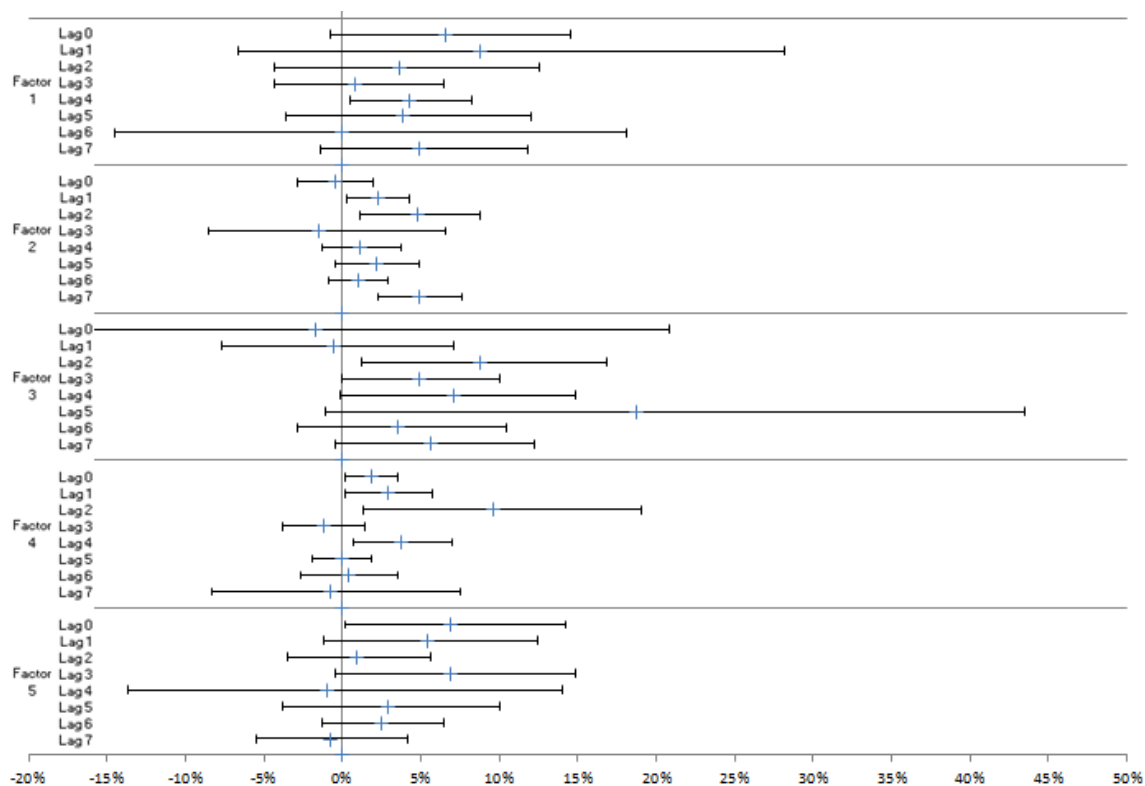


Figure 18. Percent change in pH associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 6 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements.

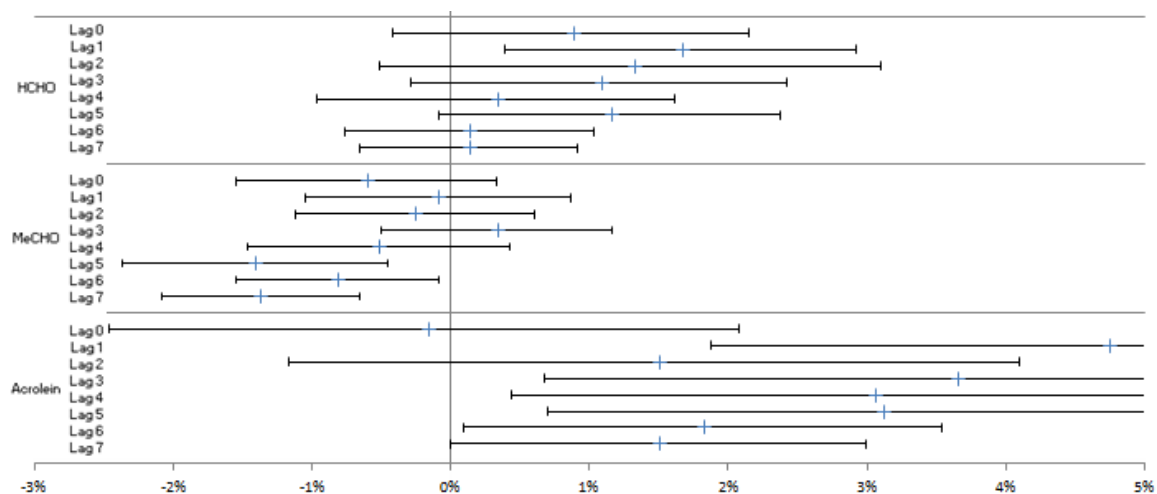


Figure 19. Percent change in EBC Nitrite associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=2), relative humidity (ns=1), 7 day moving average of temperature (ns=3), 3 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

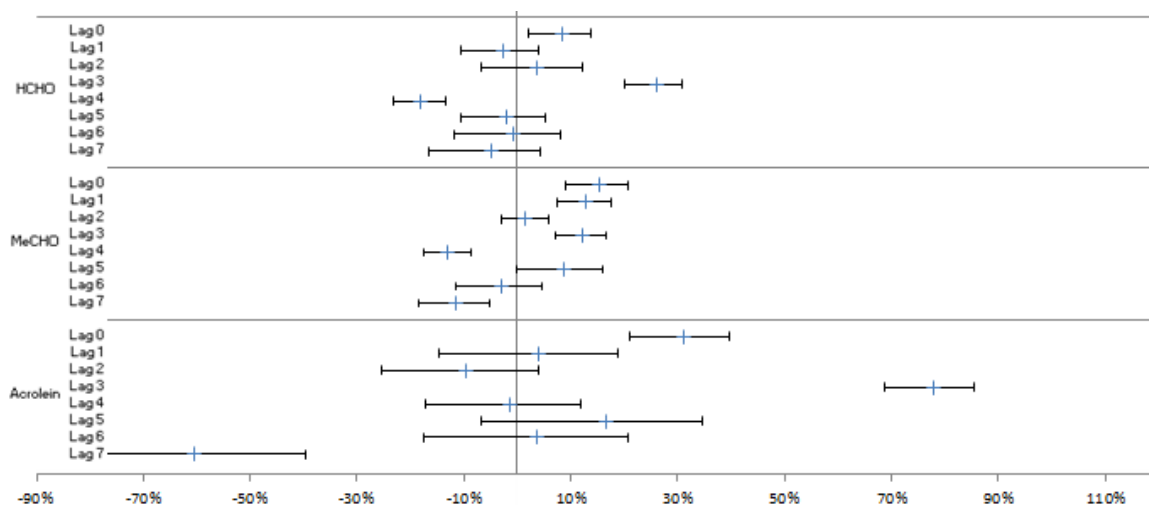


Figure I10. Percent change in eNO associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=2), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 7 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

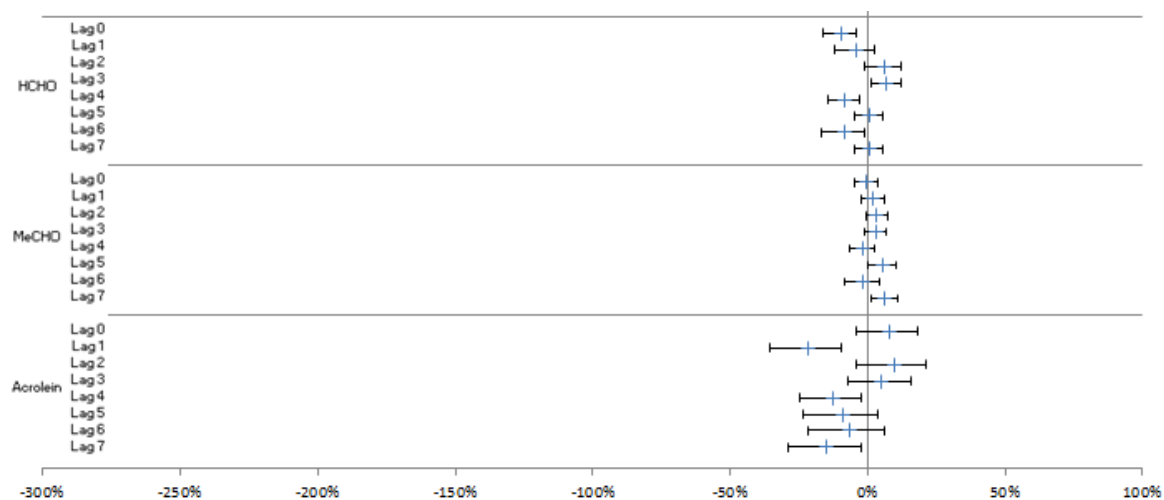


Figure I11. Percent change in vWF associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=3), relative humidity (ns=3), 7 day moving average of temperature (ns=3), 6 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.

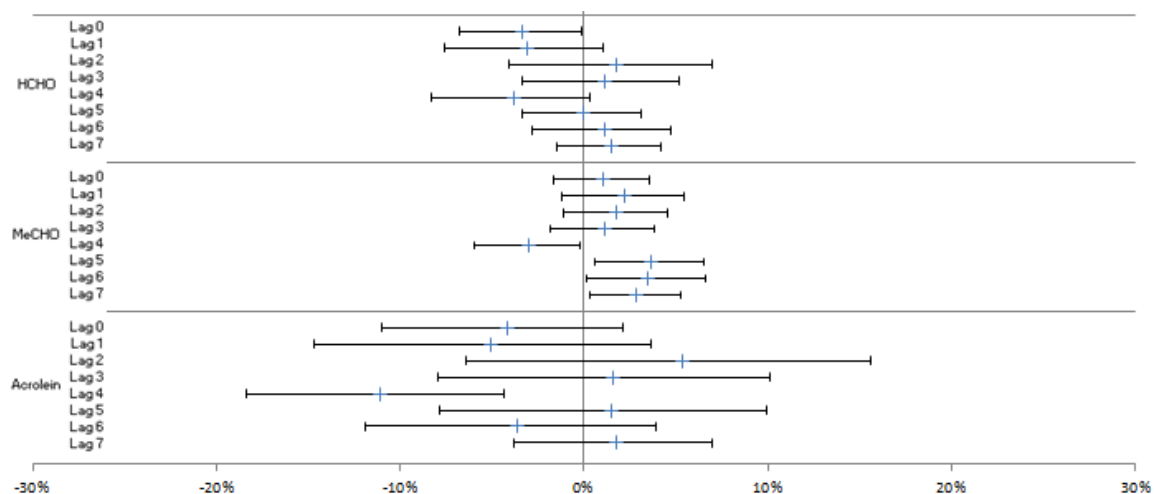


Figure I12. Percent change in sCD62p associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=3), 7 day moving average of temperature (ns=2), 4 day moving average of relative humidity (ns= 2), gender, and day of week for biomarker measurements.

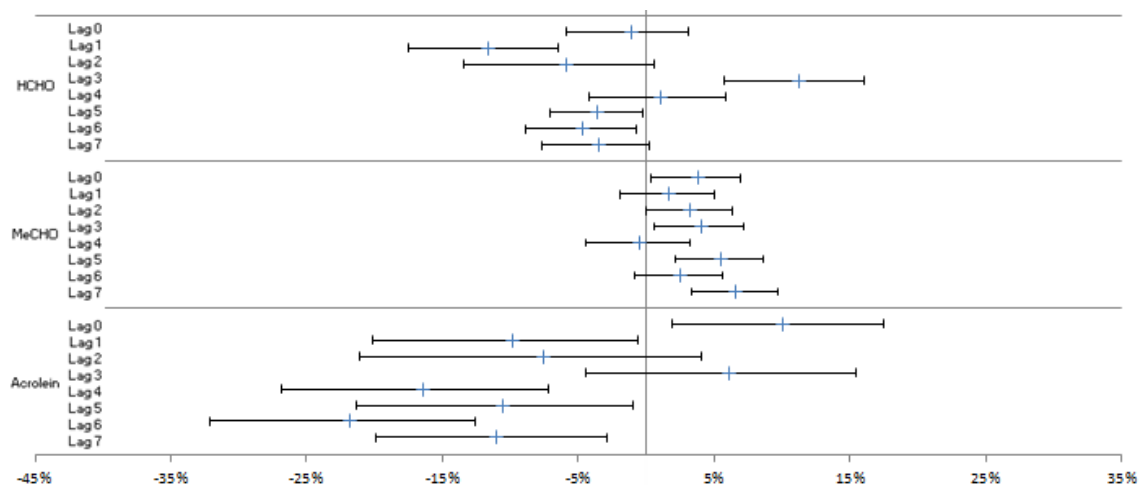


Figure I13. Percent change in sCD40L associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 5 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 1), gender, and day of week for biomarker measurements

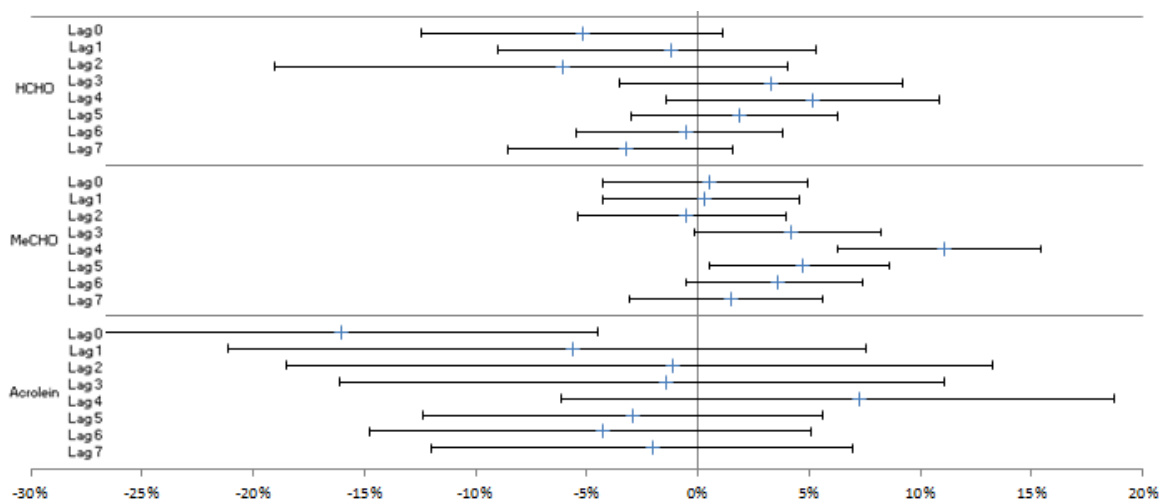
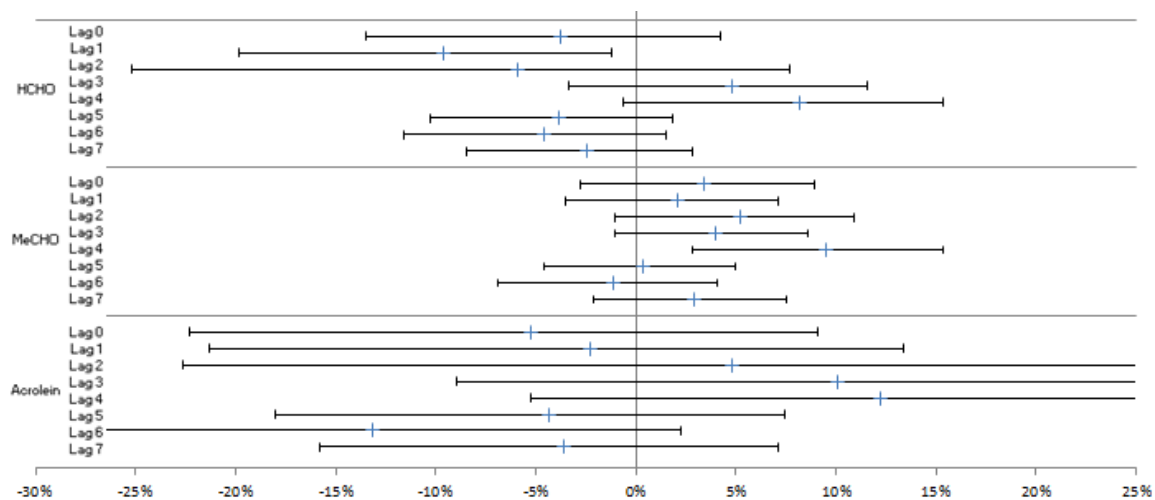


Figure I14. Percent change in log(8-OHdG) associated with one interquartile increase in aldehyde concentration, fall data omitted, controlling for temperature (ns=1), relative humidity (ns=1), 7 day moving average of temperature (ns=1), 2 day moving average of relative humidity (ns= 3), gender, and day of week for biomarker measurements.



References

- Akbar-Khanzadeh F, Mlynek JS. 1997. Changes in respiratory function after one and three hours of exposure to formaldehyde in non-smoking subjects. *Occupational and Environmental Medicine* 54:296-300.
- Altshuller AP. 1993. Production of aldehydes as primary emissions and from secondary atmospheric reactions of alkenes and alkanes during the night and early morning hours. *Atmospheric Environment Part a-General Topics* 27:21-32.
- Andreini BP, Baroni R, Galimberti E, Sesana G. 2000. Aldehydes in the atmospheric environment: Evaluation of human exposure in the north-west area of Milan. *Microchemical Journal* 67:11-9.
- Artaxo P, Oyola P, Martinez R. 1999. Aerosol composition and source apportionment in Santiago de Chile. *Nuc Inst Meth Phys Res* 150:409-416.
- Baez AP, Belmont R, Padilla H. 1995. Measurements of formaldehyde and acetaldehyde in the atmosphere of Mexico City. *Environmental Pollution* 89:163-7.
- Ballester RF, Tenias JM, Perez-Hoyos S. 2001. Air pollution and emergency hospital admissions for cardiovascular diseases in Valencia, Spain. *J Epidemiol Community Health* 55(1):57-65.
- Barregard L, Sallsten G, Gustafson P, Andersson L, Johansson L, Basu S, Stigendal L. 2006. Experimental exposure to wood-smoke particles in healthy humans: effects on markers of inflammation, coagulation, and lipid peroxidation. *Inhal Toxicol* 18(11):845-53.
- Benjebria A, Marthan R, Rossetti M, Savineau JP, Ultman JS. 1994. Human bronchial smooth-muscle responsiveness after in-vitro exposure to acrolein. *American Journal of Respiratory and Critical Care Medicine* 149:382-6.
- Botto, N., Masetti, S., Petrozzi, L., Vassalle, C., Manfredi, S., Biagini, A., Andreassi, M. G., 2002 Elevated levels of oxidative DNA damage in patients with coronary artery disease. *Coron Artery Dis* 13, (5), 269-74.
- Burnett R, Brook J, Dann T, Delocia C, Phillips O, Cakmak S, Vincent R, Goldberg M, Krewski D. 2000. Association between particulate and gas phase components of urban air pollution and daily mortality in eight Canadian cities. *Inh Tox* 12(s4):15-39.
- Burnett R, Smith-Doiron M, Stieb D, Cakmak S, Brook J. 1999. Effects of particulate and gaseous air pollution on cardiorespiratory hospitalizations. *Arch Environ health* 54:130-139.

Cao L, Tian W, Ni B, Zhang Y, Wang P. 2002. Preliminary study of airborne particulate matter in a Beijing sampling station by instrumental neutron activation analysis. *Atmospheric Environment* 36: 1951–1956.

Cassee FR, Arts JHE, Groten JP, Feron VJ. 1996a. Sensory irritation to mixtures of formaldehyde, acrolein, and acetaldehyde in rats. *Archives of Toxicology* 70:329-37.

Cassee FR, Groten JP, Feron VJ. 1996b. Changes in the nasal epithelium of rats exposed by inhalation to mixtures of formaldehyde, acetaldehyde, and acrolein. *Fundamental and Applied Toxicology* 29:208-18.

Chan CK, Yao X. 2008. Air pollution in mega cities in China. *Atmospheric Environment* 42:1-42.

Creason J, Neas L, Walsh D, Williams R, Sheldon L, Liao D, Shy C. 2001. Particulate matter and heart rate variability among elderly retirees: the Baltimore 1998 PM study. *J Exp Analysis Environ Epidemiol* 11:116-122.

Demirbag, R.; Yilmaz, R.; Erel, O.; Gultekin, U.; Asci, D.; Elbasan, Z., 2005 The relationship between potency of oxidative stress and severity of dilated cardiomyopathy. *Can J Cardiol* 21, (10), 851-5.

Devlin RB, Ghio AJ, Kerhl H, Sanders G, Cascio W. 2003. Elderly human exposed to concentrated air pollution particles have decreased heart rate variability. *Eur Respir J* 21(Suppl 40):76s-80s.

D'Ippoliti D, Forastiere F, Ancona C, et al. 2003. Air pollution and myocardial infarction in Rome: a case-crossover analysis. *Epidemiology* 14:528-35.

Dockery DW, Luttmann-Gibson H, Rich DQ, et al. 2005. Association of air pollution with increased incidence of ventricular tachyarrhythmias recorded by implanted cardioverter defibrillators. *Environ Health Perspect* 113:670-4.

Dockery DW, Luttmann-Gibson H, Rich DQ, et al. 2005. Particulate air pollution and nonfatal cardiac events. Part II. Association of air pollution with confirmed arrhythmias recorded by implanted defibrillators. *Health Effects Institute Research Report* 124. Particulate air pollution and nonfatal cardiac events.

Feng YL, Wen S, Chen YJ, Wang XM, Lu HX, Bi XH, et al. 2005. Ambient levels of carbonyl compounds and their sources in Guangzhou, China. *Atmospheric Environment* 39:1789-800.

Feng YL, Wen S, Wang XM, Sheng GY, He QS, Tang JH, et al. 2004. Indoor and outdoor carbonyl compounds in the hotel ballrooms in Guangzhou, China. *Atmospheric Environment* 38:103-12.

Forastiere F, Stafoggia M, Picciotto S, et al. 2005. A case-crossover analysis of out-of-hospital coronary deaths and air pollution in Rome, Italy. *Am J Respir Crit Care Med* 172:1549-55.

Friedman MS, Powell KE, Hutwagner L, Graham LM, Teague WG. 2001. Impact of changes in transportation and commuting behaviors during the 1996 Summer Olympic Games in Atlanta on air quality and childhood asthma. *JAMA* 285(7):897-905.

Frye C, Hoelscher B, Cyrus J, Wjst M, Wichmann HE, Heinrich J. 2003. Association of lung function with declining ambient air pollution. *Environ Health Perspect* 111(3):383-7.

Gold DR, Litonjua A, Schwartz J, Lovett E, Larson A, Nearing B, Allen G, Verrier M, Cherry R, Verrier R. 2000. Ambient air pollution and heart rate variability. *Circulation* 101:1267-1273.

Goldberg MS, Burnett RT, Bailar JC, 3rd, et al. 2001. Identification of persons with cardiorespiratory conditions who are at risk of dying from the acute effects of ambient air particles. *Environ Health Perspect* 109 Suppl 4:487-94.

Goldberg MS, Burnett RT, Bailar JC, 3rd, et al. 2001. The association between daily mortality and ambient air particle pollution in Montreal, Quebec. 1. Nonaccidental mortality. *Environ Res* 86:12-25.

Grosjean D, Grosjean E, Moreira LFR. 2002. Speciated ambient carbonyls in Rio de Janeiro, Brazil. *Environmental Science & Technology* 36:1389-95.

Hao JM, Hu JN, Fu LX. 2006. Controlling vehicular emissions in Beijing during the last decade. *Transportation Research Part A*. 40:639-51.

Hedley AJ, Wong CM, Thach TQ, Ma S, Lam TH, Anderson HR. 2002. Cardiorespiratory and all-cause mortality after restrictions on sulphur content of fuel in Hong Kong: an intervention study. *Lancet* 360(9346):1646-52.

Heinrich J, Hoelscher B, Wichmann HE. 2000. Decline of ambient air pollution and respiratory symptoms in children. *Am J Respir Crit Care Med* 161(6):1930-6.

Henneberger A, Zareba W, Ibal-Mulli A, et al. 2005. Repolarization changes induced by air pollution in ischemic heart disease patients. *Environ Health Perspect* 113:440-6.

Henry R, Lewis C, Collins J. 1994. Vehicle-related hydrocarbon source compositions from ambient data: the GRECE/SAFER Method. *Environ Sci Technol* 28:823-832.

Herrington J, Zhang L, Whitaker D, Sheldon L, Zhang J. 2005. Optimizing a dansylhydrazine (DNSH) based method for measuring airborne acrolein and other unsaturated carbonyls. *Journal of Environmental Monitoring* 7:969-76.

Holguin F, Tellez-Rojo MM, Hernandez M, Cortez M, Chow JC, Watson JG, Mannino D, Romieu I. 2003. Air pollution and heart rate variability among the elderly in Mexico City. *Epidemiol* 14:521-527.

Huang W, Wang G, Lu S, Kipen H, Wang Y, Hu M, Lin W, Rich D, Ohman-Strickland P, Diehl S, Zhu P, Tong J, Gong J, Zhu T, Zhang J. 2012a. Inflammatory and oxidative stress responses of health young adults to changes in air quality during the Beijing Olympics. *Am J Resp Crit Care Med*. 186: 1150-1159.

Huang W, Cao J, Tao Y, Dai L, Lu S, Hou B, Wang Z, Zhu T. 2012b. Seasonal variation of chemical species associated with short-term mortality effects of PM_{2.5} in Xi'an, a central city in China. *Am J Epidemiol*. 175(6): 556–566.

Huang XF, He LY, Hu M, Canagaratna MR, Sun Y, Zhang Q, et al. 2010. Highly time-resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne High-Resolution Aerosol Mass Spectrometer. *Atmospheric Chemistry and Physics* 10:8933-45.

Jacobs L, et al. 2010. Air pollution–related prothrombotic changes in persons with diabetes. *Environ Health Perspect*. 118(2): 191–196.

Jerrett M, Burnett R, Ma R, Pope CA, Krewski D, Newbold KB, Thurston G, Shi Y, Finkelstein N, Calle E, Thun M. 2005. Spatial analysis of air pollution and mortality in Los Angeles. *Epidemiology* 16(6): 727-736.

Jolliffe IT. 2002. *Principal Component Analysis*, 2nd Ed. New York: Springer.

Kipen H, Gandhi S, Rich D, Ohman-Strickland P, Laumbach R, Fan Z, Chen L, Laskin D, Zhang J, Madura K. 2011. Acute decreases in proteasome pathway activity after inhalation of fresh diesel exhaust or secondary organic aerosol. *Environ Health Perspect*. 119(5): 658–663.

Li Y, Shao M, Lu SH, Chang CC, Dasgupta PK. 2010a. Variations and sources of ambient formaldehyde for the 2008 Beijing Olympic Games. *Atmospheric Environment* 44:2632-9.

Li Y, Wang W, Kan HD, Xu XH, Chen BH. 2010b. Air quality and outpatient visits for asthma in adults during the 2008 Summer Olympic Games in Beijing. *Science of the Total Environment* 408:1226-7.

Liao D, Creason J, Shy C, Williams R, Watts R, Zweidinger R. 1999. Daily variation of particulate air pollution and poor cardiac autonomic control in the elderly. *Environ Health Perspect* 107(7):521-5.

Linn WS, Szlachcic Y, Gong H, Jr., Kinney PL, Berhane KT. 2000. Air pollution and daily hospital admissions in metropolitan Los Angeles. *Environ Health Perspect* 108:427-34.

Lipari F, Dasch JM, Scruggs WF. 1984. Aldehyde emissions from wood-burning fireplaces. *Environmental Science and Technology* 18(5):326-30.

Liso D, Creason J, Shy C, Williams R, Watts R, Zweidinger R. 1999. Daily variations of particulate air pollution and poor cardiac autonomic control in the elderly. *Environ Health Perspect*. 107:521-525.

Liu XH, Zhang Y, Cheng SH, Xing J, Zhang Q, Streets DG, Jang C, Wang WX, Hao JM. 2010. Understanding of regional air pollution over China using CMAQ, part I performance evaluation and seasonal variation. *Atmospheric Environment* 44(20): 2415-2426.

Liu XH, Zhang Y, Xing J, Zhang Q, Streets DG, Jang C, Wang WX, Hao JM. 2010. Understanding of regional air pollution over China using CMAQ, part II. Process analysis and sensitivity of ozone and particulate matter to precursor emissions . *Atmospheric Environment* 44(30): 3719-3727.

Luttmann-Gibson H, Huh HH, Coull BA, Dockery DW, Sarnat SE, Schwartz J, Stone PH, Gold DR. 2006. Short-term effects of air pollution on heart rate variability in senior adults in Steubenville, Ohio. *J Occup Environ Med* 48:780-788.

MacIntosh DL, Zimmer-Dauphinee SA, Manning RO, Williams PL. 2000. Aldehyde concentrations in ambient air of coastal Georgia, USA. *Environmental Monitoring and Assessment* 63:409-29.

Magari SR, Hauser R, Schwartz J, Williams PL, Christiani DC. 2001. Association of heart rate variability with occupational and environmental exposure to particulate air pollution. *Mayo Clin Proc* 104:986-91.

Manoli E, Voutsas D, Samara C. 2002. Chemical characterization and source identification/ apportionment of fine and coarse air particles in Thessaloniki, Greece. *Atmospheric Env*. 36(6): 949-961.

Mar T, Norris G, Koenig J, Larson T. 2000. Associations between air pollution and mortality in Phoenix, 1995-1997. *Env Health Perspectives*. 108(4):347-353.

Metzger KB, Tolbert PE, Klein M, et al. 2004. Ambient air pollution and cardiovascular emergency department visits. *Epidemiology* 15:46-56.

Mills N, et al. 2007. Ischemic and thrombotic effects of dilute diesel-exhaust inhalation in men with coronary heart disease. *N Engl J Med*. 357:1075-1082.

Moolgavkar SH. 2000. Air pollution and hospital admissions for diseases of the circulatory system in three U.S. metropolitan areas. *J Air Waste Manag Assoc* 50:1199-206.

Ostro B. 1995. Fine particulates air pollution and mortality in two Southern California countries. *Environ res* 70:98-104.

Ozkaynak H, Thurston G. 1987. Associations between 1980 U.S. mortality rates and alternative measures of air particulate concentration. *Risk Anal* 7:449-461.

Paget-Brown AO, Ngamtrakulpanit L, Smith A, Bunyan D, Hom S, Nguyen A, Hunt JF. 2006. Normative data for pH exhaled breath condensate. *Chest* 129(2): 426-30.

Park S, Kim Y, Kang C. 2002. Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. *Atmospheric Environment* 36(17): 2917-2924.

Peters A, Dockery DW, Muller JE, Mittleman MA. 2001. Increased particulate air pollution and the triggering of myocardial infarction. *Circulation* 103:2810-5.

Peters A, Heier M. 2005. Particular air pollution and nonfatal cardiac events. Part 1 Air pollution, personal activities and onset of myocardial infarction in a case-crossover study. *HEI* 124:15-82.

Peters A, Liu E, Verrier RL, et al. 2000. Air pollution and incidence of cardiac arrhythmia. *Epidemiology* 11:11-7.

Pope CA III, Hansen ML, Long RW, Nielsen KR, Eatough NL, Wilson WE, Eatough DJ. 2004. Ambient particulate air pollution, heart rate variability, and blood markers of inflammation in a panel of elderly subjects. *EHP* 112(3):339-345.

Pope CA III, Schwartz J, Ransom M. 1992. Daily mortality and PM₁₀ pollution in Utah Valley. *Arch Environ Health* 47:211-217.

Pope CA III, Verrier RL, Lovett ED, Larson AC, Raizenne ME, Kanner RE, Schwartz J, Villegas GM, Gold DR, Dockery DW. 1999. Heart rate variability associated with particulate air pollution. *Am Heart J* 138(5):890-899.

Possanzini M, Di Palo V, Cecinato A. 2002. Sources and photodecomposition of formaldehyde and acetaldehyde in Rome ambient air. *Atmospheric Environment* 36:3195-201.

Possanzini M, Dipalo V, Petricca M, Fratarcangeli R, Brocco D. 1996. Measurements of lower carbonyls in Rome ambient air. *Atmospheric Environment* 30:3757-64.

Prevedouros K, Brorstrom-Lunden E, Halsall C, Jones K, Lee R, Sweetman A. 2004. Seasonal and long-term trends in atmospheric PAH concentrations: evidence and implications. *Environmental Pollution* 128(1-2): 17-27.

Pusede SE, Cohen RC, 2012. On the observed response of ozone to NO_x and VOC reactivity reductions in San Joaquin Valley California 1995-present. *Atmospheric Chemistry and Physics*. 12:8323-8339.

Rich DQ, Freudenberger R, Ohman-Strickland P, Cho Y, Kipen H. 2008. Right heart pressure increases after acute increases in ambient particulate concentration. *Environ Health Perspect*. 116(9): 1167–1171.

Rich DQ, Kim M, Turner J, et al. 2006. Association of ventricular arrhythmias detected by implantable cardioverter defibrillator and ambient air pollutants in Saint Louis, Missouri. *Occup Environ Med* 63: 591-596.

Rich DQ, Kipen H, Zhang J, Kamat L, Wislon A, Kostis J. 2010. Triggering of transmural infarctions, but not nontransmural infarctions, by ambient fine particles. *Environ Health Perspect*. 118(9): 1229–1234.

Rich DQ, Schwartz J, Mittleman MA, et al. 2005. Association of short-term ambient air pollution concentrations and ventricular arrhythmias. *Am J Epidemiol* 161:1123-32.

Rich, DQ, Kipen, HM, Huang, W, Wang, G, Wang, Y, Zhu, P, Ohman-Strickland, P, Hu, M, Philipp, C; Diehl, SR, Lu, SE, Tong, J, Gong, J, Thomas, D, Zhu, T, Zhang, JF. 2012. Association between changes in air pollution levels during the Beijing Olympics and biomarkers of inflammation and thrombosis in healthy young adults. *JAMA*. 307(19): 2068-2078.

Rich KE, Petkau J, Vedal S, Brauer M. 2004. A case-crossover analysis of particulate air pollution and cardiac arrhythmia in patients with implantable cardioverter defibrillators. *Inhal Toxicol* 16:363-72.

Riediker M, Cascio WE, Griggs TR, et al. 2004. Particulate matter exposure in cars is associated with cardiovascular effects in healthy young men. *Amer J Res Crit Care Med* 169:934-940.

Ruckerl R, Ibal-Mulli A, Koenig W, Schneider A, Woelke G, Cyrys J, Heinrich J, Marder V, Frampton M, Wichmann H and others. 2006. Air pollution and markers of inflammation and coagulation in patients with coronary heart disease. *Am J resp Crit Care Med* 173(4):432-441.

Sarnat S. 2006. Ambient particulate air pollution and cardiac arrhythmia in a panel of older adults in Steubenville, Ohio. *Occup Environ Med* Epub ahead of print.

Schauer J, Rogge W, Hildemann L, Mazurek M, Cass G, Simoneit B. 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment* 30(22): 3837-3855.

Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT. 2001. Measurement of emissions from air pollution sources. 3. C-1-C-29 organic compounds from fireplace combustion of wood. *Environmental Science & Technology* 35:1716-28.

Schwartz J, Litonjua A, Suh H, Verrier M, Zanobetti A, Syring M, Nearing B, Verrier R, Stone P, MAcCallum G, Speizer FE, Gold DR. 2005. Traffic related pollution and heart rate variability in a panel of elderly subjects. *Thorax* 60:455-461.

Schwartz J. 1993. Air pollution and daily mortality in Birmingham, Alabama. *Am J of Epidemiol* 137:1136-1146.

Schwartz J. 1994. What are people dying of on high air pollution days? *Environ Res* 64:26-35.

Schwartz J. 1997. Air pollution and hospital admissions for cardiovascular disease in Tuscon. *Epidemiology* 8:371-377.

Seaton A, MacNee W, Donaldson K, Godden D. 1995. Particulate air pollution and acute health effects. *Lancet* 345:176-178.

Seaton A, Soutar A, Crawford V, Elton R, McNerlan S, Cherrie J, Watt M, Agius R, Stout R. 1999. Particulate air pollution and the blood. *Thorax* 54:1027-1032.

Seinfeld JH, Pandis SN. 1998. Chemistry of the atmospheric aqueous phase. In: *atmospheric chemistry and physics: from air pollution to climate change*. New York: John Wiley and Sons p. 357-8.

Sharovsky R, Cesar LA, Ramires JA. 2004. Temperature, air pollution, and mortality from myocardial infarction in Sao Paulo, Brazil. *Braz J Med Biol Res* 37:1651-7.

Son J, Lee J, Kim K, Jung K, Bell M. 2012. Characterization of fine particulate matter and associations between particulate chemical constituents and mortality in Seoul, Korea. *Environ Health Perspect* 120(6): 872–878.

Song Y, Tang X, Xie S, Zhang Y, Wei Y, Zhang M, Zeng L, Lu S. 2007. Source apportionment of PM_{2.5} in Beijing in 2004. *Journal of Hazardous Materials*. 146(1-2): 124-130.

Song Y, Xie S, Zhang Y, Zeng L, Salmon L, Zheng M. 2006. (1) Source apportionment of PM_{2.5} in Beijing using principal component analysis/absolute principal component scores and UNMIX. *Science of the Total Environment* 372(1): 278-286.

Song Y, Zhang Y, Xie S, Zeng L, Zheng M, Salmon L, Shao M, Stanina S. 2006. (2) Source apportionment of PM_{2.5} in Beijing by positive matrix factorization. *Atmospheric Environment* 40(8): 1526-1537.

Stahl, QR. 1969. Air pollution aspects of aldehydes. Prepared for the National Air Pollution Control Administration Consumer Protection & Environmental Health Service. Department of Health, Education, and Welfare (Contract No. PH-22-68-25).

Statheropoulos M, Vassiliadis N, Pappa A. 1998. Principal component and conical correlation analysis for examining air pollution and meteorological data. *Atmospheric Env* 32(6): 1087-1095.

Streets DG, Fu JS, Jang CJ, Hao JM, He KB, Tang XY, et al. 2007. Air quality during the 2008 Beijing Olympic Games. *Atmospheric Environment* 41:480-92.18

Sullivan JH, Schreuder AB, Trenga CA, et al. 2005. Association between short term exposure to fine particulate matter and heart rate variability in older subjects with and without heart disease. *Thorax* 60:462-6.

Symons JM, Wang L, Guallar E, et al. 2006. A case-crossover study of fine particulate matter air pollution and onset of congestive heart failure symptom exacerbation leading to hospitalization. *Am J Epidemiol* 164(5):421-433.

Tang XY. 2004. Urbanization, energy, and air pollution in china. Washington DC: The National Academies Press p 47-54.

Timonen KL, Vanninen E, De Hartog J, Ibaldo-Mulli A, Brunekreef B, Gold DR, Heinrich J, Hoek G, Lanki T, Peters A, Tarkkiainen P, Kreyling W, Pekkanen J. 2006. Effects of ultrafine and fine particulate and gaseous air pollution on cardiac autonomic control in subjects with coronary artery disease: the ULTRA study. *J Exp Sci Environ Epidemiol* 16:332-341.

Tolbert PE, Klein M, Metzger KB, et al. 2000. Interim results of the study of particulates and health in Atlanta (SOPHIA). *J Expo Anal Environ Epidemiol* 10:446-60.

Tsai SS, Goggins WB, Chiu HF, Yang CY. 2003. Evidence for an association between air pollution and daily stroke admissions in Kaohsiung, Taiwan. *Stroke* 34:2612-6.

Vassalle, C., Petrozzi, L., Botto, N., Andreassi, M. G., Zucchelli, G. C., 2004 Oxidative stress and its association with coronary artery disease and different atherogenic risk factors. *J Intern Med* 256, (4), 308-15.

Vedal S, Rich K, Brauer M, White R, Petkau J. 2004. Air pollution and cardiac arrhythmias in patients with implantable cardioverter defibrillators. *Inhal Toxicol* 16:353-62.

- Wang H, Zhuang Y, Wang Y, Sun Y, Yuan H, Zhuang G, Hao Z. 2008. Long-term monitoring and source apportionment of PM_{2.5}/PM₁₀ in Beijing, China. *Journal of Environmental Sciences* 20(11):1323-1327.
- Wang M, Zhu T, Zheng J, Zhang RY, Zhang SQ, Xie XX, et al. 2009a. Use of a mobile laboratory to evaluate changes in on-road air pollutants during the Beijing 2008 Summer Olympics. *Atmospheric Chemistry and Physics* 9:8247-63.
- Wang SX, Zhao M, Xing J, Wu Y, Zhou Y, Lei Y, et al. 2010a. Quantifying the air pollutants emission reduction during the 2008 Olympic Games in Beijing. *Environmental Science & Technology* 44:2490-6.
- Wang T, Nie W, Gao J, Xue LK, Gao XM, Wang XF, et al. 2010b. Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact. *Atmospheric Chemistry and Physics Discussion* 10:12433-63.
- Wang T, Nie W, Gao J, Xue LK, Gao XM, Wang XF, et al. 2010c. Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact. *Atmospheric Chemistry and Physics* 10:7603-15.
- Wang T, Xie SD. 2009. Assessment of traffic-related air pollution in the urban streets before and during the 2008 Beijing Olympic Games traffic control period. *Atmospheric Environment* 43:5682-90.
- Wang X, Westerdahl D, Chen LC, Wu Y, Hao JM, Pan XC, et al. 2009b. Evaluating the air quality impacts of the 2008 Beijing Olympic Games: On-road emission factors and black carbon profiles. *Atmospheric Environment* 43:4535-43.
- Wang XS, Li JL, Zhang YH, Xie SD, Tang XY. 2009c. Ozone source attribution during a severe photochemical smog episode in Beijing, China. *Science in China Series B-Chemistry* 52:1270-80.
- Wang Y, Hao J, McElroy MB, Munger JW, Ma H, Chen D, et al. 2009d. Ozone air quality during the 2008 Beijing Olympics: effectiveness of emission restrictions. *Atmospheric Chemistry and Physics* 9:5237-51.
- Weisel CP, Zhang J, Turpin BJ, Morandi MT, Colome S, Stock TH, et al. 2005. Investigators' report: Relationships of Indoor, Outdoor, and Personal Air (RIOPA). Part I. Collection methods and descriptive analyses. Research Report 130. Health Effects Institute (HEI) and the Mickey Leland National Urban Air Toxics Center. Boston, MA.
- Wellenius GA, Bateson TF, Mittleman MA, Schwartz J. 2005. Particulate air pollution and the rate of hospitalization for congestive heart failure among medicare beneficiaries in Pittsburgh, Pennsylvania. *Am J Epidemiol* 161:1030-6.

Wellenius GA, Schwartz J, Mittleman MA. 2005. Air pollution and hospital admissions for ischemic and hemorrhagic stroke among medicare beneficiaries. *Stroke* 36:2549-53.

Wellenius GA, Schwartz J, Mittleman MA. 2006. Particulate air pollution and hospital admissions for congestive heart failure in seven United States cities. *Am J Cardiol* 97:404-8.

Wordley J, Walters S, Ayres J. 1997. Short term variations in hospital admissions and mortality and particulates air pollution. *Occup Environ Med* 54:108-116.

Xin JY, Wang YS, Tang GQ, Wang LL, Sun Y, Wang YH, et al. 2010. Variability and reduction of atmospheric pollutants in Beijing and its surrounding area during the Beijing 2008 Olympic Games. *Chinese Science Bulletin* 55:1937-44.

Yan X, Ohara T, Akimoto H. 2006. Bottom-up estimate of biomass burning in mainland China. *Atmospheric Environment* 40(27): 5262-5273.

Zanobetti A, Schwartz J, Dockery DW. 2000. Airborne particles are a risk factor for hospital admissions for heart and lung disease. *Environ Health Perspect* 108:1071-1077.

Zanobetti A, Schwartz J. 2005. The effect of particulate air pollution on emergency admissions for myocardial infarction: a multicity case-crossover analysis. *Environ Health Perspect* 113:978-82.

Zhang J, Zhang L, Fan Z, Ilacqua V. 2000. Development of the personal aldehydes and ketones sampler based upon DNSH derivatization on solid sorbent. *Environmental Science & Technology* 34:2601-7.

Zhang JF, He QC, Liyo PJ. 1994. Characteristics of aldehydes - concentrations, sources, and exposures for indoor and outdoor residential microenvironments. *Environmental Science & Technology* 28:146-52.

Zhang JF, Smith KR. 1999. Emissions of carbonyl compounds from various cookstoves in China. *Environmental Science & Technology* 33:2311-20.

Zhang JF, Zhu T, Kipen H, Wang G, Huang W, Rich D, Zhu P, Wang Y, Lu S, Ohman-Strickland P, Diehl S, Hu M, Tong J, Gong J, and Thomas D, 2013. Cardiorespiratory biomarker responses in healthy young adults to drastic air quality changes surrounding the 2008 Beijing Olympics. *Health Effects Institute Report #*: 174, 2013-03-11.

Zhang JJ, McCreanor JE, Cullinan P, Chung KF, Ohman-Strickland P, Han IK, Järup L, Nieuwenhuijsen MJ. 2009. Health effects of real-world exposure to diesel exhaust in persons with asthma. *Res Rep Health Eff Inst*. 138: 5-109.

Zheng M, Salmon L, Schauer J, Zeng L, Kiang C, Zhang Y, Cass G. 2005. Seasonal trends in PM_{2.5} source contributions in Beijing, China. *Atmospheric Environment* 39: 3967-3976.

Zhou Y, Wu Y, Yang L, Fu LX, He KB, Wang SX, et al. 2010. The impact of transportation control measures on emission reductions during the 2008 Olympic Games in Beijing, China. *Atmospheric Environment* 44:285-93.

Zmirou D, Schwartz J, Saez M, Zanobetti A, Wojtyniak B, Touloumi G, Spix C, Ponce de Leon A, Le Moullec Y, Bacharove L, et al. 1998. Time-series analysis of air pollution and cause-specific mortality. *Epidemiology* 9:495-503.