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Millsboro Inhalation Exposure and Biomonitoring Study

Final Report

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Executive Summary

The Millsboro Inhalation Exposure and Biomonitoring Study (MIEBS) was initiated to improve our understanding of the exposures of residents of Sussex County, Delaware to fine particulate matter ($PM_{2.5}$) and associated inorganic species. The study is focused on out of state, local regional and local point sources, in particular, the NRG Energy power plant near Millsboro, that contribute to the overall exposures of the residents. The study is designed to estimate the relative contributions of these sources by sampling indoor, outdoor, and personal air for $PM_{2.5}$ in locations both upwind and downwind of the power plant. Samples are assessed for PM mass, environmental tobacco smoke (ETS) in personal samples, and a suite of inorganic elements with selenium, arsenic, mercury, nickel, and chromium of special interest. The environmental samples are supplemented with blood, urine, and hair samples for analysis of volatile organic compounds (VOCs) and metals in blood and metals in urine and, in the future, hair. The sampling plan was designed to capture exposures during the Fall of 2011 and 2012. During the Fall 2011 season, the NRG Energy power plant was not operating while engineering upgrades designed to reduce pollutant emissions were installed. The Fall 2012 sampling period was conducted while the power plant was operational, though not at 100% capacity. This sampling design allowed for an indication of the power plant contribution to local PM exposures.

The Fall 2011 and Fall 2012 sample collection periods included 32 participants recruited from the vicinity of the NRG Energy power plant in Sussex County, Delaware. The participants allowed personal, indoor residential and outdoor residential particulate matter samples to be collected over 3 consecutive days. Surveys characterized participant demographics and residence characteristics. Meteorological records permitted assessment of upwind or downwind location relative to the power plant when both phases of sampling were completed and data were analyzed. Participants also provided blood, urine, and hair samples. Regional background particulate matter samplers were deployed to obtain a broader picture of the regional air quality.

The average outdoor residential $PM_{2.5}$ mass concentration over the course of both sampling seasons was 11.4 $\mu g/m^3$, which is below the Federal annual standard of 15 $\mu g/m^3$. Indoor residential samples during this period indicated an average $PM_{2.5}$ level of 11.7 $\mu g/m^3$. This difference was not statistically significant. Personal concentrations (avg. 21.4 $\mu g/m^3$), however, were statistically higher than outdoor and indoor concentrations. One possible reason for this is that personal samples were influenced by the proximity and source strength of common indoor activities (e.g. smoking, cooking, cleaning, use of personal care products, etc.). Regional background average particulate concentrations were the lowest of all four measurement locations. The inter-comparison between ambient monitors located around NRG Energy power plant and the Seaford FRM monitor showed excellent agreement with average $PM_{2.5}$ concentrations between these samplers over the course of both sampling periods being 9.3 $\mu g/m^3$ and 8.9 $\mu g/m^3$, respectively.

Elemental analysis of filters collected during the Fall 2011 and Fall of 2012 sampling periods displayed similar elements and concentrations as has been found elsewhere in the Northeastern United

States (Ondov, 2006) The exception to this occurred with personal level samples. Personal samples were enriched with Bromine (avg. 686.4 ng/m^3) when compared to outdoor samples collected during this study (avg. 3.9 ng/m^3). These elements have several potential indoor sources, including environmental tobacco smoke, which would require further sampling and data analysis to identify.

Results for the blood biospecimen samples showed that none of the analytes were above the reference values for the 32 participants during either season. Urinary Arsenic and Selenium were above the reference ranges in 12 of the participants during Season 1 while these same two metals were similarly above reference values in 8 of the participants during Season 2. Although uncertain, this may be attributable to dietary exposure. Further investigation would be needed to better understand this finding.

The MIEBS resulted in high quality data that could serve as a baseline for additional studies in the future. The motivated Sussex County residents willing to participate in this exposure health study contributed significantly to the quality of the data collected. Data revealed expected spatial and elemental distributions with concentration differences being observed between indoor, personal, outdoor, and background sampling locations. Significantly, data demonstrated that ambient background $PM_{2.5}$ concentrations in southern Delaware are driven by long-range airborne transport from neighboring upwind states and metropolitan areas.

Table of Contents

Executive Summary.. i

Table of Contents.. iii

List of Figures v

List of Tables vii

Forward.. viii

Acknowledgments.. ix

List of Acronyms.. x

Introduction 1

  Background 1

  Study Purpose and Goals 1

    Data for Objective 1—Evaluation of IRPP Operating Capacity 2

    Data for Objective 2—Contribution of Out-of-State Sources to Sussex County $PM_{2.5}$ Exposures........ 2

    Data for Objective 3—Contribution of Other Sources to $PM_{2.5}$ Exposure 2

    Data for Objective 4—Collect Biological Specimens.. 2

  Hypotheses 3

  Report Framework.. 3

Study Methodology.. 4

  Sample Analysis.. 7

    Gravimetric Analysis 7

    Environmental Tobacco Smoke/Brown Carbon and Black Carbon Analysis.. 7

    X-Ray Fluorescence Analysis 8

    Urine Analysis.. 8

    Blood Analysis 8

Data Quality Results.. 8

Sample Results.. 9

  Seaford Site 9

  Fixed Site Data 10

  Outdoor $PM_{2.5}$ Residential Data.. 16

  Indoor $PM_{2.5}$ Residential Data.. 21

  Personal $PM_{2.5}$ Data 26
  Residential Temperature and Humidity 32
  Questionnaires 32
  Biospecimen Samples 32
Evaluation of Study Objectives and Hypothesis 49
  Objective 1 49
  Objective 2 50
  Objective 3 53
  Objective 4 57
Conclusions 57
Recommendations 58
References 61
Appendices I
  Appendix A: Questionnaire Data I
  Appendix B: Reference Ranges for Analytes in Blood or Serum (Provided by DHSS) VI
  Appendix C: Reference Ranges for Analytes in Urine (Provided by DHSS) VII
  Appendix D: Data Quality Indicator Determination Methods VIII
Glossary XVI

List of Figures

Figure 1. Participant Sampling area (Red circle) with number of participants in each sector denoted (including two replacement participants for 2012), Fixed Sites (Green), and NRG Energy power plant (Yellow) during both Season 1 and 2 of the MIEBS Study. Note the Seaford monitor is not shown. 6

Figure 2. Distributions of Seaford Site $PM_{2.5}$, BrC, and BC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 11

Figure 3. Comparison of XRF data Collected at the Seaford Site from 2011 and 2012. 11

Figure 4. Comparison of collocated Seaford FRM and RTI PEM during both seasons. 12

Figure 5. Distributions of Fixed Site $PM_{2.5}$ concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 13

Figure 6. Distributions of Fixed Site BrC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 14

Figure 7. Distributions of Fixed Site BC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 15

Figure 8. XRF Results from 2011 Fixed Site ambient samplers, Trace elements above MDL not shown. .. 17

Figure 9. XRF Results from 2012 Fixed Site ambient samplers, Trace elements above MDL not shown. .. 17

Figure 10. Distributions of outdoor residential $PM_{2.5}$ concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 18

Figure 11. Distributions of outdoor residential BrC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 19

Figure 12. Distributions of outdoor residential BC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 20

Figure 13. XRF analysis of outdoor residential samples from 2011 & 2012. 21

Figure 14. Distributions of indoor residential $PM_{2.5}$ concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 22

Figure 15. Distributions of indoor residential ETS concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 23

Figure 16. Distributions of indoor residential BC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 24
Figure 17. Comparison of XRF analysis for indoor residential $PM_{2.5}$ during 2011 & 2012. 25
Figure 18. Indoor residential-outdoor residential ratio of select elements. 25
Figure 19. Distributions of personal level $PM_{2.5}$ concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 27
Figure 20. Distributions of personal level ETS concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 28
Figure 21. Distributions of personal level BC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2. 29
Figure 22. 24-hr Trend of 5-minute averaged $PM_{2.5}$ from high and low ETS participants. 30
Figure 23. XRF analysis of RTI MicroPEM filters from Seasons 1 and 2. 31
Figure 24. Blood metals distribution for all participants during 2011 (Red) and 2012 (Blue). 38
Figure 25. Urine metals distributions for all participants during 2011 (Red) and 2012 (Blue). 39
Figure 26. Upwind/downwind ratios of fixed site monitors during both sampling seasons. 50
Figure 27. Comparison of Seaford and four fixed site monitors $PM_{2.5}$ concentrations during 2011 (Red, NRG Energy power plant not operating) and 2012 (Blue, power plant operating) sampling seasons. 51
Figure 28. Wind direction and ambient $PM_{2.5}$ concentrations during 2011. 52
Figure 29. Wind direction and ambient $PM_{2.5}$ concentrations during 2012. 53
Figure 30. Back trajectory analysis for November 7th, 2012. Different color traces represent air masses initiated at 6-hour time points during the 72-hour analysis. 53
Figure 31. Panel A) Log-probability graph highlighting those participant days with $PM_{2.5}$ exposure greater than 35 µg/m3. Panel B) Log-probability graph showing the majority of those same participant days as also having the highest ETS concentrations. 55
Figure 32. Contributions of $PM_{2.5}$ from each sampling location to the overall $PM_{2.5}$ for Season 1(NRG Energy power plant not operting) and Season 2 (power plant operating). The large influence of personal level sources to $PM_{2.5}$ can be seen, with lesser contributions from indoor and outdoor residential as well as ambient sources. Values above each source represent the geometric mean for that source during that sampling year. 57

List of Tables

Table 1. Detailed list of sampling days for Season 1. 6
Table 2. Detail list of sampling days for Season 2. 7
Table 3. Data validity distributions for $PM_{2.5}$ samples for season 1 by sampling location. 9
Table 4. Data validity distributions for $PM_{2.5}$ samples for season 2 by sampling location. 9
Table 5. Average temperatures and relative humidities for Season 1 & Season 2 participants. 32
Table 6. 2011 Concentrations of metals in urine (ppb).[i] 33
Table 7. 2012 Concentrations of metals in urine (ppb). [i] 34
Table 8. 2011 and 2012 blood metals concentrations (ppb). 35
Table 9. Participants for whom any of the analytes in blood or urine exceeded high reference value (* indicates a measurement above the reference value). 37
Table 10. Pearson correlations of PM mass with biospecimen elements by year. 40
Table 11. Pearson correlations of ETS mass with biospecimen elements by year. 41
Table 12. Pearson correlations of BC mass with biospecimen elements by year. 43
Table 13.Pearson correlations of elements on personal filters by XRF with biospecimen elements by year. 46
Table 14. Pearson correlations of elements on personal filters by XRF with biospecimen elements across years. 47
Table 15. Evaluation of exceedances for Arsenic and Selenium in the context of possible ingestion routes. 48
Table 16. Percentage of the personal PM2.5 exposure due to ambient, indoor residential, and other sources. Data are presented by season, and stratified by residences without significant ETS and all residences (ETS and non-ETS). Average and standard deviation for each source are presented. Ambient and indoor percentages are calculated from the personal, indoor, and outdoor data. The “Other” source consists of proximity to localized sources within the participant’s home, transportation, and indoors at other locations; it is calculated by difference. 56
Table 17. Summarized participant questionnaire results Season 1. I
Table 18. Summarized participant questionnaire results Season 2. II
Table 19. Summarized residential questionnaire results Season 1. III
Table 20. Summarized residential questionnaire results Season 2. IV
Table 21. Summarized additional questionnaire data taken during season 2. V
Table 22. Target DQI's for each metric and analyte. IX
Table 23. Target quantitative DQI's for XRF analysis. XI
Table 24. Actual DQIs from MIEBS Seasons 1 & 2. XIII
Table 25. Actual DQIs for XRF Analysis of MIEBS Season 1 & 2 data. XIII

Forward

The Millsboro Inhalation Exposure and Biomonitoring Study (MIEBS) was performed to assess the role of the NRG Energy power plant in Millsboro, Delaware in increasing the exposure of Sussex County residents to particulate matter, metals, and selected organic contaminants. The study involved the collection of outdoor air quality data, indoor air quality data, personal air quality data, biospecimen data, and questionnaire data in the Fall of 2011 and the Fall of 2012. This report presents the objectives, methods, results, and conclusions of the study.

This study has been a partnership between the Delaware Department of Natural Resources and Environmental Control (DNREC) and the Delaware Department of Health and Social Services (DHSS), with technical assistance from RTI International who was contracted to perform the environmental sampling and analysis.

Acknowledgments

Foremost, this study would not be possible without the participation and support of the Sussex County residents. Thirty-five Sussex County residents participated in the study, while numerous others expressed a willingness to participate.

This project was underwritten by the Delaware Department of Natural Resources and Environmental Control and the Delaware Cancer Consortium, in collaboration with the Delaware Health Fund.

Several RTI International (RTI) staff contributed significantly to this project. Dr. Jonathan Thornburg and Dr. James Raymer were co-Principal Investigators. Dr. Quentin Malloy managed the daily technical details of sample collection and analysis. Michael Philips recruited the study participants. Cortina Johnson and Jocelin Deese-Spruill spent six weeks in Delaware in 2011 and 2012 working with the participants to collect the particulate matter samples. Meaghan McGrath and Andrea McWilliams analyzed the collected environmental samples. Larry Michael performed the statistical analysis of the data. Lastly, Wayne Dawson is a Sussex County resident hired by RTI as a temporary contractor to assist with sample collection.

RTI conducted this project in conjunction with the Delaware Department of Natural Resources and Environmental Control (DNREC) and Delaware Health and Social Services Division of Public Health (DPH). Elizabeth Frey (DNREC), Lisa Henry (DPH), and Richard Perkins (DPH) provided oversight of the project. Mohammed Majeed (DNREC) performed air dispersion modeling to aid siting of the fixed site air monitors and identify areas for participant recruitment. Susan Mitchell, R.N. (DPH) collected the biological specimens from the participants. The Delaware Public Health Laboratory, under the direction of Tara Lydick, analyzed the biological specimens. Richard Greene (DNREC) provided extensive comments that improved the quality of this report.

List of Acronyms

µg: Microgram
BC: Black Carbon
BrC: Brown Carbon
C_m: Measured concentration of a spiked sample
C_s: Measured concentration of a spiked solution
C_{sample}: Measured concentration of a sample
C_{std}: Measured concentration of a certified standard
C_u: Measured concentration of an unspiked sample
DHSS: Delaware Department of Health and Social Services
DNREC: Delaware Department of Natural Resources and Environmental Control
DPHL: Delaware Public Health Laboratory
DQI: Data Quality Indicator
ETS: Environmental Tobacco Smoke
FRM: Federal Reference Method
ICP-DRC/MS: Inductively Coupled Plasma-Dynamic Reaction Cell/Mass Spectrometry
ICP-MS: Inductively Coupled Plasma-Mass Spectrometry
LPM: Liter Per Minute
MDL: Minimum Detection Limit
MIEBS: Millsboro Inhalation Exposure and Biomonitoring Study
MQL: Minimum Quantification Limit
P/I: Personal-to-Indoor ratio
PEM: Personal Exposure Monitor
PM: Particulate Matter
$PM_{2.5}$: Particulate Matter with an aerodynamic diameter equal to or less than 2.5 micrometers
RSD: Relative Standard Deviation
RTI: Research Triangle Institute
SD: Standard Deviation
SPME-GC: Solid-Phase Micro Extraction-Gas Chromatography
TAD: Time Activity Diary
VOC: Volatile Organic Compound
XRF: X-Ray Fluorescence

Introduction

Background

Evidence is increasing that long-term human exposure to particulate matter (PM) has negative impacts on human health, including adverse respiratory and cardiovascular effects (Dockery 2001; Ito et al. 2011). It has also been demonstrated that acute exposures to elevated PM can lead to a myriad of health end points, including non-accidental mortality, total mortality, respiratory deaths, and morbidity (Goldberg et al. 2001; Laden et al. 2000; Hoek et al. 2001; Zanobetti, Schwartz, and Dockery 2000). However, there exists a need for more information about the amount and composition of this PM as it relates to health end points of the exposed population. Those who live close to sources of $PM_{2.5}$ (PM with an aerodynamic diameter equal to or less than 2.5 micrometers) are especially vulnerable to the negative impacts; therefore, federal and state agencies have made it a priority to gather more information concerning the health outcomes of long-term exposure to these particles.

Research has shown the spatial gradients in $PM_{2.5}$ to be smaller than PM_{10} (PM with an aerodynamic diameter equal to or less than 10 micrometers) with concentrations being higher in urban areas and close to point sources, but temporal trends are stronger with $PM_{2.5}$ (Environment Canada-Health Canada 2000; Thornburg et al. 2009; Rodes et al. 2010). It has also been noted that strong diurnal trends exist with the chemical composition of $PM_{2.5}$ (Cheung et al. 2011). Many factors influence these gradients, including temperature, wind direction, and human activity patterns. Because of the regional nature of $PM_{2.5}$, the adverse health effects associated with it are more widespread and can be harder to link to specific sources. This is especially compounded by the paucity of personal exposure data.

Study Purpose and Goals

This study centers around the DESIGN I plan presented to the Department of Natural Resources and Environmental Control (DNREC) by RTI International in June 2008 (DNREC-OTS, 2008). The DESIGN I plan described a multi-media exposure study in Sussex County that would serve as a pilot effort as a prelude to a statewide study. The scope of the DESIGN I plan was reduced in accordance with the available budget resources. The final study design yielded the Millsboro Inhalation Exposure and Biomonitoring Study (MIEBS). Although MIEBS was developed to explore inhalation exposure pathways, it is possible alternative exposure routes, such as seafood consumption, may be of interest though outside the scope of MIEBS (Greene and Crecelius, 2006). MIEBS addressed four objectives over the course of an 18-month study. MIEBS had the following objectives:

1) Evaluate the impacts of the NRG Energy power plant operating capacity on $PM_{2.5}$ exposure levels of the Sussex County population.
2) Ascertain the relative contributions of upwind sources in Virginia, Maryland, Pennsylvania, New York, and the New England area on the $PM_{2.5}$ exposure of the Sussex County population.
3) Establish the contribution of point, local, and personal sources to the Sussex County population's exposure to $PM_{2.5}$.
4) Collect biological samples for dose measurements of the Sussex County population.

Objectives one, two, and three focused on the NRG Energy power plant, other ambient sources, and residential sources and their impact on the inhalation exposures of the surrounding Sussex County population. Objective four attempted to link the participants PM2.5 exposures to their dose of specific chemical species.

Data for Objective 1—Evaluation of NRG Energy Power Plant Operating Capacity

To evaluate the effect of the NRG Energy power plant operating capacity on $PM_{2.5}$ exposures of the Sussex County population, air samples were collected in a variety of locations over the course of two periods (non-operating and operating). The locations included fixed site monitors located upwind and downwind of the power plant. In addition to the fixed sites, samples were taken outside and inside participants' houses along with personal air samples. It should be noted that NRG Energy power electricity generation load fluctuated daily during the second season.

Measurements for this objective included not only $PM_{2.5}$ mass, but also $PM_{2.5}$ composition, which included environmental tobacco smoke (ETS), brown carbon (BrC), black carbon (BC), and metals. Metals were identified for analysis based on previous studies by DNREC (DNREC, 2006) along with the current U.S. Environmental Protection Agency (EPA) criteria document (U.S. EPA 2004).

Data for Objective 2—Contribution of Out-of-State Sources to Sussex County $PM_{2.5}$ Exposures

In addition to evaluating the effect of the NRG Energy power plant operating capacity, RTI determined the relative contribution of sources in upwind states such as Pennsylvania, Maryland, and Virginia to Sussex County $PM_{2.5}$. For this objective, meteorological data and optimal spatial distribution of monitors was key. Data from the same samples were used to address Objectives 1 and 2 through proper spatial planning of sampler deployment.

Data for Objective 3—Contribution of Other Sources to $PM_{2.5}$ Exposure

Data collection for Objective 3 used the same sampling platforms as used in Objective 1. This information was used to locate potential sources of $PM_{2.5}$ other than the NRG Energy power plant, which could significantly contribute to the exposure of the Sussex County population. The questionnaires and permitting database mining were used in conjunction with the personal sampling to gather detailed data concerning personal exposures.

Data for Objective 4—Collect Biological Specimens

Blood, hair, and urine samples were collected from each participant once during each sampling campaign. These biospecimens were used to investigate changes in personal $PM_{2.5}$ measures (mass, ETS) with changes in human exposure. Of particular interest were changes in $PM_{2.5}$ that might be associated with the NRG Energy power plant. Blood and urine samples were analyzed by DHSS. Blood samples were analyzed for VOCs and metals and urine samples were analyzed for metals. Blood, urine, and hair were archived for potential future analysis of other environmental pollutants. Blood and urine samples were archived at -80C.

Hypotheses

The hypotheses for each objective are outlined below. The details describing how each hypothesis was tested are provided in more detail in the following section.

Objective 1

Hypothesis 1: Contributions of the NRG Energy power plant to ambient $PM_{2.5}$ concentrations in Sussex County will increase with increasing usage of the electricity generating capacity of the power plant. Indoor residential and personal $PM_{2.5}$ concentrations will not be affected.

Objective 2

Hypothesis 2: Upwind source contributions to ambient Sussex County $PM_{2.5}$ levels will be detectable, and their relative contribution to the $PM_{2.5}$ concentration will decrease as the load on the NRG Energy power plant increases. However, exact sources will be difficult to determine unless a unique emissions profile exists.

Hypothesis 3: The relative contribution of upwind sources from bordering states to the ambient $PM_{2.5}$ concentration will decrease as usage of the energy generating capacity from the NRG Energy power plant increases.

Objective 3

Hypothesis 4: Relative contributions of other point $PM_{2.5}$ sources to ambient concentrations will decrease after the NRG Energy power plant increases its electricity generation.

Hypothesis 5: Personal sources will contribute more to $PM_{2.5}$ exposure relative to during the low electricity generation period than during the high generation sampling period.

Objective 4

Hypothesis 6: Markers for $PM_{2.5}$ exposure from NRG Energy power plant emissions in biological specimens will increase as the load demand on the power plant increases.

Report Framework

The structure of this report presents the study methodology, data quality summary, PM2.5 concentration and biospecimen data presentation, evaluation of the hypotheses, and the study conclusions/recommendations. The study methodology summarizes the study area, participants, and sample collection methods. The data quality summary provides an overview of data capture for each metric, including reasons for invalid samples. Subsequent sections present PM2.5 concentrations from each sampling season along with corresponding environmental tobacco smoke (ETS) and black carbon (BC) measurements. Particulate metals analysis performed by X-ray fluorescence (XRF) is also presented during discussion of results from each sample type. Following the data presentation, discussion of the study objectives and hypotheses in the context of the previously presented data is performed followed by conclusions and recommendations by RTI.

Study Methodology

RTI conducted two sampling periods for the MIEBS in October through November of 2011 and October through November of 2012. Data acquired during the first sampling campaign (hereinafter referred to as Season 1) captured PM concentrations while the NRG Energy power plant was shut-down for the installation of pollution control technologies. The second campaign (hereinafter referred to Season 2) took place after the power plant had resumed operation. Sample collection consisted of personal exposure, residential indoor, residential outdoor, and ambient fixed site monitoring. Figure 1 presents the area of Sussex County sampled, and the three sectors where recruited participants reside. Four fixed site ambient monitors near the power plant are also shown; the DNREC ambient monitoring site, not shown, is located in Seaford, Delaware.

Multiple types of personal exposure monitors collected $PM_{2.5}$ filter samples. RTI used the MicroPEM™ to collect $PM_{2.5}$ personal exposure samples. Participants wore the MicroPEM unit during their normal, daily activities. Participants did not wear the unit while bathing or sleeping. The MicroPEM operated at 0.5 LPM and collected $PM_{2.5}$ on a 25 mm Teflo® filter (Gelman Sciences, Ann Arbor, Michigan, 3 µm porosity) during both seasons. Participants during the second season used MicroPEM units that also contained nephelometers which permitted real-time $PM_{2.5}$ mass concentration to be collected. RTI deployed Personal Exposure Monitors (PEMS, MSP Corporation, Minneapolis, MN) as stationary residential indoor, residential outdoor, and ambient $PM_{2.5}$ samplers. A PEM unit is a single channel $PM_{2.5}$ inlet operating at either 2 or 4 liters per minute (LPM) with a 37 mm Teflo filter and 2 µm porosity.

RTI recruited and enrolled 32 participants for each season. Participant retention was high, with 29 recruits (91%) participating in both sampling seasons. Three replacement participants were recruited in 2012 from the same sector (Figure 1) as the participants that withdrew. Participants were grouped into eight cohorts of 4 participants each. There was no constraints put on participant involvement for smokers, nor was questionnaire data collected that related to their smoking habits. Eight participants per week were scheduled to complete the campaign within the 4-week window available. The exception to this was during the second sampling season when Hurricane Sandy forced a suspension in all sampling activities during the course of four days (October 29-November 1).

The five fixed sites operated continuously with filters being replaced every 24 hours, except at the Seaford site, which operated on a 1-in-3 day schedule corresponding to the DNREC $PM_{2.5}$ FRM monitor. The four 24-hour fixed site monitors were located within a 2.5 mile radius of the power plant, whereas the Seaford site was located 21-miles west of the power plant, therefore data obtained from the Seaford site is presented separately in order to uncover potential regional transport of power plant associated $PM_{2.5}$. Tables 1 and 2 provide a detailed overview of the sampling schedule and frequency of visits during the each campaign. The appointment schedule minimized time burdens on the participants and avoided conflict with the Thanksgiving holiday. Personal, indoor, and outdoor sampling occurred daily for each participant. After each 24-hour period, technicians arrived at a prearranged time to retrieve the used samplers and replace them with fresh samplers. Also during this time, technicians administered a short questionnaire (time-activity diary or TAD) about the participant's activities the previous day. At the beginning of each participant 3-day sampling period technicians also conducted a residential survey to gather information about each residence. Lastly, a temperature and humidity sensor (HOBO) was placed within each participant's household during the 3-day sampling period.

Hair, blood, and urine samples were collected from all participants by a registered DHSS nurse at the first appointment time. Due to scheduling constraints and minimization of time burden to the participant, the urine samples were not always the first morning void. All biospecimen samples were immediately transported to the Delaware Public Health Laboratory. Blood and urine were kept at 0°C during transport. Metals in both blood and urine samples were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). No metals were speciated or creatinine adjusted because creatinine data was not collected during the 2011 period.

Figure 1. Participant Sampling area (Red circle) with number of participants in each sector denoted (including two replacement participants for 2012), Fixed Sites (Green), and NRG Energy power plant (Yellow) during both Season 1 and 2 of the MIEBS Study. Note the Seaford monitor is not shown.

Table 1. Detailed list of sampling days for Season 1.

Participant Sampling Schedule: Season 1			
Cohort 1	**Cohort 2**	**Cohort 3**	**Cohort 4**
Oct 27-29	Oct 30-Nov 1	Nov 3 -5	Nov 6-8
Cohort 5	**Cohort 6**	**Cohort 7**	**Cohort 8**
Nov 10-12	Nov 13-15	Nov 17-19	Nov 19-21
Fixed Site Sampling Schedule			
Northwest	**Southeast**	**Northeast**	**West-SW**
Oct 27-Nov 21	Oct 27-Nov 21	Oct 27-Nov 21	Oct 27-Nov 21
Seaford Site Sampling Schedule			
Oct 27, Oct 30, Nov 2, Nov 5, Nov 8, Nov 11, Nov 14, Nov 17, Nov 20			

Table 2. Detail list of sampling days for Season 2.

<table>
<tr><th colspan="4">Participant Sampling Schedule: Season 2</th></tr>
<tr><th>Cohort 1</th><th>Cohort 2</th><th>Cohort 3</th><th>Cohort 4</th></tr>
<tr><td>Oct 19-21</td><td>Oct 22-24</td><td>Oct 26 -28</td><td>Nov 2-4</td></tr>
<tr><th>Cohort 5</th><th>Cohort 6</th><th>Cohort 7</th><th>Cohort 8</th></tr>
<tr><td>Nov 5-7</td><td>Nov 9-11</td><td>Nov 12-14</td><td>Nov 16-18</td></tr>
<tr><th colspan="4">Fixed Site Sampling Schedule</th></tr>
<tr><th>Northwest</th><th>Southeast</th><th>Northeast</th><th>West-SW</th></tr>
<tr><td>Oct 19-Nov 18</td><td>Oct 19-Nov 18</td><td>Oct 19-Nov 18</td><td>Oct 19-Nov 18</td></tr>
<tr><th colspan="4">Seaford Site Sampling Schedule</th></tr>
<tr><td colspan="4">Oct 21, Oct 24, Oct 27, Nov 2, Nov 5, Nov 8, Nov 11, Nov 14, Nov 17</td></tr>
</table>

Sample Analysis

Gravimetric Analysis

Filter samples collected by the PEM were analyzed by gravimetric analysis following a minimum of 24 hours of equilibration in an environmental weighing chamber. The techniques used to perform the gravimetric analysis and considerations to successfully perform these at low mass loadings have been reported elsewhere (Lawless and Rodes, 1999; Williams et al., 2000d, 2003a).

Environmental Tobacco Smoke/Brown Carbon and Black Carbon Analysis

Quantification of ETS/BrC and BC was performed following gravimetric analysis by means of a novel optical absorbance analysis method. This technique involved a multi-wavelength spherical photometer to speciate the $PM_{2.5}$ determining the absorbance of the collected $PM_{2.5}$ across several different wavelengths. Since ETS/BrC absorbs at near UV wavelengths and BC absorbs much more strongly than ETS at wavelengths near the IR region, this method allows for non-destructive speciation of filter bound $PM_{2.5}$. Details of this method are described elsewhere (Lawless et al., 2004). BrC is generally defined as light absorbing organic matter in atmospheric particulate matter of various origins, including humic like substances, tarry material from combustion or bioaerosols (Andreae and Gelencsér 2006). However, distinguishing BrC from ETS requires wavelengths that are not currently available with the instrumentation. Previous research however has demonstrated that ETS concentrations outdoors are typically much lower than BrC concentrations; therefore, for purposes of this report, BrC is used during discussion of outdoor $PM_{2.5}$ speciation, while ETS is used when discussing indoor or personal level speciation.

X-Ray Fluorescence Analysis

Following gravimetric and optical analysis, the Teflon filters were analyzed for selected elements by X-ray fluorescence (XRF). Details about the normal XRF operational procedures employed for these types of samples have been reported by Dzubay et al. (1988) and Landis et al. (2001).

Urine Analysis

Urine samples were tested by Delaware Public Health Laboratory (DPHL) for trace metals (Ba, Be, Cd, Co, Cs, Mo, Pb, Pt, Sb, Tl, U, W) by inductively coupled plasma mass spectrometry (ICP/MS) and inductively coupled dynamic reaction cell-plasma mass spectrometry (ICP-DRC/MS) (As, Se). This method utilizes small volumes of urine that are spiked with known internal standard solution in an acidified dilute matrix. The method is based upon that utilized by the Centers for Disease Control and Prevention. Plasma is used to ionize the sample and mass spectrometric scanning of resulting specific isotopes to identify the metal species in question. A DRC is used for As and Se to reduce the possibility of interferences from isobaric, doubly charged, and polyatomic species. This provides excellent accuracy, specificity, dynamic range, precision, and multi-element capability. No metals were speciated or creatinine adjusted.

Blood Analysis

DPHL analyzed blood metals (Cd, Hg, Pb) by ICP/MS. This method utilizes small volumes of blood that are spiked with known internal standard solution in a basic diluent matrix. Similar to urine analysis, blood samples are ionized and then a mass spectrometer scans the resulting specific isotopes to identify the metals in question.

Blood Volatile Organic Compounds (VOCs) were analyzed by isotope dilution solid phase micro extraction gas chromatography (SPME-GC/MS). This method utilizes small volumes of blood that are spiked with known isotopically labeled internal standard solution. A microfiber is used to absorb the volatile components released from the blood in the head space of the vial when heated. The components are then desorbed into a heated inlet, separated via GC, ionized, then fragmented into charged fragments which are collected and separated on the basis of their mass / charge ratio with the mass spectrometer. This method is based on a method used by the Centers for Disease Control and Prevention.

Data Quality Results

Tables 3 and 4 present data capture rate for 2011 and 2012 by sample type. Sample collection during each sampling season was generally in excess of 90%.

Table 3. Data validity distributions for $PM_{2.5}$ samples for season 1 by sampling location.

validity code	Outdoor	Indoor	Personal (MicroPEM)	Fixed Sites	Seaford
0	4	6	21	1	0
1	1	0	11	4	0
2	101	104	64	110	11
% valid	95.28	94.55	66.67	95.65	100.00

Reasons for invalid samples during the first season can be divided into three categories:

- Hardware issues (e.g. pump failure; 20 samples)
- Sample issues (e.g. filters physically damaged; 7 samples)
- Participant coordination issues (e.g. participant not home at time of visit; 5 samples)

Table 4. Data validity distributions for $PM_{2.5}$ samples for season 2 by sampling location.

validity code	Outdoor	Indoor	Personal (MicroPEM)	Fixed Sites	Seaford
0	6	7	18	7	1
1	3	0	7	6	0
2	94	95	71	103	8
% valid	91.26	93.13	73.96	88.79	88.88

Reasons for invalid samples during the second season can be divided into three categories:

- Hurricane Sandy (18 samples)
- Filter weight issues (filter weight exceeded 2 standard deviation or negative; 11 samples)
- Hardware issues (7 samples)
- Other (e.g. missing data file, voided filter; 3 samples)

Sample Results

Seaford Site

RTI operated a PEM sampler at the DNREC Seaford site during the MIEBS. This PEM was collocated with a FRM sampler operated by DNREC. Filter sampling for this location followed the 1-in-3 day cycle of the DNREC FRM sampler. Distributions of $PM_{2.5}$, BrC, and BC concentrations for the PEM operated at the Seaford site for both seasons are presented in Figure 2. Lower and upper whiskers within Figure 2 represent the minimum and maximum values, the box encompasses the interquartile range (25th percent to 75th percent) of the data; the horizontal line in the box represents the median or 50th percentile value; and the star represents the arithmetic average of the data. All subsequent data presented as box-and-whisker plots within this report all conform to this standard.

$PM_{2.5}$ data for the Seaford monitoring site were lognormally distributed. Geometric mean $PM_{2.5}$ concentrations during Season 2 (6.7 ± SD 1.6 $\mu g/m^3$) were reduced by 40% in comparison to Season 1 concentrations (11.1 ± SD 1.5 $\mu g/m^3$). BrC was also reduced from Season 1 to Season 2, with concentrations dropping from 1.7 ± SD 1.4 $\mu g/m^3$ during Season 1 to 0.01 ± SD 31.6 $\mu g/m^3$ during Season 2. This trend in decreasing $PM_{2.5}$ from Season 1 to Season 2 continued with BC decreasing between Season 1 (0.6 ± SD 1.7 $\mu g/m^3$) and Season 2 (0.34 ± SD 8.8 $\mu g/m^3$). After transformation of the data to a normal distribution, T-Test's of the $PM_{2.5}$, BrC, and BC indicate that the differences of means between seasons were not significant at an alpha value of 0.01. Operating capacity of the NRG Energy power plant was not available during the 2012 sampling period, therefore a correlation between $PM_{2.5}$ reductions with power plant operation was not possible.

Evaluation of the XRF data (Figure 3) collected during the two sampling seasons reveals that although there was a 26% increase in Sulfur content during this time, it was accompanied by reductions in most other elements, including Calcium (56%), Chlorine (22%), Iron (21%), Magnesium (51%), Sodium (37%), and Silicon (41%). T-Tests ($\alpha=0.01$) of the normally transformed results between seasons indicates that there are no significant differences with the exception of Magnesium, which had a P-value of 0.0002. Because most of the elements that were reduced in mass between the two seasons originate from crustal material, they are most prevalent in their oxide form, a fact which could account for the overall mass reduction from Season 1 to Season 2.

Figure 4 illustrates the comparison between the Seaford FRM $PM_{2.5}$ concentration and the RTI collocated PEM sampler for both seasons (not blank corrected). The first season showed a reasonable correlation (R-squared =0.85). However, the Seaford FRM samples were biased low, possibly due to the increased face velocity of the FRM inducing additional volatilization of filter bound nitrate as has been documented in comparison of $PM_{2.5}$ filters with different filter face velocities (CARB, 1998). The FRM has a face velocity five times greater than the 2 LPM PEM. In contrast to Season 1, comparison of RTI PEM from Season 2 and Seaford FRM samples showed extremely good agreement, with a correlation coefficient of 0.98. This increased correlation could be due to increased filter face velocity of RTI PEMs during the switch to 4 LPM samplers which have a face velocity equal to 40% of the FRM.

Fixed Site Data

PEM samplers were attached to permanent structures at four locations (North, South, East, and West) within approximately 2.5 miles of the NRG Energy power plant. These fixed site samplers operated continuously for 24 hours, with filters from these samplers being collected each day throughout the sampling phase. Fixed site samplers during Season 1 operated at 2 LPM, while Season 2 samplers were operated at 4 LPM. Figures 5-7 below detail the $PM_{2.5}$, BrC, and BC concentration distributions at these sites during Season 1 and Season 2.

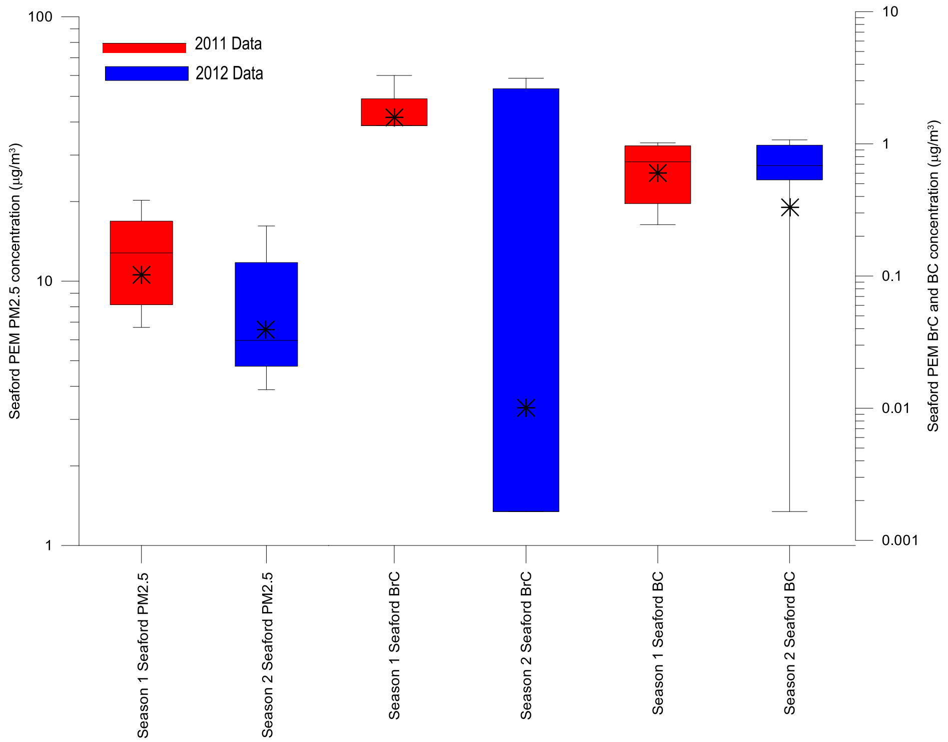

Figure 2. Distributions of Seaford Site $PM_{2.5}$, BrC, and BC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

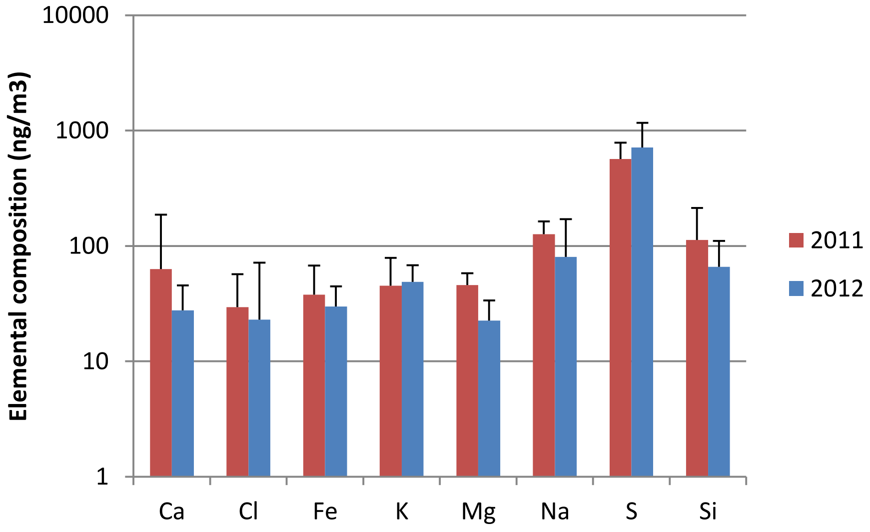

Figure 3. Comparison of XRF data Collected at the Seaford Site from 2011 and 2012.

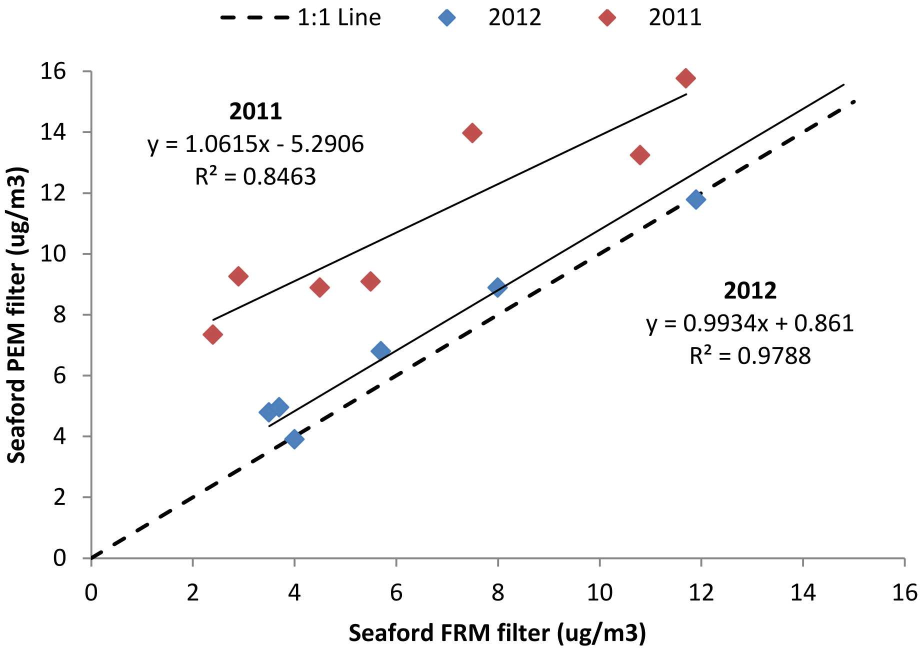

Figure 4. Comparison of collocated Seaford FRM and RTI PEM during both seasons.

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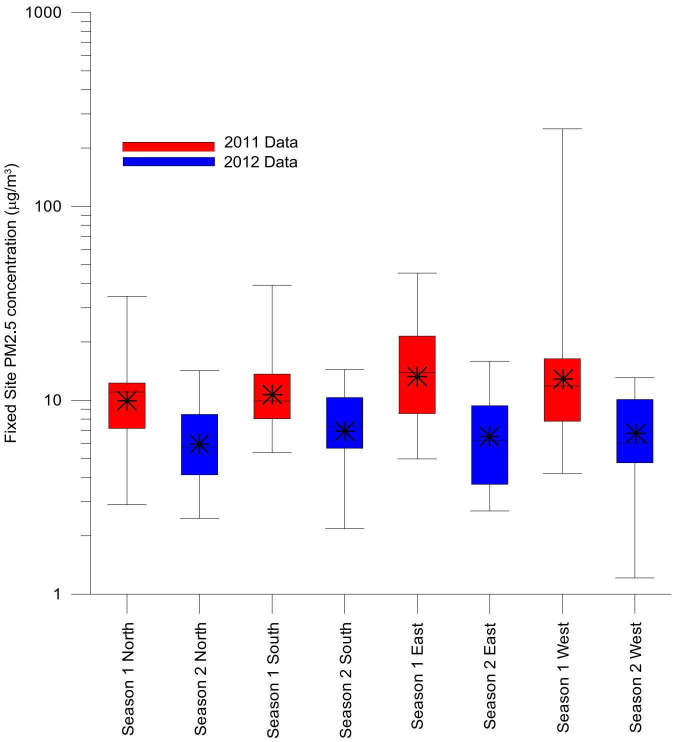

Figure 5. Distributions of Fixed Site PM$_{2.5}$ concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

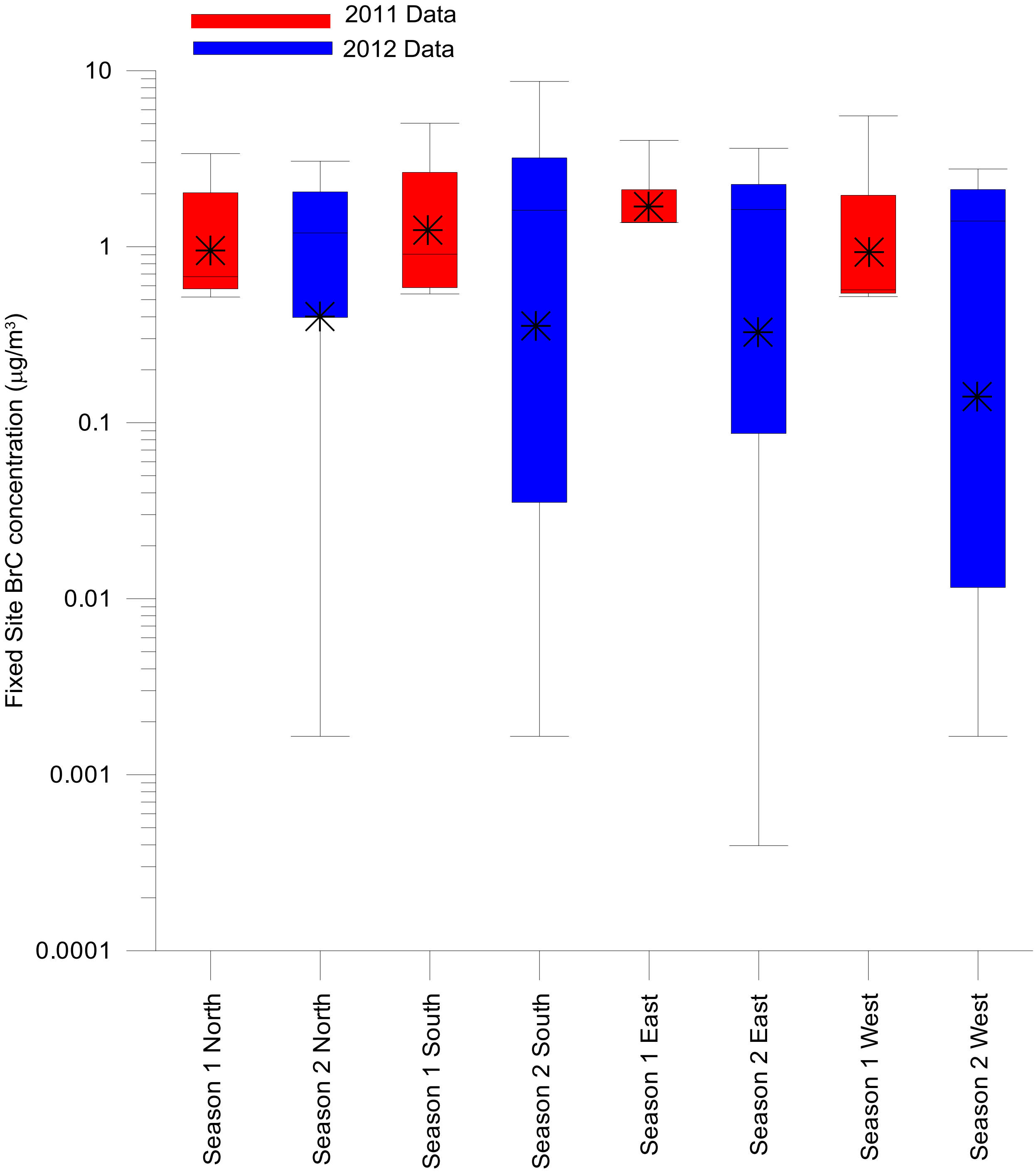

Figure 6. Distributions of Fixed Site BrC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

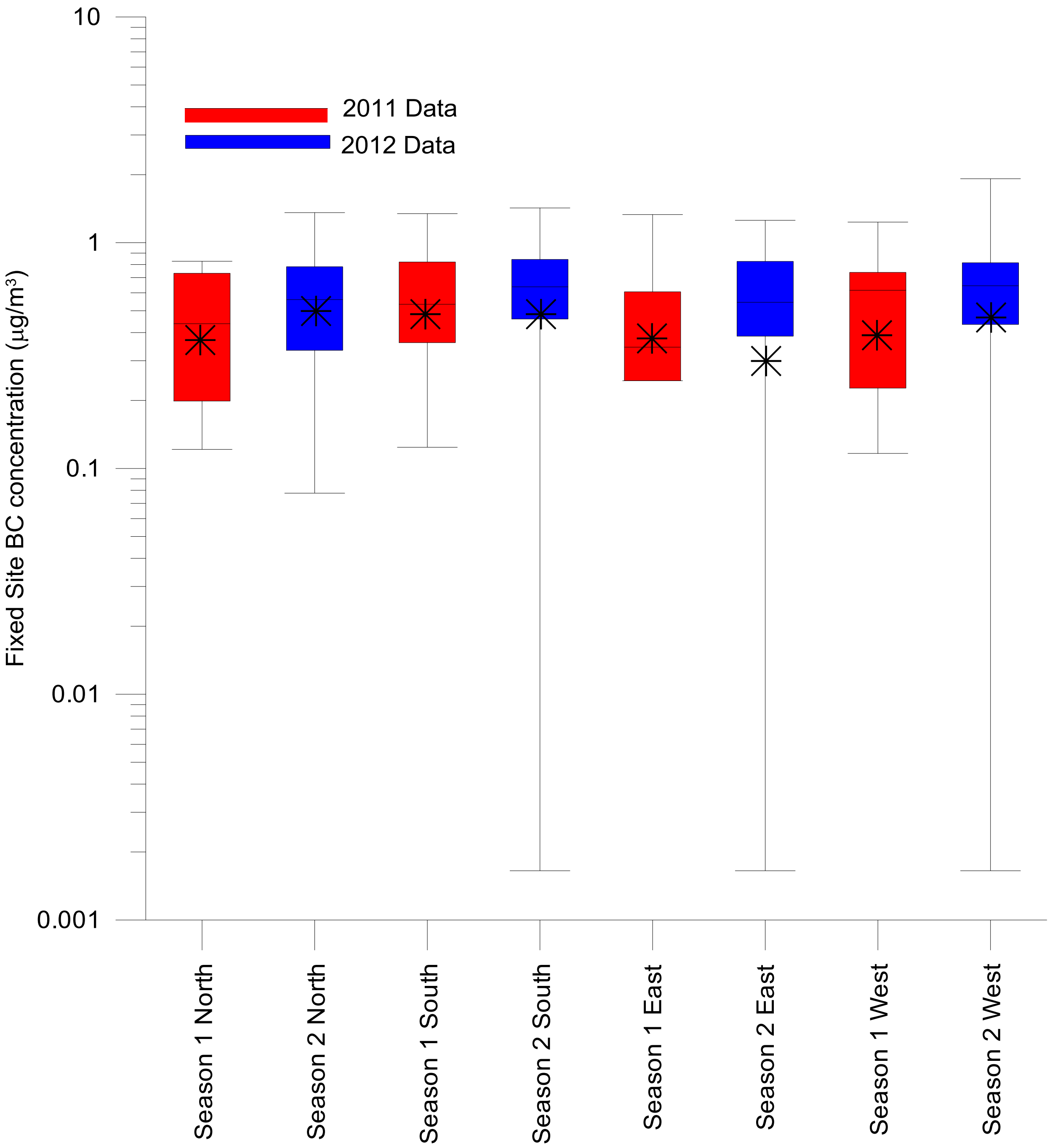

Figure 7. Distributions of Fixed Site BC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

$PM_{2.5}$ was lower during Season 2 (when the NRG Energy power plant was operational) as compared to Season 1 (when the power plant was not operational), with average concentrations being reduced to 6.5 ± SD 1.7 $\mu g/m^3$ from 12.1 ± SD 2.0 $\mu g/m^3$. T-Tests of normally transformed fixed site $PM_{2.5}$ data indicated this measured reduction was significant at a level of 0.01. This difference in significance despite similar measured $PM_{2.5}$ concentrations between Seaford and the fixed sites is most likely due to the lower number of total samples collected at Seaford (n=17) versus the fixed sites (n=204). BrC concentrations decreased from Season 1 to Season 2 with average BrC concentrations being 1.2 ± SD 2.0 $\mu g/m^3$ during Season 1 and 0.3 ± SD 16.8 $\mu g/m^3$ during Season 2, representing a significant change when evaluated at a significance level of 0.01. BC was similar between seasons (0.4 ± SD 2.0 $\mu g/m^3$ during Season 1 versus 0.4 ±SD 3.9 $\mu g/m^3$ during Season 2), and therefore the change between seasons was determined to be not significant at the same test levels as used in other T-tests.

The near 46% reduction in observed ambient $PM_{2.5}$ from Season 1 to Season 2 for the 4 fixed sites can be understood by examining the XRF data collected during each season (Figures 8 and 9). A 47% reduction in average Silicon concentration (significant at a level of $\alpha=0.01$) was seen between seasons. The clear spatial trends observed with Silicon between sites during Season 1 indicate that there is a strong source to the West-Southwest of the study area. This is in contrast to Season 2, during which a homogenous distribution of Silicon was observed, indicating the source during Season 1 either reduced emissions or ceased emission of Silicon altogether. Silicon is a common crustal element, therefore, the reduction may be linked to the 39% increase in precipitation between seasons. Also of note is an approximately 11% increase in Sulfur detected in Season 2 $PM_{2.5}$ samples (not significant at a level of $\alpha=0.01$). Although it is presumable the increased Sulfur content is a result of the power plant, no other metals commonly associated with coal-fired power plants, such as Selenium, Iron, and Cadmium, were detected. Therefore, linking the increased Sulfur to the NRG Energy power plant is not supported by the XRF analysis

Outdoor $PM_{2.5}$ Residential Data

Figures 10-12 show a general overall decrease in outdoor residential $PM_{2.5}$ and the associated BrC and BC from 2011 (NRG Energy power plant not operating) to 2012 (power plant operating), with the average $PM_{2.5}$ decreasing from 16.2 ± SD 1.5 $\mu g/m^3$ in Season 1 to 6.5 ± SD 2.0 $\mu g/m^3$ in Season 2. At the same time, BrC and BC were reduced from 2.9 ± SD 2.3 and 0.9 ± SD 2.0 $\mu g/m^3$ respectively to 0.3 ± SD 15.4 and 0.6 ± SD 2.4 $\mu g/m^3$. Reductions in all three $PM_{2.5}$ mean concentrations were determined to be significant at a test level of 0.01. Similar to the fixed sites and the Seaford site, all metrics in outdoor residential samples were reduced between seasons, with $PM_{2.5}$, BrC, and BC being reduced by 60%, 90%, and 33% respectively. Further examination of the outdoor residential $PM_{2.5}$ elemental composition revealed a significant ($\alpha=0.01$) increase in Chlorine content (Figure 13). Additional species that were found to vary between seasons include Sulfur and Iron, though these variations were determined to not be significant. Elucidating the origin of the observed $PM_{2.5}$ reduction requires incorporation of additional measurements of atmospheric constituents, such as sulfur dioxide, nitrogen dioxide, and PM speciation (nitrate, organic carbon fractions), which was beyond the scope of the current work.

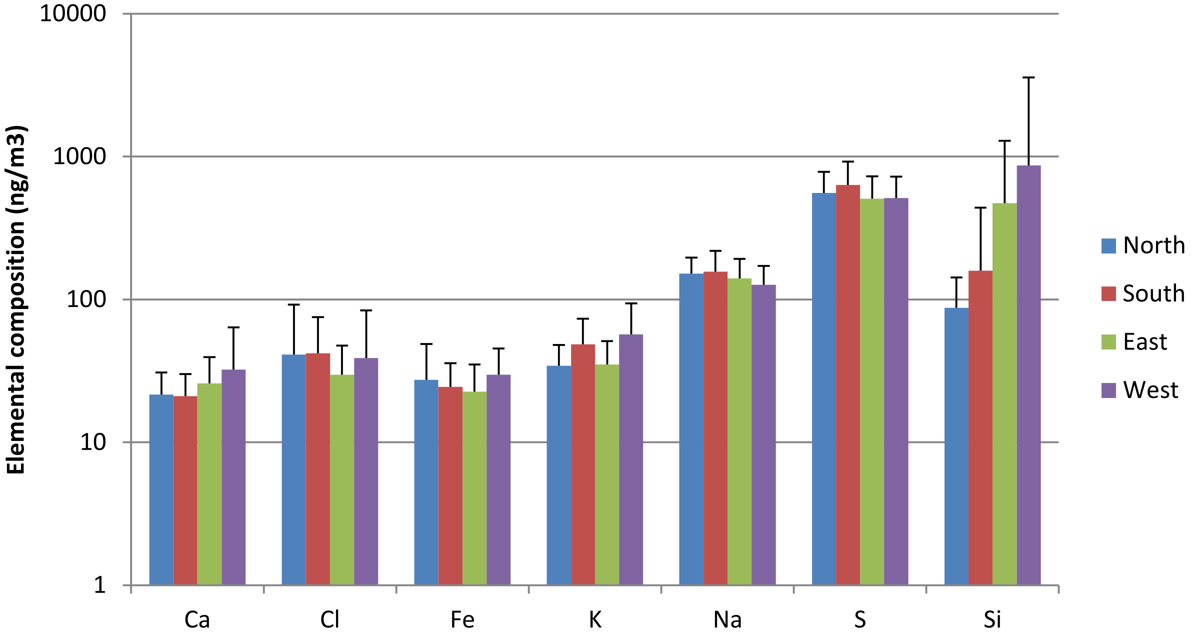

Figure 8. XRF Results from 2011 Fixed Site ambient samplers, Trace elements above MDL not shown.

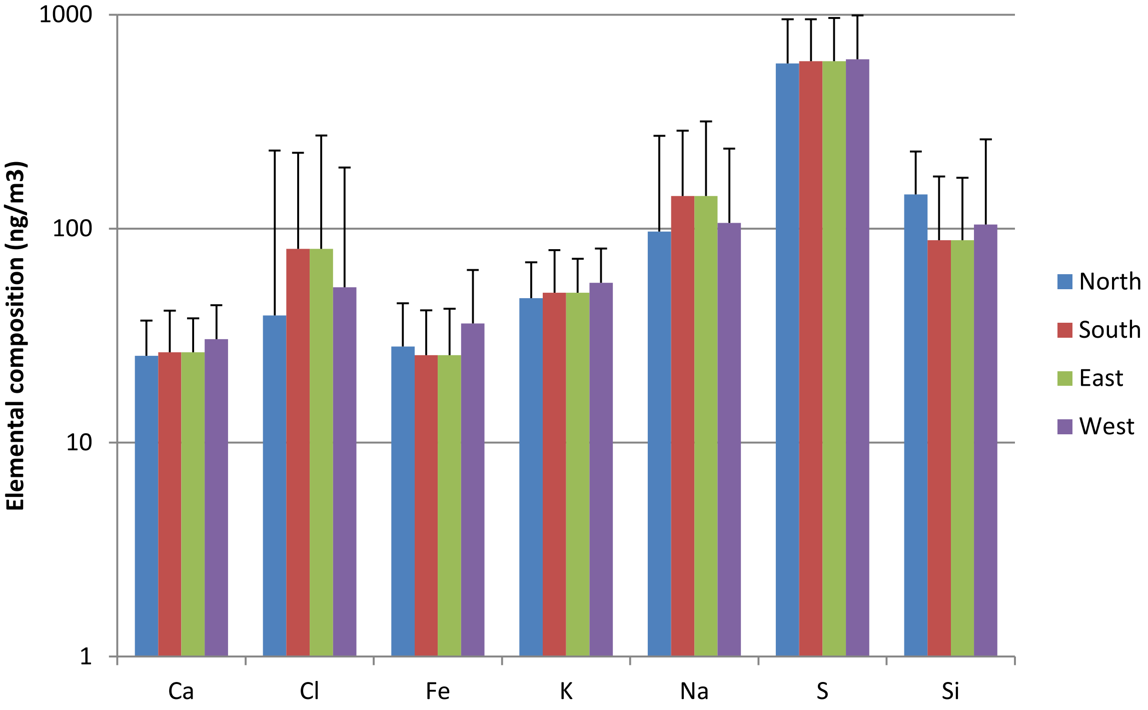

Figure 9. XRF Results from 2012 Fixed Site ambient samplers, Trace elements above MDL not shown.

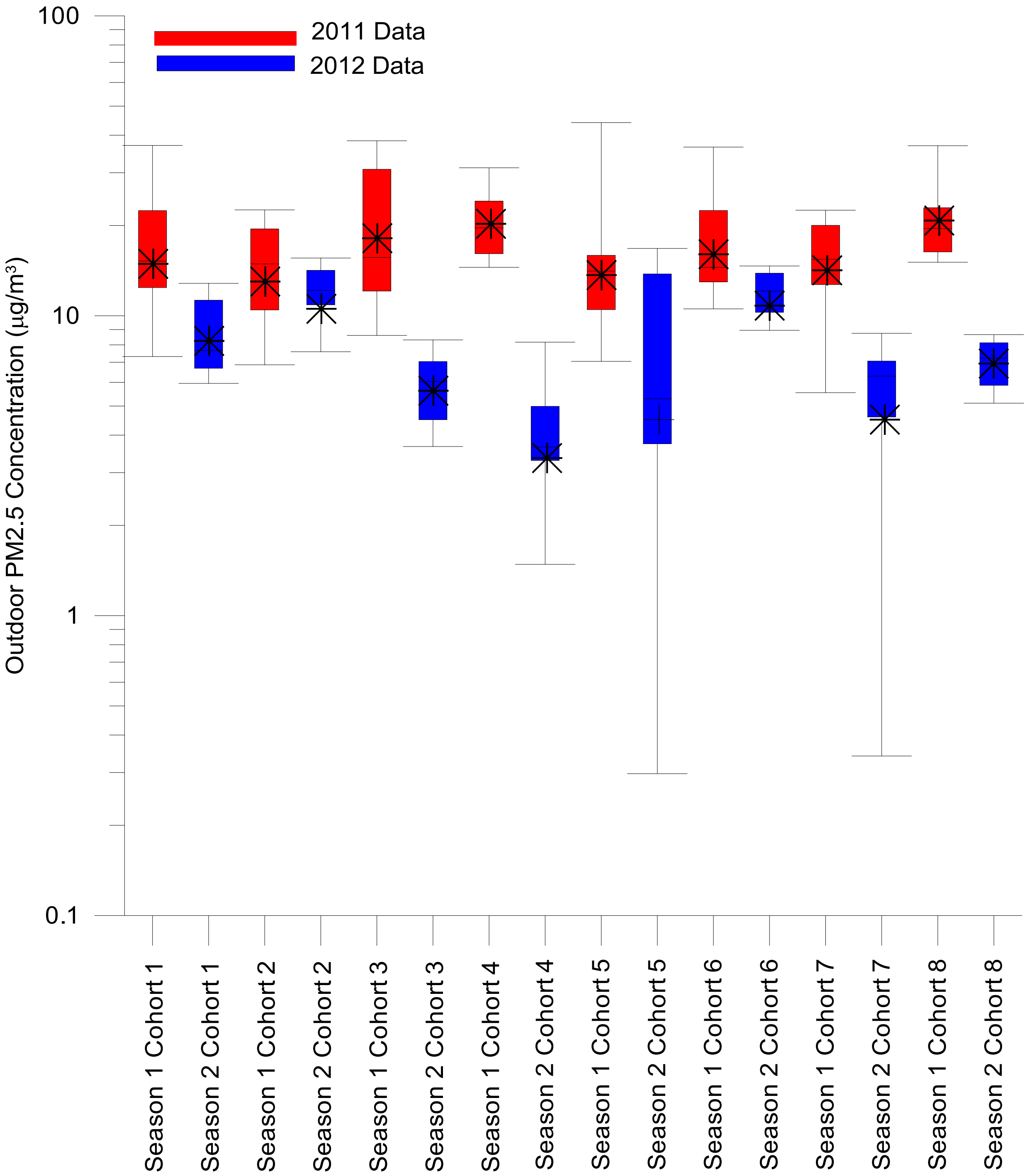

Figure 10. Distributions of outdoor residential $PM_{2.5}$ concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

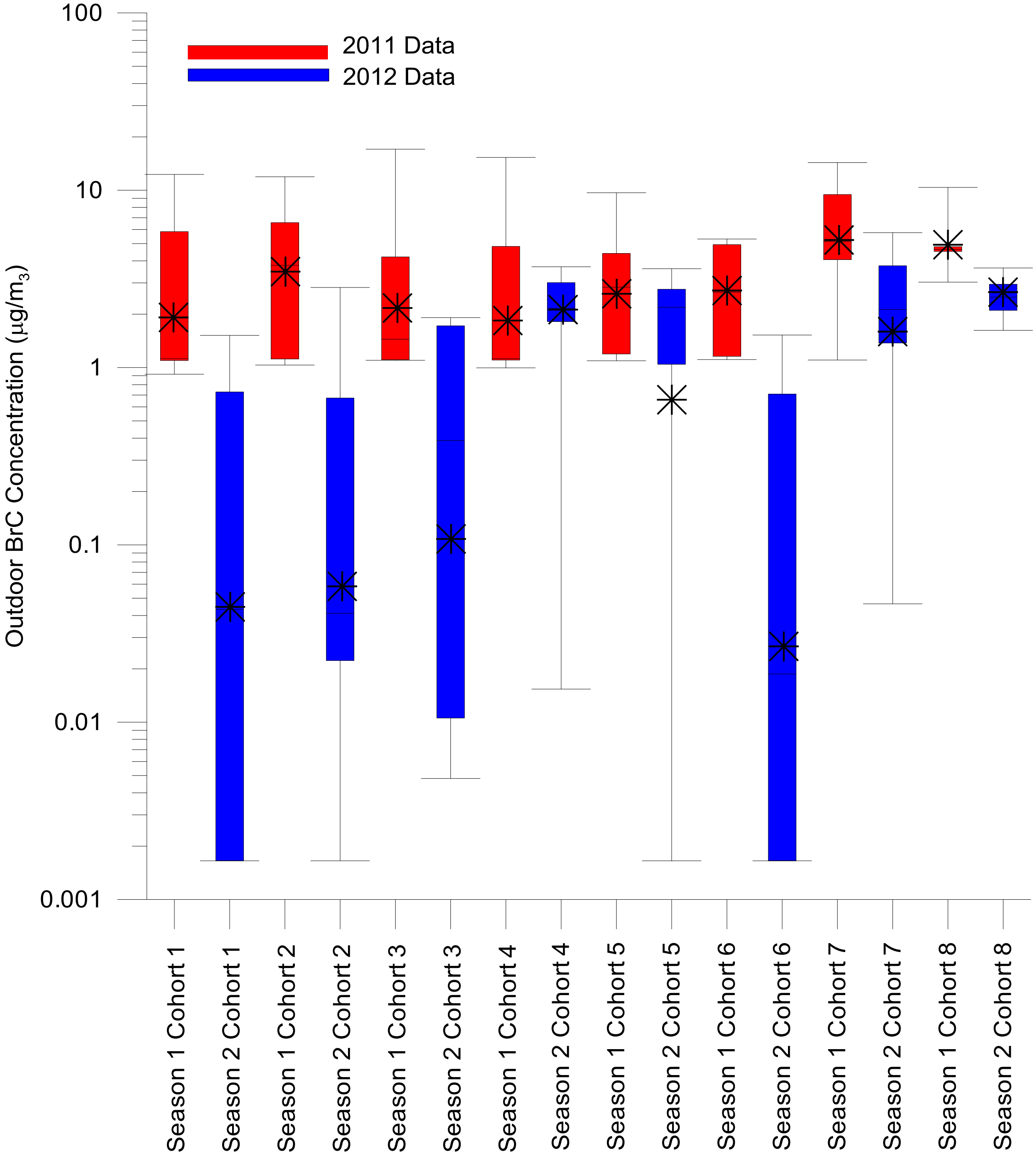

Figure 11. Distributions of outdoor residential BrC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

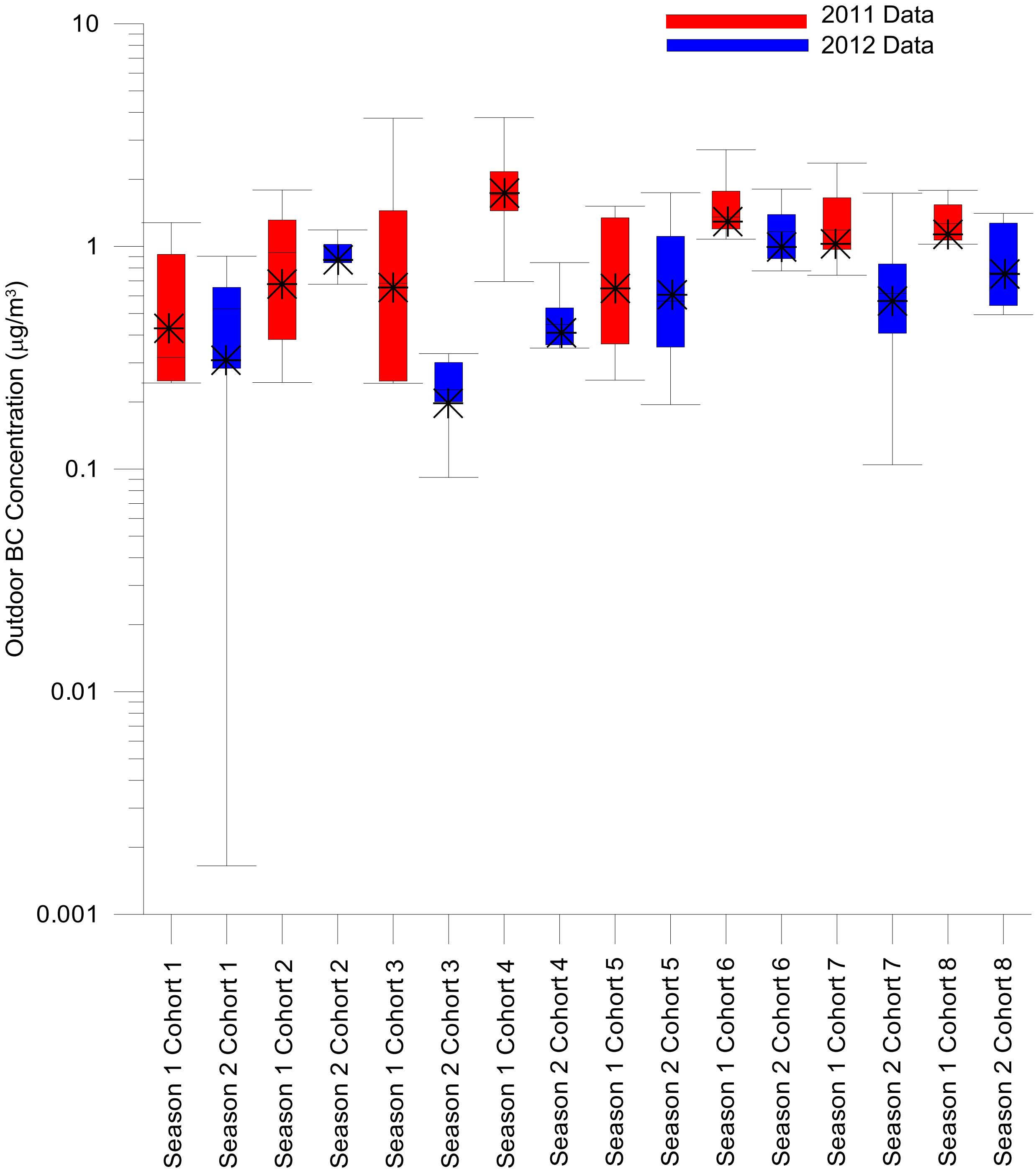

Figure 12. Distributions of outdoor residential BC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

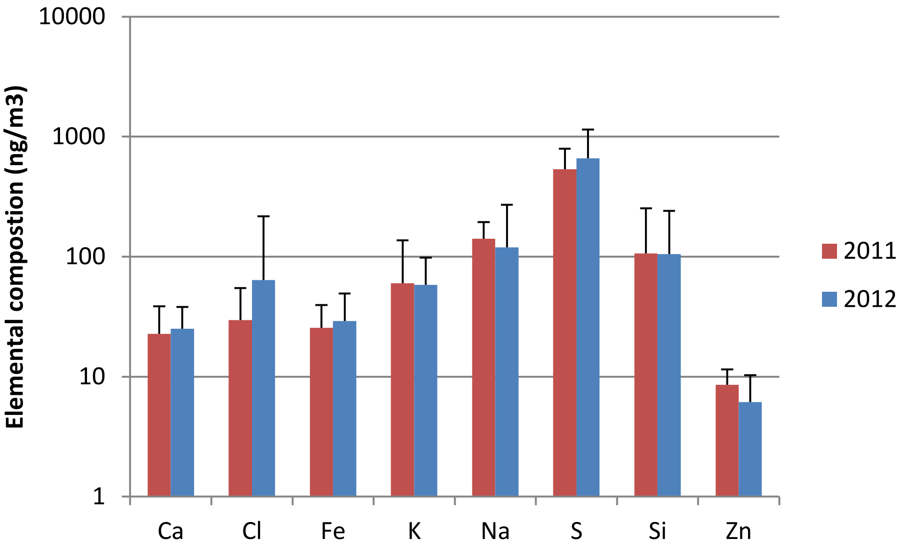

Figure 13. XRF analysis of outdoor residential samples from 2011 & 2012.

Indoor $PM_{2.5}$ Residential Data

Distributions of indoor $PM_{2.5}$, ETS, and BC are presented in Figures 14-16 below. Similar to outdoor residential $PM_{2.5}$, indoor $PM_{2.5}$ results indicate a decrease in geometric mean $PM_{2.5}$, ETS, and BC concentrations across all participants from Season 1 (NRG Energy power plant not operating) to Season 2 (power plant operating). Of particular interest are the elevated concentrations of $PM_{2.5}$ and ETS in the indoor residential air samples compared to the outdoor residential air samples. Indoor $PM_{2.5}$ levels were 12.6 ± SD 3.8 $\mu g/m^3$ during Season 1 and 10.9 ± SD 3.3 $\mu g/m^3$ during Season 2, with geometric mean ETS concentrations (Season 1, 2.8 ± SD 6.3 $\mu g/m^3$; Season 2, 2.9 ± SD 15.2 $\mu g/m^3$). BC remained nearly unchanged from Season 1 (0.5 ± SD 3.7 $\mu g/m^3$) to Season 2 (0.6 ± SD 2.5 $\mu g/m^3$). The yearly change in all three metrics was determined not to be significant. However, the larger SD in measured ETS during Season 2 with a similar geometric mean as Season 1 indicates the presence of more extreme values during Season2.

Details of the XRF analysis of indoor $PM_{2.5}$ collected during both seasons are presented in Figure 17. Many of the same elements detected outdoors are also found indoors (albeit at reduced concentrations for several elements). Additionally, trace amounts of new elements, such as Bromine and Cerium appear indoors. Presumably, these are due to sources that are unique to indoor settings, such as flame retardants and ETS (Suzuki, 2009; Böhlandt, 2012). The commonality of elements detected in both indoor and outdoor samples indicates infiltration of outside air inside. The potential infiltration of outside air is supported by the fact that during Season 1, 73% of the elements detected in indoor air were also detected in outdoor air, this percentage rose to 79% during Season 2, although without data of a non-reactive gas, such as Carbon Monoxide the degree of infiltration cannot be determined.

Figure 18 illustrates the indoor to outdoor ratio of the common elements between indoor and outdoor samples for both sampling seasons. A ratio greater than 1 suggests the sources for an element

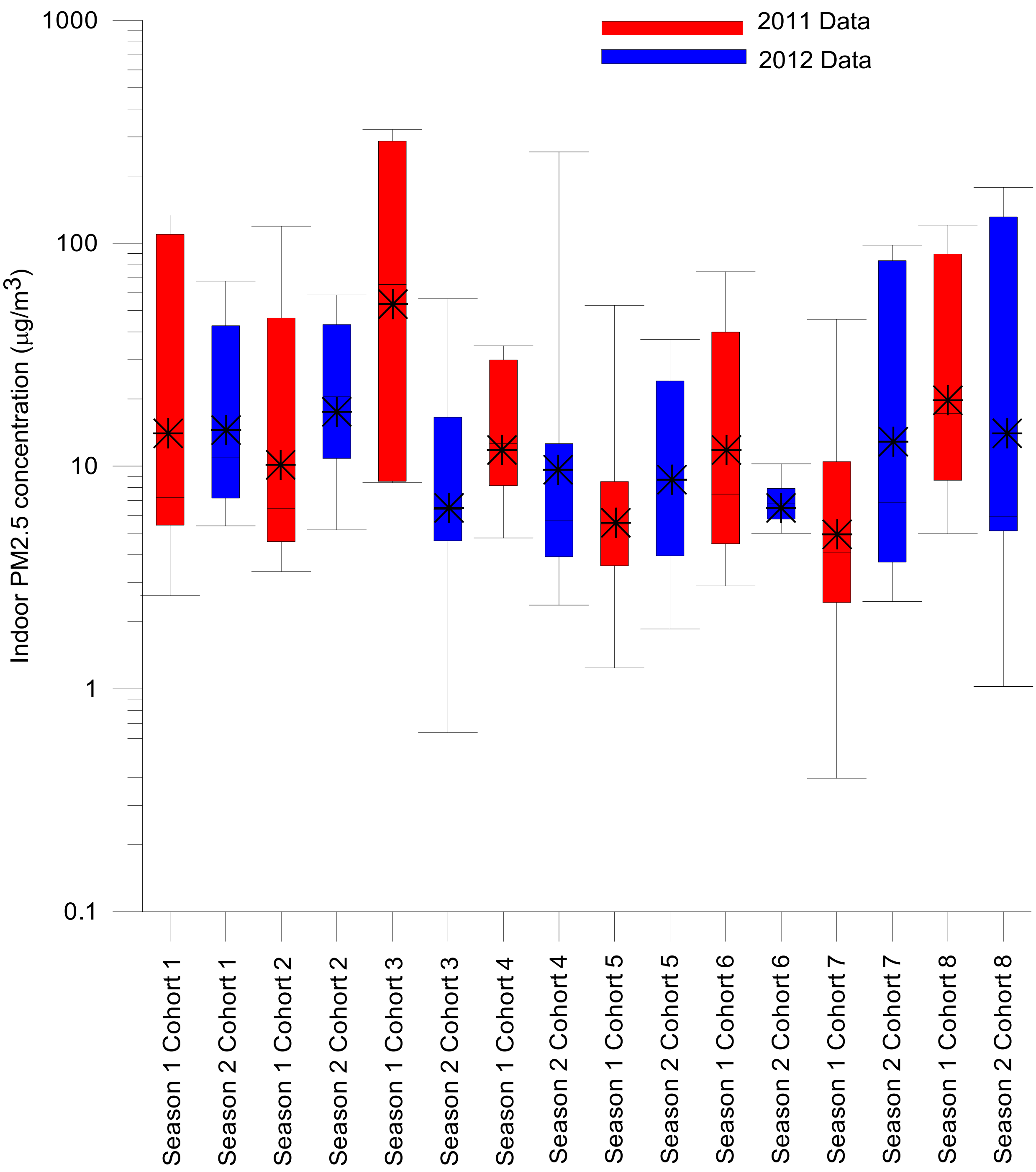

Figure 14. Distributions of indoor residential $PM_{2.5}$ concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

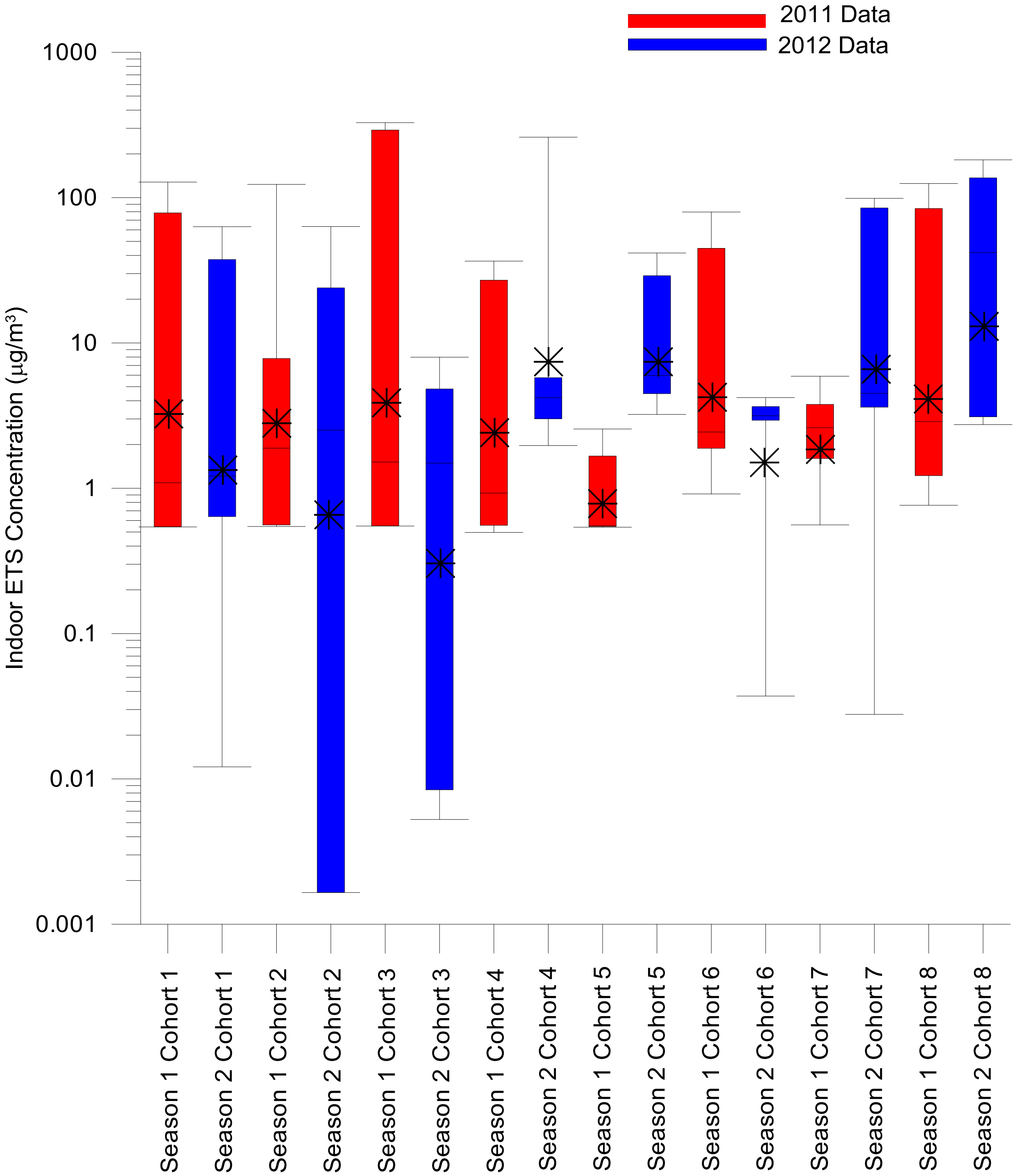

Figure 15. Distributions of indoor residential ETS concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

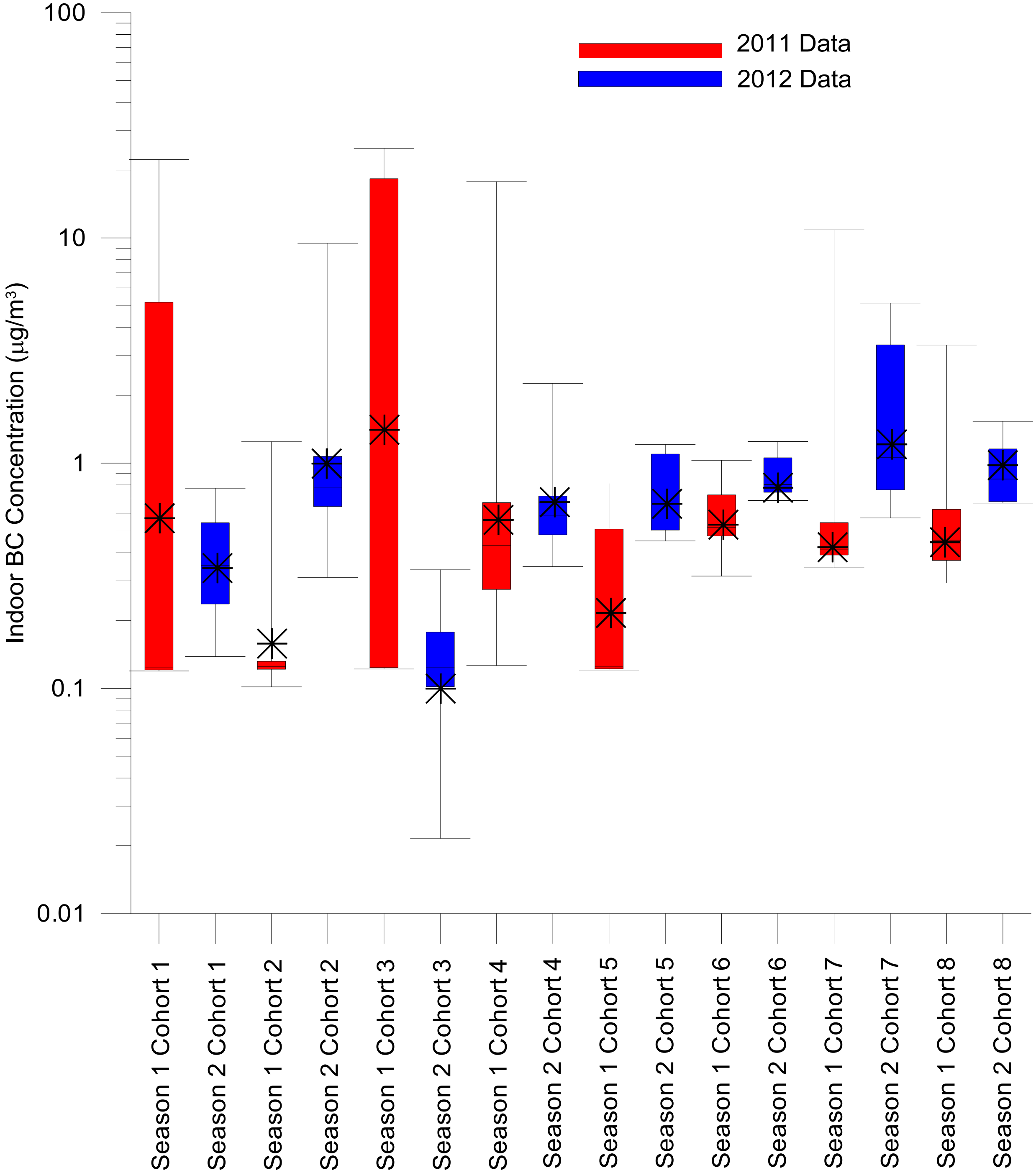

Figure 16. Distributions of indoor residential BC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

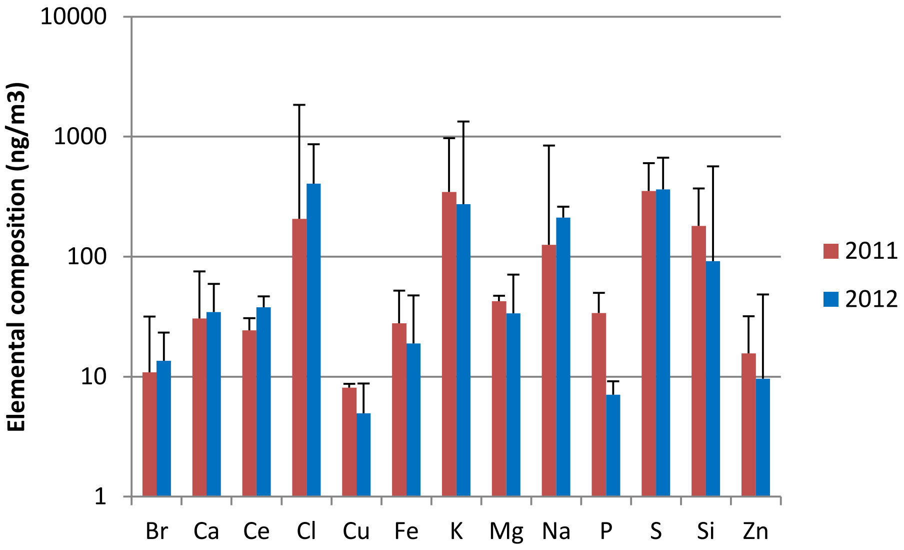

Figure 17. Comparison of XRF analysis for indoor residential $PM_{2.5}$ during 2011 & 2012.

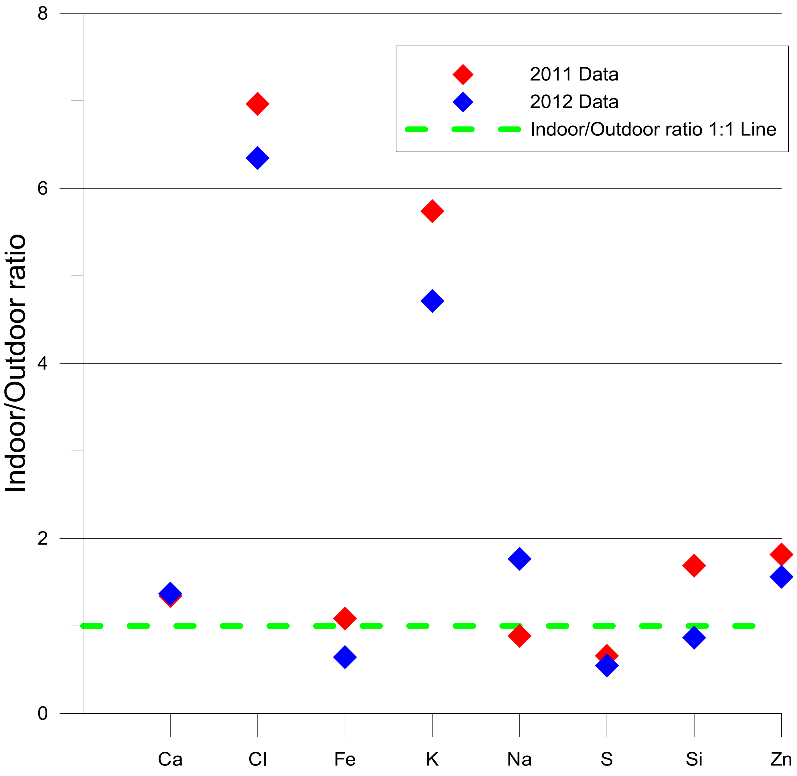

Figure 18. Indoor residential-outdoor residential ratio of select elements.

originate indoors, whereas a ratio less than 1 suggests the majority of an element originates from outdoor sources. The ratios greater than or near unity found during this study are consistent with other residential studies (Brown et al., 2012). For most elements, such as Calcium, Sulfur, and Zinc, the ratios were consistent from season to season. This consistency suggests the emission rate of these elements remained the same during each season. Other elements, such as Potassium, Sodium, and Silicon, showed decreases in their indoor/outdoor ratio. This decrease could be linked to either a decrease in their emission rate while the number of sources remained consistent or reduction of emission sources during the time period between the first and second sampling season. The lower emission rate or reduction of sources would result from changes in the residents' activity patterns. Furthermore, the consistent indoor/outdoor ratio of elements between seasons coupled with previous research suggests that indoor/outdoor ratios of elements provide insight into the degree of infiltration (Johnson, 2008).

Personal $PM_{2.5}$ Data

The RTI MicroPEM units monitored personal level exposure to $PM_{2.5}$. These units contained filters on which $PM_{2.5}$ was captured. Additionally the MicroPEMs used during Season 2 contained nephelometers which permitted real-time measurement of $PM_{2.5}$ concentrations. Figures 19-21 show the variability in personal level $PM_{2.5}$, ETS, and BC measurements made during both sampling seasons.

Personal level exposure to $PM_{2.5}$ was considerably higher than outdoor or indoor concentrations. This is consistent with findings of previous studies conducted elsewhere (Williams et al., 2003; Rodes et al., 2010; Williams et al., 2012). Season 1 personal level $PM_{2.5}$ concentrations had a geometric mean of 19.6 ± SD 3.4 $\mu g/m^3$, while Season 2 concentrations were 23.2 ± SD 5.7 $\mu g/m^3$ (gravimetric) and 24.1 ± SD 2.7 $\mu g/m^3$ (nephelometer). T-Test of these values indicated there was no significant difference between gravimetric or nephelometer data between seasons. However, these concentrations are 55% and 113% more than the indoor concentrations observed during the same time period and 21% and 257% more than the outdoor concentrations seen during the respective seasons.

The high personal level concentrations are primarily driven by ETS exposure. Examination of individual level data supports this conclusion. Of the 20 participants during Season 1 whose personal exposure levels were in excess of the Federal 24 hour $PM_{2.5}$ standard of 35 $\mu g/m^3$, 65% of them were also within the top 20 participants in terms of ETS concentration. This percentage increased during Season 2, where 89% of the top 18 participants in terms of ETS exposure also had personal $PM_{2.5}$ exposure levels in excess of 35 $\mu g/m^3$. Therefore, although ETS concentrations averaged 1.0 ± SD 7.5 $\mu g/m^3$ for Season 1 and 2.1 ± SD 31.3 $\mu g/m^3$ during Season 2, they accounted for the vast majority of samples with elevated $PM_{2.5}$ concentrations. To further illustrate the impact of ETS on personal exposure, Figure 22 compares real-time $PM_{2.5}$ acquired with the MicroPEM nephelometer from a participant with high ETS concentrations to that of a participant with low ETS concentrations. The household with high ETS tended to have a higher background concentration and several spikes in $PM_{2.5}$ mass were observed. These spikes are thought to be due to the passive combustion and extinguishing of cigarettes, an act which leads to large amounts of $PM_{2.5}$, however without questionnaire data indicating the presence of smokers within households, a definitive correlation cannot be determined. Black carbon plays a lesser role in terms of the overall mass concentration of personal exposure than does ETS with

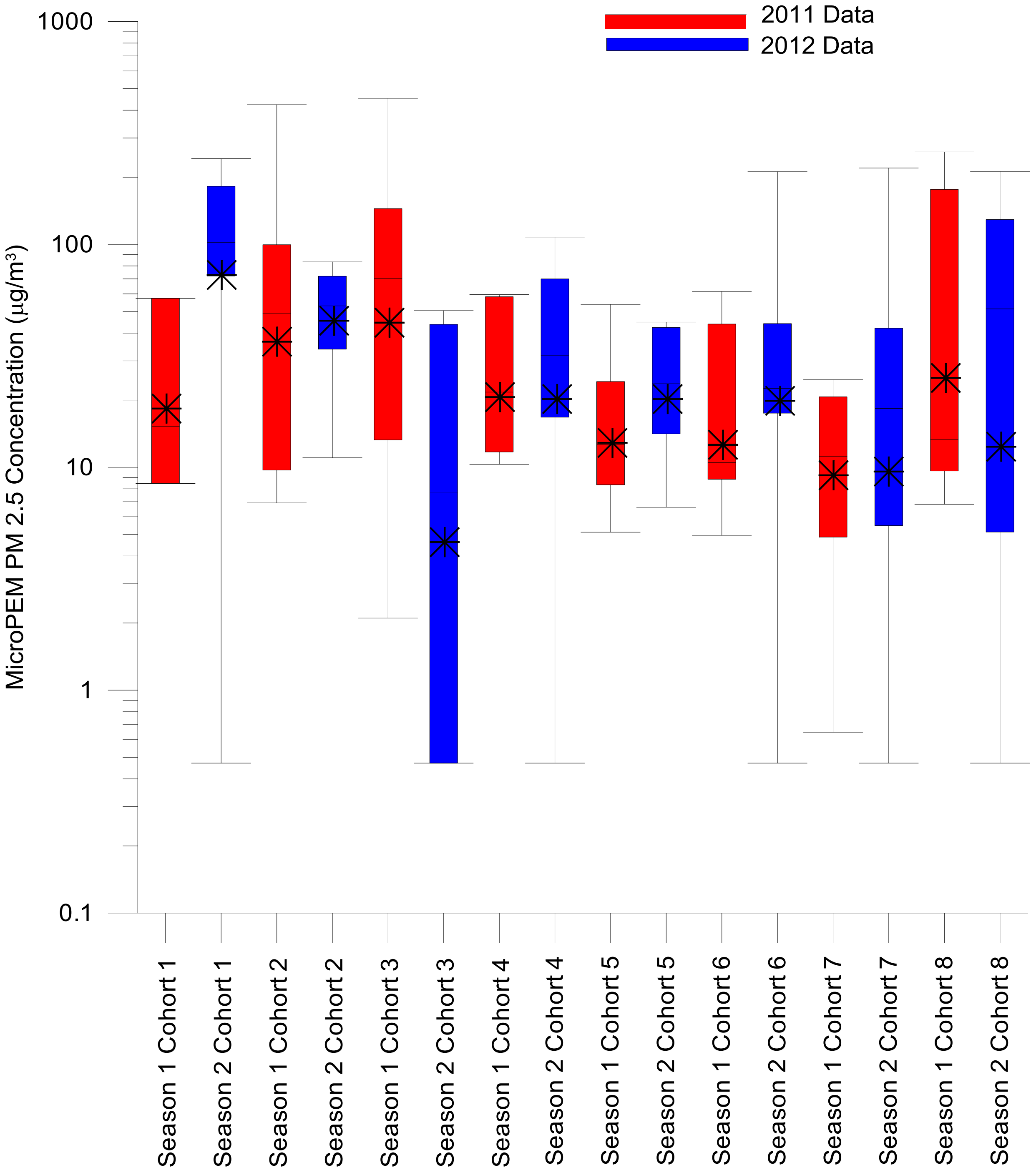

Figure 19. Distributions of personal level $PM_{2.5}$ concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

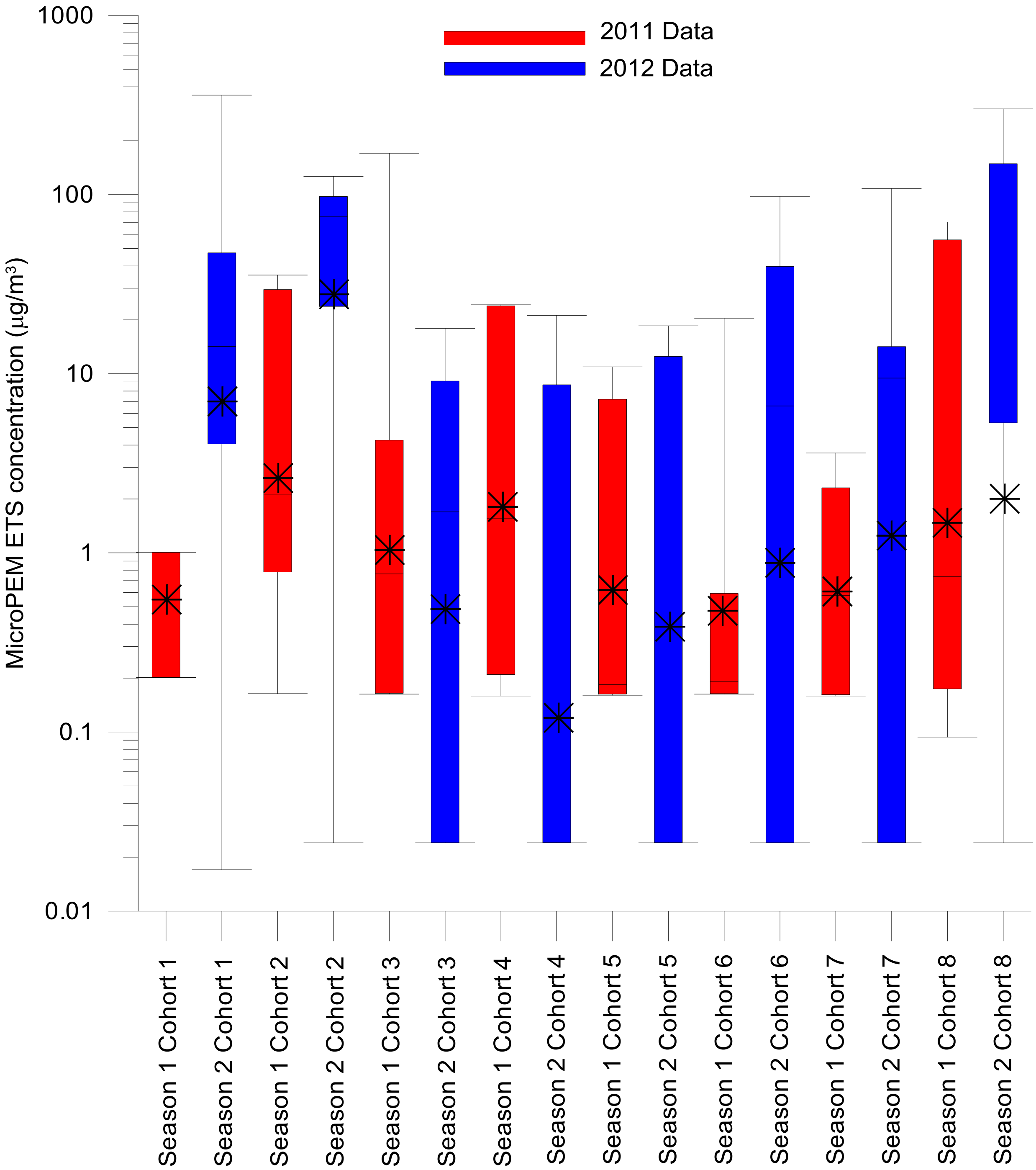

Figure 20. Distributions of personal level ETS concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

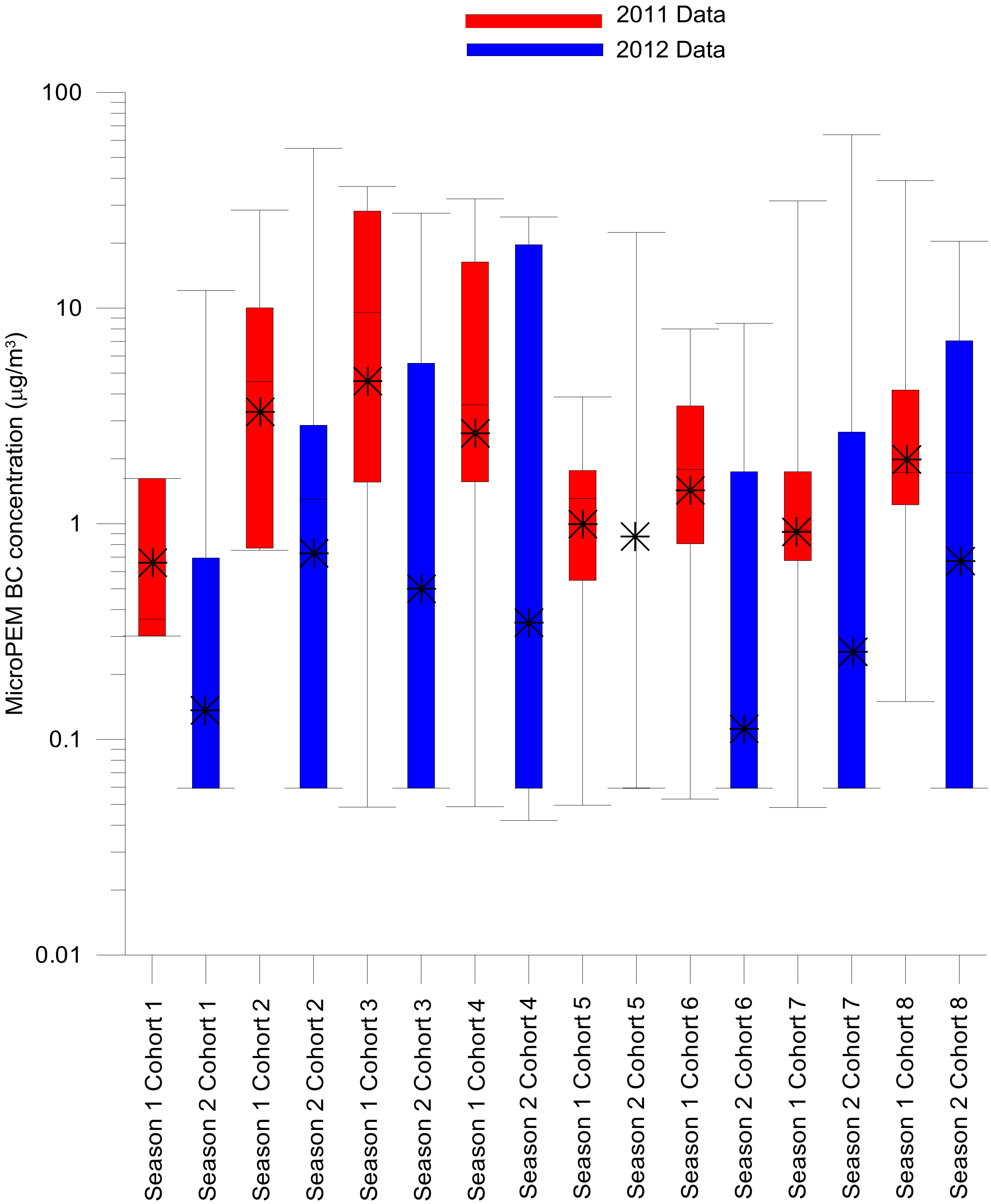

Figure 21. Distributions of personal level BC concentrations during Season 1 (Red, NRG Energy power plant not operating) & Season 2 (Blue, power plant operating) along with geometric means (asterisks). Values below the MDL were assigned a value of the MDL divided by square root of 2.

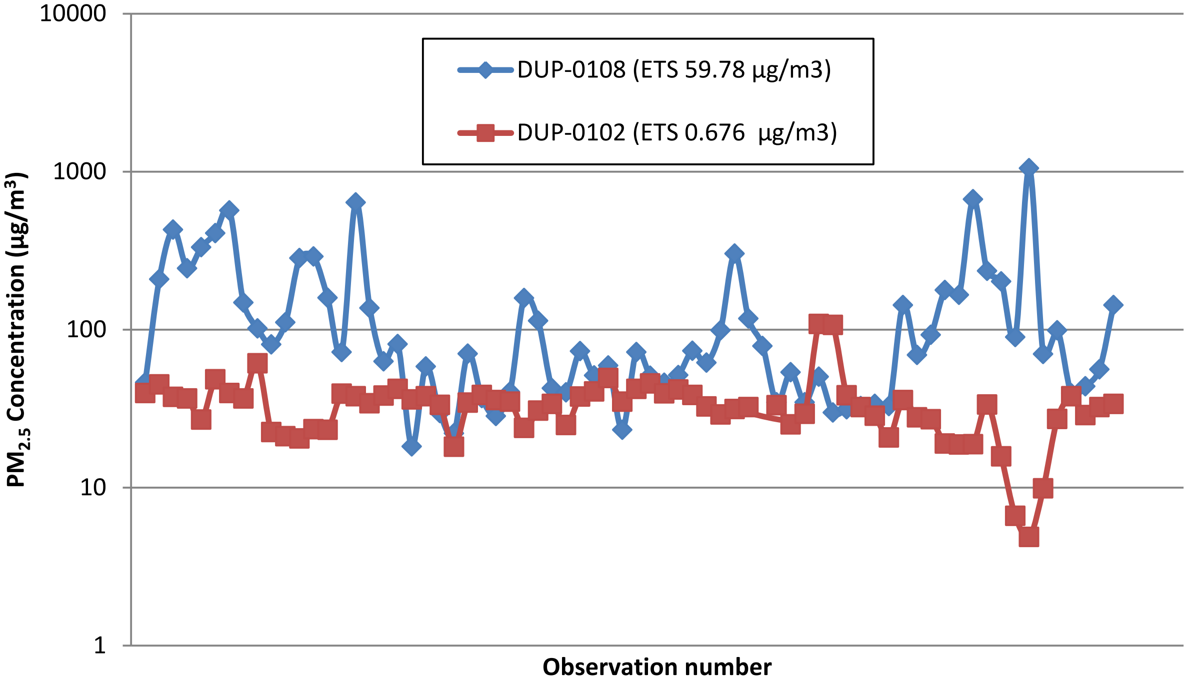

Figure 22. 24-hr Trend of 5-minute averaged PM$_{2.5}$ from high and low ETS participants.

1.7 ± SD 5.1 μg/m^3 and 0.4 ± SD 10.2 μg/m^3 being observed in seasons 1 and 2 respectively, though it was determined to be significantly different (p-value $2.8x10^{-7}$) it is due to less than 10 instances of BC measurements greater than 10 μg/m^3 and therefore the significant difference should be viewed as unlikely.

XRF analysis of MicroPEM filters indicated a wide variation in 15 different metals. The overall trend of XRF analysis indicated an increase from Season 1 (NRG Energy power plant not operating) to Season 2 (power plant operating) with the exception of Sulfur as shown in Figure 23. The additional elements detected in personal level samples as compared in outdoor samples coupled with elevated $PM_{2.5}$ concentrations underscore the fact that understanding the local population exposure and potential sources of cancer-causing chemicals associated with $PM_{2.5}$ requires additional study of indoor sources and participant habits.

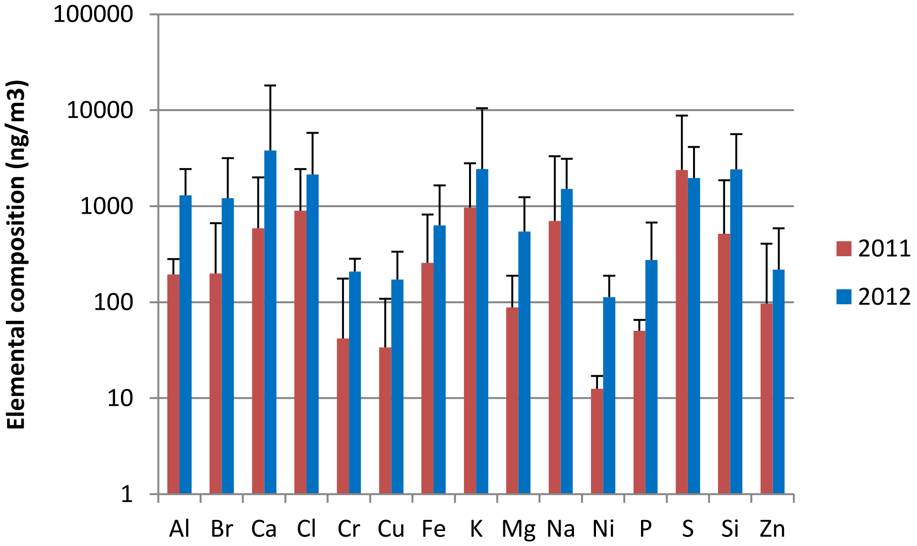

Figure 23. XRF analysis of RTI MicroPEM filters from Seasons 1 and 2.

Residential Temperature and Humidity

Technicians placed temperature and humidity sensors inside each participant's household at the beginning of the three-day sampling period. Average temperatures for all households during both sampling seasons were 69.8 ± SD 3.0 (Season 1) and 71.3 ± SD 4.7 (Season 2) degrees Fahrenheit. The average relative humidity for households during both seasons was 51.1 percent. Table 9 below presents summarized data for all participants during both seasons.

Table 5. Average temperatures and relative humidities for Season 1 & Season 2 participants.

Season	Average Temperature (°F)	Average Relative Humidity (%)
Season 1	69.8 ± SD 3.0	51.1 ± SD 6.4
Season 2	71.3 ± SD 4.7	51.1 ± SD 8.2

Questionnaires

Residents were given two questionnaires during the first season three-day sampling period. The first questionnaire (Residential Survey) covered details about the physical residence participants were living in including age of dwelling, types of heating, number of persons living there, etc. During Season 2, additional questions were asked about consumption of certain foods and dietary supplements. These changes were made because of the measurement of higher than expected concentrations of As and Se in some samples during Season 1; such elevations were thought to be possibly associated with diet. The second questionnaire was a time activity diary. Participants were asked to keep track of their movements and actions during the course of the three sampling days. Summarized data from both questionnaires and both seasons are included in Appendix A.

Biospecimen Samples

The urine and blood specimen results are listed in Tables 6-8. During Season 1, Arsenic and Selenium were greater than reference values in 12 of the participant's urine (Table 6). Urine samples were greater than reference values for various metals, especially arsenic and selenium in 9 of the participants (Table 7) during Season 2. Additionally, blood metals (Table 8) were elevated for some of the participants in both seasons, but none of the elements (Cadmium, Mercury, and Lead) were above the high values shown in Appendix C. Participants with elevated concentration of Mercury and Lead in 2011 generally had elevated concentrations in 2012; the significance of these differences was not tested. No VOCs were detected in blood above the lower reporting threshold during either season. Reference values for metals and VOCs in blood and urine are presented in Appendices B and C, respectively. Hair samples were not tested but were archived for later testing, along with remaining aliquots of the blood and urine samples.

Table 6. 2011 Concentrations of metals in urine (ppb).[i]

Subject ID	As	Se	Be	Co	Mo	Cd	Sb	Cs	Ba	W	Pt	Tl	Pb	U
557	9.118	28.766	<0.25	0.125	14.525	<0.1250	<0.10	1.506	0.638	<0.1	<0.125	<0.0500	<0.3750	<0.0125
168	<8.125	40.244	<0.25	0.236	38.066	0.276	<0.10	4.714	1.796	<0.1	<0.125	0.116	<0.3750	<0.0125
190	**234.524**	52.994	<0.25	0.264	32.782	0.742	<0.10	6.656	<0.50	<0.1	<0.125	0.304	0.664	<0.0125
551	12.37	29.917	<0.25	1.208	16.538	<0.1250	<0.10	3.152	<0.50	<0.1	<0.125	<0.0500	<0.3750	<0.0125
139	<8.125	44.465	<0.25	0.362	<7.50	0.128	0.134	1.245	1.209	<0.1	<0.125	0.059	<0.3750	<0.0125
238	**14.048**	**251.126**	<0.25	1.132	**337.449**	2.095	<0.10	**20.661**	2.423	0.379	<0.125	0.392	1.286	<0.0125
156	9.53	59.135	<0.25	0.249	41.108	0.132	<0.10	4.307	1.172	<0.1	<0.125	0.134	1.01	<0.0125
342	<8.125	57.772	<0.25	0.267	55.01	0.746	<0.10	6.917	7.757	<0.1	<0.125	0.266	0.5	<0.0125
559	26.692	31.569	<0.25	0.151	25.205	0.125	<0.10	3.601	<0.50	<0.1	<0.125	0.148	<0.3750	<0.0125
169	<8.125	24.955	<0.25	0.644	8.775	0.762	<0.10	4.153	0.668	<0.1	<0.125	0.05	<0.3750	<0.0125
136	<8.125	33.252	<0.25	0.125	17.347	<0.1250	<0.10	<0.5	<0.50	<0.1	**0.133**	0.072	<0.3750	<0.0125
566	**>650**	56.821	<0.25	0.719	51.201	0.191	0.167	5.852	3.065	0.171	<0.125	0.473	2.601	0.016
177	<8.125	21.302	<0.25	0.181	<7.50	<0.1250	<0.10	1.071	0.22	<0.1	<0.125	<0.0500	<0.3750	<0.0125
561	<8.125	52.915	<0.25	0.541	29.862	0.277	<0.10	3.421	2.685	0.1	<0.125	0.163	1.16	<0.0125
553	**88.202**	36.07	<0.25	0.472	61.705	<0.1250	0.115	13.378	4.86	0.213	<0.125	0.339	1.895	0.034
554	<8.125	**98.551**	<0.25	0.511	73.711	0.167	<0.10	4.957	3.581	0.278	<0.125	0.349	0.988	<0.0125
352	11.678	44.381	<0.25	0.203	56.152	0.172	<0.10	3.706	1.458	0.127	<0.125	0.114	0.773	0.002
325	<8.125	23.054	<0.25	0.125	9.117	0.149	<0.10	<0.5	<0.50	<0.1	<0.125	<0.0500	<0.3750	<0.0125
249	<8.125	12.192	<0.25	0.125	<7.50	<0.1250	<0.10	1.141	<0.50	<0.1	<0.125	<0.0500	<0.3750	<0.0125
552	<8.125	31.305	<0.25	0.125	12.38	<0.1250	<0.10	<0.5	1.45	<0.1	<0.125	<0.0500	<0.3750	<0.0125
564	<8.125	**92.909**	<0.25	0.31	69.406	0.5	0.15	5.771	3.034	<0.1	<0.125	0.104	0.878	<0.0125
346	<8.125	**123.634**	<0.25	0.167	17.617	0.238	<0.10	2.639	<0.50	<0.1	<0.125	0.09	<0.3750	<0.0125
560	62.788	**72.161**	<0.25	0.413	80.512	1.817	<0.10	8.839	2.243	0.158	<0.125	0.129	1.26	<0.0125
556	0.503	<0.0500	<0.1250	<0.5	<0.3750	0.125	**19.948**	<7.50	<0.25	0	<0.10	<0.0125	<0.125	<0.1
290	24.004	**74.835**	<0.25	0.609	59.696	1.048	<0.10	5.095	2.252	<0.1	<0.125	0.216	1.013	<0.0125
298	<8.125	27.154	<0.25	0.307	<7.50	0.202	<0.10	1.201	3.939	<0.1	<0.125	0.3	<0.3750	<0.0125
567	<8.125	20.866	<0.25	0.125	<7.50	<0.1250	<0.10	3.03	<0.50	<0.1	<0.125	<0.0500	<0.3750	<0.0125
211	**86.361**	**210.974**	<0.25	0.539	180.421	0.794	<0.10	7.248	2.562	<0.1	<0.125	0.102	1.427	<0.0125
563	11.005	**96.178**	<0.25	0.483	97.092	1.08	<0.10	6.147	1.294	<0.1	<0.125	0.163	<0.3750	<0.0125
565	8.204	27.648	<0.25	0.456	13.613	<0.1250	<0.10	1.533	1.001	<0.1	<0.125	<0.0500	<0.3750	<0.0125
558	15.458	**105.83**	<0.25	0.242	41.082	0.226	<0.10	12.306	1.143	<0.1	<0.125	0.441	0.48	<0.0125
562	<8.125	19.596	<0.25	0.125	<7.50	<0.1250	<0.10	<0.5	<0.50	<0.1	<0.125	<0.0500	<0.3750	<0.0125

[i] Comparison or reference values are shown in Appendix C. Values in bold are those that exceeded the DHHS "high" value, defined as repeat upper boundary levels measured during analysis; samples with results greater than this are reanalyzed for confirmation. These values are higher than the 95th percentile from NHANES. Actual precisions do not exceed three significant figures.

[ND] Element was not detected

[<LOD] Element was detected, but was below the method quantification limit

[<#] value was below the lowest calibration point

Table 7. 2012 Concentrations of metals in urine (ppb). [i]

Subject ID	As	Se	Be	Co	Mo	Cd	Sb	Cs	Ba	W	Pt	Tl	Pb	U
603	ND	13.696	ND	<0.125	11.098	0.517	<LOD	3.681	<LOD	<LOD	ND	0.106	<0.375	<LOD
557	ND	6.565	ND	ND	<7.5	ND	<LOD	<0.5	<LOD	<LOD	ND	ND	ND	ND
168	<LOD	50.565	ND	0.438	207.975	0.436	<0.1	10.639	<0.5	0.157	<LOD	0.185	ND	ND
190	<8.125	55.435	ND	0.577	67.755	1.611	0.134	11.615	<LOD	0.102	ND	0.282	1.391	<LOD
551	ND	9.011	ND	0.206	16.579	0.152	<0.1	2.508	0.539	<0.1	ND	0.063	<0.375	ND
602	10.555	49.296	ND	0.306	51.98	0.133	<0.1	8.406	0.703	0.102	ND	0.236	<0.375	<LOD
238	19.389	26.808	ND	0.218	24.479	<0.125	<LOD	3.754	1.121	<0.1	ND	0.072	ND	ND
156	**103.321**	**129.571**	ND	**8.511**	97.035	0.276	0.121	8.799	3.501	0.155	ND	0.133	1.603	<LOD
342	<8.125	36.077	ND	0.349	68.228	0.658	<0.1	7.667	15.231	<LOD	<0.125	0.171	0.404	<LOD
559	<8.125	46.312	ND	0.268	79.601	0.313	<LOD	6.324	0.948	<0.1	ND	0.199	0.434	<LOD
136	<8.125	11.014	ND	<0.125	13.03	<LOD	<0.1	1.664	<LOD	<LOD	ND	0.065	<0.375	ND
566	<8.125	43.112	ND	0.583	76.021	0.421	<0.1	7.328	3.078	<0.1	ND	0.407	2.232	0.013
177	12.964	**70.07**	ND	0.786	81.886	0.707	<0.1	11.058	2.868	0.121	ND	0.177	0.726	ND
561	ND	6.633	ND	<0.125	25.219	<LOD	<LOD	<0.5	0.521	ND	ND	<0.05	<0.375	ND
553	37.099	39.935	ND	0.283	186.522	1.134	0.147	10.543	3.185	0.873	ND	0.356	2.087	0.055
554	<8.125	26.903	ND	0.505	61.046	0.318	<0.1	6.404	8.036	<0.1	ND	0.347	1.195	<0.0125
352	19.021	59.199	ND	0.302	57.393	0.173	<0.1	6.421	2.379	0.126	<LOD	0.219	1.083	<0.0125
325	<LOD	56.47	ND	0.295	62.625	0.665	<0.1	5.376	2.449	<0.1	ND	0.183	<0.375	ND
249	<LOD	15.475	ND	0.308	29.231	0.166	<LOD	5.487	1.67	ND	ND	0.085	<0.375	ND
564	<8.125	55.053	ND	0.556	66.725	0.325	<0.1	11.643	4.69	<0.1	<LOD	0.147	1.123	<0.0125
346	<LOD	**154.425**	ND	0.436	214.234	0.651	<0.1	10.463	1.148	0.222	ND	0.291	<0.375	ND
290	<8.125	51.64	ND	0.757	46.874	0.605	<0.1	3.65	6.709	<0.1	**0.146**	0.208	0.501	<0.0125
601	<8.125	43.04	ND	1.44	50.15	0.301	<0.1	5.672	2	<0.1	ND	0.145	0.392	<LOD
567	ND	62.242	ND	0.522	53.986	0.785	<LOD	**19.576**	2.691	<0.1	ND	0.196	0.615	ND
211	44.588	**229.533**	ND	0.603	196.139	0.829	<0.1	7.797	2.797	0.135	ND	0.115	0.445	<LOD
563	ND	**PGC**	ND	0.417	99.434	**4.705**	<LOD	4.746	0.672	0.208	**PGC**	0.41	<0.375	<0.0125
565	<8.125	42.077	ND	**4.022**	37.136	0.579	<0.1	6.307	1.418	<0.1	ND	0.299	0.487	<LOD
558	22.637	**152.996**	ND	0.428	115.341	0.466	<0.1	15.526	2.65	<0.1	ND	0.317	0.754	<LOD
562	ND	23.49	ND	0.155	10.005	<0.125	<LOD	1.066	<0.5	ND	ND	<0.05	0.39	ND
169	ND	38.831	ND	0.749	32.284	0.921	<0.1	5.337	<LOD	<0.1	ND	0.075	<0.375	ND
560	<8.125	16.851	ND	0.276	60.02	0.411	<LOD	1.956	3.464	0.124	ND	0.074	0.661	<0.0125
556	<8.125	**72.151**	ND	0.571	65.865	0.359	<0.1	6.814	3.249	0.128	ND	0.194	0.902	<LOD

[i] Comparison or reference values are shown in Appendix C. Values in bold are those that exceeded the DHHS "high" value, defined as repeat upper boundary levels measured during analysis; samples with results greater than this are reanalyzed for confirmation. These values are higher than the 95th percentile from NHANES. Actual precisions do not exceed three significant figures.

[ND] Element was not detected

[<LOD] Element was detected, but was below the method quantification limit

[<#] value was below the lowest calibration point

Table 8. 2011 and 2012 blood metals concentrations (ppb).

2011 (Season 1)

Subject ID

	557	168	190	551	139	238	156	342	559	169	136	566	177	561	553	554
Cd	<0.5	<0.5	0.698	1.316	1.329	<0.5	<0.5	<0.5	<0.5	0.788	<0.5	<0.5	<0.5	<0.5	0.681	<0.5
Hg	<1	<1	<1	<1	<1	<1	2.886	<1	<1	<1	1.212	1.474	<1	<1	2.088	2.324
Pb	<10	<10	26.652	<10	10.931	<10	16.699	<10	<10	<10	19.016	14.736	12.723	<10	23.818	<10

Subject ID

	352	325	249	552	564	346	560	556	290	298	567	211	563	565	558	562
Cd	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.15	0.812	0.644	<0.5	0.681	<0.5	<0.5	<0.5
Hg	2.04	<1	<1	<1	<1	1.43	<1	1.854	1.69	1.144	<1	3.048	<1	1.3	<1	<1
Pb	21.6	<10	<10	<10	17.537	<10	<10	<10	<10	11.31	<10	10.89	<10	<10	<10	11.63

2012 (Season 2)

Subject ID

	603	557	168	190	551	602	238	156	342	559	136	566	177	561	553	554
Cd	<1	<1	<LOD	<1	1.034	ND	<LOD	ND	<LOD	ND	<LOD	ND	<LOD	<1	<1	ND
Hg	<2	<2	<LOD	<2	<LOD	<LOD	<LOD	2.462	ND	ND	<2	<2	<LOD	<LOD	6.074	<2
Pb	<LOD	<LOD	<20	25.173	<LOD	<LOD	<LOD	<20	<LOD	<20	<20	<20	<20	<20	32.912	<20

Subject ID

	352	325	249	564	346	290	601	567	211	563	565	558	562	169	560	556
Cd	ND	<LOD	<LOD	<LOD	<LOD	<1	<LOD	<1	<LOD	<1	<LOD	ND	<LOD	<1	<LOD	<LOD
Hg	<2	ND	<2	ND	<2	<2	ND	ND	3.06	ND	<2	<LOD	<2	<LOD	<LOD	<2
Pb	28.3	<20	<20	28.988	<20	<LOD	<LOD	<LOD	<20	ND	<LOD	<LOD	<20	<20	<20	<LOD

[ND] Element was not detected

[<LOD] Element was detected, but was below the method quantification limit

[<#] value was below the lowest calibration point

The measurement of an environmental chemical in a person's blood or urine does not by itself mean that the chemical causes disease. Research studies are required to determine whether blood or urine concentrations are safe or are associated with disease or adverse effects. Many of the reference levels contained in this report were obtained from the National Health and Nutrition Examination Survey (NHANES) Studies conducted by the Centers for Disease Control and Prevention (e.g., Fourth National Report on Human Exposure to Environmental Contaminants, Centers for Disease Control and Prevention, 2009; http://www.cdc.gov/exposurereport/). The NHANES studies are probability-based population studies and reflect the analyte concentrations representative of the US population. In most cases in this report, reference is made to the 95th percentiles, which means that the indicated concentrations are equal to or higher than those measured for 95% of the population. This value is useful for determining whether or not a concentration measured in any particular public health study is unusual. The reader is encouraged to visit the website shown above for more information about many of the analytes measured.

Distributions of the biospecimen results for each season are shown below for blood (Figure 24) and for urine (Figure 25) for both seasons. Note that for these results, values below MDL or those that were not detected were reported as 0.5 times the limit of detection. On average, there do not appear to be any significant changes across seasons. However, several participants had concentrations that exceeded the high reference value for various elements in one or both seasons (Table 9). By far the most common exceedances were for Arsenic and Selenium. For those 2012 participants with urinary concentrations of As or Se that were above the high reference values, we evaluated their responses to the dietary questions added for the 2012 sampling season. Participant 156 consumed locally caught fish (tautog), ate meat, poultry, and locally-grown produce on a on a regular basis but did not report taking any multivitamins or Selenium containing supplements. Those participants with elevated concentrations of Se only (346, 211. 558, and 556) reported regular consumption of meats, poultry, grains, and local produce. Participants 346, 211, 558, and 556 all took multivitamins with participants 211 and 556 reporting taking a fish oil supplement. A key parameter in evaluation of the effect of these actions on urinary metals concentrations is the time between providing a urine sample and consumption. In the case of grains and local seafood, these actions were taken within the past 48 hours of providing a urine sample; therefore the linkage between these actions is potentially stronger than those actions with no time-related information.

An important component of this study was to evaluate how exposure to particulate matter is associated with measures from the biospecimens. Measured PM permitted evaluation of four characteristics: mass, ETS, Black carbon, and elemental composition. Relationships of each PM measure to each analyte/matrix combination in the biospecimens were examined. PM measurement characteristics were averaged over the course of the three day sampling period since there was only one biospecimen data point to reflect each participant. Non-ranked correlations were performed with the following tables indicating how predictive each PM characteristic was for each biospecimen analyte. The scatter plots were examined to ensure that the correlation was not being driven by a single extreme value.

Table 10 shows the results for PM mass to be predictive of elements in blood and urine. Blood lead appears to be associated with PM mass each year, but it is also persistent in the body. Table 11 shows the correlation of ETS with elements in blood and urine. Although significance was found for blood mercury, blood lead, and urinary uranium, all of these appeared to be driven by a single, high value. Table 12 shows associations of BC with elements in blood and urine. P-values <0.05 were found for blood Cd and Pb in 2011 and blood Hg in 2012; other significant associations were clearly driven by extreme values and should not be believed. In general, some associations were observed between some elements with total mass, ETS, and BC, but they were not consistent across all elements or across the two years of the study.

Table 9. Participants for whom any of the analytes in blood or urine exceeded high reference value (* indicates a measurement above the reference value).

Participant Id.	Specimen	Measurement Type	Analyte	2011 Result (ppb)	2012 Result (ppb)	Reference Value
136	URINE	Metals	PT	0.133 *	ND	0.10
156	URINE	Metals	AS	9.53	103.321 *	64.50
156	URINE	Metals	CO	0.249	8.511 *	2.83
156	URINE	Metals	SE	59.1	129.571 *	68.00
177	URINE	Metals	SE	21.3	70.07 *	68.00
190	URINE	Metals	AS	235 *	<8.125	64.50
211	URINE	Metals	AS	86.4 *	44.588	64.50
211	URINE	Metals	SE	211 *	229.533 *	68.00
238	URINE	Metals	MO	337 *	24.479	293.50
238	URINE	Metals	SE	251 *	26.808	68.00
290	URINE	Metals	PT	<0.125	0.146 *	0.10
290	URINE	Metals	SE	74.8 *	51.64	68.00
346	URINE	Metals	SE	124 *	154.425 *	68.00
553	URINE	Metals	AS	88.2 *	37.099	64.50
554	URINE	Metals	SE	98.6 *	26.903	68.00
556	URINE	Metals	SE	19.9	72.151 *	68.00
558	URINE	Metals	SE	106 *	152.996 *	68.00
560	URINE	Metals	SE	72.2 *	16.851	68.00
563	URINE	Metals	CD	1.08	4.705 *	2.54
563	URINE	Metals	SE	96.2 *	PGC†	68.00
564	URINE	Metals	SE	92.9 *	55.053	68.00
565	URINE	Metals	CO	0.456	4.022 *	2.83
566	URINE	Metals	As	>650 *	<8.125	64.5

[†]Participant 563 also had very high levels of Pt in urine that was reported by DPHL as "PGC" or "parameter greater than calibration"

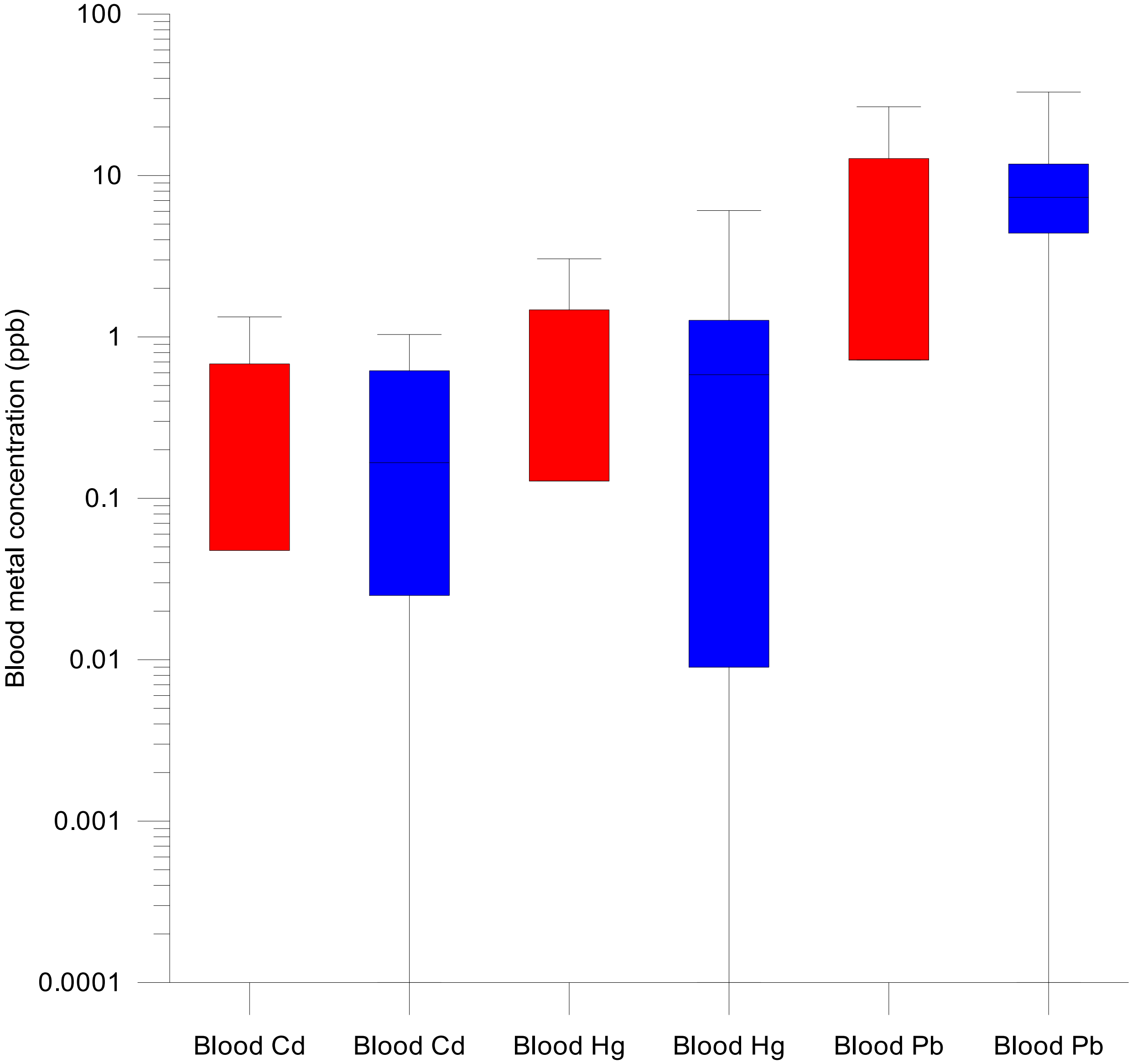

Figure 24. Blood metals distribution for all participants during 2011 (Red) and 2012 (Blue).

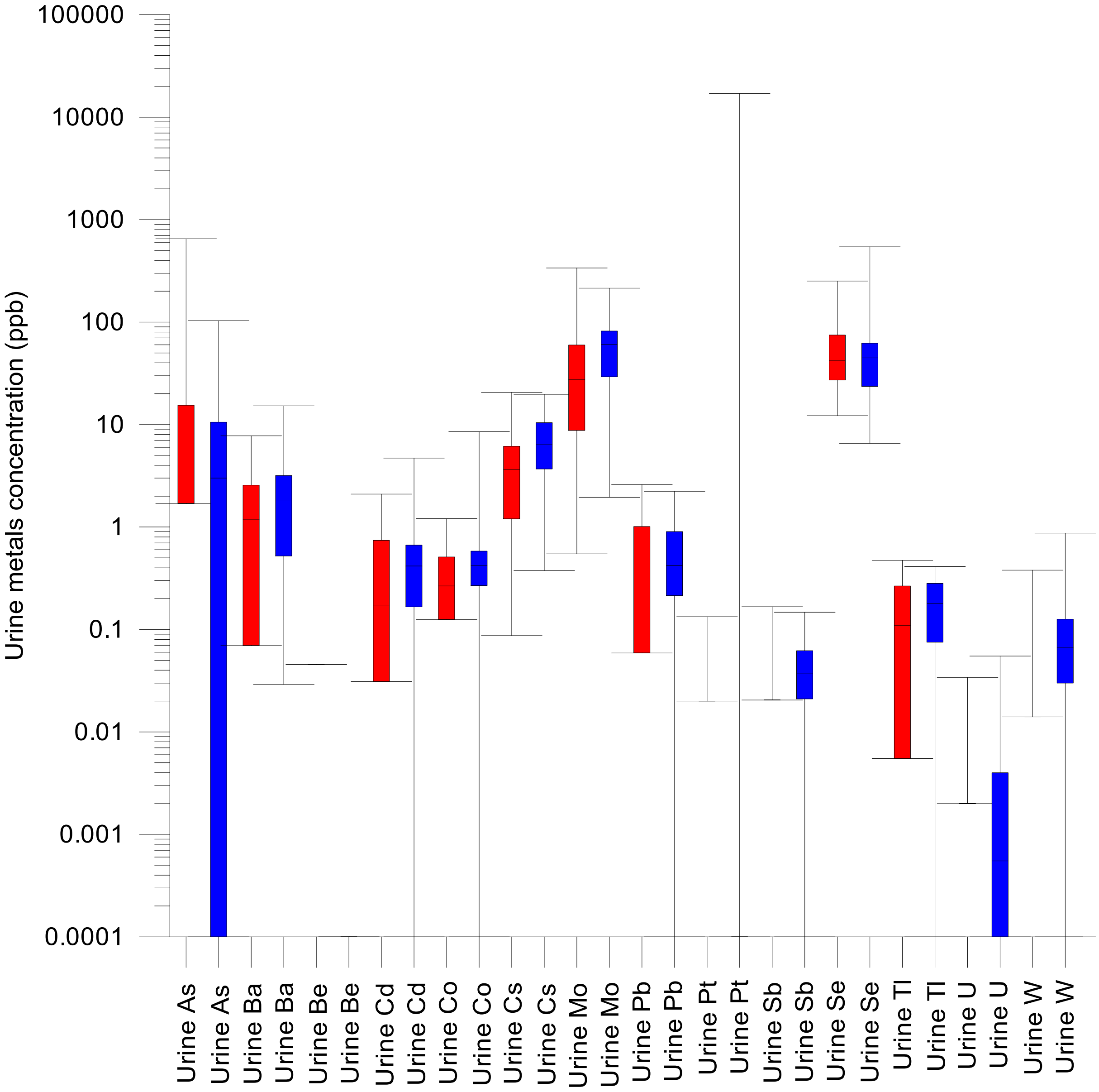

Figure 25. Urine metals distributions for all participants during 2011 (Red) and 2012 (Blue).

Table 10. Pearson correlations of PM mass with biospecimen elements by year.

Sample Matrix	Analyte	Year	No. Meas.	r-Square	p-value
BLOOD	CD	2011	28	0.2124	0.2778
BLOOD	CD	2012	31	0.2800	0.1271
BLOOD	HG	2011	28	-.2164	0.2687
BLOOD	HG	2012	31	0.2914	0.1117
BLOOD	PB	2011	28	0.4260	**0.0238**
BLOOD	PB	2012	31	0.3664	**0.0426**
URINE	AS	2011	28	0.0500	0.8007
URINE	AS	2012	31	0.1100	0.5559
URINE	BA	2011	28	0.0424	0.8305
URINE	BA	2012	31	-.0323	0.8632
URINE	BE	2011	28	Not Detected	Not Detected
URINE	BE	2012	31	Not Detected	Not Detected
URINE	CD	2011	28	0.0279	0.8880
URINE	CD	2012	31	-.0324	0.8626
URINE	CO	2011	28	-.0624	0.7526
URINE	CO	2012	31	0.0298	0.8736
URINE	CS	2011	28	0.0781	0.6930
URINE	CS	2012	31	0.3493	0.0541
URINE	MO	2011	28	-.0064	0.9741
URINE	MO	2012	31	-.0201	0.9146
URINE	PB	2011	28	0.0810	0.6819
URINE	PB	2012	31	0.3773	**0.0364**
URINE	PT	2011	28	-.0812	0.6812
URINE	PT	2012	31	-.1659	0.3726
URINE	SB	2011	28	0.5306	**0.0037**

Sample Matrix	Analyte	Year	No. Meas.	r-Square	p-value
URINE	SB	2012	31	0.2284	0.2165
URINE	SE	2011	28	0.0454	0.8185
URINE	SE	2012	31	-.1953	0.2924
URINE	TL	2011	28	-.0255	0.8975
URINE	TL	2012	31	0.0266	0.8869
URINE	U	2011	28	0.0276	0.8892
URINE	U	2012	31	0.4241	**0.0174***
URINE	W	2011	28	-.1465	0.4568
URINE	W	2012	31	0.3259	0.0736

[*] an extreme value may be driving the association

Table 11. Pearson correlations of ETS mass with biospecimen elements by year.

Sample Matrix	Analyte	Year	No. Meas.	r-Square	p-value
BLOOD	CD	2011	28	0.3449	0.0722
BLOOD	CD	2012	31	0.3139	0.0855
BLOOD	HG	2011	28	-.2830	0.1445
BLOOD	HG	2012	31	0.4748	**0.0070***
BLOOD	PB	2011	28	0.3591	0.0605
BLOOD	PB	2012	31	0.3788	**0.0356***
URINE	AS	2011	28	0.1839	0.3488
URINE	AS	2012	31	0.0559	0.7650
URINE	BA	2011	28	-.2425	0.2138
URINE	BA	2012	31	-.0820	0.6609
URINE	BE	2011	28	Not Detected	Not Detected
URINE	BE	2012	31	Not Detected	Not Detected

Sample Matrix	Analyte	Year	No. Meas.	r-Square	p-value
URINE	CD	2011	28	0.0462	0.8153
URINE	CD	2012	31	0.1258	0.5001
URINE	CO	2011	28	-.1543	0.4330
URINE	CO	2012	31	-.1180	0.5271
URINE	CS	2011	28	0.0042	0.9830
URINE	CS	2012	31	0.2761	0.1327
URINE	MO	2011	28	-.1087	0.5820
URINE	MO	2012	31	0.1107	0.5532
URINE	PB	2011	28	-.0715	0.7178
URINE	PB	2012	31	0.3315	0.0685
URINE	PT	2011	28	-.0741	0.7080
URINE	PT	2012	31	-.0702	0.7073
URINE	SB	2011	28	0.0860	0.6636
URINE	SB	2012	31	0.3471	0.0557
URINE	SE	2011	28	-.0862	0.6627
URINE	SE	2012	31	-.1206	0.5182
URINE	TL	2011	28	0.0022	0.9910
URINE	TL	2012	31	0.1492	0.4231
URINE	U	2011	28	-.1056	0.5927
URINE	U	2012	31	0.6256	**0.0002***
URINE	W	2011	28	-.2074	0.2897
URINE	W	2012	31	0.5687	**0.0008***

[*] an extreme value may be driving the association

Table 12. Pearson correlations of BC mass with biospecimen elements by year.

Sample Matrix	Analyte	Year	No. Meas.	r-Square	p-value
BLOOD	CD	2011	28	0.5787	**0.0013**
BLOOD	CD	2012	31	0.1856	0.3176
BLOOD	HG	2011	28	0.0541	0.7845
BLOOD	HG	2012	31	0.5403	**0.0017**
BLOOD	PB	2011	28	0.4651	**0.0126**
BLOOD	PB	2012	31	0.1780	0.3379
URINE	AS	2011	28	0.0253	0.8983
URINE	AS	2012	31	0.2155	0.2442
URINE	BA	2011	28	0.2339	0.2309
URINE	BA	2012	31	-.1501	0.4203
URINE	BE	2011	28	Not Detected	Not Detected
URINE	BE	2012	31	Not Detected	Not Detected
URINE	CD	2011	28	-.1942	0.3221
URINE	CD	2012	31	-.0536	0.7747
URINE	CO	2011	28	-.0438	0.8249
URINE	CO	2012	31	-.0900	0.6301
URINE	CS	2011	28	0.1050	0.5948
URINE	CS	2012	31	0.0130	0.9447
URINE	MO	2011	28	-.1547	0.4317
URINE	MO	2012	31	0.2729	0.1375
URINE	PB	2011	28	0.0978	0.6204
URINE	PB	2012	31	0.2402	0.1930
URINE	PT	2011	28	-.1257	0.5238
URINE	PT	2012	31	-.1372	0.4616
URINE	SB	2011	28	0.3605	0.0595

Sample Matrix	Analyte	Year	No. Meas.	r-Square	p-value
URINE	SB	2012	31	0.2533	0.1691
URINE	SE	2011	28	-.2487	0.2019
URINE	SE	2012	31	-.0045	0.9808
URINE	TL	2011	28	0.1461	0.4581
URINE	TL	2012	31	-.0396	0.8324
URINE	U	2011	28	0.5728	**0.0014***
URINE	U	2012	31	0.4540	**0.0103***
URINE	W	2011	28	0.0461	0.8157
URINE	W	2012	31	0.4087	**0.0224***

[*] an extreme value may be driving the association

Lastly, a comparison was performed between the elemental concentrations measured of the collected personal level $PM_{2.5}$ to those measured in urine or blood. Table 13 indicates the associations of elements on personal PM filters, as measured by XRF, to the same elements measured in biospecimen samples by year, while Table 14 compares across both years of sampling. When examined by year, three associations were identified, but they were all found to have been driven by one or a few extreme values and are not predictive. No significant associations were observed when the data from both years were combined.

It does not appear that the personal PM characteristics measured in this study have strong and consistent contributions to the analytes measured in the blood and urine from the study participants. The lack of relationship may mean that current exposures do not result in large biospecimen changes on the time scale of this study. In other words, measures for some of the analytes in biospecimens might reflect long-term equilibria that are not perturbed to any great extent by the short-term change in PM. These data might also indicate the possibility of non-inhalation routes of exposure. When considering the biospecimen analyte concentrations that exceeded reference values (Table 9), most of the excursions are measured for Arsenic and Selenium, two elements known to have dietary sources. Exposure to these metals has health consequences that range from cancer to other less severe consequences which depend on both exposure amount and length. As described earlier, questions were added to the participant survey for Season 2 to examine some potential dietary sources.

Table 15 examines the relationship between elevated urinary concentrations of Arsenic and Selenium and various ingestion sources. Specific potential contributors to individual excursions were examined previously. The purpose of the correlations presented in Table 15 is an attempt to see how generalizable the findings might be to the rest of the study participants, whether or not their particular biospecimen results where high or more typical of this group. Some of the dependent variables in the table are categorical, i.e., they have a “yes” or “no” response. Such variables include eating grains, local produce, rice, or meat, drinking filtered water, taking dietary supplements, eating fish/seafood, or whether a participant’s source of drinking water was a private well or municipal water supply. Another factor to consider is the relative amount of time spent indoor versus outdoors. This would not be expected to influence exposure to Arsenic or Selenium, unless there is an inhalation source (not supported by the results shown above), but could for other pollutants. This was not explored further in this work. In any event, the data show that the consumption of seafood within 48 hours of providing a urinary sample is significantly linked to increased urinary Arsenic levels. It is important to recognize, however, that this study measured total (inorganic + organic) arsenic in urine, while arsenic in fish is predominantly organic arsenic (Greene and Crecelius, 2006). Inorganic arsenic is considered toxic, while organic arsenic is not. Further, organic arsenic is quickly excreted from the body. Total urinary arsenic values can occasionally increase to several thousands of ug/L after seafood consumption (Caldwell et. al., 2009), which is well above values seen in the current study. It is also important to note that arsenic concentrations in fish and shellfish from the local Inland Bays are not greater than concentrations in fish and shellfish from the entire East and Gulf Coasts of the U.S. (Greene, 2010). The data also suggest that the regular consumption of grains significantly decreases exposure to Arsenic. The reason is not immediately obvious, but could reflect associated dietary factors or food interactions.

Table 13.Pearson correlations of elements on personal filters by XRF with biospecimen elements by year.

Sample Matrix	Analyte	YEAR	No. Meas.	r-square	p-value
BLOOD	CD	2011	28	-.2079	0.2914
BLOOD	CD	2012	32	0.3086	0.0858
BLOOD	PB	2011	28	-.2007	0.3090
BLOOD	PB	2012	32	-.2826	0.1177
URINE	AS	2011	28	-.0827	0.6786
URINE	AS	2012	32	0.2072	0.2576
URINE	BA	2011	28	0.6012	**0.0005***
URINE	BA	2012	32	-.0341	0.8544
URINE	CD	2011	28	0.3484	0.0690
URINE	CD	2012	32	-.0708	0.7023
URINE	CO	2011	28	0.3437	0.0732
URINE	CO	2012	32	0.1749	0.3413
URINE	CS	2011	28	0.3982	**0.0351***
URINE	CS	2012	32	0.1198	0.5167
URINE	PB	2011	28	0.1293	0.5155
URINE	PB	2012	32	0.0025	0.9891
URINE	SB	2011	28	-.1556	0.4327
URINE	SB	2012	32	0.1181	0.5228
URINE	SE	2011	28	0.4625	**0.0123***
URINE	SE	2012	32	0.3040	0.0909

[*] an extreme value may be driving the association

Table 14. Pearson correlations of elements on personal filters by XRF with biospecimen elements across years.

Sample Matrix	Analyte	No. Meas.	r-square	p-value
BLOOD	CD	60	-.1596	0.2243
BLOOD	PB	60	-.2048	0.1169
URINE	AS	60	0.0001	0.9996
URINE	BA	60	0.2411	0.0634
URINE	CD	60	0.1024	0.4377
URINE	CO	60	0.0027	0.9839
URINE	CS	60	0.1561	0.2346
URINE	PB	60	0.0688	0.6031
URINE	SB	60	-.1323	0.3150
URINE	SE	60	0.1714	0.1913

[*] an extreme value may be driving the association

Table 15. Evaluation of exceedances for Arsenic and Selenium in the context of possible ingestion routes.

Obs	Sample Matrix	Analyte	Dependent Variable	p-value
1	URINE	AS	EATGRAINS (yes)	**0.0197**
2	URINE	SE	EATGRAINS (yes)	0.7692
3	URINE	AS	LOCALPRODUCE (yes)	0.5434
4	URINE	SE	LOCALPRODUCE (yes)	0.0932
5	URINE	AS	EATMEAT (yes)	0.5398
6	URINE	SE	EATMEAT (yes)	0.5162
7	URINE	AS	FILTERWATER (yes)	0.4991
8	URINE	SE	FILTERWATER (yes)	0.3070
9	URINE	AS	DIETSUPPL (yes)	0.4545
10	URINE	SE	DIETSUPPL (yes)	0.2693
11	URINE	AS	HERBSUPPL (yes)	0.4605
12	URINE	SE	HERBSUPPL (yes)	0.2525
13	URINE	AS	MULTIVITA (yes)	0.7515
14	URINE	SE	MULTIVITA (yes)	0.8090
15	URINE	AS	EATFISH W/in 48 hours (yes)	**0.0130**
16	URINE	SE	EATFISH W/in 48 hours (yes)	0.5183
17	URINE	AS	EATRICE W/in 48 hours (yes)	0.5341
18	URINE	SE	EATRICE W/in 48 hours (yes)	0.4590
19	URINE	AS	DRINKSOURCE	0.8090
20	URINE	SE	DRINKSOURCE	0.1388
21	URINE	AS	HRS_INSIDE	0.3316
22	URINE	SE	HRS_INSIDE	0.6585

Evaluation of Study Objectives and Hypothesis

Based on the data presented in the preceding sections, the hypotheses listed in the hypotheses section can be evaluated and answers to the study objectives can be posited.

Objective 1

Hypothesis 1: Contributions of the NRG Energy power plant to ambient $PM_{2.5}$ concentrations in Sussex County will increase with increasing usage of the electricity generating capacity of the power plant. Indoor residential and personal $PM_{2.5}$ concentrations will not be affected.

Results: Contributions of the NRG Energy power plant to ambient $PM_{2.5}$ was not found to increase with electrical generating capacity of the power plant. According to data collected, indoor and personal $PM_{2.5}$ concentrations did not appear to be affected by the operation of the power plant. This is supported by the average 46% reduction in overall $PM_{2.5}$ from Season 1 to Season 2 in all samplers with the exception of personal monitors. The 6.8% increase in personal level $PM_{2.5}$ concentrations is thought to be due to changes in habits of the participants as indicated by the increase in XRF concentrations across a wide variety of elements not typically associated with coal-fired power plants. However, the NRG Energy power plant operates on a variable load that depends on electricity generation needs in the Northeast. The inconsistent operation of the power plant prevented any conclusive evidence about its operational capacity on local $PM_{2.5}$ levels from being discerned. Additionally, without additional gas and particle speciation data, specific linkages between power plant and local $PM_{2.5}$ cannot be established. Such specific information required for the source apportionment would involve particle phase ammonium nitrate, ammonium sulfate, and organic carbon. Gas phase Sulfur dioxide would also be required to generate linkages between local $PM_{2.5}$ and the power plant.

To support the finding that the NRG Energy power plant did not affect the Sussex County $PM_{2.5}$ concentrations average daily wind directions identified the fixed site monitors located downwind and upwind of the power during each day of the study for both seasons (Figure 26). A ratio of upwind/downwind mass concentrations less than unity indicates a source of $PM_{2.5}$ between the two monitors in question. During the first season the average upwind/downwind ratio of 1.7 ± SD 1.6 indicated no significant sources of $PM_{2.5}$ between the two monitors. The same analysis carried out during Season 2 resulted in an upwind/downwind ratio of 0.9 ± SD 0.2. At a level of $\alpha=0.01$, the upwind/downwind ratios between seasons are not statistically different, resulting in the conclusion that the operating conditions of the power plant during the second season do not contribute to the local $PM_{2.5}$ in an appreciable amount in comparison to regional and long-range transport.

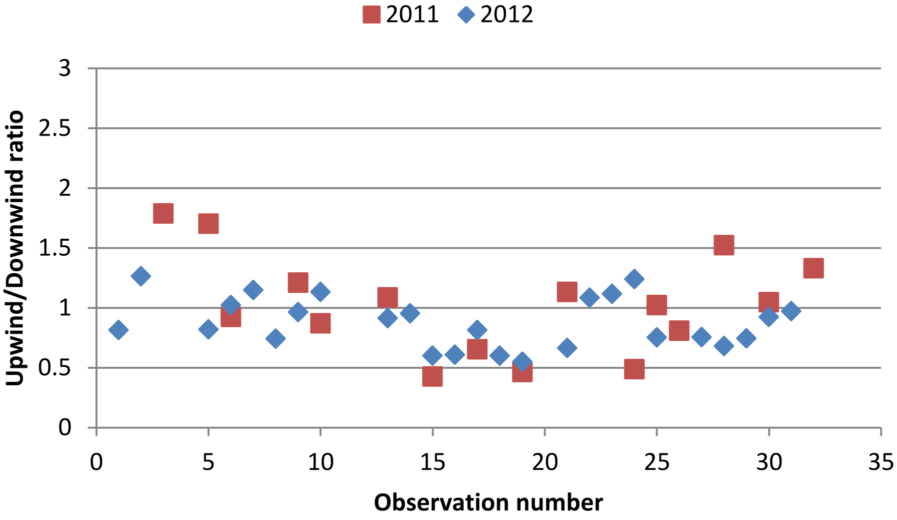

Figure 26. Upwind/downwind ratios of fixed site monitors during both sampling seasons.

Objective 2

For the purposes of this report, Hypothesis 2 and 3 will be combined due to the similar nature of the questions and data used to reach conclusions for each.

Hypothesis 2: Upwind source contributions to ambient Sussex County $PM_{2.5}$ levels will be detectable, and their relative contribution to the $PM_{2.5}$ concentration will decrease as the load on the NRG Energy power plant increases. However, exact sources will be difficult to determine unless a unique emissions profile exists.

Hypothesis 3: The relative contribution of upwind sources from bordering states to the ambient $PM_{2.5}$ concentration will decrease as usage of the energy generating capacity from the NRG Energy power plant increases.

Results: Localized upwind sources were not detectable primarily due to influence of long-range transport and atmospheric mixing during the transport process which created a uniformly disperse air mass. Because of the heavy influence of long-range transport and mixing, precise localized sources of ambient $PM_{2.5}$ could not be identified. This finding is supported by the similarity between the Seaford site and four fixed site monitors indicated the predominant source of $PM_{2.5}$ within Sussex County is likely due to regional or long-range transport (Figure 27).

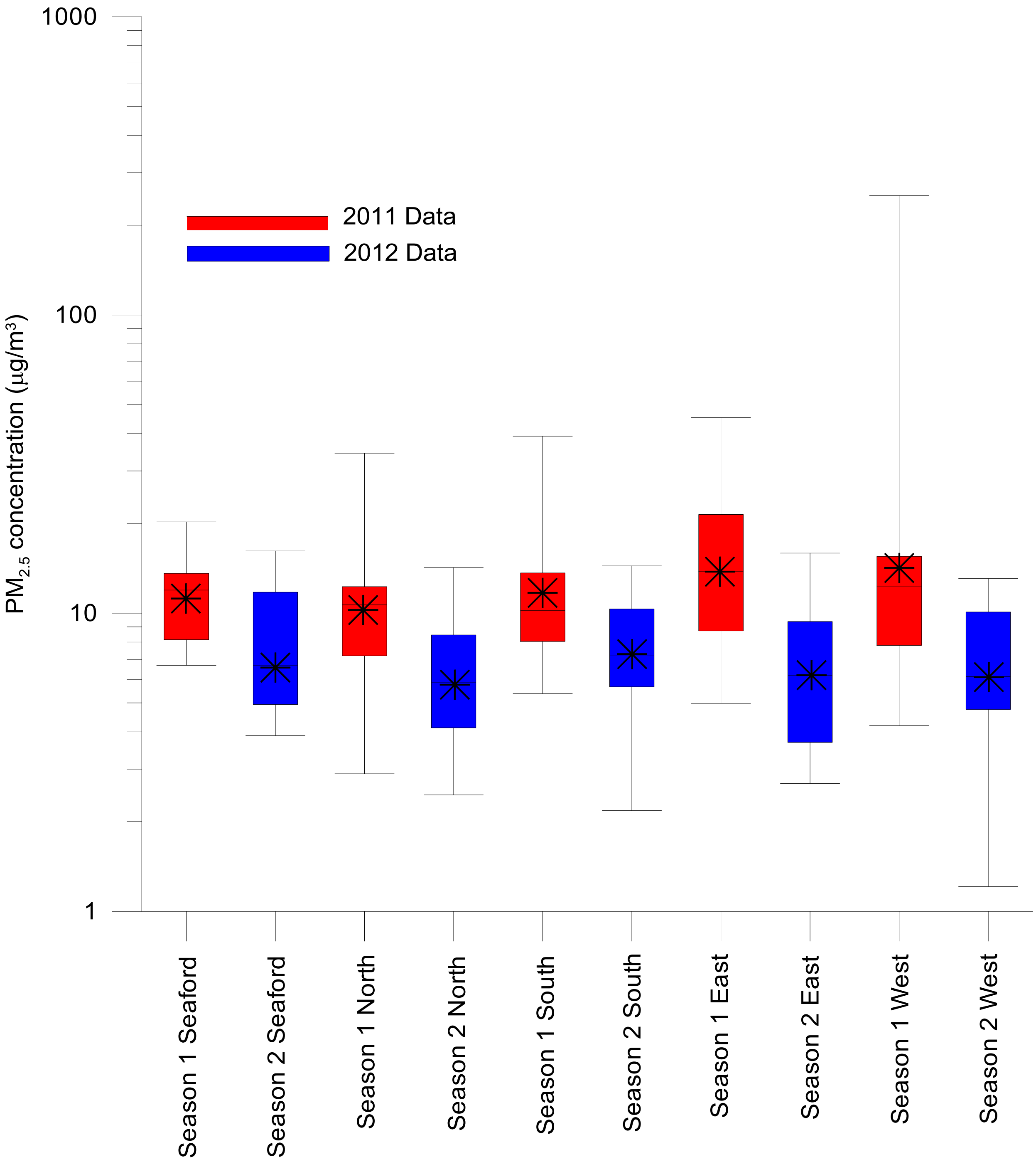

Figure 27. Comparison of Seaford and four fixed site monitors $PM_{2.5}$ concentrations during 2011 (Red, NRG Energy power plant not operating) and 2012 (Blue, power plant operating) sampling seasons.

Figures 28 and 29 illustrate the $PM_{2.5}$ concentration of the four fixed sites (averaged together) and wind direction. Figure 29 illustrates an approximately 3 day delay between wind directed from Northwest-North and maximum $PM_{2.5}$ concentrations. 72-hr HYSPLIT back trajectory analysis of wind patterns (Figure 30) during the $PM_{2.5}$ maxima indicate air masses during this time point originated from major metropolitan areas such as New York, Boston, Baltimore, and Washington D.C.

Furthermore, the transient operation of the NRG Energy power plant prevented establishment of relative contribution of upwind sources to Sussex County $PM_{2.5}$. Without NRG Energy power plant operational data, a qualitative conclusion that upwind sources contributed to a significant proportion of Sussex County $PM_{2.5}$ would be consistent with the similarity in $PM_{2.5}$ levels and chemical signatures observed between Seasons 1 and 2 samples across semi-rural, semi-urban, and urban sites. The homogeneity in samples indicates a more likely source of $PM_{2.5}$ within Sussex County would be regional or long-range transport.

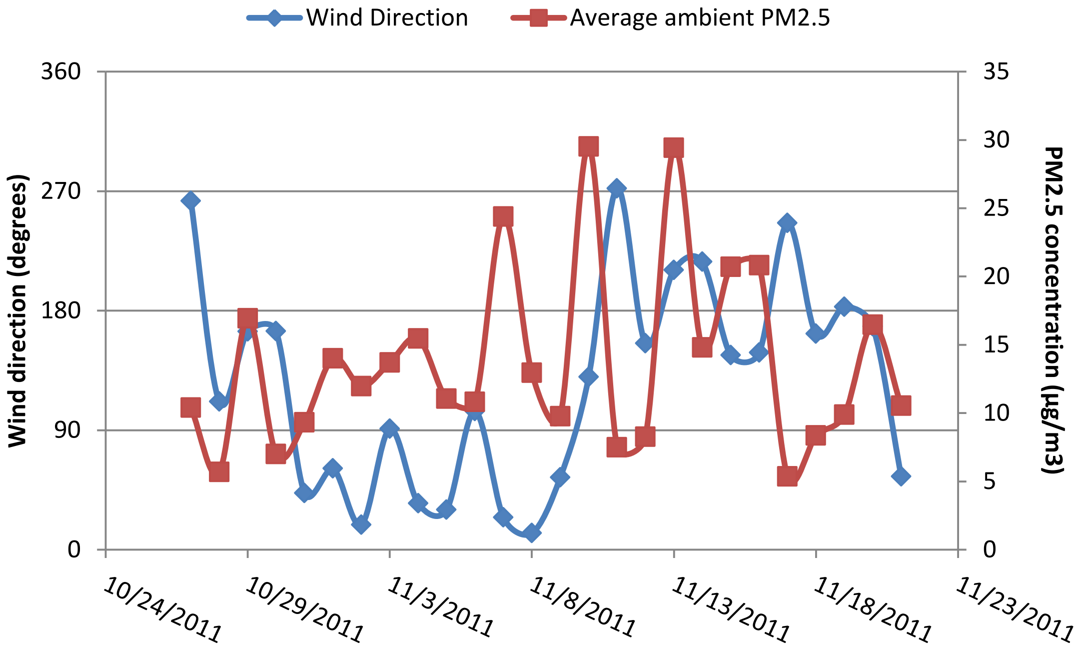

Figure 28. Wind direction and ambient $PM_{2.5}$ concentrations during 2011.

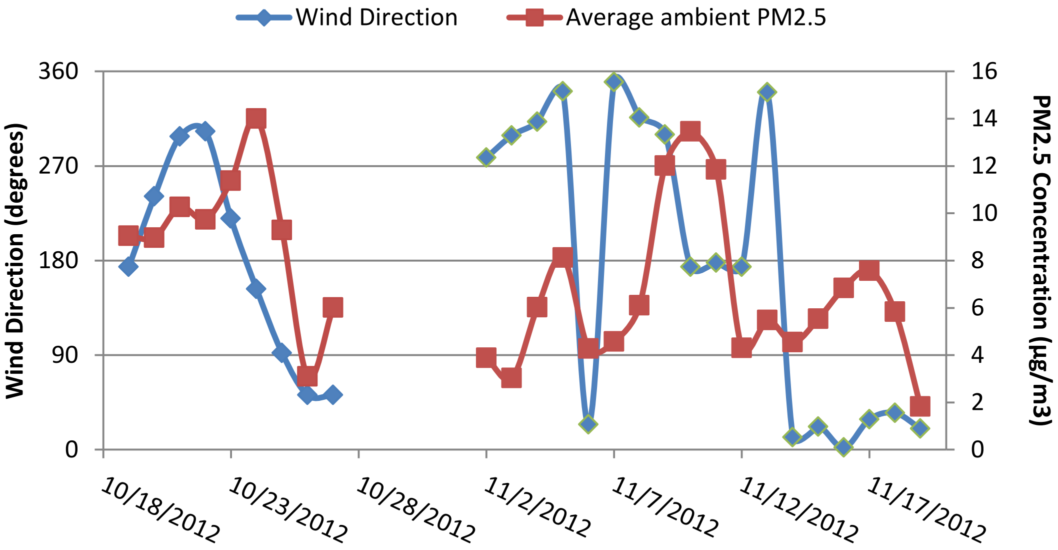

Figure 29. Wind direction and ambient $PM_{2.5}$ concentrations during 2012.

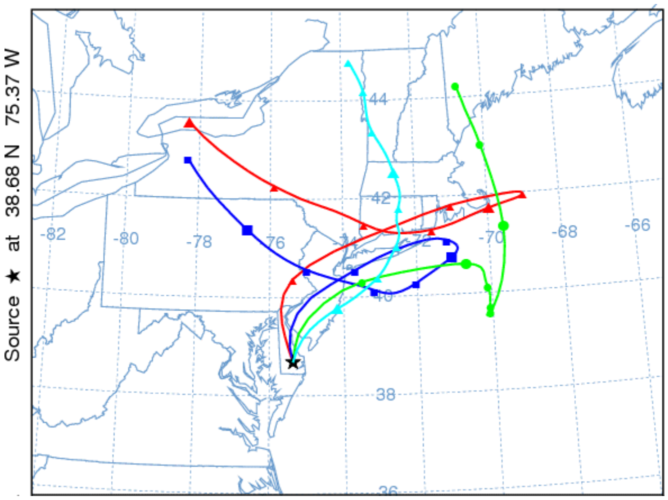

Figure 30. Back trajectory analysis for November 7th, 2012. Different color traces represent air masses initiated at 6-hour time points during the 72-hour analysis.

Objective 3

Hypothesis 4: Relative contributions of other point $PM_{2.5}$ sources to ambient concentrations will decrease after the NRG Energy power plant increases its electricity generation.

Results: The relative contribution of local point sources were not significant enough to evaluate their relative contribution to local $PM_{2.5}$ with respect to regional and long-range $PM_{2.5}$ as indicated through the homogenous nature of the $PM_{2.5}$ concentration and chemical signature in both background and fixed sites. Additional data of higher spatial and temporal resolution in Sussex County are needed to assess the relative contribution of local point sources to $PM_{2.5}$ with respect to the NRG Energy power plant operating capacity.

Hypothesis 5: Personal sources will contribute more to $PM_{2.5}$ exposure relative to during the low electricity generation period than during the high generation sampling period.

Results: Throughout both sampling seasons, personal sources were the predominate source of $PM_{2.5}$ exposure (19.6 ± SD 3.4 $\mu g/m^3$ Season 1, 20.9 ± SD 6.5 $\mu g/m^3$ Season 2). Figure 31 Panel A shows the probability of personal $PM_{2.5}$ exposures greater than 35 $\mu g/m^3$ for all participants, these values are marked as red symbols. Panel B of the same figure shows these same participant days (again marked as red symbols) plotted as the probability of personal ETS exposures. These two figures illustrate that during both seasons ETS was the primary cause for elevated $PM_{2.5}$ exposures, although less so during Season 1.

Sources of these ETS exposures were investigated by evaluating personal/indoor (P/I) ratios. During Season 1, 79% of the participant days had P/I $PM_{2.5}$ ratios greater than 1, however of analysis of these same participants also indicated that only 17% of them had P/I ETS ratios greater than 1. During Season 2, 89% of the participant days had personal/indoor ratios in excess of 1, and 66% of the participants had P/I ETS ratios greater than 1. Thus, the majority of exposure to $PM_{2.5}$ is occurring inside of residences; however the indoor monitors were not able to capture the degree of exposure. The personal exposure monitor worn by the participants was needed to capture their proximity to highly transient ETS $PM_{2.5}$. The elevated ETS concentrations in the personal samples during Season 2 was not observed in the corresponding indoor monitors which indicates the participant was near the guest, spouse, or family member that smoked cigarettes.

ETS had a profound influence on the calculated contribution of different sources to the personal $PM_{2.5}$ concentration. Following Wallace and Williams (2005), the percentage of the personal exposure due to ambient, indoor residential, and "other" sources was calculated. The critical data required for this calculation were 1) valid outdoor, indoor, and personal $PM_{2.5}$ concentrations, 2) valid sulfur concentration data for each sample, 3) the ETS concentration on the personal and indoor residential sample, and 4) percentage of time spent inside the home, outside, and in other locations.

The sulfur data is used to estimate the infiltration of ambient $PM_{2.5}$ into the residence, as described in Wallace and Williams (2005). This approach is only valid if ETS concentrations within the home are less than 5 $\mu g/m^3$. Research has shown that ETS is the primary source of indoor generated sulfur. As a result, ETS concentrations greater than 5 $\mu g/m^3$ confound the calculation of the infiltration factor. As noted earlier, the participant selection criteria allowed cigarette smoking by the participant or other residents of the home to increase recruitment rates. For houses that had indoor ETS concentrations greater than the 5 $\mu g/m^3$ threshold, the mean infiltration factor for non-ETS homes was used.

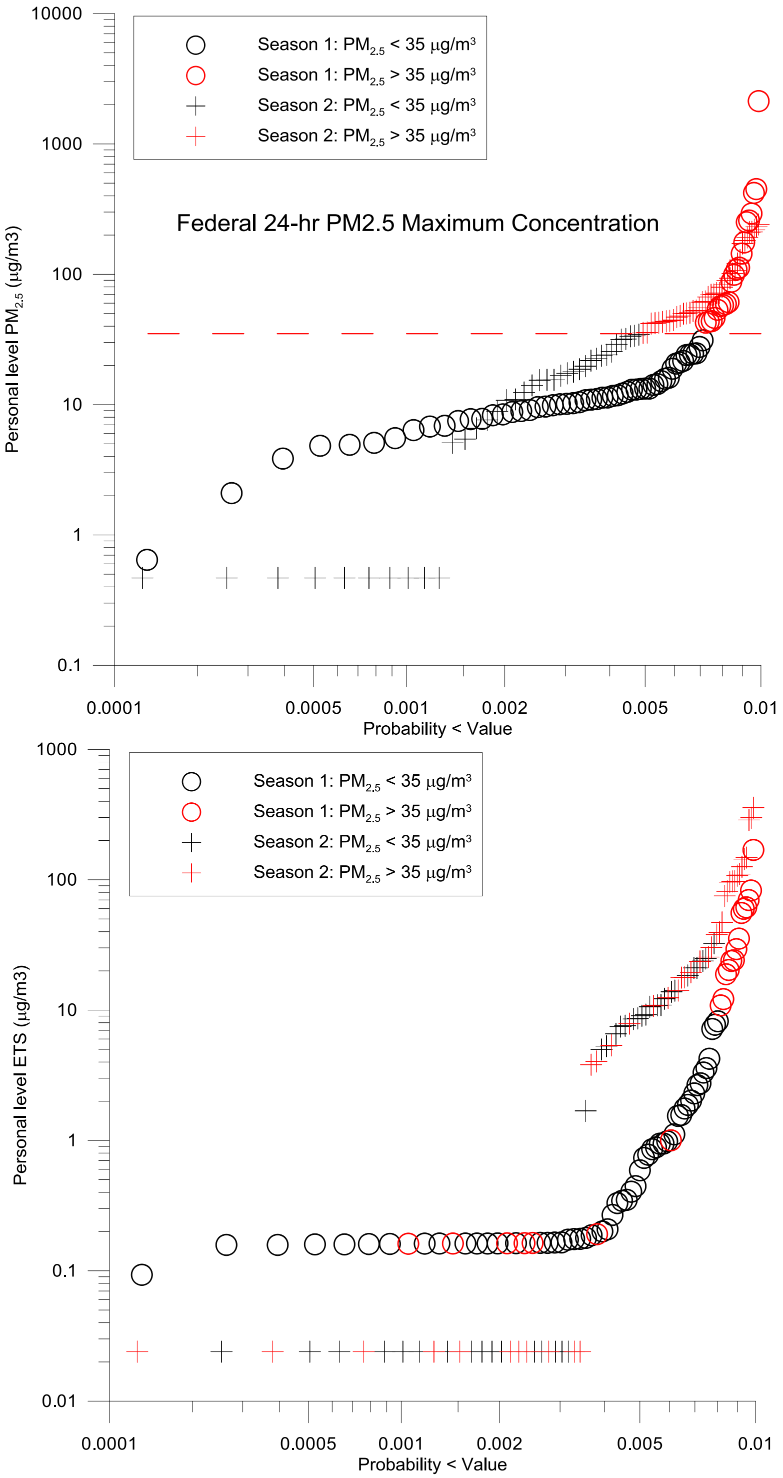

Figure 31. Panel A) Log-probability graph highlighting those participant days with $PM_{2.5}$ exposure greater than 35 µg/m3. Panel B) Log-probability graph showing the majority of those same participant days as also having the highest ETS concentrations.

Table 16 presents the apportionment of the participant's $PM_{2.5}$ exposure due to ambient, indoor residential and "other" sources. The "other" sources category has three components. The main component is the participant's proximity to localized sources within the home since they may be performing the activity or near the resident that is. Typical indoor sources with strong spatial gradients include cigarette smoking, cooking, and cleaning (Rea et al., 2002). The indoor residential portion is the $PM_{2.5}$ concentration sampled by the indoor stationary $PM_{2.5}$ sampler. This sampler is usually placed in a common area of the house (e.g., family room), but not always. The ambient portion is $PM_{2.5}$ that infiltrates into the home via open windows, opening/closing doors, ventilation systems, and gaps around windows, doors, and other exterior openings.

Table 16. Percentage of the personal PM2.5 exposure due to ambient, indoor residential, and other sources. Data are presented by season, and stratified by residences without significant ETS and all residences (ETS and non-ETS). Average and standard deviation for each source are presented. Ambient and indoor percentages are calculated from the personal, indoor, and outdoor data. The "Other" source consists of proximity to localized sources within the participant's home, transportation, and indoors at other locations; it is calculated by difference.

Source	Season 1 (No ETS)	Season 1 (All)	Season 2 (No ETS)	Season 2 (All)
Ambient	57% ± SD 30%	44% ± SD 30%	48% ± SD 53%	14% ± SD 15%
Indoor Residential	23% ± SD 33%	26% ± SD 34%	46% ± SD 65%	15% ± SD 17%
Other	22%	30%	8%	71%
# Observations	42	60	18	64

The impact of ETS on the apportionment of the three sources is clearly evident. The Season 1 and Season 2 apportionment for non-ETS residences are consistent with previous studies conducted in the U.S. (Wallace and Williams, 2005; Rodes et al., 2010). When ETS is added, the percentage contributed by ambient and indoor residential sources decreases and the "other" category increases. This change is expected because of the strong source-proximity effect resulting from ETS. The impact of ETS on the source contribution percentages is especially large in Season 2 since only 28% of the comparisons came from non-ETS homes, as opposed to 70% from non-ETS homes in Season 1.

Furthermore, indoor and personal samples contained additional elements not found in outdoor samples, such as Bromine, Copper, and Phosphorus. These factors coupled with the greater than 80% of time spent indoors by the participants (as determined from questionnaire data) leads to the conclusion that the greatest exposure to $PM_{2.5}$ of the Sussex County population is occurring within indoor environments (Figure 32), while the most extreme events resulted from ETS, cooking, and cleaning. Elevated exposure during these events is expected and has been previously documented (Rea et al., 2002).

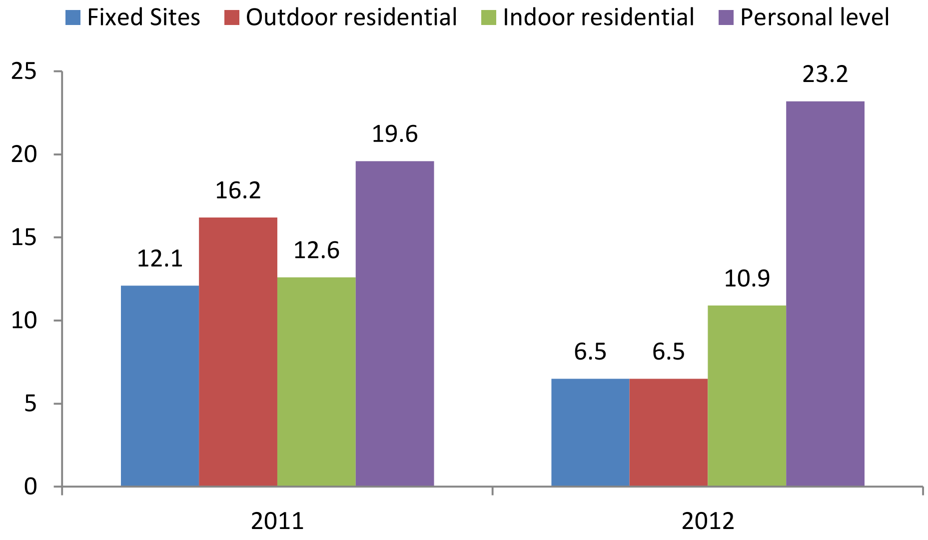

Figure 32. Contributions of $PM_{2.5}$ from each sampling location to the overall $PM_{2.5}$ for Season 1(NRG Energy power plant not operting) and Season 2 (power plant operating). The large influence of personal level sources to $PM_{2.5}$ can be seen, with lesser contributions from indoor and outdoor residential as well as ambient sources. Values above each source represent the geometric mean for that source during that sampling year.

Objective 4

Hypothesis 6: Markers for $PM_{2.5}$ exposure from the NRG Energy power plant emissions in biological specimens will increase as the load demand on the power plant increases.

Results: Metals measured in blood and urine by analyte across seasons are summarized in Figures 24 and 25.

Inorganic elements were measured in both biological matrices in each season, but there was no consistent increase in analytes during Season 2. Apparent increases for some analytes during Season 2, such as Tungsten, Antimony, and Barium, are for elements not associated with coal-fired power plants. This suggests sources other than the power plant are contributors to exposure for those elements. Measures for Arsenic and Selenium from some individuals were high during both seasons, but values in excess of high reference values were not related to power plant operation; both of these elements can arise from dietary sources.

Conclusions

Participant recruitment and retention exceeded study expectations. More than 80 residents of Sussex County contacted RTI and expressed interest in the study. Of the 32 original participants, 29 (91%) returned for the second sampling campaign. The high public interest and high retention rate indicated Sussex County residents are interested in their health and quality of life. The community interest and data quality achievements indicate statewide, longitudinal, multimedia exposure studies are feasible.

Sampling conducted for $PM_{2.5}$ during the fall of 2011 and 2012 indicated the geometric mean ambient $PM_{2.5}$ concentrations of the Millsboro area was 9.3 $\mu g/m^3$. The semi-rural location of Seaford had an average $PM_{2.5}$ concentration of 8.9 $\mu g/m^3$, both below the Federal Standard of 15 $\mu g/m^3$ and were not statistically different at a test value of $\alpha=0.01$. Sampling conducted outdoors and indoors of 35 distinct participants (32 each season) resulted in average $PM_{2.5}$ concentrations of 11.3 $\mu g/m^3$ and 11.8 $\mu g/m^3$ respectively. The higher elevated indoor concentration is expected due to the strength and proximity of $PM_{2.5}$ sources found indoors (e.g. cooking, cleaning, candle burning, smoking, etc.). Personal level sampling conducted during both seasons revealed geometric mean $PM_{2.5}$ concentrations of 20.3 $\mu g/m^3$ across both seasons. Similar to indoor $PM_{2.5}$ measurements that were elevated with respect outdoor and ambient measurement, higher personal level concentrations were presumably due to personal proximity and strength of sources and is to be expected based on previous studies.

Analysis of the chemical and time-series analysis of the ambient $PM_{2.5}$ of Sussex county reveals the predominate source of $PM_{2.5}$ within Sussex county to be regional and long-range transport of $PM_{2.5}$ from upwind metropolitan locations such as Baltimore, New York City, and Boston. This can be observed from the homogeneity of $PM_{2.5}$ from a concentration as well as a compositional standpoint.

Additionally, though not part of the MIEBS, it is conceivable that due to the design of the NRG Energy power plant stacks, the exhaust plume may lead to the majority of the $PM_{2.5}$ to be deposited at great distance from the stack, perhaps in the Atlantic. However, pollutants deposited by this mechanism would be subject to significant dilution.

Despite the fact that control of much of the $PM_{2.5}$ within Sussex County is beyond the control of Delaware officials, the majority of participants spent more than 80% of their day inside their own homes. Thus RTI recommends performing a more detailed study of indoor $PM_{2.5}$ sources as these sources dominate the exposure of the Sussex County population to $PM_{2.5}$. Results from this follow-up study can be used to design an educational plan for the local population in an effort to reduce their exposure and improve their long-term health.

The personal PM species measured do not have a strong and consistent contribution to the analytes measured in the blood and urine from the study participants. The lack of a relationship may mean that current exposures do not result in large biospecimen changes on the time scale of this study. These data might also indicate the possibility of non-inhalation routes of exposure. Dietary and non-dietary ingestion of inorganic species should be considered for future investigation.

Recommendations

The findings from this study suggest several recommendations for future research into the environmental exposures that impact the health of Delaware residents. The recommendations are easily separated into two groups: 1) additional analyses that can be performed using the collected biological, $PM_{2.5}$ and survey data and 2) future data collection and analysis efforts.

Recommendations for further analysis of the existing samples and dataset are summarized below.

- The $PM_{2.5}$ emission from the NRG Energy power plant and the resulting concentration in the ambient air within the study area should be modeled. This analysis will estimate the fraction of the ambient $PM_{2.5}$ contributed by the power plant. RTI wanted to perform this modeling for this report. However, the fact the power plant operated under a variable load during Fall 2012 prohibits performing any modeling until NRG Energy reports $PM_{2.5}$ emission data to DNREC (expected in late 2013). If this modeling is performed, this report should be updated to incorporate the results and revised conclusions.

- Detailed statistical analysis of the $PM_{2.5}$ and biospecimen data against the collected metadata is recommended. The objectives of this report did not include a detailed analysis of the survey, geospatial, or meteorological data in relation to the $PM_{2.5}$ and biospecimen results. A multivariate cluster analysis, such as principal component analysis, will identify variables or classes of variables that predict the $PM_{2.5}$ and biospecimen results. The findings from this analysis would provide valuable information into the design of a larger, statewide multimedia exposure study.

- The additional analysis of $PM_{2.5}$ and biospecimen samples will provide additional details to clarify some of the findings or provide additional data for the multivariate analysis discussed previously. The detailed recommendations listed below can be performed individually, as a subset, or in total.

    - The total arsenic mass in the urine should be speciated into organic and inorganic fractions. CDC has a standard method for this analysis. This data will provide insight into the toxicity and sources of the arsenic exposure noted in the report.

    - The personal $PM_{2.5}$ filters should be analyzed by inductively coupled plasma – mass spectrometry (ICP-MS) to increase the number of elements per filter that are detected. This data would be useful for the multivariate cluster analysis.

    - Measure the urinary cotinine (biomarker of ETS exposure) to confirm ETS is a major source of $PM_{2.5}$ exposure in this study. The data from this inexpensive analysis would provide further confirmation that the study participants were exposed to high levels of tobacco smoke.

Multiple future studies are recommended to provide the information necessary to understand the $PM_{2.5}$ exposures of Sussex County residents and all Delaware residents.

- There is a need to confirm long-range transport of $PM_{2.5}$ from upwind urban areas is the primary contributor to ambient $PM_{2.5}$ concentrations in Delaware. A combination of ambient $PM_{2.5}$

concentration measurements and Hysplit modeling will provide the information. RTI recommends that daily $PM_{2.5}$ samples be collected at an urban, suburban, and rural location for at least four weeks in each season (Winter, Spring, Summer, Fall). The three sites can be existing DNREC monitoring locations. Hysplit back-trajectory analysis, similar to the one conducted for this study, will identify the origin of the ambient air up to 72 hours previously. A time series correlation analysis will determine if the highest $PM_{2.5}$ concentrations at the three monitoring locations are correlated to air that originated over the metropolitan areas surrounding Delaware.

- A source apportionment study conducted at the DNREC Seaford site and one additional site near the NRG Energy power plant would confirm the impact of long-range transport, regional sources, and local sources (including the power plant) on $PM_{2.5}$ concentrations and the Sussex County residents' exposure. This study would require detailed PM2.5 speciation data, including metals (as measured for this study), nitrate, sulfate, and organic carbon fractions. Nitrogen dioxide and sulfur dioxide gas concentration data would also be required.

- Establish multimedia (air, dietary, and non-dietary ingestion) carcinogen exposure and biospecimen distributions on a statewide level. This study would assess the broader, temporal contribution of multiple sources to the total body burden of environmental contaminants and account for individual behavior patterns. Exposure distributions would be captured by enrolling participants in urban, suburban, and rural areas of Delaware and would help to establish the baseline to monitor future exposures. This study would combine the Design I and Design II study designs developed in 2008 (RTI, 2008).

  As an initial step towards establishing a baseline, a study similar to that performed around Millsboro could be conducted in the Wilmington area. This would provide for a comparison of the rural Sussex County to an urban area with regard to the same pollutants. An expansion of the methods to provide more data about the exposures (additional chemical measures in both environmental and biological specimens) will begin to define those measures of greatest use in the broader study.

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Appendices

Appendix A: Questionnaire Data

Table 17. Summarized participant questionnaire results Season 1.

					race	transportation to work			
males	females	average age	average weight (lbs.)	average height (inches)	white	car, truck, or van	bus or trolley	average transit time (minutes)	average number of years lived in Sussex County
11	21	63.2	173.2	64.6	32	8	1	26	18.7

		numbers reporting knowingly been exposed to any of the following							
average hours away from home	average hours outside	asbestos	chemicals	coal/dust	coal tar/asphalt	diesel engine exhaust	dyes	formaldehyde	gasoline exhaust
4.2	2.3	4	6	2	0	1	9	4	0

numbers reporting knowingly been exposed to any of the following, continued			
pesticides	textile fibers	wood dust	x-rays / radioactive material
6	1	3	17

Table 18. Summarized participant questionnaire results Season 2.

					race	transportation to work			
males	females	average age	average weight (lbs.)	average height (inches)	white	car, truck, or van	bus or trolley	average transit time (minutes)	average number of years lived in Sussex County
11	21	63.4	181.7	66.9	32	7	0	27.1	19.8

		numbers reporting knowingly been exposed to any of the following							
average hours away from home	average hours outside	asbestos	chemicals	coal/dust	coal tar/asphalt	diesel engine exhaust	dyes	formaldehyde	gasoline exhaust
3.6	2.4	6	6	3	0	4	3	4	3

numbers reporting knowingly been exposed to any of the following, continued			
pesticides	textile fibers	wood dust	x-rays / radioactive material
6	3	2	10

Table 19. Summarized residential questionnaire results Season 1.

type of home					
mobile home	one-family detached	one family attached	building with 2 or more apartments	boat, RV, van, etc	other
9	19	1	0	0	2

location and use of garage							
none, detached, or separate carport	attached	underneath	parking one car	parking two cars	parking more than 2 cars	storage only	N/A
19	12	0	12	3	0	4	10

Type of heating							
forced air gas	forced air oil	forced air electric	forced water, radiator	heat pump	wood burning stove	fireplace, gas	fireplace, wood
12	2	6	0	5	3	1	1

Type of heating, continued				
gas space heater	kerosene space heater	electric space heater	open stove/oven	other
1	0	4	0	5

average number of years resident of this building	average age of building (years)	average # of people	average # of children	how many central AC units (per residence)	how many window AC units	storm windows present	kitchen exhaust fan (yes)
12.9	**23.1**	**2**	**0**	**1**	**1**	**20**	**27**

Table 20. Summarized residential questionnaire results Season 2.

type of home					
mobile home	one-family detached	one family attached	building with 2 or more apartments	boat, RV, van, etc	other
10	21	1	0	0	2

location and use of garage							
none, detached, or separate carport	attached	underneath	parking one car	parking two cars	parking more than 2 cars	storage only	N/A
21	13	0	13	3	0	5	13

Type of heating							
forced air gas	forced air oil	forced air electric	forced water, radiator	heat pump	wood burning stove	fireplace, gas	fireplace, wood
14	2	6	0	6	4	1	1

Type of heating, continued				
gas space heater	kerosene space heater	electric space heater	open stove/oven	other
1	0	4	0	5

average number of years resident of this building	average age of building (years)	average # of people	average # of children	how many central AC units (per residence)	how many window AC units	storm windows present	kitchen exhaust fan (yes)
12.9	**22.3**	**2**	**0**	**1**	**1**	**16**	**21**

Table 21. Summarized additional questionnaire data taken during season 2.

What is your source of drinking water	Do you filter your drinking water*	Do you eat meat or poultry on a regular basis*	Do you eat grains, nuts, or bread products on a regular basis*	Do you eat locally grown produce*	In the past 48 hrs, have you eaten rice or rice products*	How many servings of rice or rice products did you have
Community Source 19 Private well 12 Community 1	17	29	24	25	6	2
In the past 48 hrs, have you eaten fish or shellfish*	**Was the fish or shellfish caught locally***	**How many servings or fish or shellfish did you have**	**Do you take dietary supplements***	**average # of supps.**	**Do you take multi-vitamins***	**Do you take herbal supplements***
8	2	1	23	2	14	6

*Numbers represent average number of positive responses to the question

Appendix B: Reference Ranges for Analytes in Blood or Serum

Analyte Monitored	**Fluid**	**Reference Range, 95th Percentile NHANES 2013, ng/mL [i]**	**Reference Ranges [ii]**	**High Value (µg/L) [iii, iv]**
Cadmium	Blood	1.55	<5 µg/L	>5 µg/L
Lead	Blood	3.57 µg/dL	<30 µg/dL	>40 µg/dL
Mercury	Blood	5.75	<10 µg/L	>200 µg/L
1,2-Dichloroethane	Serum	Not Available	Not defined	Not defined
Benzene	Serum	0.34	Not defined	Not defined
Carbon tetrachloride	Serum	<LOD	Not defined	Not defined
Chloroform	Serum	Not Available	Not defined	Not defined
Ethylbenzene	Serum	0.15	Not defined	Not defined
m- & p-Xylene	Serum	0.43	Not defined	Not defined
o-Xylene	Serum	0.11	Not defined	Not defined
Styrene	Serum	0.15	Not defined	Not defined
Tetrachloroethylene	Serum	0.13	Not defined	Not defined
Toluene	Serum	0.90	Not defined	Not defined

[i] Fourth National Report on Human Exposure to Environmental Chemicals, updated Tables for Adults over 20 years, March 2013, Centers for Disease Control and Prevention National Center for Environmental Health (NCEH), Environmental Health Laboratory.

[ii] Tietz Textbook of Clinical Chemistry, edited by C.A. Burtis and E.R. Ashwood, 1999

[iii] Carson, B.L., Ellis III H.V., and McCann, J.L., Toxicology and Biological Monitoring of Metals in Humans, Lewis Publishers, 1986.

[iv} "High" levels are repeat upper boundary levels; samples with results greater than this range are reanalyzed for confirmation.

Appendix C: Reference Ranges for Analytes in Urine

Element/ Isotope Monitored	**Fluid**	**Reference Range, 95th Percentile NHANES 2013, ng/mL [i]**	**High Value (µg/L, PPB) [ii]**
Beryllium	Urine	<LOD	0.2
Cobalt	Urine	1.35	2.83
Molybdenum	Urine	144	293.5
Cadmium	Urine	1.13	2.54
Antimony	Urine	0.220	0.8
Cesium	Urine	11.1	16.5
Barium	Urine	6.80	17.1
Tungsten	Urine	0.370	1.38
Platinum	Urine	0.017	0.1
Thallium	Urine	0.410	0.62
Lead	Urine	1.71	7.8
Uranium	Urine	0.36	0.277
Arsenic, total	Urine	93.1	64.5
Selenium, total	Urine	30.9 [iii]	68

[i] Second National Report on Human Exposure to Environmental Chemical, hhtp://cdc.gov/exposurereport/2nd/metal.htm, Centers for Disease Control and Prevention, 2013.

[ii] Values provided by DE DHSS (Call level). "High "values are repeat upper boundary levels; samples with results greater than this are reanalyzed for confirmation

[iii] value provided by DE DHSS; referenced as NHANES 1999-2000

Appendix D: Data Quality Indicator Determination Methods

Quantitative data quality indicators (DQIs) targeted for each metric collected are presented in Tables 3 and 4. DQIs include method detection limit (MDL), precision, accuracy, and completeness. Qualitative DQIs include representativeness and comparability. Quality control sample results from the outdoor, indoor, and fixed sites were combined to increase the statistical strength of the DQIs. Collocated duplicate samples from all locations were combined to calculate the precision of the PEMs. Field blanks and standard weight analyses were combined when calculating the MDL and MQL values for the PEMs. This approach is reasonable given the same sampler (PEMs) was deployed at each location and the filter underwent identical analysis (gravimetric, ETS/BrC, and BC).

Precision

Precision is the agreement between the measurements collected by two identical devices or measures under similar conditions. Collection of collocated duplicate samples provides information on the variability in the sample collection, handling, storage, and analysis. Precision is reported as percent relative standard deviation (% RSD) between replicate samples or sample analyses and is defined as

$$\%\,RSD = \frac{SD}{Mean} \times 100$$

where SD is the standard deviation and *Mean* is the mean value of the measurements from each replicate set.

Accuracy and Bias

Accuracy is the measure of the closeness of a measured value to a known or true value and includes both random error (precision) and systematic error (bias). Precision was discussed previously. Bias is the distortion of the data in a consistent direction due to measurement or analytical error. Measurement and analytical bias should be estimated using materials as independent as possible from the measurement system.

Measurement accuracy is used to assess sample collection with the integrated and continuous instrumentation. Measurement accuracy will be reported as a comparison between the measured value and the known value of a standard. Accuracy is defined as

$$\%\,Accuracy = \frac{C_{sample} - C_{std}}{C_{std}} \times 100$$

where C_{std} and C_{sample} are the values for the standard and the sample, respectively. Measurement accuracy for instrumentation typically is determined by the validation of the instrument performance during instrument development. For continuous monitors, accuracy also is determined during instrument calibration certification.

Analytical accuracy will be reported as recovery from spiked control samples during sample analysis. The composition and concentration of the spiked sample will come from a standard reference material (e.g., National Institute of Standards and Technology [NIST]). Recovery is defined as

$$\%\,Recovery = \frac{C_m - C_u}{C_s} \times 100$$

where C_m, C_u, and C_s are the concentration of each target analyte measured in the spiked sample, in the unspiked sample, and the spiking solution, respectively. This definition of analytical accuracy incorporates matrix recovery into the assessment. A documented, consistent spiking protocol is essential to obtain useful accuracy estimates.

Table 22. Target DQI's for each metric and analyte.

Metric	Analysis	MDL/MQL	Precision	Accuracy	% Complete	
					Collection	Analysis
RTI MicroPEM	Gravimetric	1.4/4.2 µg/m^3	±10%	±15%	95%	99%
	ETS	2.4/7.2 µg/m^3	±10%	±15%	95%	99%
	BC	0.4/1.2 µg/m^3	±10%	±15%	95%	99%
	XRF	See Table 2-2				
2 Lpm PEM	Gravimetric	0.2/0.6 µg/m^3	±10%	±10%	95%	99%
	ETS/BrC	0.3/0.9 µg/m^3	±10%	±10%	95%	99%
	BC	0.1/0.3 µg/m^3	±10%	±10%	95%	99%
	XRF	See Table 2-2				
Questionnaires	NA	NA	NA	NA	99%	NA
HOBO	NA	NA	NA	NA	99%	NA

Completeness

Completeness is a measure of valid data obtained from each metric. Completeness consists of sample collection and analysis components. Completeness requirements for sample collection and analysis aspects are presented because their relative importance varies between metrics. Completeness is typically defined by RTI as follows for all chemical and physical measurements:

$$\%\,Completeness = \frac{V}{N} \times 100$$

where V is the number of measurements judged valid, and N is the number of measurements planned. The anticipated influence of completeness for each metric on the ability to answer the study hypotheses should be considered when the statistical design for the study is being developed.

Other Quality Criteria

Instrument Detection Limit (IDL)

The quantity of the target analyte that can be measured and distinguished from zero on a continuous monitor provides direct output of the metric of interest. It is the lowest level readable on a display or recorded that can be distinguished from background.

Method Detection Limit (MDL), Corrected for Optimal Sample Volume

The method detection limit (MDL) is defined as the minimum concentration of substance that can be measured and reported with a known confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. For all applicable metrics, the equation to determine the MDL for a given analyte is:

$$\mathrm{MDL} = t_{(n\text{-}1,\ a=0.68)}S$$

where, $t(n\text{-}1, a = 0.68)$ represents the Students' t-test t value appropriate for a 68% confidence level (84% one-tailed) and a standard deviation estimate with n-1 degrees of freedom. S is equal to the standard deviation of the replicate (usually seven samples) analyses. This value is obtained from analyzing standard samples containing the target mass between the MDL and the lowest target analyte mass expected to be observed (or blank filters for filter media). This value is then divided by the theoretical sample volume. For example, the theoretical volume for a 24 h PM sample collected on a PEM sampler operating at 4 L per minute is 5,760 L or 5.76 cubic meters.

Method Quantitation Limit (MQL)

For other analyses, such as gravimetric, the MQL is three times the MDL [MQL = 3 x MDL] and within the specified limits of precision and accuracy during routine analytical operating conditions. Tables 4 and 5 contain the current values of MQL.

Table 23. Target quantitative DQI's for XRF analysis.

Element	MDL/MQL ng/filter	Precision	Accuracy	% Completeness	
				Collection	Analysis
Sodium	70/210	20	10	95%	99%
Magnesium	70/210	20	10	95%	99%
Aluminum	500/1,500	20	10	95%	99%
Silicon	170/510	20	10	95%	99%
Phosphorous	120/360	20	10	95%	99%
Sulfur	70/210	20	10	95%	99%
Chlorine	50/150	20	10	95%	99%
Potassium	30/90	20	10	95%	99%
Calcium	40/120	20	10	95%	99%
Titanium	70/210	20	10	95%	99%
Vanadium	25/75	20	10	95%	99%
Chromium	10/30	20	10	95%	99%
Manganese	10/30	20	10	95%	99%
Iron	30/90	20	10	95%	99%
Cobalt	20/60	20	10	95%	99%
Nickel	15/45	20	10	95%	99%
Copper	15/45	20	10	95%	99%
Zinc	10/30	20	10	95%	99%
Arsenic	15/45	20	10	95%	99%
Selenium	8/24	20	10	95%	99%
Bromine	10/30	20	10	95%	99%
Rubidium	10/30	20	10	95%	99%
Strontium	10/30	20	10	95%	99%
Zirconium	80/240	20	10	95%	99%
Silver	50/150	20	10	95%	99%
Cadmium	60/180	20	10	95%	99%
Tin	80/240	20	10	95%	99%
Antimony	90/270	20	10	95%	99%

Element	MDL/MQL ng/filter	Precision	Accuracy	% Completeness	
				Collection	Analysis
Cesium	133/400	20	10	95%	99%
Barium	170/510	20	10	95%	99%
Cerium	467/1,400	20	10	95%	99%
Mercury	23/70	20	10	95%	99%
Lead	24/72	20	10	95%	99%

Table 24. Actual DQIs from MIEBS Seasons 1 & 2.

Metric	Analysis	MDL/MQL	Precision*	Accuracy	% Complete	
					Collection	Analysis
RTI MicroPEM	Gravimetric:					
	Season 1	0.1/0.4 μg/m^3	-	0.1%	See Table 7	See Table 7
	Season 2	0.2/0.7 μg/m^3	-	0.1%	See Table 8	See Table 8
	ETS:					
	Season 1	0.04/0.1 μg/m^3	-	-	See Table 7	See Table 7
	Season 2	0.01/0.03 μg/m^3	-	-	See Table 8	See Table 8
	BC					
	Season 1:	0.01/0.03 μg/m^3	-	-	See Table 7	See Table 7
	Season 2:	0.03/0.08 μg/m^3	-	-	See Table 8	See Table 8
	XRF	See Table 7				
PEM:	Gravimetric:					
2 LPM season 1	Season 1	0.3/0.9 μg/m^3	10.1%	-5.5%	See Table 7	See Table 7
4 LPM season 2	Season 2:	0.02/0.08 μg/m^3	14.8%	-5.5%	See Table 8	See Table 8
	ETS/BrC:					
	Season 1	0.3/1.0. μg/m^3	17.6%	-	See Table 7	See Table 7
	Season 2	0.008/0.002 μg/m^3	10.0%	-	See Table 8	See Table 8
	BC:					
	Season 1	0.3/1.0. μg/m^3	2.6%	-	See Table 7	See Table 7
	Season 2	0.008/0.002 μg/m^3	6.0%	-	See Table 8	See Table 8
	XRF	See Table 7				
Questionnaires	Season 1	NA	NA	NA	91%	NA
	Season 2				100%	
HOBO	Season 1	NA	NA	NA	100%	NA
	Season 2				100%	

[*]Precision values are averages of all filters collocated filters: n = 7 Season 1; n= 14 Season 2

Table 25. Actual DQIs for XRF Analysis of MIEBS Season 1 & 2 data.

	MDL (ng/filter)		MQL (ng/filter)		Median Precision		Accuracy	
	Season 1	Season 2	Season 1	Season 2	Season 1	Season 2	Season 1	Season 2
Ag	211.9	223.5	635.7	670.4	0.0	0.0	-	-
Al	119.1	95.2	357.3	285.7	0.0	0.0	-	-
As	12.1	10.8	36.2	32.5	0.0	0.0	-	-
Ba	59.4	67.2	178.3	201.5	0.0	0.0	-	-
Br	12.5	11.4	37.5	34.3	0.0	0.0	-	-

	MDL (ng/filter)		MQL (ng/filter)		Median Precision		Accuracy	
Ca	22.7	18.8	68	56.3	0.0	22.5	-	-
Cd	283.1	299.5	849.4	898.6	0.0	0.0	0.0	-2.0
Ce	30.2	50.1	90.6	150.2	0.0	0.0	-	-
Cl	22.6	18.4	67.8	55.1	0.0	0.0	-	-
Co	6.4	5.8	19.2	17.3	0.0	0.0	-	-
Cr	10.9	11.6	32.8	34.9	0.0	0.0	-	-
Cs	60.7	70.7	182.2	212.0	0.0	0.0	-	-
Cu	10.1	6.6	30.4	19.9	0.0	0.0	-	-
Fe	10.7	9.5	32	28.5	19.6	10.5	0.6	0.8
In	367.4	383.8	1102.1	1151.3	0.0	0.0	-	-
K	19.1	17.9	57.2	53.8	9.4	10.9	-	-
Mg	56.7	44.5	170.2	133.4	0.0	0.0	-	-
Mn	8.8	8.8	26.4	26.5	0.0	0.0	-	-
Na	131.4	92.4	394.2	277.3	0.0	0.0	-	-
Ni	5.9	5.0	17.8	15.0	0.0	0.0	-	-
P	45.7	4.7	137.2	14.0	0.0	0.0	-	-
Pb	25.0	19.3	75	58.0	0.0	0.0	-0.8	1.8
Rb	13.7	13.8	41.2	41.3	0.0	0.0	-	-
S	29.6	23.6	88.8	70.7	5.3	7.2	-	-
Sb	712.5	709	2137.6	2127.1	0.0	0.0	-	-
Se	13.5	11.7	40.4	35.1	0.0	0.0	1.3	-0.3
Si	57.4	47.7	172.3	143.2	33.1	27.1	1.1	-0.2
Sn	497.3	552.2	1491.8	1656.7	0.0	0.0	-	-
Sr	18.2	154.7	54.7	464.0	0.0	0.0	-	-
Ti	22.7	28.8	68.2	86.3	0.0	0.0	0.2	1.5
V	15.2	18.7	45.7	56.0	0.0	0.0	-	-
Zn	10.1	7.7	30.2	23.0	0.0	27.7	-	-
Zr	139.3	197.5	418	592.5	0.0	0.0	-	-

Data validity was determined on three levels: 1) review of data collection sheets recorded by field technicians during sampling, 2) physical inspection of filters, and 3) comparison of analysis results against other filters collected. During each of these steps filters were given one of three levels of validity:

- Invalid (code = 0; noted handling issue or obvious filter damage which precludes analysis)
- Suspect (code = 1; no noted issues, but reported value is more or less than twice the standard deviation of the mean)
- Valid (code = 2; no noted issues and data value is within two standard deviations of the mean)

During the first level of data validation, any filters that were noted as incorrectly handled were marked as invalid due to possible contamination. The second level of data review involved visual inspection of filters for any holes which might induce errors in analytical analysis. The final level of data validation resulted from comparison of analytical data amongst all filters of similar sample collection parameters. All data was entered into a comprehensive file in order to provide a unified space for data to be housed. Results from the validation procedures are displayed in Tables 7 and 8.

Glossary

Particulate Matter (PM): Any material, except pure water, that exists in the solid or liquid state in the atmosphere, such as soot, dust, smoke, fumes, and aerosols. The size of particulate matter can vary from coarse, wind-blown dust particles to fine particle combustion products.

Particulate Matter less than 2.5 micrometers ($PM_{2.5}$): A major air pollutant consisting of tiny solid or liquid particles, generally soot and aerosols. The size of the particles (2.5 micrometers or smaller, about 0.0001 inches or less) allows them to easily enter the air sacs deep in the lungs where they may cause adverse health effects, as noted in several recent studies. $PM_{2.5}$ also causes visibility reduction.

Volatile Organic Compound (VOC): This term is generally used similarly to the term "reactive organic compounds" but excludes ethane, which the federal government does not consider to be reactive. VOCs are hydrocarbon compounds that exist in the ambient air and contribute to the formation of smog and/or may themselves be toxic. VOCs often have an odor, and some examples include gasoline, alcohol, and the solvents used in paints.

Minimum Detection Limit (MDL): The minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Minimum Quantification Limit: The smallest detectable concentration of analyte greater than the detection limit where the required* accuracy (precision & bias) is achieved for the intended purpose.