# Tacoma and Seattle Area Air Toxics Evaluation

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# Executive Summary

In a joint air monitoring and data analysis effort, the Puget Sound Clean Air Agency and the University of Washington collaborated to collect information characterizing the similarities and differences in air toxics between Seattle and Tacoma from 11/02/2008 to 10/28/2009. This work was funded primarily through a competitive EPA monitoring grant. Prior to this study, the only air toxics monitoring conducted in Puget Sound was in Seattle. This study was primarily designed to better understand air toxics in the Tacoma area.

Air toxics are a group of air pollutants known or suspected to cause serious health problems. Potential health effects include cancer, lung damage, and nerve damage.[1] People exposed to toxic air pollutants at sufficient concentrations and durations may have an increased chance of getting cancer or experiencing other serious health effects. In this report, the term "air pollutant" and "pollutant" are general terms encompassing "criteria air pollutants" and "air toxics". At times, one or more air toxics are referred to in a more general sense as a pollutant or air pollutant.

The Environmental Protection Agency's (EPA) National-Scale Air Toxics Assessment (NATA) shows that those living in urban areas of the US are in the top 5th percentile of the country for potential health (cancer) risk from air toxics. Assessing urban areas like Tacoma and Seattle air toxics is important to understand how to use available resources best and mitigate these potential risks.

## Monitoring Locations

The fixed monitoring sites used in this study included two sites in Seattle and four in Tacoma. The sites included: Seattle Beacon Hill, Seattle Duwamish, Tacoma Tideflats, Tacoma Portland Ave, Tacoma South L St, and Tacoma Alaska St. These monitoring sites are mapped on the image below. The Seattle Beacon Hill site was operated by the Washington State Department of Ecology, and is a National Air Toxics Trends Station (NATTS). As such, there is a historical record of air toxics since 2000 at this location. All other sites were run by the Puget Sound Clean Air Agency. Collectively, Tacoma sites were chosen to capture the spatial distribution of Tacoma air toxics for intra-city comparisons. In addition, Seattle sites were chosen to make inter-city and historical comparisons.

**Fixed Monitoring Sites for the Study**

## Priority Pollutants

We measured over 100 different pollutants, of which only 9 were found to be at concentrations above Washington State established screening levels. Concentrations above screening levels present potential health risk. Eight of the nine were above screening levels specifically for potential cancer risk. Therefore, this report puts more emphasis on the potential cancer risks due to air toxics.

For non-cancer effects, acrolein was the only pollutant we monitored with a concentration exceeding a level of concern. This pollutant is associated with upper respiratory irritation. Concentrations were similar among the study sites and were also similar compared to the national sites.

Non-cancer health effects associated with particulate matter-related combustion mixtures (e.g., wood smoke and diesel soot) are not evaluated here, as only air toxics were directly monitored, but these still present serious non-cancer health risks.[2]

This study identified 8 individual pollutants and pollutant mixtures with the highest contribution to potential cancer risk, which are, in order, **diesel particulate matter[*], wood smoke particulate matter[*], carbon tetrachloride, benzene, 1,3-butadiene, formaldehyde, naphthalene, acetaldehyde, chloroform, and tetrachloroethene**. These are the same air toxics highlighted in the Seattle 2003 study,[3] EPA's 2002 NATA,[4] and other national studies.

The main underlying sources for these priority pollutants in both Seattle and Tacoma are the same: motor vehicle traffic and residential wood burning. Both of these important sources can be further reduced with policy changes aimed at reducing diesel emissions, wood smoke, and motor vehicle emissions. By reducing these emission sources, the highest risk pollutants except carbon tetrachloride would be reduced.

Although the same pollutants are contributors to potential cancer risk in both Tacoma and Seattle, the relative importance of different pollutants and the fractional contribution to risks vary between the cities. In Seattle, diesel exhaust emissions dominate risk, while in Tacoma wood smoke and air toxics make a larger contribution (see figure below).

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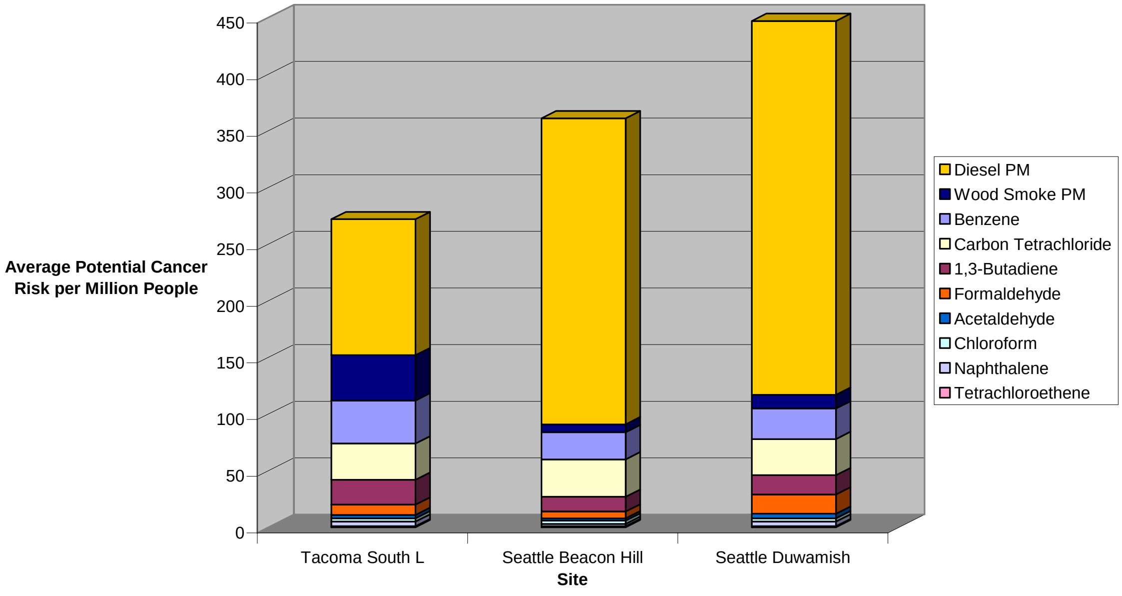
[*] Diesel and wood smoke concentrations were estimated from other studies [Ogulei (2010); Kim, Hopke (2008)].

**Total Potential Cancer Risk per Million People for Tacoma South L Street (270), Seattle Beacon Hill (360), and Seattle Duwamish (450), Subdivided into Largest Contributors**



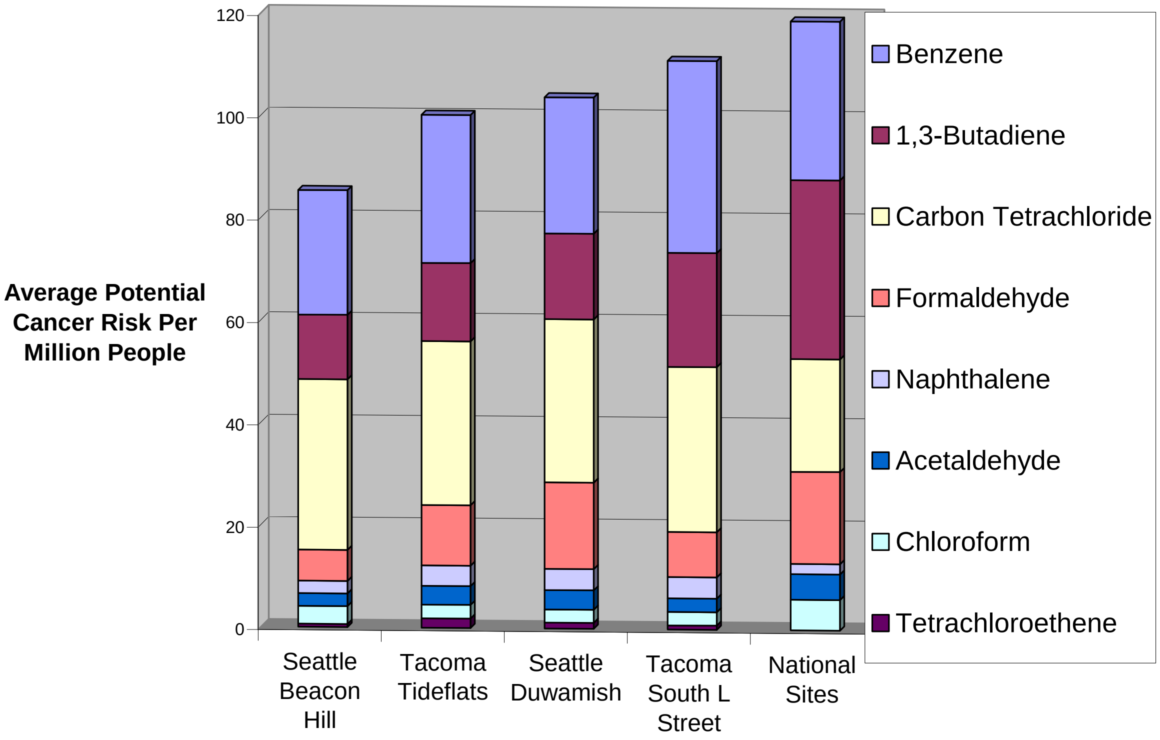
## Diesel Impact

Diesel is still the largest contributor to potential cancer risk throughout Puget Sound. Diesel risk contributed over 70% of the potential cancer risk at the Seattle sites. This study is consistent with results from 2003, which energized the Agency's diesel emission reduction program.

## Wood Smoke Impact

The Tacoma area is currently nonattainment for the 24-hour National Ambient Air Quality Standard (NAAQS) for fine particulate ($PM_{2.5}$). Adverse health effects from breathing air with a high $PM_{2.5}$ concentration include: premature death, increased respiratory symptoms and disease, chronic bronchitis, and decreased lung function particularly for individuals with asthma and increased cardiovascular disease.[5,6] Recent work[7] has confirmed that the most significant source contribution of $PM_{2.5}$ in Tacoma is from wood smoke.

**Potential Cancer Risk per Million People for Monitored Pollutants (excluding diesel and wood smoke particulate) at Selected Sites including NATTS 2007-2008 average, Subdivided into Largest Contributors**



The results of this study demonstrate that in addition to having elevated $PM_{2.5}$ concentrations, the Tacoma residential sites have elevated air toxics concentrations. The Tacoma South L Street residential site, which violates the 24-hour $PM_{2.5}$ standard, was found to have the highest cancer risk attributed to monitored air toxics in this study (excluding diesel and wood smoke particulate estimates). It is noteworthy that this site is higher than the industrial centers like the Seattle Duwamish and the Tacoma Tideflats sites. Additionally, the Tacoma sites appear to be higher than the Seattle sites for higher risk pollutants like benzene and 1,3-butadiene.

This study also compared air toxics concentrations to the National Air Toxics Trends Sites Network. The network of roughly 30 sites contains a mix of mostly urban areas with some rural sites across the US (e.g. Houston, St. Louis, Portland, San Jose, Tampa, Boston). Air toxics linked to wood smoke (e.g. benzene and naphthalene) were much higher in Tacoma residential sites than these national sites. However, total cancer risk was lower at all the sites compared to the NATTS as other pollutants like formaldehyde, chloroform, and acetaldehyde made the national risk higher than Puget Sound.

Levoglucosan, a stable chemical marker for wood burning, was used to estimate daily average wood smoke contributions to ambient particulate matter and to correlate air toxics to wood smoke contributions. Levoglucosan was correlated with most priority air toxics (1,3-butadiene, benzene, black carbon, chloroform, elemental carbon, organic carbon, naphthalene, $PM_{2.5}$) moderately to strongly suggesting wood smoke as a significant source of these pollutants.

## Spatial Variability

In this study, mobile monitoring of ambient air was conducted to observe any spatial variations in the Tacoma area. Benzene, fine particulate matter, and other air pollutants were sampled on a mobile platform. Sampling occurred during air stagnation events in the winter and summer to capture the highest pollution levels.

A principle component analysis (PCA) resulted in a wood smoke factor that correlated to benzene and appeared exclusively on winter nights. Additionally, the spatial distribution of the pollutants demonstrated that the residential neighborhoods were the source for the emissions.

Moreover, this study confirms the results of a temporary study performed by the Agency in 2007 that monitored fine particulate matter distribution in South Tacoma. The temporary study demonstrated that particulate matter was relatively evenly distributed in the southern end of Tacoma within residential neighborhoods.

## Air Toxics Concentrations Have Decreased Since 2001-2002

Historical data from the 2001-2002 air toxics monitoring campaign, in addition to Seattle Beacon Hill annual data show that air toxics have decreased over time. The one exception is carbon tetrachloride, which remains a national concern for potential cancer risk. Although this chemical has been banned from most applications for many years, low level emissions continue to impact the area and country. The chemical is stable in the atmosphere, and there are no known reduction or mitigation methods available. Concentrations in Puget Sound are somewhat higher than national concentrations and have increased since 2000. As the pollutant is banned from most applications, the sources and methods of mitigation are not yet understood.

**Summary**

In conclusion, screening risk estimates were used as a tool to focus attention on those pollutants and mixtures that are likely to present the greatest risk of cancer and some non-cancer effects. Concentrations, and corresponding risks, were relatively consistent among areas measured and modeled throughout the Puget Sound region. Although some differences were apparent, overall it is clear that the sites and the region as a whole have similar emission sources of concern (e.g., diesel particulate matter, mobile-source-related air toxics, and wood smoke).

The Puget Sound Clean Air Agency along with local, regional, and national partners has been engaged in reducing air toxics. Since 2001, the Agency has been involved with our partners in programs to lower air toxics in our regions, such as *Diesel Solutions* and our on-going wood stove replacement programs, funded largely through the State of Washington. However, more still needs to be done to continue to reduce our exposure to these harmful pollutants in our area and to improve the public health as our region continues to grow and thrive.

## 1. Introduction

Air toxics are a group of air pollutants known or are suspected to cause serious health problems. Potential health effects include cancer, birth defects, lung damage, and nerve damage.[1] People exposed to toxic air pollutants at sufficient concentrations and durations may have an increased chance of getting cancer or experiencing other serious health effects. In this report, the term "air pollutant" and "pollutant" are general terms encompassing "criteria air pollutants" and "air toxics". At times, one or more air toxics are referred to in a more general sense as a pollutant or air pollutant.

Sources of air toxics are most commonly human-generated, although natural sources like forest fires and volcanic eruptions can contribute. Typical anthropogenic sources include mobile sources (e.g. cars, buses, trucks) and stationary sources (e.g. power plants, refineries). Average households also are sources for air toxics (e.g. wood stoves and fireplaces, cleaning solvents, building materials).

The Puget Sound region is home to two major metropolitan areas in King and Pierce Counties: Seattle and Tacoma. Both cities have major ports and industrial areas, and are connected by the Interstate-5 corridor. The Environmental Protection Agency's (EPA) National Air Toxics Assessment (NATA) places urban areas in the top 5th percentile of the country for potential health (cancer) risk from air toxics.[8,9] Assessing urban areas like Tacoma and Seattle air toxics is important to understand how to use available resources best and mitigate these potential risks.

Seattle is home to a National Air Toxics Trend Site (NATTS) at Beacon Hill. Beginning in 2001, the Washington State Department of Ecology has measured a suite of air toxics at this site. Also beginning in 2001, the Washington State Department of Ecology (Ecology) conducted supplemental toxics monitoring through an EPA grant at five additional sites in the Seattle urban area. These five additional monitoring sites were located in different areas to capture the impacts from different sources. This supplemental monitoring, combined with receptor modeling performed on Beacon Hill speciation data, contributed to an air toxics evaluation for the Seattle area.[7] This evaluation, published by the Puget Sound Clean Air Agency (the Agency) and Ecology and partners, prioritized risk from diesel particulate matter and wood smoke, as well as priority urban area air toxics such as formaldehyde, hexavalent chromium, and benzene.

While there are many similarities between Seattle and Tacoma, one air quality difference is the higher concentrations of fine particles ($PM_{2.5}$) observed in some residential areas of Tacoma during winter. Fine particle levels in South Tacoma are the highest in Washington State, leading EPA to designate the Tacoma/Pierce County area as nonattainment for the 2006 $PM_{2.5}$ daily standard.[10] Monitoring has shown that elevated $PM_{2.5}$ levels mainly occur during the heating months, when a main source of fine particulate is wood smoke. Most of the focus in the Tacoma area has been "fine particle-centric"; prior to this study, no air toxics monitoring had been conducted in the Tacoma area.

Therefore, a main objective of this study was to determine base-line air toxics concentrations for the Tacoma area, and provide information at select sites in the Seattle area for comparison. Knowledge of air toxics concentrations, especially their spatial and seasonal variation, contributes to our understanding of major air toxics emissions sources in the area. Here we report not only the variability between fixed sites, but also supplement this information with even greater spatial resolution using a mobile monitoring platform.

The results of this study are summarized in four main chapters. Chapter 2 of this report describes how fixed monitoring sites were selected in the Seattle and Tacoma area, and also describes the monitoring methods that were used to determine air toxics concentrations at fixed sites. A description of the mobile monitoring is also included. Chapter 3 reports ambient air quality results from both the fixed sites and the mobile monitoring platform. Comparisons between the Seattle and Tacoma sites are provided, as well as comparisons within cities and neighborhoods. In addition, seasonal patterns of select air toxics are provided. Chapter 4 ranks priority air toxics according to health risk, including potential cancer and non-cancer health endpoints. Chapter 5 compares results of this monitoring study to the EPA's national air toxics assessment (NATA), which models air toxics concentrations nationally. Finally, Chapter 6 summarizes the results of the study, highlighting the main findings and uncertainties, and discusses implications for both monitoring strategies and regulatory policy.

## 2. Air Monitoring Methodology

### 2.1. Fixed Sites

The Agency chose monitoring sites in Seattle and Tacoma to primarily gain perspective on $PM_{2.5}$ and air toxics gradients between Seattle data, and the data collected in Tacoma during this study. Fixed sites were used so that reference levels could be compared to historic pollution levels; furthermore, the fixed sites were used as reference levels to the mobile monitors to gain spatial resolution. For this study, the Agency monitored at one Seattle and four Tacoma fixed sites. Not all sites were monitored for all pollutants. In addition, the Washington State Department of Ecology monitored at the Seattle Beacon Hill Site.

The fixed monitoring sites used in this study included: Seattle Beacon Hill, Seattle Duwamish, Tacoma Tideflats, Tacoma Portland Ave, Tacoma South L St, and Tacoma Alaska St. These monitoring sites are shown in Figure 2.1.1. A brief description of each site is provided below, and more detailed information about each monitoring site can be found in Appendix A.

#### *Seattle Duwamish Site*

The Seattle Duwamish monitoring site has been in place since 1971 and is located in the center of the Duwamish industrial valley. The site is located on the property of the Washington State Liquor Control Board warehouse facility. The site is a neighborhood scale site that is representative of South Seattle neighborhoods and ambient exposure in the industrial valley. The site is influenced by a very complex mixture of mobile sources, port and marine sources, industrial sources, winter home heating wood smoke, and other pollution sources. The site is 80 meters west of E. Marginal Way, which is a main arterial for many large haul trucks, as well as service vehicles and personal automobiles.

#### *Seattle Beacon Hill Site*

Air pollution data has been collected at the Seattle Beacon Hill site since 1979, and air toxics data since 2001. The site is located on the property of the Seattle Water Beacon Hill reservoir adjacent to the Jefferson Park Golf Course and Park. The site is a neighborhood scale site that is representative of Seattle neighborhoods. The site is influenced by a mixture of mobile sources, industrial sources, winter home heating wood smoke, and other pollution sources.

**Figure 2.1.1: Fixed Monitoring Sites**

### *Tacoma Tideflats Site*

The Tacoma Tideflats monitoring site has been in place since 1987 in the tideflats area collecting air pollution data. The site is neighborhood scale that is located near the Port of Tacoma, and several other air pollution sources. The sources that impact the area are a mixture of mobile sources, port and marine sources, industrial sources, and winter home heating from wood burning.

### *Tacoma South L Street Site*

The Tacoma South L Street monitoring site has been in place since 1999 at the South End Community Center. The site is a neighborhood scale site that is representative of Tacoma neighborhoods that use wood heating in winter. The site is around 1 km from any significant traffic (I-5, Hwy 512, and neighborhood arterials). While multiple sources contribute to $PM_{2.5}$ levels here, winter home heating from wood burning is the dominant source. This monitoring site has the highest design value in the Puget Sound region for $PM_{2.5}$ for the 24-hour standard.

### *Tacoma Portland Ave Site*

The Tacoma Portland Ave fixed site was installed for this study at the Tacoma Water Portland Avenue Reservoir facility located at the intersection of Fairbanks Street and Portland Avenue. The Puget Sound Clean Air Agency sought out and received feedback from several City of Tacoma and Pierce County stakeholders to identify an appropriate site. The reservoir is located on the side of a hill that separates typical Tacoma neighborhoods and the port/industrial area in the river valley. This site is a neighborhood-scale site that was located to assess the gradient between pollution generated from mainly mobile and industrial sources in the Tideflats area and pollution that is generated in the neighborhoods from winter wood heating. This area was also identified as having a lower-income surrounding population, and so was sited with environmental justice considerations.

### *Tacoma Alaska St Site*

The Tacoma Alaska St site was used to collect fine particulate matter data for this study using a continuous nephelometer and a regressed $PM_{2.5}$ estimation equation. The site would have been used to collect additional samples if any data indicated hot spots during the mobile monitoring runs. No hot spots were identified.

## 2.2. Fixed Site Pollutants and Methods

The pollutants monitored in this study are summarized below in Table 2.2.1. Most pollutants were sampled on a schedule of once every six days. Puget Sound Clean Air Agency operated the monitoring sites listed below except Seattle Beacon Hill. As needed, collocated samplers collected data for quality assurance purposes of assessing accuracy and precision.

**Table 2.2.1: Summarized List of Methods Monitored by Fixed Site. Note: 1/3 and 1/6 refer to the sampling taking place on a 1 day out of every 3 day, or 1 day out of every 6 day schedule.**

| Site<br>Method | Major Toxic Species (Other species were analyzed based on the available suite of the analysis) | Seattle Beacon Hill | Seattle Duwamish | Tacoma Portland Ave | Tacoma Alaska St | Tacoma South L Street | Tacoma Tideflats |
|---|---|---|---|---|---|---|---|
| PM$_{2.5}$ Filter by FRM | PM$_{2.5}$ (1/3 or 1/6) | X | X | X |  | X | X |
| 1/6 PM$_{2.5}$ Filter Levoglucosan | Levoglucosan (wood smoke tracer) |  | X | X |  | X | X |
| 1/6 PM$_{2.5}$ Filter Speciation by URG Carbon and Met One SASS | Carbons<br>Cations<br>Metals<br>60 total PM2.5 species | X | X |  |  | X | X |
| PM$_{2.5}$ Hourly by Continuous | PM$_{2.5}$ Hourly by nephelometer or TEOM | X | X | X | X | X | X |
| 1/6 Canister Sampling by TO-15 (24 hour sampling period) | Benzene<br>1,3-butadiene<br>Carbon tetrachloride<br>Chloroform<br>56 other gas phase species | X | X | X** |  | X | X |
| 1/6 PUF Sampling by TO-13a (24 hour sampling period) | Naphthalene<br>Pyrene<br>20 other PAH's | X | X |  |  | X | X |
| 1/6 Carbonyl DNPH Tube Sampling by TO-11a (24 hour sampling period) | Acetaldehyde<br>Formaldehyde<br>10 other aldehydes | X | X |  |  | X | X |
| PM$_{2.5}$ Hourly Continuous Aethalometer | BC (Absorption)<br>UV (Absorption) | X | X | X |  | X | X |
| Met Parameters (Hourly) | WD, WS, T, RH, BP | X | X | X |  | X | X |

**Certain analytes were invalidated due to an initially undetected sampling problem.

During this study, where possible, we used existing equipment and methods that are common to the EPA NATTS (National Air Toxics Trends Network) and UATMP (Urban Air Toxics Monitoring Program). Appendix B provides detailed descriptions of the methods used. Each monitoring method used during the study is summarized below. In previous studies[3], we found that metals are not major health risk contributors to Puget Sound. Consequently, $PM_{10}$ metals sampling and analysis were not completed. Instead, we utilized readily available toxic metals data in our analysis from the Seattle Beacon Hill site. Hexavalent chromium is an air toxic of concern in our area, but was not addressed in this project due to large uncertainty in the reliability of existing monitoring and analysis methods. During the study sampling, $PM_{2.5}$ metals collection occurred concurrently at the Seattle Duwamish, Seattle Beacon Hill, Tacoma Tideflats, and Tacoma South L Street sites, but was not used for the potential cancer risk estimate as $PM_{10}$ metals are typically used in potential risk estimates.

The following basic descriptions are detailed in Appendix B, which includes our entire Quality Assurance Project Plan:

- $PM_{2.5}$ Daily Sampling by Federal Reference Method (FRM). The operator installs 47 mm Teflon filters into the Partisol 2025 sequential sampler (manufactured by Rupprecht & Patashnik). The sampler operates at 16.67 Lpm flow rate. This flow rate (in combination with the $PM_{10}$ aerodynamic head and the $PM_{2.5}$ impactor) separates the coarser PM from the $PM_{2.5}$ fraction. $PM_{2.5}$ collects onto the pre-weighed filters for a period of 24 hours. The filters are collected in accordance with the EPA Standard Operating Procedure and then weighed by a microbalance to quantitatively determine the daily average $PM_{2.5}$ pollution for the integrated 24-hour period.
- 1/6 $PM_{2.5}$ Daily Levoglucosan. The operator collects a FRM filter each 6 days. After the gravimetric analysis, the filter is sent to the University of Washington laboratory for Levoglucosan analysis. See Appendix B for more information.
- 1/6 $PM_{2.5}$ Daily Speciation Sampling by URG 3000N and Met One SASS Samplers. The operator installs nylon, Teflon, and quartz filters into the two speciation samplers. The speciation samplers use the EPA Speciation Standard Operating Procedure to collect the pollution onto the filters. The operators collect and ship the filters to the RTI laboratory (Research Triangle Institute) for analysis. See Appendix B for more information.
- $PM_{2.5}$ Hourly by Continuous Sampling. $PM_{2.5}$ is estimated by either nephelometer or TEOM. The nephelometer collects air and measures light scattering. The light scattering coefficient is linearly proportional to the $PM_{2.5}$ in the aerosol. There is a standard method

used by the Puget Sound Clean Air Agency for determining a multiplicative factor which converts light scattering to estimated $PM_{2.5}$ in micrograms per cubic meter. The factor is based on the slope and intercept of the regression of a nephelometer and FRM. Data is validated for each hour. The TEOM (tapered element oscillating microbalance) samples air at 16.67 liters per minute (separated similarly to the FRM method) and pollution is collected on an oscillating filter. The pollution collected is proportional to the frequency change of the oscillating filter. The frequency change is then converted to $PM_{2.5}$ in micrograms per cubic meter.

- 1/6 Daily Canister Sampling by EPA Method TO-15. Standard SUMMA canisters are humid-zeroed, evacuated, and certified in the laboratory. The laboratory ships the canisters to the operator. The operator prepares the canister and sets up the Xontech 910 canister sampler to collect the proper amount of air for the scheduled 24-hour period. Once the sampling run is complete, the sample is shipped to the laboratory where the sample is drawn into a cryogenic trap and cooled with liquid nitrogen. The concentrated sample extracts are then analyzed using GC-MS (gas chromatography by mass spectrometer). Method calibration and quality control procedures, as well as acceptance criteria are all described in the Appendix B.
- 1/6 Daily PUF Sampling by EPA Method TO-13a. The operator sets up Standard PUF (polyurethane foam) cartridges into a sampler for the scheduled 24-hour period. The samples are collected and shipped to the laboratory. The laboratory extracts and then injects the PUF components into the GC-MS. Method calibration and quality control procedures, as well as acceptance criteria are all described in Appendix B.
- 1/6 Daily Carbonyl DNPH (dinitrophenylhydrazine) Tube Sampling by EPA Method TO-11a. DNPH cartridges are placed into the Xontech 925 sampler. The operator sets up the sample to run on the scheduled day for 24 hours. The sample is collected and shipped to the laboratory. The laboratory extracts the sample and injects it into a high-pressure liquid chromatography system. Method calibration and quality control procedures, as well as acceptance criteria are all described in Appendix B.
- $PM_{2.5}$ Continuous Aethalometer. The sampler collects $PM_{2.5}$ pollution (separated by a $PM_{2.5}$ aerodynamic head) at 5 Lpm flow rate. The filter tape is made of quartz fibers. The aethalometer measures light absorbance at two wavelengths – Black Carbon (880nm) and Ultraviolet (370 nm). A standard calibration was determined by the manufacturer, and the light absorbance is converted to units of micrograms per cubic meter. The instrument data is collected by a data logger, and the data is validated as 1 hour averages.

- Meteorological Parameters. Wind speed and wind direction are determined by ultrasonic wind sensors located throughout the Agency network. Temperature, barometric pressure and relative humidity are determined by sensors located throughout the network. Data is collected and validated as hourly averages.

### 2.3. Mobile Air Monitoring Methods

Mobile air monitoring was used to study the spatial gradients of toxic pollutants. Where possible, the mobile monitoring platform used identical instrumentation to the fixed sites. An example is the Radiance Research M903 Nephelometer, used to measure light scattering and estimated $PM_{2.5}$ continuously.

Mobile monitoring was conducted in the winter and the summer, during the day and during the evening hours. Specific routes are described in Appendix D and more detail is also included in Chapter 3. The project team used air quality forecasts of high pollution events to determine when mobile monitoring runs would begin and end.

There were two mobile monitoring platforms used in the study. The first mobile monitoring platform focused on fine particles. The mobile monitoring van provided highly spatially resolved maps of a relatively limited number of pollution measures within each neighborhood studied in Tacoma. The instrumentation was placed inside a vehicle and connected to a sampling manifold inlet placed out an otherwise sealed window – away from the vehicle exhaust plume. A field log recorded any close encounters with heavy-duty diesel vehicles that would otherwise cause excessively high spikes in the data record. Sampling instruments included:

- A nephelometer (Radiance Research M903) to measure light scattering, equipped with a small air blower and air pre-heater with the averaging time set at 15 seconds.
- A GPS receiver logging position every 5 seconds.
- A particle soot absorption photometer to measure the light absorption coefficient.
- An EcoChem PAS 2000 instrument to measure particle bound polycyclic aromatic hydrocarbons set at a 15 second averaging time.

The neighborhood sampling routes were established prior to sampling and traversed in either a clockwise or counterclockwise direction on any given evening, as determined randomly. These routes were established based on neighborhood characteristics such as location of major roads and populated areas and census tract level wood smoke use surveys, as well as air quality monitoring the Agency has recently conducted in the Tacoma area. Routes were constrained based on the time it takes to traverse them. Temporal adjustments of night-to-night variations in measured concentrations were necessary. These normalizations were performed by taking the nearest fixed site data and using a normalizing ratio where the mobile data was divided by the fixed site data. These fixed-site measurements sufficiently controlled for temporal variation and allowed us to composite the mobile measurements over time.

The second mobile monitoring platform focused on gaseous sampling measurement. The mobile platform consisted of a moving van with a MIMS (Membrane Introduced Mass Spectrometer) system powered by a towed diesel generator.

- MIMS (membrane introduced mass spectrometer) system uses a semi-permeable polymer membrane to reject the sample matrix and enrich certain analytes from gaseous or liquid samples. These separated analytes are then directly transferred as a mixture (often using a helium carrier gas acceptor phase) to a mass spectrometer for their subsequent resolution and measurement. Analytes amenable to MIMS are those that can readily permeate a silicone™ (polydimethylsiloxane, PDMS) membrane (typically volatile organic compounds (VOCs), as well as some semi-volatile organic compounds - SVOCs).

The diesel generator was operating when sampling occurred, but the exhaust was away from the sampling manifold, and the sample was taken from air not contaminated by the vehicle or diesel generator exhaust. The data analysts were able to confirm that the possible contaminated sources did not affect the data results. Additional detail about the MIMS system is contained in Appendix D.

The neighborhood sampling routes were established prior to sampling and focused on neighborhoods that were impacted by wood smoke sources, or traffic sources. Data analysis methods are described in more detail in Chapter 3.

## 3. Monitoring Results

### Background

In 2001, an evaluation published by the Puget Sound Clean Air Agency (the Agency) and Washington State Department of Ecology (Ecology) and partners, prioritized risk from diesel particulate matter and wood smoke, as well as formaldehyde, hexavalent chromium, and benzene. Our monitoring campaign extended the air toxics evaluation for the Seattle area by monitoring at the Duwamish valley site, and 3 sites in the Tacoma area, and using Seattle Beacon Hill data (a NATTS site operated by Ecology). The data described in this chapter was collected at 4 sites (see Chapter 2) on a fixed 1 in 6 day sampling schedule over the course of a year from November 2, 2008 to October 28, 2009.

EPA's 2002 National-Scale Air Toxics Assessments (NATA) identified several species of air toxics as well as polycyclic organic matter (including PAHs) as contributing to an elevated potential cancer risk for this area. NATA did not include estimates for wood smoke particulate matter. Currently, the Agency continues to publish NATTS data from Seattle Beacon Hill in its annual data summary, and rank toxics according to potential cancer risk based on this site.

In the industrial Duwamish valley neighborhoods of Seattle and in neighborhoods around the Port of Tacoma and southward, there is a great deal of community interest in air pollution impacts from the port and nearby industrial sources. The Tacoma urban area, connected to Seattle via the Interstate 5 corridor, is host to many of the same pollution sources as the Seattle urban area, including a major port, an interstate corridor, some industry, and neighborhood woodstoves and fireplaces. Census tracts in the Tacoma area were among those ranked highest in the 2002 NATA for potential cancer risk of any census tracts in the Puget Sound area (King, Snohomish, Pierce, and Kitsap counties). More recently, the monitor in the South End area of Tacoma has been designated non-attainment under EPA's stricter daily $PM_{2.5}$ standards. Monitoring has shown that elevated $PM_{2.5}$ levels predominantly occur during the heating months, when a main source of fine particulate is wood smoke.

The Agency partners with the local health department and community environmental justice groups in these areas, and has begun actively working with neighborhood councils in the South End neighborhoods to address air quality issues. Most of the focus of prior work in the Tacoma area was on criteria pollutants ($PM_{2.5}$). This study is one of the first to include air toxics monitoring in this area. A secondary aim of this 2010 study was to characterize spatial variations in air toxics in these areas and compare them to the Seattle Beacon Hill site as a regional reference. Further, since wood smoke has impacts mainly during the winter, this chapter examines patterns in air toxics across the heating and non-heating seasons. It is important to note that both meteorology and sources of air toxics differ in winter months.

Wood smoke is known to present health risks and was recently assessed as a category 2A carcinogen by the International Agency for Research on Cancer (IARC).[11] As with diesel exhaust, wood smoke has both a particulate component, as well as several vapor phase air toxics that have been demonstrated to present health risks. These include, but are not limited to: PAHs, benzene, formaldehyde, acetaldehyde, 1,3-butadiene, and acrolein.[12,13]

The following air toxics are the primary focus of the summary analysis presented in this chapter because they exceed the cancer risk screening levels discussed in Chapter 4: **naphthalene, benzene, 1,3-butadiene, formaldehyde, acetaldehyde, carbon tetrachloride, chloroform, and acrolein.** In addition, graphical results are presented for black carbon, elemental carbon, levoglucosan (a wood smoke tracer), and $PM_{2.5}$. While these four are not air toxics, their results help to determine possible sources. Tetrachloroethene was not included in this chapter as contributions to cancer risk were relatively lower (near one cancer risk per million) and there was a large fraction of samples that were below method detection, complicating comparisons. A summary table, consisting of results for the 12 months of monitoring across all sites in the study, is shown in Table 3.13 at the end of this chapter. A large suite of additional analytes were monitored in the study, and data for these appear in summary form in Appendix E of this report.

In addition to the summary tables, a series of graphs were created to compare the range of values collected in this study to the data derived from the NATTS sites across the nation. Data used for the NATTS comparison were derived from daily values reported over 24 months in 2006 and 2007 from the EPA-AQS (Air Quality System) Database. Data for tetrachloroethene from the NATTS survey was also not useful due to the proportion of results below detection limit. NATTS data from the 2008-2009 periods were not available for comparison, because these values were being revised at the time of this report due to laboratory analytical corrections.

## 3.1. Fixed Sites Monitoring Results

### 3.1.1. Data Review and Non-Detects

Prior to all analyses, the data was screened through QA processes, including identifying potential outliers by reviewing typical patterns, reviewing collocated (duplicate) sample precision, reviewing lab QA spikes, and ensuring that all QA criteria were met according to the Quality Assurance Project Plan (Appendix B). The data used in this analysis passed all QA criteria for blanks, precision, and recoveries.

From QA review, acetonitrile was fully invalidated as there were obvious interferences, from contamination on the cartridges used for sampling aldehydes which use acetonitrile as a solvent. On a few samples, there were high concentrations of methylene chloride that were over 1000 times baseline levels that were invalidated, although the potential contamination source was never identified.

Data from the Tacoma Portland Ave study site were not reported for several compounds because an equipment malfunction in a sampler resulted in invalid data that did not meet QA requirements. Data completeness for all other sites and parameters was higher than 86%.

All valid data were compiled and screened against Washington state established screening levels for ambient air toxics concentrations. The screening of air toxics for health risk is described in more detail in Chapter 4. Of the air toxics above screening levels, all values were above detection limit, except for tetrachloroethylene and hexavalent chromium. For these pollutants, Kaplan-Meier estimation was used to derive the means (see Appendix C).

Because of the sheer enormity and diversity of the data set, NATTS data below detection was substituted with one-half the detection limit for means, medians, and quartile range calculations. Nevertheless, as found with our study sites, the priority air toxics (benzene, 1,3-butadiene, formaldehyde, etc) are mostly detects, even in some of the more rural NATTS sites.

### 3.1.2. Statistical Methodology

Comparisons of the annual sampling results are presented in Figures 3.1.1 to 3.1.12, which display the data from this study across all sites by season and in relation to national survey data from the NATTS. The box and whisker plots all have the same format: the shaded bar shows the interquartile range of the data; the dark line in the middle represents the median; the lower and upper whiskers show the corresponding 5th and 95th percentile values.

In addition to box and whisker plots, the data was further statistically analyzed using a two-way Analysis of Variance (ANOVA). ANOVA is a statistical method used for comparing three or more means in a null hypothesis test to determine if all the means are statistically different from each other. In this study, the means of the sites are compared.

The two-way ANOVA allows the addition of another variable for comparison, which in our study is heating vs. non-heating season. Additional comparisons can be made to determine if the *pattern* of the sites changes in a different season. For example, if the null hypothesis is true, Tacoma South L Street site may be the highest in the heating season, but lower than another site in the non-heating season.

As ANOVA compares means, it should not be confused with the medians, which are plotted in the box plots. The black bar on the box plot is the median and no means are displayed in the box plots.

Post-hoc Scheffe tests were completed to determine if individual site means are the same or different than each other. Using this test identifies differences between individual sites with 95% confidence. The Scheffe method tests as many possible statistical contrasts as allowed all at the same time, allowing for comparisons among individual sites.

ANOVA uses all the data and requires the same number of samples (run days) from each site. Where there were an unequal number of samples due to sample loss, the samples from the same sampling date was dropped. That is, if there were 59 runs at 3 sites and 58 runs at 1 site, the other 3 sites had the sample dropped for that same sample date where there was data loss.

Additionally, as ANOVA assumes normal distributions, the data was log-transformed to make the data normally distributed. Normality was tested using the Lilliefors test, which uses normal distributions for the null hypothesis. Prior to applying a log transformation to the data, results of the Lilliefors test demonstrated the all the data was not normal.

The analysis revealed several important differences between sites and across seasons, and did not show a single pattern of results that applied to all the compounds that were analyzed. To further understand the results, our analysis included bivariate correlations between the measured chemical species using both Spearman (rank) correlation and Pearson (product-moment) correlations (the latter applied to log transformed data). Because of the strong seasonal influence on some species, the correlation analysis was applied separately to data for the heating and non-heating seasons. Tables of the ANOVA results and the correlation results are included in Appendix E.

### 3.1.3. Summary of Results

The most apparent feature of these comparisons is that regional and seasonal differences exist for several of the air toxics. In particular, benzene, naphthalene and carbon tetrachloride are elevated in some regions particularly during the heating season (October - March) relative to the NATTS national values. However, 1,3-butadiene, chloroform, formaldehyde, and acetaldehyde are generally lower than the NATTS results.

The industrial/port sites at Tacoma Tideflats and Seattle Duwamish results were very similar for all measured pollutants, except for levoglucosan. At the Tacoma Tideflats site, levoglucosan concentrations were higher demonstrating more of a wood smoke impact there.

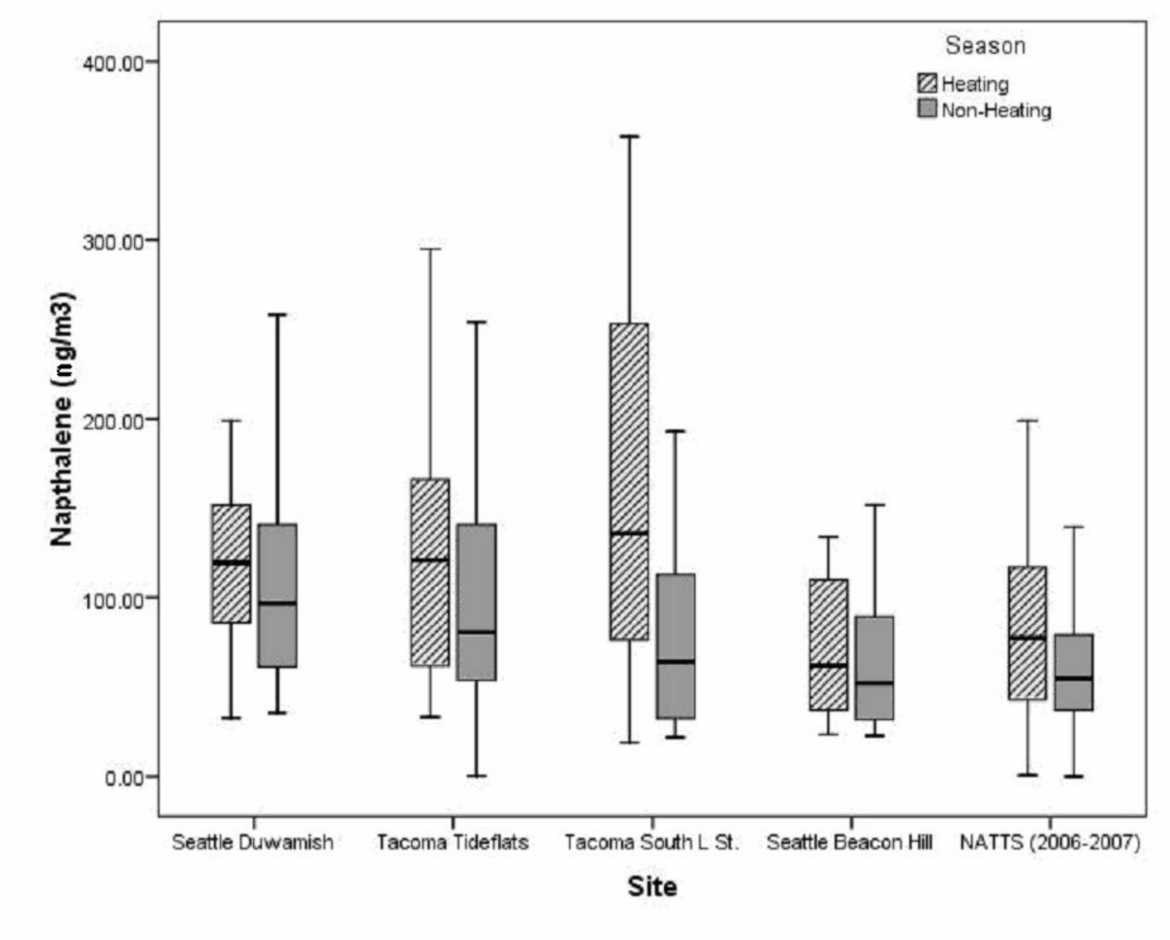


**Figure 3.1.1: Box and Whisker Plots for Naphthalene: results by site and season**

The plot in Figure 3.1.1 displays the naphthalene results. Naphthalene is designated as a possible human carcinogen by EPA, and is also associated with eye damage.[14] Sources of naphthalene include combustion/smoke. The median values, shown by the dark line in the middle of each hatched bar, are elevated in the two Tacoma sites (Portland Ave missing) and at the Seattle Duwamish site during heating season, compared to the median of the NATTS data. In addition, the upper 75th and 95th percentiles in these three sites are elevated above the corresponding NATTS values and the Seattle Duwamish site 25th percentile values exceed the median of the national data. The ANOVA results indicate significant differences ($p<0.001$) exist with between all the sites together, and also by heating and non-heating season. However, the ANOVA post-hoc comparisons indicate that Seattle Beacon Hill is the only site that is statistically different than the others and there is no significant difference between each of the other sites. The Seattle Beacon Hill site is the lowest across all sites and seasons, and these values appear to have a similar range compared to the national data.

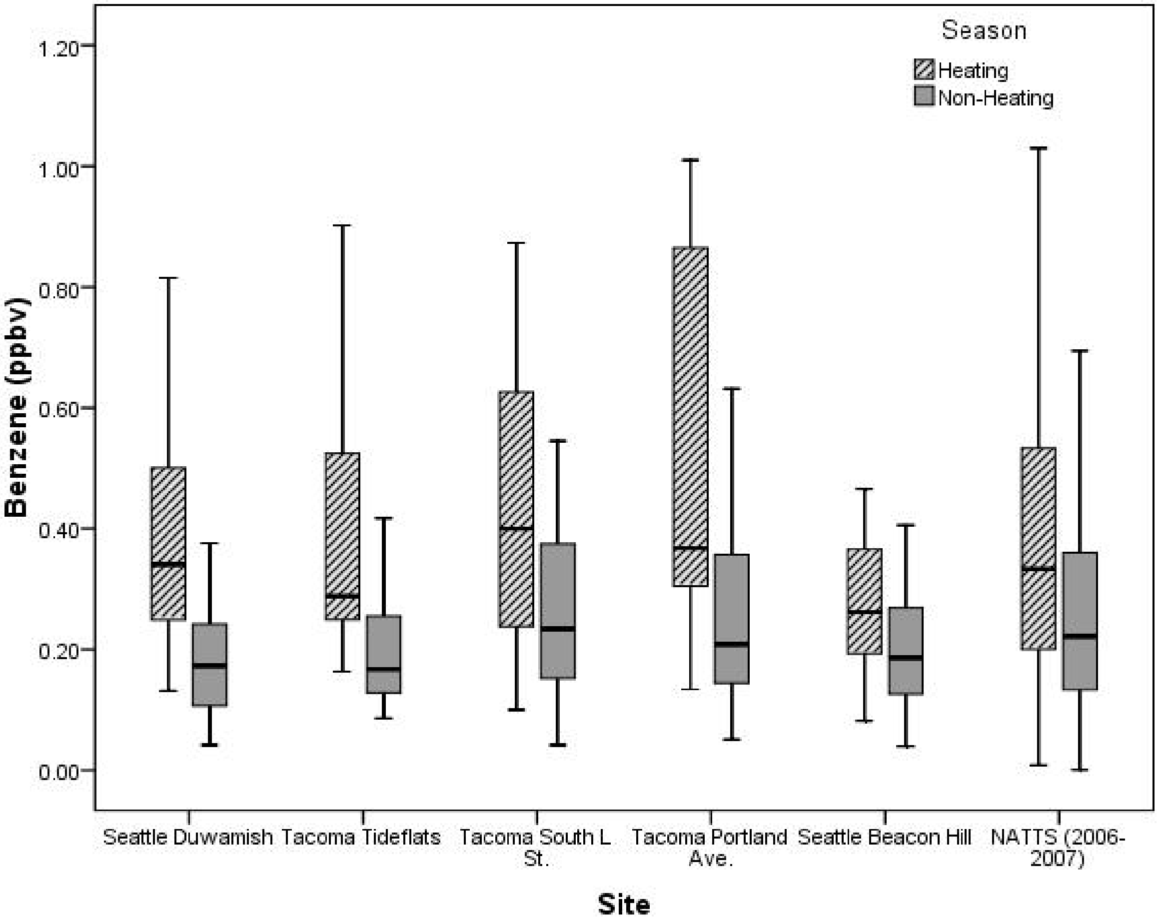


**Figure 3.1.2: Box and Whisker Plots for Benzene: results by site and season**

Figure 3.1.2 illustrates the benzene results from the study. EPA lists benzene as a known human carcinogen, and it is also linked with blood, immune, and nervous system disorders.[15] This air toxic comes from a variety of sources, including motor vehicle exhaust, wood burning, evaporation of industrial solvents, and other combustion. The benzene values at Tacoma South L St, Tacoma Portland Ave and Seattle Duwamish are elevated in the heating season compared to both Beacon Hill and NATTS sites. The median values are more similar across all sites, but the 75th and 95th percentiles are considerably higher in the Tacoma sites. The ANOVA results indicate some differences both between sites as a group ($p<0.02$) and seasons ($p<0.001$), but the pattern of results for the sites were the same when examining one season and then the other. Although the box plots show strikingly different 75th percentiles, the post-hoc comparisons show no significant differences between the means when comparing individual sites to one another. In the non-heating season, all sites appear to be similar to the national data.

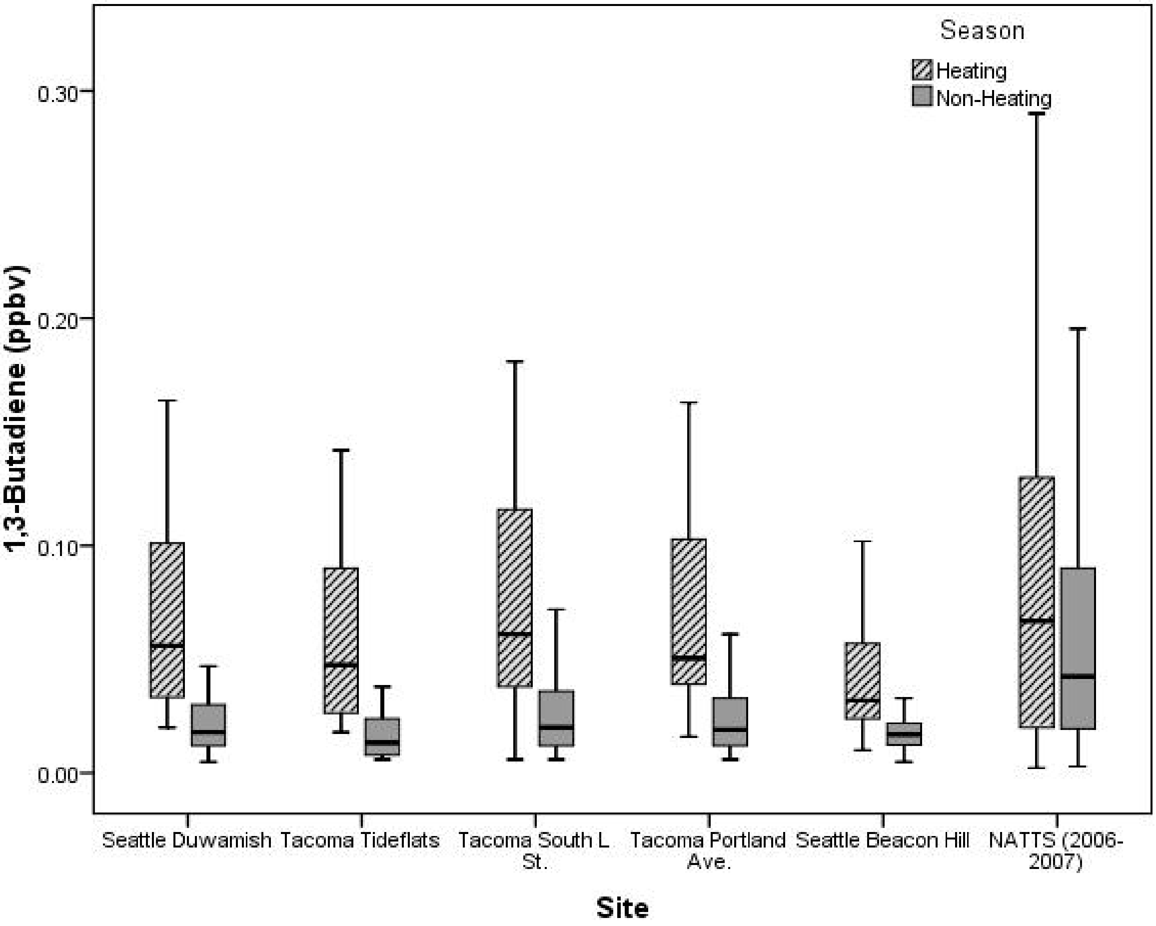


**Figure 3.1.3: Box and Whisker Plots for 1,3-butadiene: results by site and season**

The plot in Figure 3.1.3 displays the 1,3-butadiene results. Primary sources of 1,3-butadiene include vehicle emissions and wood burning. The median values appear elevated in the three Tacoma sites and at the Seattle Duwamish site relative to the Beacon Hill site during heating season, with all the sites lower than the NATTS. However the results appear to fall well within the range of values for national NATTS sites during the heating season. In the non-heating season, all the Tacoma and Seattle sites appear to be quite low compared to the median and range of the NATTS data. The ANOVA results indicate significant differences between sites ($p<0.02$) and seasons ($p<0.001$), and the pattern of results is not different for from heating vs. non-heating season across all the sites ($p=0.62$). For example, Tacoma South L Street is highest during heating and non-heating seasons. Like benzene, post-hoc results show no significant difference between any individual sites compared to each other.

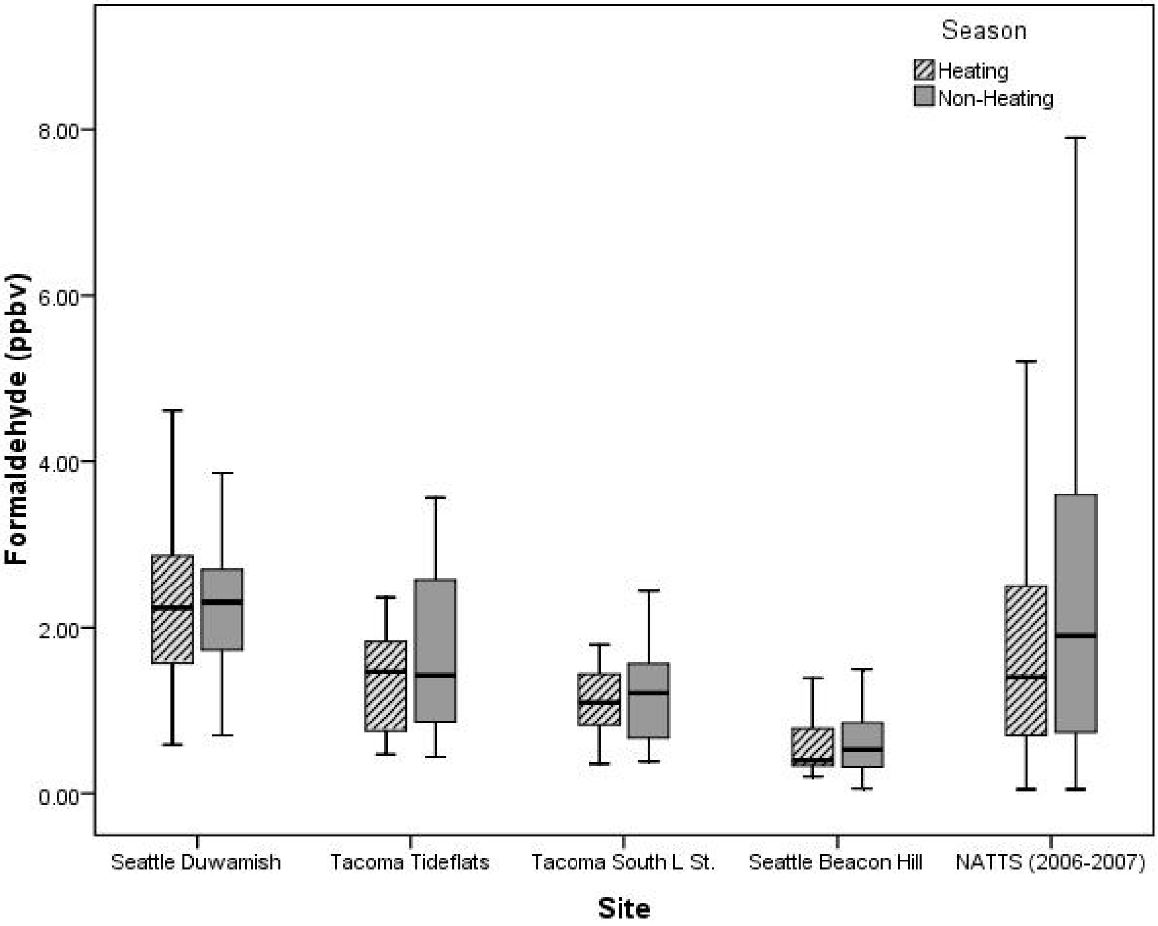


**Figure 3.1.4: Box and Whisker Plots for Formaldehyde: results by site and season**

The plot in Figure 3.1.4 displays the formaldehyde results. The EPA lists formaldehyde as a probable human carcinogen. Formaldehyde inhalation is also associated with eye, nose, throat, and lung irritation.[16] Sources of ambient formaldehyde include automobile and other mobile source emissions, and combustion. The median values appear elevated at the Seattle Duwamish and the two Tacoma sites relative to the Beacon Hill site during heating and non-heating season. However the results appear to fall well within or below the range of values for national NATTS sites during both seasons. The ANOVA results indicate significant differences between sites ($p<0.001$) but not between seasons ($p<0.6$). Also, the pattern of results for the sites remains unchanged across seasons ($p<0.86$). That is, Seattle Duwamish is highest during heating and non-heating seasons and Beacon Hill is lowest in both seasons. The ANOVA post-hoc comparisons indicate that the Tideflats and Duwamish sites have significantly different means ($p<0.001$). However, the difference in means between the Tacoma South L Street and the Tideflats sites were not found to be statistically significant.

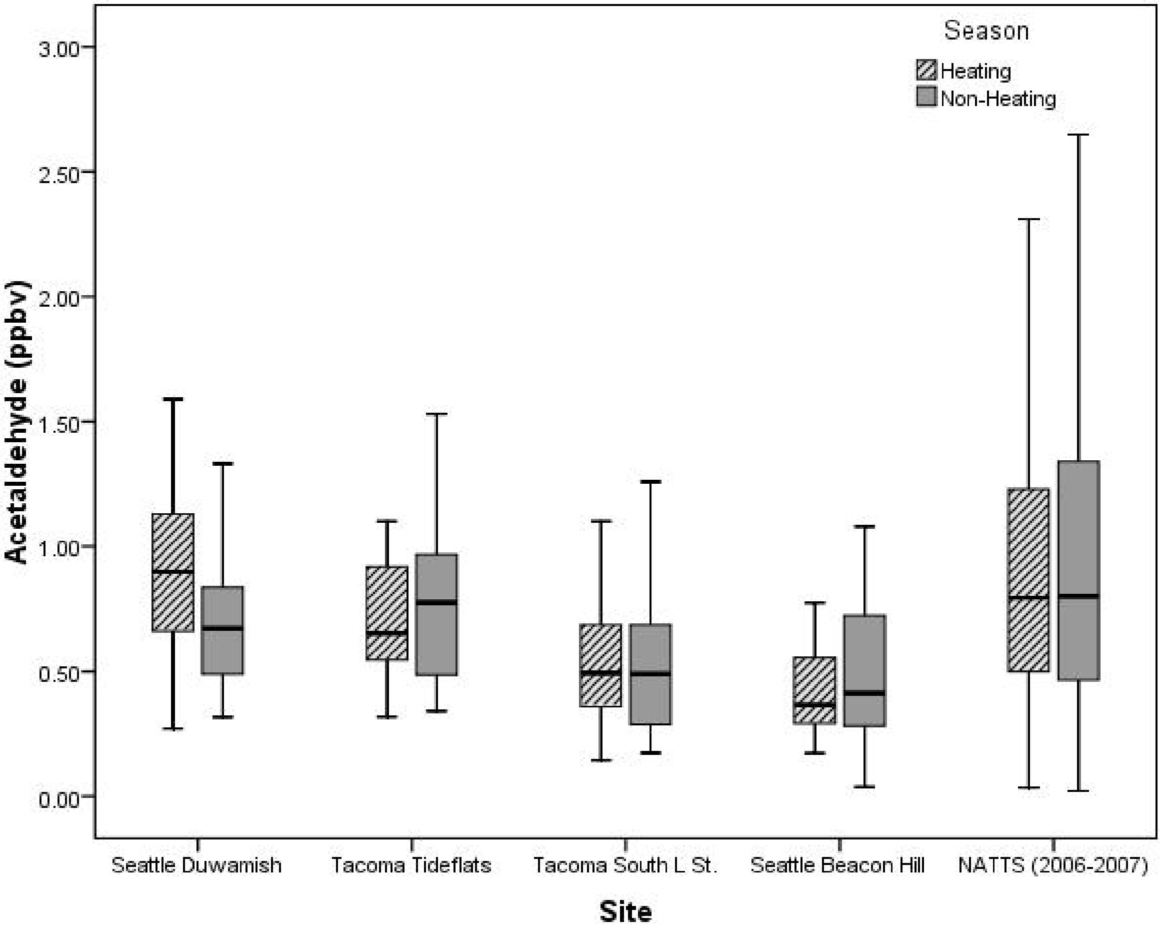


**Figure 3.1.5: Box and Whisker Plots for Acetaldehyde: results by site and season**

The plot in Figure 3.1.5 displays the acetaldehyde results. The EPA lists acetaldehyde as a probable human carcinogen. Acetaldehyde inhalation is also associated with irritation of eyes, throat, and lungs, and effects similar to alcoholism.[17] Main sources of acetaldehyde include wood burning and car/truck exhaust. The pattern of results is similar to the previous figure for formaldehyde, although with smaller differences across sites in the region and across seasons. The median values appear elevated at the Seattle Duwamish and the Tacoma Tideflats sites relative to the Beacon Hill site during heating and non-heating season. However the results appear to fall well within or below the range of values for national NATTS sites during both seasons. The ANOVA results indicate significant differences between sites (p<0.001) but not between seasons (p<0.3), and the pattern of results is modestly different from one season to the other (p<0.03). The ANOVA post-hoc comparisons show that the Tideflats and Duwamish sites show no significant difference but the Tacoma sites are significantly different from one another (p<0.001).

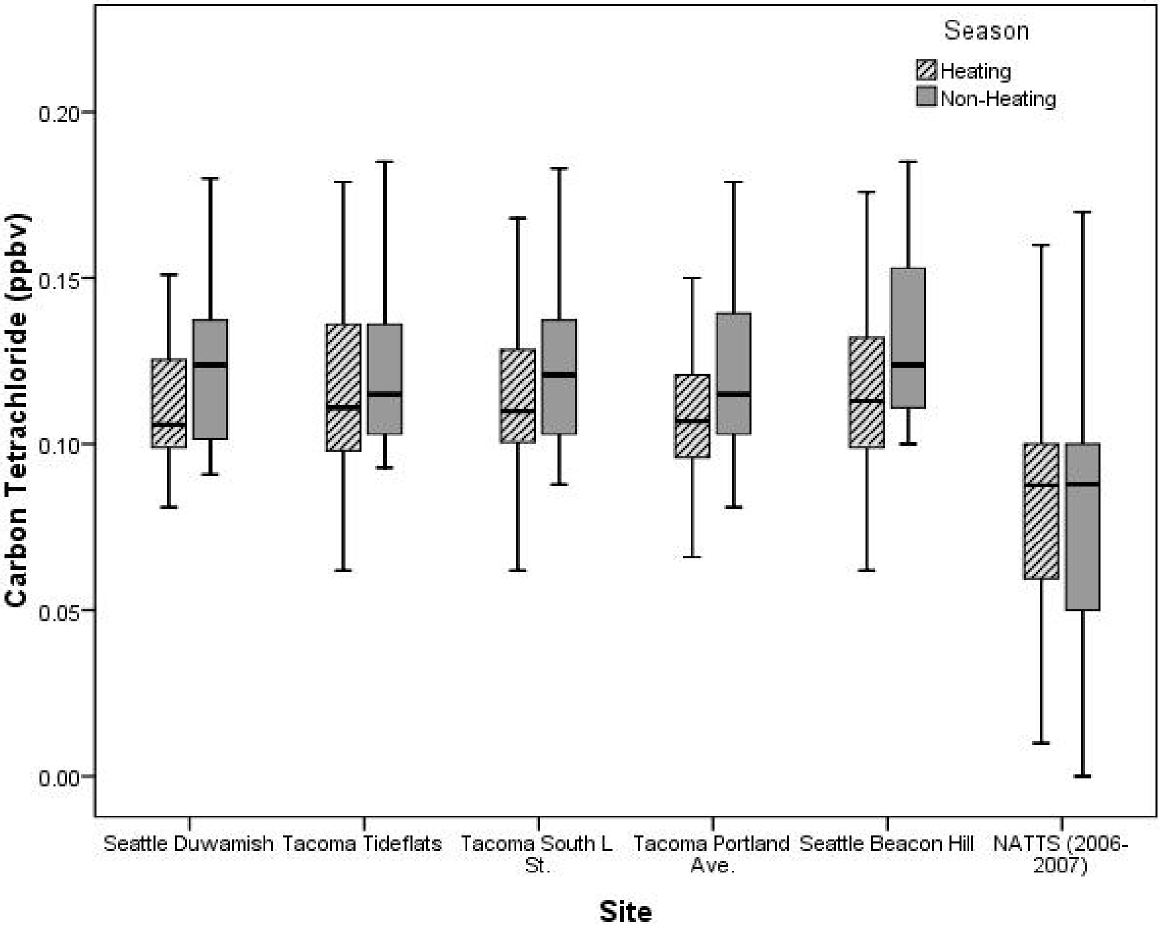


**Figure 3.1.6: Box and Whisker Plots for Carbon Tetrachloride: results by site and season**

The plot in Figure 3.1.6 displays the carbon tetrachloride results. The EPA lists carbon tetrachloride as a probable human carcinogen. Carbon tetrachloride inhalation is also associated with liver and kidney damage.[18] It was widely used in chlorofluorocarbon production (CFCs) and as a solvent for both industry and consumer use, and was banned from most applications in 1996. It has a long atmospheric lifetime (30-100 years), and is still in use for some small essential laboratory research applications.

The pattern of results is quite distinct from the previous figures with very small differences across sites in the region and across seasons. Values recorded during heating season are slightly lower compared to non-heating season. Interestingly, our study sites appear higher than the NATTS sites.

At this time, it is unclear why this is the case. The ANOVA results indicate differences between seasons ($p<0.003$), but not between sites ($p<0.6$), and the pattern of results for the sites remains unchanged across seasons ($p<0.9$). The ANOVA post-hoc comparisons indicate that no statistically significant differences occur between each individual site compared to each other.

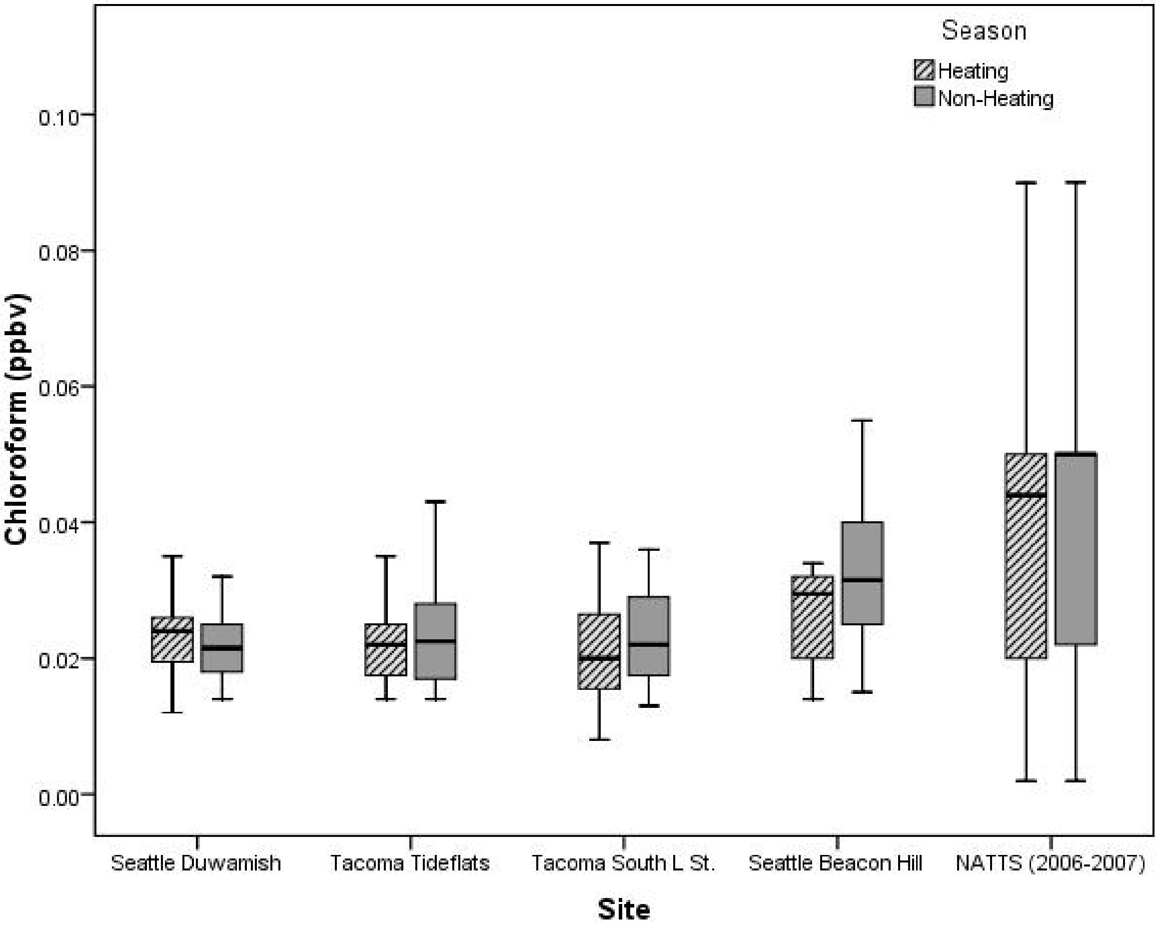


**Figure 3.1.7: Box and Whisker Plots for Chloroform: results by site and season**

The plot in Figure 3.1.7 displays the chloroform results. The EPA lists chloroform as a probable human carcinogen. Chloroform inhalation is also associated with central nervous system effects and liver damage.[19] Main sources of chloroform are water treatment plants and reservoirs. The pattern of results is distinct from the previous figures with only small variations across sites in Tacoma and the Duwamish valley across seasons. The median values in all the Tacoma and Seattle Duwamish sites appear to be similar to each other, but well below the Beacon Hill site in contrast to other pollutants measured in the study. It's noteworthy that the Beacon Hill site is located near a reservoir, a possible source. Values recorded during heating season are slightly lower in most cases compared to non-heating season. However the results appear to fall well below the range of values for national NATTS sites during both seasons with median values that routinely fall near or below the 25th percentile of the NATTS sites. The ANOVA results indicate small differences between seasons ($p<0.03$), and the pattern of results for the sites remains unchanged across seasons ($p<0.28$). The ANOVA post-hoc comparisons of means indicate that no statistically significant differences occur between each individual site compared to each other.

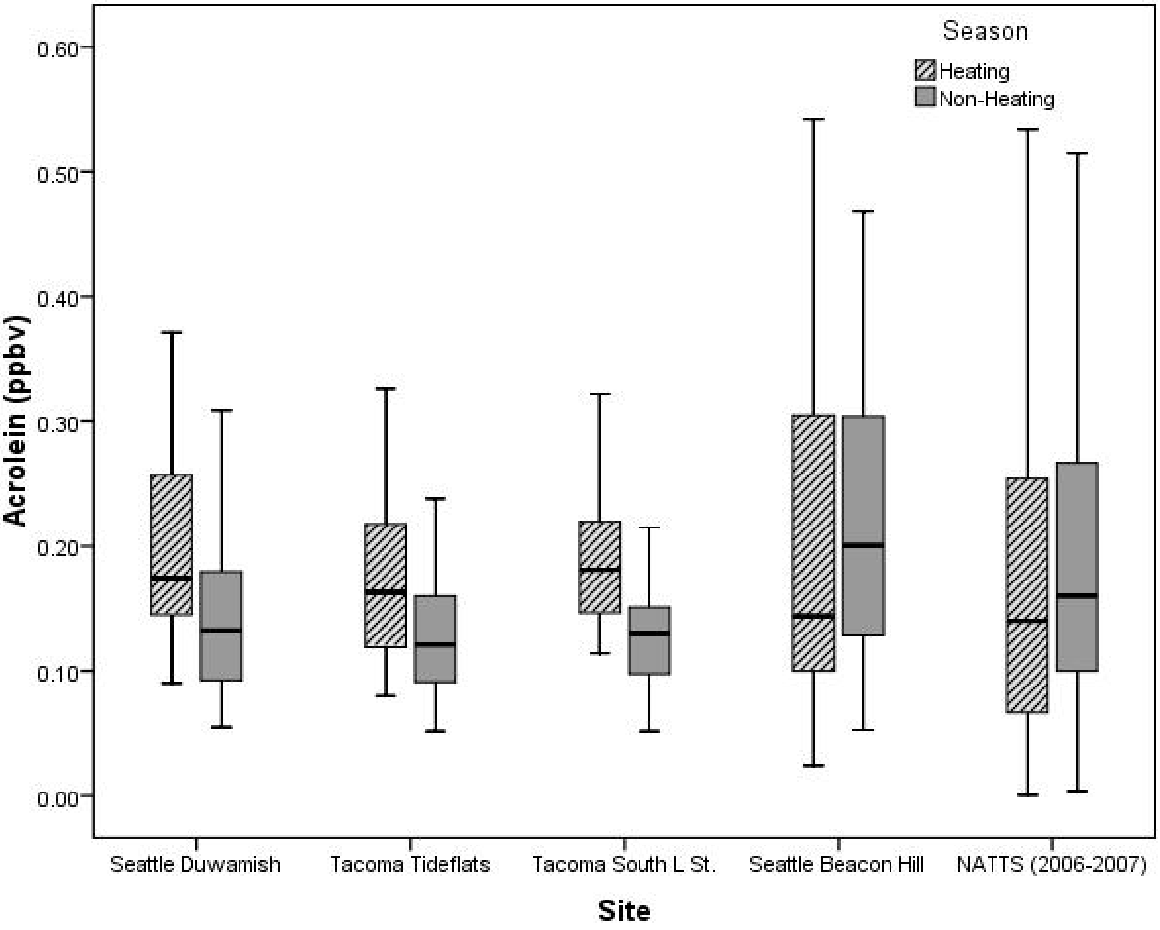


**Figure 3.1.8: Box and Whisker Plots for Acrolein: results by site and season**

The plot in Figure 3.1.8 displays the acrolein results. Acrolein is associated with respiratory irritation, and its main source is combustion of fuels (for example, gasoline, wood, etc.).[20] The median values of all the sites appear to be similar to each other. The Beacon Hill site appears to have a lower median compared to the other sites in the heating season, but this trend is reversed in the non-heating season. Meanwhile, values recorded during heating season are slightly higher compared to non-heating season for the Tacoma and Duwamish sites. The ANOVA results indicate significant differences between seasons ($p<0.001$) but not between sites ($p<0.07$). The ANOVA post-hoc comparisons indicate that the means are not statistically distinguishable.

It is important to highlight that acrolein monitoring data has a high level of uncertainty. In 2009, the EPA conducted a short term laboratory study that raised questions about the consistency and reliability of acrolein monitoring results[21]. Acrolein is one of the most difficult chemicals to measure using TO-15 because of inconsistent sampling canister preparation methods and other uncertainties. Acrolein can react easily with other chemicals to form compounds that complicate laboratory analysis. Even though we used a very consistent method of preparing canisters and did not find indications to show our data was in question, a comparison to other NATTS sites is inconclusive due to the measurement inconsistencies nationally.

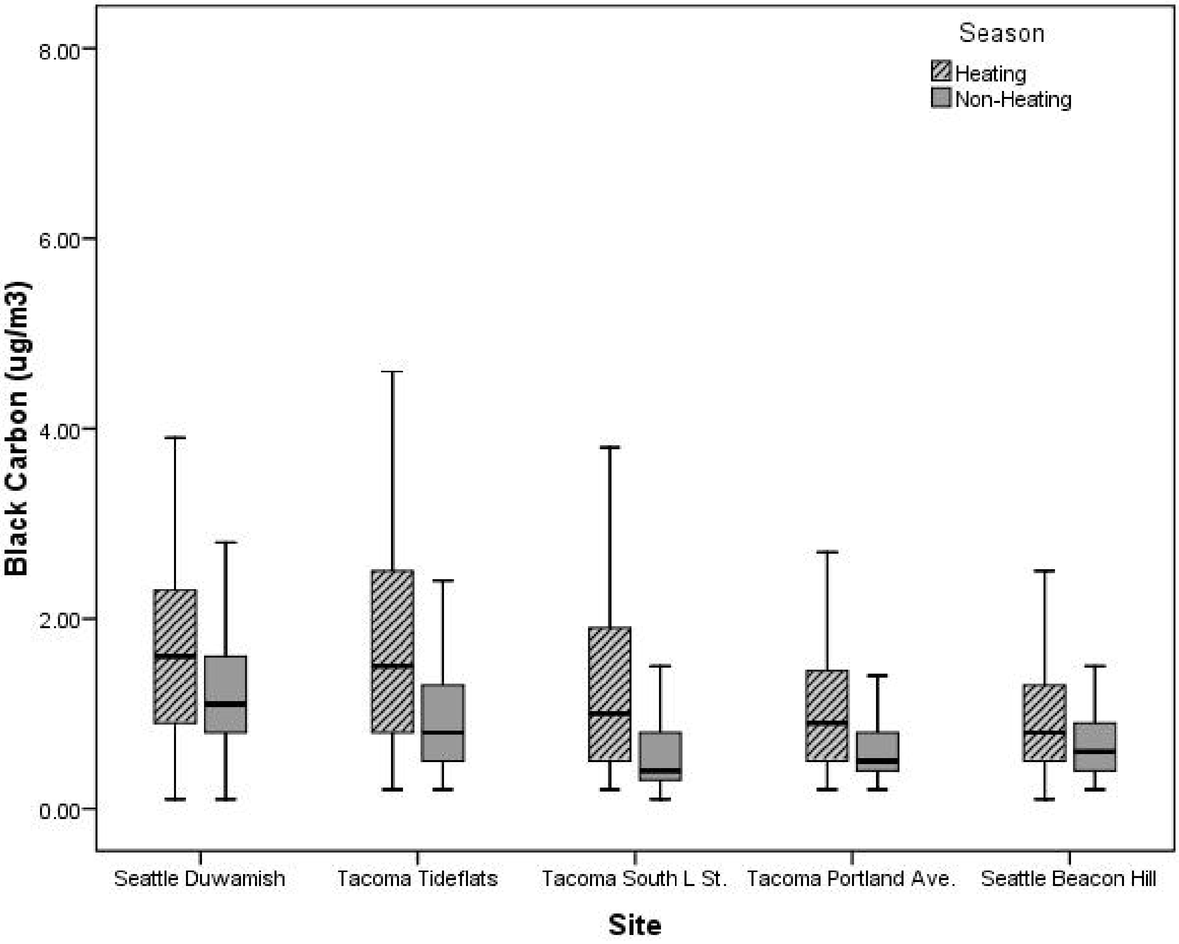


**Figure 3.1.9: Box and Whisker Plots for Black Carbon: results by site and season**

Figure 3.1.9 illustrates the black carbon results from the study. Black carbon, commonly referred to as "soot", is a component of fine particles. It is associated with diesel exhaust, as well as other combustion sources. It is monitored by measuring the absorption from a lamp at 880 nanometer wavelength. The median values are similar across all sites, but the 75th and 95th percentiles are higher in the industrial sites (Seattle Duwamish and Tacoma Tideflats). The ANOVA results indicate significant differences both between sites ($p<0.001$) and seasons ($p<0.001$), but the pattern of results for the sites changes across seasons ($p<0.001$), largely due to a decrease in levels at the South L St site in the non-heating season. The ANOVA post-hoc comparisons indicate that the values at the Duwamish and Tideflats sites are significantly different ($p<0.05$) and that the Tideflats site shows significant differences in values compared to the two other Tacoma sites ($p<0.001$).

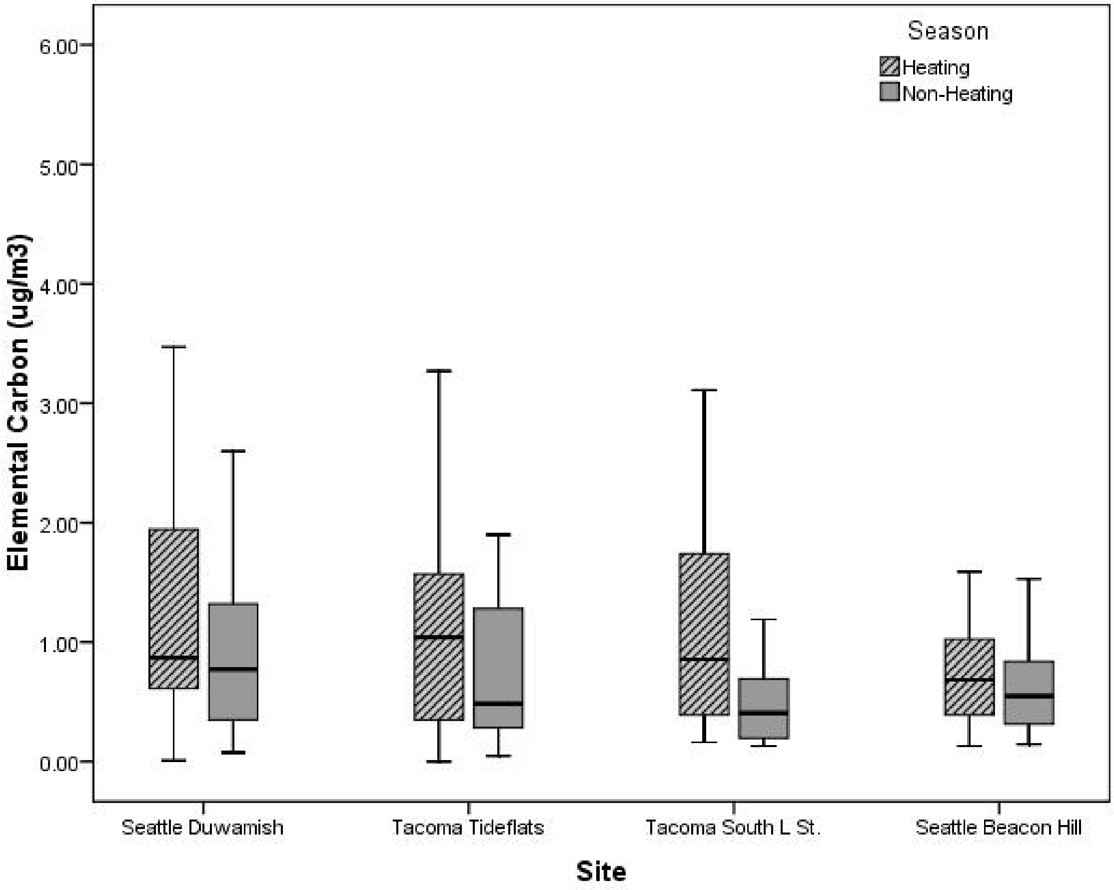


**Figure 3.1.10: Box and Whisker Plots for Elemental Carbon: results by site and season**

The plot in Figure 3.1.10 displays the elemental carbon results. Elemental carbon is also a component of fine particles, from combustion sources. Although similar in concept to black carbon, it is measured using thermo-optical transmittance. In this technique, elemental carbon is defined as a quantity from which a filter sample is heated to an appropriate temperature for "elemental carbon" to oxidize and volatilize. The median values in all the Tacoma and Seattle sites appear to be similar to each other. The South L St site appears to have a lower median compared to the other sites in the non-heating season, but this trend is not carried over into the heating season. Median values in heating season are slightly higher for the Tacoma Tideflats site compared to South L St or Duwamish sites. However, the ANOVA results indicate significant differences between seasons ($p<0.001$), but not between sites ($p<0.12$), and the pattern of results for all sites is not significantly different between heating and non-heating seasons ($p<0.33$). The ANOVA post-hoc comparisons indicate there were no significant differences between each individual site.

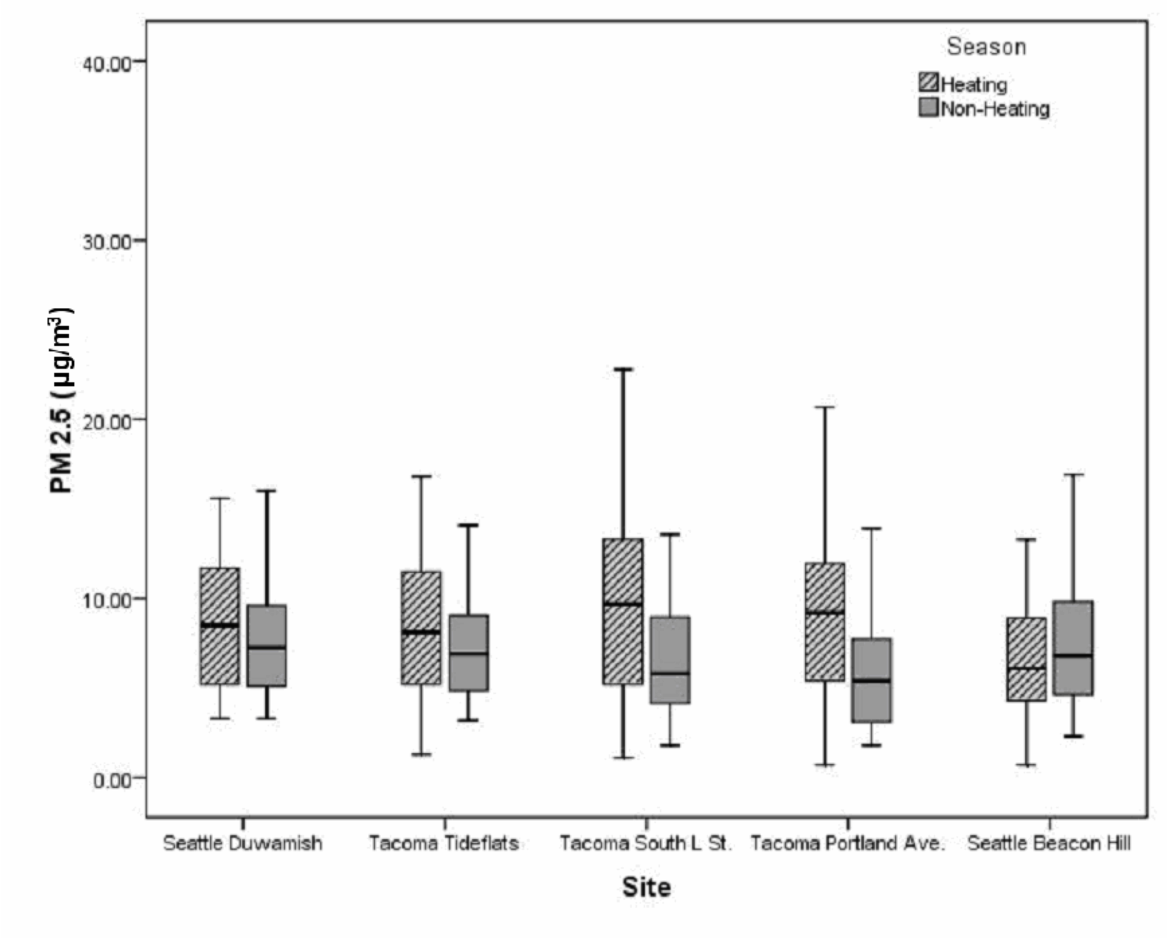


**Figure 3.1.11: Box and Whisker Plots for $PM_{2.5}$: results by site and season**

The plot in Figure 3.1.11 displays the $PM_{2.5}$ results. $PM_{2.5}$ is the one pollutant in this study that is regulated as a criteria pollutant, and has a National Ambient Air Quality Standard. Exposure to $PM_{2.5}$ can have serious health effects. Fine particles are most closely associated with increased respiratory disease, decreased lung function, and premature death.[22,23,24,25] $PM_{2.5}$ primarily comes from wood burning and engine exhaust including cars, diesel trucks, and buses. Fine particulate can also be formed in the atmosphere through chemical reactions of pollutant gases. The median values at the Tacoma and Seattle Duwamish sites appear to be similar to each other. The Beacon Hill site appears to have a slightly lower median compared to the other sites in the heating season, but this trend is not carried over into the non-heating season. Values recorded during heating season are slightly higher for the Tacoma South L St site compared to Tacoma Tideflats or Seattle Duwamish sites. The ANOVA results indicate significant differences between seasons ($p<0.01$) but no difference between sites ($p<0.25$), and the pattern of results for the sites only minor changes across seasons ($p<0.052$). The ANOVA post-hoc comparisons indicate that there is no significant difference between the Duwamish and Tideflats sites, and no significant differences between the Tacoma sites.

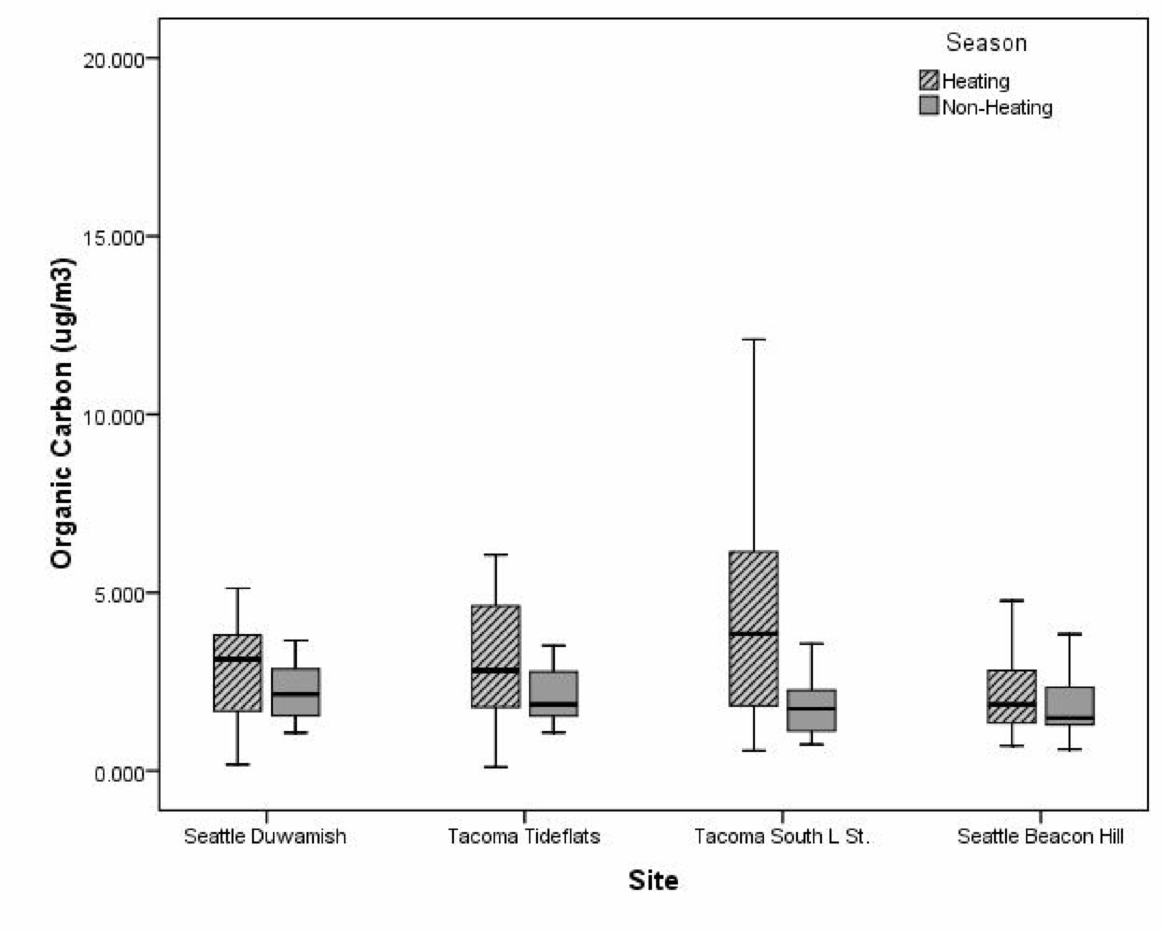


**Figure 3.1.12: Box and Whisker Plots for Organic Carbon: results by site and season**

The plot in Figure 3.1.12 displays the organic carbon results. Organic carbon, like elemental carbon, is a component of fine particles. It also comes from combustion sources. Like elemental carbon, it is measured using thermo-optical transmittance and it is defined as a component that volatilizes at a certain temperature *without* oxidation. The results show that organic carbon levels are higher during the heating season at all of the monitoring sites, where Tacoma South L St. has the highest heating season results. Results in the non-heating season are fairly constant across all sites. The ANOVA results indicate significant differences between seasons ($p<0.001$), but not between sites ($p<0.063$), and the pattern of all the sites is not significantly different for heating versus non-heating season ($p<0.126$). The ANOVA post-hoc comparisons indicate that the Duwamish and Tideflats sites were not significantly different from each other and there are no significant differences between the values at the Tacoma sites.

### 3.1.4. Levoglucosan Analysis

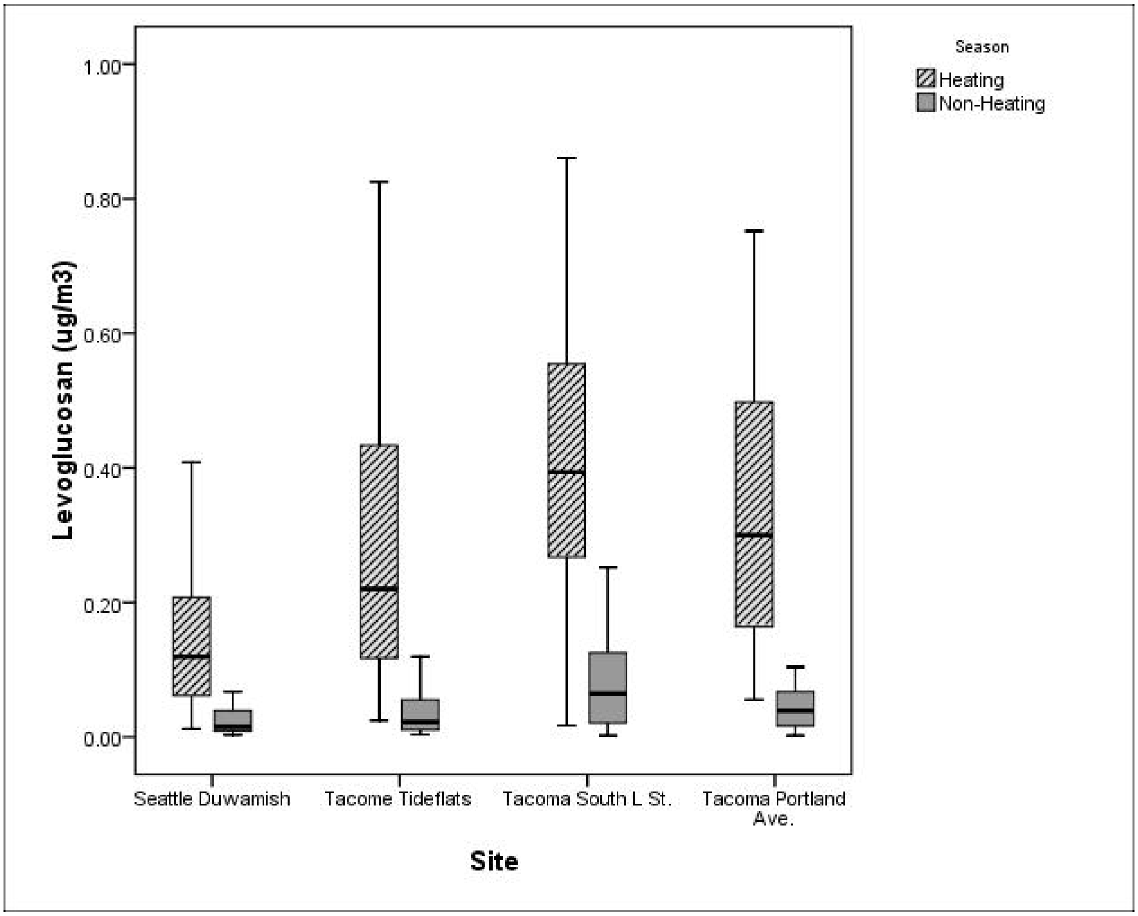


**Figure 3.1.13: Box and whisker Plots for Levoglucosan: results by site and season**

The plot in Figure 3.1.13 displays the levoglucosan results. Levoglucosan is a specific marker for wood burning, and shows a clear difference by season and by site. The median values in all the Tacoma sites appear to be elevated compared to the Seattle Duwamish site during the heating season. During the non-heating season, levels are much lower, with Tacoma sites remaining higher than Duwamish. The ANOVA results indicate significant differences between seasons (p<0.001) and between sites (p<0.001), and the pattern of results for the sites does not change across seasons (p<0.7). That is, Tacoma South L Street is highest in both the heating and non-heating seasons. The ANOVA post-hoc comparisons indicate that the Duwamish and Tideflats sites are not significantly different, but there is some heterogeneity in the results amongst the Tacoma sites. Tacoma South L is not different than the Portland Ave site (p=0.09), but it is different than the Tacoma Tideflats and Duwamish sites (p<0.005). Since levoglucosan is a marker applied only in measurements from this study and is not routinely analyzed, no results were available for comparison with national NATTS sites or for Beacon Hill.

The results for levoglucosan can provide some insight into the specific contribution of wood burning to the mixture of air toxics observed at the sites. Levoglucosan, an anhydrous sugar derived from the pyrolysis of the major wood polymer cellulose, is one of the most abundant organic compounds associated with particles in wood smoke.[26,27] This chemical marker is stable in the environment and has been used extensively to estimate wood smoke levels in ambient particulate matter (PM) samples.[28,29] As noted earlier, levoglucosan shows strong seasonal variations, and the time-series plot in Figure 3.1.14 illustrates the pattern in these daily values (1 in 6 frequency) reported over the 1 year period of this study. This figure also plots the daily benzene values measured in the same time series, and there is remarkable correspondence to the two compounds plotted in the graph. This correspondence in day-to-day fluctuations suggests that benzene and levoglucosan are co-varying, and probably originate from the same source, that is, residential wood burning in neighborhoods around the monitoring sites. Although meteorology is a potential confounder, higher benzene/levoglucosan ratios in winter also suggests wood burning as the likely source of benzene.

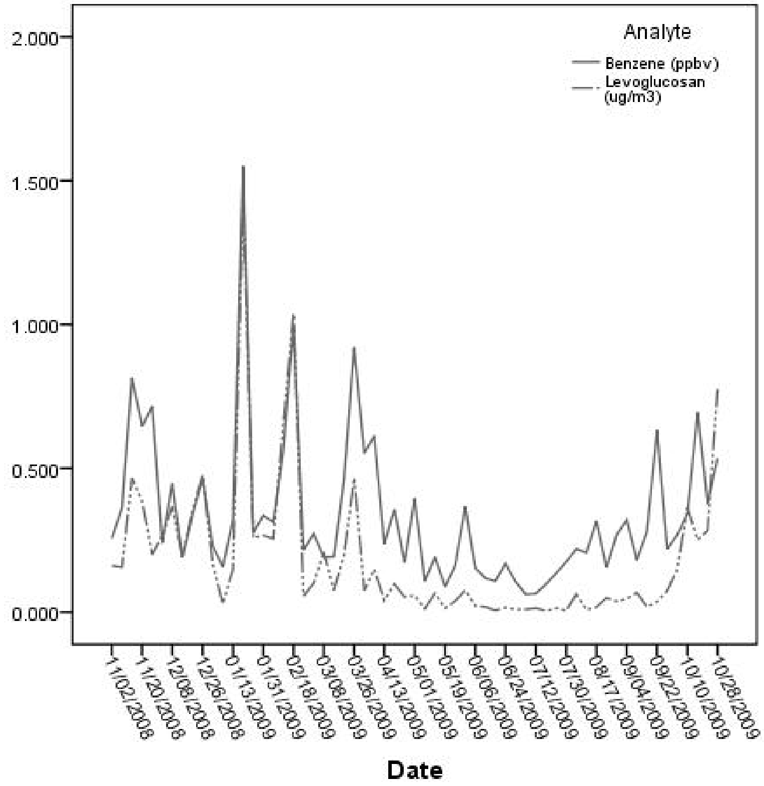


**Figure 3.1.14: Time Series Plot for Benzene and Levoglucosan: results averaged across Tacoma sites.**

As noted in the previous figure, some chemical species measured in the study show similar co-varying patterns of day-to-day changes in concentration. One common method of examining the data is to search for pair-wise associations between the compounds and to conduct a correlation analysis. The usual basis for interpreting this analysis is a scatter plot, as shown below in Figure 3.1.15 for levoglucosan (abscissa or X) and benzene (ordinate or Y) during the heating season. A plot of the data for the non-heating season shows very similar results. Observations taken on each day for these two chemicals are plotted as an (X,Y) data pair, and the values are plotted over the time period (or season) of interest.

As illustrated here, the scatter plot shows the trend of this association between the two species, and this can be summarized by a linear regression through the data points. (Note, all the data were log transformed to normalize the distributions.) The Pearson product-moment correlation coefficient (rho) is a measure of the strength of this association, with a coefficient of ±1 representing a perfect linear association and a coefficient of 0 showing no association. The square of the Pearson correlation coefficient (denoted by $R^2$) can be interpreted as the amount of variability in Y that is explained by X.  Since levoglucosan is a specific marker for wood smoke, this suggests that a substantial amount of the benzene measured at the sites is due to wood burning near the sites.

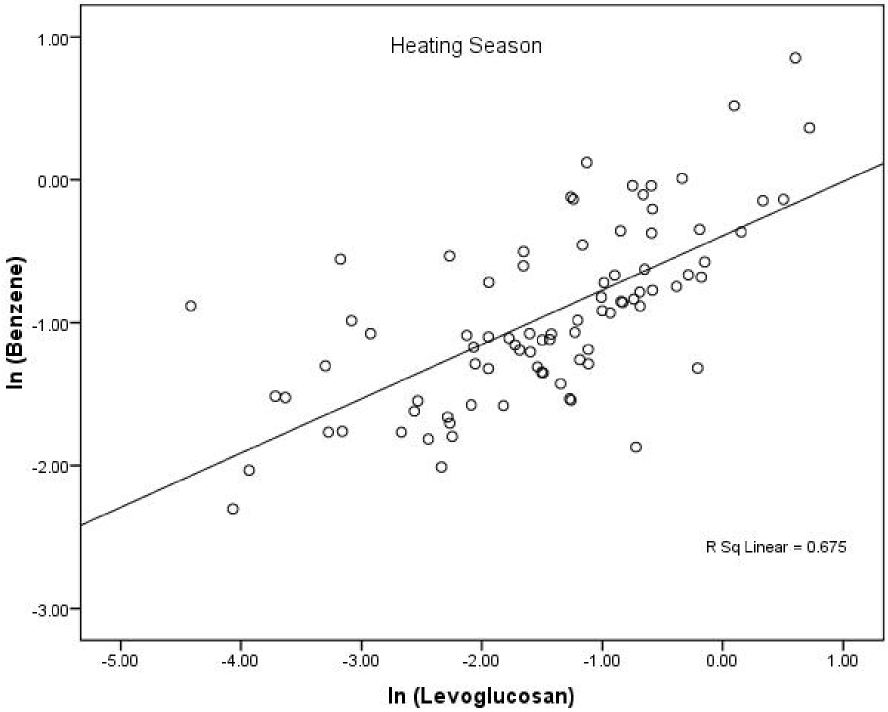


**Figure 3.1.15: Bivariate Scatter Plot for ln(Benzene) and ln(Levoglucosan): Heating Season, all sites**

Figure 3.1.16 displays a scatter plot for the paired levoglucosan and benzene results (log transformed) across all seasons. The overall association is relatively strong and consistent with the heating season.  This reinforces the observation that much of the benzene impact at the sites is likely due to wood burning in surrounding areas.  The slightly better fit across all seasons is likely due to having a larger data set.

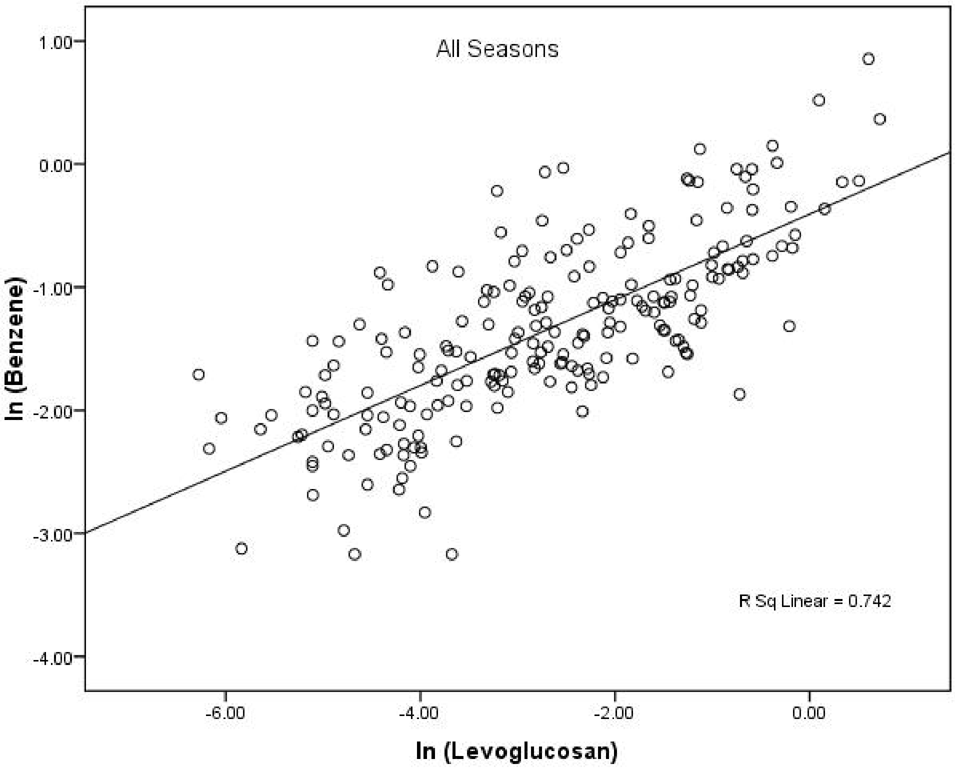


**Figure 3.1.16: Bivariate Scatter Plot for ln(Benzene) and ln(Levoglucosan): All Seasons, all sites**

The preceding analysis was extended to examine pair-wise associations for all the compounds discussed earlier in these results, by constructing a correlation matrix. A separate matrix was created for each season, to account for seasonal changes in emission and source patterns which were noted earlier in the ANOVA analysis. In addition, we also used the Spearman rank correlation (Spearman's rho) which provides a robust estimator of the ordinal (ranked) association between the paired measurements. Associations based on Spearman's rho are not dependent on the distribution of the data, and therefore are not sensitive to the use of a log transform to normalize the values for analysis. However, the rank correlation cannot be interpreted as an 'explained variance' in the same way as Pearson's rho, so both measures were retained.

Tables 3.1.1 and 3.1.2 below show the results of the correlation analysis. The diagonal of the tables separates the Spearman and Pearson correlation results. The upper half of the table shows Spearman (rank) correlations and significance values for the bivariate rank association; the lower half of the table shows Pearson correlations and their corresponding significance values. Data pairs that are significantly correlated at $p < 0.01$ are shaded in green, to highlight these associations. Aside from the large number of correlated pairs, the most striking feature is that carbon tetrachloride, formaldehyde, carbon tetrachloride, and acrolein appear to be the only compounds that do *not* have associations with most of the other measured air toxics.  This suggests that these compounds arise from some other regional source that is not due to the main site contributors, vehicle traffic and wood burning.

# Table 3.1.1: Heating Season Correlation Matrix for Seattle and Tacoma Fixed Sites

| | 1,3-Butadiene | Acetaldehyde | Acrolein | Benzene | Black Carbon | Carbon Tetrachloride | Chloroform | Elemental Carbon | Formaldehyde | Levoglucosan | Naphthalene | PM 2.5 | Organic Carbon |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,3-Butadiene | Correlation | .577** | .400** | .903** | .748** | -.274** | .438** | .674** | .510** | .637** | .761** | .728** | .733** |
| | Sig. (2-tailed) | .000 | .000 | .000 | .000 | .003 | .000 | .000 | .000 | .000 | .000 | .000 | .000 |
| | N 175 | 114 | 94 | 118 | 116 | 118 | 96 | 85 | 114 | 85 | 89 | 115 | 85 |
| Acetaldehyde | .424** | 1.000 | .362** | .586** | .585** | -.244** | .452** | .646** | .852** | .252* | .731** | .586** | .698** |
| | .000 | . | .000 | .000 | .000 | .009 | .000 | .000 | .000 | .019 | .000 | .000 | .000 |
| | 114 | 180 | 91 | 114 | 116 | 114 | 93 | 83 | 118 | 86 | 89 | 117 | 83 |
| Acrolein | .106 | .136 | 1.000 | .394** | .244* | -.232* | .082 | .227* | .360** | .261* | .324** | .149 | .175 |
| | .308 | .199 | . | .000 | .019 | .024 | .434 | .039 | .000 | .039 | .002 | .157 | .113 |
| | 94 | 91 | 141 | 94 | 92 | 94 | 94 | 83 | 91 | 63 | 87 | 92 | 83 |
| Benzene | .945** | .449** | .089 | 1.000 | .751** | -.347** | .464** | .667** | .466** | .682** | .735** | .751** | .752** |
| | .000 | .000 | .392 | . | .000 | .000 | .000 | .000 | .000 | .000 | .000 | .000 | .000 |
| | 118 | 114 | 94 | 177 | 116 | 118 | 96 | 85 | 114 | 85 | 89 | 115 | 85 |
| Black Carbon | .689** | .576** | .118 | .727** | 1.000 | -.301** | .503** | .825** | .450** | .578** | .835** | .852** | .802** |
| | .000 | .000 | .263 | .000 | . | .001 | .000 | .000 | .000 | .000 | .000 | .000 | .000 |
| | 116 | 116 | 92 | 116 | 1043 | 116 | 94 | 100 | 116 | 89 | 93 | 141 | 100 |
| Carbon Tetrachloride | -.291** | -.275** | -.152 | -.354** | -.360** | 1.000 | .198 | -.245* | -.198* | -.107 | -.280** | -.233* | -.290** |
| | .001 | .003 | .143 | .000 | .000 | . | .053 | .024 | .035 | .331 | .008 | .012 | .007 |
| | 118 | 114 | 94 | 118 | 116 | 177 | 96 | 85 | 114 | 85 | 89 | 115 | 85 |
| Chloroform | .390** | .425** | .024 | .408** | .449** | .175 | 1.000 | .481** | .218* | .484** | .380** | .454** | .468** |
| | .000 | .000 | .819 | .000 | .000 | .088 | . | .000 | .036 | .000 | .000 | .000 | .000 |
| | 96 | 93 | 94 | 96 | 94 | 96 | 141 | 85 | 93 | 64 | 89 | 94 | 85 |
| Elemental Carbon | .662** | .667** | .083 | .637** | .798** | -.273* | .487** | 1.000 | .513** | .472** | .753** | .784** | .827** |
| | .000 | .000 | .454 | .000 | .000 | .011 | .000 | . | .000 | .000 | .000 | .000 | .000 |
| | 85 | 83 | 83 | 85 | 100 | 85 | 85 | 164 | 83 | 63 | 82 | 101 | 104 |
| Formaldehyde | .144 | .513** | .166 | .141 | .196* | -.151 | .106 | .260* | 1.000 | .131 | .638** | .386** | .523** |
| | .127 | .000 | .116 | .133 | .035 | .109 | .311 | .017 | . | .230 | .000 | .000 | .000 |
| | 114 | 118 | 91 | 114 | 116 | 114 | 93 | 83 | 180 | 86 | 89 | 117 | 83 |
| Levoglucosan | .738** | .175 | .010 | .744** | .595** | -.148 | .424** | .538** | .026 | 1.000 | .579** | .693** | .649** |
| | .000 | .106 | .937 | .000 | .000 | .177 | .000 | .000 | .815 | . | .000 | .000 | .000 |
| | 85 | 86 | 63 | 85 | 89 | 85 | 64 | 63 | 86 | 125 | 65 | 91 | 63 |
| Naphthalene | .677** | .640** | .070 | .675** | .822** | -.302** | .380** | .799** | .213* | .691** | 1.000 | .802** | .838** |
| | .000 | .000 | .517 | .000 | .000 | .004 | .000 | .000 | .045 | .000 | . | .000 | .000 |
| | 89 | 89 | 87 | 89 | 93 | 89 | 89 | 82 | 89 | 65 | 141 | 92 | 82 |
| PM 2.5 | .779** | .563** | .024 | .798** | .867** | -.296** | .412** | .797** | .166 | .783** | .825** | 1.000 | .905** |
| | .000 | .000 | .817 | .000 | .000 | .001 | .000 | .000 | .073 | .000 | .000 | . | .000 |
| | 115 | 117 | 92 | 115 | 141 | 115 | 94 | 101 | 117 | 91 | 92 | 203 | 101 |
| Organic Carbon | .779** | .594** | .040 | .823** | .848** | -.385** | .368** | .763** | .170 | .747** | .854** | .952** | 1.000 |
| | .000 | .000 | .720 | .000 | .000 | .000 | .001 | .000 | .124 | .000 | .000 | .000 | . |
| | 85 | 83 | 83 | 85 | 100 | 85 | 85 | 104 | 83 | 63 | 82 | 101 | 104 |

**. Correlation significant @ P<0.01(2-tailed)

* Correlation significant @ P<0.05 (2-tailed)

Spearman's rho (upper half)

Pearson rho (Lower half)

## Table 3.1.2: Non-Heating Season Correlation Matrix for Seattle and Tacoma Fixed Sites

| | 1,3-Butadiene | Acetaldehyde | Acrolein | Benzene | Black Carbon | Carbon Tetrachloride | Chloroform | Elemental Carbon | Formaldehyde | Levoglucosan | Naphthalene | PM 2.5 | Organic Carbon |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,3-Butadiene | Correlation | .388** | .330** | .814** | .633** | -.019 | .312** | .725** | .305** | .561** | .669** | .360** | .479** |
| | Sig. (2-tailed) | .000 | .000 | .000 | .000 | .804 | .000 | .000 | .000 | .000 | .000 | .000 | .000 |
| | N 175 | 172 | 139 | 175 | 170 | 175 | 139 | 129 | 172 | 122 | 130 | 166 | 129 |
| Acetaldehyde | .337** | 1.000 | .161 | .313** | .522** | .094 | .498** | .633** | .798** | -.063 | .813** | .426** | .722** |
| | .000 | . | .059 | .000 | .000 | .217 | .000 | .000 | .000 | .487 | .000 | .000 | .000 |
| | 172 | 180 | 138 | 174 | 175 | 174 | 138 | 135 | 180 | 124 | 135 | 170 | 135 |
| Acrolein | .109 | .138 | 1.000 | .107 | .203* | -.125 | .343** | .242** | .022 | .033 | .229** | .223** | .259** |
| | .200 | .106 | . | .207 | .017 | .140 | .000 | .005 | .799 | .757 | .008 | .010 | .003 |
| | 139 | 138 | 141 | 141 | 138 | 141 | 141 | 131 | 138 | 88 | 132 | 133 | 131 |
| Benzene | .898** | .301** | .096 | 1.000 | .487** | .095 | .244** | .605** | .189* | .691** | .446** | .354** | .448** |
| | .000 | .000 | .258 | . | .000 | .211 | .004 | .000 | .013 | .000 | .000 | .000 | .000 |
| | 175 | 174 | 141 | 177 | 172 | 177 | 141 | 131 | 174 | 123 | 132 | 168 | 131 |
| Black Carbon | .500** | .422** | .144 | .404** | 1.000 | .160* | .450** | .862** | .566** | .056 | .786** | .653** | .716** |
| | .000 | .000 | .092 | .000 | . | .036 | .000 | .000 | .000 | .543 | .000 | .000 | .000 |
| | 170 | 175 | 138 | 172 | 1043 | 172 | 138 | 159 | 175 | 121 | 137 | 197 | 159 |
| Carbon Tetrachloride | -.099 | .043 | -.025 | -.021 | .123 | 1.000 | .423** | .029 | .116 | -.175 | .071 | .297** | .169 |
| | .192 | .571 | .766 | .783 | .108 | . | .000 | .743 | .128 | .053 | .416 | .000 | .053 |
| | 175 | 174 | 141 | 177 | 172 | 177 | 141 | 131 | 174 | 123 | 132 | 168 | 131 |
| Chloroform | .239** | .505** | .401** | .186* | .367** | .313** | 1.000 | .392** | .203* | .013 | .456** | .622** | .582** |
| | .005 | .000 | .000 | .027 | .000 | .000 | . | .000 | .017 | .902 | .000 | .000 | .000 |
| | 139 | 138 | 141 | 141 | 138 | 141 | 141 | 131 | 138 | 88 | 132 | 133 | 131 |
| Elemental Carbon | .595** | .660** | .201* | .494** | .888** | -.027 | .296** | 1.000 | .441** | .249* | .706** | .546** | .613** |
| | .000 | .000 | .022 | .000 | .000 | .757 | .001 | . | .000 | .019 | .000 | .000 | .000 |
| | 129 | 135 | 131 | 131 | 159 | 131 | 131 | 164 | 135 | 88 | 131 | 152 | 164 |
| Formaldehyde | .249** | .687** | -.011 | .175* | .587** | .125 | .241** | .457** | 1.000 | -.242** | .672** | .430** | .581** |
| | .001 | .000 | .898 | .021 | .000 | .100 | .004 | .000 | . | .007 | .000 | .000 | .000 |
| | 172 | 180 | 138 | 174 | 175 | 174 | 138 | 135 | 180 | 124 | 135 | 170 | 135 |
| Levoglucosan | .639** | -.094 | .010 | .605** | .055 | -.148 | .082 | .200 | -.189* | 1.000 | .077 | .111 | .169 |
| | .000 | .298 | .930 | .000 | .547 | .103 | .449 | .062 | .035 | . | .481 | .219 | .116 |
| | 122 | 124 | 88 | 123 | 121 | 123 | 88 | 88 | 124 | 125 | 86 | 124 | 88 |
| Naphthalene | .609** | .809** | .186* | .441** | .737** | .039 | .428** | .659** | .674** | .301** | 1.000 | .568** | .718** |
| | .000 | .000 | .033 | .000 | .000 | .655 | .000 | .000 | .000 | .005 | . | .000 | .000 |
| | 130 | 135 | 132 | 132 | 137 | 132 | 132 | 131 | 135 | 86 | 141 | 129 | 131 |
| PM 2.5 | .331** | .343** | .235** | .317** | .616** | .355** | .567** | .509** | .461** | .131 | .568** | 1.000 | .882** |
| | .000 | .000 | .006 | .000 | .000 | .000 | .000 | .000 | .000 | .146 | .000 | . | .000 |
| | 166 | 170 | 133 | 168 | 197 | 168 | 133 | 152 | 170 | 124 | 129 | 203 | 152 |
| Organic Carbon | .379** | .564** | .206* | .357** | .592** | .306** | .474** | .479** | .515** | .273* | .630** | .900** | 1 |
| | .000 | .000 | .018 | .000 | .000 | .000 | .000 | .000 | .000 | .010 | .000 | .000 | |
| | 129 | 135 | 131 | 131 | 159 | 131 | 131 | 164 | 135 | 88 | 131 | 152 | 164 |

**. Correlation significant @ P<0.01(2-tailed)
* Correlation significant @ P<0.05 (2-tailed)

Spearman's rho (upper half)
Pearson rho (Lower half)

## Table 3.1.3: Summary of Key Results from 1 in 6 daily monitoring over 12 months in the study area

| Analyte | Concentration (ug/m3) | Site | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Statistic | CEWA | EQWA | ESWA | EYWA | NATTS | SEWA | SEWA 00-01 | Six Sites 00-01 |
| 1,3-Butadiene | Mean | 0.099 | 0.090 | 0.131 | 0.107 | 0.204 | 0.074 | 0.137 | 0.114 |
| | Median | 0.064 | 0.051 | 0.077 | 0.064 | 0.111 | 0.049 | | |
| | Percentile 05 | 0.022 | 0.013 | 0.013 | 0.018 | 0.022 | 0.022 | | |
| | Percentile 25 | 0.033 | 0.024 | 0.031 | 0.033 | 0.044 | 0.033 | | |
| | Percentile 75 | 0.111 | 0.113 | 0.148 | 0.119 | 0.243 | 0.071 | | |
| | Percentile 95 | 0.281 | 0.314 | 0.400 | 0.360 | 0.688 | 0.186 | | |
| | % NDs | 0% | 0% | 1.69% | 0% | . | 1.61% | | |
| Acetaldehyde | Mean | 1.403 | 1.365 | 0.972 | . | 1.883 | 0.919 | 1.260 | 1.230 |
| | Median | 1.346 | 1.203 | 0.884 | . | 1.440 | 0.682 | | |
| | Percentile 05 | 0.589 | 0.635 | 0.313 | . | 0.341 | 0.385 | | |
| | Percentile 25 | 0.909 | 0.928 | 0.560 | . | 0.900 | 0.508 | | |
| | Percentile 75 | 1.744 | 1.696 | 1.240 | . | 2.340 | 1.197 | | |
| | Percentile 95 | 2.592 | 2.565 | 2.088 | . | 4.644 | 1.944 | | |
| | % NDs | 0% | 0% | 0% | . | . | 0% | | |
| Acrolein | Mean | 0.389 | 0.374 | 0.356 | . | 0.496 | 0.543 | | |
| | Median | 0.344 | 0.298 | 0.319 | . | 0.344 | 0.412 | | |
| | Percentile 05 | 0.165 | 0.167 | 0.156 | . | 0.038 | 0.133 | | |
| | Percentile 25 | 0.238 | 0.227 | 0.275 | . | 0.213 | 0.275 | | |
| | Percentile 75 | 0.467 | 0.405 | 0.426 | . | 0.595 | 0.698 | | |
| | Percentile 95 | 0.724 | 0.623 | 0.733 | . | 1.402 | 1.072 | | |
| | % NDs | 0% | 1.69% | 0% | . | . | 1.61% | | |
| Benzene | Mean | 0.918 | 0.998 | 1.294 | 1.167 | 1.077 | 0.840 | 1.180 | 1.320 |
| | Median | 0.692 | 0.777 | 0.928 | 0.938 | 0.828 | 0.691 | | |
| | Percentile 05 | 0.236 | 0.303 | 0.226 | 0.274 | 0.160 | 0.262 | | |
| | Percentile 25 | 0.501 | 0.482 | 0.590 | 0.581 | 0.479 | 0.482 | | |
| | Percentile 75 | 1.088 | 1.085 | 1.439 | 1.448 | 1.329 | 1.053 | | |
| | Percentile 95 | 2.600 | 2.877 | 3.700 | 3.062 | 2.839 | 1.487 | | |
| | % NDs | 0% | 0% | 0% | . | . | 0% | | |
| Carbon Tetrachloride | Mean | 0.759 | 0.762 | 0.768 | 0.741 | 0.528 | 0.793 | 0.610 | 0.627 |
| | Median | 0.717 | 0.711 | 0.739 | 0.711 | 0.554 | 0.764 | | |
| | Percentile 05 | 0.516 | 0.535 | 0.554 | 0.516 | 0.315 | 0.585 | | |
| | Percentile 25 | 0.629 | 0.635 | 0.635 | 0.616 | 0.375 | 0.679 | | |
| | Percentile 75 | 0.843 | 0.855 | 0.855 | 0.855 | 0.629 | 0.899 | | |
| | Percentile 95 | 1.107 | 1.145 | 1.151 | 1.101 | 0.818 | 1.107 | | |
| | % NDs | 0% | 0% | 0% | 0% | . | 0% | | |
| Chloroform | Mean | 0.111 | 0.115 | 0.115 | . | 0.254 | 0.151 | 0.230 | 0.167 |
| | Median | 0.107 | 0.107 | 0.107 | . | 0.244 | 0.146 | | |
| | Percentile 05 | 0.068 | 0.073 | 0.063 | . | 0.041 | 0.083 | | |
| | Percentile 25 | 0.088 | 0.083 | 0.078 | . | 0.100 | 0.117 | | |
| | Percentile 75 | 0.127 | 0.132 | 0.142 | . | 0.244 | 0.166 | | |
| | Percentile 95 | 0.171 | 0.210 | 0.181 | . | 0.634 | 0.249 | | |
| | % NDs | 0% | 0% | 0% | . | . | 0% | | |
| Formaldehyde | Mean | 2.816 | 1.964 | 1.465 | . | 2.921 | 1.013 | 1.720 | 1.310 |
| | Median | 2.804 | 1.784 | 1.451 | . | 2.030 | 0.563 | | |
| | Percentile 05 | 1.390 | 0.628 | 0.477 | . | 0.615 | 0.255 | | |
| | Percentile 25 | 2.079 | 0.978 | 0.900 | . | 0.861 | 0.405 | | |
| | Percentile 75 | 3.518 | 2.632 | 1.870 | . | 3.825 | 1.039 | | |
| | Percentile 95 | 4.711 | 4.010 | 3.001 | . | 8.364 | 1.882 | | |
| | % NDs | 0% | 0% | 0% | . | . | 0% | | |
| Naphthalene | Mean | 0.122 | 0.118 | 0.123 | . | 0.071 | 0.072 | | |
| | Median | 0.101 | 0.102 | 0.092 | . | 0.064 | 0.054 | | |
| | Percentile 05 | 0.037 | 0.032 | 0.024 | . | 0.002 | 0.024 | | |
| | Percentile 25 | 0.068 | 0.057 | 0.035 | . | 0.038 | 0.035 | | |
| | Percentile 75 | 0.146 | 0.146 | 0.164 | . | 0.103 | 0.097 | | |
| | Percentile 95 | 0.279 | 0.274 | 0.341 | . | 0.153 | 0.199 | | |
| | % NDs | 0% | 0% | 0% | . | . | 0% | | |
| Tetrachloroethene | Kaplan-Meier Mean | 0.199 | 0.312 | 0.138 | 0.145 | . | 0.105 | 0.156 | 0.216 |
| | Percentile 95 | 0.576 | 0.759 | 0.400 | 0.427 | . | 0.339 | | |
| | Maximum | 1.756 | 4.746 | 0.678 | 1.017 | | 0.570 | | |
| | 95% KM UCL (Chebushev) | 0.361 | 0.676 | 0.224 | 0.239 | . | 0.188 | | |
| | % NDs | 5.08% | 3.45% | 22.4% | 6.90% | . | 8.06% | | |

| | | | |
|---|---|---|---|
| CEWA | Seattle Duwamish | EYWA | Tacoma Portland Ave. |
| EQWA | Tacoma Tideflats | NATTS | NATTS 2006 and 2007 |
| ESWA | Tacoma South L St. | SEWA | Seattle Beacon Hill |

Table 3.1.3 shows summary statistics for key pollutants across monitoring sites during this study period. In the right-hand columns, the historical data above is from the 2000-2001 Seattle air toxics study (for Beacon Hill and for the 6 sites averaged).

### 3.1.5. Comparison of Beacon Hill Results with Historic Results

For comparison to the 2001 study results in the Seattle area, a comparison can be made by analyzing Seattle Beacon Hill data over time. This study, along with results from the previous monitoring campaign in 2001, and the 2006-2007 NATTS data acquired for this report, provides 24-hour average results for several compounds. Figure 3.1.17 shows a comparison of data for these compounds measured at the Seattle Beacon Hill site over time. Carbon tetrachloride is the only pollutant to have a higher concentration in this study than the previous 2001 study. All others showed small decreases.

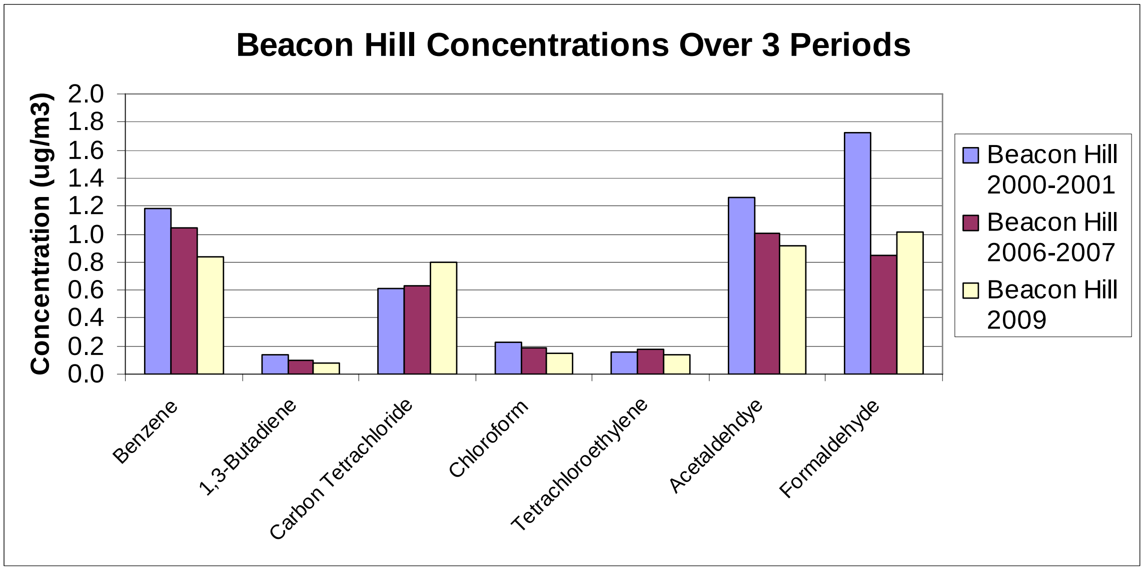


**Figure 3.1.17: Beacon Hill Concentrations Over 3 Periods**

**Plot of average 24-hr measurements of selected air toxics values taken at the Beacon Hill site in 2009, with measurements at Beacon Hill in past studies.**

## 3.2. Mobile Monitoring: MIMS

### 3.2.1. Intro/Background

Membrane introduction mass spectrometry (MIMS) has been employed for over thirty years as an on-line analytical technique[30] for the direct resolution of complex mixtures, most notably the increased use of tandem mass spectrometry (MS/MS).

The objective of the MIMS analysis in this project was to characterize seasonal and spatial patterns of key air toxics. The MIMS was put on a mobile trailer to capture hourly concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX compounds). This information was used to determine how wood smoke concentrations and diesel exhaust, and the air toxics associated with them, vary spatially across and within neighborhoods.

### 3.2.2. Methods and Materials

Monitoring took place in the neighborhoods surrounding the three fixed air toxics sites in Tacoma, WA. Monitoring took place during two periods, one in summer and one in winter. The winter monitoring was undertaken during a stagnation event January 15-21, 2009. During this period, the Agency issued a Stage 1 Burn Ban on January 17, and a Stage 2 Burn Ban on January 19. The bans were cancelled on January 20 as air quality began to improve. Summer monitoring took place July 23-24, 2009 and July 28-30, 2009. Although no smog alerts were issued, there was a stagnation event during this period.

Two separate strategies were used to identify spatial and temporal variation in select VOCs associated with traffic-related and wood smoke-related pollution respectively.

For wood smoke-related air pollution, three separate routes were identified, each consisting of a central site (three of the fixed sites in the study: Tacoma South L St, Tacoma Portland Ave and Tacoma Tideflats) and three satellite sites (see Figure 3.2.1). The mobile platform began each route by slowly driving (~15-20 mph) around the central site for that route and sampling air quality for 15-20 minutes. The mobile platform then drove out to the first satellite location and data was acquired over another 15-20 minute period. The route continued with the mobile platform moving from the satellite location back to the central site to sample for a further 15-20 minutes prior to moving to the next satellite site. In this way, the sampling design is able to tightly control for variations over time that could otherwise confound analysis of the spatial variability across sites. One route was completed each evening, between 9:00 p.m.-1:00 a.m. when impact from wood smoke is expected to be greatest. The satellite locations for each route were chosen *a priori* as likely to have consistently higher or lower air pollutant concentrations than the corresponding central site, and were identified based on satellite photography, GIS data, and mobile light scattering measurements.

For traffic related pollution, seven locations were selected, which included two of the fixed sites used in this study (Tacoma Portland Ave and Tacoma South L St, sites A and C in Figure 3.2.2), and five additional satellite sites which were located near major roadway intersections (see Figure 3.2.2). The seven sites were divided into two routes (four sites/route), with the Portland Avenue site (Site A) being common to both routes. Traffic Route 1 comprised sites A, B, C and D, whereas Traffic Route 2 comprised sites A, E, F and G. On each sampling day, the mobile platform completed two circuits of one of the routes, circling each of the four sites per route (typically in a clover-leaf pattern) for 15 minutes to accumulate air quality data, before moving on to the next site. Sampling for traffic related pollutants took place during the afternoon rush hour, between 2:00 p.m.-6:00 p.m. when impacts from traffic related air pollutants was anticipated to be highest.

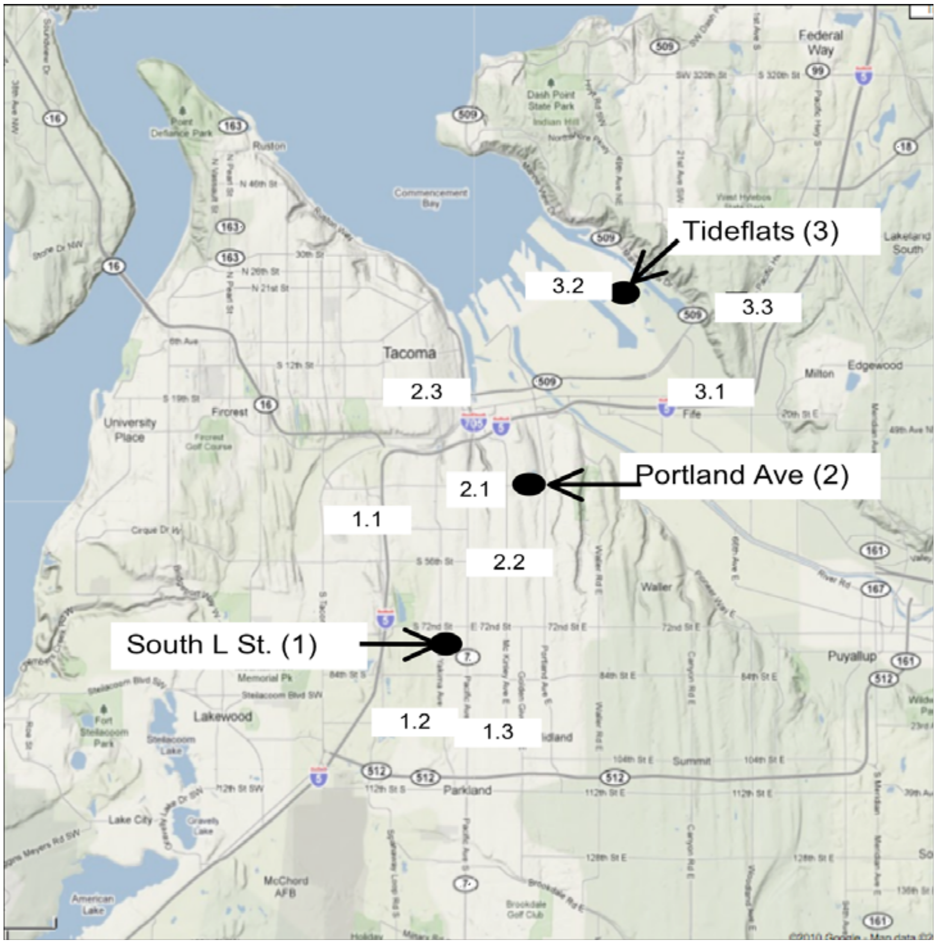


Figure 3.2.1: Wood Smoke Sampling Routes

**First digit number represents sampling route, second digit represents label for each satellite site (e.g., 2.3 is satellite site 3 on route 2).**

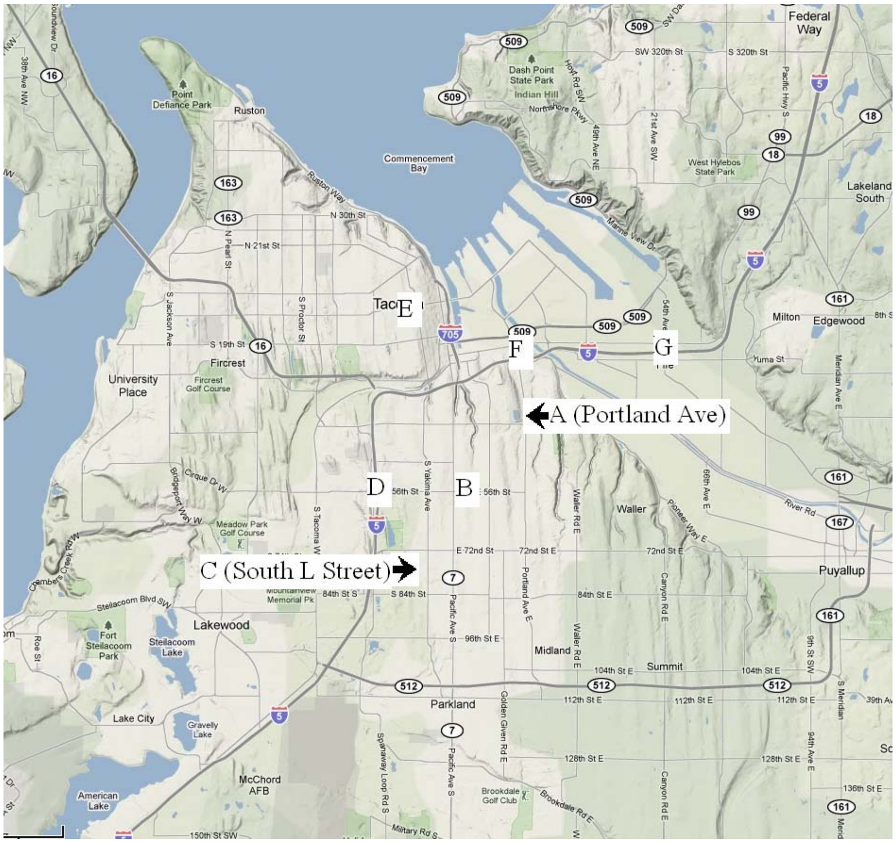


**Figure 3.2.2: Traffic Sampling Routes**
**Instrumentation and analytical procedures used are described in Appendix D.**

### 3.2.3. Results and Discussion

Table 3.2.1 lists the response factors, MS/MS transitions, and detection limits for targeted analytes in air as determined via gravimetrically calibrated permeation tube standards used with the gas dilution apparatus.

**Table 3.2.1: Target VOCs and SVOCs Monitored in Air by MIMS**

| Analyte | MW | MS/MS Transition [a] | Response Factor [b] | Detection Limit (ppbv) [c] |
|---|---|---|---|---|
| Toluene | 92.14 | 91 → 65 | 1.75 | 0.08 |
| Benzene | 78.11 | 78 → 51 | 1.22 | 0.44 |
| Ethylbenzene/Xylene | 106.17 | 106 → 79, 91 | 0.94 | 0.19 |
| Guaiacol | 124.14 | 124 → 81, 109 | 2.13 | 0.06 |
| Naphthalene | 128.17 | SIM 102, 128 | 2.10 | 0.15 |

[a] parent ion → monitored progeny ion
[b] response relative to toluene-d8 internal standard
[c] 3 x signal/noise

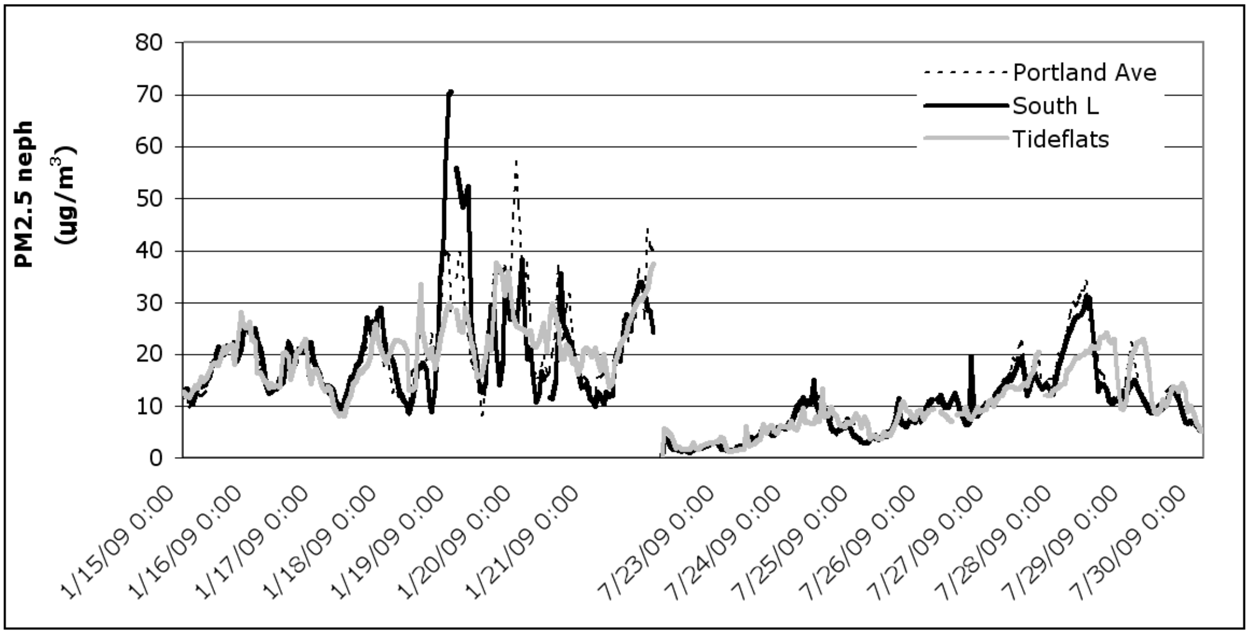


**Figure 3.2.3: Hourly $PM_{2.5}$ Variation at the 3 "Central" Sites during the winter and summer monitoring periods**

Figure 3.2.3 illustrates variation in $PM_{2.5}$ concentrations in the Tacoma area during the winter and summer intensive monitoring periods. Average and 1-hour peak $PM_{2.5}$ concentrations were similar across all three sites, and were consistently higher in winter (21 $\mu$g/m$^3$) compared to summer (9.7 $\mu$g/m$^3$). During the winter stagnation event, the highest hourly $PM_{2.5}$ concentrations occurred on January 19 and 20. During the summer sampling period, $PM_{2.5}$ concentrations steadily increased to the peak at 20 $\mu$g/m$^3$ on July 28 and 29.

A polytetrafluoroethylene (PTFE) filter was placed in the sampling line upstream of the MIMS inlet, to remove particles that might otherwise contaminate the MIMS membrane. The filters were installed prior to each sampling route, and removed at the end of the sampling route. Therefore particles collected on the filter represent an integrated sample corresponding to each of the sampling routes. (For more information on the specific method of sampling and data collection, see Appendix B). Concentrations of several source-specific tracers, namely levoglucosan (wood smoke specific), 1-nitropyrene (marker for diesel exhaust) and 2-nitrofluoranthene (a potential marker for secondary aerosol) were measured on the filter samples, and the results are summarized in Table 3.2.2.

**Table 3.2.2: Concentrations of Levoglucosan and Nitro-PAH measured coincident with MIMS sampling**

| | Levoglucosan ($\mu g/m^3$) | 2-nitrofluoranthene ($fg/m^3$) | 1-nitropyrene ($fg/m^3$) |
|---|---|---|---|
| **Winter Samples:** | | | |
| Fraction of samples >LOQ | 15/15 | 11/15 | 11/15 |
| Mean | 0.17 | 829 | 3252 |
| Standard deviation | 0.12 | 381 | 3304 |
| **Summer Samples:** | | | |
| Fraction of samples >LOQ | 0/11 | 4/10 | 4/10 |
| Mean | - | 3074 | 749 |
| Standard deviation | - | 2871 | 547 |
| t-test, summer vs. winter | 0.003* | 0.216 | 0.033* |

- p values for 2-tailed comparison of means, summer vs. winter

As expected, levoglucosan was significantly higher in filters collected during the winter sampling periods (mean 0.17 $\mu g/m^3$) compared to the summer sampling periods (where no samples were above the limit of quantification for levoglucosan). For the winter samples, levoglucosan concentrations were almost two-fold higher for the wood smoke routes compared to the traffic routes, but this difference was not statistically significant (0.22±0.14 $\mu g/m^3$ vs. 0.14±0.10 $\mu g/m^3$, p=0.303). 1-Nitropyrene concentrations were also significantly higher in winter compared to summer. The intensity of diesel exhaust emissions are not expected to exhibit significant seasonal variation, so our observation of higher 1-nitropyrene concentrations in winter vs. summer likely indicates reduced atmospheric mixing in winter (leading to high concentrations of air pollutants generally), or greater chemical stability of the 1-nitropyrene during the winter months. In contrast, average levels of 2-nitrofluoranthene were over 3-fold higher in summer vs. winter. This is consistent with formation of 2-nitrofluoranthene from photochemical reactions.

Table 3.2.3 summarizes concentrations of five specific compounds measured using the MIMS system at each of the central site and satellite locations.

### Table 3.2.3: Spatial Variation in VOC Concentrations (ppbv)

| | | | Toluene | | Benzene | | Ethylbenzene | | Guaiacol | | Naphthalene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | summer | winter | summer | winter | summer | winter | summer | winter | summer | winter |
| Woodsmoke Route 1 | Central | mean | 1.08 | 1.05 | 4.36 | 3.71 | 1.55 | 1.10 | 0.20 | 0.15 | 3.44 | 2.02 |
| | | SD | 0.99 | 0.42 | 4.68 | 1.02 | 1.03 | 0.35 | 0.11 | 0.09 | 2.91 | 0.55 |
| | Satellite 1 | mean | 0.63 | 1.03 | 4.34 | 3.66 | 1.28 | 1.06 | 0.19 | 0.16 | 3.86 | 1.94 |
| | | SD | 0.25 | 0.23 | 4.02 | 0.83 | 0.48 | 0.39 | 0.09 | 0.09 | 2.34 | 0.52 |
| | Satellite 2 | mean | 1.10 | 1.30 | 4.99 | 4.67 | 1.75 | 1.25 | 0.21 | 0.14 | 4.31 | 2.36 |
| | | SD | 0.76 | 0.35 | 5.44 | 1.85 | 0.78 | 0.42 | 0.11 | 0.10 | 3.41 | 0.91 |
| | Satellite 3 | mean | 1.13 | 1.02 | 4.99 | 3.68 | 1.95 | 1.09 | 0.21 | 0.14 | 3.51 | 2.11 |
| | | SD | 0.83 | 0.28 | 5.58 | 0.74 | 1.44 | 0.34 | 0.14 | 0.08 | 3.34 | 0.57 |
| Woodsmoke Route 2 | Central | mean | 0.74 | 1.60 | 2.20 | 3.75 | 0.93 | 1.89 | 0.18 | 0.15 | 1.78 | 2.11 |
| | | SD | 0.26 | 1.26 | 0.58 | 1.58 | 0.32 | 0.66 | 0.08 | 0.07 | 0.82 | 0.39 |
| | Satellite 1 | mean | 1.08 | 2.41 | 2.13 | 4.48 | 1.63 | 2.24 | 0.16 | 0.17 | 1.37 | 2.04 |
| | | SD | 0.34 | 1.48 | 0.54 | 2.14 | 0.55 | 0.82 | 0.08 | 0.07 | 0.47 | 0.63 |
| | Satellite 2 | mean | 0.98 | 1.56 | 1.88 | 3.98 | 0.89 | 2.06 | 0.18 | 0.19 | 2.17 | 2.26 |
| | | SD | 0.28 | 1.48 | 0.45 | 1.63 | 0.22 | 0.48 | 0.03 | 0.08 | 0.31 | 0.38 |
| | Satellite 3 | mean | 0.53 | 0.92 | 2.14 | 3.30 | 0.70 | 1.34 | 0.16 | 0.20 | 2.89 | 2.49 |
| | | SD | 0.25 | 0.73 | 0.29 | 1.07 | 0.21 | 0.20 | 0.07 | 0.08 | 0.36 | 0.33 |
| Woodsmoke Route 3 | Central | mean | 0.96 | 1.85 | 2.92 | 4.28 | 1.38 | 1.32 | 0.19 | 0.15 | 3.94 | 1.81 |
| | | SD | 0.64 | 0.82 | 1.30 | 0.90 | 0.64 | 0.55 | 0.08 | 0.06 | 1.25 | 0.38 |
| | Satellite 1 | mean | 1.31 | 1.58 | 3.21 | 3.86 | 1.95 | 1.19 | 0.24 | 0.16 | 3.99 | 1.67 |
| | | SD | 0.69 | 0.67 | 1.21 | 0.62 | 0.38 | 0.52 | 0.10 | 0.07 | 1.49 | 0.20 |
| | Satellite 2 | mean | 0.70 | 1.66 | 2.34 | 4.05 | 0.92 | 1.15 | 0.17 | 0.12 | 3.76 | 1.73 |
| | | SD | 0.28 | 0.70 | 0.61 | 0.46 | 0.29 | 0.50 | 0.08 | 0.06 | 0.66 | 0.20 |
| | Satellite 3 | mean | 1.13 | 1.40 | 1.99 | 3.56 | 1.05 | 0.99 | 0.15 | 0.13 | 2.81 | 1.61 |
| | | SD | 0.51 | 0.66 | 0.43 | 0.54 | 0.45 | 0.48 | 0.09 | 0.07 | 0.44 | 0.23 |
| Traffic Route | Central (Site A | mean | 1.09 | 1.17 | 6.38 | 3.92 | 1.82 | 1.13 | 0.25 | 0.14 | 10.69 | 2.31 |
| | | SD | 0.57 | 0.56 | 5.01 | 1.33 | 0.66 | 0.49 | 0.14 | 0.06 | 9.44 | 0.89 |
| | Site B | mean | 0.85 | 1.85 | 4.83 | 5.08 | 2.38 | 2.05 | 0.17 | 0.16 | 6.63 | 3.00 |
| | | SD | 0.37 | 0.88 | 1.03 | 1.37 | 0.79 | 0.85 | 0.07 | 0.06 | 1.39 | 0.71 |
| | Site C | mean | 0.55 | 1.14 | 4.19 | 4.61 | 1.43 | 1.56 | 0.15 | 0.16 | 6.06 | 2.84 |
| | | SD | 0.27 | 0.59 | 0.49 | 0.83 | 0.38 | 0.58 | 0.07 | 0.06 | 0.73 | 0.43 |
| | Site D | mean | 0.51 | 1.08 | 4.37 | 4.96 | 1.57 | 1.80 | 0.15 | 0.15 | 6.36 | 3.05 |
| | | SD | 0.21 | 0.59 | 0.51 | 1.01 | 0.28 | 0.54 | 0.06 | 0.06 | 0.62 | 0.45 |
| | Site E | mean | 1.57 | 1.72 | 10.31 | 5.43 | 2.47 | 1.59 | 0.32 | 0.15 | 18.92 | 2.74 |
| | | SD | 0.77 | 0.88 | 4.50 | 1.81 | 0.64 | 0.89 | 0.14 | 0.07 | 8.90 | 1.17 |
| | Site F | mean | 2.33 | 1.73 | 12.48 | 6.29 | 3.11 | 1.59 | 0.34 | 0.18 | 22.03 | 3.72 |
| | | SD | 1.74 | 0.76 | 3.88 | 1.97 | 3.05 | 1.02 | 0.13 | 0.09 | 9.03 | 1.46 |
| | Site G | mean | 1.88 | 2.30 | 12.80 | 6.48 | 3.28 | 1.76 | 0.39 | 0.17 | 22.13 | 3.88 |
| | | SD | 0.58 | 1.35 | 2.14 | 2.45 | 0.93 | 1.00 | 0.11 | 0.08 | 5.64 | 1.40 |

Wood Smoke Route 1 Central Site = Tacoma South L Street; Wood Smoke Route 2 Central Site = Tacoma Portland Ave; Wood Smoke Route 3 Central Site = Tacoma Tideflats. Traffic Route Central Site = Tacoma Portland Ave. See Figure 3.2.2 for site locations.

Paired t-tests were used to evaluate whether there were significant seasonal differences in analyte concentrations. For the wood smoke routes, toluene and benzene were significantly higher in winter vs. summer, where as guaiacol and naphthalene were significantly higher in summer compared to winter. For the traffic routes, only guaiacol and naphthalene showed significant seasonal differences (higher in summer vs. winter). Ethylbenzene concentrations did not differ significantly by season for either the wood smoke or the traffic routes. Guaiacol (2-methoxyphenol) is a pyrolysis product of lignin, and it was therefore anticipated that the primary source of guaiacol would be wood combustion, and hence that guaiacol concentrations would be higher in winter compared to summer. Our observation that guaiacol concentrations were in fact higher in summer compared to winter therefore runs counter to our *a priori* expectations. Our MIMS system relies on MS/MS to separate and quantify individual analytes in the mixture of air pollutants. Guaiacol concentrations in both seasons were close to the limit of detection that we previously determined for this compound in our MIMS system. It is possible that other compounds present in the air were interfering with the measurement of guaiacol at these low concentrations.

To remove the potential for temporal variation in contaminant concentrations confounding the spatial analysis, a temporal correction was applied to data from the wood smoke routes. For each analyte, the median concentration at a satellite site during each 15-20 minute sampling period was divided by the median concentration for that analyte measured at the central site for the time periods 10 minutes before and after the satellite site measurement. This expresses the analyte concentrations at each satellite site as a ratio in relation to the central site. Box plots illustrating the spatial variation in benzene relative to the central sites for the three wood smoke routes are shown in figure 3.2.4. Similar plots for the other five analytes are included in Appendix D. A ratio of 1.0 indicates the benzene concentration at a specific satellite site is the same as for the central site. As can be seen in Figure 3.2.4, the benzene concentration ratios for all satellite sites are close to 1 (range 0.7-1.4). This suggests that community-scale spatial variation in benzene concentrations was relatively small for the locations and time periods studied, and that the central sites provide a reasonable representation of benzene levels within each of these communities. This finding is consistent with the hourly PM data illustrated in Figure 3.2.3, which showed that $PM_{2.5}$ concentrations were highly correlated amongst the three central sites. These results are perhaps not surprising given that both the summer and winter sampling took place during periods of air stagnation. Greater spatial variation may exist at other times of the year when wind currents may lead rapid dilution of air pollutants, and steeper concentration gradients between source and receptor.

Similar to the wood smoke routes, a correction was applied to data from the traffic routes to remove the potential for temporal variation in contaminant concentrations that confounds the spatial analysis. For each analyte, the median concentration for all data from a specific satellite on a given day was divided by the median concentration measured for that analyte at the central site (Tacoma Portland Ave) on the same day. This expresses the analyte concentrations at each satellite site as a ratio in relation to the central site. Because the Portland Ave site was common to both traffic routes, it is possible to compare all traffic sites in a single figure. Box plots illustrating the spatial variation in benzene and toluene relative to the Portland Ave site are shown in Figure 3.2.5. Similar plots for the other analytes are included in Appendix D.

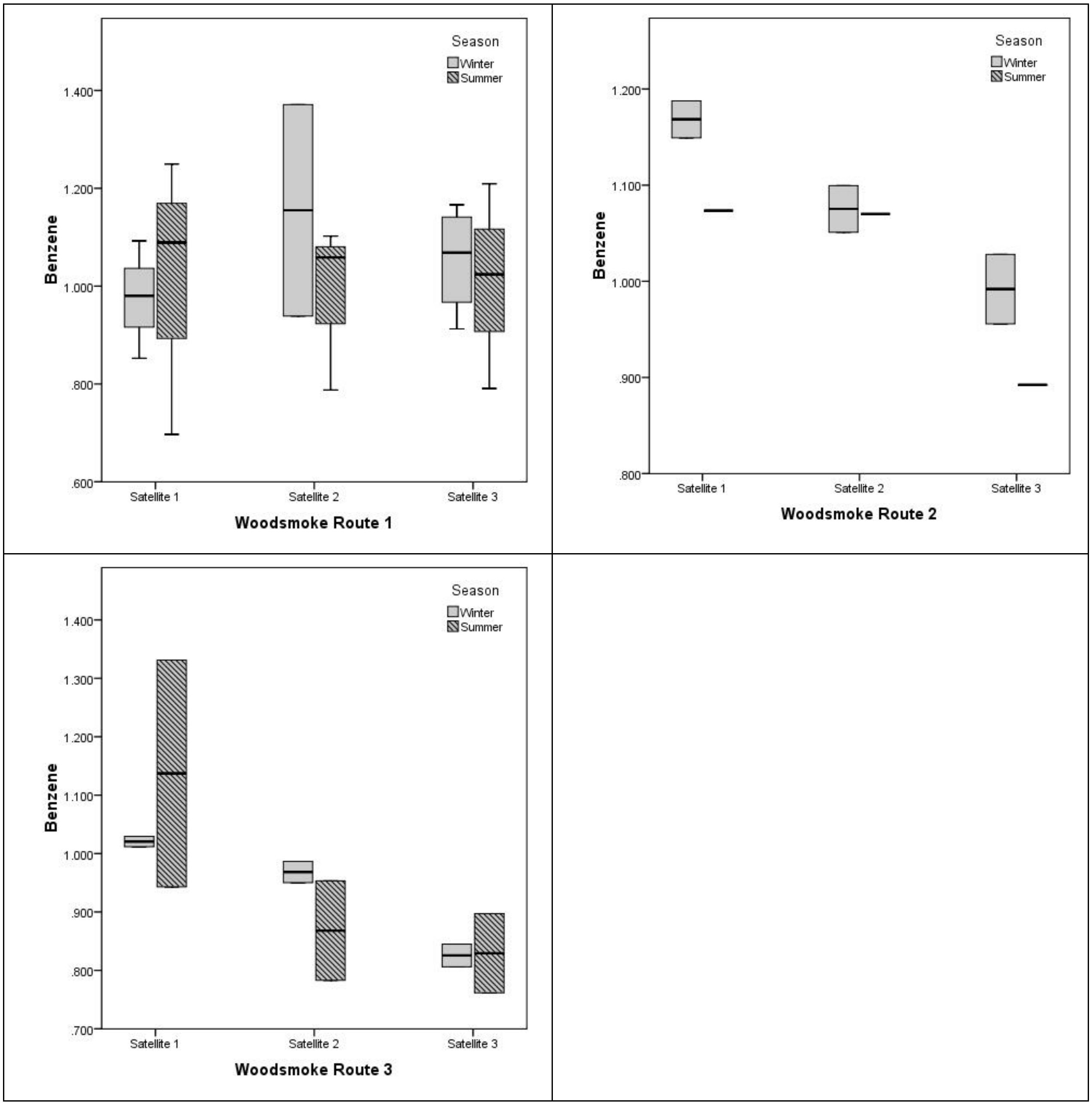


**Figure 3.2.4: Box Plots Illustrating Benzene Concentrations at satellite sites as a ratio, relative to the central site for each route. For some routes (e.g., route 2, summer) the route was only sampled on one day. On these occasions only a single concentration ratio is reported. For other routes sites, variation in the concentration ratio is shown as the 25th-75th percentiles (box) and the 5th to 95th percentiles (whiskers).**

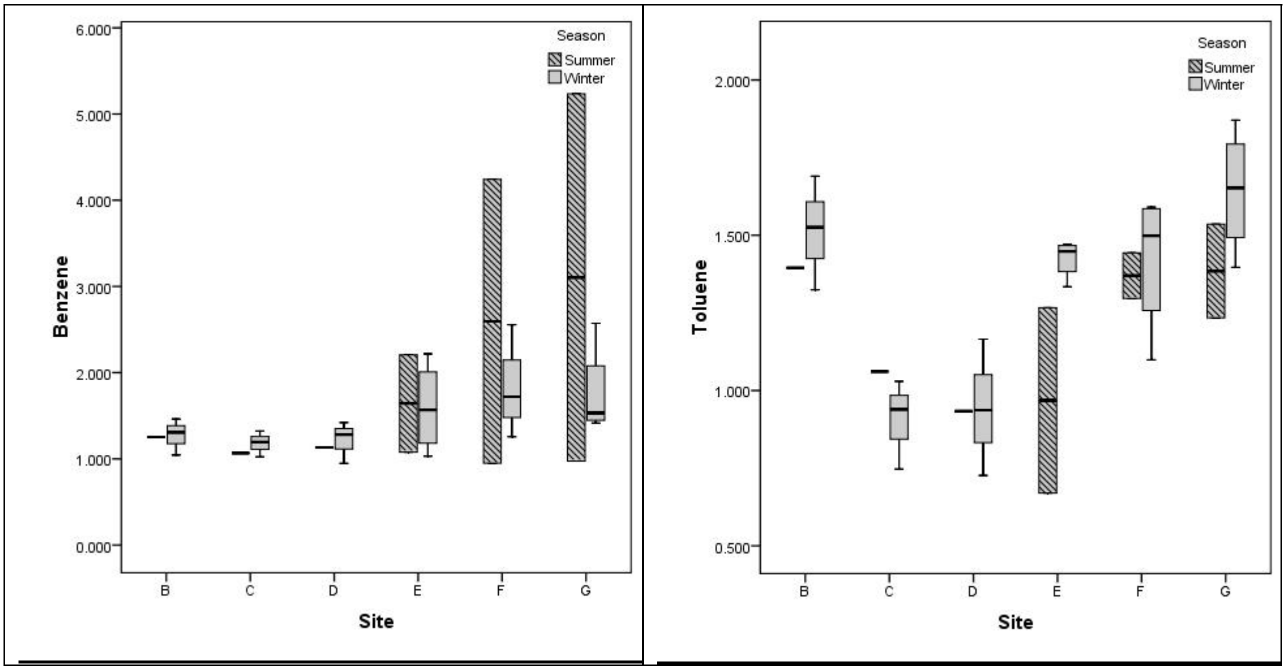


**Figure 3.2.5: Box Plots Illustrating Benzene and Toluene Concentrations measured at the traffic sites as a ratio, relative to the Tacoma Portland Ave central site. For some sites (e.g., B, C, and D, summer) the route was only sampled on one day. On these occasions only a single concentration ratio is reported. For other routes' sites, variation in the concentration ratio is shown as the 25th-75th percentiles (box) and the 5th to 95th percentiles (whiskers).**

Benzene concentrations at sites B, C and D were similar to the Portland Ave central site in both summer and winter (ratios close to 1.0, Figure 3.2.5). In contrast benzene concentrations at the other traffic sites E, F and G are substantially higher than the Portland Ave site, especially during the summer (average concentration ratios 1.5-3, Figure 3.2.5). The spatial pattern for toluene is somewhat different compared to benzene: toluene concentrations at sites B, E (winter only), F and G are approximately 50% higher than the Portland Ave central site, whereas at sites C, D and E (summer) toluene concentration is similar to the Portland Ave central site. Consequently, in contrast to the wood smoke sites and routes, for the traffic sites and routes substantial spatial variation was observed for some compounds. In these cases, measurements made at the central site tended to underestimate concentrations measured at the other locations.

## 3.3. Mobile Monitoring of Particles

In a separate monitoring campaign, mobile monitoring was conducted in Tacoma for particles measured by light scattering, light absorption coefficient, and particle-bound polyaromatic hydrocarbons (PAH) during selected afternoon and evening periods from December 2008 to February 2009 and again from July to August 2009. Data was collected over 10 afternoons and 16 evenings in the summer, and 10 afternoons and 10 evenings in the Winter. The time periods for afternoon and evening sampling were 4:00 p.m.-7:00 p.m. and 9:00 p.m.-1:00 a.m. The morning commute hours were not sampled because particle concentrations during this period are affected by the rapidly increasing morning mixing height, in addition to the spatially varying emission densities.[31,32,33] 30-second averages of particle light scattering coefficient ($b_{sp}$), particle light absorption coefficient ($b_{ap}$), and particle-bound PAHs (PAH) were collected along with relevant location information by GIS. Details of the deployment of this mobile platform are described in Appendix D.

Table 3.3.1 shows the means of the observed values of $b_{sp}$, $b_{ap}$, and PAH. These data were merged with relevant, contemporaneous fixed site data collected during this study to adjust for short-term temporal variability within each sample period. The resulting details of these adjustments are described in Appendix D.

Figures 3.3.1 through 3.3.3 summarize the spatial distribution of the temporally adjusted observations for the entire experiment. These results indicate that the high $b_{sp}$ values occur in residential areas of southern Tacoma in the winter during evening hours. In contrast, the high $b_{ap}$ values were observed near the major roads during both afternoon and evening periods in both summer and winter.

**Table 3.3.1: Summary of Mobile Measurements of Particles on Selected Days between 12/08 and 2/09 (winter) and between 7/09 and 8/09 (summer). Afternoon and evening sampling occurred between 4:00 p.m.-7:00 p.m. and 9:00 p.m.-1:00 a.m., respectively.**

| Measurement | | Winter Mean | Summer Mean |
|---|---|---|---|
| $b_{sp}$ ($10^{-6}m^{-1}$) | Afternoon | 78.9 | 21.9 |
| | Evening | 83.2 | 20.8 |
| $b_{ap}$ ($10^{-6}m^{-1}$) | Afternoon | 21.8 | 9.4 |
| | Evening | 24.7 | 10.4 |
| PAH (ng/m$^3$) | Afternoon | 18.4 | 4.9 |
| | Evening | 20.7 | 4.5 |

We noticed that during most mobile sampling runs, we encountered occasional short-lived peaks of particle-bound PAHs that occurred without corresponding increases in either $b_{ap}$ or $b_{sp}$. These peaks usually lasted for 30 seconds or less and were at least five times the sampling period median. They were observed to be caused by the presence of nearby heavy duty vehicle plumes. A map of the locations of these PAH peaks is found in Appendix D. This data was not excluded from the means.

A principal component analysis (PCA) identified three factors contributing to the observed spatial variability. Details of this analysis are included in Appendix D The analysis indicated three contributing factors to the observed spatial variability, one high in $b_{sp}$ and moderately high in $b_{ap}$ (Factor 1), another high in PAH (factor 2), and a third high in $b_{ap}$ and moderately high in $b_{sp}$ (Factor 3). The factor loadings are shown in Table 3.3.2.

**Table 3.3.2: Principal Component Factor Loadings**

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| $b_{sp}$ | 0.92 | 0.18 | 0.36 |
| PAH | 0.17 | 0.96 | 0.23 |
| $b_{ap}$ | 0.42 | 0.29 | 0.86 |

The resulting factor scores were then temporally adjusted using the method described in Section 3.2.

This PCA is useful for understanding the underlying sources of spatial variability and to clarify the location of the highly impacted wood smoke areas that have relatively high levels of $b_{sp}$, moderate levels of $b_{ap}$, and low levels of PAHs. Figure 3.3.4 compares the relative contribution of this temporally adjusted wood smoke factor with the results of a wood stove use Census survey data from 2000. Given the limited (and outdated) nature of the data, it is difficult to discern specific correlations, but some minor relationships are visible, particularly in the center of the monitored area.

For a subset of evenings, the particle mobile platform followed the MIMS vehicle and were able to combine the benzene measurements with the particle measurements. A principal component analysis of this combined data revealed the three factors seen with the particle data alone. Details of this analysis are given in Appendix D. However, with the added benzene variable in the model, we could reconstruct the contribution of each factor to the observed benzene. Figure 3.3.5 shows that the observed benzene concentrations are highly correlated with the light scattering factor that is elevated in winter at night in residential areas, consistent with a nighttime wood burning source.

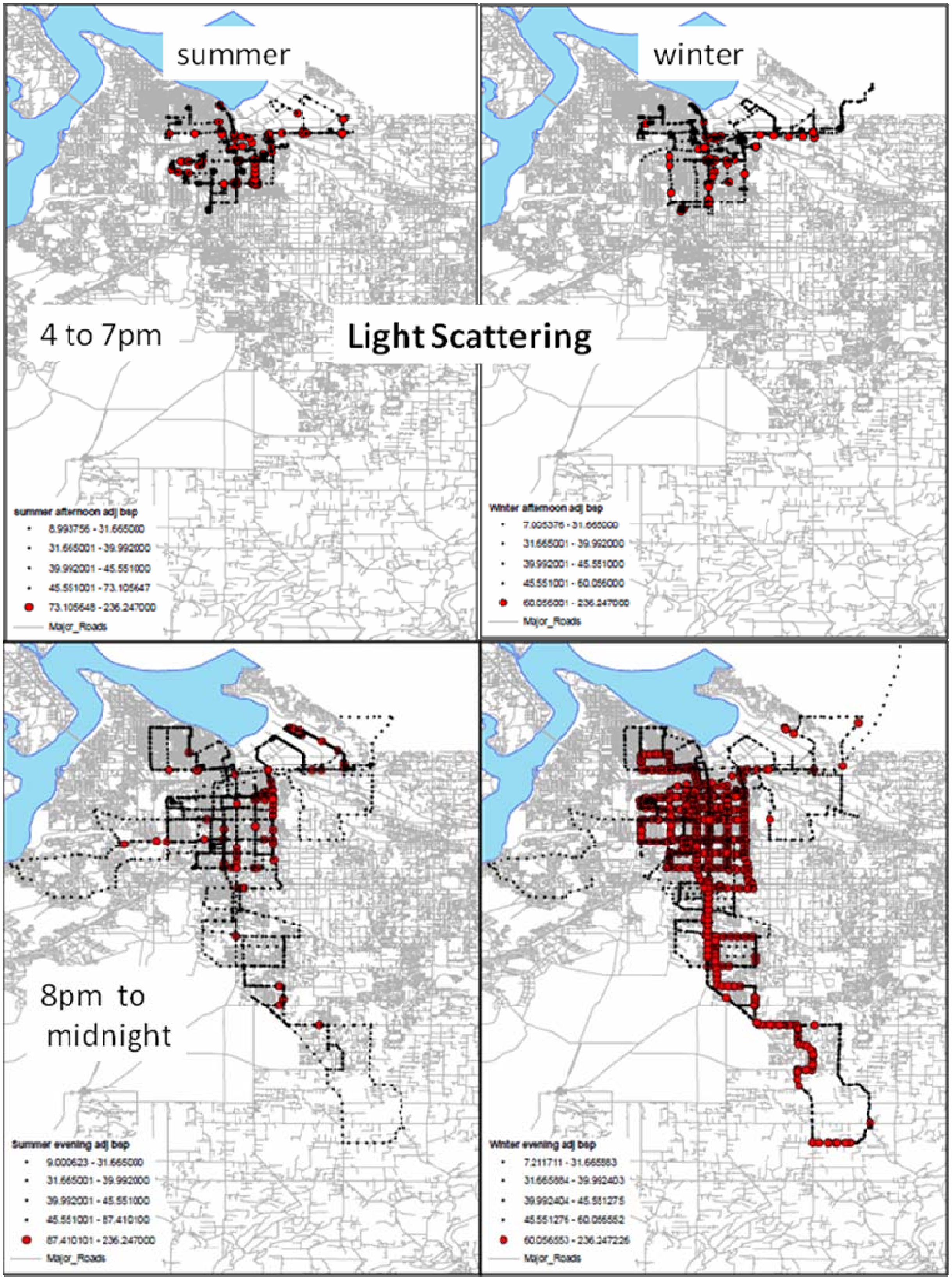


Figure 3.3.1: Spatial Distribution of Temporally Adjusted Particle Light Scattering Coefficient (measurements were taken in the late afternoon and evening on selected winter days between December 2008 and February 2009 and on selected summer days between July and August 2009)

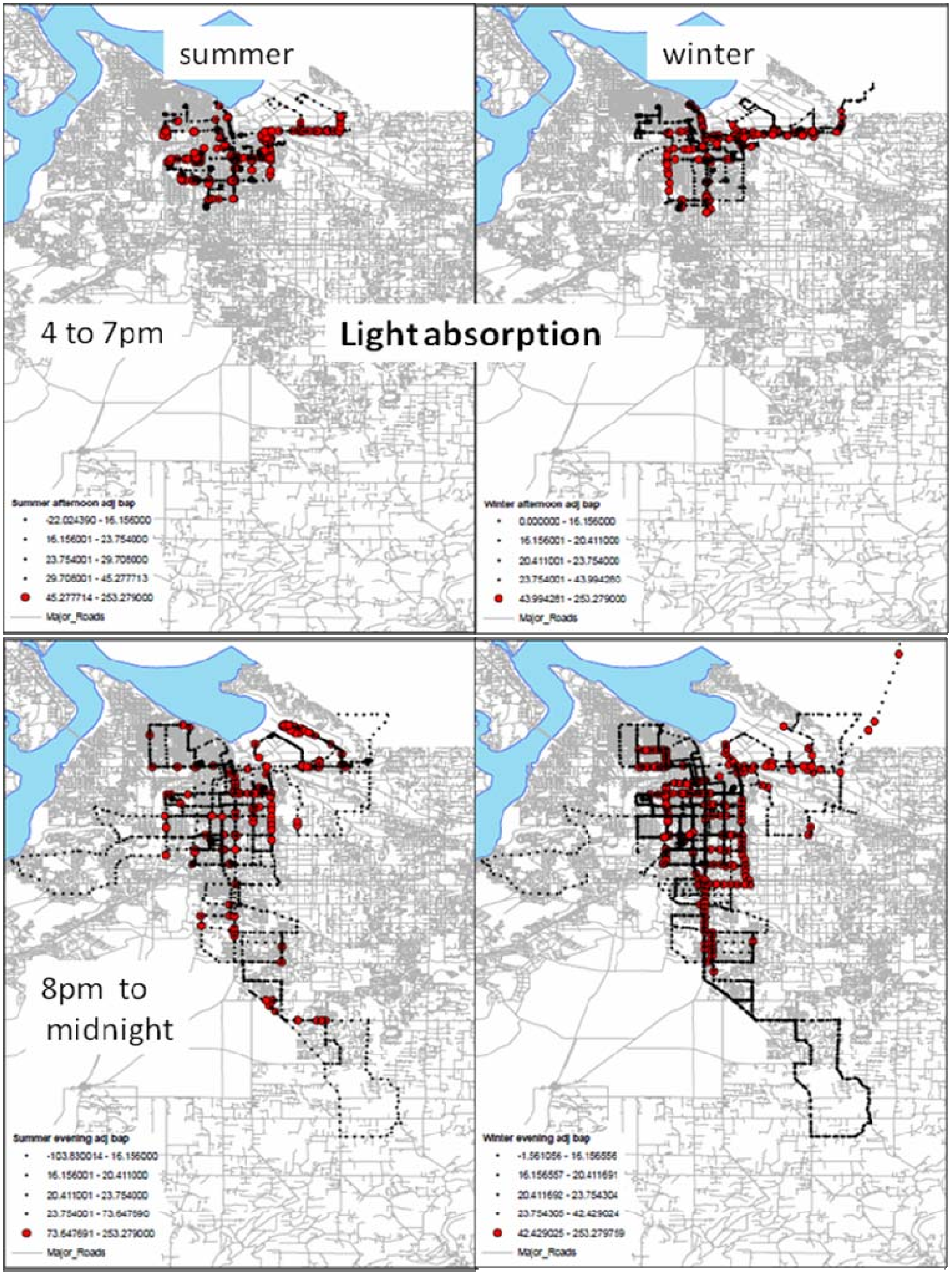


Figure 3.3.2: Spatial Distribution of Temporally Adjusted Particle Light Absorption Coefficient (measurements were taken in the late afternoon and evening on selected winter days between December 2008 and February 2009 and on selected summer days between July and August 2009)

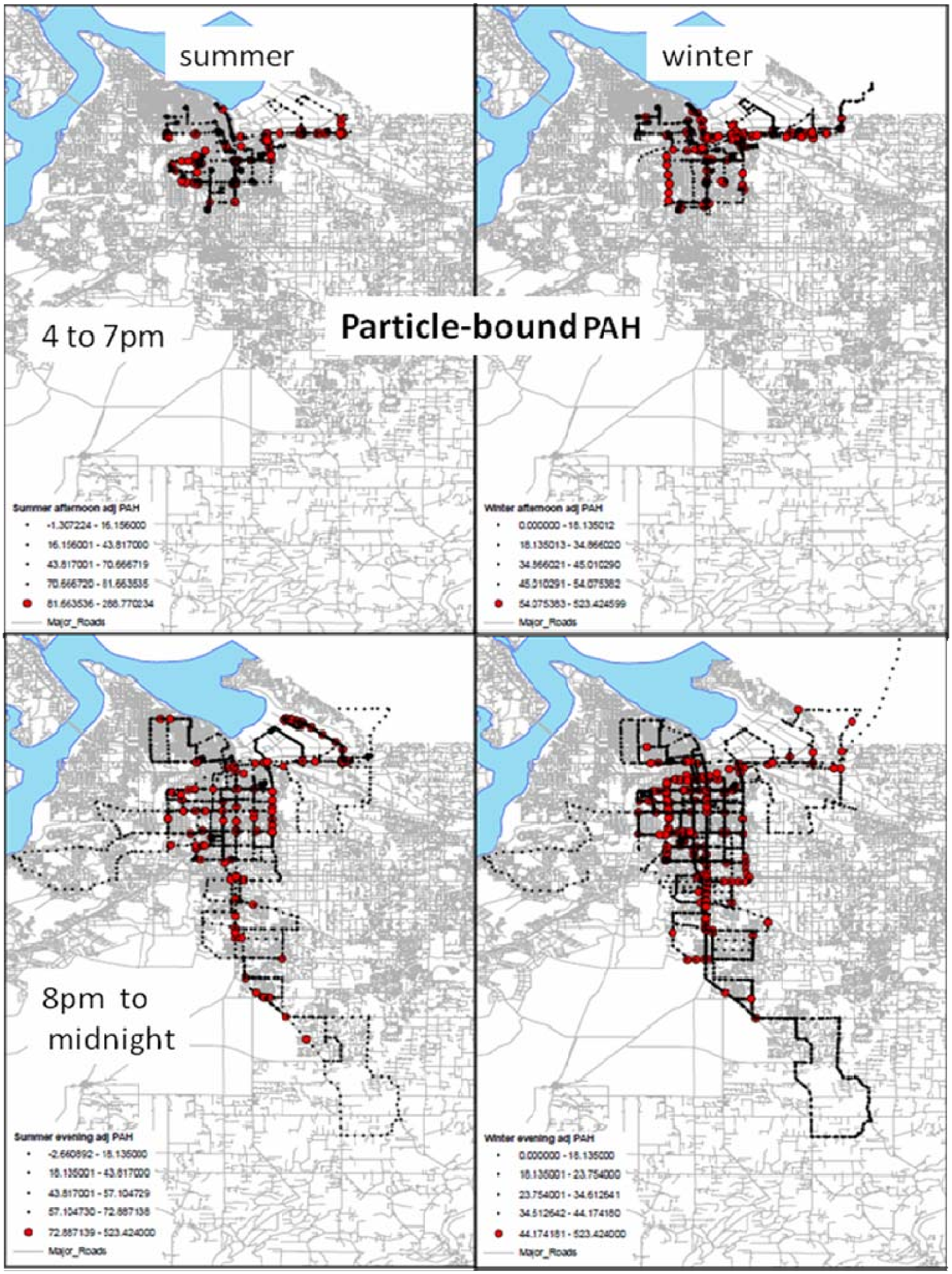


Figure 3.3.3: Spatial Distribution of Temporally Adjusted Particle-Bound PAHs (measurements were taken in the late afternoon and evening on selected winter days between December 2008 and February 2009 and on selected summer days between July and August 2009)

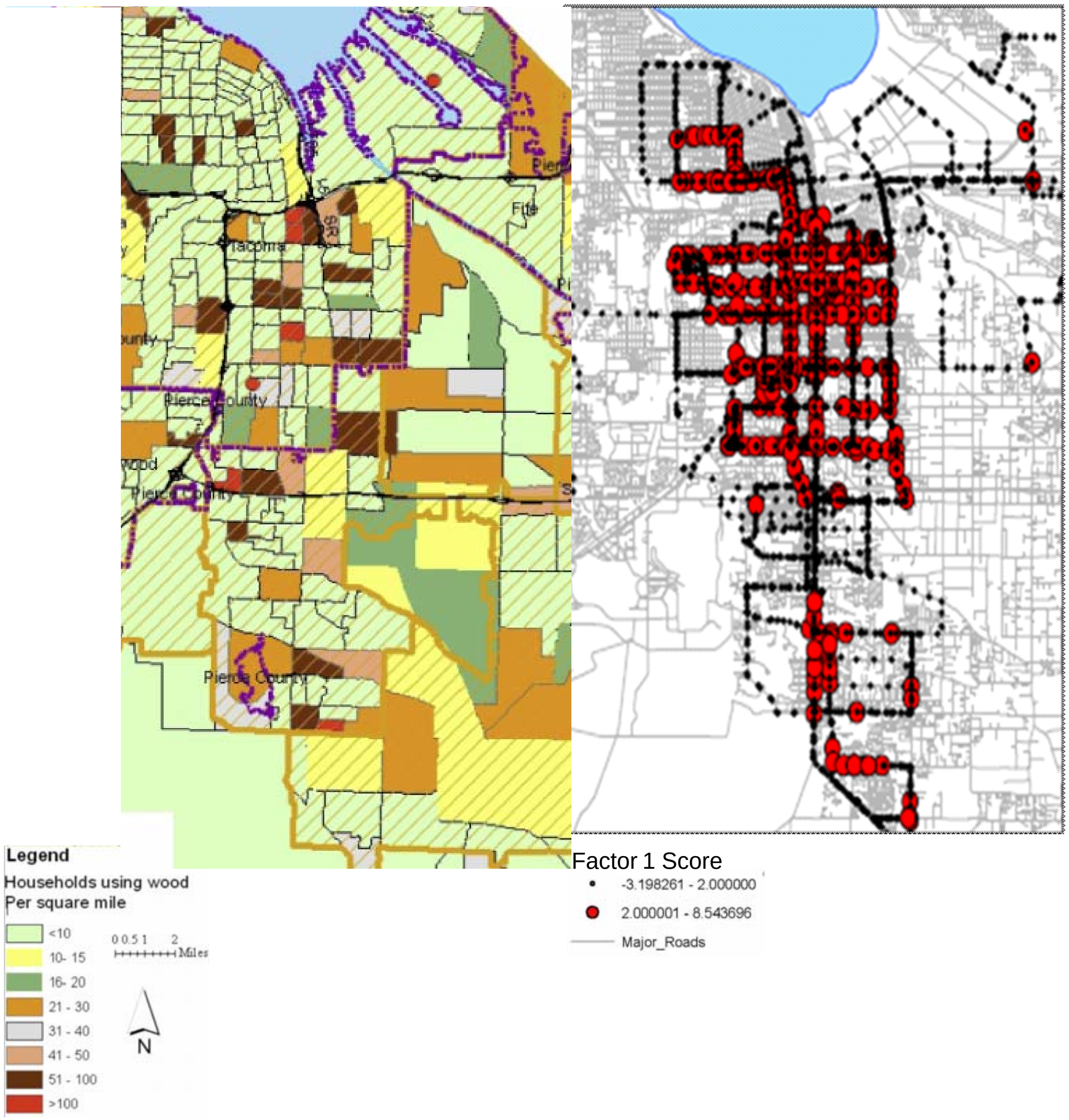


**Figure 3.3.4: Spatial Distribution of Woodstove Use Survey Data versus winter, nighttime contributions from a multivariate factor derived from principal component analysis**

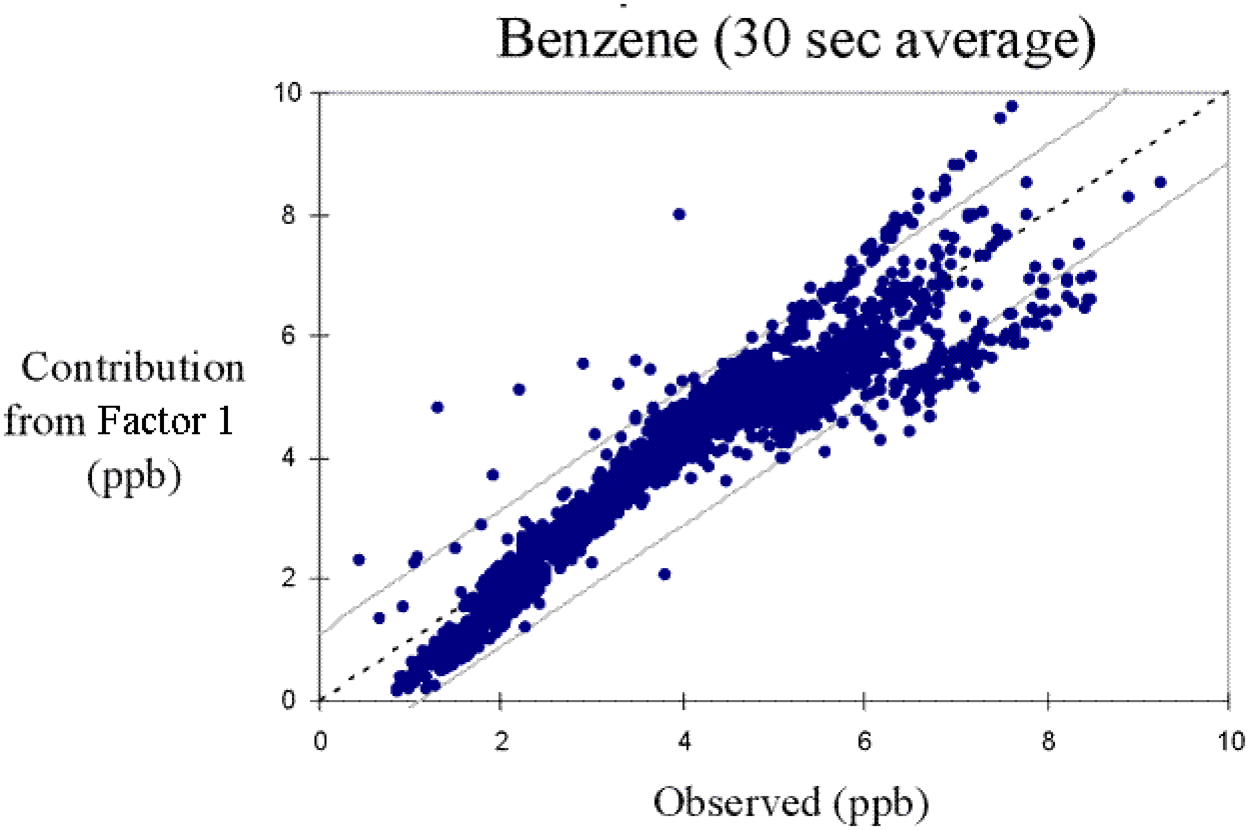


**Figure 3.3.5: 30-Second Average Benzene Concentrations (measured from the MIMS platform versus the predicted contribution from the principal component factor associated with high light scattering values at night in winter in residential areas)**

## 4. Health Risk Screening and Priority Air Toxics

In this section, the Agency describes how health risks were evaluated, and presents a ranking of air toxics based on monitored concentrations and available health information.

First, the Agency reviewed pollutants to determine whether we found data that was complete and valid, and consistently above the method's minimum level of detection (MDL). Then, we compared valid datasets to the Washington State Department of Ecology's (Ecology's) Acceptable Source Impact Levels (ASIL), using them as screening values.[34] If a pollutant's mean was greater than the ASIL, then it was of potential health concern and highlighted in this report. We grouped air toxics monitoring parameters into four screening categories through this process:

- Air toxics with detection limits above the ASIL, with concentrations below the MDL. These air toxics levels and risks are indeterminate. These two air toxics are shown in Table C-1 in Appendix C.
- Air toxics without ASILs for comparison. Table C-2 in Appendix C shows air toxics that do not have a corresponding ASIL. Several air toxics also had invalid datasets, below detection limits or with few detects. While some air toxics have valid datasets, potential health risks are indeterminate because there's no screening level for comparison.
- Air toxics with valid datasets with concentrations below ASILs. Table C-3 in Appendix C shows air toxics that were not detected and the MDL is below the ASIL, and air toxics that were detected and found to be consistently below the WA 460 ASIL. Although the table lists mean concentrations, it is noteworthy that in many instances maximum concentrations were below the ASIL. Because these air toxics have known levels below health screening values, they do not likely present health risk, and were not further explored in this study.
- Air toxics with valid datasets above ASILs. These air toxics are listed in Table C-4 of the Appendix. With concentrations greater than health screening levels, these air toxics present potential health risk and are the focus of this chapter and study. In the following sections, the Agency evaluates and ranks these air toxics based on chronic cancer and non-cancer health effects.

The Agency did not evaluate pollutants for short-term/acute health effects, because data collected (24 hour samples) do not allow for this type of evaluation.

## 4.1. Carcinogenic Health Screening: Unit Risk Factors

Carcinogenic health effects are presented as a probability or risk of developing cancer over a lifetime. Typically, this is interpreted as potential cancer cases over the population of potentially exposed individuals. For example, a one in a million potential cancer risk can be viewed as one additional cancer case for every million people equally exposed to that concentration. This is in addition to those cancer cases that would normally occur in an unexposed population of one million people over a lifetime.

Potential cancer risk is estimated by multiplying a pollutant's concentration by its unit risk factor:

$$\textit{Potential Cancer Risk (risk)} = \textit{Pollutant Concentration} (\mu g/m^3) * \textit{Unit Risk Factor} (risk / (\mu g/m^3))$$

A unit risk factor (URF) represents the potency of each pollutant, and is defined as "a measure of the potential cancer risk of exposure to 1 microgram chemical per cubic meter of air over a 70-year period."[4] URFs are typically derived from animal laboratory studies, and human data from epidemiological or clinical studies can also provide dose-response information. URFs are designed to be protective of health; therefore, risks derived from URFs are upper bound estimates. Actual risks may be lower and possibly as low as zero. Upper bound estimates are used to ensure that risks are not underestimated.

Table 4.1.1 shows the URFs that were used for pollutants in this study whose annual average concentrations exceeded a screening threshold of 1 in a million potential cancer risk. The threshold of 1 in a million potential cancer risk is used as the starting point for defining a risk level of concern by most environmental agencies, including the Agency, Washington State Department of Ecology, and EPA. Those pollutants whose ambient concentrations present risk below 1 in a million potential cancer risk are shown in Table C.3 in Appendix C.

The URFs shown in Table 4.1.1 are consistent with those used by the Washington State Department of Ecology in their rulemaking for acceptable source impact levels (ASILs) for air toxics.[34] The source for the URF is also listed in the table. Most of the URFs were obtained from the US EPA IRIS (Integrated Risk Information System) database and from California EPA's Office of Environmental Health and Hazard Assessment (OEHHA).[35,36] Both are credible, extensively peer-reviewed sources. Cancer confidence ratings are also included. US EPA IRIS assigns the weight of evidence rating, with Group A being associated with the greatest certainty of evidence for causing cancer in humans and Group E having evidence that the chemical does not cause cancer in humans.[37] Where IRIS gave no assignment, IARC's (International Agency for Research on Cancer's) rating was used. Weight of evidence ratings are shown in Table C-6 in Appendix C. While diesel particulate matter and wood smoke particles were not measured explicitly in this study, we use their estimates from other studies because these are key air toxics. Thus, their unit risk factors are included in Table 4.1 and are discussed below.

**Table 4.1.1: Unit Risk Factors and Cancer Ratings for Air Toxics with average potential cancer risk greater than 1 in a million**

| Air Toxic | URF (risk/$\mu$g/m$^3$) | Weight of Evidence* | Source |
|---|---|---|---|
| Benzene | 2.9E-05 | A | CA EPA/OEHHA |
| 1,3-Butadiene | 1.7E-04 | A | CA EPA/OEHHA |
| Carbon tetrachloride | 4.2E-05 | B2 | CA EPA/OEHHA |
| Chloroform | 2.3E-05 | B2 | US EPA/IRIS |
| Diesel particulate matter | 3.0E-04 | B2 | CA EPA/OEHHA |
| Tetrachloroethylene | 5.9E-06 | IARC 2A ~ B1 | CA EPA/OEHHA |
| Acetaldehyde | 2.7E-06 | B2 | CA EPA/OEHHA |
| Formaldehyde | 6.0E-06 | B1 | CA EPA/OEHHA |
| Naphthalene | 3.4E-05 | C | CA EPA/OEHHA |
| Hexavalent chromium** | 1.5E-01 | A | CA EPA/OEHHA |
| Arsenic** | 3.3E-03 | A | CA EPA/OEHHA |
| Nickel** | 4.8E-04 | A*** | US EPA/IRIS |
| Wood smoke particles* | 1.0E-05 | IARC 2A ~ B1 | Lewtas, 1988 |

* Weight of Evidence ratings are described by category in Appendix C, Table C-6.
** $PM_{10}$ metals and hexavalent chromium total suspended particulate (TSP) only at Beacon Hill site
*** As nickel subsulfide from refinery dust.

### 4.1.1. Wood Smoke Unit Risk Factor

Wood smoke is comprised of a variety of constituents, including but not limited to: particulate matter, nitrogen oxides, carbon monoxide, sulfur oxides, volatile organic compounds, and polycyclic aromatic hydrocarbons (PAHs).[38] Many of the chemicals listed as constituents in wood smoke have been identified as probable or likely human carcinogens.

The unit risk factor for wood smoke was developed through a comparative potency method where the mutagenicity and tumor initiating potency from particles emitted from several sources (e.g., diesels, wood smoke and gasoline-powered automobiles) are systematically evaluated.[39] Lewtas uses bioassay-directed fractionation, a combination of several chemical separation and bioassay techniques, to identify the more toxic elements of several complex mixtures. In the Lewtas study, mutagenicity tests are conducted on different segments of the total mixtures. Segments showing higher mutagenic potencies are further divided into groups and tested until the components or segments with the highest potencies are identified.[39]

We recognize the Lewtas wood smoke URF has not undergone the same rigorous evaluation as the other URFs used in our analysis. Nonetheless, it is developed through a method recommended by the National Academy of Sciences and is published in a respected peer-reviewed journal.[40]

Further, the International Agency for Research in Cancer (IARC) evaluated wood smoke, and determined it to be a Group 2A carcinogen – probably carcinogenic to humans. In reaching this evaluation, IARC considered mechanistic and other relevant data. These data included the presence of polycyclic aromatic hydrocarbons and other carcinogenic compounds in wood smoke; evidence of mutagenicity of wood smoke; and multiple studies that show cytogenetic damage in humans who are exposed to wood smoke.[41]

### 4.1.2. Diesel Particulate Matter Unit Risk Factor

DPM is a component of diesel exhaust. DPM contains elemental carbon, organic carbon, and small amounts of nitrate, metals, and unidentified compounds. We focus on the particulate component of diesel exhaust because it is thought to contain the majority of the toxicity associated with the mixture. Some experiments have shown the tumorigenicity of diesel exhaust is from the particulate components, not the vapor components. The vast majority of animal and human exposure studies use DPM as a measure of diesel engine exhaust. These particles and their adsorbed toxics penetrate deep into the lung during inhalation.

While specific knowledge of the role of the adsorbed chemicals is not known, it is hypothesized that the presence of such substances may influence particle toxicity. However, relatively little is known about the cumulative toxicity of the multiple toxics present in certain combustion mixtures. For example, it is possible that antagonism or synergism occurs among the chemicals and/or particles. In addition, there may be a variety of carcinogenic or toxic chemicals present in the mixture that have not yet been identified.[42] Therefore, we use unit risk factors for the whole mixture to estimate potential risk for diesel particulate and wood smoke, rather than unit risk factors for individual carcinogens and summing the individual risks.

The carcinogenicity of diesel particulate matter is widely recognized by a number of health agencies including the US EPA,[8] California EPA,[43] the US Department of Health and Human Services,[44] and the International Agency for Research on Cancer (IARC).[45] The Washington State Department of Ecology conducted an extensive review of the literature on diesel exposures and health, and endorses the California EPA URF.[46]

The Clean Air Agency uses an appropriate approach based on the California OEHHA DPM unit risk factor, which has been widely cited and is the basis for the diesel retrofit program in place for several years in California. This approach evaluates 100% of the highly toxic diesel particulates as a complete and complex mixture. Risk assessment using the single DPM URF is likely to account for potential interactions (i.e., synergism and antagonism) among the hundreds and/or thousands of chemicals in DPM. To the extent that diesel exhaust contains priority air toxics like benzene, formaldehyde, and acetaldehyde, there is the possibility for ‘double counting’ some of the potential risk for these air toxics. However, the benefits of the complex mixture approach outlined above far outweigh any downside of potential double-counting. Also, these three air toxics have other known sources, so the potential for ‘double counting’ for them is small.

## 4.2. Carcinogenic Risk Ranking

### 4.2.1. Cancer Risk Ranking for Air Toxics Measured at Multiple Sites

Potential cancer risk per million is presented for those air toxics with measured average concentrations in this study greater than the health screening value (set at 1 in a million potential cancer risk) in table 4.2.1 below. It is important to note that these risks are based on ambient concentrations, not exposure concentrations. The concentrations that people are actually exposed to depend on a variety of factors, including penetration into indoor environments; peoples' commuting and daily activity patterns; and the length of time and proximity to given monitors/sources. These factors would be required for a comprehensive risk assessment. Rather, the potential cancer risks are presented as a mechanism to rank priority air toxics in a relative sense.

The air toxics highlighted in Table 4.2.1 are consistent with the priority air toxics highlighted in the 2003 Seattle area air toxics evaluation, as well as other monitoring and modeling air toxics reports. The top priority air toxics include **benzene**, **carbon tetrachloride**, **1,3-butadiene** and **formaldehyde**.

Caution should be used when comparing risk values from the 2003 Seattle air toxics study to this current study, as we have applied different unit risk factors in some instances. Where these differences exist, it is typically because Washington State Department of Ecology and the Agency have chosen to apply a more protective unit risk factor (e.g., using a California EPA OEHHA URF instead of an EPA IRIS URF). Because of this difference the more appropriate comparison is concentration level (Chapter 3).

**Table 4.2.1: Average Potential Cancer Risk Per Million at Seattle and Tacoma Sites, and average National Air Toxics Trend Sites**

| | Average Potential Cancer Risk per Million | | | | | | |
|---|---|---|---|---|---|---|---|
| **Pollutant** | **Seattle Duwamish** | **Seattle Beacon Hill** | **Tacoma South L** | **Tacoma Portland Ave Res** | **Tacoma Tideflats** | **5-site Mean** | **All NATTS** |
| Benzene | 27 | 24 | 38 | 34 | 29 | 30 | 31 |
| Carbon Tetrachloride | 32 | 33 | 32 | 31 | 32 | 32 | 22 |
| 1,3-Butadiene | 17 | 13 | 22 | 18 | 15 | 17 | 35 |
| Formaldehyde | 17 | 6 | 9 | n/a | 12 | 11 | 18 |
| Acetaldehyde | 4 | 2 | 3 | n/a | 4 | 3 | 5 |
| Naphthalene | 4 | 2 | 4 | n/a | 4 | 4 | 2 |
| Chloroform | 3 | 3 | 3 | n/a | 3 | 3 | 6 |
| Tetrachloroethene | 1 | 1 | 1 | 1 | 2 | 1 | n/a |
| Total Risk* | 104 | 85 | 111 | n/a** | 100 | 101 | 119 |

*Based on rounding convention, not all numbers add to total risk

**Total risk for the Tacoma Portland Avenue site should not be compared.

Figure 4.2.1 below shows relative contributing risks for pollutants that were measured at all four sites. Again, these risks are based on annual average concentrations. Details on data treatment are found in Chapter 3.

The concentrations and corresponding risks at the two port/industrial sites (Seattle Duwamish and Tacoma Tideflats) are, not surprisingly, similar.

Potential cancer risk at the Tacoma South L Site, a residential site that is heavily impacted by wood smoke, exceeds the two port industrial sites and also the Seattle Beacon Hill *for the pollutants that were measured at all sites.* It is important to note that risks included in Figure 4.2.1 do not include risks for diesel particulate matter and wood smoke particles. The Agency addresses this further in Section 4.2.3.

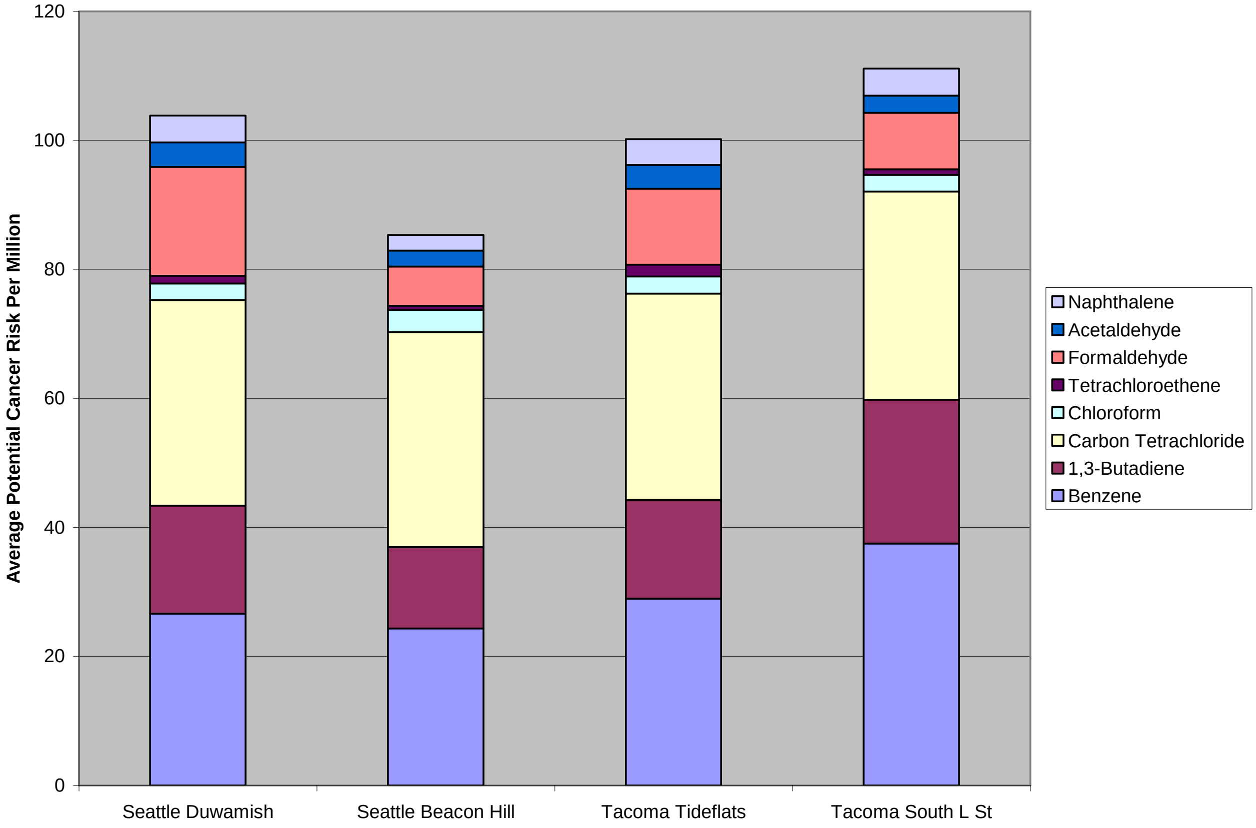


**Figure 4.2.1: Average Potential Cancer Risks for Pollutants Measured at all 4 Sites**

### 4.2.2. $PM_{10}$ Metals and Hexavalent Chromium at Beacon Hill

Health risks for $PM_{10}$ metals (metals measured in particles with diameters of 10 micrometers or less) monitored at the Seattle Beacon Hill site are discussed in this section. While $PM_{2.5}$ metals were also measured at Tacoma South L, Tacoma Tideflats, and Seattle Duwamish, the methods and size fraction are different, making comparison inappropriate.

When compared with health screening levels, only three metals exceeded concentrations that could result in additional potential cancer risk greater than 1 in one million: arsenic, nickel, and hexavalent chromium. When the URFs from Table 4.1 were applied to estimate an average potential cancer risk for each, it amounted to 1 in a million for nickel, and 2 in a million for arsenic, and 5 in a million for hexavalent chromium. Hexavalent chromium is monitored at Beacon Hill as total suspended particulate (TSP).

### 4.2.3. Comprehensive Cancer Risk — with Diesel Particulate and Wood Smoke

It is important to note that there is no direct method to monitor diesel particulate and wood smoke particulate matter.

While we do not have estimates of diesel and wood smoke particulate at all of the sites in this study, we do have estimates of diesel and wood smoke at the Tacoma South L site, the Seattle Beacon Hill site, and the Seattle Duwamish site.

The Tacoma South L St site estimate is based on positive matrix factorization (PMF) receptor modeling conducted by the Department of Ecology on $PM_{2.5}$ speciation samples collected from January 11, 2006 to May 7, 2009. PMF modeling uses speciated data and a mathematical algorithm to estimate the independent sources that contribute to concentrations at the monitor. Details of the methods used can be found in "*Sources of Fine Particles in the Wapato Hills-Puyallup River Valley $PM_{2.5}$ Nonattainment Area*." The average concentrations estimated in the report for DPM and wood smoke are 0.4 $\mu g/m^3$ and 4 $\mu g/m^3$, respectively.[1] Combined with the URFs listed in Table 4.1, this yields potential cancer risk estimates of 120 and 40 potential cancer risk per million for DPM and wood smoke.[2]

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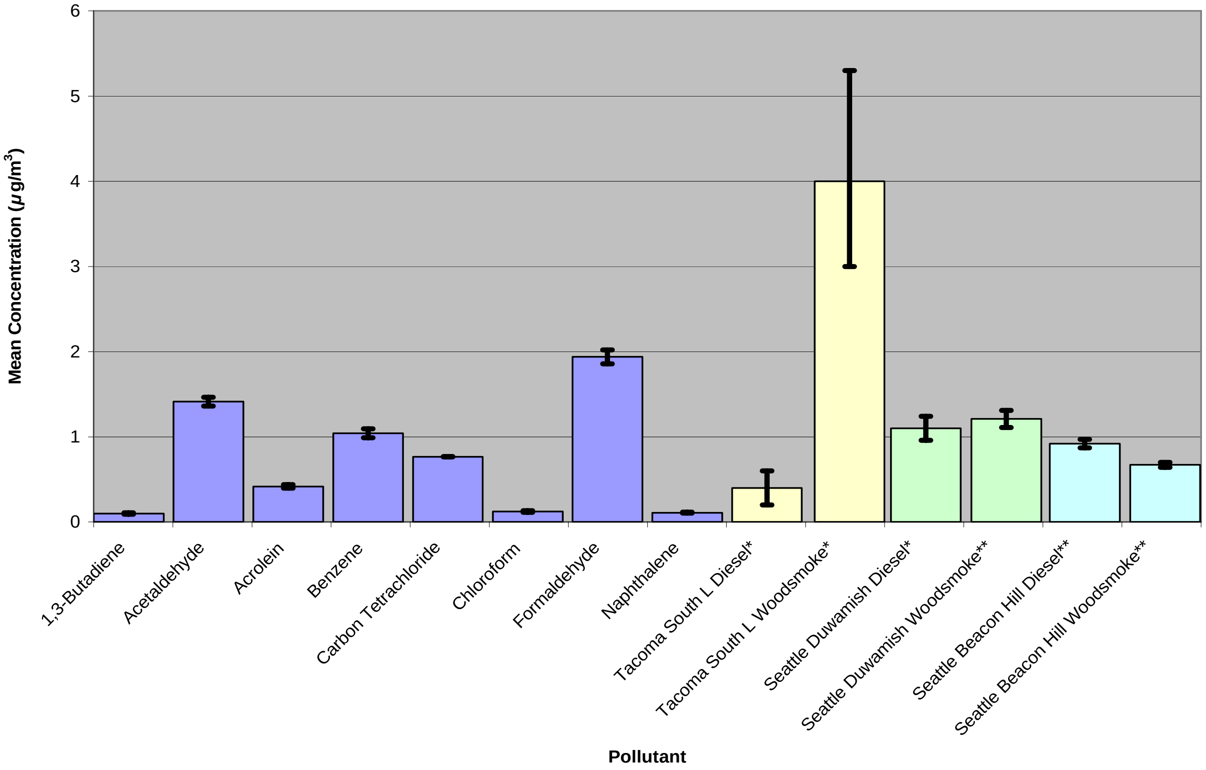
[1] The concentration for diesel particulate matter includes 0.3 $\mu g/m^3$ identified as diesel by the model, and 0.1 $\mu g/m^3$ identified as marine sources/oil.

[2] The concentration for DPM at Duwamish includes 0.65 $\mu g/m^3$ identified as diesel and 0.44 $\mu g/m^3$ identified as oil combustion. The concentration for DPM at Beacon Hill includes 0.45 $\mu g/m^3$ identified as diesel and 0.47 identified as oil combustion.

The Seattle Duwamish and Seattle Beacon Hill estimates are based on PMF2 receptor modeling conducted by Kim and Hopke on $PM_{2.5}$ speciation samples collected from 2000 to 2005. Details of the methods used can be found in "*Source characterization of ambient fine particles at multiple sites in the Seattle area*".[47] The average DPM concentrations estimated in the report at Seattle Duwamish and Seattle Beacon Hill are 1.1 $\mu g/m^3$ and 0.9 $\mu g/m^3$, respectively. Combined with the URF listed in Table 4.1.1, this yields DPM potential cancer risk estimates of 330 and 270 per million at the sites. The average wood smoke concentrations estimated in the report at Seattle Duwamish and Seattle Beacon Hill are 1.2 $\mu g/m^3$ and 0.7 $\mu g/m^3$, respectively. Combined with the URF listed in Table 4.1.1, this yields wood smoke potential cancer risk estimates of 12 and 7 per million at the sites.

PMF receptor modeling is endorsed and provided by US EPA, and Washington State Dept of Ecology followed modeling procedures recommended by EPA for its estimates. Despite the fact that this modeling is considered the 'gold standard' to estimate fine particle contributing sources, results have a substantial amount of uncertainty. Average concentrations for each site are given in Figure 4.2.2 with their respective uncertainties. The modeled diesel and wood smoke results are also given. Kim and Hopke's model for Seattle used PMF2, which underestimates the uncertainty that newer EPA algorithms provide. The analysis conducted on South Tacoma data uses newer statistical techniques that estimate the uncertainties more accurately.



*The Tacoma South L wood smoke and diesel uncertainty is based on the 95th percent Confidence Interval.
**The Seattle Duwamish and Beacon Hill uncertainties are based on PMF2 results.

**Figure 4.2.2: Study Means and Standard Errors for all Sites**

Figures 4.2.3, 4.2.4, and 4.2.5 use potential cancer risks from this air toxics monitoring study, as well as potential cancer risks estimated for DPM and wood smoke particles from receptor modeling studies.

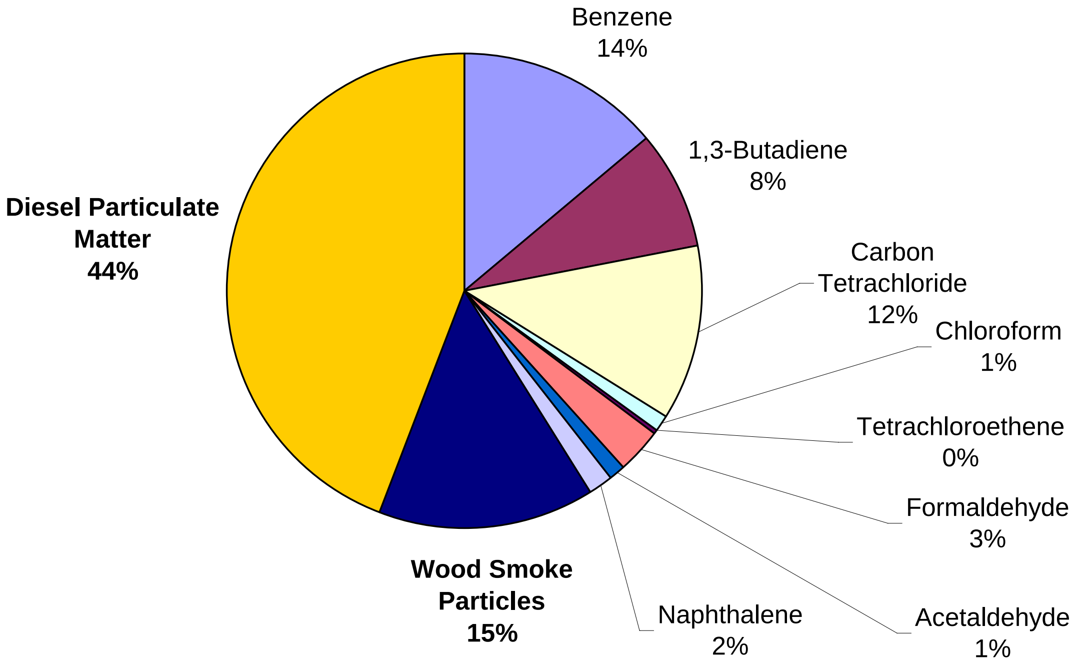


**Figure 4.2.3: Contributors to Average Potential Cancer Risk at South L Monitor, including estimates for DPM and wood smoke**

**Total potential cancer risk approximately 270 per million**

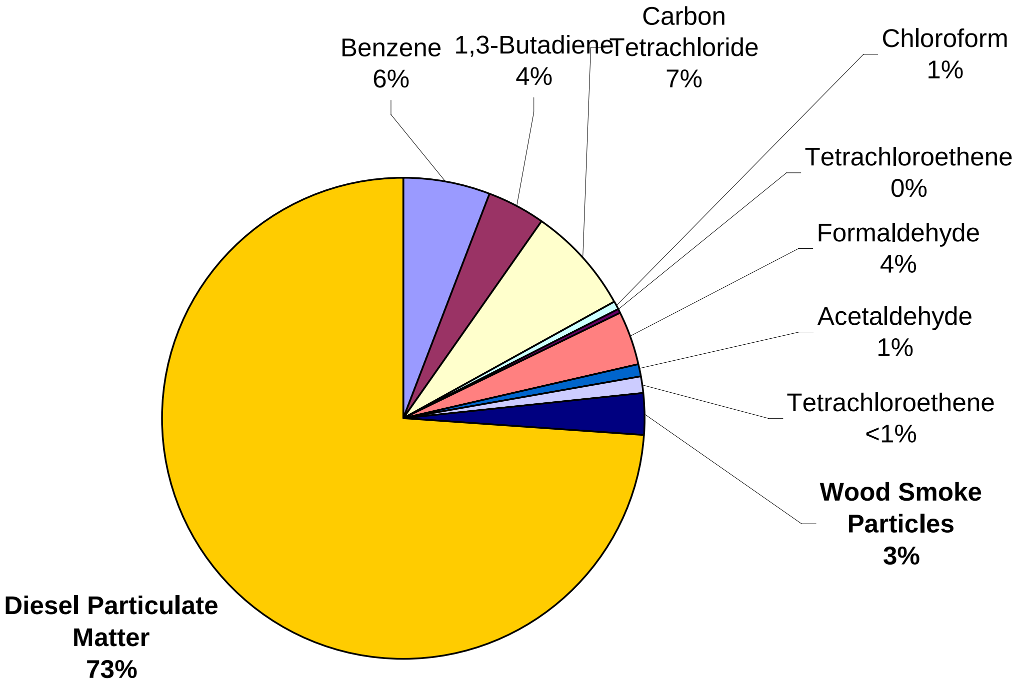


**Figure 4.2.4: Contributors to Average Potential Cancer Risk at Seattle Duwamish Monitor, including estimates for DPM and wood smoke**

**Total potential cancer risk approximately 450 per million**

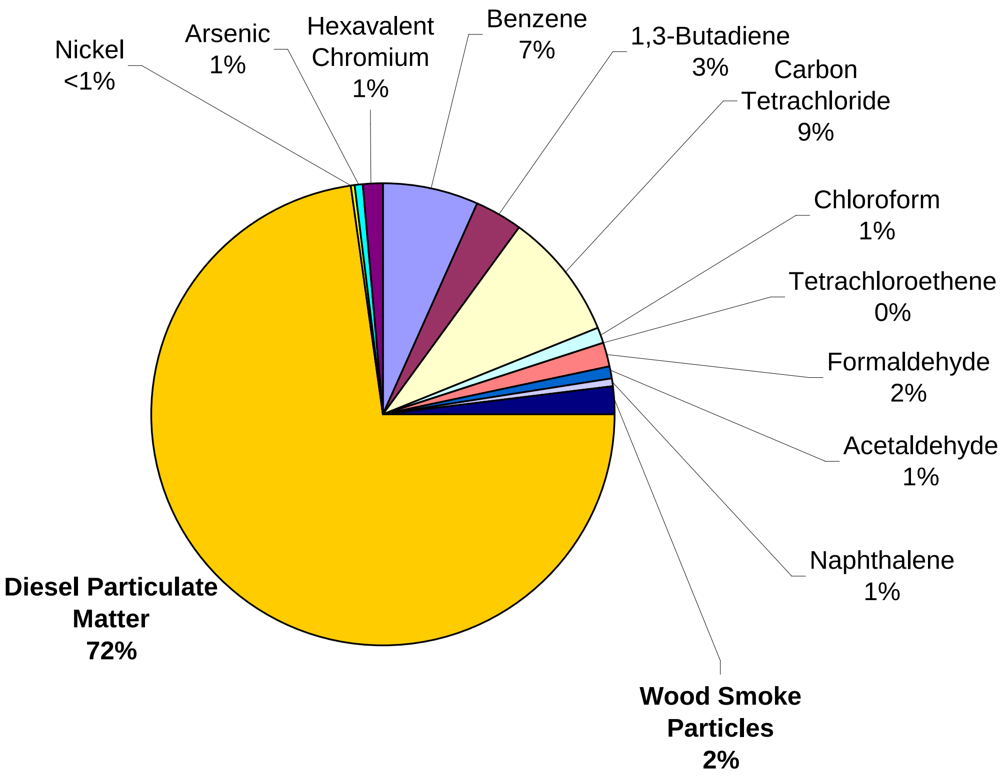


**Figure 4.2.5: Contributors to Average Potential Cancer Risk at Seattle Beacon Hill Monitor, including estimates for DPM and wood smoke**

**Total potential cancer risk approximately 360 per million**

Again, it should be reiterated that the estimates for diesel particulate matter and wood smoke particles have greater uncertainty because their concentration estimates are based on modeling, rather than direct monitoring.

The air toxics contributors for potential cancer risk at Seattle Duwamish and Beacon Hill sites are consistent with previous studies, which place the contribution of DPM at greater than 70%. The Tacoma South L site, located in a residential area that is highly impacted by wood smoke, shows a different picture: DPM presents less than half of the overall potential air toxics cancer, while wood smoke and benzene combined contribute almost 30%.

Although Seattle Beacon Hill and Duwamish have similar contributors to the overall cancer risk, it is worth noting that the magnitudes vary. When potential risks associated with wood smoke and diesel are added to risks shown in Table 4.2.1, it yields overall potential cancer risks from air toxics of 450 per million at Seattle Duwamish, 360 per million at Seattle Beacon Hill, and 270 at Tacoma South L. As noted above in section 4.2.3, the diesel and wood smoke concentrations at Seattle and Tacoma sites were estimated in different studies and come with large uncertainty. Kim and Hopke's model for Seattle used PMF2,[47] which underestimates the uncertainty that newer EPA algorithms provide. South Tacoma uses newer statistical techniques that estimate the uncertainties more accurately.

## 4.3. Non-carcinogenic Screening – Reference Concentrations

Non-carcinogenic effects are evaluated as exceeding (or not exceeding) a particular health guideline, referred to as a reference concentration. This non-carcinogen evaluation does not calculate a probability but instead determines whether a particular exposure is below the threshold at which there could be an adverse effect.

Reference concentrations (RfCs), like unit risk factors, are based on animal or human studies. RfCs are derived from toxicity studies that report the lowest concentration of inhalation exposure at which adverse (but non-cancer) health effects occur, and or the highest concentration at which no such adverse effects are observed. This concentration is then divided by factors to account for uncertainties and variability such as extrapolating from animals to humans, from healthy adult individuals to sensitive individuals, or from sub-chronic to chronic exposures.

A hazard quotient is a ratio of the estimated exposure concentration, divided by a reference concentration (RfC) deemed to have no adverse effect from a lifetime exposure to that level.

$$\textit{Hazard Quotient (HQ)} = \textit{Pollutant Concentration } (\mu g/m^3) / \textit{ Reference Concentration } (\mu g/m^3)$$

A hazard quotient of less than 1 is typically considered to not present health risk, per pollutant. The Agency factored in an additional safety factor, and considered hazard indices less than 0.1 to not present health risk. This is to account for the fact that people are exposed to multiple air toxics simultaneously and to be protective.

Acrolein was the only air toxic with a hazard index greater than 1, and formaldehyde and acetaldehyde had a hazard index greater than 0.1 and less than 1.0. Their reference concentrations as established by EPA IRIS or OEHHA and adopted by the Washington State Department of Ecology are shown in Table 4.3.1 below.

**Table 4.3.1: Reference Concentrations for Air Toxics with Average Hazard Indices >0.1**

| Chemical | RfC ($mg/m^3$) | Target Organ for Critical Effect | Source |
|---|---|---|---|
| Acetaldehyde | 9.E-03 | Nasal epithelium | IRIS |
| Acrolein | 2.E-05 | Nasal epithelium | IRIS |
| Formaldehyde | 9.0E-03 | Respiratory System, Eyes | OEHHA |

### 4.4. Non-Carcinogenic Health Risk Ranking

Acrolein was the only priority air toxic with a hazard quotient greater than 1 at all sites. Formaldehyde and acetaldehyde had a hazard quotient greater than 0.1. All other air toxics hazard quotients were well below 0.1, as shown in Table 4.4.1.

**Table 4.4.1: Average Health Quotients for all Pollutants over the ASIL Screening Level**

| Chemical | Seattle Duwamish | Tacoma Tideflats | Tacoma South L | Tacoma Portland Ave Reservoir | All NATTS | Seattle Beacon Hill |
|---|---|---|---|---|---|---|
| Acrolein | 1.1 | 1.1 | 1.0 | - | 1.4 | 1.6 |
| Formaldehyde | 0.3 | 0.2 | 0.2 | - | 0.3 | 0.1 |
| Acetaldehyde | 0.2 | 0.2 | 0.1 | - | 0.2 | 0.1 |
| 1,3-Butadiene | 0.05 | 0.05 | 0.07 | 0.05 | 0.10 | 0.04 |
| Benzene | 0.03 | 0.03 | 0.04 | 0.04 | 0.04 | 0.03 |
| Naphthalene | 0.04 | 0.04 | 0.04 | - | 0.02 | 0.02 |
| Carbon tetrachloride | 0.008 | 0.008 | 0.008 | 0.007 | 0.005 | 0.008 |
| Chloroform | 0.0004 | 0.0004 | 0.0004 | - | 0.0008 | 0.0005 |
| Tetrachloroethylene | 0.0003 | 0.0005 | 0.0002 | 0.0002 | - | 0.0002 |

## 5. Comparison to Modeled Concentrations

In this chapter, the Agency compares average ambient concentrations of priority air toxics monitored in this study to average ambient concentrations estimated by US EPA in their national air toxics assessment (NATA).[9]

EPA estimates health risks from air toxics on a national level using NATA. NATA ambient air concentration estimates are based on emissions from the national emissions inventory (NEI). EPA uses the emissions estimates as inputs to the Assessment System for Population Exposure Nationwide (ASPEN) dispersion model to estimate ambient concentrations. EPA also estimates exposure concentrations in NATA using the Hazardous Air Pollutant Exposure Model (HAPEM). To date, EPA has released results on three NATA assessments based on 1996, 1999, and 2002 emissions inventories. At the time of publication, the 2002 NATA is the latest available information available from EPA. As 2005 information is available in limited form, but not finalized, we compare monitored and modeled concentrations based on the 2002 NATA. Because the data from NATA was modeled on emission estimates from 7 years prior to the study data, our comparison here is quite limited to assess potential divergence between the model and monitoring data. As shown in Chapter 3, many priority air toxics have decreased in concentration since 2001 (based on Beacon Hill monitoring). Therefore, a comparison of the 2002 NATA to 2009 monitored results is limited.

To assess the 2002 NATA, model-to-monitor ratios were calculated as shown in Table 5.1.1 below. It is worth noting there are significant uncertainties in the model that must be considered in the analysis. Additionally, a one-year monitoring event is not necessarily an accurate or complete representation due to meteorological differences. Another variation from monitor to model may be a result of model resolution. As the model's smallest unit is census tract level, there may be sources within the tract that the monitor does not represent due to topographic, meteorological, or other pollutant barriers. Pollutant lifetimes may not be long enough to monitor effectively, and result in a higher model bias.

Often, EPA suggests a model/monitor ratio between 0.5 and 2 as adequate model performance.[48] However, with the differences in time frames and other unique uncertainties, ratios over or under this suggested threshold may not be significant.

**Table 5.1.1: Model-to-Monitor Ratios Using the 2002 NATA and the Study Monitor Results***

| **Pollutant** | **Seattle Duwamish** | **Tacoma Tide Flats** | **Tacoma South L St** | **Tacoma Portland Ave Reservoir** | **Seattle Beacon Hill** |
|---|---|---|---|---|---|
| **1,3-Butadiene** | 8.5 | 3.0 | 1.1 | 1.7 | 3.3 |
| **Acetaldehyde** | 3.8 | 2.4 | 2.5 | N/A | 4.1 |
| **Acrolein** | 1.0 | 0.5 | 0.4 | N/A | 0.5 |
| **Benzene** | 13.0 | 4.6 | 2.0 | 2.8 | 5.7 |
| **Carbon Tetrachloride** | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| **Chloroform** | 1.3 | 1.1 | 0.8 | N/A | 1.1 |
| **Diesel Engine Emissions*** | 6.3 | N/A | 3.1 | N/A | 2.3 |
| **Formaldehyde** | 2.0 | 2.0 | 1.6 | N/A | 2.7 |
| **Naphthalene** | 2.3 | 0.9 | 0.4 | N/A | 1.7 |
| **Tetrachloroethylene** | 1.1 | 0.5 | 0.8 | 0.7 | 1.5 |

*The study results for diesel emissions for South Tacoma are derived from the 2009 WA State Dept of Ecology Source Apportionment analysis7 and the diesel emissions for Seattle Duwamish and Beacon Hill are derived from Kim, Hopke, 2008.[47]

Overall, the model performance was acceptable for carbon tetrachloride, chloroform, tetrachloroethylene, and acrolein. The remaining compounds were generally overestimated, including diesel emissions, benzene, 1,3-butadiene, acetaldehyde, and formaldehyde. Lastly, naphthalene was over estimated at the Seattle sites, but underestimated at the Tacoma sites. Some portion of the general overestimates is likely due to declines in air toxics in the area since 2002.

The highest difference from NATA to our study results was found at the Seattle Duwamish site. NATA generally over-predicted most analytes at this site. Benzene, 1,3-butadiene, diesel emissions, and acetaldehyde were vastly over predicted and are all significant mobile source pollutants. The monitor at the site is within 50 meters of Highway 99 with around 60,000 vehicles per day. However, the model still appears to be high and may be overestimating some of the risk in this area. Again, it is important to note that declines in air toxics emissions since 2002 likely account for some of this difference.

NATA estimates of benzene concentrations at other sites are 2-5.7 times higher than in our study. Likely this is due to early actions that our Northwest refiners have made to reduce benzene content, in part in anticipation of EPA's Mobile Source Air Toxics Rule (MSATII), which substantially reduces benzene content in gasoline in the northwest.[49] As such, concentrations in the Northwest, including Oregon[50] and Washington[51], have dropped considerably. To compare to 2002, measured benzene concentration at the Seattle Beacon Hill site was 1.2 $\mu g/m^3$, while the 2009 study levels were measured to be 0.8 $\mu g/m^3$.[51] Clearly, this difference in concentration over time makes comparing to a model (2002) to monitor (2009) ratio problematic.

Diesel emissions were not monitored during the study, but source apportionment studies were completed for South Tacoma[7], and Seattle Duwamish and Beacon Hill[47]. From these reports, diesel emissions were estimated and used in Table 5.1.1 above to compare to the NATA results. NATA also seemingly over predicts the diesel emissions at each of the sites. As diesel is such a significant source for cancer risk in our region, the 2002 NATA may be over estimating 2002 risks for the region. Once more, it is worthwhile for the Agency to explore how potential diesel risks compare with more recent modeling efforts (for example, the 2005 NATA).

As anticipated, carbon tetrachloride has consistent concentrations across the sites – typical of a background pollutant. However, as stated in Chapter 3, the Puget Sound region's background carbon tetrachloride levels found in our study sites are higher than the NATTS. Moreover, NATA is more similar to the national background levels, and the Puget Sound sites are showing higher levels than the model consistently. Method limitations may be ruled out as a source of the difference as Seattle Beacon Hill site was operated by another entity (Washington State Department of Ecology), and the Agency used the same national lab as the other NATTS sites. It is worth noting that carbon tetrachloride concentrations were higher in 2009 than in 2002 at Beacon Hill. The 2002 NATA also reflects this difference as it predicts lower concentrations than were observed during our study. The increased concentrations of carbon tetrachloride are still not well understood.

## 6. Findings and Limitations

### 6.1 Findings

**This study validated results from 2003, and other studies which show that the priority air toxics and priority pollution sources have been well identified.**

A main objective of this study was to determine base-line air toxics concentrations for the Tacoma area, and provide measurements at sites in the Seattle area for comparison. This study provides a follow-up to previous assessments conducted by the Agency and Ecology in October 2003[1]. The priority air toxics were found to be in order: diesel PM, wood smoke PM, benzene, carbon tetrachloride, 1,3 butadiene, formaldehyde, acetaldehyde, naphthalene, chloroform, and tetrachloroethene. The results of this study confirm that many of the same air toxics identified previously remain as important risk drivers in Tacoma. However, the relative importance of different pollutants and the fractional contribution to risks in Tacoma vary somewhat from the results in Seattle. While diesel exhaust emissions continue to dominate potential cancer risk in both Seattle and Tacoma, wood smoke makes a larger risk contribution at Tacoma sites.

The main underlying sources in both areas are the same: motor vehicle traffic and residential wood burning. Both of these important source profiles can be controlled further with policy changes aimed at reducing wood smoke, motor vehicle emissions, and diesel emissions. By reducing these emission sources, the toxics risks for all of the major risk drivers except carbon tetrachloride will be reduced.

The finding that wood smoke from residential burning is associated with a larger contribution to air toxics risk in Tacoma has larger regional and national implications. Wood smoke is a common source of air pollution during the winter heating season in many areas of Washington State and across the Western US. Based on these results, we can expect that most other communities with significant residential wood burning will experience elevated levels of air toxics from this source.

Carbon tetrachloride remains as both a national and regional risk driver. Although this chemical has been banned from most applications for many years, it previously was used widely in dry cleaning and industrial processes. However, low level emissions continue to impact Puget Sound. The chemical is extremely stable in the atmosphere, and there are no known reduction or mitigation methods available. Since 2002, it appears that carbon tetrachloride concentrations are increasing and the sources are not well understood. Concentrations may vary with altitude and meteorology, which could account for the difference between results from this study and national surveys.[52]

**Benzene is still a risk driver, and results from this study indicate that wood smoke, as well as mobile sources, is a significant contributor.**

In past assessments, benzene risk was generally perceived to come mostly from motor vehicles.
Based on benzene data collected at the fixed sites and data analyzed using the mobile MIMS platform, benzene and levoglucosan were co-variant, indicating that wood smoke is the likely source of benzene. Both fixed and mobile monitoring independently reflected the same conclusion. It is clear that more progress needs to be made to reduce wood smoke particulate matter and benzene risks in the wood smoke impacted neighborhoods.

**The study provided a more detailed picture of the pattern in seasonal and spatial variability of air toxics in the Puget Sound area. Specifically, Seattle air toxics monitoring is not fully representative of Tacoma.**

Tacoma air toxics data from the Tideflats site shows that there is some similarity between the industrial areas in Seattle and Tacoma. However, the fixed Tacoma neighborhood sites are different than both Seattle neighborhood and Tacoma Industrial areas. These findings are supported by several independent data analysis tools and findings from this study.

Benzene emissions appear to make a larger contribution to air toxics risk in Tacoma compared to Seattle. The highest benzene levels were found at the Tacoma South L and Tacoma Portland Avenue monitors during the heating season. Benzene is present in wood smoke[15] and the elevated levels in this area likely reflect the impacts of wood burning in nearby residential neighborhoods. Principal components analysis (PCA) of mobile particulate data confirmed that a wood smoke source factor produces the highest levels of air toxic pollution during heating season. Additionally, the spatial distribution pattern of benzene in Tacoma as measured by the mobile gaseous platform (MIMS) is strongly correlated with the spatial distribution of wood smoke during the evening in the heating season

Levoglucosan is a stable chemical marker for wood burning that was used to estimate daily average wood smoke contributions to ambient particulate matter (PM). This wood smoke marker shows a clear seasonal difference in the study areas, and the Tacoma sites appear to have elevated concentrations compared to the Seattle site during the heating season. During the non-heating season, levels in Tacoma are much lower, but remain higher than Seattle. The highest levoglucosan levels were found at the Tacoma South L and Tacoma Portland Avenue monitors during the heating season. Furthermore, levoglucosan and benzene as monitored by canister samples and the mobile MIMS platform confirmed these results. This study indicates that levoglucosan measurements can be applied more routinely to provide a reliable and specific indicator of wood smoke impacts in areas where wood burning is suspected to have adverse impacts.

Levoglucosan was correlated with most priority air toxics (1,3-butadiene, benzene, black carbon, elemental carbon, organic carbon, chloroform, naphthalene, $PM_{2.5}$) strongly suggesting wood smoke as a major source of air toxics. Independently, $PM_{2.5}$ speciation data collected previously in the Tacoma area was analyzed using Positive Matrix Factorization[33] and it was reported that annual wood smoke accounted for 42% of all of the $PM_{2.5}$ collected in the Tacoma neighborhood. The remaining emissions are mainly dominated by mobile sources. The results of the current report with several independent monitoring methods have confirmed that wood smoke from residential burning is an important contributor to air toxics, particularly in Tacoma. Policies and programs must continue to focus on reducing winter wood smoke emissions during the heating season, which also will help to lower overall $PM_{2.5}$ levels. Additionally, across the region, motor vehicle and diesel engine emissions during all seasons continue to be a major contributor to air toxics and $PM_{2.5}$ emissions. There must be continued efforts to reduce mobile source emissions in order to reduce their associated health risks.

**The 2002 NATA Modeled results are not in agreement with the monitoring data collected during this study from Fall 2008 to Fall 2009.**

We did not expect that 2002 NATA modeling data would match the monitoring data found during the 2008-2009 campaign. This study shows a very wide range of model-to-monitor ratios across monitoring sites for a local pollutant such as 1,3-butadiene, but a very consistent modeled-to-monitor result for a regional pollutant such as carbon tetrachloride. However, NATA modeling results do diverge significantly for some air toxics from monitoring results found in this study. Comparison of the monitoring data to 2005 NATA is worth investigating once the 2005 NATA final report has been released. Although NATA is an important tool to consider when developing air pollution reduction policies, decision makers need all of the available analysis tools including both modeling and a strong complement of monitoring data to validate the models.

## 6.2 Limitations and Uncertainties

Clearly, a main limitation of this study is that we do not have more consistent estimates for diesel particulate matter (DPM) and wood smoke particles, two primary risk drivers. We rely on two reports that used different versions of the positive matrix factorization (PMF) model. Thus, it is difficult to compare the risk of DPM and wood smoke particles at the Tacoma and Seattle sites. A source apportionment study using a consistent receptor model and more data (sites) would reduce uncertainties associated with diesel and wood smoke emission estimates. Also, it would be ideal to have receptor modeling results that were consistent with respect to time periods modeled. Additionally, having the Tacoma Tideflats site, when there is enough speciation data gathered, will be helpful as well.

Another limitation of the study is that we did not monitor for a full suite of pollutants, i.e. $PM_{10}$ metals. It's possible that some risks are understated due to not including metals. However, past studies and concentrations at the Beacon Hill monitor demonstrate that $PM_{10}$ metals are not typically risk drivers.

The large number of assumptions necessary in our study reflects the amount of uncertainty and variability associated with the health risk estimates. It is possible that risk is underestimated because (1) not all air toxics are considered in this analysis, and (2) many chemicals have been shown to accumulate in indoor micro-environments, which could increase exposure. In addition, potential cancer estimates will underestimate risk for those individuals living near large point sources or directly adjacent to key transportation corridors. Alternatively, risk may be underestimated or overestimated by assuming that the concentration at the monitor accurately reflects lifetime exposure to ambient pollutants. Obviously, chemical concentrations could increase or decrease throughout the lifetime exposure period.

It is important to note that this analysis does not evaluate indoor sources of air pollution (i.e., from paints, home furnishings, cleaning products, cooking emissions, building materials, and other indoor sources). Uncertainties in the toxicity information could also serve to over- or underestimate potential risk estimates. These are only a few of the uncertainties associated with this study. A more detailed discussion can be found in Chapter 4.

Finally, acrolein appears to present a potential non-cancer risk as well. As stated earlier, the non-cancer health effects associated with the particulate-matter-related combustion mixtures (e.g., wood smoke and diesel soot) are not evaluated here, but present serious non-cancer health risks.[53] As discovered in the EPA School Air Toxics Monitoring Study in 2009,[21] acrolein measurement using EPA method TO-15 has been unreliable and limited as uncertainty has been large due to the unique chemical nature of acrolein.

In summary, we use screening risk estimates as a tool to focus Agency attention on those pollutants and mixtures that are likely to present the greatest risk of cancer and some non-cancer effects. Concentrations, and corresponding risks, were relatively consistent among areas measured and modeled throughout the Puget Sound region. Although some differences were apparent, overall it is clear that the sites and the region as a whole have similar emission sources of concern (e.g., diesel particulate matter, mobile-source-related pollutants, and wood smoke).

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# Appendix A: Fixed Monitoring Site Descriptions

The monitoring sites used in this study are described in this appendix according to language, figures, and tables similar to past EPA UATMP (Environmental Protection Agency Urban Air Toxics Monitoring Program) Annual Reports. The intent of this approach is to describe the monitoring sites in a way that is comparable to national monitoring sites that are part of the UATMP program. In 2007 there were 100 monitoring sites located in many of the major urban areas of the country that have collected data that is considered comparable to the fixed site data collected in this study because standard monitoring methods were used. Each fixed site has a description of representativeness scale, likely source impacts, meteorology, topography, land use, and demographics.

The fixed monitoring sites used in this study include Seattle Beacon Hill, Seattle Duwamish, Tacoma Tideflats (Alexander Ave), Tacoma Portland Ave, Tacoma South L St, and Tacoma Alaska Ave. These monitoring sites are shown in Figure A.1.

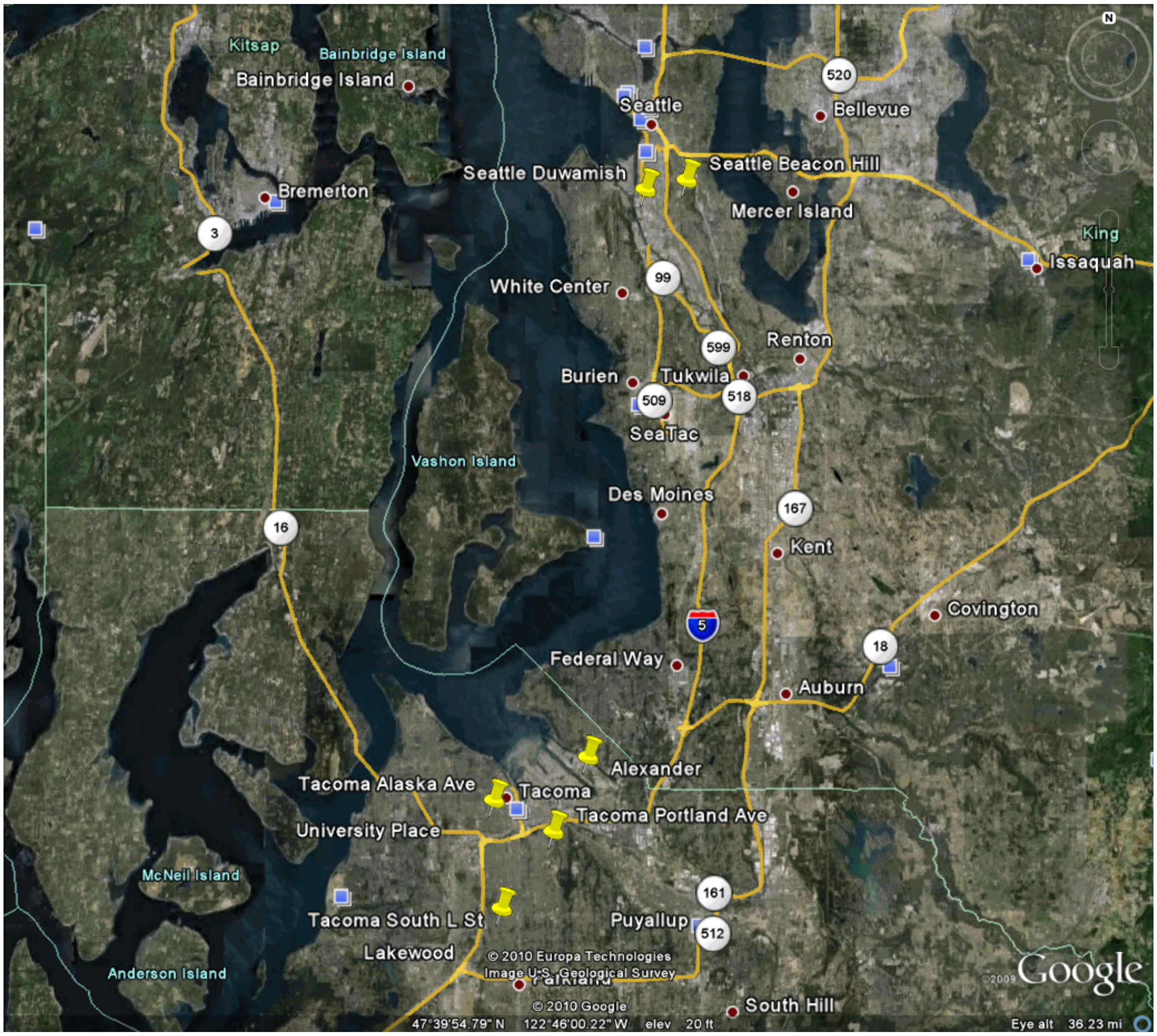


Figure A.1: Seattle and Tacoma area at a 36 mile wide view with all 6 fixed sites.

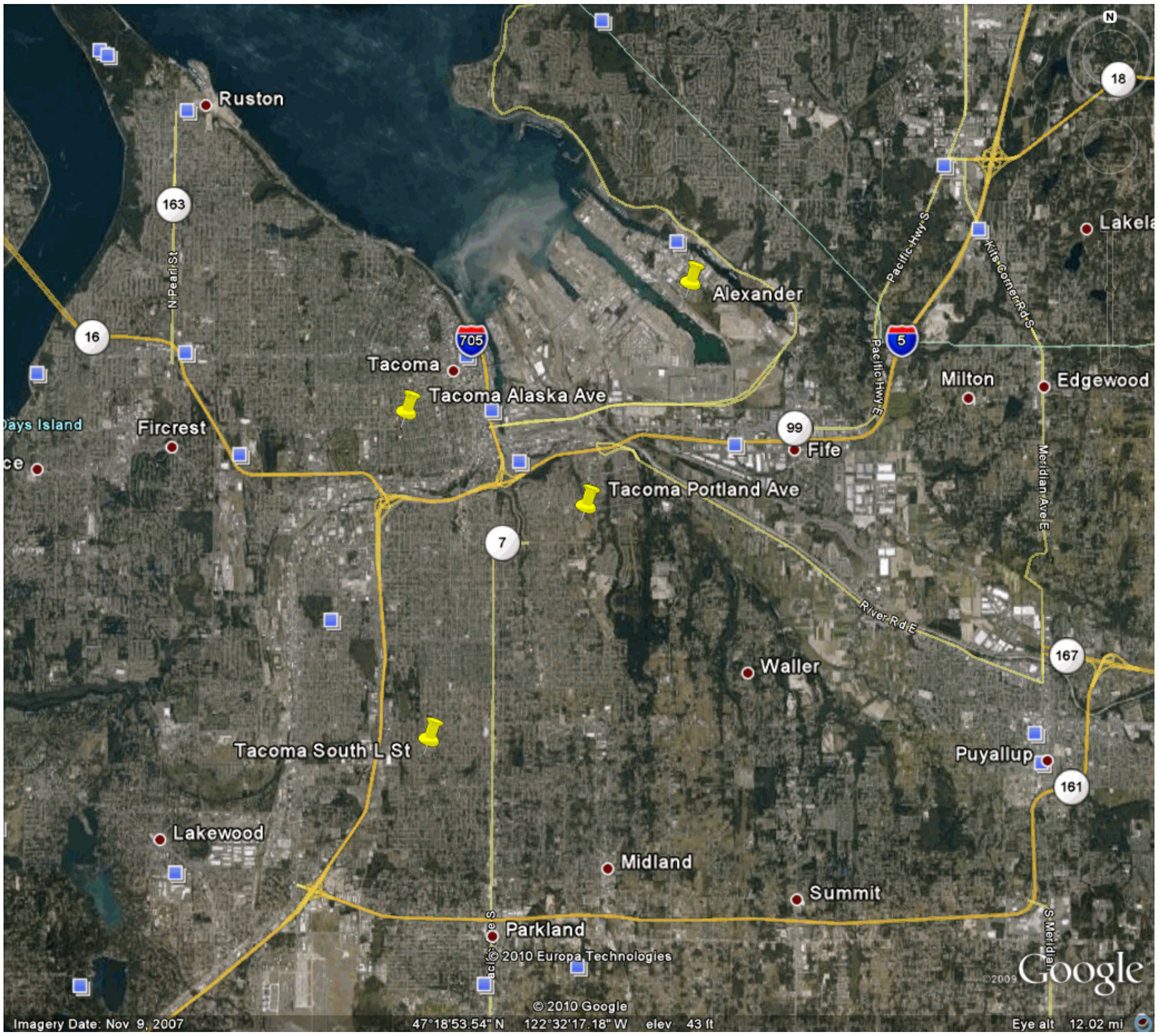


**Figure A.2: Tacoma study sites with a 12 mile wide view.**

Figure A.2 shows the study sites in the Tacoma area using a 12 mile wide view. Google Earth was used to highlight the location of major highways and to highlight land use and to give geographic reference. The fixed monitoring sites chosen for this study are designed to indicate source gradients across the Tacoma area for major air pollutants such as fine particulate matter and air toxics including benzene, formaldehyde, and others. As shown, the Tacoma Tideflats (Alexander Ave) site is located in an industrialized area, and is representative of air that is impacted by industry and mobile sources (transportation sources such as diesel trucks, trains, and delivery vehicles). Tacoma South L, Tacoma Alaska Ave, and Tacoma Portland Ave are located in neighborhoods and are representative of the neighborhood area sources such as wood smoke, and mobile sources such as what is found along the Interstate 5 corridor. The three neighborhood sites are all at a neighborhood scale and are at least 100 yards from the nearest chimney.

It is important to note that the fixed sites were used as references during the mobile monitoring periods. The mobile monitoring assessed areas throughout Tacoma to determine the spatial gradients for the air toxics.

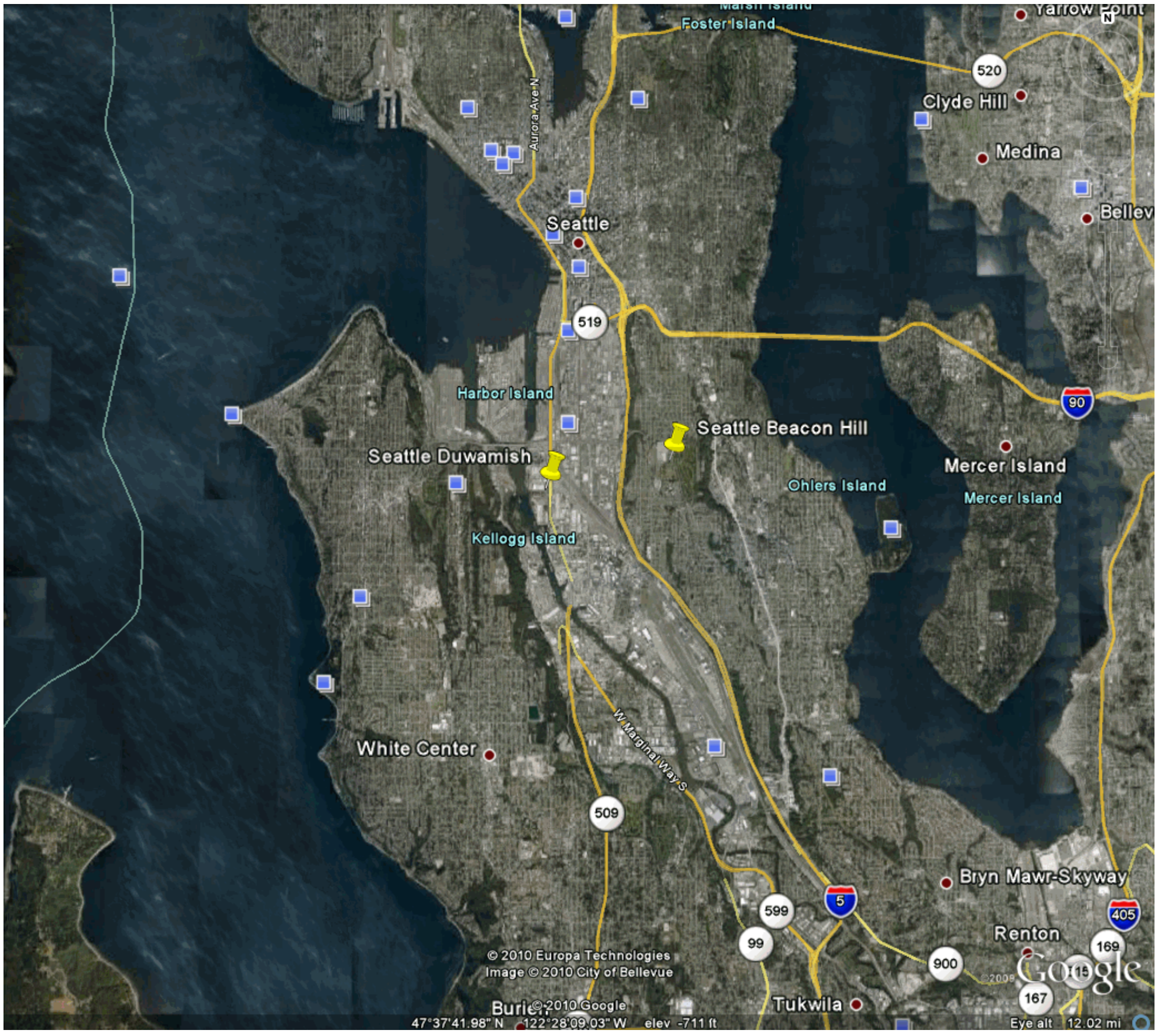


**Figure A.3: Seattle study sites with a 12 mile wide view.**

Figure A.3 shows the study sites in the Seattle area using a 12 mile wide view. Google Earth was used to highlight the location of major highways and to highlight land use and to give geographic reference. The fixed monitoring sites chosen for this study are designed to indicate representative gradients across Seattle for major air pollutants such as fine particulate matter and air toxics including benzene, formaldehyde, and others. Both sites are at the neighborhood scale, and represent the neighborhoods in which they are located. The Duwamish site is representative of air that is impacted by mobile sources (transportation sources such as diesel trucks, trains, and delivery vehicles) and industrial sources in the river valley. The Beacon Hill monitoring site is located in a typical Seattle residential neighborhood impacted by a mixture of mobile sources (motor vehicles) in the neighborhood and along the Interstate 5 corridor, residential wood smoke, and other sources. The Beacon Hill monitoring site has an extensive history of air toxics monitoring data that is considered representative of Seattle, and is used in this study to give historical perspective and reference.

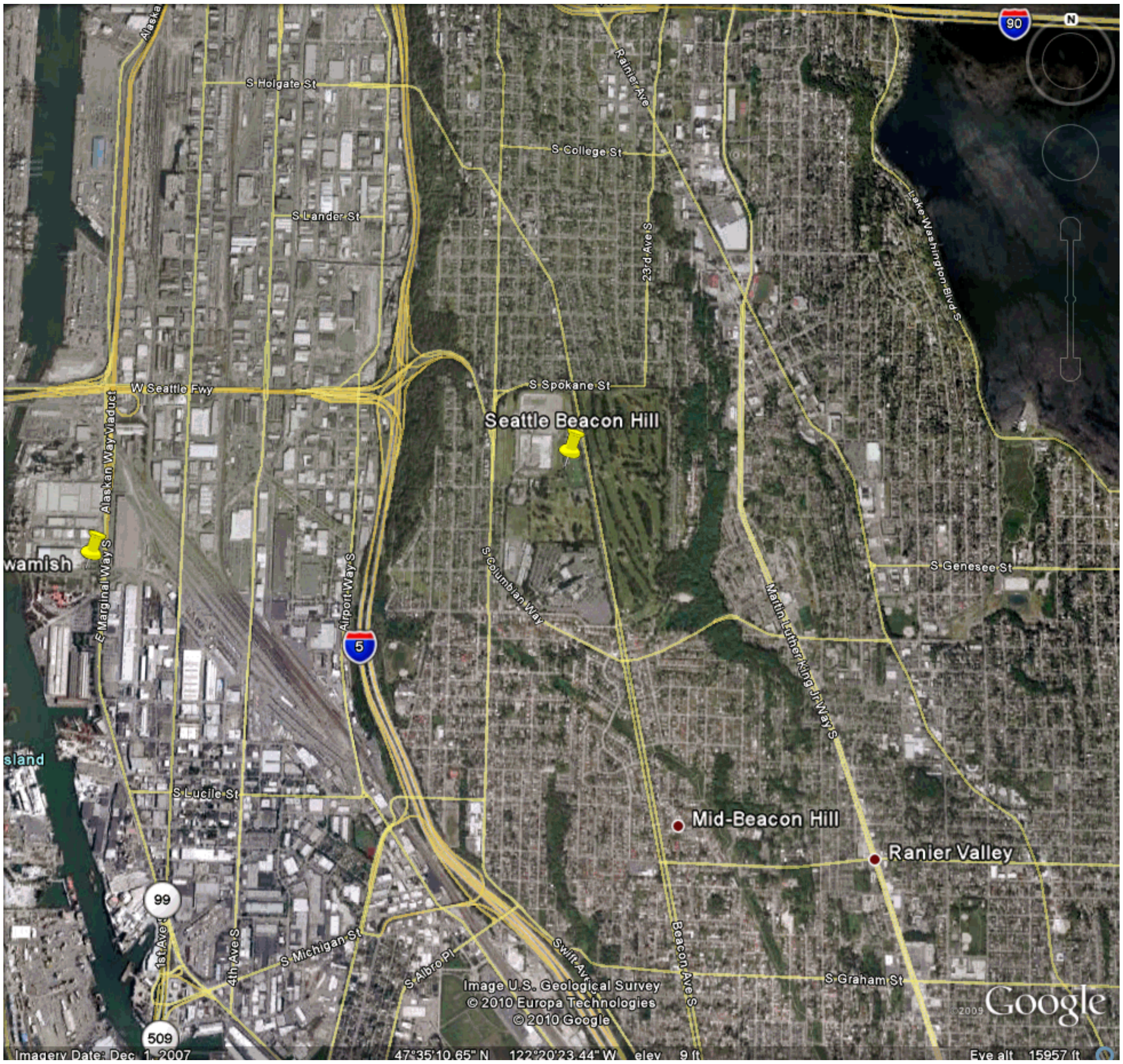


**Figure A.4: Seattle Beacon Hill site with a 4 mile wide view.**

The Seattle Beacon Hill monitoring site has been collecting air pollution data since 1979. The site is located on the property of the Seattle Water Beacon Hill reservoir adjacent to the Jefferson Park Golf Course and Park. The site is a neighborhood scale site that is representative of Seattle neighborhoods. The site is influenced by a mixture of mobile sources, industrial sources, winter home heating wood smoke, and other pollution sources.

Data collected here included continuous fine PM data, continuous BC, Federal Reference Method (FRM) $PM_{2.5}$ filters, speciated fine particle filters, metals, and meteorology data. Additionally, VOCs, PAHs, and aldehyde samples were collected using canisters, PUF sample media, and DNPH tubes, respectively.

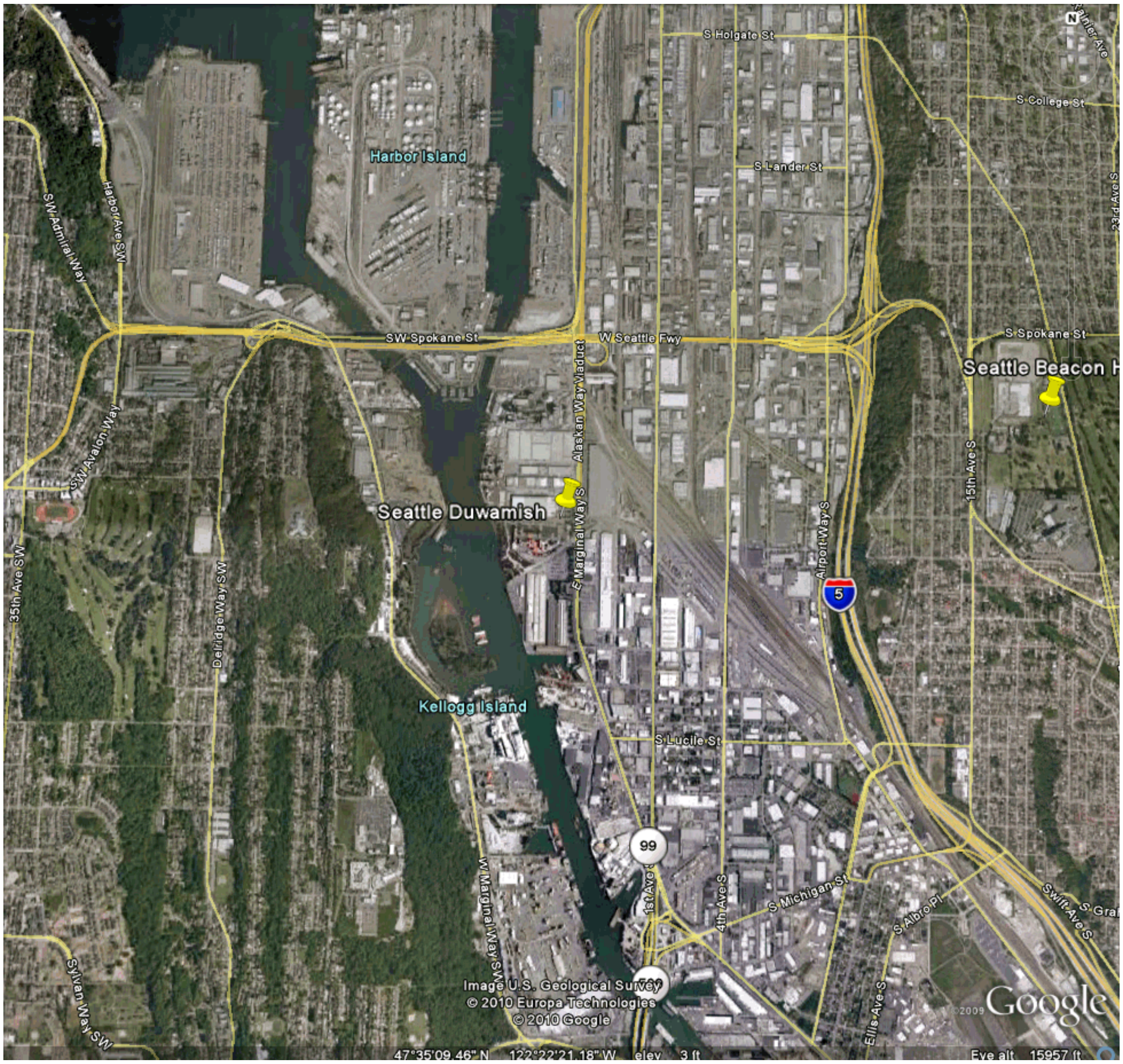


Figure A.5: Seattle Duwamish site with a 4 mile wide view.

The Seattle Duwamish monitoring site has been in place since 1971 in the heart of the Duwamish industrial valley. The site is located on the property of the WA State Liquor Control Board warehouse facility. The site is a neighborhood-scale site that is representative of South Seattle neighborhoods and ambient exposure in the industrial valley. The site is influenced by a very complex mixture of mobile sources, marine sources, industrial sources, winter home heating wood smoke, and other pollution sources. The site is 80 meters west of E. Marginal Way, which is a main arterial for many large haul trucks as well as service vehicles, and personal automobiles. This monitoring site consistently has the highest annual average of any other monitoring site in Western Washington, but is below the Federal Standard indicating that the area is in attainment of the current fine particle NAAQS levels.

Data collected here included continuous fine PM data, speciated fine particle data, continuous BC, Federal Reference Method $PM_{2.5}$ filters, which were then analyzed for levoglucosan content and 1-nitropyrene content, and meteorology data. Additionally, VOCs, PAHs, and aldehyde samples were collected using canisters, PUF sample media, and DNPH tubes, respectively.

Additionally temporary MIMS mobile monitoring data and Ecochem Particle-bound PAH data were collected.

**Figure A.6: Tacoma Tideflats (Alexander Ave) site.**

The Tacoma Tideflats (Alexander Ave) monitoring site has been in place since 1987 in the tideflats area collecting air pollution data. The site is a neighborhood scale site that is representative of ambient exposure in the tideflats area. The site is located near the Port of Tacoma, and several other air pollution sources. The sources that impact are a mixture of winter home heating from wood burning, mobile sources, and industrial sources.

Data collected here included continuous fine PM data, continuous BC, Federal Reference Method $PM_{2.5}$ filters, which were then analyzed for levoglucosan content and meteorology data. Additionally, VOCs, PAHs, and aldehyde samples were collected using canisters, PUF sample media, and DNPH tubes, respectively.

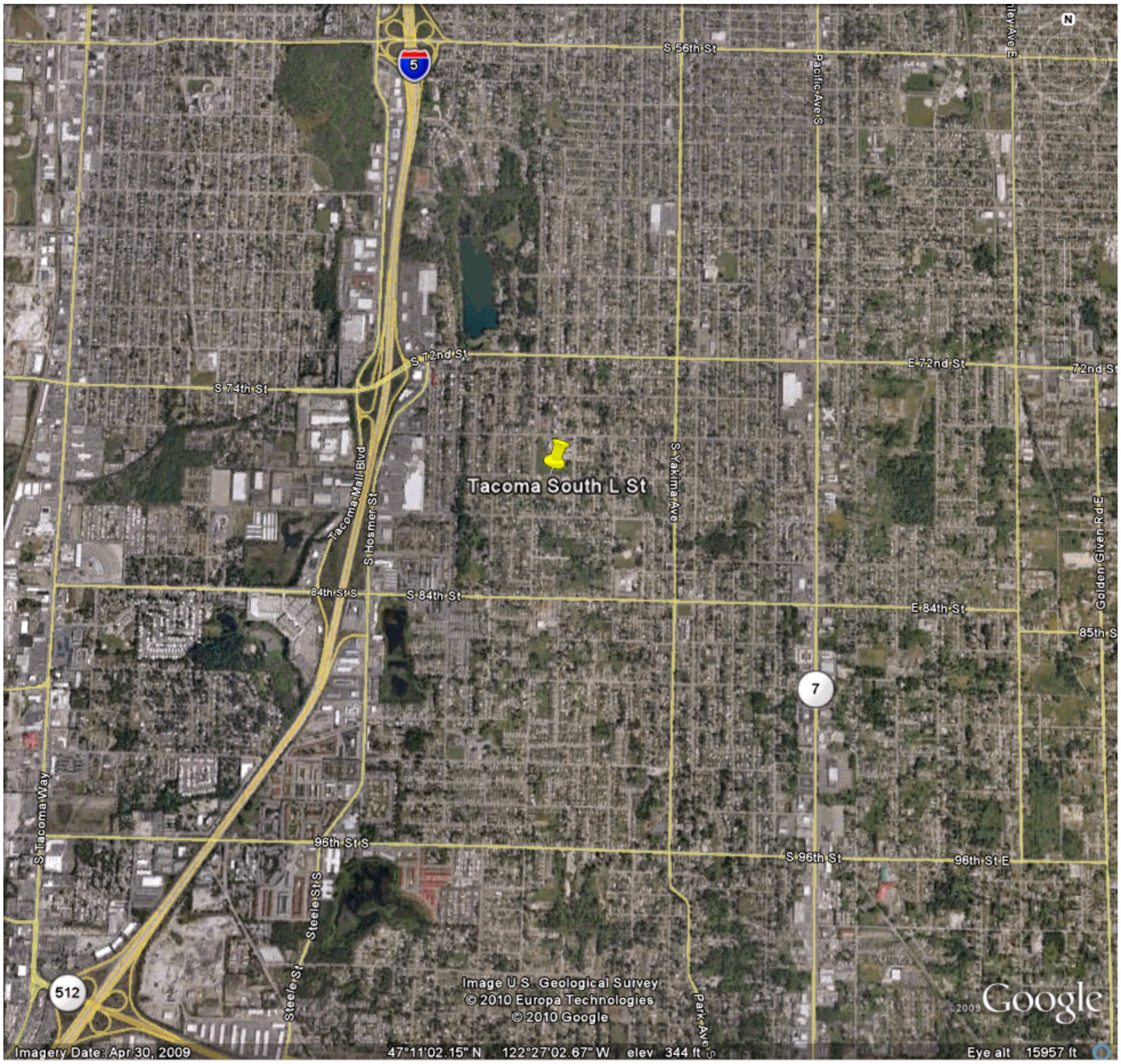


**Figure A.7: Tacoma South L St. site with a 4 mile wide view.**

The Tacoma South L Street monitoring site has been in place since 1999 at the South End Community Center. The site is a neighborhood scale site that is representative of Tacoma neighborhoods that use wood heating in winter. The site is set back from any significant traffic (from I-5, Hwy 512, and neighborhood arterials). The site is ~ 1 mile away from I-5. Winter home heating from wood burning is the dominant source that impacts this monitoring site. This monitoring site indicates that Tacoma is in violation of the NAAQS for fine particulate matter for the 98th percentile form of the standard.

Data collected here included continuous fine PM data, continuous BC, Federal Reference Method $PM_{2.5}$ filters, which were then analyzed for levoglucosan content and meteorology data. Additionally, VOCs, PAHs, and aldehyde samples were collected using canisters, PUF sample media, and DNPH tubes, respectively.

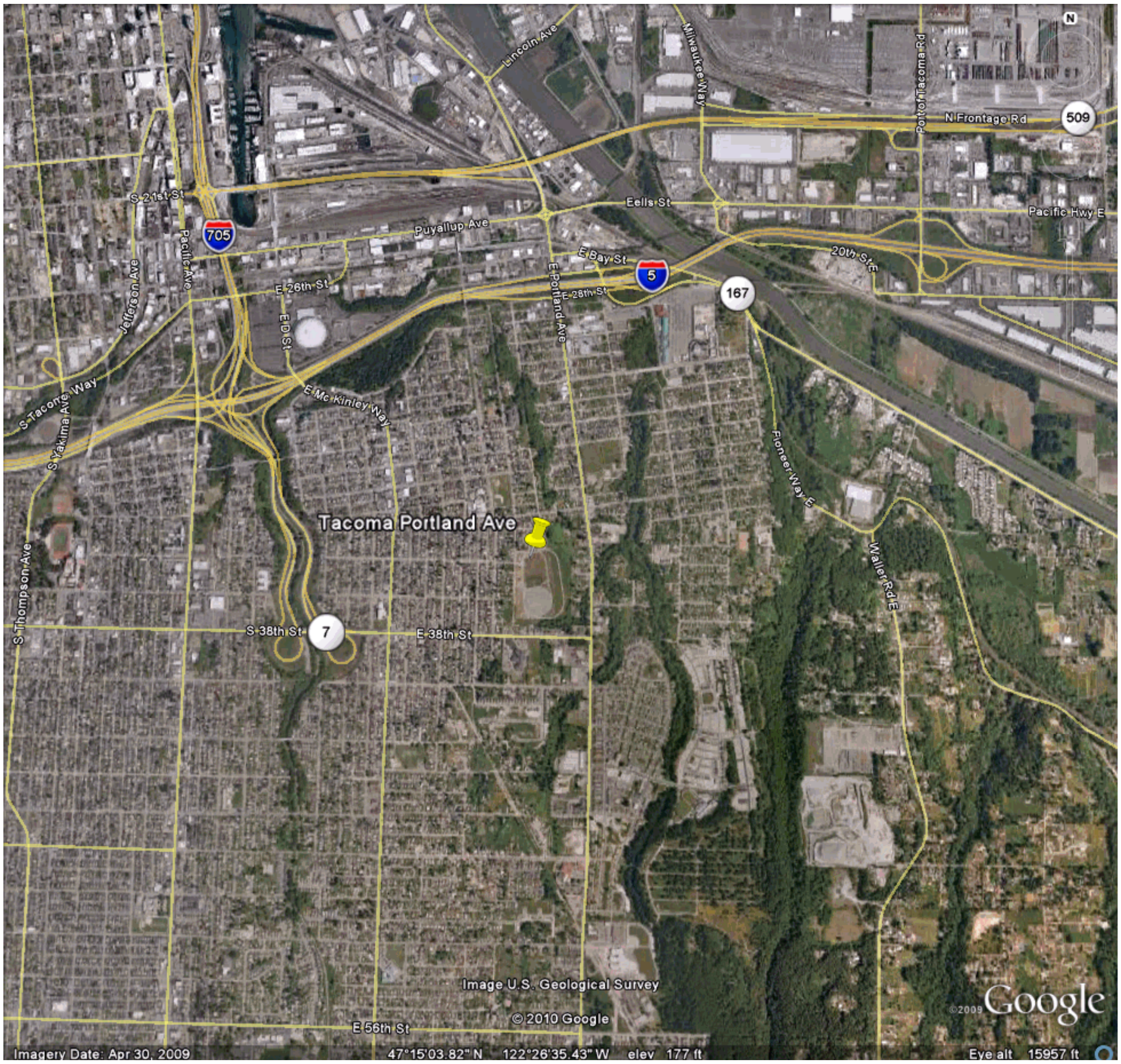


**Figure A.8: Tacoma Portland Ave. site with a 4 mile wide view.**

The Tacoma Portland Ave. site was located at the Tacoma Water Portland Avenue Reservoir campus located at the intersection of Fairbanks Street and Portland Avenue. The reservoir is located on the side of a hill that separates typical Tacoma neighborhoods and tribal property in the river valley. This site is a neighborhood scale site that is designed to assess the gradient between pollution generated from mobile and point sources in the industrial valley and pollution that is generated in the neighborhoods from winter wood heating.

Data collected here included continuous fine PM data, continuous BC, Federal Reference Method $PM_{2.5}$ filters, which were then analyzed for levoglucosan content and meteorology data. Additionally, VOCs and aldehyde samples were collected using canisters and DNPH tubes, respectively, but a significant section of VOC data was flagged in AQS after a glass denuder crack was found toward the end of the sampling period. All of the aldehyde samples were invalidated.

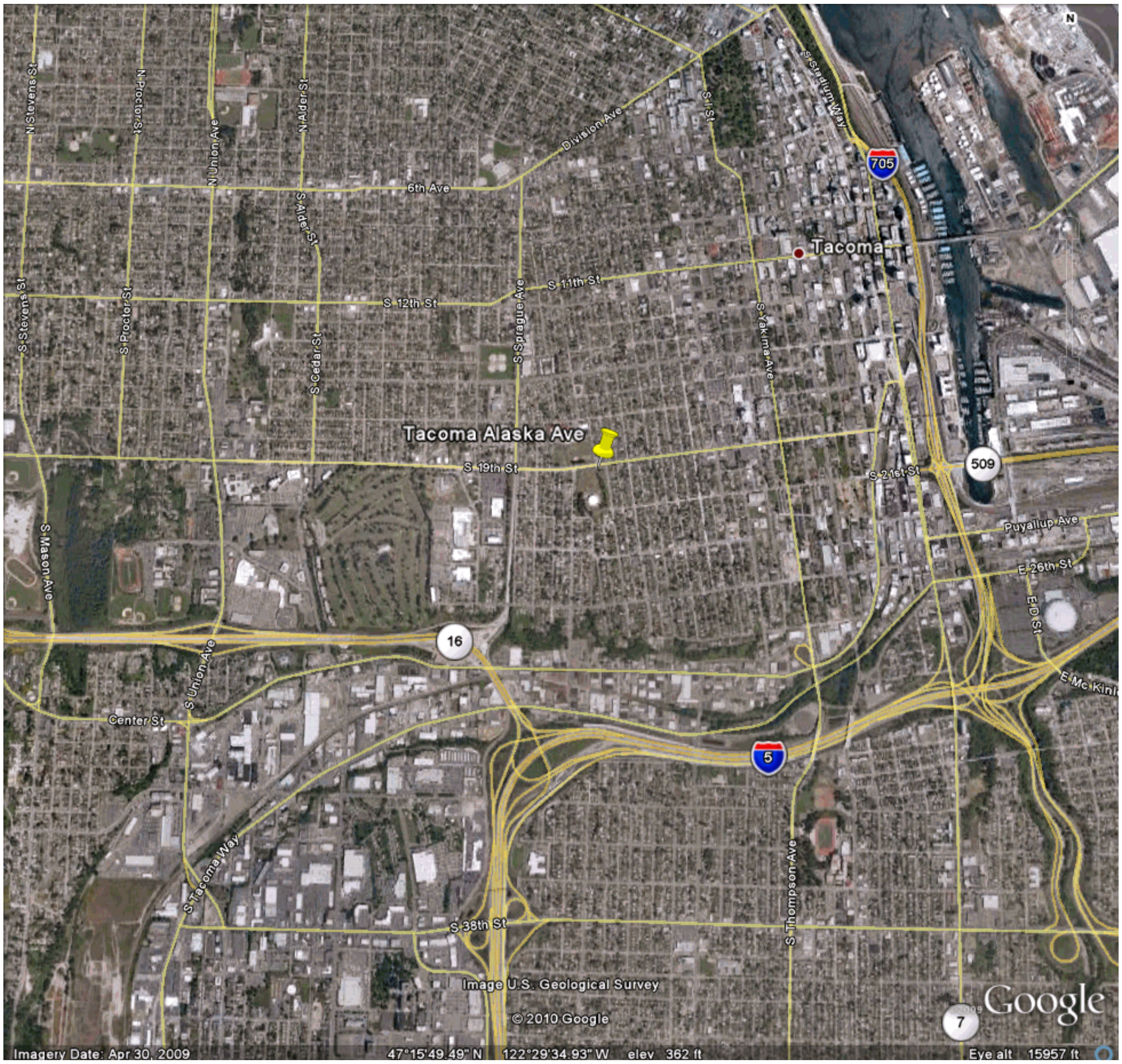


**Figure A.9: Tacoma Alaska Ave. site with a 4 mile wide view**

The Tacoma Alaska Ave. site was used to collect fine PM data for this study using a continuous nephelometer and a standard $PM_{2.5}$ estimation equation. The site would have been used to collect additional samples if any data indicated hot spots during the mobile monitoring runs. No hot spots were identified during the course of the mobile monitoring in this neighborhood, so additional TO-15, TO-11, and TO-13 sampling was not necessary.

The Alaska Ave. site was located at the Tacoma Water Alaska Avenue Reservoir campus located at the intersection of 19th Street and Alaska Avenue. The site is located in a typical residential neighborhood. Within 1 mile are St. Joseph's Medical Center, and Multicare Allenmore Hospital. Tacoma Stanley Elementary School is across 19th Avenue. This monitoring site was representative of neighborhood exposure to air pollution in the area of Tacoma bounded on the South by Interstate 5 and Highway 16. The fine PM data is very close and comparable to continuous fine PM data obtained at both the Tacoma South L Street monitor, and the Tacoma Portland Ave. monitor. The Alaska Avenue monitor represented pollution from sources such as home heating wood smoke, mobile sources from neighborhoods and from the major highways.

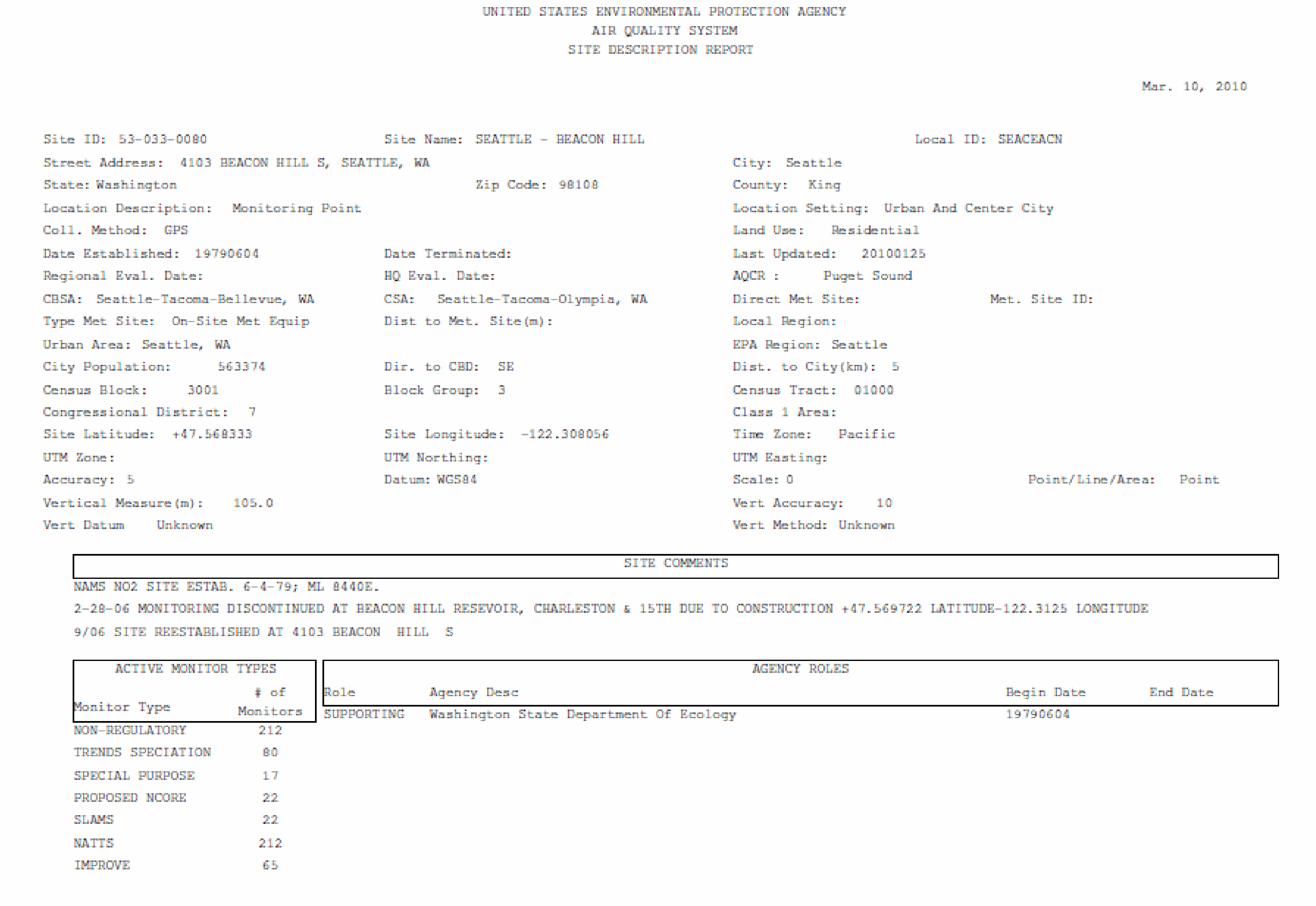
## Table A.1: Geographical Information for the study sites

| Site Code | AQS Code | Location | County | Micro- or Metropolitan Statistical Area | Latitude and Longitude | Land use | Location Setting | Description of the Immediate Surroundings |
|---|---|---|---|---|---|---|---|---|
| SEWA | 53-033-0080 | Seattle | King | Seattle-Tacoma-Bellevue, WA | 47.5683, -122.3081 | Industrial | Suburban | The Beacon Hill site is centrally located within the Seattle urban area. The site is isolated within the confines of the city's water reservoir. The nearest roads are at least 1 km away. It is surrounded by residential neighborhoods, Jefferson Park and a middle school. It is about 100 meters above sea level. The hill is part of a larger ridge defining the eastern edge of an area of light industry including a major seaport, and airport and warehousing and trucking activity about 4 km west of the site. Interstate freeways and arterial roads carrying large amounts of traffic are closely situated 2 to 4 km northwest of the site. The site is considered to be representative of 24 hour average PM2.5 levels within a 20 km radius (Goswami 2002). |
| CEWA | 53-033-0057 | Seattle | King | Seattle-Tacoma-Bellevue, WA | 47.5633, -122.3406 | Industrial | Urban Center | The Seattle Duwamish site is located within the Seattle Duwamish river industrial valley. The site is located in a parking lot area of the WA state liquor control board warehouse |

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | property. The nearest road, Hwy 99, is 80 meters East of the site. The dominant wind pattern is from the South. Likely source impacts include diesel mobile sources, motor vehicle exhaust, industrial emissions, and winter home heating wood smoke. |
| EQWA | 53-053-0031 | Tacoma | Pierce | Seattle-Tacoma-Bellevue, WA | 47.2656, -122.3858 | Industrial | Urban Center | The Tacoma Tideflats Alexander Avenue site is located on Puyallup tribal property in the industrial area of the Tacoma Port. The area monitored has been included in the EPA Superfund program. The dominant wind pattern is from the South and from the Northwest during winter stagnations. Likely source impacts include industrial emissions, mobile sources such as diesel trucks and port activities, marine sources from the port, and winter home heating wood smoke. |
| ESWA | 53-053-0029 | Tacoma | Pierce | Seattle-Tacoma-Bellevue, WA | 47.1864, -122.4517 | Residential | Suburban | The Tacoma South L Street site is on the property of the South End Community Center on L Street. The site is located next to a baseball diamond, and the Birney Elementary school. The site is at the neighborhood scale and has, year after year, been the highest fine PM concentrations recorded in Western Washington on stagnant winter nights. The dominant |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | wind pattern is from the south and the east during winter stagnant events. The wind pattern at other times of the year is from the north or the south and west. The dominant source is winter home heating wood smoke. |
| EYWA | 53-053-0034 | Tacoma | Pierce | Seattle-Tacoma-Bellevue, WA | 47.2267, -122.4121 | Residential | Suburban | The Tacoma Portland Avenue site is located on the property of Tacoma Water's Portland Avenue Reservoir. The reservoir is on the side of a hill boundary between Tacoma neighborhoods and the Puyallup river valley 0.8 miles south of Interstate 5. The dominant wind pattern is generally from the south. Dominant sources include local mobile sources and winter home heating wood smoke. |
| EZWA | 53-053-0033 | Tacoma | Pierce | Seattle-Tacoma-Bellevue, WA | 47.2428, -122.4578 | Residential | Suburban | The Tacoma Alaska Avenue site is located on the property of Tacoma Water's Alaska Avenue reservoir. The building that housed the monitor was adjacent to 19th Avenue. Met parameters weren't monitored at this site, but the wind pattern was consistent through our Tacoma sites to assume that the winds at this site were similar. Dominant sources include a mixture of local mobile sources, winter home heating wood smoke, and other sources present in the urban air shed. |

# Table A.2: AQS Site Descriptions



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
AIR QUALITY SYSTEM
SITE DESCRIPTION REPORT

Mar. 10, 2010

Site ID: 53-033-0080    Site Name: SEATTLE - BEACON HILL    Local ID: SEACEACN

Street Address: 4103 BEACON HILL S, SEATTLE, WA    City: Seattle

State: Washington    Zip Code: 98108    County: King

Location Description: Monitoring Point    Location Setting: Urban And Center City

Coll. Method: GPS    Land Use: Residential

Date Established: 19790604    Date Terminated:    Last Updated: 20100125

Regional Eval. Date:    HQ Eval. Date:    AQCR : Puget Sound

CBSA: Seattle-Tacoma-Bellevue, WA    CSA: Seattle-Tacoma-Olympia, WA    Direct Met Site:    Met. Site ID:

Type Met Site: On-Site Met Equip    Dist to Met. Site(m):    Local Region:

Urban Area: Seattle, WA    EPA Region: Seattle

City Population: 563374    Dir. to CBD: SE    Dist. to City(km): 5

Census Block: 3001    Block Group: 3    Census Tract: 01000

Congressional District: 7    Class 1 Area:

Site Latitude: +47.568333    Site Longitude: -122.308056    Time Zone: Pacific

UTM Zone:    UTM Northing:    UTM Easting:

Accuracy: 5    Datum: WGS84    Scale: 0    Point/Line/Area: Point

Vertical Measure(m): 105.0    Vert Accuracy: 10

Vert Datum Unknown    Vert Method: Unknown

SITE COMMENTS

NAMS NO2 SITE ESTAB. 6-4-79; ML 8440E.

2-28-06 MONITORING DISCONTINUED AT BEACON HILL RESEVOIR, CHARLESTON & 15TH DUE TO CONSTRUCTION +47.569722 LATITUDE-122.3125 LONGITUDE

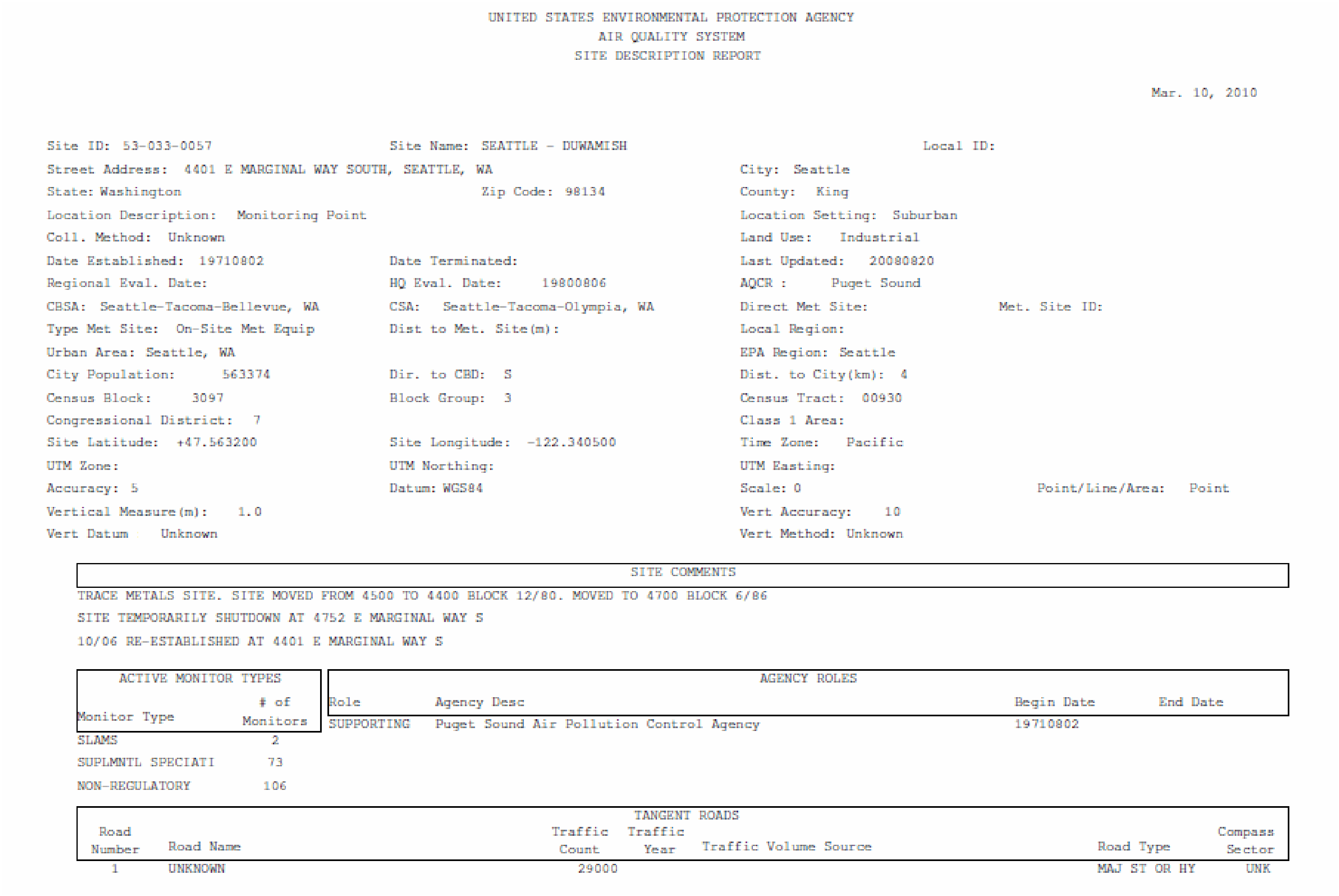
9/06 SITE REESTABLISHED AT 4103 BEACON HILL S

ACTIVE MONITOR TYPES

| Monitor Type | # of Monitors |
|---|---|
| NON-REGULATORY | 212 |
| TRENDS SPECIATION | 80 |
| SPECIAL PURPOSE | 17 |
| PROPOSED NCORE | 22 |
| SLAMS | 22 |
| NATTS | 212 |
| IMPROVE | 65 |

AGENCY ROLES

| Role | Agency Desc | Begin Date | End Date |
|---|---|---|---|
| SUPPORTING | Washington State Department Of Ecology | 19790604 | |



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
AIR QUALITY SYSTEM
SITE DESCRIPTION REPORT

Mar. 10, 2010

Site ID: 53-033-0057 Site Name: SEATTLE - DUWAMISH Local ID:
Street Address: 4401 E MARGINAL WAY SOUTH, SEATTLE, WA City: Seattle
State: Washington Zip Code: 98134 County: King
Location Description: Monitoring Point Location Setting: Suburban
Coll. Method: Unknown Land Use: Industrial
Date Established: 19710802 Date Terminated: Last Updated: 20080820
Regional Eval. Date: HQ Eval. Date: 19800806 AQCR : Puget Sound
CBSA: Seattle-Tacoma-Bellevue, WA CSA: Seattle-Tacoma-Olympia, WA Direct Met Site: Met. Site ID:
Type Met Site: On-Site Met Equip Dist to Met. Site(m): Local Region:
Urban Area: Seattle, WA EPA Region: Seattle
City Population: 563374 Dir. to CBD: S Dist. to City(km): 4
Census Block: 3097 Block Group: 3 Census Tract: 00930
Congressional District: 7 Class 1 Area:
Site Latitude: +47.563200 Site Longitude: -122.340500 Time Zone: Pacific
UTM Zone: UTM Northing: UTM Easting:
Accuracy: 5 Datum: WGS84 Scale: 0 Point/Line/Area: Point
Vertical Measure(m): 1.0 Vert Accuracy: 10
Vert Datum Unknown Vert Method: Unknown

SITE COMMENTS

TRACE METALS SITE. SITE MOVED FROM 4500 TO 4400 BLOCK 12/80. MOVED TO 4700 BLOCK 6/86
SITE TEMPORARILY SHUTDOWN AT 4752 E MARGINAL WAY S
10/06 RE-ESTABLISHED AT 4401 E MARGINAL WAY S

ACTIVE MONITOR TYPES

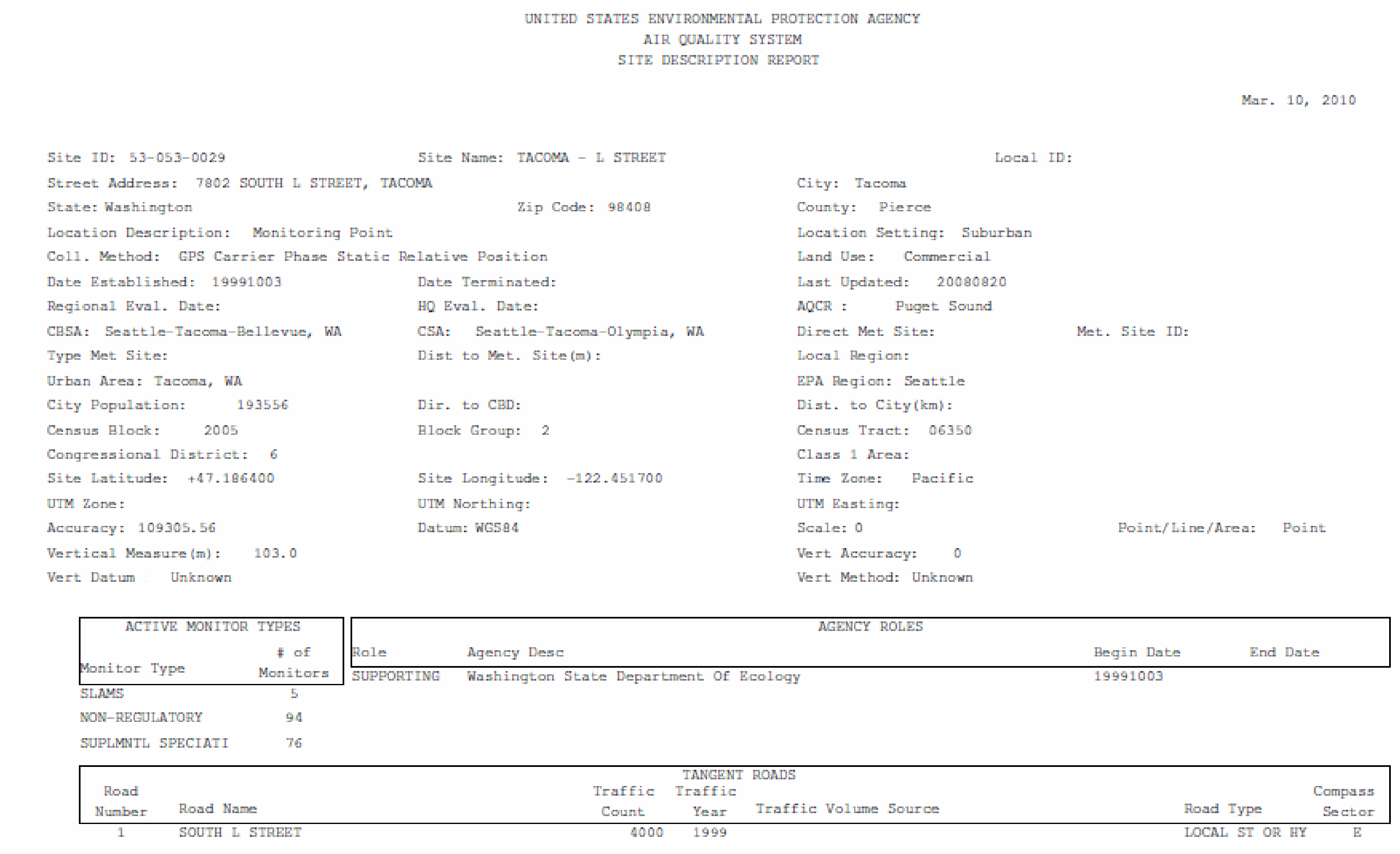
| Monitor Type | # of Monitors |
|---|---|
| SLAMS | 2 |
| SUPLMNTL SPECIATI | 73 |
| NON-REGULATORY | 106 |

AGENCY ROLES

| Role | Agency Desc | Begin Date | End Date |
|---|---|---|---|
| SUPPORTING | Puget Sound Air Pollution Control Agency | 19710802 | |

TANGENT ROADS

| Road Number | Road Name | Traffic Count | Traffic Year | Traffic Volume Source | Road Type | Compass Sector |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 29000 | | | MAJ ST OR HY | UNK |



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
AIR QUALITY SYSTEM
SITE DESCRIPTION REPORT

Mar. 10, 2010

Site ID: 53-053-0029 Site Name: TACOMA - L STREET Local ID:
Street Address: 7802 SOUTH L STREET, TACOMA City: Tacoma
State: Washington Zip Code: 98408 County: Pierce
Location Description: Monitoring Point Location Setting: Suburban
Coll. Method: GPS Carrier Phase Static Relative Position Land Use: Commercial
Date Established: 19991003 Date Terminated: Last Updated: 20080820
Regional Eval. Date: HQ Eval. Date: AQCR : Puget Sound
CBSA: Seattle-Tacoma-Bellevue, WA CSA: Seattle-Tacoma-Olympia, WA Direct Met Site: Met. Site ID:
Type Met Site: Dist to Met. Site(m): Local Region:
Urban Area: Tacoma, WA EPA Region: Seattle
City Population: 193556 Dir. to CBD: Dist. to City(km):
Census Block: 2005 Block Group: 2 Census Tract: 06350
Congressional District: 6 Class 1 Area:
Site Latitude: +47.186400 Site Longitude: -122.451700 Time Zone: Pacific
UTM Zone: UTM Northing: UTM Easting:
Accuracy: 109305.56 Datum: WGS84 Scale: 0 Point/Line/Area: Point
Vertical Measure(m): 103.0 Vert Accuracy: 0
Vert Datum Unknown Vert Method: Unknown

ACTIVE MONITOR TYPES

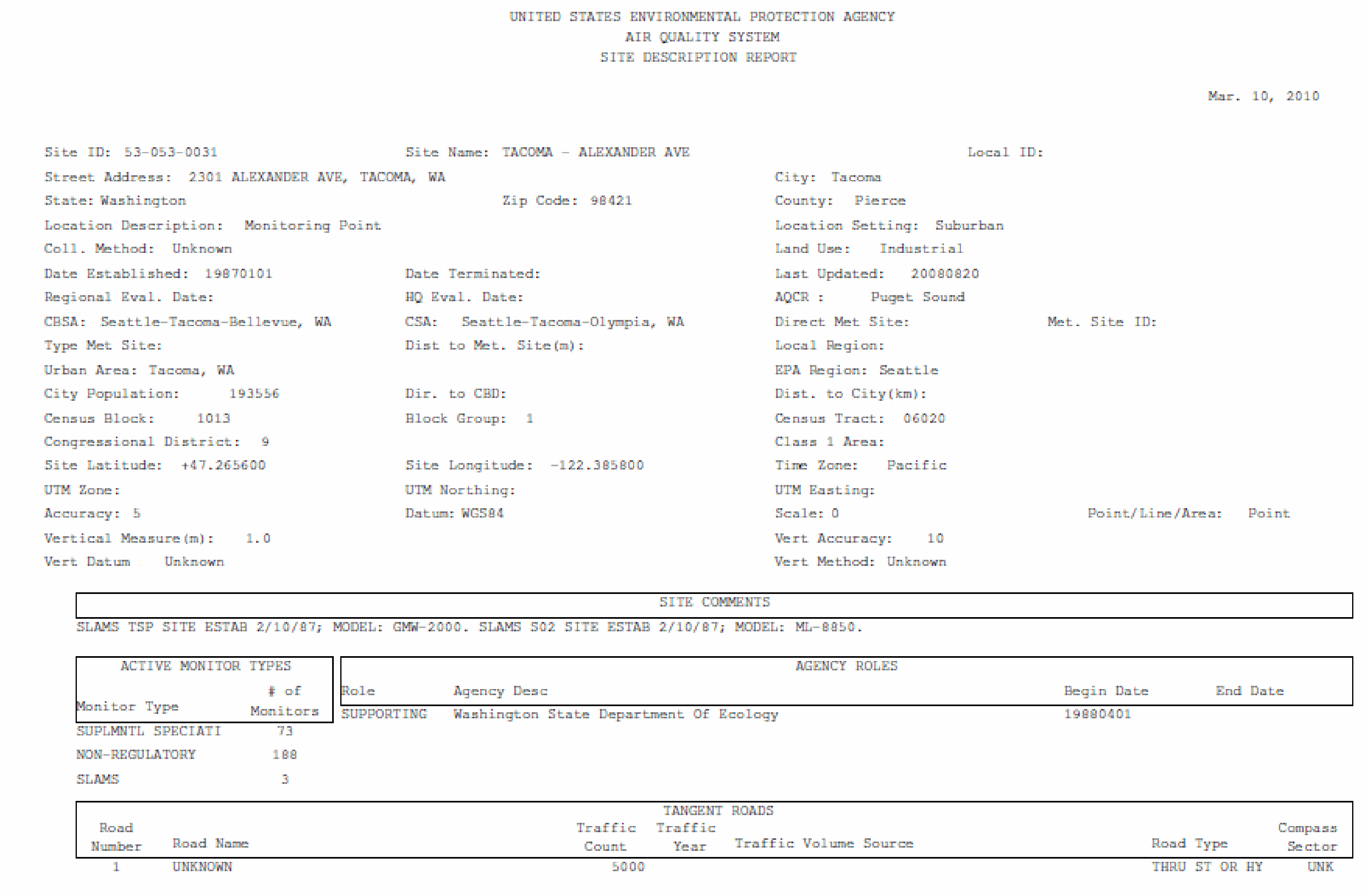
| Monitor Type | # of Monitors |
|---|---|
| SLAMS | 5 |
| NON-REGULATORY | 94 |
| SUPLMNTL SPECIATI | 76 |

AGENCY ROLES

| Role | Agency Desc | Begin Date | End Date |
|---|---|---|---|
| SUPPORTING | Washington State Department Of Ecology | 19991003 | |

TANGENT ROADS

| Road Number | Road Name | Traffic Count | Traffic Year | Traffic Volume Source | Road Type | Compass Sector |
|---|---|---|---|---|---|---|
| 1 | SOUTH L STREET | 4000 | 1999 | | LOCAL ST OR HY | E |



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
AIR QUALITY SYSTEM
SITE DESCRIPTION REPORT

Mar. 10, 2010

Site ID: 53-053-0031 Site Name: TACOMA - ALEXANDER AVE Local ID:
Street Address: 2301 ALEXANDER AVE, TACOMA, WA City: Tacoma
State: Washington Zip Code: 98421 County: Pierce
Location Description: Monitoring Point Location Setting: Suburban
Coll. Method: Unknown Land Use: Industrial
Date Established: 19870101 Date Terminated: Last Updated: 20080820
Regional Eval. Date: HQ Eval. Date: AQCR : Puget Sound
CBSA: Seattle-Tacoma-Bellevue, WA CSA: Seattle-Tacoma-Olympia, WA Direct Met Site: Met. Site ID:
Type Met Site: Dist to Met. Site(m): Local Region:
Urban Area: Tacoma, WA EPA Region: Seattle
City Population: 193556 Dir. to CBD: Dist. to City(km):
Census Block: 1013 Block Group: 1 Census Tract: 06020
Congressional District: 9 Class 1 Area:
Site Latitude: +47.265600 Site Longitude: -122.385800 Time Zone: Pacific
UTM Zone: UTM Northing: UTM Easting:
Accuracy: 5 Datum: WGS84 Scale: 0 Point/Line/Area: Point
Vertical Measure(m): 1.0 Vert Accuracy: 10
Vert Datum Unknown Vert Method: Unknown

SITE COMMENTS

SLAMS TSP SITE ESTAB 2/10/87; MODEL: GMW-2000. SLAMS SO2 SITE ESTAB 2/10/87; MODEL: ML-8850.

ACTIVE MONITOR TYPES

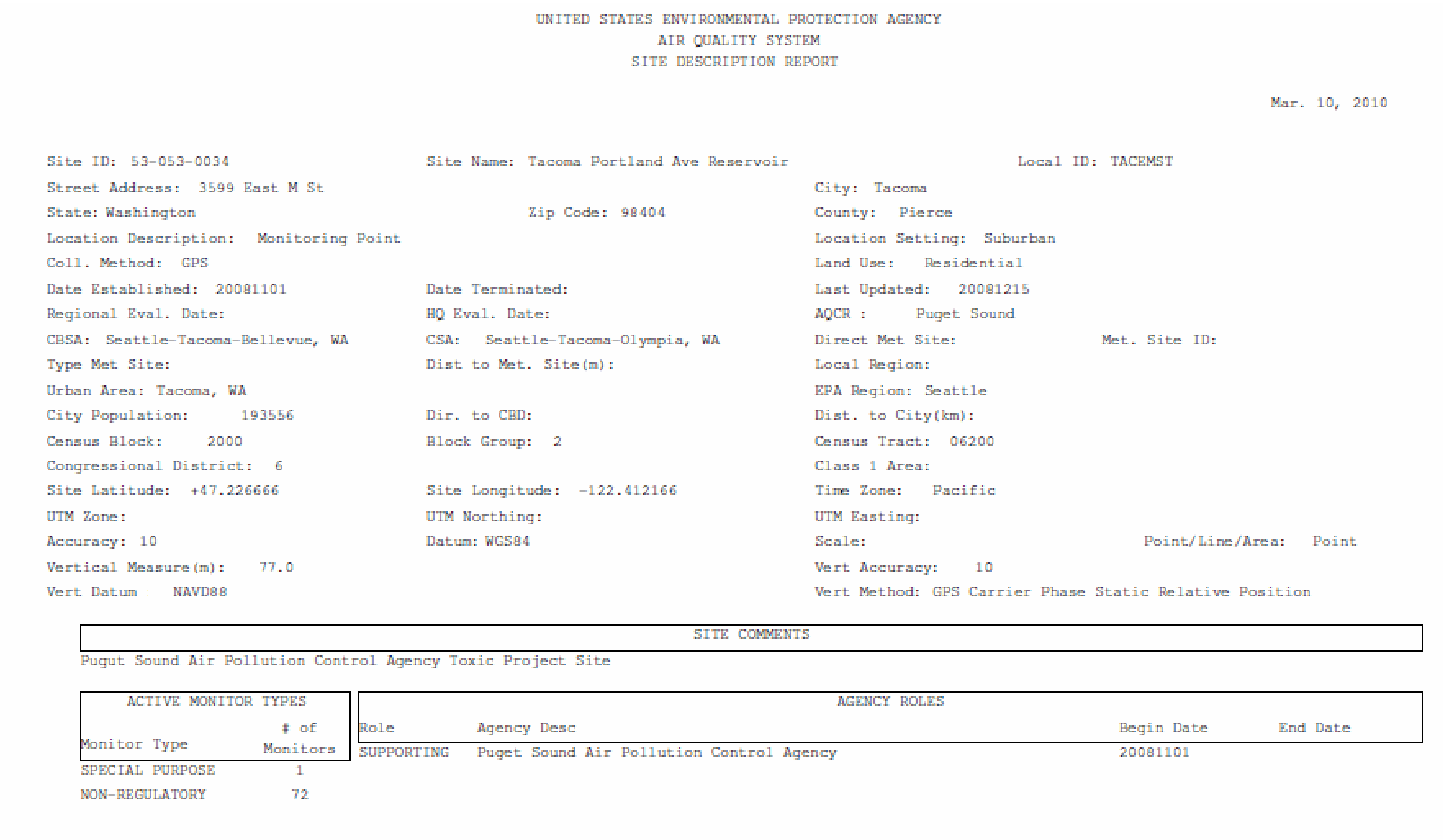
| Monitor Type | # of Monitors |
|---|---|
| SUPLMNTL SPECIATI | 73 |
| NON-REGULATORY | 188 |
| SLAMS | 3 |

AGENCY ROLES

| Role | Agency Desc | Begin Date | End Date |
|---|---|---|---|
| SUPPORTING | Washington State Department Of Ecology | 19880401 | |

TANGENT ROADS

| Road Number | Road Name | Traffic Count | Traffic Year | Traffic Volume Source | Road Type | Compass Sector |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 5000 | | | THRU ST OR HY | UNK |



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
AIR QUALITY SYSTEM
SITE DESCRIPTION REPORT

Mar. 10, 2010

Site ID: 53-053-0034 Site Name: Tacoma Portland Ave Reservoir Local ID: TACEMST
Street Address: 3599 East M St City: Tacoma
State: Washington Zip Code: 98404 County: Pierce
Location Description: Monitoring Point Location Setting: Suburban
Coll. Method: GPS Land Use: Residential
Date Established: 20081101 Date Terminated: Last Updated: 20081215
Regional Eval. Date: HQ Eval. Date: AQCR : Puget Sound
CBSA: Seattle-Tacoma-Bellevue, WA CSA: Seattle-Tacoma-Olympia, WA Direct Met Site: Met. Site ID:
Type Met Site: Dist to Met. Site(m): Local Region:
Urban Area: Tacoma, WA EPA Region: Seattle
City Population: 193556 Dir. to CBD: Dist. to City(km):
Census Block: 2000 Block Group: 2 Census Tract: 06200
Congressional District: 6 Class 1 Area:
Site Latitude: +47.226666 Site Longitude: -122.412166 Time Zone: Pacific
UTM Zone: UTM Northing: UTM Easting:
Accuracy: 10 Datum: WGS84 Scale: Point/Line/Area: Point
Vertical Measure(m): 77.0 Vert Accuracy: 10
Vert Datum NAVD88 Vert Method: GPS Carrier Phase Static Relative Position

SITE COMMENTS

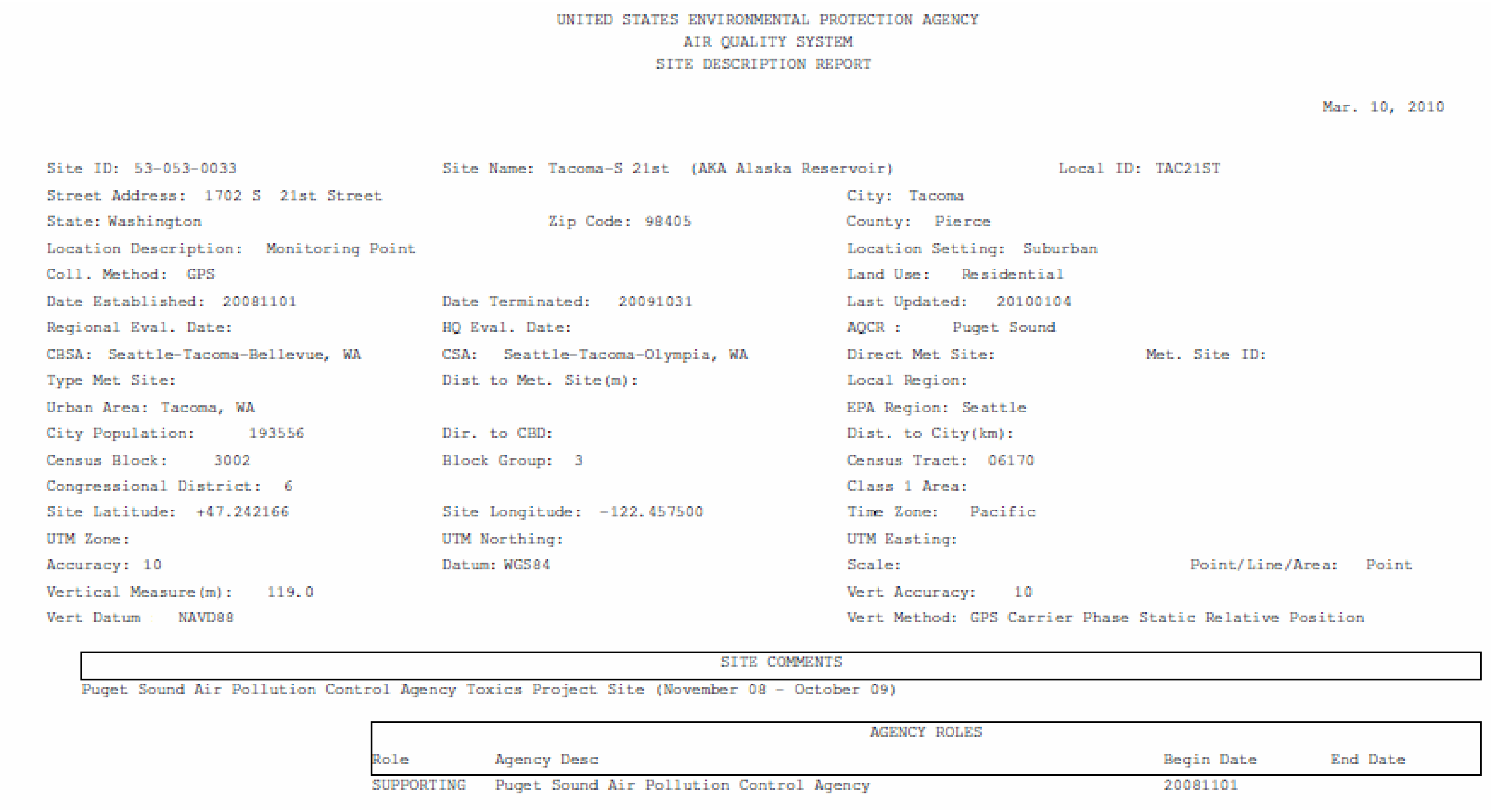
Puqut Sound Air Pollution Control Agency Toxic Project Site

ACTIVE MONITOR TYPES

| Monitor Type | # of Monitors |
|---|---|
| SPECIAL PURPOSE | 1 |
| NON-REGULATORY | 72 |

AGENCY ROLES

| Role | Agency Desc | Begin Date | End Date |
|---|---|---|---|
| SUPPORTING | Puget Sound Air Pollution Control Agency | 20081101 | |



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
AIR QUALITY SYSTEM
SITE DESCRIPTION REPORT

Mar. 10, 2010

Site ID: 53-053-0033 Site Name: Tacoma-S 21st (AKA Alaska Reservoir) Local ID: TAC21ST
Street Address: 1702 S 21st Street City: Tacoma
State: Washington Zip Code: 98405 County: Pierce
Location Description: Monitoring Point Location Setting: Suburban
Coll. Method: GPS Land Use: Residential
Date Established: 20081101 Date Terminated: 20091031 Last Updated: 20100104
Regional Eval. Date: HQ Eval. Date: AQCR : Puget Sound
CBSA: Seattle-Tacoma-Bellevue, WA CSA: Seattle-Tacoma-Olympia, WA Direct Met Site: Met. Site ID:
Type Met Site: Dist to Met. Site(m): Local Region:
Urban Area: Tacoma, WA EPA Region: Seattle
City Population: 193556 Dir. to CBD: Dist. to City(km):
Census Block: 3002 Block Group: 3 Census Tract: 06170
Congressional District: 6 Class 1 Area:
Site Latitude: +47.242166 Site Longitude: -122.457500 Time Zone: Pacific
UTM Zone: UTM Northing: UTM Easting:
Accuracy: 10 Datum: WGS84 Scale: Point/Line/Area: Point
Vertical Measure(m): 119.0 Vert Accuracy: 10
Vert Datum NAVD88 Vert Method: GPS Carrier Phase Static Relative Position

SITE COMMENTS

Puget Sound Air Pollution Control Agency Toxics Project Site (November 08 - October 09)

AGENCY ROLES

| Role | Agency Desc | Begin Date | End Date |
|---|---|---|---|
| SUPPORTING | Puget Sound Air Pollution Control Agency | 20081101 | |

# Appendix B: Approved Project Quality Assurance Plan

(the report is attached in the following pages)

pscleanair.org
Puget Sound Clean Air Agency

# SEASONAL AND SPATIAL CHARACTERIZATION OF TACOMA AND SEATTLE AREA AIR TOXICS COMMUNITY-SCALE MONITORING PROJECT

**November 2008 - October 2010**

## QUALITY ASSURANCE PROJECT PLAN
**Revision 1.1**

**Puget Sound Clean Air Agency**

**Air Monitoring Department**

**November 2008**

## PROJECT PLAN IDENTIFICATION AND APPROVAL

The attached Quality Assurance Project Plan for the Seasonal and Spatial Characterization of Tacoma and Seattle Area Air Toxics Community Scale Monitoring Project is approved and commits the Department to follow the elements described within.

**Puget Sound Clean Air Agency**

1) Signature:__________ Date: 11/24/08
Mike Gilroy – Air Monitoring Manager, Puget Sound Clean Air Agency

2) Signature:__________ Date: 11/24/08
Matt Harper – Air Monitoring Lead, Puget Sound Clean Air Agency

3) Signature:__________ Date: 11/24/08
Erik Saganic – Quality Assurance Specialist, Puget Sound Clean Air Agency

4) Signature:__________ Date: 11/24/08
Walter Zylowski – Quality Assurance Specialist, Puget Sound Clean Air Agency

**United States Environmental Protection Agency**

1) Signature:__________ Date: 12/1/08
Keith Rose - Air Monitoring Officer - Office of Air Quality
USEPA Region 10

2) Signature:__________ Date: 11/26/08
Chris Hall, Quality Assurance Officer, Office of Air Quality
USEPA Region 10

3) Signature:__________ Date: 12/02/08
Gina Grepo-Grove, Quality Assurance Manager
USEPA Region 10

# TABLE OF CONTENTS

# 2 DISTRIBUTION

A hardcopy of this Quality Assurance Project Plan for the Seasonal and Spatial Characterization of Tacoma and Seattle Area Air Toxics Community Scale Monitoring Project has been distributed to the individuals listed in Table 2-1. The document is also available on the Department's shared network drive under \\Chinook\TechServices\Monitoring documents\Procedures\SOPs and Manuals\Speciation and Toxics.

**Table 2-1. Seasonal and Spatial Characterization of Tacoma and Seattle Area Air Toxics Community Scale Monitoring Project QAPP Distribution List**

| Name | Position |
|---|---|
| ***Puget Sound Clean Air Agency*** | |
| Mike Gilroy | Manager, Air Monitoring |
| Matt Harper | Lead, Air Monitoring |
| Erik Saganic | Quality Assurance Specialist |
| Walter Zylowski | Quality Assurance Specialist |
| Greg Sandau | Air Monitoring Specialist |
| Adam Petrusky | Air Monitoring Specialist |
| Mary Hoffman | Data Specialist |
| Kathy Himes | Lead, Air Resources |
| ***University of Washington, Seattle*** | |
| Mike Yost | Principle Investigator, Professor, Environmental & Occupational Health Sciences |
| Tim Larson | Co-Investigator, Professor, Civil and Environmental Engineering |
| Chris Simpson | Co-Investigator, Assistant Professor, Environmental & Occupational Health Sciences |
| Ming Tsai | Post-Doctoral Researcher, Environmental & Occupational Health Sciences |
| Rob Crampton | Research Scientist, Environmental & Occupational Health Sciences |
| Maria Tchong-French | Research Scientist, Environmental & Occupational Health Sciences |
| Cole Fitzpatrick | Research Scientist, Environmental & Occupational Health Sciences |
| TBD | Research Scientist, Environmental & Occupational Health Sciences |
| ***Research Triangle Institute*** | |
| R. K. M. Jayanty | Senior Fellow in Environmental Analytical Chemistry |

| Name | Position |
|---|---|
| ***Eastern Research Group, Inc.*** | |
| Julie Swift | Senior Program Manager and Technical Director |
| ***EPA Region 10*** | |
| Keith Rose | Air Analyst |
| Chris Hall | Quality Assurance Analyst |

# 3 PROJECT ORGANIZATION

## 3.1 ROLES AND RESPONSIBILITIES

Federal, State, tribal and local agencies all have important roles in developing and implementing satisfactory air toxics monitoring programs. As part of the planning effort, EPA is responsible for setting national objectives, establishing methods for data gathering, and defining the quality of the data necessary to meet those objectives. State, tribal and local organizations are responsible for using this information to implement a quality system that will meet the data quality requirements. It is the responsibility of all the agencies to assess the quality of the data and to take corrective action when appropriate.

### *3.1.1 EPA Office of Air Quality Planning and Standards (OAQPS)*

The OAQPS is charged under the authority of the Clean Air Act (CAA) to protect and enhance the quality of the nation's air resources. OAQPS sets standards for pollutants considered harmful to public health or welfare and, in cooperation with EPA's Regional Offices and the States, enforces compliance with the standards through state implementation plans (SIPs) and regulations controlling emissions from stationary sources. With respect to Hazardous Air Pollutants the OAQPS:

- evaluates the need to regulate potential air pollutants and develops national standards;
- monitors national air quality trends and maintains a database of information on air pollution and controls;
- provides technical guidance and training;
- ensures that the methods and procedures used in making air pollution measurements are adequate to meet the programs objectives and that the resulting data are of satisfactory quality; and
- renders technical assistance to the EPA Regional Offices and air pollution monitoring community.

### *3.1.2 EPA Region 10 Office*

EPA Regional Offices have been developed to address environmental issues related to the states within their jurisdiction, and to administer and oversee regulatory and congressionally mandated programs. The major responsibilities of EPA's Region 10 Office, in regards to air toxics monitoring, are the coordination of monitoring projects and quality assurance matters with the State and local agencies. EPA Regional Project Officers are responsible for the technical aspects of the program including:

- reviewing Project Work Plans and Quality Assurance Project Plans;
- evaluating quality system performance; and
- acting as a liaison between EPA Headquarters and the State and local agencies by making available technical and quality assurance information.

### *3.1.3 Puget Sound Clean Air Agency (PSCAA)*

One major responsibility of PSCAA is the operation of an air quality monitoring program, which must include an appropriate quality assurance program. Ambient air quality data is used for multiple objectives, including:

- providing the people of Puget Sound with information about air contaminants;
- determining if ambient air standards are being met;
- assessing the effectiveness of emissions reduction programs; and
- identifying sources of pollution having significant impacts on public health and the environment.

Monitoring the air for toxic contaminants requires that a variety of specialists work together to define and accomplish the objectives specific to this task. The following information lists the responsibilities of each individual and is grouped by function of the Division related to Environmental Data Generation, Quality Assurance, Technical Support, and Program Support.

*AIR MONITORING DEPARTMENT*

The Air Monitoring Division is responsible for coordinating all aspects (quality assurance, data collection, and data processing) of the PSCAA Ambient Air Monitoring Program.

**Air Monitoring Manager**
The Administrator of the Air Monitoring Division has direct access to the Director on all matters relating to the Department's operation. The Administrator's duties include:

- ensuring that the QA requirements are implemented;
- maintaining overall responsibility for the monitoring network design and review; and
- reviewing budgets, contracts, grants and proposals.

**Air Monitoring Lead**
The Monitoring Lead reports to the Air Monitoring Manager and is responsible for coordinating the activities of the local-monitoring program. The Monitoring Lead's duties include:

- data collection, verification, and reporting, and
- evaluating the effectiveness of the network system.

**Quality Assurance Specialist**

The Quality Assurance Specialist has direct access to the Air Monitoring Manager on all matters relating to the Department's quality assurance and quality control activities. The Quality Assurance Specialist is responsible for verifying that division policies, programs, and procedures are implemented. The Quality Assurance Specialist has the independent ability to determine the validity of data collected based on this QAPP and the other referenced QAPPs and procedures.

**Air Monitoring Specialist**

The Air Monitoring Specialist reports to the Air Monitoring Manager and is responsible for maintenance and oversight of the PSCAA ambient air monitoring network, in addition to the quality assurance and submittal of the data collected to the Data Specialist.

**Data Specialist**

The Data Specialist reports to the Air Monitoring Manager and is responsible for review of the PSCAA ambient air monitoring network, in addition to the quality assurance and submittal of the data collected for the EPA AQS database.

*AIR RESOURCES DEPARTMENT*

**Air Resources Lead**

The Air Resources Lead reports to the Air Resources Manager and is responsible for operational oversight of the project's routine activities ensuring that milestones are being met and that required reports are generated and submitted promptly. As Operations Coordinator, along with the Air Monitoring Manager, the Lead will interact routinely with the University of Washington participants providing project guidance and support ensuring they are delivering expected products and showing required progress toward the successful outcome of the overall project.

### *3.1.4 Eastern Research Group, Inc. (ERG), Morrisville, NC*

**Program Manager**

The Program Manager's primary responsibility is ensuring client satisfaction by verifying that components of effective management are in place and active at all times during the contract performance period. The manager coordinates with the ERG Quality Assurance (QA) Officer, and task leaders to provide insight and communicate technical issues and needs, and to ensure that the program staff facilitates management decisions appropriate to their roles on the contract. The Program Manager prepares all budgetary and schedule information and is responsible for the technical operation of the program on a day-to-day basis. She leads the analytical task and provides technical direction and support. She assists in the resolution of technical issues and serves as a resource for Task Leaders regarding any project issues.

**Program Technical Adviser**

The Program Technical Adviser assists in the resolution of technical issues. He communicates with management, and the technical staff for discussion of real and potential technical problems.

**Program QA Officer**

The Program QA Officer is responsible for ensuring the overall integrity and quality of the project results. He reviews the ERG and PSCAA Quality Assurance Project Plans and coordinates data and laboratory audits that will provide information relative to data quality and determine whether procedures are in accordance with the QAPP. The lines of communication between management, the Program QA Officer, and the technical staff are formally established and allow for discussion of real and potential problems, preventive actions, and corrective procedures. At any time during the program, additional QA/QC measures may be initiated upon consultation between the Task Leaders, Program Managers, and Program QA Officer.

**Deputy Program QA Officer**

The Deputy Program QA Officer is responsible for ensuring the integrity and quality of results. The officer will do a QA review for all sample analyses delivered for reporting to the Program Manager and will work closely with the Program QA Officer to ensure the overall quality of the Program.

**Analytical Coordinator**

The Analytical Coordinators are responsible for ensuring that schedules for analysis of samples and delivery of the resulting data to the Program Manager are met.

**Task Leaders**

ERG Task Leaders are responsible for meeting the project objectives, meeting budgets and schedules, and directing the technical staff in execution of the technical effort for their respective task(s). The Task Leaders manage the day-to-day technical activities. They assess and report on the project's progress and results (e.g., recordkeeping, data validation procedures, sample turnaround time) and ensure timely, high-quality services and adherence to the project QA plan.

### *3.1.5 Research Triangle Institute International (RTI), RTP, NC*

**Services Program Manager**

The Services Program Manager maintains liaisons with the PSCAA, the RTI Delivery Order Project Officer (DOPO), and RTI QA Manager in the following ways:

- Written communications and e-mails to document planning and decisions
- Facilitating interaction among team personnel
- Ensuring that proper techniques and procedures are followed
- Ensuring that reporting requirements are satisfied
- Maintaining cost and schedule control
- Adjusting schedules to meet the needs of the client
- Reviewing and approving deliverables submitted to the client.

**Financial Services Program Coordinator**

The Financial Services Program Coordinator will be responsible for financial and other coordination of activities within RTI.

**QA Manager**

The QA Manager reports to the Services Program Manager and works closely with technical area supervisors and staff. The manager is responsible for monitoring all aspects of the QA/QC program, including following, updating, and enforcing the QAPP. The manager is administratively independent from the staff performing the project work and data generation. The QA Manager will also perform periodic in-lab and data review audits.

**Technical Area Supervisors**

Technical Area Supervisors are responsible for maintaining technical quality, data handling and transfer, and identifying and resolving technical problems. They are responsible for staff training and assessment. The supervisors report to the Services Program Manager and work closely with the QA Manager.

### *3.1.6 University of Washington, Seattle*

**Principle Investigator**

The Principle Investigator is responsible for all phases of the University of Washington's work plan, and for reporting results and coordinating effort with other investigators. This includes supervising data collection, QA practices and policies, and for resolving QA issues identified through PSCAA and the contract lab. Major QA related responsibilities of the Principle Investigator include:

- assuring that the University develops and maintains a current and relevant quality system, and
- assuring that the University develops and implements a QAPP for each data generating project.
- assuring that the University validates and stores the data according to the QAPP or any QAPPs generated by the University.

**Co-Investigator A**

The Co-Investigator A supervises the MIMS and levoglucosan measurements. The Co-Investigator is responsible for overseeing the MIMS procedure, QA process, and data handling. This also includes managing communications between the contract lab, the University, and PSCAA. Additionally, the procedure, QA process, and data handling for levoglucosan measurement are also supervised by the Co-Investigator A.

**Co-Investigator B**

The Co-Investigator B supervises the mobile monitoring. Data collected include: nephelometer, particle soot absorption photometer, total polycyclic aromatic hydrocarbon sampler, and GPS. All procedures, QA processes, and data handling for these methods are supervised by Co-Investigator B.

**Post-Doctoral Researcher**

The Post-Doctoral Researcher is responsible for aspects of data collection and analysis of the above methods and reports to the Principle Investigator.

**Research Scientist**
The Research Scientist is responsible for project management, creating and maintaining the GIS database, sampling logistics and sample collection and reports to the Principle Investigator.

**Research Assistant A**
The Research Assistant A reports to Co-Investigator A and is responsible for analysis of filter samples for levoglucosan. The Assistant is also responsible for following the QA procedures outlined for the method.

**Research Assistant B**
Research Assistant B reports to Co-Investigator B and is responsible for execution of the mobile monitoring in year one, and will be responsible for data analysis and source apportionment modeling in year 2. The Assistant is also responsible for following the QA procedures outlined for the methods.

## 3.2 SPECIAL TRAINING REQUIREMENTS/CERTIFICATION

Adequate education and training are critical to any monitoring program that strives for reliable and comparable data. Training is aimed at increasing the effectiveness of employees and the Department. Personnel assigned to ambient air toxics monitoring activities and for laboratory analysis activities will meet the educational, work experience, responsibility, personal attributes, and training requirements for their positions.

## 3.3 PROBLEM STATEMENT AND BACKGROUND

> ***Underlined** air toxics in this section are of top priority locally and/or nationally, and are included for study in this project.*

***Seattle and Tacoma Urban Areas***
The Environmental Protection Agency's (EPA) National Air Toxics Assessment (NATA) places the Seattle, Washington and Tacoma, Washington urban areas (in King and Pierce counties) in the top 5th percentile of the country for potential health (cancer) risk from air toxics.[1]

Seattle is home to a National Air Toxics Trend Site (NATTS) at Beacon Hill. In 2001, the Washington State Department of Ecology (Ecology) conducted toxics monitoring through an EPA grant at five additional sites in the Seattle urban area. These five additional monitoring sites were run for one year, and were located in a variety of areas to represent different source impacts. This monitoring, combined with receptor modeling performed on Beacon Hill speciation data, contributed to an air toxics evaluation for the Seattle area.[2] This evaluation, published by the Puget Sound Clean Air Agency and Ecology and partners, prioritized risk from diesel particulate matter and wood smoke, as well as priority urban area air toxics such as formaldehyde, hexavalent chromium, and benzene (polycyclic aromatic hydrocarbons (PAHs) were not included in this evaluation).

These same air toxics, as well as polycyclic organic matter (including PAHs) were identified in

EPA's 1999 NATA at elevated potential cancer risk for this area.[3] NATA did not include estimates for wood smoke particulate matter. Currently, the Agency continues to publish NATTS data from Seattle Beacon Hill in its annual data summary, and rank toxics according to potential cancer risk.[4,5] In the industrial Duwamish valley neighborhoods, there is a great deal of community interest in air toxics from the port and nearby industrial sources. The Agency partners with the local health department and community environmental justice groups in these areas.

The Tacoma urban area, connected to Seattle via the Interstate 5 corridor, is host to many of the same air toxics sources as the Seattle urban area, including a major port, an interstate corridor, some industry, and neighborhood woodstoves and fireplaces. Census tracts in the Tacoma area were among those ranked highest in the 1999 NATA for potential cancer risk of any census tracts in the Puget Sound area (King, Snohomish, Pierce, and Kitsap counties). Additionally, the monitor for the South End area of Tacoma indicates that the area is not in attainment under EPA's stricter daily $PM_{2.5}$ standards. Monitoring has shown that elevated $PM_{2.5}$ levels mainly occur during the heating months, when a main source of fine particulate is wood smoke. The Agency has taken the initiative to begin actively working with a neighborhood council in the South End neighborhood to address air quality issues, and has performed temporary monitoring (using integrating nephelometers) during the last heating season to determine the extent of elevated $PM_{2.5}$ levels. Most of the focus in the Tacoma area has been "criteria pollutant-centric" – no air toxics monitoring has yet been conducted in the Tacoma area. Community members in the Tacoma area have expressed interest in local air toxics monitoring.

Both Seattle and Tacoma have major ports predicted to have major expansion in the next decade, due largely to increased demand for goods from Asia. There is growing interest in marine diesel emissions, and the Agency and partners in the Puget Sound Maritime Air Forum recently completed a comprehensive marine inventory including ports of Seattle and Tacoma.[6]

### *Air Toxics – A mixture of Particulates and Vapor Phase Pollutants*

Air toxics encompass a diversity of chemicals, including both particulate and vapor phase components. Diesel exhaust and wood smoke are two of the highest priority sources of air toxics in Region 10 and nationally. Both of these sources emit complex chemical mixtures including both particulate and vapor phase air toxics. This project is unique in that it will address both components of air toxics, for a more comprehensive understanding of the concentrations and variability of these sources and toxics.

Diesel exhaust, and specifically <u>diesel particulate matter</u>, is considered a top air toxic of concern in the Puget Sound area, with over 75% of the potential cancer risk from air toxics attributed to DPM.[2] Resource-intensive receptor modeling based on fine particulate speciation data is considered the "gold standard" to estimate DPM concentrations. In addition, continuous methods measuring black carbon, related to elemental carbon, are used to inform on the scale and variation of DPM. While these continuous measurements are not specific to diesel, data collected in this study can be used for future analysis of DPM.

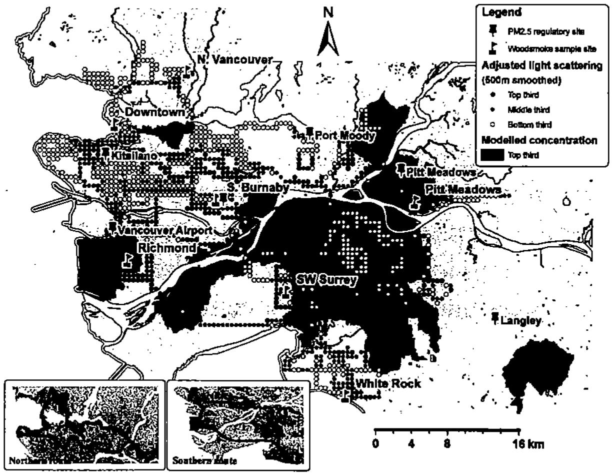
Diesel exhaust has been shown to present health risk and is classified as a probable human carcinogen (classified 2A by IARC). [7,8] The California Air Resources Board has established a quantitative risk factor based on the particulate matter portion of diesel exhaust.[9] The gases contained in diesel exhaust are also listed as priority air toxics by EPA. These include but are not limited to: PAHs, benzene, formaldehyde, and acrolein.[10]

Wood smoke, known to present health risk, was recently assessed as a category 2A carcinogen by the International Agency for Research on Cancer (IARC).[11] As with diesel exhaust, wood smoke has both a particulate component demonstrated to present health risk, as well as several vapor phase air toxics. These include but are not limited to: PAHs, benzene, formaldehyde, acetaldehyde, 1,3-butadiene, and acrolein.[12,13]

Several useful metrics have been established to estimate wood smoke. These metrics are much less labor and resource intensive than the gold standard of receptor modeling with fine particulate speciation data. Levoglucosan and methoxyphenols are two of these metrics. Levoglucosan, an anhydrous sugar derived from the pyrolysis of the major wood polymer cellulose, is one of the most abundant organic compounds associated with particles in wood smoke.[14,15] It is stable in the environment and has been used extensively to estimate wood smoke levels in ambient particulate matter (PM) samples.[16,17] Methoxyphenols are derived from the pyrolysis of the wood polymer lignin – their presence in atmospheric samples is a unique tracer for biomass combustion. Guaiacol is the simplest and most abundant of the methoxyphenols in wood smoke, and it exists almost exclusively in the vapor phase.[18] Several methoxyphenols have been used in source attribution models to determine the contribution of wood smoke to ambient PM.[19]

### *Spatial Variability of Air Toxics*

**Figure 3-1. Regions of High, Medium, and Low Wood Smoke in British Columbia**



A number of recent studies have shown that there can be substantial spatial variability of selected air pollutants within urban areas.[20,21,22,23,24] These findings have important implications for the design and interpretation of epidemiological analyses and for air quality management.[25,26,27,28,29,30]

A better understanding of the neighborhood scale spatial variability in urban wintertime wood smoke will aid in the interpretation of the resulting measurements and emissions reduction strategies. Likewise, a better understanding of variability in summertime vehicle pollutants will similarly aid in prioritizing areas for emissions reductions.

The University of Washington in collaboration with the University of British Columbia recently used a combination of mobile and fixed-location monitoring to collect a set of spatially resolved fine particle mass and levoglucosan measurements in Vancouver and Victoria, British Columbia.[31] These measurements were incorporated into a geographic information systems (GIS)-based model framework in order to identify sub-regions of 20-to-50 square kilometers within an urban area that are categorized as having high, medium or low wood smoke (see Figure 1). The overall approach resulted in the ability to identify the location of elevated, persistent night-time levels of fine particles that are consistent with the presence of wood smoke and that are not captured by a relatively dense regulatory ambient monitoring network.

## 3.4 PROJECT DESCRIPTION

The main project objectives are:

1. Determine base-line (fixed site) air toxics concentrations for the Tacoma area and provide select sites in the Seattle area for comparison.
2. Characterize seasonal spatial patterns of key air toxics.
3. Determine health risks from exposure to air toxics, and communicate them clearly to the community.

**Objective 1.** Determine base-line air toxics concentrations for the Tacoma area and provide select sites in the Seattle area for comparison. Seattle sites will complement the NATTS site at Beacon Hill and will also build on the pilot study conducted in 2001 as part of an EPA air toxics community grant. Concentrations at Seattle sites will be compared to Tacoma sites to inform intra-city variability. The Agency will monitor at up to four fixed sites, potentially including:

1. South End Tacoma site – This site has $PM_{2.5}$ concentrations that will likely violate EPA's new, stricter $PM_{2.5}$ daily standard, and is representative of a "maximum concentration urban wood smoke" site in our 4-county jurisdiction. This site is situated in an area with an active neighborhood council concerned about air quality. We will leverage speciated trends network (STN) speciation data currently being collected at this site.
2. Port of Tacoma site – This site will be representative of port impacts as well as community impact. The Agency may consider conducting $PM_{2.5}$ speciation sampling at this site to better understand the composition and sources of $PM_{2.5}$.
3. Tacoma neighborhood scale site – The Agency will identify a third air toxics monitoring site in the Tacoma area. This site will be situated in an area near several high volume arterials and with high population density, and will ideally be placed in an environmental justice community.
4. Port of Seattle/Urban industrial site – This site will be impacted by both the Port of Seattle, as well as industry. The Agency will leverage the existing Duwamish site, which currently has STN speciation data. This site is located in the Duwamish valley, near the South Park and Georgetown environmental justice community. This Agency has a relationship with this community who is very involved in air quality concerns. In addition, this site is very close to the Georgetown 2001 pilot study site.

Table 3-1 summarizes a few of the air toxics the Agency proposes to monitor at up to four sites throughout the Tacoma and Seattle area. Fixed site monitoring will be conducted at each site at a sampling frequency of 1 in 6 days, for one year. This list will likely include more compounds than listed.

**Table 3-1. Some of the proposed air toxics at fixed sites**

| Air Toxic | Method | 3. Tacoma Neighborhood | 1. Tacoma South End<br>2. Tacoma Port<br>4. Seattle Port/Industrial |
|---|---|---|---|
| Benzene | TO-15 | X | X |
| 1,3-Butadiene | TO-15 | X | X |
| Carbon Tetrachloride | TO-15 | X | X |
| Chloroform | TO-15 | X | X |
| Dichloromethane | TO-15 | X | X |
| 1,2-Dichloropropane | TO-15 | X | X |
| Tetrachloroethylene | TO-15 | X | X |
| Trichloroethene | TO-15 | X | X |
| PAHs | TO-13A | | X |
| Acetaldehyde | TO-11A | X | X |
| Formaldehyde | TO-11A | X | X |

In the interest of maximizing resources, the Agency will not measure air toxic metals at these four sites. Instead, the Agency will leverage the $PM_{2.5}$ metals data that are already collected at STN sites at the Tacoma South End (1), Seattle Port/Industrial (4), and Seattle roadway (5) sites. Although air toxics and STN metals data are different particle sizes (<10 and <2.5 $\mu$m) and represent different analytical techniques, our comparison of the two at Beacon Hill reflects the differences to be inconsequential. In the Seattle and Tacoma urban areas, $PM_{10}$ levels are typically very low, so one would expect $PM_{10}$ metals to be roughly equivalent to $PM_{2.5}$ levels. In addition, in our area, metals do not drive risk, with the exception of hexavalent chromium. Hexavalent chromium is an air toxic of concern in our area, but is not addressed in this current project largely due to uncertainty in the reliability of existing monitoring and analysis methods.

The Agency proposes to monitor PAHs at only three sites in the interest of conserving resources. These three sites include the South End Tacoma site and the two sites located near ports (sites 1, 2, and 4 in Table 3-1). Presumably, these will be most impacted by wood smoke and diesel emissions, both primary sources of PAHs.

For fixed site monitoring, the Agency will send samples for analysis at an EPA-approved contract lab, such as Eastern Research Group.

The Agency will conduct meteorology measurements at most of the sites: wind speed, wind direction, temperature, humidity. The Agency will also conduct $PM_{2.5}$ and black carbon (aethalometer) measurements at all sites.

The Agency will leverage resources available to them, rather than purchasing new monitoring equipment. For example, the Washington State Department of Ecology can provide equipment as available, which may include: canister samplers for VOCs, carbonyl samplers and cans, and samplers for PAHs. In addition, the University of Washington has agreed to provide canisters for VOC samples, as available.

**Objective 2.** Characterize seasonal spatial patterns of key air toxics. The Agency and partners will collect monitoring information that better informs how wood smoke concentrations and diesel exhaust, and the air toxics associated with them (PAHs, volatile organic compounds

[VOCs]), vary spatially across and within neighborhoods. This monitoring will be conducted seasonally with a "tiered approach."

Previous experience in Seattle and Vancouver using mobile light scattering measurements have proved successful in identifying elevated nighttime levels of fine particles in certain residential areas not captured by traditional fixed-site regulatory monitors.[32,33] and in identifying "hot spots" of particulate black carbon during evening rush hour in the summertime.[34] We will be employing these same methods and complementing them with additional air toxics measurements.

**Table 3-2. Measurements to characterize community-wide spatial variation in ambient concentrations of wood smoke and diesel exhaust associated air toxics**

| Tier | Activity Description | Instruments Used (measurements collected) | Frequency |
|---|---|---|---|
| 1 | "Preliminary identification" via mobile monitoring to identify air pollution "hotspots" | Nephelometer (PM); PSAP (black carbon); EcoChem (particle bound PAHs); GPS | Up to 20 nights/ season (heating & non-heating) |
| 2 | Intensive continuous measurements of HAPs at approximately 3 "hotspots" identified in Tier 1 | Nephelometer (PM); PSAP (black carbon); EcoChem (particle bound PAHs); MIMS (guaiacol; BTEX); GPS | Up to 2 weeks/ season |
| 3 | 24-hr fixed site measurements at selected "hotspots" to validate continuous data and to compare with community monitors | Filters ($PM_{2.5}$, levoglucosan); sorbent tubes (aldehydes); summa canisters (BTEX, other VOCs) | Up to 10 days/ season |

***Sampling plan overview***

Monitoring will be conducted, at a minimum, in the neighborhoods surrounding the three fixed air toxics sites in Tacoma. These are neighborhoods that will potentially be designated non-attainment under EPA's new $PM_{2.5}$ daily standard, and have previously not been monitored for air toxics. Where resources allow, we will include the Seattle air toxics sites. Monitoring will be conducted in each of two seasons (heating, non-heating).

Tier 1 and 2 monitoring will be conducted during periods of poor ventilation using meteorological data to forecast these periods, and are thus dependent on meteorology. For wood smoke, winter monitoring will be performed on cold, calm winter evenings at times when wood burning is expected to be relatively high and traffic is at a minimum. For diesel exhaust, monitoring periods will favor daytime afternoon traffic peaks when the daytime mixing depths are relatively constant.

### Tier 1 – Preliminary identification mobile monitoring

Tier 1 "qualitative" monitoring will involve a continuously moving platform and will provide a highly spatially resolved map of a relatively limited number of pollution measures within each neighborhood (within 10 km of the community monitoring site). As in our previous studies, the instrumentation will be placed inside a vehicle and connected to a sampling manifold inlet placed out an otherwise sealed window. A field log will record any close encounters with heavy-duty diesel vehicles that would otherwise cause excessively high spikes in the data record. Sampling instruments will include:

- A nephelometer (Radiance Research M903, Seattle, WA.), equipped with a small air blower and air pre-heater and the averaging time set at 15 seconds.
- A GPS receiver logging position every 5 seconds.
- A particle soot absorption photometer (this instrument has been shown to be successful in a moving vehicle/resistant to vibration interference).
- An EcoChem PAS 2000 instrument set at a 15 second averaging time for PAHs.

The neighborhood sampling routes will be established prior to sampling and traversed in either a clockwise or counterclockwise direction on any given evening as determined randomly. These routes will be established based on neighborhood characteristics such as location of major roads and populated areas and census tract level wood smoke use surveys, as well as air quality monitoring the Agency has recently conducted in the Tacoma area. Routes will be constrained based on the time it takes to traverse them. Temporal adjustments of night-to-night variations in measured concentrations will likely be necessary. For this reason, we will site a nephelometer and an aethalometer at the appropriate fixed air quality monitoring site during the nightly traverses. These fixed-site measurements should sufficiently control for temporal variation and allow us to composite the mobile measurements over time.

Refer to the Mobile Monitoring QAPPs to find the respective measures taken to ensure quality of analysis.

***Tier 2 – Intensive continuous samples***

Tier 2 quantitative monitoring will be done at five to seven "Tier 2 satellite" locations surrounding each of the three air toxics sites in Tacoma. These locations will be identified by Tier 1 measurements as being consistently higher, lower or similar in magnitude to the corresponding Tier 1 values at the community monitoring site locations. These Tier 2 satellite sites will be visited for 15 to 30 minutes each during a given sampling day. The mobile platform will move from one of these locations back to the community monitoring site to sample for a similar length of time prior to moving to the next Tier 2 satellite site. In this way, we will tightly control for variations over time that could otherwise confuse our understanding of the spatial variability across sites.

We anticipate completing two sets of measurements at each satellite location in a single evening. The Tier 2 studies will use the sample equipment used for the Tier 1 characterization [Nephelometer (PM); PSAP (black carbon); EcoChem (particle bound PAHs)], with the addition of an MIMS system. The MIMS instrument will provide simultaneous measurement of guaiacol (a wood smoke specific VOC), BTEX and other selected VOCs, with 10-15 minute resolution, as described below.

***Membrane introduction mass spectrometry (MIMS):***

Membrane introduction mass spectrometry (MIMS) has been used for over 25 years as a direct sampling interface for mass spectrometry. Over the last decade, its use for volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in air has been well documented.[35]

A coaxially heated MIMS system, operated in the pulsed heating mode, provides temporally resolved measurements in the parts-per-billion to parts-per trillion ranges every 15 minutes for a variety of toxicologically important VOCs and SVOCs. This MIMS system can be located at a fixed site (e.g., a speciation or air quality monitoring site), or it can be mounted on a mobile platform and used to measure VOC and SVOC levels in transects through an air shed. MIMS data are shown below in Figure 2 for VOCs as part of a study in British Columbia. Figure 3 shows MIMS data for both VOCs and methoxyphenols.

***Tier 3 – Fixed site filter sampling for $PM_{2.5}$, levoglucosan, aldehydes and selected VOCs***
Tier 3 monitoring will involve establishing and operating fixed "Tier 3 satellite" sites at two locations near the South End Tacoma site (site 1 in Table 1) and two locations near the Port of Tacoma site (site 2). The Tier 3 satellite site locations will be chosen based on the Tier 2 results such that one site is co-located with the fixed monitor and at a site with higher air toxics concentrations. In the unlikely case that no gradients are seen at a site, then the Agency and partners will not conduct Tier 3 sampling at that location.

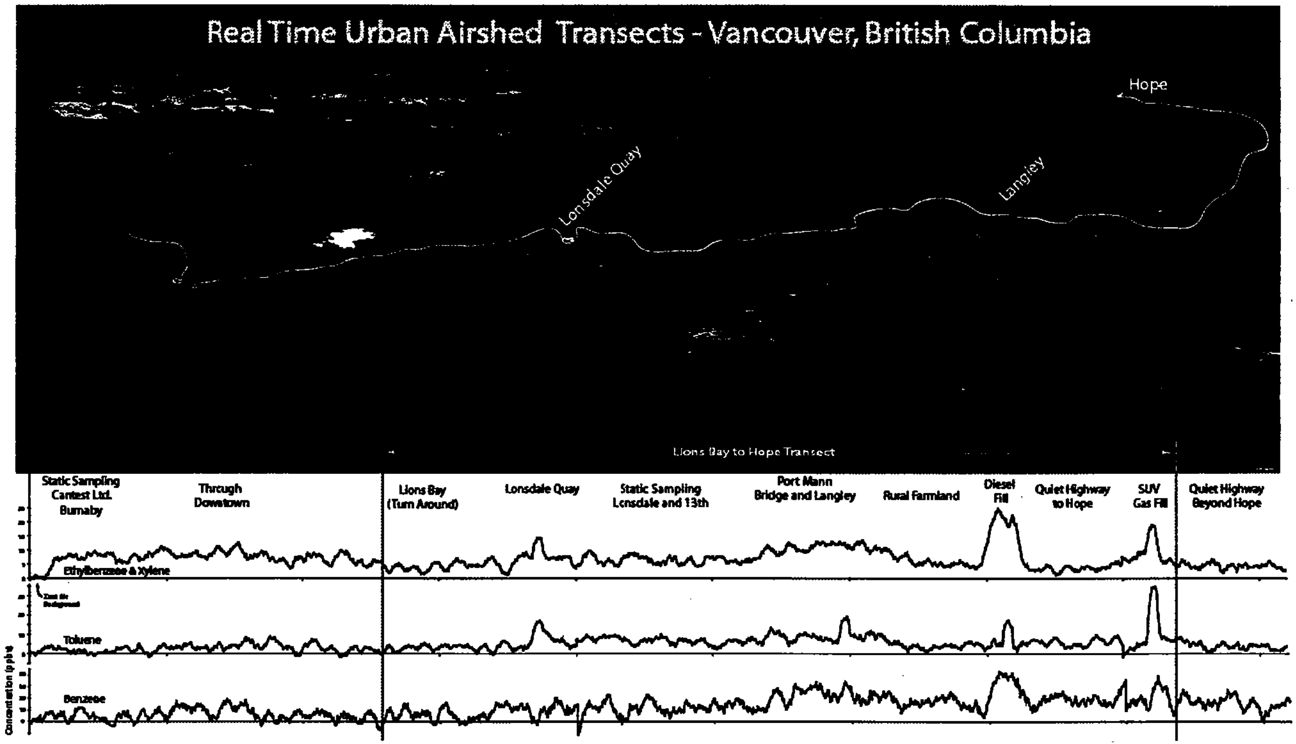
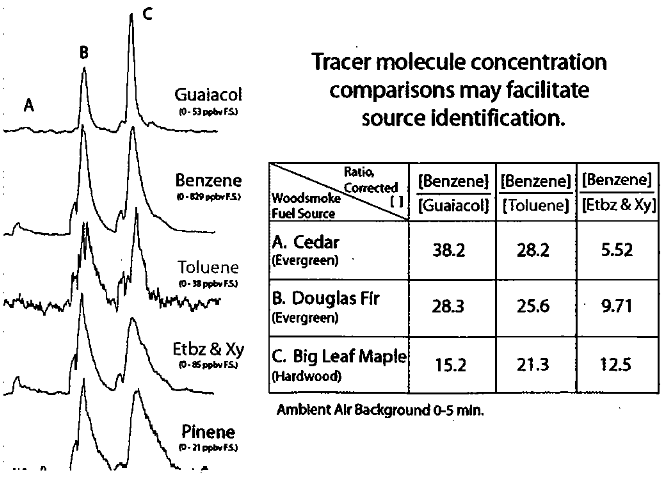


**Figure 3-2. Urban Airshed Transects from British Columbia using MIMS**



Tracer molecule concentration comparisons may facilitate source identification.

| Woodsmoke Fuel Source / Ratio, Corrected [ ] | [Benzene] / [Guaiacol] | [Benzene] / [Toluene] | [Benzene] / [Etbz & Xy] |
|---|---|---|---|
| A. Cedar (Evergreen) | 38.2 | 28.2 | 5.52 |
| B. Douglas Fir (Evergreen) | 28.3 | 25.6 | 9.71 |
| C. Big Leaf Maple (Hardwood) | 15.2 | 21.3 | 12.5 |

Ambient Air Background 0-5 min.

**Figure 3-3. MIMS Data**

The Tier 3 satellite monitors will be operated for approximately 10 days in each of the two sampling seasons at times when the community sites are also sampling. Samples will include Teflon filters for measurement of $PM_{2.5}$, and levoglucosan (wood smoke tracer); sorbent tubes for measurement of aldehydes (formaldehyde, acetaldehyde) and summa canisters for measurement of BTEX and other VOCs. These time-integrated samples will also be sent to the same EPA-approved contract lab as the fixed site samples. For each measured species, the relative ranking of each site's average concentration compared with the community monitor will be compared with that derived from the measurements taken with the mobile MIMS platform. Refer to the MIMS QAPP for more on the method and quality assurance methods.

***Spatial characterization of air toxics concentrations and identifying areas of peak concentrations for top air toxics of concern will contribute to the most effectively targeted emissions reductions.***

**Objective 3.** Determine health risks from exposure to air toxics, and communicate them clearly to the community. The Agency and partners will use annual ambient air toxic statistics to estimate potential health risk. These will be summarized and communicated in a report to the community.

**Data Analysis.** Fixed site monitoring data will be statistically summarized, with any outliers flagged/addressed. Potential cancer risk estimates will be generated from annual concentrations at fixed sites. Additional non-cancer risk reference concentrations will also be compared to ambient concentrations.

**Air toxics evaluation.** The Agency and partners will publish an air toxics evaluation following conclusion of monitoring. The report will include both quantitative and qualitative components to describe the results of fixed site and mobile monitoring. The evaluation will help the Agency to communicate air toxics risk to the community and prioritize air toxics for reduction. The evaluation will include, at a minimum:

- A statistical summary of fixed site monitors. The Beacon Hill NATTS site data for the same time period will also be included in the summary.
- A complete description of the fixed sites, including what scale they represent, what sources they're likely impacted by, meteorology, topography, land use, demographics, etc.
- A potential cancer risk ranking of air toxics at fixed monitors.
- A screening and discussion of non-cancer health risks.
- A discussion/comparison of fixed sites, both inter- and intra-city.
- A comprehensive discussion of the spatial variation of air toxics near fixed monitors (a summary of Objective 2).
- Correlations of the fine scale spatial variations of several air toxics with fine particulate and particle bound wood smoke tracers (levoglucosan and guaiacol).
- GIS-based displays of concentrations overlaid with relevant demographic information.
- Results of this evaluation will influence areas that the Agency targets for wood smoke/air toxics reductions. Also, results of this mobile monitoring will be shared with the community to help highlight the health risks associated with wood smoke.

- The Agency is well-positioned with community groups and local health departments in both the Tacoma and south Seattle (Duwamish) area, and will perform outreach and education to share results of this report.

## 3.5 PROJECT SCHEDULE

All tasks are dependent upon funding availability in November 2008. Because the mobile sampling has a strong seasonal component, any change to the funding award date may significantly change the Tier 1, 2, and 3 sampling schedule.

**Table 3-3. Tasks, deliverables, responsible parties, and timelines**

| Task | Deliverable | Responsible Party/ Accountable Party | Timeline |
|---|---|---|---|
| EPA awards grant and funding | Region makes funding available | EPA | November 2008 |
| Quarterly progress reports to EPA | Quarterly report | Puget Sound Clean Air Agency(PSCAA) | Quarterly – to be established |
| Complete, submit quality assurance (QA) plan for mobile monitoring | QA plan | University of Washington (UW) | November 2008 |
| Complete and submit data quality objectives (DQOs) | Data quality objectives | PSCAA/UW | November 2008 |
| Determine mobile monitoring routes, begin Tier 1 sampling | Memo with rationale | UW/PSCAA | November/December 2008 |
| Finalize fixed site monitor locations, set up monitoring logistics | Memo with rationale | PSCAA/UW | December 2008 |
| Fixed site sampling (5 sites) | All data uploaded to AQS | PSCAA/UW/EPA contract lab | Monitoring: approx. October 2008- October 2009. AQS data will be uploaded within 4 months after conclusion of monitoring |
| Tier 2 mobile sampling | Data collection and analysis completed | PSCAA/UW | Winter 2008 and 2009, Summer 2009 and 2010 |
| Tier 3 mobile sampling | Data collection and analysis completed | PSCAA/UW/EPA contract lab | Winter 2008 and 2009, Summer 2009 and 2010 |
| Draft air toxics evaluation | Draft air toxics evaluation | PSCAA/UW | 5 months after data collected |
| Final air toxics evaluation | Final air toxics evaluation | PSCAA/UW | 2 months after draft |
| Community outreach – | Outreach events/ | PSCAA | Summer/fall 2010 |

| | | | |
|---|---|---|---|
| results and recommendations from air toxics evaluation | community feedback | | |
| Final report to EPA | Final report | PSCAA | <90 days after end of project |
| Presentation at EPA national monitoring conference | Presentation | PSCAA/UW | To be determined |

## 3.6 LIST OF PARAMETERS MEASURED

The list of parameters to be monitored and the methods of analysis for the proposed program are listed in Table 3-4. All valid samples will be analyzed and compounds beyond the core group will be reported.

**Table 3-4. List of Hazardous Air Pollutants to be Measured and Reported**

| Substance | Method | Equipment |
|---|---|---|
| **Volatile Organic Compounds** | | |
| 1,1,1-Trichloroethane | TO-15 | XonTech 910PC |
| 1,1,2,2-Tetrachloroethane | | |
| 1,1,2-Trichloroethane | | |
| 1,1-Dichloroethane | | |
| 1,1-Dichloroethene | | |
| 1,2,4-Trichlorobenzene | | |
| 1,2,4-Trimethylbenzene | | |
| 1,2-Dibromo-3-Chloropropane | | |
| 1,2-Dibromoethane | | |
| 1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114) | | |
| 1,2-Dichlorobenzene | | |
| 1,2-Dichloroethane | | |
| 1,2-Dichloropropane | | |
| 1,3,5-Trimethylbenzene | | |
| 1,3-Butadiene | | |
| 1,3-Dichlorobenzene | | |
| 1,4-Dichlorobenzene | | |
| 1,4-Dioxane | | |
| 2-Butanone (MEK) | | |
| 2-Hexanone | | |
| 4-Ethyltoluene | | |
| 4-Methyl-2-pentanone | | |
| Acetone | | |
| Acetonitrile | | |

| | | |
|---|---|---|
| Acrolein | | |
| Acrylonitrile | | |
| Allyl Chloride | | |
| alpha-Pinene | | |
| Benzene | | |
| Benzyl Chloride | | |
| Bromodichloromethane | | |
| Bromoform | | |
| Bromomethane | | |
| Carbon Disulfide | | |
| Carbon Tetrachloride | | |
| Chlorobenzene | | |
| Chloroethane | | |
| Chloroform | | |
| Chloromethane | | |
| cis-1,2-Dichloroethene | | |
| cis-1,3-Dichloropropene | | |
| Cumene | | |
| Dibromochloromethane | | |
| Dichlorodifluoromethane (CFC 12) | | |
| d-Limonene | | |
| Ethanol | | |
| Ethylbenzene | | |
| Hexachlorobutadiene | | |
| Isopropyl Alcohol | | |
| m,p-Xylenes | | |
| Methyl tert-Butyl Ether | | |
| Methylene Chloride | | |
| Naphthalene | | |
| n-Butyl Acetate | | |
| n-Hexane | | |
| n-Nonane | | |
| o-Xylene | | |
| Styrene | | |
| Tetrachloroethene | | |
| Toluene | | |
| trans-1,2-Dichloroethene | | |
| trans-1,3-Dichloropropene | | |
| Trichloroethene | | |
| Trichlorofluoromethane | | |
| Trichlorotrifluoroethane | | |
| Vinyl Acetate | | |
| Vinyl Chloride | | |

| | | |
|---|---|---|
| **Aldehydes (Carbonyls)** | | |
| 2,5-Dimethylbenzaldehyde | TO-11A | XonTech 925 |
| Acetaldehyde | | |
| Acetone | | |
| Benzaldehyde | | |
| Butyraldehyde | | |
| Crotonaldehyde | | |
| Formaldehyde | | |
| Hexanaldehyde | | |
| Isovaleraldehyde | | |
| Methyl ethyl ketone | | |
| m-Tolualdehyde | | |
| o-Tolualdehyde | | |
| p-Tolualdehyde | | |
| Propionaldehyde | | |
| Valeraldehyde | | |
| **Polycyclic Aromatic Hydrocarbons** | | |
| Acenaphthene | TO-13A | Tisch Environmental TE-1000 PUF Sampler |
| Acenaphthylene | | |
| Anthracene | | |
| Benzo(b)fluoranthene | | |
| Benz(a)anthracene | | |
| Benzo(a)pyrene | | |
| Benzo(e)pyrene | | |
| Benzo(g,h,i)perylene | | |
| Benzo(k)fluoranthene | | |
| Chrysene | | |
| Coronene | | |
| Dibenz(a,h)anthracene | | |
| Fluoranthene | | |
| Fluorene | | |
| Indeno(1,2,3-cd)pyrene | | |
| Naphthalene | | |
| Phenanthrene | | |
| Pyrene | | |
| Perylene | | |
| **Miscellaneous** | | |
| BTEX and other VOCs | MIMS | |
| Levoglucosan | Aqueous Extraction, GC/MS | |
| Total PAHs | EcoChem PAS 2000 PAH Monitor | |
| Soot | Particle Soot Absorption Photometer | |
| $PM_{2.5}$ | Nephelometer, TEOM, Federal Reference Method | |

| | | |
|---|---|---|
| Black Carbon Channel | McGee Aethalometer | |
| UV Channel | | |
| Relative Humidity | EPA Air Quality QA Handbook Volume IV: Meteorological Measurement | Met One 083D |
| Ambient Temperature | | |
| Ambient Pressure | | Met One 092, R&P TEOM |
| Wind Direction | | RM Young 85004 |
| Wind Speed | | |
| **$PM_{2.5}$ Speciation** | | |
| Ammonium Ion | Speciation Trends Network (STN) Sampling | Met One SASS or SuperSASS |
| Antimony | | |
| Arsenic | | |
| Aluminum | | |
| Barium | | |
| Bromine | | |
| Cadmium | | |
| Calcium | | |
| Chromium | | |
| Cobalt | | |
| Chlorine | | |
| Cerium | | |
| Cesium | | |
| Europium | | |
| Gallium | | |
| Gold | | |
| Indium | | |
| Iridium | | |
| Iron | | |
| Hafnium | | |
| Lanthanum | | |
| Lead | | |
| Manganese | | |
| Magnesium | | |
| Mercury | | |
| Molybdenum | | |
| Nickel | | |
| Niobium | | |
| Phosphorus | | |
| Potassium | | |
| Potassium Ion | | |
| Rubidium | | |
| Samarium | | |
| Scandium | | |
| Selenium | | |

| | | |
|---|---|---|
| Silicon | | |
| Silver | | |
| Sodium | | |
| Sodium Ion | | |
| Strontium | | |
| Tantalum | | |
| Terbium | | |
| Tin | | |
| Titanium | | |
| Vanadium | | |
| Wolfram | | |
| Yttrium | | |
| Zirconium | | |
| Crustal | | |
| Nitrate | | |
| Volatile Nitrate | | |
| Non-volatile Nitrate | | |
| Sulfate | | |
| **Carbonaceous $PM_{2.5}$** | | |
| Elemental Carbon Fraction 1 | Speciation Trends Network (STN) Sampling | URG 3000N |
| Elemental Carbon 2 | | |
| Elemental Carbon 3 | | |
| Organic Carbon Fraction 1 | | |
| Organic Carbon 2 | | |
| Organic Carbon 3 | | |
| Organic Carbon 4 | | |
| Pyrolyzed Organic Carbon | | |

## 3.7 QUALITY OBJECTIVES AND CRITERIA

It is the policy of PSCAA that air toxics data generated for internal and external use shall meet specific qualitative and quantitative requirements, referred to as Quality Objectives. The process used to determine these objectives is performed in accordance to the guidelines stated in the "EPA Quality Manual for Environmental Programs". The process is also detailed in US-EPA's "Guidance on Systematic Planning Using the Data Quality Objectives Process", EPA QA/G-4.

The Quality Objectives are used to develop a resource-effective data collection design. It provides a systematic procedure for defining the criteria that a data collection design should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision errors for the study, and how many samples to collect. By using such a process, the PSCAA will help to assure that the type, quantity, and quality of environmental data used in decision making will be appropriate for the decisions to be made.

This QAPP focuses on the role of ambient measurement data as one key element of the full air toxics assessment process. Currently, PSCAA does not have sufficient amount of data to define the spatial and temporal characteristics of the monitoring area at a neighborhood scale.

## 3.8 DATA QUALITY INDICATORS

Data Quality Indicators (DQIs) are established so that data can be evaluated and controlled to ensure that it is maintained within the established acceptance criteria. DQIs are established to evaluate and control various phases (sampling, preparation, and analysis) of the measurement process to ensure that total measurement uncertainty is within the range prescribed.

**Precision** - a measure of mutual agreement among individual measurements of the same property usually under prescribed similar conditions. This is the random component of error. Precision is estimated by various statistical techniques using some limit of the standard deviation.

**Bias** - the systematic or persistent distortion of a measurement process which causes error in one direction. Bias will be determined by estimating the positive and negative deviation from the true value as a percentage of the true value.

**Representativeness** - a measure of the degree which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

**Detectability** - a determination of the lowest concentration value (Minimum Detectable Limit) that a method-specific analysis can reliably discern.

**Completeness** - a measure of the amount of valid data obtained from a measurement system compared to the expected total.

Quality Control procedures are used to maintain the measurement systems within prescribed limits of acceptability, and Quality Assurance procedures assess whether these systems have achieved the desired DQIs shown in Table 3-5.

**Table 3-5. Data Quality Indicators**

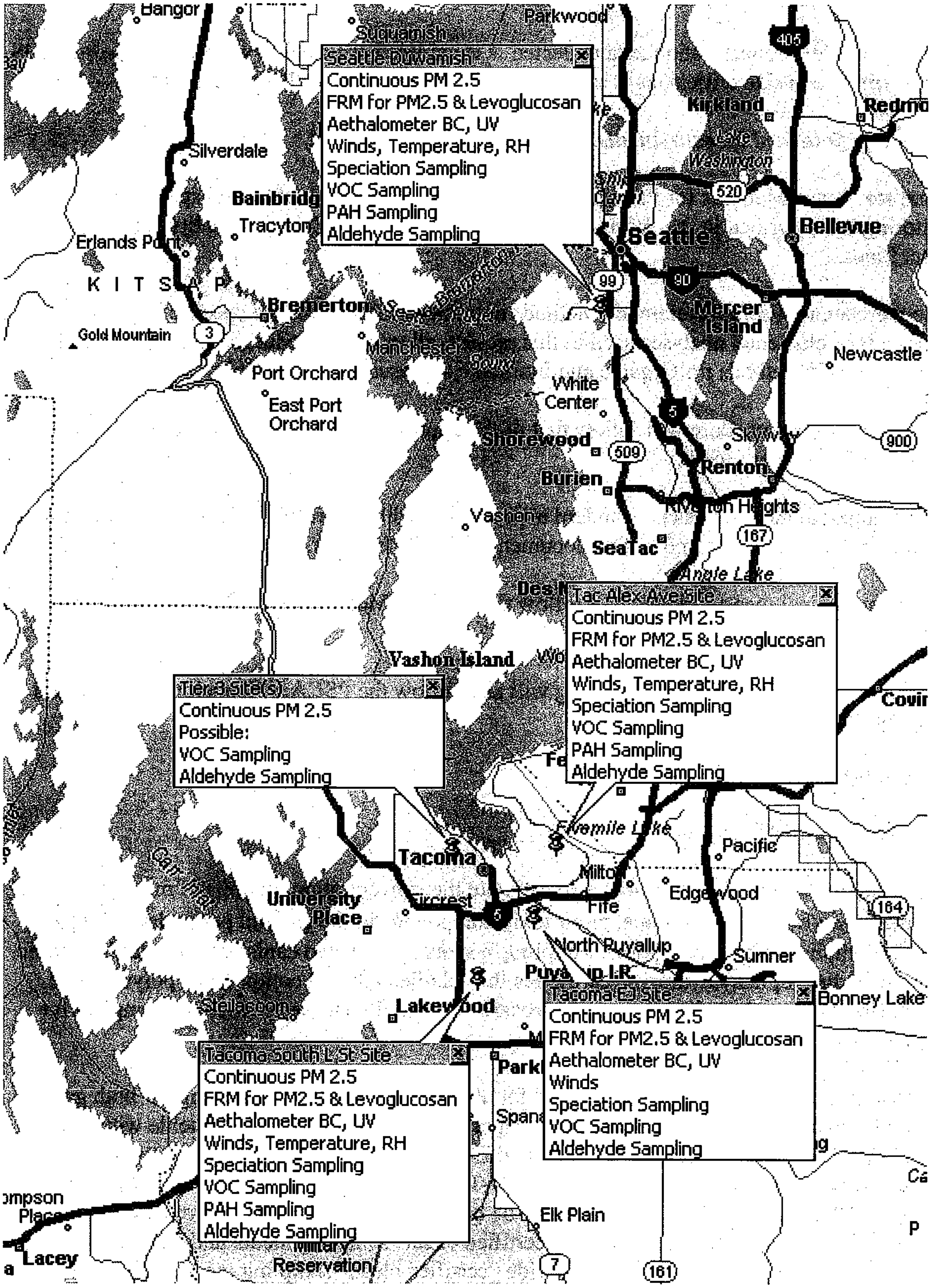
| Parameter | Reporting Units | Precision (CV) (Duplicate Samples) | Accuracy (Replicate Samples) | Representativeness | Comparability (Method Selection) | Completeness | Minimum Detection Limits (ug/m$^3$) |
|---|---|---|---|---|---|---|---|
| Speciation | $\mu g/m^3$ | 50% XRF<br>10% IC<br>15% FID<br>>10*MDL | 10% XRF<br>15% IC<br>15% FID<br>>10*MDL | Urban<br>Neighborhood<br>Middle | XRF, IC, FID | >75% | 0.01 - 0.001 |
| Aldehydes (Carbonyls) | $\mu g/m^3$ | 20% | ± 10% | Urban<br>Neighborhood<br>Middle | Liquid Chromatography | >75% | 0.02 - 0.07 |
| Volatile Organic Compounds | ppbv | 20% | ± 10% | Urban<br>Neighborhood<br>Middle | Gas Chromatography - Mass Spectrometry | >75% | 0.1 – 1.0 |
| Polycyclic Aromatic Hydrocarbons | $\mu g/m^3$ | 30% | ± 30% | Urban<br>Neighborhood<br>Middle | Gas Chromatography - Mass Spectrometry | >75% | 0.01 – 0.1 |
| Black Carbon and UV Channels | $\mu g/m^3$ | 10% | – | Urban<br>Neighborhood<br>Middle | Aethalometer | >75% | 1.0 |

# 4 AMBIENT AIR DATA COLLECTION

## 4.1 SAMPLING DESIGN

The purpose of this Section is to describe all of the relevant components of the monitoring network. This includes: the frequency of sampling; the types of samplers used at each site; the laboratory support provided to sampling; and the frequency and scope of sampler performance evaluations.

**Figure 4-1. Planned monitoring sites with their respective measured parameters**



Seattle Duwamish
- Continuous PM 2.5
- FRM for PM2.5 & Levoglucosan
- Aethalometer BC, UV
- Winds, Temperature, RH
- Speciation Sampling
- VOC Sampling
- PAH Sampling
- Aldehyde Sampling

Tac Alex Ave Site
- Continuous PM 2.5
- FRM for PM2.5 & Levoglucosan
- Aethalometer BC, UV
- Winds, Temperature, RH
- Speciation Sampling
- VOC Sampling
- PAH Sampling
- Aldehyde Sampling

Tier 3 Site(s)
- Continuous PM 2.5
- Possible:
- VOC Sampling
- Aldehyde Sampling

Tacoma EJ Site
- Continuous PM 2.5
- FRM for PM2.5 & Levoglucosan
- Aethalometer BC, UV
- Winds
- Speciation Sampling
- VOC Sampling
- Aldehyde Sampling

Tacoma South L St Site
- Continuous PM 2.5
- FRM for PM2.5 & Levoglucosan
- Aethalometer BC, UV
- Winds, Temperature, RH
- Speciation Sampling
- VOC Sampling
- PAH Sampling
- Aldehyde Sampling

### *4.1.1 Critical Measurements*

All of the ambient concentration data collected is considered critical and will be provided to AQS. Site information is also critical, as is sampling and measurement method identification.

### *4.1.2 Non-Standard Measurements*

Federal Reference Methods for $PM_{2.5}$ mass determination and $PM_{2.5}$ chemical speciation monitoring are described in the Washington State Department of Ecology Quality Assurance Project Plans.

While there are no Federal Reference Methods currently available for the specific organic compounds or elemental analyses used in this project, all of the procedures are taken from EPA's Compendium of Methods for Organic and Inorganic analyses where possible.

The Aethalometer procedure will follow that of the approved Washington State Department of Ecology Aethalometer QAPP.

The levoglucosan analysis has no standard approval but will follow the University Washington procedure referenced at the end of this document under References.

The meteorological measurements will follow the PSCAA Meteorological Monitoring Standard Operating Procedure.

Nephelometer sampling and data handling will also follow the PSCAA Nephelometer Standard Operating Procedure.

## 4.2 SAMPLING METHODS

### *4.2.1 Background / Purpose*

The measurement goal of this project is to estimate the concentration, in units of micrograms per cubic meter ($\mu g/m^3$) or ppb-volume, of air toxic compounds in the gas and particulate phases. This is accomplished by four separate sampling systems: passivated canisters for volatile organic compounds, dinitrophenylhydrazine cartridges for volatile carbonyl compounds, polyurethane foam cartridges for polycyclic aromatic hydrocarbons, and filter-based particulate samplers for $PM_{2.5}$, speciation, and levoglucosan.

Integrated 24-hour samples will be collected for all HAP analyses. All sampling for both gas phase and particulate analyses will be done on a one in six day schedule to coincide with the national particulate network schedule. Standard EPA Method TO-15 will be used to measure volatile organic compounds (VOC). Method TO-11A will be used to measure carbonyls, i.e. aldehydes and ketones. Method TO-13A will be used to measure polycyclic aromatic hydrocarbons (PAHs). ERG will provide “certified clean” sampling media and canisters for carbonyls, VOCs, and PAHs. RTI will provide “certified clean” sampling media for the speciation samples.

### *4.2.2 Volatile Organic Compound Sampling*

A detailed description of sampling for volatile organic compounds using SUMMA canisters can be found in EPA Method TO-15 Section 8. An evacuated stainless steel canister is connected to the sampling system and a timer is used to begin and end sampling at midnight. A steady sampling rate is maintained over the 24-hour period with the pump, solenoid valve, and critical orifice. Table 4-1 provides design and performance specifications for this method.

**Table 4-1. SUMMA Canister Sampler - Volatile Organic Compounds**

| Equipment | Frequency | Acceptance Criteria | Reference |
|---|---|---|---|
| **Canister Design Specifications** | 1 in 6 days | | |
| Size | | 317.5 mm, spherical | Vendor Spec. |
| Medium | | Passivated SUMMA Electropolished Stainless Steel Canister | |
| Pore size | | 6.35 mm | Vendor Spec. |
| Max Pressure | | 30 psig | Vendor Spec. |
| Max. pressure drop | | 14 psig | Vendor Spec. |
| Collection efficiency | | 99% | Vendor Spec. |
| Lower Detection Limit | | compound specific, usually >0.1 ppbc | Vendor Spec |
| **Sampler Performance Specifications** | 1 in 6 days | | |
| Sample Flow Rate | | 200 cc/min. | Vendor Spec. |
| Flow Regulation | | 20 cc/min. | Vendor Spec. |
| Flow Rate Precision | | ±10% | TO-15 |
| Flow Rate Accuracy | | ±10% | TO-15 |
| External Leakage | | Vendor specs | NA |
| Internal Leakage | | Vendor specs | NA |
| Timer | | 24 hour ± 2 min accuracy | Vendor Spec. |

### *4.2.3 Carbonyl Compound Sampling*

Sampling for gaseous carbonyl compounds occurs concurrently with VOC collection. A dinitrophenylhydrazine cartridge is attached to the sampling line and air is drawn through an ozone scrubber prior to passing through the cartridge. Details of the method are given in EPA Method TO-11A. Design and performance specifications are given in Table 4-2.

**Table 4-2. Dinitrophenylhydrazine (DNPH) Sampler - Aldehydes**

| Equipment | Frequency | Acceptance Criteria | Reference |
|---|---|---|---|
| **Filter Design Specs.**<br>Size<br>Medium | 1 in 6 days | 100 mm Cylindrical silica cartridge coated with 2,4-dinitro-phenyl hydrazine | TO-11A |

| | | | |
|---|---|---|---|
| **Sampler Performance Specifications** | 1 in 6 days | | |
| Sample Flow Rate | | 2 L/min. | Vendor Spec. |
| Flow Rate Precision | | ± 10% | Vendor Spec. |
| Flow Rate Accuracy | | ± 10% | Vendor Spec. |
| External Leakage | | Vendor specs | NA |
| Internal Leakage | | Vendor specs | NA |
| Clock/Timer | | 24 hour ± 2 min accuracy | Vendor Spec. |

### 4.2.4 *Particulate Sampling (including Speciation)*

MetOne SASS or SuperSASS $PM_{2.5}$ samplers will be used for collecting speciation samples using a Speciation Trends Network approach (STN). R&P Partisol 2025 Samplers will be used to collect $PM_{2.5}$ for gravimetric analysis and for levoglucosan analysis. Details are provided in the Washington State QAPPs for $PM_{2.5}$ FRM sampling. The URG 3000N will be used for the measurement of elemental and organic carbon. Tables 4-3 through 4-5 give the design and performance details for these methods.

**Table 4-3. $PM_{2.5}$ Met One SASS or SuperSASS Samplers – Speciation**

| Equipment | Frequency | Acceptance Criteria | Reference |
|---|---|---|---|
| **Filter Design Specs.** | 1 in 6 days | | EPA $PM_{2.5}$ Speciation Guidance Document |
| Glass Fiber Quartz, Teflon, and Nylon | | | |
| Size | | 47mm diameter | |
| Medium | | Quartz, Teflon, and Nylon Filters | |
| Alkalinity | | <25 meq/g | |
| Collection Efficiency | | 99.0% | |
| **Sampler Performance Specifications** | 1 in 6 days | | |
| Sample Flow Rate | | 6.7 Lpm | Vendor Specifications |
| Flow Regulation | | ± 2% | Vendor Specifications |
| Flow Rate Precision | | ± 10% | Vendor Specifications |
| Flow Rate Accuracy | | ± 10% | Vendor Specifications |
| Clock/Timer | | 24 hour ± 15 minutes | EPA $PM_{2.5}$ Speciation Guidance Document |

**Table 4-4. $PM_{2.5}$ R&P Partisol 2025 Samplers – $PM_{2.5}$ and Levoglucosan**

| Equipment | Frequency | Acceptance Criteria | Reference |
|---|---|---|---|
| **Filter Design Specs.** | 1 in 3 days – $PM_{2.5}$<br>1 in 6 days – Levoglucosan | | |
| Teflon | | | |
| Size | | 47mm diameter | 40 CFR 50 Appendix L |
| Medium | | Teflon Filter | 40 CFR 50 Appendix L |
| Alkalinity | | <25 meq/g | 40 CFR 50 Appendix L |
| Collection Efficiency | | 99.0% | 40 CFR 50 Appendix L |

| | | | |
|---|---|---|---|
| **Sampler Performance Specifications** | | | |
| Sample Flow Rate | 1 in 3 days – $PM_{2.5}$<br>1 in 6 days – Levoglucosan | 16.67 Lpm | 40 CFR 50 Appendix L |
| Flow Regulation | | ± 4% | 40 CFR 50 Appendix L |
| Flow Rate Precision | | ± 10% | 40 CFR 50 Appendix L |
| Flow Rate Accuracy | | ± 10% | 40 CFR 50 Appendix L |
| Clock/Timer | | 24 hour ± 5 minutes | 40 CFR 50 Appendix L |
| Temperature Check | | ± 4°C | 40 CFR 50 Appendix L |
| Ambient Pressure | | ± 10 mmHg | 40 CFR 50 Appendix L |

**Table 4-5. $PM_{2.5}$ URG 3000N Samplers – Elemental and Organic Carbon**

| Equipment | Frequency | Acceptance Criteria | Reference |
|---|---|---|---|
| **Filter Design Specs.** | | | |
| Glass Fiber Quartz | | | |
| Size | 1 in 6 days | 25mm diameter | Vendor Specifications |
| Medium | | Glass Fiber Quartz Filter | Vendor Specifications |
| Alkalinity | | <25 meq/g | Vendor Specifications |
| Collection Efficiency | | 99.0% | Vendor Specifications |
| **Sampler Performance Specifications** | | | |
| Sample Flow Rate | 1 in 6 days | 22.7 Lpm | Vendor Specifications |
| Flow Regulation | | ± 4% | Vendor Specifications |
| Flow Rate Precision | | ± 10% | Vendor Specifications |
| Flow Rate Accuracy | | ± 10% | Vendor Specifications |
| Clock/Timer | | 24 hour ± 15 minutes | EPA $PM_{2.5}$ Speciation Guidance Document |

### *4.2.5 Black Carbon and UV Channels*

The McGee Scientific Aethalometer will be used to measure black carbon and UV Channels. This is a continuous measurement and concentrations are averaged on an hourly basis. Table 4-6 gives the design and performance details for this method.

**Table 4-6. Aethalometer – Black Carbon and UV Channels**

| Equipment | Frequency | Acceptance Criteria | Reference |
|---|---|---|---|
| **Sampler Performance Specs** | | | |
| Sample Flow Rate | Continuous | 5.0 Lpm ± 10% | Vendor Specifications |
| Medium | | Quartz Tape | |
| Temperature Range | | 0 – 40 °C | |
| Wavelength | | 880 nm, 370 nm | |
| Time Resolution | | 1 hour | |
| Sensitivity | | 0.1 ug/m$^3$ | |

### *4.2.6 Polycyclic Aromatic Hydrocarbon Sampling*

Details of the method are given in EPA Method TO-13A. Design and performance specifications are given in Table 4-7.

**Table 4-7. Polyurethane Foam Sampler - PAHs**

| Equipment | Frequency | Acceptance Criteria | Reference |
|---|---|---|---|
| **Filter Design Specs.** | | | |
| Size | 1 in 6 days | 60mm x 3" | TO-11A |
| Medium | | Polyurethane foam plug | |
| **Sampler Performance Specifications** | | | |
| Sample Flow Rate | | 8 scfm | Vendor Specifications |
| Flow Rate Precision | 1 in 6 days | ± 10% | Vendor Specifications |
| Flow Rate Accuracy | | ≤ 20% RPD | Vendor Specifications |
| External Leakage | | Vendor Specifications | NA |
| Clock/Timer | | 24 hour ± 2 min accuracy | Vendor Specifications |

## 4.3 SAMPLE PREPARATION AND COLLECTION

Laboratory activities associated with sampling for the air toxics program include preparing the filters, canisters, and cartridges for the field operator prior to sampling and receiving the samples after they have been collected.

### *4.3.1 Pre-Sampling*

- Receiving filters, canisters or cartridges from the vendors
- Checking sample integrity
- Conditioning filters, storing canisters and cartridges
- Weighing filters
- Storing prior to field use
- Packaging filters, canisters and cartridges for field use

### *4.3.2 Post-Sampling*

- Receiving filters, canisters and cartridges from the field
- Checking sampling media integrity
- Logging samples into tracking systems
- Routing samples to the appropriate analytical section
- Stabilizing/weighing filters
- Storing filters, canisters and cartridges
- Loading analytical results into LIMS system and eventually AQS

The details for these activities are included in various sections of this QAPP as well as the references to other procedures and contract lab QAPPs.

## 4.4 SAMPLE INTEGRITY

### *4.4.1 Sample Contamination Prevention*

There are rigid requirements for preventing sample contamination throughout the sampling and analysis process. Powder free gloves are worn while handling DNPH cartridges. Filters and cartridges are to be held in storage containers (static resistant zip lock bags) as provided by the sample media manufacturer during transport to and from the laboratory.

Particulate filters are equilibrated/conditioned and stored in the same room where they are weighed. The filters are then kept in their filter holders until readied for setup. The filters are then placed in pre-cleaned filter holders which are put in site specific canisters.

For the VOC analysis, the best way to prevent contamination is not opening the canister in the laboratory. After cleaning and evacuating each canister a "cap nut" is tightened on top of the valve orifice. All post-sampling canisters that enter the laboratory should be under pressure. With positive pressure, it is less likely that the sample will be contaminated. However, care must be taken when the canisters are under vacuum and stored in the laboratory. If there is a slight leak in the canister cap or valve, then laboratory air can enter into the canister and contaminate it.

For DNPH cartridges, the best prevention is to not take the cartridges out of the shipping packet until they are loaded into the sampler in the field. After receipt and log in, the cartridges are immediately stored in a refrigerator within the sealed package. To load the cartridges into the aldehyde sampler, the DNPH cartridges are removed from their package and immediately installed.

### *4.4.2 Temperature Preservation Requirements*

The temperature requirements of the laboratory and field situations are detailed in FRM and TO methods.

In the weighing room, particulate filters must be conditioned for a minimum of 24 hours prior to pre-sample weighing, although a longer period of conditioning may be required. Control filters are weighed before and after sample filter weighing.

During transport from the laboratory to the sample location there are no specific requirements for temperature control of the sampling media, with the exception of DNPH cartridges and $PM_{2.5}$ filters. Filters will be kept in their protective container and in the transport container. Excessive heat must be avoided (e.g., do not leave in direct sunlight or a closed-up car during summer). DNPH cartridges, PUF cartridges, and $PM_{2.5}$ filter cartridges need to be stored at 4°C until they are transported to the sampler.

Speciation filters should NOT be frozen as it may alter the ionic species prior to analysis. The samples should be stored in a refrigerator from 0 to 4°C.

### *4.4.3 Holding Times*

Permissible holding times for the various samples are provided in Table 4-8.

**Table 4-8. Holding Times**

| Item | Holding Time | From: | To: | Reference |
|---|---|---|---|---|
| Speciation Filters | As soon as possible | Receipt from field | Time/date of analyses | EPA $PM_{2.5}$ Speciation Guidance Document |
| $PM_{2.5}$ Teflon Filters | ≤30 days | Completion of sample period | Time/date of analysis | 40 CFR 50 Appendix L |
| VOC canister | < 30 days | Completion of sample period | Time/date of analysis | TO-15 |
| DNPH Cartridge Filter | ≤ 14 days<br>≤ 30 days | Sample end date/time<br>Sample end date/time | Time/date of extraction<br>Time/date of analysis | TO-11A |
| PUF Cartridge | ≤ 7 days<br>≤ 40 days | Sample end date/time<br>Sample end date/time | Time/date of extraction<br>Time/date of analysis | TO-13A |

## 4.5 SAMPLE CUSTODY

Proper sample custody minimizes accidents by assigning responsibility for all stages of sample handling and ensures that problems will be detected and documented if they occur. A sample is in custody if it is in actual physical possession or it is in a secured area that is restricted to authorized personnel. Chain of Custody forms will be used to track the stages of sampling media handling throughout the data collection operation.

### *4.5.1 Pre-Sampling*

PSCAA has made arrangements with the ERG and RTI Laboratories to prepare and ship sample cartridges and canisters to them for sampling. The contract labs' pre-sampling SOPs define how the samples will be enumerated, conditioned, weighed, placed into the protective shipping container, sealed, and stored or refrigerated.

### *4.5.2 Post Sampling*

Documentation of sample collection and post-collection sample handling will be in accordance to the contract labs' field sampling SOPs.

### *4.5.3 Sample Receipt*

The samples will be received at the RTI and ERG Laboratories and logged in according to SOP.

### *4.5.4 Sample Archival*

Once the laboratory analysis has been completed, the entire sample, an aliquot, or an extract may be archived for future analysis according to SOP.

## 4.6 QUALITY ASSURANCE SAMPLING

According to the network design, PSCAA will deploy and operate one collocated aldehyde, PAH, and VOC sampler for this study. 40 CFR Part 58, Appendix A, requires at least 25% (minimum of one) of the samplers be collocated. Although these requirements do not directly relate to air toxics monitoring, PSCAA uses them as guidelines. More specifically, PSCAA will run a collocated sampler at the Alexander Ave site, which will act as the network wide duplicate sample site. PSCAA will be collecting a duplicate sample for aldehydes, PAHs, and VOCs once a month. This frequency of duplicate collection will be reviewed for adequacy as data becomes available.

Field blanks will similarly be tested once a month for aldehydes and PAHs at each of the sites.

## 4.7 SAMPLING/MEASUREMENT SYSTEM CORRECTIVE ACTION

Corrective action measures will be taken to ensure the data quality objectives are attained. Table 4-9 attempts to detail expected problems and corrective actions needed for a well-run network.

**Table 4-9. Field Corrective Actions**

| Item | Problem | Action | Notification |
|---|---|---|---|
| Filter Inspection (Pre-sample) | Pinhole(s) or torn | 1) If additional filters have been brought, use one of them. Void filter with pinhole or tear.<br>2) Use new field blank filter as sample filter.<br>3) Obtain a new filter from lab. | 1) Document on field data sheet.<br>2) Document in logbook. |
| Filter Inspection (Post-sample) | Torn or otherwise suspect particulate bypassing filter. | 1) Flag for possible invalidation of sample | 1) Document on field data sheet.<br>2) Document in logbook. |
| Flow rate erratic | Heavy loading or motor/motor brushes are worn. | 1) Replace brushes or motor.<br>2) Recalibrate flow rate. | 1) Document in logbook |
| Sample Flow Rate Verification | Out of Specification | 1) Reset flows to design flow rates with operator's site orifice.<br>2) Confirm that operator's site flow orifice agrees within ±7.5% of transfer standard flow orifice. | 1) Document on data sheet. Notify QA Specialist<br>2) Document on data sheet. Notify QA Specialist |
| Sample Flow Rate | Consistently low flows documented during sample run | 1) Repair or replace pump.<br>2) Perform leak check. | 1) Document on field data sheet. QA Specialist<br>2) Document on data sheet. Notify QA Specialist |
| Elapsed Sample Time | Out of Specification | 1) Check time clock setting. Verify Power Outages | 1) Notify QA Specialist |
| Power | Power Interruptions | 1) Check Line Voltage | 1) Notify QA Specialist |
| Leak Test | Canister/Sampler won't hold pressure | 1) Repair, Recalibrate; flag data | 1) Document on field data sheet. Document in logbook. Notify QA Specialist |

# 5 ANALYTICAL METHODS

At the heart of the data gathering process are the analytical systems used to provide the ambient air measurements of pollutant concentrations. The ERG, UW, and RTI Laboratories will perform analyses for all specified compounds. No federal reference or equivalent methods have been specified for the determination of these compounds. PSCAA will require analysis by methods contained in EPA's Compendium of Methods for Organic and Inorganic analyses. These analytical procedures will provide results consistent with this project's data quality objectives, since these same methods are also being used by other air quality agencies throughout the United States.

## 5.1 BACKGROUND

Four separate sampling and analysis protocols will be used in order to measure gaseous volatile and carbonyl compounds, and particulate metals. The collected samples will be logged in at the PSCAA Laboratory then distributed to either the inorganic or the organic laboratory sections for analysis.

## 5.2 METHODS

### *5.2.1 Particulate Matter, Speciation, and Levoglucosan*

Particulate filters are weighed prior to any analysis for elemental content. Subsequently, sample preparation and analysis procedures follow 40 CFR 50 Appendix L, and details can be found in the references.

Filters for speciation will be analyzed using XRF, akin to EPA Compendium Method IO-3.5 procedures, but for $PM_{2.5}$. The EPA QAPP for $PM_{2.5}$ Speciation Trends Network Sampling will also be followed closely. Calibration and quality control procedures, along with acceptance criteria are specified in these references.

Filters for organic and elemental carbon analysis will be analyzed using a thermal/optical carbon analyzer as in NIOSH Method 5040. Calibration and quality control procedures, along with acceptance criteria are specified in the reference.

Filters for levoglucosan measurement will be analyzed after standard FRM weighing by the Standard Operating Procedure for Levoglucosan Analysis.

### *5.2.2 Volatile Organic Compounds*

Sample preparation and analysis procedures are from the EPA Compendium Method TO-15. Details of these procedures can be found in the references.

A specific volume of sample is drawn from the SUMMA canister into a cryogenic trap and cooled with liquid nitrogen. The concentrated sample extracts are then analyzed using gas chromatography with mass spectrometry detection and identification. Surrogate compounds and internal standards, are spiked into all samples during this process. SUMMA canisters require humid zero air sampler certification.

Method calibration and quality control procedures, as well as acceptance criteria are all described in the reference methods.

### *5.2.3 Carbonyl Compounds*

EPA Compendium Method TO-11A is followed for sample preparation and analysis. Details of these procedures can be found in the references.

Components on the DNPH cartridge are extracted and then injected into a high-pressure liquid chromatography system. Method calibration and quality control procedures, as well as acceptance criteria are described in the reference.

### *5.2.4 Polycyclic Aromatic Hydrocarbons*

EPA Compendium Method TO-13A is followed for sample preparation and analysis. Details of these procedures can be found in the references.

Components on the polyurethane foam cartridge are extracted and then injected into a Gas Chromatography-Mass Spectrometer. Method calibration and quality control procedures, as well as acceptance criteria are described in the reference.

## 6 QUALITY CONTROL

Quality Control (QC) is the overall system of activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the project plan. QC is both pro-active and corrective in preventing the generation of unacceptable data.

To assure the quality of data from air monitoring measurements, two distinct and important inter-related functions must be performed. One is the control of the measurement process through broad quality assurance activities, such as establishing policies and procedures, developing data quality objectives, assigning roles and responsibilities, conducting oversight and reviews, and implementing corrective actions. The other is the control of the measurement process through the implementation of specific quality control procedures, such as audits, calibrations, checks, replicates, routine self-assessments, etc. In general, the greater the control of a given monitoring system, the better will be the resulting quality of the monitoring data.

Figure 6-1 shows a number of QC activities that help to evaluate and control data quality for the program.

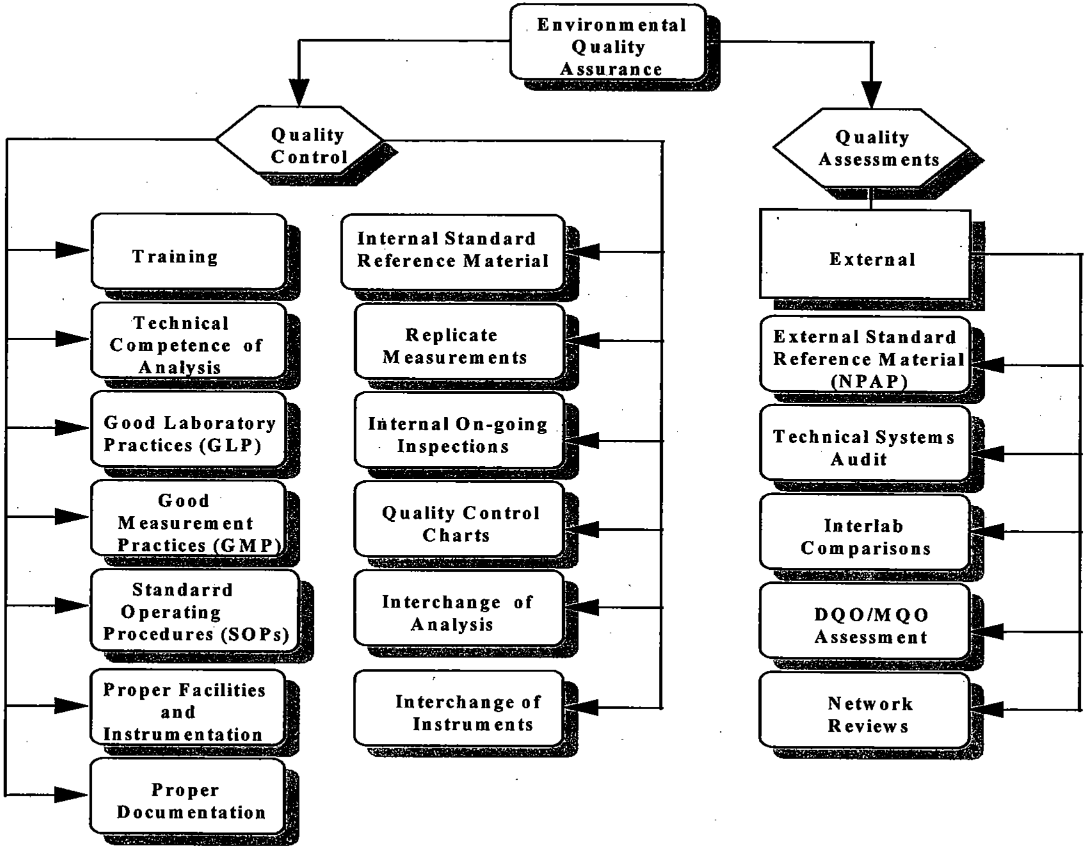


**Figure 6-1**

## 6.1 QUALITY CONTROL PROCEDURES

Day-to-day quality control is implemented through the use of various check samples or instruments that are used for comparison. Table 3-3 contains a complete listing of measurement quality objectives for this program. Detailed method-specific procedures are included in the field and analytical methods sections of this QAPP.

### *6.1.1 QC Records*

A QC notebook or database (with disk backups) will be maintained which will contain QC data, including the calibrations, maintenance information, routine internal QC checks of mass reference standards and laboratory and field or lab filter blanks, and external QA audits. These data will duplicate data recorded on laboratory data forms but will consolidate them so that long-term trends can be identified.

At the beginning of each analysis day, after zeroing and calibrating the instruments and measuring the working standard, the laboratory filter blanks for the current sample batches are analyzed. The zero, working standards, and blank measurements are recorded on the laboratory data form and in the laboratory QC notebook or database.

Corrective action measures will be taken as appropriate to ensure good quality data. These are also recorded.

### *6.1.2 Calibrations*

Calibration is the comparison of a measurement standard or instrument with another standard or instrument to determine and correct any variation (deviation) in the accuracy of the item being compared and thus minimize bias.

In general these calibration activities follow a two step process:

1. Certifying the calibration standard and/or transfer standard against an authoritative standard, and

2. Comparing the calibration standard and or transfer standard against the routine sampling/analytical instruments.

Calibration requirements for the critical field and laboratory equipment are found in the respective SOP for each analysis method.

### *6.1.3 Blanks*

Concentrations of air toxics in the ambient air can be extremely low and contamination introduced by the measurement process itself can be significant. Blank samples are used to determine the extent and source of this potential contamination. Three types of blanks will be used in the air toxics program:

**Lot blanks** - provide an estimate of contamination resulting from preparation of the sampling medium. Each group of sampling media must be tested prior to use to determine the extent of contamination.

**Lab blanks** - provide an estimate of contamination occurring at the laboratory facility. Details of the use of lab blanks can be found in the analytical method SOP. Blank contamination for VOC measures result from the laboratory cleaning system, while for metals and aldehydes blank contamination results from the suppliers of the filters and absorber tubes.

**Field blanks** - provide an estimate of total measurement system contamination. By comparing information from laboratory blanks against the field blanks, one can assess contamination from field activities. Details of the use of the field blanks can be found in field SOP.

**Blank Evaluation** - The following general procedures will be used:

**Percent Difference for a Single Check** ($d_i$) - The percentage difference, $d_i$, for each check is calculated using the following equation, where $X_i$ represents the original concentration and $Y_i$ represents the concentration reported for the duplicate concentration.

$$d_i = \frac{Y_i - X_i}{(Y_i + X_i)/2} x\,100$$

**Mean difference for batch** ($d_z$) - The mean difference $d_z$ for both field and lab blanks within an analysis batch, is calculated using the following equation, where $d_1$ through $d_n$ represent individual differences (calculated from equation 1) and $n$ represents the number of blanks in the batch.

$$d_z = \frac{d_1 + d_2 + d_3 \cdots d_n}{n}$$

**Corrective action** - The percent difference calculation is used for control charting purposes and can be used to determine status. Acceptance criteria for blanks are discussed in the individual method SOP.

## 6.2 QUALITY CONTROL MEASURES

### *6.2.1 Precision*

Precision measurements will be obtained using co-located monitoring and replicate analysis.

**Collocated Monitoring** - Duplicate samples for aldehydes, PAHs, and VOCs will be collected once a month for each method. These samples will be designated as either from the primary or the duplicate sampler. Analysis and comparison of these two samples will provide a measure of sampling precision.

**Replicate Analyses** - Duplicate aliquots from a sample will be analyzed on ten percent of the samples, for each lab sample type. Analysis and comparison of these two aliquots will provide a measure of analytical precision.

The following algorithms will be used to evaluate co-located and replicate data.

**Percent Difference ($d_i$).** The percentage difference, $d_i$, for each check is calculated by using the following equation, where $X_i$ represents the concentration produced from the primary sample, or aliquot, and $Y_i$ represents the concentration reported for the duplicate sample, or aliquot.

$$d_i = \frac{Y_i - X_i}{(Y_i + X_i)/2} * 100$$

**Precision of a Single Sampler or Analysis - Quarterly Basis.** For any sampler or analysis *i*, the individual 95% confidence limits produced during each quarter are pooled using the following equations where $S_i$ = sample standard deviation. Each individual compound must have the precision data generated.

$$\text{Upper 95\% Percent Limit} = d_i + 1.96 * S_i$$

$$\text{Lower 95\% Percent Limit} = d_i - 1.96 * S_i$$

**Quarterly Corrective Action -** Corrective action will be initiated before a calendar quarter of data fails to meet the 15% Confidence Limits. However, when the Confidence Limit is greater than 20% the routine data for that monitor for that quarter will be flagged. The QA Specialist and the Air Monitoring Manager will work together to identify the problem and a solution. The problem and solution will be reported and appropriately filed under response and corrective action. This information will also be included in the final project report.

### *6.2.2 Accuracy*

Two accuracy checks are used in the air toxics monitoring program:

**Flow Rate Audits (Field) -** The flow rate audit is accomplished by measuring the sampler's normal operating flow rate using a certified flow rate transfer standard. Details are provided in the method SOP. Calculation of measurement uncertainty is described by:

**Accuracy of a Single Sampler - Single Check Basis ($d_i$).** The percentage difference ($d_i$) for a single flow rate audit $i$ is calculated, where $X_i$ represents the audit standard flow rate (known) and $Y_i$ represents the indicated flow rate.

$$d_i = \frac{Y_i - X_i}{X_i} * 100$$

**Instrument Checks (Lab) -** Balance checks are frequent checks of the working standards. RTI and PSCAA use ASTM class 1 weights for their primary and secondary (working) balance standards and NIST supplied standards for both metals and gases.

**Instrument Accuracy - single check ($d_y$).** The difference, $d_y$, for each check is calculated, where $X$ represents the certified value (known) and $Y$ represents the reported value.

$$d_y = Y - X$$

### *6.2.3 Completeness*

Completeness is a quality measure that is determined at the end of the project. Percent completeness is calculated as the ratio of the number of valid samples obtained to the number of scheduled samples. This value is provided in the final project report.

### *6.2.4 Representativeness*

This is a measure of how well the reported results reflect the actual ambient air concentrations and is primarily determined by the project design and the siting of the measurement stations. This will be provided in the final project report.

### *6.2.5 Comparability*

Comparability is a measure of the similarity of this data to ambient air toxics data collected in other geographic areas. It is primarily ascertained through the use of standard methods of sampling and analysis. However, since standard methods of air toxics measurement have not been specified, PSCAA will require analysis by methods commonly used by other agencies.

At times a laboratory audit will be performed, usually under EPA auspices, as an independent check of the laboratory's entire analytical system. An audit sample, generated by an outside laboratory, will be mailed directly to the laboratory. RTI and ERG will log the sample into the laboratory system as it would a normal sample and the lab technician will handle the audit sample in the same manner as all other samples. Once the analysis is performed, the lab section manager will review the results and send them to the initiating laboratory. The equation used to define percentage difference ($d_i$) for each individual compound audit, $i$, is calculated as:

$$d_i = \frac{Y_i - X_i}{X_i} * 100$$

where $X_i$ represents the audit standard concentration from a certified laboratory (known) and $Y_i$ represents the indicated value obtained from the ERG or RTI laboratory.

Comparability can also be determined by comparing measured concentrations to modeled concentrations provided by EPA's National Scale Air Toxics Assessment or to NW-AIRQUEST modeling data, when available. Results of any laboratory audits or monitor-to-model comparisons will be provided in the final project report.

### *6.2.6 Minimum Detection Limit (MDL)*

The MDL are determined individually for each pollutant analyzed by each method employed. Details are provided in each of the method SOP.

Method specific quality control measures are listed in Table 6-1.

**Table 6-1. QC Measures by Method.**

| | Instrument Performance Check Standard | Matrix Spike/ Daily Calibration Standard | Matrix Spike Duplicate | Process Blank (Cartridge/ Canister) | Field Blank | Solvent Blank | Deuterated Surrogate Recovery/ Internal Standard |
|---|---|---|---|---|---|---|---|
| TO-11A | Each analytical run** | | | √N, where N=DNPH lot size*** | Each sampling event*** | | |
| TO-13A | Each analytical run | Each analytical run | | Each analytical run | Each sampling event | Each analytical run | Run for each analytical run |
| TO-15 | Each analytical run | Each analytical run* | | Each analytical run | | Each analytical run | Each sample and standard analyzed |
| $PM_{2.5}$ Speciation | Each analytical run | Each Analytical run | No | Each run | (Samplers decide) | | Internal Standard, Each sample and standard analyzed |

* If response of daily calibration standard is not within 30% of calibration value, corrective action such as cleaning of the ion source, column replacement. Repeat daily calibration sample to verify performance.
** If response of daily calibration standard is not within 10% of calibration value, a new 5-point calibration is necessary.
*** The average of 3 cartridge blanks = Certification Blank (Lot Blank). Remaining cartridges from this set are used as Field Blanks.

## 6.3 DOCUMENT CONTROL

The Department will follow its standard procedures for the timely preparation, review, approval, issuance, use, control, revision and maintenance of documents and records. Table 6-2 shows the categories and types of records and documents to which document control applies for air toxics information.

**Table 6-2. Critical Documents and Records**

| Categories | Record/Document Types |
|---|---|
| Management and Organization | State Implementation Plan<br>Organizational structure<br>Personnel qualifications and training<br>Grant allocations |
| Site Information | Network description/review<br>Site characterization file<br>Site maps<br>Site Pictures |
| Data Reporting | Air quality index report<br>Annual SLAMS air quality information<br>Data/summary reports |
| Data Management | Data algorithms<br>Data management plans/flowcharts<br>Air Toxics Data<br>Any original data (routine and QC data) entry forms |

| Categories | Record/Document Types |
|---|---|
| Quality Assurance | Network reviews<br>Data quality assessments<br>QA reports<br>System audits<br>Response/Corrective action reports<br>Site Audits<br>QA Project Plans<br>Standard operating procedures (SOP)<br>Field notebooks<br>Sample handling/custody records<br>Inspection/maintenance records |

# 7 INSTRUMENTS AND EQUIPMENT

## 7.1 PURPOSE / BACKGROUND

The purpose of this element of the QAPP is to describe the procedures used to verify that all instruments and equipment are maintained in sound operating condition and are capable of operating at acceptable performance levels. Good maintenance procedures not only are essential for obtaining reliable data but are also important for minimizing instrument downtime.

## 7.2 TESTING AND INSPECTION

All samplers used in the project will meet the instrument requirements described in the Compendium of EPA Methods. Therefore, they are assumed to be of sufficient quality for the data collection operation. Field operators will perform external and internal checks to verify continuing performance within specifications. If any of these checks are out of specification, the field technicians will attempt to correct them or if necessary request assistance from the equipment's manufacturer.

Equipment used in the laboratory for analysis will likewise meet requirements specified in their respective methods. Laboratory analysts will perform periodic checks to verify continuing performance and will attempt to correct any instruments operating outside specifications.

## 7.3 MAINTENANCE

There are many items that need maintenance attention in the network. This section describes the field and laboratory procedures that will be used.

### *7.3.1 Field Equipment Maintenance*

Preventive maintenance checks of the samplers and their frequency are detailed in Table 7-1.

**Table 7-1. Preventive Maintenance on Field Instruments**

| Instrument | Item | Maintenance Frequency | Responsible Party |
|---|---|---|---|
| VOC, PAH, and Carbonyl Sampler | Inspect pump, seals and gaskets | 6 months | *Field Operator* |
| | Replace canister and cartridge filters | 6 Months | *Field Operator* |
| | Replace ozone scrubber | Annually | *Field Operator* |
| | Calibrate mass flow controller | Annually | *Field Operator* |
| | Calibrate pressure transducer | Annually | *Field Operator* |
| Particulate Sampler | Flow check | Quarterly | *Field Operator* |
| | Clean inlet | 6 Months or as needed | *Field Operator* |
| | Inspect tubing, collar, impactor | 3 months or as needed | *Field Operator* |
| | Rebuild Pump | Annually | *Field Operator* |
| | Elapsed time indicator check | Annually | *Field Operator* |
| Aethalometer | Leak check | 1 months | *Field Operator* |
| Nephelometer | Clean Unit | Annually | *Field Operator* |
| TEOM | Replace filters | 3 months or as needed | *Field Operator* |
| Propeller Anemometer | Replace Bearings | 6 months | *Field Operator* |
| Relative Humidity | Clean Screen | Annually | *QA Specialist* |

### *7.3.2 Laboratory Equipment Maintenance*

The following tables details the maintenance items, how frequently they will be replaced, and who will be responsible for performing the maintenance.

**Table 7-2. Preventive Maintenance in Balance Room**

| Item | Maintenance Frequency | Responsible Party |
|---|---|---|
| Multi-point Micro-balance maintenance calibration | Yearly | *Contractor* |
| Comparison of NIST Standards to laboratory working and primary standards | 3 Months | *Lab Analyst* |
| Cleaning weigh room | Monthly | *Lab Analyst* |
| Computer Back-up | Daily | *Lab Analyst* |
| Computer Virus Check | Daily | *Lab Analyst* |

**Table 7-3. Preventive Maintenance in Organic Laboratory**

| Item | Maintenance Frequency | Responsible Party |
|---|---|---|
| Multi-point maintenance calibration | As necessary | *Lab Analyst* |
| Replace Chromatography Column | As necessary | *Lab Analyst* |

| | | |
|---|---|---|
| Replace Detector | As necessary | *Lab Analyst* |
| Computer Virus Check | Continuous | *Network Admin* |
| Computer system preventive maintenance (clean out old files, compress hard-drive, inspect) | As needed | *PC support personnel* |

**Table 7-4. Preventive Maintenance in Inorganic Laboratory**

| Item | Maintenance Frequency | Responsible Party |
|---|---|---|
| Multi-point maintenance calibration | Yearly | *Lab Analyst* |
| Comparison of NIST Standards to laboratory working and primary standards | Monthly | *Lab Analyst* |
| Equipment maintenance | Yearly | *Lab Analyst* |
| Computer Back-up | Daily | *Lab Analyst* |
| Computer Virus Check | Daily | *Lab Analyst* |

# 8 CALIBRATION METHODS AND STANDARDS

This section describes the calibration procedures and standards used for both the sampling and analytical phases of this project.

## 8.1 CALIBRATION METHODS

### *8.1.1 Meteorological Equipment Calibration*

The EPA Quality Assurance Handbook, Volume IV (EPA, 2008) gives information on calibration equipment and methods for assessing response characteristics of temperature sensors. The PSCAA Meteorological Monitoring Procedure will be used for measurement of ambient pressure, temperature, relative humidity, and wind parameters. Table 8-1 summarizes the adjustment and invalidation levels of the equipment.

**Table 8-1. Meteorological Instrument Adjustment and Invalidation Levels**

| **Instrument** | **Parameter** | **Action Level** | **Failure Level** |
|---|---|---|---|
| Propeller/Vane Windbird | Wind Speed | None | > ± 0.005V – replace bearings or windbird |
| | Wind Direction | > ± 0.005V – replace windbird, or adjust translator if the max voltage ≠ 0.986 | > ± 0.014V or > 5° – total error inclusive with mast alignment |
| | Azimuth Torque | > 8 gm-cm – replace windbird | > 11 g-cm |
| | Wind Speed Torque | > 0.5 gm-cm – replace bearings | > 1 gm-cm |
| Mast Alignment | Wind Direction | Adjust to zero after every audit; when > 3° off, audit alignment | > 5° - total error inclusive with windbird azimuth |
| Ultrasonic Windbird | Wind Speed | None* | Manufacturer audit result > ± 1 mph |

| | | | |
|---|---|---|---|
| | Wind Direction | None* | > 5° – total error inclusive with mast alignment |
| Temperature Probe | Temperature | > ± 2.5°C – recalibrate | > ± 4°C |
| Humidity Probe | RH | > ± 6% – recalibrate | > ± 10% |
| Pressure Probe | Barometric Pressure | 7 mmHg | 10 mmHg |

### *8.1.2 Flow Calibration*

The EPA Quality Assurance Handbook, Volume IV (EPA, 1995) provides information on calibration equipment and methods for assessing response characteristics of flow sensors. The flow sensors will be sent to the manufacturer for recertification against a NIST standard yearly.

Upon initial receipt of a new, repaired, or replaced air toxics sampler, a technician will perform a multi-point flow rate calibration verification on the sampler flow rate (if applicable) to determine if performance is acceptable.

Samplers are connected to the calibration device after equilibrating to ambient conditions. A leak check is performed according to the manufacturer's operational instruction manual. The sampler is then placed in calibration or "run" mode and a one-point calibration verification or one-point flow rate verification is performed.

### *8.1.3 Analytical Equipment*

The EPA Quality Assurance Handbook, Volume IV (EPA, 1995), provides detailed information on laboratory equipment calibration and methods. In general:

- For balances, NIST-traceable weights (100 and 200mg) are used to verify that the balance is weighing within the tolerance limits. This is performed before and after each batch of filter weighings. Any difference in weight is noted.

- For Gas Chromatographs, laboratory standards are attached to a mass flow control calibration unit. Reference components are measured before and after each set of samples. Recoveries and retention times are noted.

- For Liquid Chromatographs, the procedure is the same with the exception of the compounds injected. Response peaks are observed and recorded. This procedure is repeated at the end of the analysis batch run.

- For XRF, calibration is necessary only when a change is made in fluorescers, x-ray tubes, or detectors, or when a serious malfunction occurs requiring significant repairs. Calibration establishes the elemental sensitivity factors and the magnitude of the interference or overlap coefficients. Thin film standards are used for calibration because they most closely resemble the layer of particles on a filter.

## 8.2 CALIBRATION STANDARDS

### *8.2.1 Temperature Standard*

The PSCAA Lab uses a NIST-traceable mercury in glass thermometer for calibration of the weigh room digital thermometer. The lab temperature transfer standards measure the temperatures of the weighing lab at ≤ 1 minute intervals. Each probe comes with a certificate of NIST-traceability with the same kind of information as the thermometer certificate.

Other temperature devices used for field use will be NIST-certified yearly.

### *8.2.2 Flow Standard*

NIST traceable flow standards will be used for calibrations and flow-rate verifications. The devices are factory certified to NIST-primary standards at least annually. PSCAA will maintain a record of the difference or percent difference between the flow-rate standards and the NIST-traceable primary flow-rate or standards.

### *8.2.3 Analytical Equipment Standards*

Instruments are calibrated using NIST traceable standards (if available) once a year. PSCAA, ERG, and RTI laboratories maintain a set of standards for each of the laboratory systems. Calibrations are performed using these standards as described below.

**Table 8-2. Analytical Equipment Calibration Requirements**

| Analytical Parameter | Instrument | Type of Standard | Frequency | Acceptance Criteria |
|---|---|---|---|---|
| Particulate Mass | Electronic Balance | NIST Weights | Before and after each batch run. | Within 3 $\mu$g |
| Particulate Metals | XRF | Thin Film | After maintenance | ± 10% of NIST Certified Standard |
| Carbonyl Compounds | Liquid Chromatograph | High Purity 2,4 Dinitrophenyl hydrazine derivative crystals dissolved in Acetonitrile | Before and after each batch run | Linear Correlation Coefficient > 0.9 |
| Volatile Organic Compounds | Gas Chromatograph | Compressed Gas Cylinder | Before and after each batch run | Linear Correlation Coefficient > 0.9 |
| Polycyclic Aromatic Hydrocarbons | GC/MS | High Purity Grade Standards | Annually or after maintenance | Linear Correlation Coefficient > 0.9 |

## 9 DATA MANAGEMENT

This section describes all the aspects of data management necessary for this air toxics monitoring project. This includes an overview of the mathematical operations and analyses performed on raw, "as-collected" data. These operations include data recording, validation, transformation, transmittal, reduction, analysis, management, storage and retrieval, and reporting.

Data processing activities for air toxics data are summarized in Figure 9-1. Data processing steps are integrated, to the extent possible, into the existing data processing system used for criteria pollutant monitoring. The air monitoring database resides on a dedicated database server running the Windows XP operating system and Microsoft SQL server.

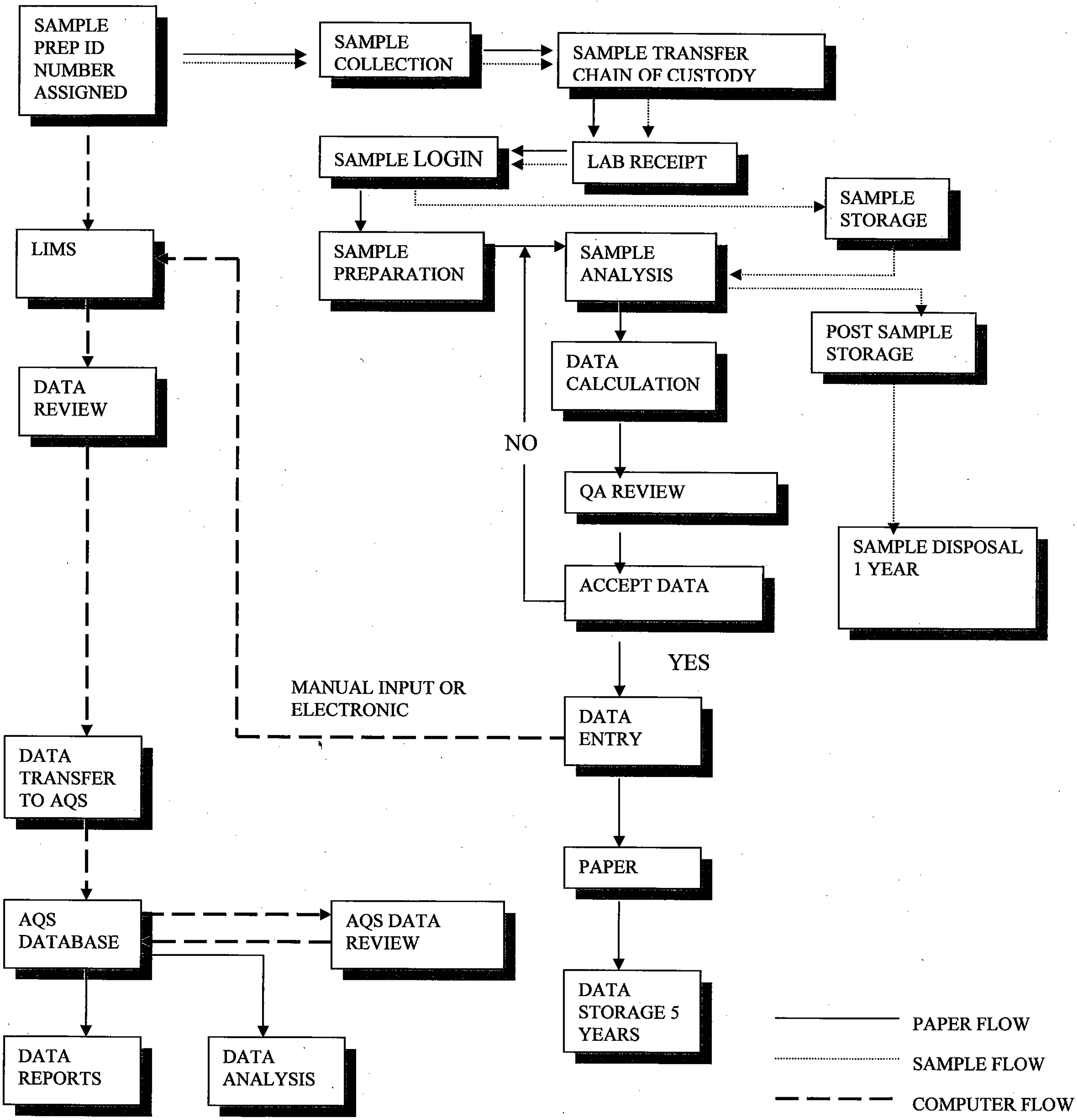
Sample tracking and chain of custody information is entered into a Laboratory Information Management System (LIMS) at two points as shown in Figure 9-1. Managers are able to obtain reports on status of samples, location of specific samples, etc. using LIMS. Different access privileges are given each authorized user depending on that person's need. The following privilege levels are defined:

- Data Entry Privilege - The individual may see and modify only data within LIMS that he or she has entered. After a data set has been "committed" to the system by the data entry operator, all further changes will generate entries in the system audit trail.
- Reporting Privilege - The individual may generate reports.
- Data Administration Privilege - Data Administrators for the LIMS are allowed to change data as a result of QA screening and related reasons. All operations resulting in changes to data values are logged to the audit trail.

The Data Administrators are responsible for performing the following tasks on a regular basis:

- merging/correcting the duplicate data entry files;
- running verification/validation routines, and correcting data as necessary;
- generating summary data reports for management, and
- uploading verified/validated data to EPA-AQS.

**FIGURE 9-1 DATA MANAGEMENT AND SAMPLE FLOW DIAGRAM**



## 9.1 DATA ACTIVITIES

### *9.1.1 Routine Data Activities*

Table 9-1 provides a list of the documents and records that will be collected and maintained.

**Table 9-1. Data Activities**

| Record/Document Types | Categories |
|---|---|
| Reporting agency information<br>Organizational structure<br>EPA Directives<br>Grant allocations<br>Support Contract | Management and Organization |
| Network description<br>Site characterization file<br>Site maps<br>Site Pictures | Site Information |
| QA Project Plans<br>Standard operating procedures (SOP)<br>Field and laboratory notebooks<br>Sample handling/custody records<br>Inspection/Maintenance records | Environmental Data Operations |
| Any original data (routine and QC data) including data entry forms | Raw Data |
| Air quality index report<br>Annual SLAMS air quality information<br>Data/summary reports<br>Journal articles/papers/presentations | Data Reporting |
| Data algorithms<br>$PM_{2.5}$ Data | Data Management |
| Network reviews<br>Data quality assessments<br>QA reports<br>System audits<br>Response/Corrective action reports<br>Site Audits | Quality Assurance |

### *9.1.2 Summary Reports for EPA*

PSCAA shall submit to the EPA Administrator, through the Region 10 Office, summary reports of all the ambient air toxics monitoring data from all the monitoring stations. These reports will be submitted according to the schedule in the work plan and will contain the following information:

**Site and Monitoring Information**

- City name (when applicable).
- County name and street address of site location.
- AQS site code.
- AQS monitoring method code.

**Summary Data**

- Quarterly and eventually annually geometric mean ($\mu g/m^3$).
- Sampling schedule used as once every 6 days, every day, etc.

## 9.2 DATA RECORDING

All raw data required for the calculation of a pollutant concentration, the submission to the AQS database, and QA/QC data, are collected electronically or on data forms that are included in the field and analytical methods sections. All hard copy information will be filled out in indelible ink. Corrections will be made by drawing one line through the incorrect entry, initialing this correction with the date, and placing the correct entry alongside the incorrect entry. If this cannot be accomplished legibly then the information should be provided on a new line.

### *9.2.1 Notebooks*

**Site logs** – PSCAA will supply logbooks or electronic logs at each field site. Any visit to a site warrants an entry in the field log regarding what was accomplished at the site.

**Instrument notebooks** - Notebooks will also be issued for each of the instruments. These notebooks will be numbered with the associated serial number of the equipment. Instrument parameters, and other information specified in the SOP, will be recorded upon each use of the instrument.

**Laboratory notebooks** – The contract lab has data entry, validation, and verification functions all integrated in the LIMS. Laboratory personnel enter bench sheets as well. Procedures for filling out the laboratory sheets and subsequent data entry are provided in the lab SOP.

### *9.2.2 Electronic data collection*

Some instruments have an automated means for collecting information that would otherwise be recorded on data entry forms. In order to reduce the potential for data entry errors, automated systems will be utilized where appropriate and will record the same information that is found on data entry forms. In order to provide a back up, the data will be stored at the site data logger as well as at the WA Ecology Central Server and on the PSCAA AQ Database.

## 9.3 DATA VALIDATION AND VERIFICATION

Data validation refers to those activities performed after the data have been collected. The difference between data validation and quality control techniques is that the quality control techniques attempt to minimize the amount of bad data being collected, while data validation seeks to prevent any bad data from getting through the data collection and storage systems.

Data validation is a combination of checking that data processing operations have been carried out correctly and of monitoring the quality of the field operations. Data validation can identify problems in either of these areas. Once problems are identified, the data can be corrected or invalidated, and corrective actions can be taken for field or laboratory operations. If possible, flags denoting error conditions or QA status are saved as separate fields in any databases, so that it is possible to recover the original data.

**Table 9-2. Validation Check Summaries**

| Type of Data Check | Person Responsible for Checks | Manual Checks | Automated Checks |
|---|---|---|---|
| Date and Time Consistency | PSCAA QA Specialist | X | |
| Completeness of Required Fields | ERG and RTI Laboratory Personnel | X | X |
| Statistical Outlier Checking | ERG and RTI Quality Assurance Manager,<br>PSCAA Data Specialist | X | X |
| Manual Inspection of Charts and Reports | ERG and RTI Laboratory Personnel | X | |
| Field and Lab Blank Checks | ERG and RTI Laboratory Personnel | X | |

### *9.3.1 Manual Validation Activities*

It is preferable that data review be performed as soon as possible after the data collection, so that the questionable data can be checked by recalling information on unusual events and on meteorological conditions which can aid in the validation. Also, timely corrective actions may be taken when indicated to minimize further generation of questionable data.

Personnel performing data review should:

- Be familiar with typical diurnal concentration variations (e.g., the time daily maximum concentrations occur and the interrelationship of pollutants.) For example, benzene, toluene, and xylene concentrations usually increase and decrease together, due to these being attributed to mobile sources, whereas, metals are usually attributable to manufacturing process, and may have a longer temporal cycle.
- Be familiar with the type of instrument malfunctions that cause characteristic trace irregularities.

- Recognize that cyclical or repetitive variations (at the same time each day or at periodic intervals during the day) may be caused by excessive line voltage or temperature variations. Nearby source activity can also cause erroneous or non-representative measurements.
- Recognize that flow traces showing little or no activity often indicate flow problems, or sample line leaks.

Data records that can be used for routine manual checks include the following:

- ***Data Identification Checks***

Data with improper identification codes are useless. Sample identification fields that must be correct are time, location, parameter and sampler ID.

- ***Unusual Event Review***

Extrinsic events (e.g., construction activity, dust storms, unusual traffic volume, and traffic jams) can sometimes help to explain unusual data. This information could also be used to explain why no data are reported for a specified time interval, or it could be the basis for deleting data from a file for specific analytical purposes. However, an unusual event does not necessitate deletion of data as it may reoccur or be relevant.

- ***Relationship Checks***

Air toxics data sets contain many physically or chemically related parameters. These relations can be routinely checked to ensure reasonableness and consistency. For example, benzene, toluene, and xylene are mobile source driven.

- ***Review of Spikes, Blanks and Replicates***

Generally, recovery of spikes in samples should be greater than 80%. Blanks should not be more than 5 times the concentration or MDL for any compound. The difference in concentration of replicates should be within ± 10%. If any of these are outside of this boundary, then appropriate corrective actions are warranted.

Some tests can check values in a data set that appear atypical when compared to the whole data set. Common anomalies of this type include unusually high or low values (outliers) and large differences in adjacent values. These tests will not detect errors that alter all values of the data set by either an additive or multiplicative factor (e.g., an error in the use of the scale). The following tests for internal consistency are used:

- Data Plots
- Ratio Test
- Students "t-test"

### *9.3.2 Validation Responsibilities*

The Data Specialist is the first reviewer of data and is the first to flag/delete data during this review. The Quality Assurance Specialist reviews the edits of the Data Specialist. The QA Specialist also does a second review of the data and flags/edits data accordingly. All forms, custody sheets, and other data entries are all reviewed by the Data Specialist first with further review by the QA Specialist.

To maintain edit records, all edits/flags/deletions to data are denoted on an "Edit File" that is reviewed by the QA Specialist. Records are reviewed as soon as possible, but are completed within 60 days of data collection. Data from contract labs are also reviewed within 60 days of receipt by PSCAA.

Erik Saganic, QA Specialist for this project, has the independent ability to determine the validity of data collected based on this QAPP and the other referenced QAPPs and procedures herein and is the ultimate decider on data validity.

## 9.4 DATA TRANSFORMATION

Calculations for transforming raw data from measured units to final concentrations are provided in the method SOP.

## 9.5 DATA TRANSMITTAL

Data transmittal occurs when data are transferred from one person or location to another, or when data are copied from one form to another. Some examples of data transmittal are copying raw data from a notebook onto a data entry form for keying into a computer file and electronic transfer of data over a telephone or computer network. Table 9-3 summarizes data transfer operations.

**Table 9-3. Data Transfer Operations**

| Description of Data Transfer | Originator | Recipient | QA Measures Applied |
|---|---|---|---|
| Keying Data into LIMS | Laboratory Technician (hand-written data form) | Data Processing Personnel | Not Applicable |
| Sample Receiving and Chain-of-Custody | Sample Tracker | LIMS (sample tracker enters data at a local terminal) | Sample numbers are verified automatically; reports indicate missing filters and/or incorrect data entries |
| Calibration and Audit Data | Regional Office/Technical Services Staff | PSCAA Air Monitoring Manager | Entries are checked by PSCAA QA Specialist |
| AQS data summaries | PSCAA Data Specialist | AQS (U.S. EPA) | Entries are checked by PSCAA QA Specialist |

## 9.6 DATA REDUCTION

Data reduction processes involve aggregating and summarizing results so that they can be understood and interpreted in different ways. Regular reports to AQS will be submitted, as specified in the project work plan. Additional data summaries to EPA Region 10 may include:

- average concentration for a station or set of stations for a specific time period;
- accuracy, bias, and precision statistics, and

- data completeness reports based on numbers of valid samples collected during a specified period.

As an integral part of all data transformations and reductions is the audit trail that provides documentation for changes made to a data set during processing. Typical reasons for data changes that would be recorded include the following:

- corrections of data input due to human error;
- application of revised calibration factors;
- addition of new or supplementary data;
- flagging of data as invalid or suspect, and
- logging of the date and times when automated data validation programs are run.

Audit trail records will include the following fields:

- operator's identity (ID code);
- date and time of the change;
- table and field names for the changed data item;
- reason for the change;
- full identifying information for the item changed (date, time, site location, parameter, etc.), and
- value of the item before and after the change.

When routine data screening programs are run, the following additional data are recorded in the audit trail:

- version number of the screening program;
- values of screening limits (e.g., upper and lower acceptance limits for each parameter), and
- numerical value of each data item flagged and the flag applied.

The audit trail is produced automatically and can only document changes; there is no "undo" capability for reversing changes after they have been made. Available reports based on the audit trail include:

- log of routine data validation, screening, and reporting program runs;
- report of data changes by station for a specified time period;
- report of data changes for a specified purpose, and
- report of data changes made by a specified person.

Because of storage requirements, the Data Specialist must periodically move old audit trail records to backup media. Audit trail information will not be moved to backup media until after the data are reported to AQS. All backups will be retained so that any audit trail information can be retrieved for at least three years.

## 9.7 DATA SUMMARY AND ANALYSIS

Procedures for Air Toxics monitoring are still being developed and it is anticipated that as the Air Toxics Monitoring Program matures, additional data analysis procedures will be developed. The following specific summary statistics will be tracked and reported:

- Mean, maximum, and minimum concentration for each pollutant.
- Single sampler bias or accuracy (based on audit flow checks and laboratory audits).
- Single sampler precision (based on co-located data).
- Comparison of concentrations between sites.
- Time series plots of concentration.
- Network-wide bias and precision.
- Data completeness.

**Table 9-4. Report Equations**

| Criterion | Equation |
|---|---|
| Accuracy of Single Sampler Flow - Single Check ($d_i$) $X_i$ is reference flow; $Y_i$ is measured flow | $d_i = \frac{Y_i - X_i}{X_i} x\,100$ |
| Bias of a Single Sampler – Annual Basis ($D_j$)- average of individual percent differences between sampler and reference value; $n_j$ is the number of measurements over the period | $D_j = \frac{1}{n_j} x \sum_{i=1}^{n_j} d_i$ |
| Percent Difference for a Single Check ($d_i$) - $X_i$ and $Y_i$ are concentrations from the primary and duplicate samplers, respectively. | $d_i = \frac{Y_i - X_i}{(Y_i + X_i)/2} x100$ |
| Upper 95% Confidence Limit* | $Limit = d_i + 1.96 * S_i$ |
| Lower 95% Confidence Limit* | $Limit = d_i - 1.96 * S_i$ |
| Completeness | $Completeness = \frac{N_{valid}}{N_{theoretical}} * 100$ |

$*S_I$ = Sample Standard Deviation

## 9.8 DATA TRACKING

The Lab LIMS system contains the necessary input functions and reports necessary to track and account for the whereabouts of samples, and the status of analytical operations for specific data. Information about sample location is updated at distributed data entry terminals at the points of significant operations. The following input locations are used to track sample location and analytical results:

- Laboratory
- Sampling media receipt (by lot).
- Pre-sampling processing or weighing (individual filter or cartridge number first enters the system).

- Canister number (VOC only).
- Filter packaged for the laboratory (filter numbers in each package are recorded).
- Sample receipt (package is opened and filter numbers are logged in).
- Filter post-sampling weighing.
- Filter archival.

In most cases the tracking database and the monitoring database are updated simultaneously. For example, when the filter is pre-weighed, the weight is entered into the monitoring database and the filter number and status are entered into the tracking database. For the VOC system, the sample handling is different. The VOC canisters are reused many times before they are retired from field use. Each canister has its own unique code that designates the can number. When the canister is sent into the field, a canister number becomes a portion of the tracking code. This allows the sample that was in the canister to be tracked.

## 9.9 DATA STORAGE AND RETRIEVAL

All of the information collected for this project will be retained for a minimum of 3 years from the date PSCAA submits its final report to EPA unless otherwise noted. However, if any litigation, claim, negotiation, audit or other action involving the records has been started before the expiration of the 3-year period, the records will be retained until completion of the action and resolution of all issues which arise from it, or until the end of the regular 3-year period, whichever is later. PSCAA will extend this regulation in order to store records for three full years past the year of collection.

All major data including concentrations, methods, and site information will be in AQS.

**Table 9-5. Data Archive Policies**

| Data Type | Medium | Location | Retention Time | Final Disposition |
|---|---|---|---|---|
| Weighing records; chain of custody forms | Hardcopy | Laboratory | 3 years | Discarded |
| Laboratory Notebooks | Hardcopy | Laboratory | 3 years | N/A |
| Field Notebooks/Logs | Hardcopy | PSCAA Office | 3 years | Discarded |
| Data Base (excluding Audit Trail records) | Electronic (on-line) | PSCAA Office | indefinite (may be moved to backup media after 5 years) | Backup tapes retained indefinitely |
| Trail record | Hardcopy and electronic reports | PSCAA Office | 3 years | N/A |
| Glass Fiber Quartz filters | Filters | Laboratory | 3 years at Lab, 2 years at rental storage | Discarded |
| VOC canisters | Metal can | Laboratory | reused after cleaning | Recycled |
| PUF Samples | Hardcopy | Laboratory | Until extracted | Discarded |
| DNPH cartridge | Hardcopy | Laboratory | Until extracted | Discarded |
| Speciation filters | Filters | Laboratory | 5 years | Discarded |

The data reside on the LIMS system on the Laboratory server. Security of data in the database is ensured by the following controls:

- Password protection on the database
- Storage of media including backup tapes in locked, restricted access areas

# 10 ASSESSMENTS AND RESPONSE ACTIONS

An assessment is defined as an evaluation process used to measure the performance or effectiveness of the monitoring network or of the quality system, and the various measurement phases of the data gathering operation.

The results of quality assurance assessments indicate whether the control efforts are adequate or need to be improved. Documentation of all quality assurance and quality control efforts implemented during the data collection, analysis, and reporting phases is important to data users, who can then consider the impact of these control efforts on the data quality. Both qualitative and quantitative assessments of the effectiveness of these control efforts will identify those areas most likely to impact the data quality and to what extent.

In order to ensure the adequate performance of the quality system, PSCAA in conjunction with the EPA Region 10 office and the EPA Office of Air Quality Planning and Standards will perform the following assessments:

- Network Reviews
- Technical Systems Audits
- Audits of Data Quality
- Data Quality Assessments

## 10.1 NETWORK REVIEWS

Conformance with the requirements of the monitoring network will be determined through an annual review. The network review will be used to determine how well the air monitoring network is achieving its required objectives, and how it should be modified to continue to meet those objectives. The Air Monitoring Program Manager will be responsible for conducting the network review.

Prior to the network review, significant data and background information for the review will be compiled and evaluated. Such information might include the following:

- network files (including updated site information and site photographs),
- AQS reports,
- air quality data summaries, and
- emission information.

**Location of Monitors** - Adequacy of the location of monitors can only be determined on the basis of stated objectives. Maps, graphical overlays, and GIS-based information will be helpful in visualizing or assessing the adequacy of monitor locations. Plots of potential emissions and/or historical monitoring data versus monitor locations may also be used.

During the network review, the stated objective for each monitoring location or site will be "reconfirmed" and the spatial scale "verified" and then compared to each location to determine whether these objectives can still be attained at the present location.

**Probe Siting Requirements** - The onsite visit will consist of the physical measurements and observations to determine that requirements are being met. Prior to the site visit, the reviewer will obtain and review the following:

- most recent hard copy of site description (including any photographs),
- data on the seasons with the greatest potential for high concentrations for specified pollutants, and
- predominant wind direction by season.

A checklist similar to the checklist used by the EPA Regional offices during their scheduled network reviews will be used. This checklist can be found in the *SLAMS/NAMS/PAMS Network Review Guidance*, which is intended to assist the reviewers. In addition to the items on the checklist, the reviewer will also perform the following tasks:

- ensure that the inlet is clean,
- record findings in field notebook and/or checklist,
- take photographs/videotape in the 8 directions, and
- document site conditions with additional photographs/videotape.

**Other Requirements** - In addition to the items included in the checklists, other aspects of the network review and determination of overall adequacy of the monitoring program will include:

- installation of new monitors,
- re-location of existing monitors,
- siting criteria problems and suggested solutions,
- problems with data submittals and data completeness,
- maintenance and replacement of existing monitors and related equipment,
- quality assurance problems, and
- air quality studies and special monitoring programs.

After the assessment, corrective actions will be implemented by PSCAA.

### 10.2 DATA QUALITY ASSESSMENTS

A data quality assessment is the statistical analysis of environmental data to determine whether the quality of data is adequate to support the decisions, which will be made by PSCAA. Data are appropriate if the level of uncertainty meets the Data Quality Objectives specified in this plan. This process is described in detail in *Data Quality Assessment: A Reviewers Guide*, EPA QA/G-9R and is summarized below.

1. Review the DQO and sampling design of the project.

2. Conduct a preliminary data review. Review Precision and Accuracy (P&A) and other available QA reports, calculate summary statistics, plots and graphs. Look for patterns, relationships, or anomalies.
3. Select the best statistical test for analysis based on the preliminary review and identify underlying assumptions about the data for that test.
4. Verify that the underlying assumptions made by the selected test hold true for the data and the consequences.
5. Perform the statistical tests, document the results, and evaluate the performance of the project for future reference.

The Data Quality assessment will be included in the final project report.

Estimates of the data quality will be calculated on the basis of single monitors and aggregated to all monitors.

**Table 10-1. Assessment Activity Summary**

| Assessment Activity | Frequency | Personnel Responsible | Schedule | Report Completion | Reporting/Resolution |
|---|---|---|---|---|---|
| Network Review | 1/year | PSCAA Air Monitoring Manager | 2009 | 30 days after activity | PSCAA Air Monitoring Department |
| Audits of Data Quality | Ongoing | PSCAA QA Specialist, ERG and RTI | Ongoing | 30 days after activity | PSCAA Air Monitoring Department |
| Data Quality Assessment | Each project | PSCAA QA Specialist | Ongoing | 120 days after activity | PSCAA Air Monitoring Department |

# 11 REPORTS TO MANAGEMENT AND EPA

This section describes the quality-related reports and communications to management necessary to support air toxics network operations and the associated data acquisition, validation, assessment, and reporting.

Important benefits of regular QA reports to management include the opportunity to alert the management of data quality problems, to propose viable solutions to problems, and to procure necessary additional resources. Management should not rely entirely upon the TSA for their assessment of the data, since they occur once every two or three years.

Effective communication among all personnel is an integral part of a quality system. Regular, planned quality reporting provides a means for tracking the following:

- adherence to scheduled delivery of data and reports,
- documentation of deviations from approved QA and test plans, and the impact of these deviations on data quality, and
- analysis of the potential uncertainties in decisions based on the data.

## 11.1 REPORTS

Required reports to management for monitoring in general are discussed in various sections of 40 CFR Parts 53 and 58. Report format and content are described in guidance developed by EPA's Quality Assurance Division (QAD) and the Office of Air Quality Planning and Standards (OAQPS). These reports are described in the following subsections.

### *11.1.1 QA Annual Report*

Periodic assessments of air toxics data should be reported to EPA. The final report for this project will provide this assessment. It will describe both the quality objectives for measurement data and how those objectives have been met.

For reporting air toxics measurement uncertainties, the report will contain the following summary information:

- Flow Rate Audit results.
- Co-located Samplers Audit results, estimating Precision and Bias.
- Laboratory Audit results, which include any “round-robin” samples that are shared among many laboratories.
- NPAP audit results.

### *11.1.2 Network Review Reports*

Section 10 describes these reviews and the reporting requirements.

### *11.1.3 Response/Corrective Action Reports*

The Response/Corrective Action Report procedure will be followed whenever a problem is found such as a safety defect, an operational problem, or a failure to comply with procedures. A Response/Corrective Action Report is one of the most important ongoing reports to management because it documents primary QA activities and provides valuable records of QA activities.

# 12 RECONCILIATION WITH DATA QUALITY OBJECTIVES

Data Quality Assessment (DQA) is a critical part of determining the value of the measurements made during this project. Following data validation and verification, it indicates how well the data can support their intended use. This section of the QAPP will outline the assessment procedures that will be followed to determine whether the sampling and the laboratory analyses are producing data that comply with the stated goals. It will also indicate what action will be taken as a result of the assessment process. This process is thoroughly described in *EPA QA/G-9R: Data Quality Assessment: A Reviewers Guide.*

## 12.1 DATA QUALITY ASSESSMENT

In order to determine if this project's stated Data Quality Objectives have been met, the assessment process must follow statistical routines. The following five steps will discuss how this will be achieved.

### *12.1.1 Review Data Quality Objectives and Sampling Design.*

Section 6 of this QAPP contains the details for the development of the DQO, including defining the objectives of the air toxics monitoring network and developing limits on the decision errors. Section 4 contains the details for the sampling design, including the rationale for the design, the design assumptions, and the sampling locations and frequency. If any deviations from the sampling design have occurred, these will be indicated and their potential effect carefully considered throughout the entire DQA. A preliminary data review will be performed to uncover potential limitations to using the data, to reveal outliers, and generally to explore the basic structure of the data.

### *12.1.2 Review Quality Assurance Reports.*

The first step is to review the quality assurance reports. All relevant quality assurance reports, internal and external, that describe the data collection and reporting process will be reviewed qualitatively. Particular attention will be directed to looking for anomalies in recorded data, missing values, and any deviations from standard operating procedures. Any concerns will be further investigated in the next two steps.

### *12.1.3 Select the Statistical Test*

The second step is to calculate basic summary statistics, generate graphical presentations of the data, and review these summary statistics and graphs. This will be done for each of the primary and QA samplers. Summary statistics will be calculated on an annual basis and will include only valid samples. These following statistical tests will be performed:

- Test to examine distribution of the data.
- Simple annual averages of all pollutants.
- Examination of bias and precision of the data.
- Seasonal averages to determine any seasonal variability.

Particular attention will be given to the impact on the statistics caused by the observations noted in the quality assurance review. PSCAA may evaluate the influence of a potential outlier by evaluating the change in the summary statistics resulting from exclusion of the outlier.

### *12.1.4 Verify assumptions of Statistical Test*

Verification of the data will be done against estimated air toxic values expected from modeling. However, before this can occur, the distribution, tests for trends, tests for outliers must be examined.

*Normal distribution for measurement error* - Assuming that measurement errors are normally distributed is common in environmental monitoring. Small departures from normality generally do not create serious problems and PSCAA will evaluate the reasonableness of the normality assumption by reviewing a normal probability plot and employing the Coefficient of Variance Test. If the plot or statistics indicate possible violations of normality, we may need to determine the sensitivity of the DQO to departures in normality.

*Trends Analysis* - A simple linear regression test can be performed to observe the temporal variations in the data sets. Air toxics emissions from mobile sources would vary with the diurnal variations of traffic in urban and suburban environment. A linear regression test would provide information on whether certain compounds are tied to mobile sources. For instance, benzene is identified as major mobile HAP. If a linear regression is performed against a compound whose source is unknown, then a small correlation coefficient would provide information on its possible source. Seasonal plots can also be useful in providing information about sources with seasonal emissions characteristics.

*Measurement precision and bias* - For each sampling system the 95% confidence limits will be determined. If any exceed the DQO the impact on data use will be considered and actions to reduce these errors identified for future studies. The algorithms from Section 6 will be used for creating the confidence intervals.

### *12.1.5 Draw Conclusions from the Data.*

If the sampling design and the statistical test bear out, it can be assumed that the network design and the uncertainty of the data are acceptable. This conclusion can then be written in the Annual Data Summary to management and the PSCAA Board. Management may then decide whether to perform risk assessments, allow the State and EPA to analyze the data or work closely with the nearby university to determine whether this data can be used to assess conclusion from health effects studies.

### *12.1.6 Create Action Plan.*

Based on the results of the DQA, PSCAA may initiate any of a number of actions. This could include such things as network siting changes, sampling or analytical changes, quality control changes, data handling changes, or no action at all. Recommendations will be presented in the project final report.

# *Appendices*

## APPENDIX A

## Puget Sound Clean Air Agency - Sampling Site Instrument Log

STATION: ______________________ AQS CODE: ______________________

| Date | Time | Tech | Instrument | Wall Value | Zero | Span | Analyzer Temp | Comments |
|---|---|---|---|---|---|---|---|---|
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# APPENDIX B – ERG DATA SHEETS

ERG

ERG Lab ID #

Site Code: ____________

City/State: ____________

AQS Code: ____________

Collection Date: ____________

Options

SNMOC (Y/N): ____________

TOXICS (Y/N): ____________

Canister Number: ____________

Lab Initial Can. Press. ("Hg): ____________

Date Can. Cleaned: ____________

Cleaning Batch # : ____________

Duplicate Event (Y/N): ____________

Duplicate Can # : ____________

Operator: ____________ Sys. #: ____________

Setup Date: ____________

Field Initial Can. Press. ("Hg): ____________

MFC Setting: ____________

Elapsed Timer Reset (Y/N): ____________

Canister Valve Opened (Y/N): ____________

Recovery Date: ____________

Field Final Can. Press. ("Hg): ____________

Sample Duration (3 or 24 hr): ____________

Elapsed Time: ____________

Canister Valve Closed (Y/N): ____________

Received by: ____________ Date: ____________

Lab Final Can. Press. ("Hg): ____________

Status: Valid Void (Circle one)

If void, why: ____________

Analyst: ____________ Date: ____________

Batch I.D.: ____________

Analyst: ____________ Date: ____________

Batch I.D.: ____________

Comments: ____________

White: Sample Traveler Canary: Lab Copy Pink: Field Copy

ERG

ERG Lab ID #

Site Code:

Collection Date:

City/State:

Cartridge Lot #:

AQS Code:

Duplicate Event (Y/N):

Set-Up Date:

Operator:

Sys. #:

Pre-Sampling Rotameter Reading (cc/min):

Elapsed Timer Reset (Y/N):

Recovery Date:

Sample Duration (3 or 24 hr):

Post Sampling Rotameter Reading (cc/min):

Elapsed Time:

Cartridges Capped (Y/N):

Received by:

Date:

Refrigerator No:

Status: Valid Void (Circle one)

If void, why:

Sample Volume (total Liters):

| | | | | | | |
|---|---|---|---|---|---|---|
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Comments:

White: Sample Traveler Canary: Lab Copy Pink: Field Copy

ERG Lab ID #

Site Code: ______________________
City/State: ______________________
AQS Code: ______________________

Collection Date: ______________
Collocated Event (Y/N): ___________

Site Operator: ___________________
Set-Up Date: ___________________
Collection Date: ___________________
Batch I.D. No.: ___________________
Batch Certification Date: _______________

Sampler ID: __________________
Elapsed Timer Reset (Y/N): _______

**Collection System Information:**

| | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
|---|---|---|---|---|---|
| [illegible] | | | | | |
| [illegible] | | | | | |
| [illegible] | | | | | |

Total Collection Time (Minutes) ___________

Total Collection Volume (std. $m^3$) ________

Received by: __________________ Date: ________ Refrigerator No.: ___________
Status: Valid Void (Circle one)
If void, why: ____________________________________________

Comments: ________________________________________________

White: Sample Traveler Canary: Lab Copy Pink: Field Copy

# APPENDIX C – PSCAA QC SHEETS

**Canister Sampler Quality Control Worksheet**

Site: ____________ Date: ________

Site Operator: ________

QC check Start Time: ____________ Stop Time: ________

Sampler ECY Number: ____________

**Leak Check** Pass Fail

**Comments**

# *P.U.F. Calibration*

| | | | |
|---|---|---|---|
| **Date** | **Site** | **Sampler I.D.** | **Operator** |

| | | | |
|---|---|---|---|
| **Orifice I.D.** | **Cal Date** | **Manometer** | **Cal Date** |

| |
|---|
| **Timer Error in minutes** |

| Oriface Slope | Oriface Intercept | Oriface Coefficent | Temp | Press |
|---|---|---|---|---|
| | | | | |
| | | | in degrees C | in mmHg |

| Y1 | Y2 |
|---|---|
| | 70 |
| | 60 |
| | 50 |
| | 40 |
| | 30 |
| | 20 |
| | 10 |

## Carbonyl Sampler Quality Control Worksheet

Site: ____________ Date: ________

Site Operator: ________

QC check Start Time: ____________ Stop Time: ________

Sampler ECY Number: ____________

Thermometer Serial #: ____________ Certification Date: ________

Barometer Field Serial #: ____________ Certification Date: ________

Flow Standard Serial #: ____________ Certification Date: ________

Ambient Temperature: ____________ °C

Barometeric Pressure: ____________ mmHg

## Leak Check

| | | |
|---|---|---|
| Channel A | Pass | Fail |
| Channel B | Pass | Fail |

| **Total Flow** | **(Qa) Flow (Lpm)** | **(Qs) Flow** | **Indicated (Lpm)** | **Percent difference** |
|---|---|---|---|---|
| Channel A | ____________ | | ____________ | |
| Channel B | ____________ | | ____________ | |

## Comments

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# Appendix C: Risk Analysis Methods

**Table C-1: Analytes Found Under Detection with a WA-460 Acceptable Source Impact Level Below Detectability.**

| Analyte | Average Detection Limit in Study ($\mu$g/m$^3$) | WA-460 Acceptable Source Impact Level ($\mu$g/m$^3$) |
|---|---|---|
| 1,1,2,2-Tetrachloroethane | 0.062 | 0.0172 |
| Acrylonitrile | 0.020 | 0.00345 |

**Table C-2: Analytes with no WA-460 Acceptable Source Impact Level**

| Analyte | Mean Concentration at Seattle Duwamish and other sites where noted ($\mu$g/m$^3$) |
|---|---|
| 1,2,4-Trimethylbenzene | 0.28 |
| 1,2,4-Trichlorobenzene | ND |
| 1,3,5-Trimethylbenzene (mesitlyene) | 0.088 |
| 2,5-Dimethylbenzaldehyde | ND |
| 9-Fluorenone | 0.002 |
| Acenaphthene | 0.00083 |
| Acenaphthylene | 0.000184 |
| Acetone | 2.4 |
| Acetylene | 1.4 |
| Anthracene | 0.00093 |
| Benzaldehyde | 0.263 |
| Benzo (e) pyrene | Max 0.0032 |
| Benzo (g,h,i) perylene | Max 0.0019 |
| Bromochloromethane | ND |
| Butyraldehyde | 0.064 |
| cis-1,2-Dichloroethylene | 1 Detect at each site, max 0.25 |
| Chloroprene | ND |
| Coronene | 0.000101 |
| Crotonaldehyde | 0.1 |
| Cyclopenta[cd]pyrene | 0.000239 |
| Ethyl acrylate | ND |
| Fluoranthene | Max 0.011 |
| Fluorene | Max 0.037 |
| Hexaldehyde | 0.224 |
| Isovaleraldehyde | Few detects - max at 0.072 |
| m-Dichlorobenzene | 1 detect at 0.012 |
| n-Octane | 0.149 |
| o-Dichlorobenzene | ND |
| Perylene | Some detects - Max 0.0008 |
| Phenanthrene | Max 0.069 |
| Pyrene | Max 0.007 |
| Retene | 0.00053 |
| tert-Amyl Methyl Ether | ND |
| Tolualdehydes | 0.119 |
| trans-1,2-Dichlorethylene | 0.063 |
| trans-1,3-Dichloropropene | 1 Detect at 0.022 |
| Trichlorofluoromethane | 1.79 |
| Trichlorotrifluoroethane | 0.857 |
| Valeraldehyde | 0.97 |

## Table C-3: Analytes Found Under the WA-460 Acceptable Source Impact Level

| Analyte | WA-460 Acceptable Source Impact Level ($\mu$g/m$^3$) | Mean Concentration at Seattle Duwamish and other sites where noted ($\mu$g/m$^3$) |
|---|---|---|
| 1,1,2,2-Tetrachloroethane | 0.0172 | ND |
| 1,1,2-Trichloroethane | 0.0625 | 2 detects at 0.027 |
| Acetonitrile | 60 | - |
| Acrylonitrile | 0.00345 | ND |
| Benzo (a) anthracene | 0.00909 | Max 0.002 |
| Benzo (a) pyrene | 0.000909 | Kaplan Meier Est. 0.000208 |
| Benzo (b) fluoranthene | 0.00909 | Max 0.0039 |
| Benzo (k) fluoranthene | 0.00909 | Max 0.0011 |
| Benzylchloride (Chloromethylbenzene) | 0.0204 | ND |
| Bromodichloromethane | 0.027 | 1 Detect at each site, max 0.034 |
| Bromoform | 0.909 | Max 0.011 |
| Carbon disulfide | 800 | 0.028 |
| Chlorobenzene | 1000 | All NDs |
| Chrysene | 0.0909 | Max 0.0029 |
| cis-1,3-Dichloropropene | 0.0625 | 1 Detect, 0.014 |
| Dibenz(a,h)anthracene | 0.00083 | Max 0.0002 |
| Dibromochloromethane | 0.037 | 1 Detect at 0.020 from 2 sites |
| Ethyl chloride (Chloroethane) | 30000 | 0.046 |
| Ethylbenzene | 0.4 | 0.312 |
| Ethylene dibromide (1,2-dibromoethane) | 0.0141 | Max 0.023 |
| Ethylene dichloride (1,2-dichloroethane) | 0.0385 | Max 0.085 |
| Ethylidene dichloride (1,1-Dichloroethane) | 0.625 | Max 0.008 |
| Hexachlorobutadiene (Hexachloro-1,3-butadiene) | 0.0455 | ND |
| Indeno(1,2,3-cd)pyrene | 0.00909 | Max 0.0019 |
| m- or p-Xylene | 221 | Max 7.3 |
| Methyl Bromide (Bromomethane) | 5 | 0.053 |
| Methyl Chloride (Choromethane) | 90 | 1.37 |
| Methyl Chloroform (1,1,1-trichloroethane) | 1000 | 0.087 |
| Methyl ethyl ketone | 5000 | 0.686 |
| Methyl isobutyl ketone | 3000 | 0.053 |
| Methyl methacrylate | 700 | Max 0.185 |
| Methyl tert-butyl ether | 3.85 | Max 1.08 |
| Methylene chloride | 1 | 0.586 |
| o-Xylene | 221 | Max 2.59 |
| p-Dichlorobenzene | 0.0909 | Max 0.030 |

| | | |
|---|---|---|
| Propylene | 3000 | 0.72 |
| Propylene dichloride (1,2-dichloropropane) | 0.1 | 1 detect at 0.083 |
| Styrene | 900 | Max 0.784 |
| Toluene | 5000 | Max 13.5 |
| Trichloroethylene | 0.5 | Max 0.44, avg 0.031 |
| Vinyl Chloride | 0.0128 | Max 0.046, 5-35% Detects depending on the site |

## Table C-4: Annual Statistics for Selected Air Toxics Above Acceptable Source Impact Level

| Concentrations in $\mu$g/m$^3$ | | Site | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Analyte | Statistic | Seattle Duwamish | Tacoma Tideflats | Tacoma South L St | Tacoma Portland Ave Reservoir | NATTS | Seattle Beacon Hill | WA-460 ASIL |
| 1,3-Butadiene | Mean | 0.099 | 0.090 | 0.131 | 0.107 | 0.204 | 0.074 | 0.00588 |
| | Median | 0.064 | 0.051 | 0.077 | 0.064 | 0.111 | 0.049 | 0.00588 |
| | Minimum | 0.011 | 0.013 | 0.013 | 0.013 | 0.005 | 0.011 | 0.00588 |
| | Maximum | 0.740 | 0.661 | 1.255 | 0.524 | 21.000 | 0.888 | 0.00588 |
| | Percentile 05 | 0.022 | 0.013 | 0.013 | 0.018 | 0.022 | 0.022 | 0.00588 |
| | Percentile 25 | 0.033 | 0.024 | 0.031 | 0.033 | 0.044 | 0.033 | 0.00588 |
| | Percentile 75 | 0.111 | 0.113 | 0.148 | 0.119 | 0.243 | 0.071 | 0.00588 |
| | Percentile 95 | 0.281 | 0.314 | 0.400 | 0.360 | 0.688 | 0.186 | 0.00588 |
| | % NDs | 0% | 0% | 1.69% | 0% | . | 1.61% | . |
| Acetaldehyde | Mean | 1.403 | 1.365 | 0.972 | . | 1.883 | 0.919 | 0.37 |
| | Median | 1.346 | 1.203 | 0.884 | . | 1.440 | 0.682 | 0.37 |
| | Minimum | 0.488 | 0.572 | 0.261 | . | 0.038 | 0.068 | 0.37 |
| | Maximum | 2.862 | 3.204 | 3.510 | . | 37.170 | 3.366 | 0.37 |
| | Percentile 05 | 0.589 | 0.635 | 0.313 | . | 0.341 | 0.385 | 0.37 |
| | Percentile 25 | 0.909 | 0.928 | 0.560 | . | 0.900 | 0.508 | 0.37 |
| | Percentile 75 | 1.744 | 1.696 | 1.240 | . | 2.340 | 1.197 | 0.37 |
| | Percentile 95 | 2.592 | 2.565 | 2.088 | . | 4.644 | 1.944 | 0.37 |
| | % NDs | 0% | 0% | 0% | . | . | 0% | . |
| Acrolein | Mean | 0.389 | 0.374 | 0.356 | . | 0.496 | 0.543 | 0.06 |
| | Median | 0.344 | 0.298 | 0.319 | . | 0.344 | 0.412 | 0.06 |
| | Minimum | 0.126 | 0.119 | 0.119 | . | 0.001 | 0.055 | 0.06 |
| | Maximum | 1.301 | 3.023 | 0.753 | . | 6.756 | 2.931 | 0.06 |
| | Percentile 05 | 0.165 | 0.167 | 0.156 | . | 0.038 | 0.133 | 0.06 |
| | Percentile 25 | 0.238 | 0.227 | 0.275 | . | 0.213 | 0.275 | 0.06 |
| | Percentile 75 | 0.467 | 0.405 | 0.426 | . | 0.595 | 0.698 | 0.06 |
| | Percentile 95 | 0.724 | 0.623 | 0.733 | . | 1.402 | 1.072 | 0.06 |
| | % NDs | 0% | 1.69% | 0% | . | . | 1.61% | . |
| Benzene | Mean | 0.918 | 0.998 | 1.294 | 1.167 | 1.077 | 0.840 | 0.0345 |
| | Median | 0.692 | 0.777 | 0.928 | 0.938 | 0.828 | 0.691 | 0.0345 |
| | Minimum | 0.134 | 0.274 | 0.134 | 0.163 | 0.003 | 0.128 | 0.0345 |
| | Maximum | 4.179 | 5.359 | 7.497 | 3.700 | 21.107 | 5.359 | 0.0345 |
| | Percentile 05 | 0.236 | 0.303 | 0.226 | 0.274 | 0.160 | 0.262 | 0.0345 |
| | Percentile 25 | 0.501 | 0.482 | 0.590 | 0.581 | 0.479 | 0.482 | 0.0345 |
| | Percentile 75 | 1.088 | 1.085 | 1.439 | 1.448 | 1.329 | 1.053 | 0.0345 |
| | Percentile 95 | 2.600 | 2.877 | 3.700 | 3.062 | 2.839 | 1.487 | 0.0345 |
| | % NDs | 0% | 0% | 0% | . | . | 0% | . |
| Carbon Tetrachloride | Mean | 0.759 | 0.762 | 0.768 | 0.741 | 0.528 | 0.793 | 0.0238 |
| | Median | 0.717 | 0.711 | 0.739 | 0.711 | 0.554 | 0.764 | 0.0238 |
| | Minimum | 0.327 | 0.390 | 0.390 | 0.415 | 0.000 | 0.390 | 0.0238 |
| | Maximum | 1.132 | 1.176 | 1.214 | 1.126 | 1.529 | 1.214 | 0.0238 |
| | Percentile 05 | 0.516 | 0.535 | 0.554 | 0.516 | 0.315 | 0.585 | 0.0238 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Percentile 25 | 0.629 | 0.635 | 0.635 | 0.616 | 0.375 | 0.679 | 0.0238 |
| | Percentile 75 | 0.843 | 0.855 | 0.855 | 0.855 | 0.629 | 0.899 | 0.0238 |
| | Percentile 95 | 1.107 | 1.145 | 1.151 | 1.101 | 0.818 | 1.107 | 0.0238 |
| | % NDs | 0% | 0% | 0% | 0% | . | 0% | . |
| Chloroform | Mean | 0.111 | 0.115 | 0.115 | . | 0.254 | 0.151 | 0.0435 |
| | Median | 0.107 | 0.107 | 0.107 | . | 0.244 | 0.146 | 0.0435 |
| | Minimum | 0.059 | 0.068 | 0.039 | . | 0.010 | 0.068 | 0.0435 |
| | Maximum | 0.234 | 0.278 | 0.273 | . | 16.299 | 0.395 | 0.0435 |
| | Percentile 05 | 0.068 | 0.073 | 0.063 | . | 0.041 | 0.083 | 0.0435 |
| | Percentile 25 | 0.088 | 0.083 | 0.078 | . | 0.100 | 0.117 | 0.0435 |
| | Percentile 75 | 0.127 | 0.132 | 0.142 | . | 0.244 | 0.166 | 0.0435 |
| | Percentile 95 | 0.171 | 0.210 | 0.181 | . | 0.634 | 0.249 | 0.0435 |
| | % NDs | 0% | 0% | 0% | . | . | 0% | . |
| Formaldehyde | Mean | 2.816 | 1.964 | 1.465 | . | 2.921 | 1.013 | 0.167 |
| | Median | 2.804 | 1.784 | 1.451 | . | 2.030 | 0.563 | 0.167 |
| | Minimum | 0.721 | 0.542 | 0.442 | . | 0.062 | 0.073 | 0.167 |
| | Maximum | 5.670 | 6.679 | 3.887 | . | 91.635 | 16.605 | 0.167 |
| | Percentile 05 | 1.390 | 0.628 | 0.477 | . | 0.615 | 0.255 | 0.167 |
| | Percentile 25 | 2.079 | 0.978 | 0.900 | . | 0.861 | 0.405 | 0.167 |
| | Percentile 75 | 3.518 | 2.632 | 1.870 | . | 3.825 | 1.039 | 0.167 |
| | Percentile 95 | 4.711 | 4.010 | 3.001 | . | 8.364 | 1.882 | 0.167 |
| | % NDs | 0% | 0% | 0% | . | . | 0% | . |
| Naphthalene | Mean | 0.122 | 0.118 | 0.123 | . | 0.071 | 0.072 | 0.0294 |
| | Median | 0.101 | 0.102 | 0.092 | . | 0.064 | 0.054 | 0.0294 |
| | Minimum | 0.033 | 0.000 | 0.019 | . | 0.000 | 0.023 | 0.0294 |
| | Maximum | 0.547 | 0.417 | 0.528 | . | 0.220 | 0.225 | 0.0294 |
| | Percentile 05 | 0.037 | 0.032 | 0.024 | . | 0.002 | 0.024 | 0.0294 |
| | Percentile 25 | 0.068 | 0.057 | 0.035 | . | 0.038 | 0.035 | 0.0294 |
| | Percentile 75 | 0.146 | 0.146 | 0.164 | . | 0.103 | 0.097 | 0.0294 |
| | Percentile 95 | 0.279 | 0.274 | 0.341 | . | 0.153 | 0.199 | 0.0294 |
| | % NDs | 0% | 0% | 0% | . | . | 0% | . |
| Chromium VI TSP | Kaplan-Meier Mean | . | . | . | . | . | 3.30E-05 | |
| | Percentile 95 | . | . | . | . | . | 1.15E-04 | |
| | Maximum | . | . | . | . | | 2.32E-04 | |
| | 95% KM UCL (Chebushev) | . | . | . | . | . | 5.56E-05 | |
| | % NDs | . | . | . | . | . | 26.7% | |
| Tetrachloroethene | Kaplan-Meier Mean | 0.199 | 0.312 | 0.138 | 0.145 | . | 0.105 | 0.169 |
| | Percentile 95 | 0.576 | 0.759 | 0.400 | 0.427 | . | 0.339 | 0.169 |
| | Maximum | 1.756 | 4.746 | 0.678 | 1.017 | | 0.570 | 0.169 |
| | 95% KM UCL (Chebushev) | 0.361 | 0.676 | 0.224 | 0.239 | . | 0.188 | 0.169 |
| | % NDs | 5.08% | 3.45% | 22.4% | 6.90% | . | 8.06% | . |

## Table C-5: 2002 NATA Comparison to Study Results

| Pollutant | Seattle Duwamish | Tacoma Tide Flats | Tacoma South L St | Tacoma Portland Ave Reservoir | Seattle Beacon Hill |
|---|---|---|---|---|---|
| **1,3-Butadiene** | 8.5 | 3.0 | 1.1 | 1.7 | 3.3 |
| **Acetaldehyde** | 3.8 | 2.4 | 2.5 | N/A | 4.1 |
| **Acrolein** | 1.0 | 0.5 | 0.4 | N/A | 0.5 |
| **Benzene** | 13.0 | 4.6 | 2.0 | 2.8 | 5.7 |
| **Carbon Tetrachloride** | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| **Chloroform** | 1.3 | 1.1 | 0.8 | N/A | 1.1 |
| **Diesel Engine Emissions*** | 6.3 | N/A | 3.1 | N/A | 2.3 |
| **Formaldehyde** | 2.0 | 2.0 | 1.6 | N/A | 2.7 |
| **Napthalene** | 2.3 | 0.9 | 0.4 | N/A | 1.7 |
| **Tetrachloroethylene** | 1.1 | 0.5 | 0.8 | 0.7 | 1.5 |

* The study results for diesel emissions for South Tacoma are derived from the 2009 WA State Dept of Ecology Source Apportionment analysis[54] and the diesel emissions for Seattle Duwamish and Beacon Hill are derived from Kim, Hopke, 2008.[55]

## Table C-6 IRIS Hazard Identification Categories

| Group | Category |
|---|---|
| A | Human carcinogen |
| B | Probable human carcinogen:<br>B1 indicates limited human evidence;<br>B2 indicates sufficient evidence in animals and inadequate or no evidence in humans |
| C | Possible human carcinogen |
| D | Not classifiable as to human carcinogenicity |
| E | Evidence of non-carcinogenicity for humans |

## References for Appendix C:

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# Appendix D: Mobile Monitoring of Airborne Particles and Gases

## D 1.1 Membrane Introduction Mass Spectrometry (MIMS)

MIMS Instrumentation:

The experimental apparatus used for this work has been described in detail elsewhere.[56] Briefly, the MIMS system used consisted of a hollow fibre polydimethylsiloxane silicone™ (Dow-Corning Silastic™, Midland, MI) membrane (10.0 cm X 0.94 mm OD X 0.51mm ID), mounted in side a 0.25” stainless steel flow cell interface. A gas chromatograph (Thermo Trace™ GC, Austin, TX) was used to supply He (~1.0 mL/min, 99.999% pure, Praxair, Seattle, WA) and act as a membrane oven (70°C). Helium sweep gas transferred analytes to a quadrupole ion trap mass spectrometer (Thermo GCQ™, EI mode, 175°C ion source, 175°C transfer line, 1.0 X $10^{-5}$ Torr base pressure). For this study, the 0.25” Teflon™ (Cole Parmer, Montreal, QC, Canada) air sampling lines were heated (70° C) via a flexible heating tape (Omegallux Model CN 7500, City, State) sheathing. PTFE membrane filters (2.0 µm, 37 mm, SKC Corp., Eighty Four, PA) were used in line for particulate removal prior to MIMS measurement. A diaphragm pump regulated by a precision ball float meter (Model FM4334, Advanced Speciality Gas Equipment, Middlesex, NJ) was used to maintain a sample flow of 4.0 L/min. Toluene-d8 internal standard was infused via a gravimetrically calibrated permeation tube (6103 ng/min at 70° C) installed downstream from a 5 m in-line heat exchanger and both upstream from the MIMS. Gas standards for the calibration and determination of interference factors were generated using a commercial gas dilution apparatus (Model 450 Dynacalibrator, VICI Metronics, Poulsbo, WA) using gravimetrically calibrated permeation tubes. The apparatus was housed in a small moving van that was retrofitted for the field experiments with an in-house constructed shock absorbing bench to support the MIMS system, associated gas cylinders, computer and vacuum/sampling pumps. A diesel generator towed behind the moving van (MQ Power WisperWatt 25 kW, Lewisville, TX) supplied all electrical power for this work. Air samples were drawn into the MIMS on the left hand side of the moving van (the exhaust was on the right hand side of the vehicle). In preliminary experiments, negligible signals were observed for the generator and for the moving van, provided the vehicle was moving in a forward direction (as was the case during the sampling runs). A global positioning system (Trimble Juno ST GPS, City, State) was used to track the travelled routes for the system over the course of the study.

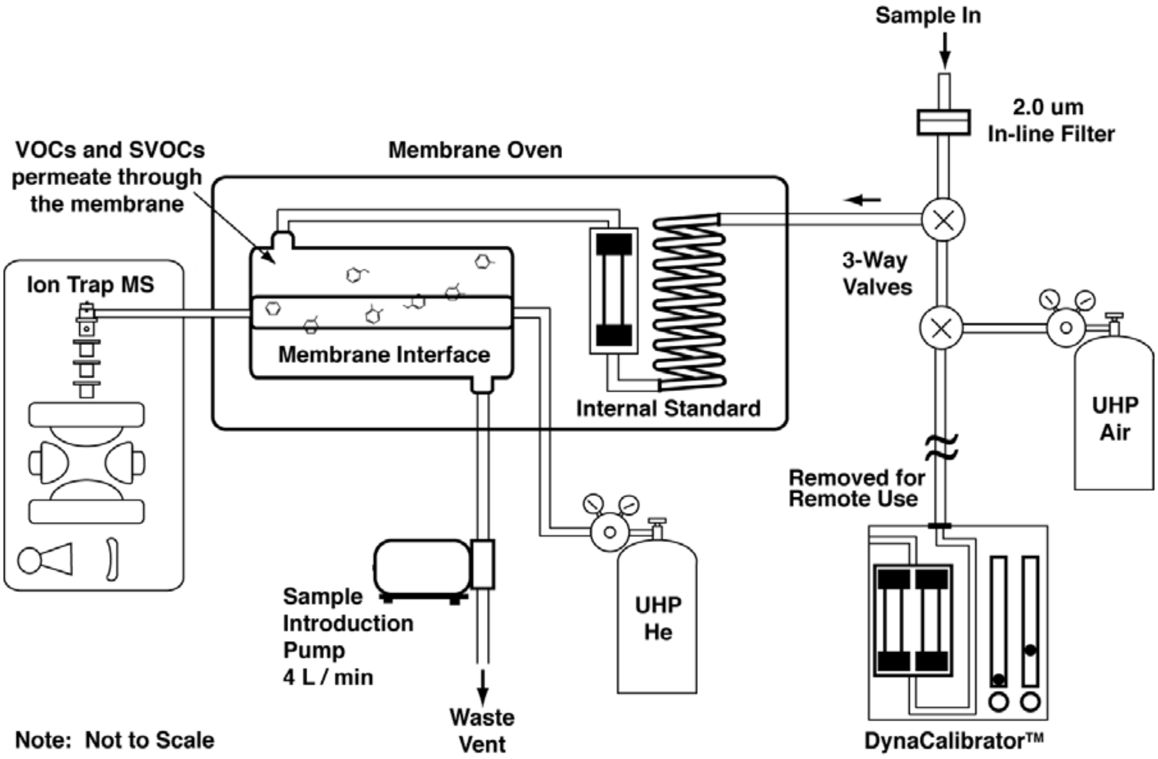

**Figure D.1: Schematic of MIMS instrumentation**

Chemical Analysis:

Levoglucosan and selected nitro- polycyclic aromatic hydrocarbons (1-nitropyrene, 2-nitropyrene and 2-nitrofluoranthene) were analyzed using previously described methods, with minor modifications[57,58]. In brief, TSP on Teflon filters were sonicated in methylene chloride, reduced in volume under nitrogen, and the extract filtered through a PTFE syringe filter. For analysis of levoglucosan, a portion of the extract was derivatized using MSTFA/pyridine prior to analysis using GC/MS with selected ion monitoring. The remainder of the extract was reduced to dryness, reconstituted in ethanol/water and NPAHs were determined using two-dimensional HPLC tandem-MS.

Statistical Analysis:

All raw signals were background corrected by subtracting the averaged zero-air baseline values for each trace. Toluene and Benzene raw signals were corrected for interference from ethylbenzene/xylene by subtracting 1.32 X ethylbenzene/xylene signal from the toluene signal and 0.4 X ethylbenzene/xylene signal from the benzene signal, based upon previously determined interference factors for each compound and the experimentally-measured ratios of ethylbenzene/xylene in the Seattle-Tacoma airshed over the course of this study. This is a potential source of error, especially for toluene, as it may result in slight over/under correction of the toluene signal, depending upon the variability in the relative concentrations of ethylbenzene and xylenes. Corrections for other (unknown) chemical species (e.g. pinenes) may also bias the results for the BTEX molecules, and although they are not suspected to be major contributors to interference, their effect on the data cannot be entirely ruled out.

Corrected signals for the five target compounds were then converted to concentration using response factors relative the toluene-d8 signal obtained from an continuously infused internal standard present in all experiments. This signal (internal standard) was stable throughout the runs (given that the flow rate is constant) except when there was dramatic variation in air sampling flows or temporary instrument operation failures as a result of large bumps etc from the instrument being located in a moving vehicle. In cases where this occurred (evidenced by disrupted internal standard signals), the data was omitted for clarity. To minimize 'noise' for near baseline signals, the data was smoothed using a moving boxcar averaging filter (7 datapoint window).

### D 1.2 Mobile Monitoring of Particles

Mobile Monitoring Sampling Instruments:

The following instruments were deployed on the mobile monitoring platform: 1) a nephelometer (Model 903) for measuring particle light scattering coefficient; 2) a particle soot absorption photometer (PSAP) for measuring light absorption coefficient; 3) an Ecochem (PAS 2000) for measuring particle-bound polycyclic aromatic hydrocarbons (PAHs); and 4) a GPS for incorporating data logger. (EcoChem, 1997)

The nephelometer (M903) was equipped with a small air blower and air pre-heater. Measurements were taken with a 15 second averaging time. The instrument zero was checked before sampling, and all the data were stored internally. A particle soot absorption photometer

(PSAP) was used to measure the particle light absorption coefficient (bap) and was equipped with an external pump and data logger . The Ecochem is equipped with its own pump and datalogger.

The instruments were located in the back seat of a vehicle and the sampling inlet was placed out of a sealed rear window. The inlet The average time of Nephelometer and Ecochem was set at 15seconds while the addition of a pump to the PSAP was 30 seconds. The datalogger clock for each equipment was synchronized in order to match that of the GPS receiver, a satellite-signaled clock, and the GPS data logger was set to record every second.

Mobile Monitoring Sampling locations:

The three afternoon routes encompass 39 intersections with heavy, moderate, and light traffic. To capture the effect of local wind direction, the vehicle followed a cloverleaf pattern at each intersection as shown in Figure D.2. Two reference intersections were visited during each afternoon for the mobile sampling, either at the beginning or end of the sampling period. The time of the cloverleaf traverse was from 5 to 15min. Our evening route covered most of the Tacoma area from east to west and from north to south. It was designed to include areas identified by the PSCAA woostove use survey (see Figure D.3). We traveled the overall routes in either a clockwise or counter-clockwise direction which was randomly chosen.

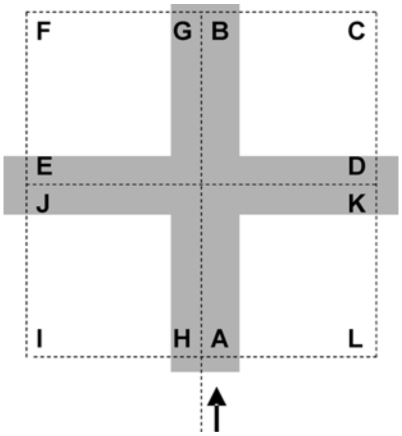

**Figure D.2. Cloverleaf pattern traversed by the vehicle at an intersection: vehicle enters intersection at A and moves to locations in alphabetical order, returning to A.**

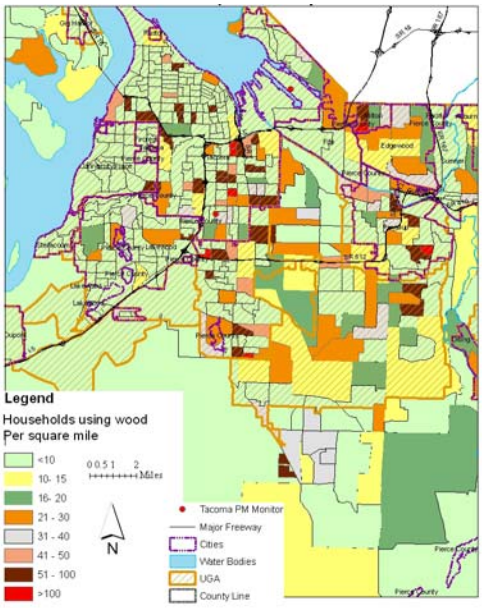

Figure D.3. Pierce County Tacoma Area Households Using Wood for Primary Heat Per Square Mile (PSCAA 2007).

Temporal adjustments:

The mobile platform data was merged with the suitable fixed site data collected by PSCAA at their reulatory monitoring sites in Tacoma. The one minute average $b_{sp}$ and $b_{ap}$ measurements sampled at the PSCAA's Portland Ave site were used in order to get the adjusted mobile measurements for within-day temporal variations. Although there is comparable data at 3 other PSCAA fixed sites in Tacoma, the Portland Ave fixed site was chosen because it was not strongly influenced by nearby local sources and therefore best represented the overall effects of within-period changes in meteorology over the entire study region. The South Tacoma L Street site was considered, but was impacted at times by local sources at night that were not representative of the overall study area.

The temporal adjustments of the observed values were computed as follows:

$$\left(\sigma_{sp}\right)_{15\text{sec}}^{\text{adjusted}} = \left(\sigma_{sp}\right)_{15\text{sec}}^{\text{mobile}} \left\{ \frac{\left(\sigma_{sp}\right)_{\text{period median}}^{\text{fixed site}}}{\left(\sigma_{sp}\right)_{\text{30-min median}}^{\text{fixed site}}} \right\}_{\text{within period}} \left\{ \frac{\left(\sigma_{sp}\right)_{\text{overall median}}^{\text{mobile}}}{\left(\sigma_{sp}\right)_{\text{period median}}^{\text{mobile}}} \right\}_{\text{between period}}$$

(1)

$$\left(\sigma_{ap}\right)_{15\text{sec}}^{\text{adjusted}} = \left(\sigma_{ap}\right)_{15\text{sec}}^{\text{mobile}} \left\{ \frac{\left(\sigma_{ap}\right)_{\text{period median}}^{\text{fixed site}}}{\left(\sigma_{ap}\right)_{\text{30-min median}}^{\text{fixed site}}} \right\}_{\text{within period}} \left\{ \frac{\left(\sigma_{ap}\right)_{\text{overall median}}^{\text{mobile}}}{\left(\sigma_{ap}\right)_{\text{period median}}^{\text{mobile}}} \right\}_{\text{between period}}$$

(2)

$$(\mathrm{PAH})_{15\mathrm{sec}}^{\mathrm{adjusted}} = (\mathrm{PAH})_{15\mathrm{sec}}^{\mathrm{mobile}} \left\{ \frac{(\sigma_{\mathrm{sp}})_{\mathrm{period\ median}}^{\mathrm{fixed\ site}}}{(\sigma_{\mathrm{sp}})_{\mathrm{30\text{-}min\ median}}^{\mathrm{fixed\ site}}} \right\}_{\mathrm{within\ period}} \left\{ \frac{(\sigma_{\mathrm{sp}})_{\mathrm{overall\ median}}^{\mathrm{mobile}}}{(\sigma_{\mathrm{sp}})_{\mathrm{period\ median}}^{\mathrm{mobile}}} \right\}_{\mathrm{between\ period}}$$

(3)

The subscripts refer to the signal averging time. The within-period adjustement was compounded from Portland fixed site values. The value of $(\sigma_{\mathrm{sp}})_{\mathrm{30\text{-}min\ median}}^{\mathrm{fixed\ site}}$ at this fixed site is the median of the thirty previous one-minute values. The value of $(\sigma_{\mathrm{sp}})_{\mathrm{period\ median}}^{\mathrm{fixed\ site}}$ is the median value at this fixed site within the overall sample period (i.e., afternoon or evening of a given day). In addition to the within-period temporal adjustment, we also made a between-period temporal adjustment to account for day to day or day to night variations. The value of $(\sigma_{\mathrm{sp}})_{\mathrm{period\ median}}^{\mathrm{mobile}}$ is the median value of mobile monitoring during a given sampling period (afternoon or evening) and the value of $(\sigma_{\mathrm{sp}})_{\mathrm{overall\ median}}^{\mathrm{mobile}}$is the overall median of all the period medians.

Short-term PAH peaks:

We noticed that during most mobile sampling runs, we encountered occasional short-lived peaks of particle-bound PAHs that occurred without corresponding to major increases in either bap or bsp. These peaks usually lasted for 30 seconds or less and were at least five times the period median. They were observed to be caused by the presence of nearby heavy duty vehicle plumes. Figure D.4 shows the locations of these PAH peaks observed at some time during the entire sampling campaign. As expected, the location of these peaks did not depend upon season and were more frequent near the major freeway and port area.

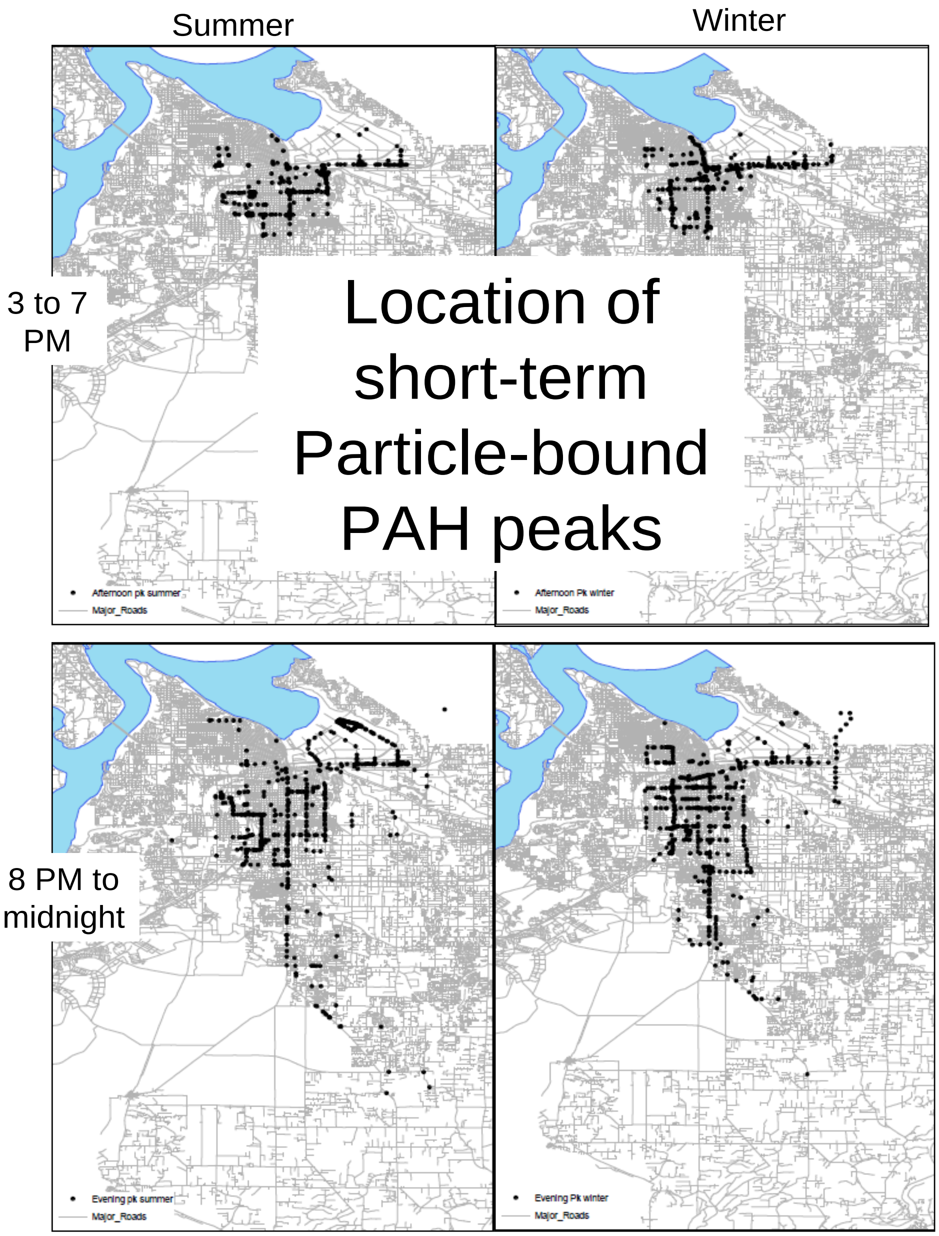

**Figure D.4. Location of particle-bound PAH peaks. Measurements were taken in the late afternoon and evening on selected winter days between December, 2008 and February, 2009 and on selected summer days between July and August, 2009.**

Principal Component Analysis:

In order to analyze the underlying sources of variability of the simultaneously observed bsp, bap and PAH values, we applied principal component analysis (PCA) to the (temporally) unadjusted measurements. The PCA included a subsequent varimax rotation of the principal components. The analysis indicated three contributing features to the observed spatial variability, one high in bsp and moderately high in bap (Factor 1), another high in PAH (factor 2), and a third high in bap and moderately high in bsp (Factor 3). The factor loadings are shown in Table D.1.

**Table D.1: Principal component factor loadings after Varimax rotation**

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| $b_{sp}$ | 0.92 | 0.18 | 0.36 |
| PAH | 0.17 | 0.96 | 0.23 |
| $b_{ap}$ | 0.42 | 0.29 | 0.86 |

The resulting factor scores were then temporally adjusted using the method described in the previous section. Figure D.5 and D.6 show maps of the temporally adjusted scores for Factors 1 and 3, respectively. As shown, this variable transformation helps to clarify the location of the highly impacted woodsmoke areas (Factor 1) as well as those highly impacted by traffic (Factor 3). The high Factor 2 scores (not shown) are similar in location to the observed PAH peaks in Figure D.4.

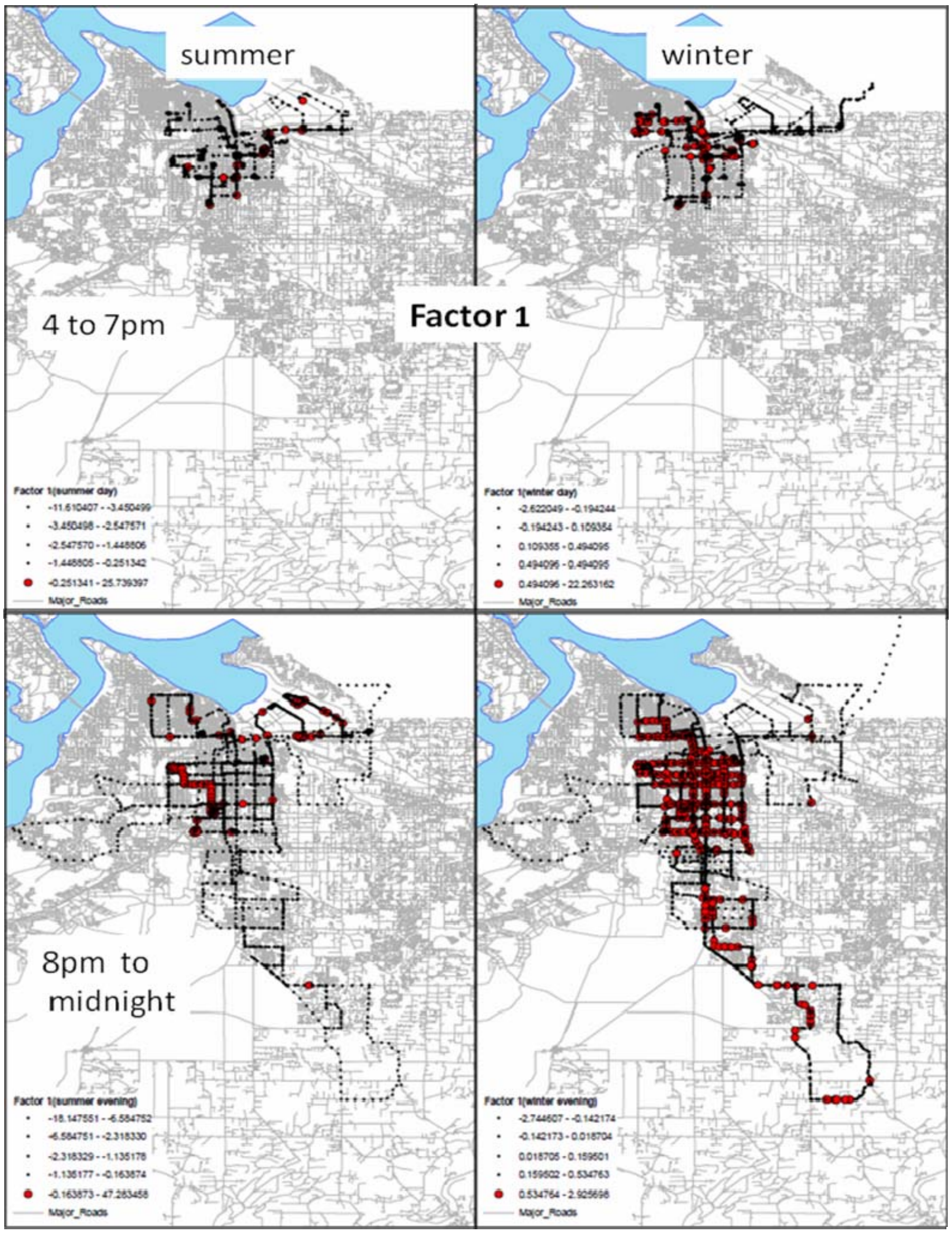

**Figure D.5: Spatial distribution of Varimax Factor #1 scores**.

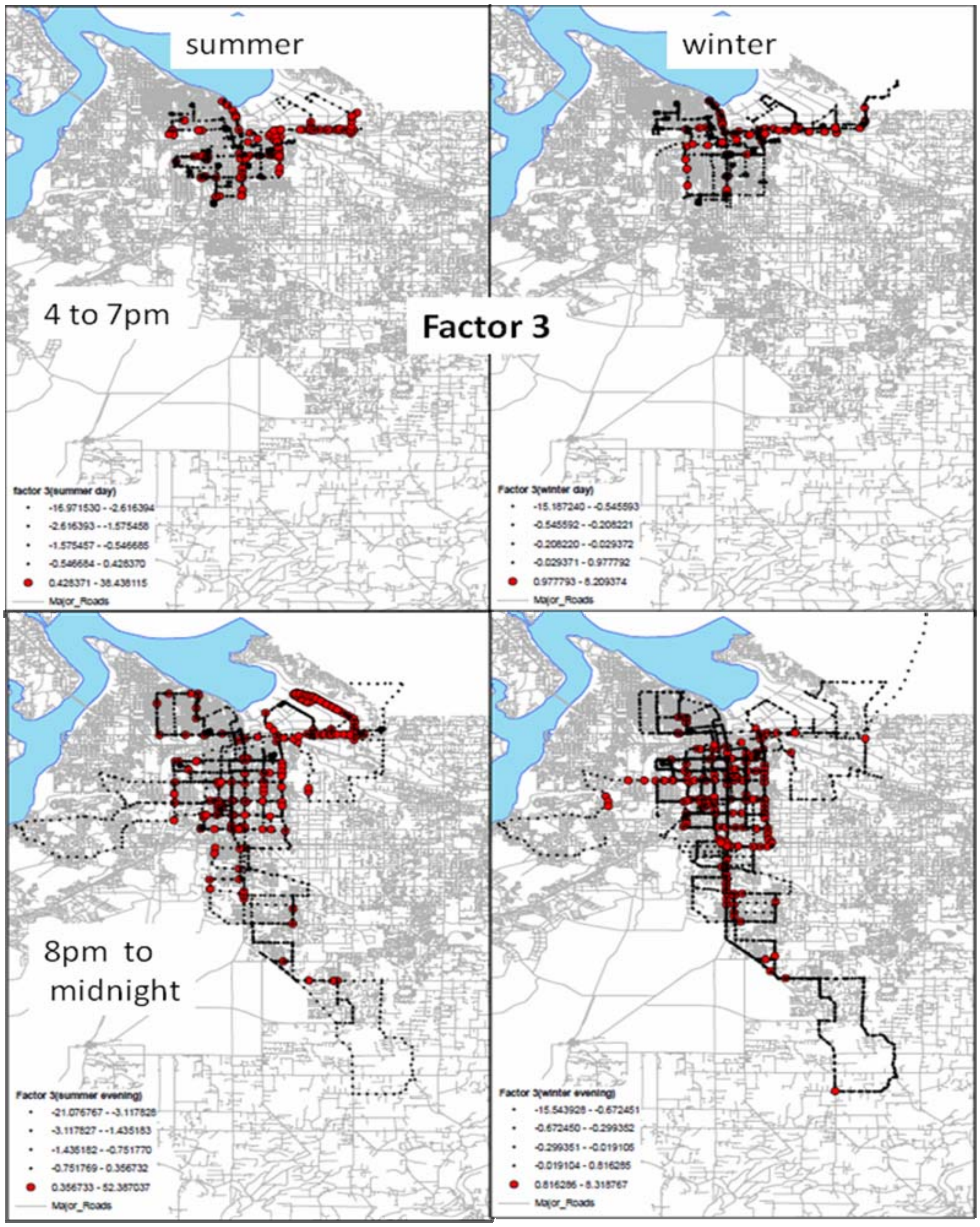

**Figure D.6. Spatial distribution of Varimax Factor #3 scores.**

Benzene concentrations:

Benzene was measured during a subset of the sampling periods on a separate mobile platform by membrane introduction mass spectrometry (MIMS). The sampling periods are shown in Figure D.7. Details of these measurements are given in Section 3.3.

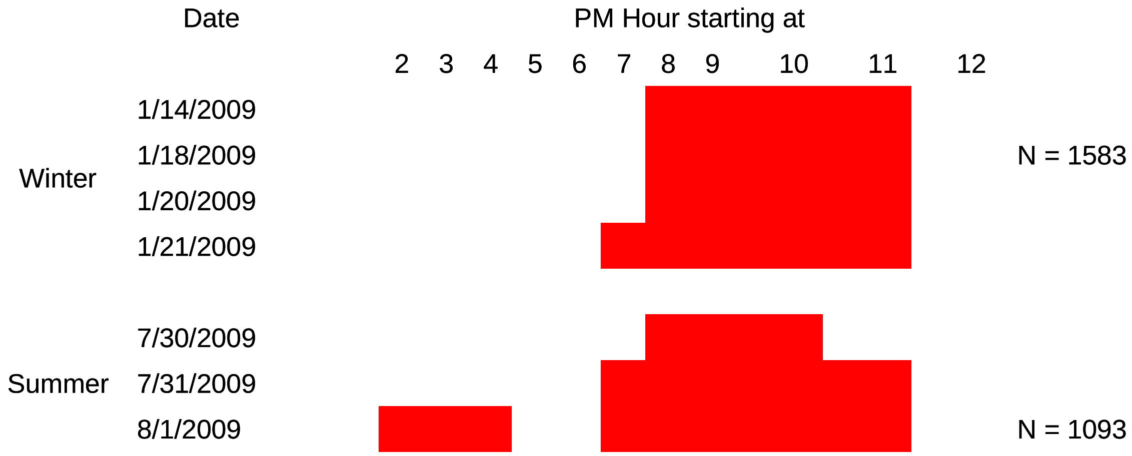

**Figure D.7: Mobile monitoring sampling periods with concurrent benzene and particle measurements.**

A principal component analysis of the concurrent particle/benzene data revealed three factors after varimax rotation. The resulting factor loadings are shown in Table D.2. These are similar factors to those found for the larger particle data set (see Table D.1). These results demonstrate that Factor 1, a woodsmoke-related feature, is highly correlated with benzene.

**Table D.2: Factor Loadings after Varimax rotation for the concurrent particle and benzene data. These concurrent data were mainly taken in the evening.**

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| $b_{sp}$ | 0.74 | 0.09 | 0.48 |
| PAH | 0.10 | 0.96 | 0.22 |
| $b_{ap}$ | 0.17 | 0.28 | 0.92 |
| Benzene | 0.93 | 0.12 | 0.08 |

It should be noted that these concurrent measurements were primarily taken during evening periods and therefore may somewhat overemphasize the contributions of wood burning to benzene relative to the contributions from traffic. However, these results are consistent with the correlations between levoglucosan and benzene observed in the fixed site monitoring data over a much longer time period. If traffic were a dominant source, the fixed site correlations between levoglucosan and benzene would not be as strong and the fixed site benzene levels would not decrease as one moves away from the residential area toward the industrial area.

Table D.2 shows the correlations between benzene and the other pollutants, but does not indicate how much each factor contributes to the benzene concentration. To do this, we regressed the absolute principal component scores (APCS) against the observed benzene concentrations across all observations. The APCS is defined as the principal component score for a given measurement set minus the hypothetical score when all the observed concentrations are zero. By defiintion, the principal component score has a value of zero when all measured species are simultaneously at their mean values. In contrast, the APCS has a value of zero when all observed concentrations are exactly zero. The APCS can be regressed against the pollutant of interest to determine how much of each principal component is contributing to the pollutant of interest for each sample. Using this approach, there was an average benzene level of 3.93 ppbv across all mobile measurements, of which 3.33 ppbv was associated with factor 1, 0.04 ppbv with factor 2, 0.1 ppbv with factor 3, and 0.48 ppbv with other unaccounted variability (the non-zero intercept in the regression model). This implies a small contribution from mobile sources during these predominantly evening measurement periods (maximum of ~ 0.6 ppbv).

**References for Appendix D:**

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[56] Etzkorn, J.M., et al., *The Use of MIMS-MS–MS in Field Locations as an On-Line Quantitative Environmental Monitoring Technique for Trace Contaminants in Air and Water.* J Chrom Sci, 2009. 47: p. 57-66.

[57] Ward, T.J., Hamilton, R., Dixon, R.W., Paulsen, M., Simpson, C.D. Characterization and evaluation of woodsmoke tracers in PM: Results from the 2003 Montana Wildfire Season, Atmos. Environ. (2006) 40(36): pp7005-7017.

[58] Miller-Schulze, J.P., Paulsen, M., Toriba,A., Tang,N., Hayakawa,K., Tamura,K., Dong,L., Zhang,X., and Simpson, C.D. Nitro Polycyclic Aromatic Hydrocarbons in Urban Air Particulate Collected in Shenyang, China and Their Relevance to Emission Sources and Atmospheric Conditions *Environ. Sci. Technol.* (2010) 44:216-221.

# Appendix E: ANOVA Results

(the report is attached in the following pages)

# Chloroform

### Tests of Between-Subjects Effects

Dependent Variable:Chloroform_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 4.562[a] | 7 | .652 | 6.303 | .000 |
| Intercept | 3209.770 | 1 | 3209.770 | 31039.825 | .000 |
| Site | 3.197 | 3 | 1.066 | 10.306 | .000 |
| Season | .544 | 1 | .544 | 5.256 | .023 |
| Site * Season | .399 | 3 | .133 | 1.287 | .280 |
| Error | 23.680 | 229 | .103 | | |
| Total | 3342.839 | 237 | | | |
| Corrected Total | 28.243 | 236 | | | |

a. R Squared = .162 (Adjusted R Squared = .136)

### Multiple Comparisons

Chloroform_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| CEWA | EQWA | -.0186 | .05946 | .992 | -.1861 | .1488 |
| | ESWA | .0007 | .05946 | 1.000 | -.1668 | .1681 |
| | SEWA | -.2856* | .05849 | .000 | -.4503 | -.1209 |
| EQWA | CEWA | .0186 | .05946 | .992 | -.1488 | .1861 |
| | ESWA | .0193 | .05971 | .991 | -.1489 | .1875 |
| | SEWA | -.2670* | .05874 | .000 | -.4324 | -.1015 |
| ESWA | CEWA | -.0007 | .05946 | 1.000 | -.1681 | .1668 |
| | EQWA | -.0193 | .05971 | .991 | -.1875 | .1489 |
| | SEWA | -.2863* | .05874 | .000 | -.4517 | -.1208 |
| SEWA | CEWA | .2856* | .05849 | .000 | .1209 | .4503 |
| | EQWA | .2670* | .05874 | .000 | .1015 | .4324 |
| | ESWA | .2863* | .05874 | .000 | .1208 | .4517 |

Based on observed means.□ The error term is Mean Square(Error) = .103.

*. The mean difference is significant at the 0.05 level.

### Chloroform_ln

Scheffe

| Site | N | Subset | |
|---|---|---|---|
| | | 1 | 2 |
| ESWA | 58 | -3.8195 | |
| CEWA | 59 | -3.8188 | |
| EQWA | 58 | -3.8002 | |
| SEWA | 62 | | -3.5332 |
| Sig. | | .991 | 1.000 |

Means for groups in homogeneous subsets are displayed.□ Based on obse

# Benzene

**Tests of Between-Subjects Effects**

Dependent Variable:Benzene_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 30.249[a] | 9 | 3.361 | 8.284 | .000 |
| Intercept | 490.358 | 1 | 490.358 | 1208.632 | .000 |
| Site | 4.903 | 4 | 1.226 | 3.021 | .018 |
| Season | 24.913 | 1 | 24.913 | 61.407 | .000 |
| Site * Season | .899 | 4 | .225 | .554 | .696 |
| Error | 115.628 | 285 | .406 | | |
| Total | 707.910 | 295 | | | |
| Corrected Total | 145.878 | 294 | | | |

a. R Squared = .207 (Adjusted R Squared = .182)

**Multiple Comparisons**

Benzene_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| CEWA | EQWA | -.0910 | .11778 | .963 | -.4562 | .2741 |
| | ESWA | -.2607 | .11778 | .301 | -.6258 | .1045 |
| | EYWA | -.2432 | .11778 | .374 | -.6084 | .1220 |
| | SEWA | .0482 | .11585 | .996 | -.3110 | .4073 |
| EQWA | CEWA | .0910 | .11778 | .963 | -.2741 | .4562 |
| | ESWA | -.1696 | .11828 | .725 | -.5364 | .1971 |
| | EYWA | -.1522 | .11828 | .799 | -.5189 | .2146 |
| | SEWA | .1392 | .11636 | .839 | -.2216 | .5000 |
| ESWA | CEWA | .2607 | .11778 | .301 | -.1045 | .6258 |
| | EQWA | .1696 | .11828 | .725 | -.1971 | .5364 |
| | EYWA | .0175 | .11828 | 1.000 | -.3493 | .3842 |
| | SEWA | .3088 | .11636 | .137 | -.0519 | .6696 |
| EYWA | CEWA | .2432 | .11778 | .374 | -.1220 | .6084 |
| | EQWA | .1522 | .11828 | .799 | -.2146 | .5189 |
| | ESWA | -.0175 | .11828 | 1.000 | -.3842 | .3493 |
| | SEWA | .2914 | .11636 | .183 | -.0694 | .6521 |
| SEWA | CEWA | -.0482 | .11585 | .996 | -.4073 | .3110 |
| | EQWA | -.1392 | .11636 | .839 | -.5000 | .2216 |
| | ESWA | -.3088 | .11636 | .137 | -.6696 | .0519 |
| | EYWA | -.2914 | .11636 | .183 | -.6521 | .0694 |

Based on observed means.□ The error term is Mean Square(Error) = .406.

**Benzene_ln**

Scheffe

| Site | N | Subset |
|---|---|---|
| | | 1 |
| SEWA | 62 | -1.5353 |
| CEWA | 59 | -1.4871 |
| EQWA | 58 | -1.3961 |
| EYWA | 58 | -1.2439 |
| ESWA | 58 | -1.2265 |
| Sig. | | .143 |

Means for groups in homogeneous subsets are displayed

# 1,3-Butadiene

**Tests of Between-Subjects Effects**

Dependent Variable:Butadiene_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 81.605[a] | 9 | 9.067 | 16.370 | .000 |
| Intercept | 3361.033 | 1 | 3361.033 | 6067.858 | .000 |
| Site | 6.978 | 4 | 1.744 | 3.149 | .015 |
| Season | 75.006 | 1 | 75.006 | 135.412 | .000 |
| Site * Season | 1.451 | 4 | .363 | .655 | .624 |
| Error | 156.756 | 283 | .554 | | |
| Total | 3954.078 | 293 | | | |
| Corrected Total | 238.361 | 292 | | | |

a. R Squared = .342 (Adjusted R Squared = .321)

**Multiple Comparisons**

Butadiene_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| CEWA | EQWA | .1732 | .13762 | .812 | -.2535 | .5999 |
| | ESWA | -.1131 | .13822 | .955 | -.5417 | .3155 |
| | EYWA | -.0542 | .13762 | .997 | -.4810 | .3725 |
| | SEWA | .2465 | .13590 | .512 | -.1748 | .6679 |
| EQWA | CEWA | -.1732 | .13762 | .812 | -.5999 | .2535 |
| | ESWA | -.2863 | .13881 | .375 | -.7167 | .1441 |
| | EYWA | -.2274 | .13820 | .609 | -.6559 | .2011 |
| | SEWA | .0734 | .13649 | .990 | -.3498 | .4966 |
| ESWA | CEWA | .1131 | .13822 | .955 | -.3155 | .5417 |
| | EQWA | .2863 | .13881 | .375 | -.1441 | .7167 |
| | EYWA | .0589 | .13881 | .996 | -.3715 | .4893 |
| | SEWA | .3597 | .13711 | .146 | -.0655 | .7848 |
| EYWA | CEWA | .0542 | .13762 | .997 | -.3725 | .4810 |
| | EQWA | .2274 | .13820 | .609 | -.2011 | .6559 |
| | ESWA | -.0589 | .13881 | .996 | -.4893 | .3715 |
| | SEWA | .3008 | .13649 | .305 | -.1224 | .7240 |
| SEWA | CEWA | -.2465 | .13590 | .512 | -.6679 | .1748 |
| | EQWA | -.0734 | .13649 | .990 | -.4966 | .3498 |
| | ESWA | -.3597 | .13711 | .146 | -.7848 | .0655 |
| | EYWA | -.3008 | .13649 | .305 | -.7240 | .1224 |

Based on observed means.□ The error term is Mean Square(Error) = .554.

**Butadiene_ln**

Scheffe

| Site | N | Subset |
|---|---|---|
| | | 1 |
| SEWA | 61 | -3.7548 |
| EQWA | 58 | -3.6814 |
| CEWA | 59 | -3.5083 |
| EYWA | 58 | -3.4540 |
| ESWA | 57 | -3.3952 |
| Sig. | | .148 |

Means for groups in homogeneous subsets are displayed

# Acetaldehyde

### Tests of Between-Subjects Effects

Dependent Variable:Acetaldehyde_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 46.292[a] | 9 | 5.144 | 20.916 | .000 |
| Intercept | 51.666 | 1 | 51.666 | 210.099 | .000 |
| Site | 38.344 | 4 | 9.586 | 38.981 | .000 |
| Season | .289 | 1 | .289 | 1.175 | .279 |
| Site * Season | 3.091 | 4 | .773 | 3.143 | .015 |
| Error | 70.823 | 288 | .246 | | |
| Total | 171.068 | 298 | | | |
| Corrected Total | 117.116 | 297 | | | |

a. R Squared = .395 (Adjusted R Squared = .376)

### Multiple Comparisons

Acetaldehyde_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| CEWA | EQWA | .0365 | .09172 | .997 | -.2479 | .3209 |
| | ESWA | .4491* | .09210 | .000 | .1636 | .7346 |
| | EYWA | -.5347* | .09210 | .000 | -.8202 | -.2492 |
| | SEWA | .5201* | .09065 | .000 | .2391 | .8012 |
| EQWA | CEWA | -.0365 | .09172 | .997 | -.3209 | .2479 |
| | ESWA | .4126* | .09092 | .001 | .1307 | .6945 |
| | EYWA | -.5712* | .09092 | .000 | -.8531 | -.2893 |
| | SEWA | .4836* | .08945 | .000 | .2063 | .7609 |
| ESWA | CEWA | -.4491* | .09210 | .000 | -.7346 | -.1636 |
| | EQWA | -.4126* | .09092 | .001 | -.6945 | -.1307 |
| | EYWA | -.9838* | .09130 | .000 | -1.2669 | -.7008 |
| | SEWA | .0710 | .08984 | .960 | -.2075 | .3495 |
| EYWA | CEWA | .5347* | .09210 | .000 | .2492 | .8202 |
| | EQWA | .5712* | .09092 | .000 | .2893 | .8531 |
| | ESWA | .9838* | .09130 | .000 | .7008 | 1.2669 |
| | SEWA | 1.0548* | .08984 | .000 | .7763 | 1.3333 |
| SEWA | CEWA | -.5201* | .09065 | .000 | -.8012 | -.2391 |
| | EQWA | -.4836* | .08945 | .000 | -.7609 | -.2063 |
| | ESWA | -.0710 | .08984 | .960 | -.3495 | .2075 |
| | EYWA | -1.0548* | .08984 | .000 | -1.3333 | -.7763 |

Based on observed means.□ The error term is Mean Square(Error) = .246.

*. The mean difference is significant at the 0.05 level.

### Acetaldehyde_ln

Scheffe

| Site | N | Subset | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| SEWA | 63 | -.8452 | | |
| ESWA | 59 | -.7742 | | |
| EQWA | 60 | | -.3617 | |
| CEWA | 57 | | -.3251 | |
| EYWA | 59 | | | .2096 |
| Sig. | | .962 | .997 | 1.000 |

Means for groups in homogeneous subsets are displayed.□ Based on observed means.□

# Acrolein

**Tests of Between-Subjects Effects**

Dependent Variable:Acrolein_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 8.760[a] | 7 | 1.251 | 4.683 | .000 |
| Intercept | 771.425 | 1 | 771.425 | 2886.886 | .000 |
| Site | 1.908 | 3 | .636 | 2.380 | .071 |
| Season | 2.981 | 1 | 2.981 | 11.154 | .001 |
| Site * Season | 2.954 | 3 | .985 | 3.685 | .013 |
| Error | 60.658 | 227 | .267 | | |
| Total | 892.618 | 235 | | | |
| Corrected Total | 69.418 | 234 | | | |

a. R Squared = .126 (Adjusted R Squared = .099)

**Multiple Comparisons**

Acrolein_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| CEWA | EQWA | .0931 | .09601 | .816 | -.1774 | .3635 |
| | ESWA | .0544 | .09558 | .955 | -.2148 | .3237 |
| | SEWA | -.1969 | .09439 | .229 | -.4628 | .0689 |
| EQWA | CEWA | -.0931 | .09601 | .816 | -.3635 | .1774 |
| | ESWA | -.0386 | .09641 | .984 | -.3102 | .2329 |
| | SEWA | -.2900* | .09523 | .028 | -.5582 | -.0218 |
| ESWA | CEWA | -.0544 | .09558 | .955 | -.3237 | .2148 |
| | EQWA | .0386 | .09641 | .984 | -.2329 | .3102 |
| | SEWA | -.2514 | .09480 | .074 | -.5184 | .0156 |
| SEWA | CEWA | .1969 | .09439 | .229 | -.0689 | .4628 |
| | EQWA | .2900* | .09523 | .028 | .0218 | .5582 |
| | ESWA | .2514 | .09480 | .074 | -.0156 | .5184 |

Based on observed means.□ The error term is Mean Square(Error) = .267.

*. The mean difference is significant at the 0.05 level.

**Acrolein_ln**

Scheffe

| Site | N | Subset | |
|---|---|---|---|
| | | 1 | 2 |
| EQWA | 57 | -1.9798 | |
| ESWA | 58 | -1.9412 | -1.9412 |
| CEWA | 59 | -1.8867 | -1.8867 |
| SEWA | 61 | | -1.6898 |
| Sig. | | .813 | .077 |

Means for groups in homogeneous subsets are displayed.□ Based on obse

# Black Carbon

### Tests of Between-Subjects Effects

Dependent Variable:Black_Carbon_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 218.225[a] | 9 | 24.247 | 54.489 | .000 |
| Intercept | 41.445 | 1 | 41.445 | 93.136 | .000 |
| Site | 101.435 | 4 | 25.359 | 56.986 | .000 |
| Season | 97.822 | 1 | 97.822 | 219.826 | .000 |
| Site * Season | 9.334 | 4 | 2.334 | 5.244 | .000 |
| Error | 775.631 | 1743 | .445 | | |
| Total | 1064.069 | 1753 | | | |
| Corrected Total | 993.856 | 1752 | | | |

a. R Squared = .220 (Adjusted R Squared = .216)

### Multiple Comparisons

Black_Carbon_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval Lower Bound | 95% Confidence Interval Upper Bound |
|---|---|---|---|---|---|---|
| CEWA | EQWA | .1573* | .05004 | .043 | .0030 | .3116 |
| | ESWA | .6417* | .05054 | .000 | .4859 | .7975 |
| | EYWA | .5571* | .05050 | .000 | .4014 | .7128 |
| | SEWA | .5308* | .05054 | .000 | .3750 | .6867 |
| EQWA | CEWA | -.1573* | .05004 | .043 | -.3116 | -.0030 |
| | ESWA | .4844* | .05015 | .000 | .3298 | .6391 |
| | EYWA | .3998* | .05011 | .000 | .2453 | .5544 |
| | SEWA | .3736* | .05015 | .000 | .2189 | .5282 |
| ESWA | CEWA | -.6417* | .05054 | .000 | -.7975 | -.4859 |
| | EQWA | -.4844* | .05015 | .000 | -.6391 | -.3298 |
| | EYWA | -.0846 | .05061 | .593 | -.2407 | .0714 |
| | SEWA | -.1109 | .05064 | .310 | -.2670 | .0453 |
| EYWA | CEWA | -.5571* | .05050 | .000 | -.7128 | -.4014 |
| | EQWA | -.3998* | .05011 | .000 | -.5544 | -.2453 |
| | ESWA | .0846 | .05061 | .593 | -.0714 | .2407 |
| | SEWA | -.0263 | .05061 | .992 | -.1823 | .1298 |
| SEWA | CEWA | -.5308* | .05054 | .000 | -.6867 | -.3750 |
| | EQWA | -.3736* | .05015 | .000 | -.5282 | -.2189 |
| | ESWA | .1109 | .05064 | .310 | -.0453 | .2670 |
| | EYWA | .0263 | .05061 | .992 | -.1298 | .1823 |

Based on observed means.□ The error term is Mean Square(Error) = .445.

*. The mean difference is significant at the 0.05 level.

### Black_Carbon_ln

Scheffe

| Site | N | Subset 1 | Subset 2 | Subset 3 |
|---|---|---|---|---|
| ESWA | 347 | -.4668 | | |
| EYWA | 348 | -.3821 | | |
| SEWA | 347 | -.3559 | | |
| EQWA | 361 | | .0177 | |
| CEWA | 350 | | | .1749 |
| Sig. | | .305 | 1.000 | 1.000 |

Means for groups in homogeneous subsets are displayed.□ Based on observed means.□

# Elemental Carbon

### Tests of Between-Subjects Effects

Dependent Variable:Elemental_Carbon_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 19.630[a] | 7 | 2.804 | 3.837 | .001 |
| Intercept | 43.174 | 1 | 43.174 | 59.070 | .000 |
| Site | 4.301 | 3 | 1.434 | 1.962 | .120 |
| Season | 13.071 | 1 | 13.071 | 17.884 | .000 |
| Site * Season | 2.528 | 3 | .843 | 1.153 | .328 |
| Error | 188.568 | 258 | .731 | | |
| Total | 272.153 | 266 | | | |
| Corrected Total | 208.199 | 265 | | | |

a. R Squared = .094 (Adjusted R Squared = .070)

### Multiple Comparisons

Elemental_Carbon_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| CEWA | EQWA | .1383 | .16024 | .862 | -.3126 | .5893 |
| | ESWA | .3549 | .15808 | .172 | -.0899 | .7997 |
| | SEWA | .3062 | .14200 | .202 | -.0934 | .7057 |
| EQWA | CEWA | -.1383 | .16024 | .862 | -.5893 | .3126 |
| | ESWA | .2166 | .16090 | .613 | -.2362 | .6694 |
| | SEWA | .1678 | .14514 | .721 | -.2406 | .5762 |
| ESWA | CEWA | -.3549 | .15808 | .172 | -.7997 | .0899 |
| | EQWA | -.2166 | .16090 | .613 | -.6694 | .2362 |
| | SEWA | -.0488 | .14275 | .990 | -.4505 | .3529 |
| SEWA | CEWA | -.3062 | .14200 | .202 | -.7057 | .0934 |
| | EQWA | -.1678 | .14514 | .721 | -.5762 | .2406 |
| | ESWA | .0488 | .14275 | .990 | -.3529 | .4505 |

Based on observed means.□ The error term is Mean Square(Error) = .731.

### Elemental_Carbon_ln

Scheffe

| Site | N | Subset |
|---|---|---|
| | | 1 |
| ESWA | 58 | -.6311 |
| SEWA | 94 | -.5823 |
| EQWA | 55 | -.4145 |
| CEWA | 59 | -.2762 |
| Sig. | | .143 |

Means for groups in homogeneous subsets are displayed

# Formaldehyde

**Tests of Between-Subjects Effects**

Dependent Variable:Formaldehyde_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 76.338[a] | 9 | 8.482 | 27.468 | .000 |
| Intercept | 13.404 | 1 | 13.404 | 43.407 | .000 |
| Site | 72.047 | 4 | 18.012 | 58.330 | .000 |
| Season | .087 | 1 | .087 | .282 | .596 |
| Site * Season | .408 | 4 | .102 | .330 | .858 |
| Error | 88.932 | 288 | .309 | | |
| Total | 177.873 | 298 | | | |
| Corrected Total | 165.269 | 297 | | | |

a. R Squared = .462 (Adjusted R Squared = .445)

**Multiple Comparisons**

Formaldehyde_ln□Scheffe

| | | | | | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | Lower Bound | Upper Bound |
| CEWA | EQWA | .4424* | .10278 | .001 | .1237 | .7611 |
| | ESWA | .6963* | .10320 | .000 | .3763 | 1.0163 |
| | EYWA | .1056 | .10320 | .902 | -.2144 | .4255 |
| | SEWA | 1.3952* | .10158 | .000 | 1.0803 | 1.7101 |
| EQWA | CEWA | -.4424* | .10278 | .001 | -.7611 | -.1237 |
| | ESWA | .2539 | .10188 | .187 | -.0620 | .5698 |
| | EYWA | -.3368* | .10188 | .029 | -.6527 | -.0210 |
| | SEWA | .9528* | .10024 | .000 | .6420 | 1.2636 |
| ESWA | CEWA | -.6963* | .10320 | .000 | -1.0163 | -.3763 |
| | EQWA | -.2539 | .10188 | .187 | -.5698 | .0620 |
| | EYWA | -.5907* | .10231 | .000 | -.9079 | -.2735 |
| | SEWA | .6989* | .10067 | .000 | .3868 | 1.0110 |
| EYWA | CEWA | -.1056 | .10320 | .902 | -.4255 | .2144 |
| | EQWA | .3368* | .10188 | .029 | .0210 | .6527 |
| | ESWA | .5907* | .10231 | .000 | .2735 | .9079 |
| | SEWA | 1.2896* | .10067 | .000 | .9775 | 1.6017 |
| SEWA | CEWA | -1.3952* | .10158 | .000 | -1.7101 | -1.0803 |
| | EQWA | -.9528* | .10024 | .000 | -1.2636 | -.6420 |
| | ESWA | -.6989* | .10067 | .000 | -1.0110 | -.3868 |
| | EYWA | -1.2896* | .10067 | .000 | -1.6017 | -.9775 |

Based on observed means.□ The error term is Mean Square(Error) = .309.

*. The mean difference is significant at the 0.05 level.

**Formaldehyde_ln**

Scheffe

| | | Subset | | |
|---|---|---|---|---|
| Site | N | 1 | 2 | 3 |
| SEWA | 63 | -.6467 | | |
| ESWA | 59 | | .0521 | |
| EQWA | 60 | | .3060 | |
| EYWA | 59 | | | .6429 |
| CEWA | 57 | | | .7484 |
| Sig. | | 1.000 | .187 | .898 |

Means for groups in homogeneous subsets are displayed.□ Based on observed means.□

# Levoglucosan

### Tests of Between-Subjects Effects

Dependent Variable:Levoglucosan_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 259.172[a] | 7 | 37.025 | 31.515 | .000 |
| Intercept | 1340.551 | 1 | 1340.551 | 1141.054 | .000 |
| Site | 33.564 | 3 | 11.188 | 9.523 | .000 |
| Season | 215.439 | 1 | 215.439 | 183.378 | .000 |
| Site * Season | 1.644 | 3 | .548 | .466 | .706 |
| Error | 244.366 | 208 | 1.175 | | |
| Total | 2049.780 | 216 | | | |
| Corrected Total | 503.538 | 215 | | | |

a. R Squared = .515 (Adjusted R Squared = .498)

### Multiple Comparisons

Levoglucosan_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| CEWA | EQWA | -.4137 | .21590 | .302 | -1.0222 | .1948 |
| | ESWA | -1.1846* | .21923 | .000 | -1.8025 | -.5667 |
| | EYWA | -.6585* | .21669 | .029 | -1.2693 | -.0477 |
| EQWA | CEWA | .4137 | .21590 | .302 | -.1948 | 1.0222 |
| | ESWA | -.7709* | .20316 | .003 | -1.3435 | -.1983 |
| | EYWA | -.2448 | .20042 | .685 | -.8097 | .3201 |
| ESWA | CEWA | 1.1846* | .21923 | .000 | .5667 | 1.8025 |
| | EQWA | .7709* | .20316 | .003 | .1983 | 1.3435 |
| | EYWA | .5261 | .20400 | .087 | -.0488 | 1.1011 |
| EYWA | CEWA | .6585* | .21669 | .029 | .0477 | 1.2693 |
| | EQWA | .2448 | .20042 | .685 | -.3201 | .8097 |
| | ESWA | -.5261 | .20400 | .087 | -1.1011 | .0488 |

Based on observed means.□ The error term is Mean Square(Error) = 1.175.

*. The mean difference is significant at the 0.05 level.

### Levoglucosan_ln

Scheffe

| Site | N | Subset | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| CEWA | 44 | -3.2670 | | |
| EQWA | 59 | -2.8533 | -2.8533 | |
| EYWA | 58 | | -2.6085 | -2.6085 |
| ESWA | 55 | | | -2.0824 |
| Sig. | | .278 | .716 | .102 |

Means for groups in homogeneous subsets are displayed.□ Based on observed means.□

# Naphthalene

**Tests of Between-Subjects Effects**

Dependent Variable:Naphthalene_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 18.579[a] | 7 | 2.654 | 4.585 | .000 |
| Intercept | 4465.306 | 1 | 4465.306 | 7713.640 | .000 |
| Site | 9.571 | 3 | 3.190 | 5.511 | .001 |
| Season | 6.661 | 1 | 6.661 | 11.507 | .001 |
| Site * Season | 1.948 | 3 | .649 | 1.122 | .341 |
| Error | 131.986 | 228 | .579 | | |
| Total | 4750.783 | 236 | | | |
| Corrected Total | 150.564 | 235 | | | |

a. R Squared = .123 (Adjusted R Squared = .096)

**Multiple Comparisons**

Naphthalene_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval Lower Bound | 95% Confidence Interval Upper Bound |
|---|---|---|---|---|---|---|
| CEWA | EQWA | .1604 | .13893 | .722 | -.2309 | .5517 |
| | ESWA | .1671 | .14008 | .700 | -.2274 | .5617 |
| | SEWA | .5597* | .14131 | .002 | .1617 | .9577 |
| EQWA | CEWA | -.1604 | .13893 | .722 | -.5517 | .2309 |
| | ESWA | .0068 | .13893 | 1.000 | -.3845 | .3981 |
| | SEWA | .3994* | .14016 | .046 | .0046 | .7941 |
| ESWA | CEWA | -.1671 | .14008 | .700 | -.5617 | .2274 |
| | EQWA | -.0068 | .13893 | 1.000 | -.3981 | .3845 |
| | SEWA | .3926 | .14131 | .055 | -.0054 | .7906 |
| SEWA | CEWA | -.5597* | .14131 | .002 | -.9577 | -.1617 |
| | EQWA | -.3994* | .14016 | .046 | -.7941 | -.0046 |
| | ESWA | -.3926 | .14131 | .055 | -.7906 | .0054 |

Based on observed means.□ The error term is Mean Square(Error) = .579.

*. The mean difference is significant at the 0.05 level.

**Naphthalene_ln**

Scheffe

| Site | N | Subset 1 | Subset 2 |
|---|---|---|---|
| SEWA | 57 | 4.0737 | |
| ESWA | 59 | 4.4663 | 4.4663 |
| EQWA | 61 | | 4.4731 |
| CEWA | 59 | | 4.6334 |
| Sig. | | .052 | .701 |

Means for groups in homogeneous subsets are displayed.□ Based on obse

# PM 2.5

### Tests of Between-Subjects Effects

Dependent Variable:PM_25_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 7.150[a] | 9 | .794 | 2.167 | .024 |
| Intercept | 1171.539 | 1 | 1171.539 | 3196.355 | .000 |
| Site | 2.095 | 4 | .524 | 1.429 | .224 |
| Season | 2.594 | 1 | 2.594 | 7.077 | .008 |
| Site * Season | 3.478 | 4 | .869 | 2.372 | .052 |
| Error | 123.885 | 338 | .367 | | |
| Total | 1398.844 | 348 | | | |
| Corrected Total | 131.035 | 347 | | | |

a. R Squared = .055 (Adjusted R Squared = .029)

### Multiple Comparisons

PM_25_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval Lower Bound | 95% Confidence Interval Upper Bound |
|---|---|---|---|---|---|---|
| CEWA | EQWA | .1117 | .11100 | .908 | -.2321 | .4555 |
| | ESWA | .1480 | .11295 | .787 | -.2018 | .4979 |
| | EYWA | .2466 | .11194 | .305 | -.1001 | .5934 |
| | SEWA | .1943 | .09695 | .405 | -.1060 | .4946 |
| EQWA | CEWA | -.1117 | .11100 | .908 | -.4555 | .2321 |
| | ESWA | .0364 | .11249 | .999 | -.3121 | .3848 |
| | EYWA | .1350 | .11148 | .832 | -.2103 | .4803 |
| | SEWA | .0826 | .09642 | .947 | -.2160 | .3813 |
| ESWA | CEWA | -.1480 | .11295 | .787 | -.4979 | .2018 |
| | EQWA | -.0364 | .11249 | .999 | -.3848 | .3121 |
| | EYWA | .0986 | .11342 | .944 | -.2527 | .4499 |
| | SEWA | .0463 | .09865 | .994 | -.2593 | .3518 |
| EYWA | CEWA | -.2466 | .11194 | .305 | -.5934 | .1001 |
| | EQWA | -.1350 | .11148 | .832 | -.4803 | .2103 |
| | ESWA | -.0986 | .11342 | .944 | -.4499 | .2527 |
| | SEWA | -.0523 | .09750 | .991 | -.3543 | .2496 |
| SEWA | CEWA | -.1943 | .09695 | .405 | -.4946 | .1060 |
| | EQWA | -.0826 | .09642 | .947 | -.3813 | .2160 |
| | ESWA | -.0463 | .09865 | .994 | -.3518 | .2593 |
| | EYWA | .0523 | .09750 | .991 | -.2496 | .3543 |

Based on observed means.□ The error term is Mean Square(Error) = .367.

### PM_25_ln

Scheffe

| Site | N | Subset 1 |
|---|---|---|
| EYWA | 58 | 1.8104 |
| SEWA | 115 | 1.8628 |
| ESWA | 56 | 1.9091 |
| EQWA | 60 | 1.9454 |
| CEWA | 59 | 2.0571 |
| Sig. | | .255 |

Means for groups in homogeneous subsets are displayed

# Carbon Tetrachloride

**Tests of Between-Subjects Effects**

Dependent Variable:Carbon_Tetrachloride_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | .646[a] | 9 | .072 | 1.429 | .175 |
| Intercept | 1294.720 | 1 | 1294.720 | 25758.382 | .000 |
| Site | .143 | 4 | .036 | .710 | .586 |
| Season | .452 | 1 | .452 | 8.988 | .003 |
| Site * Season | .034 | 4 | .009 | .170 | .953 |
| Error | 14.325 | 285 | .050 | | |
| Total | 1355.911 | 295 | | | |
| Corrected Total | 14.972 | 294 | | | |

a. R Squared = .043 (Adjusted R Squared = .013)

**Multiple Comparisons**

Carbon_Tetrachloride_ln□Scheffe

| | | Mean Difference | | | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| (I) Site | (J) Site | (I-J) | Std. Error | Sig. | Lower Bound | Upper Bound |
| CEWA | EQWA | -.0045 | .04146 | 1.000 | -.1330 | .1240 |
| | ESWA | -.0125 | .04146 | .999 | -.1410 | .1161 |
| | EYWA | .0215 | .04146 | .992 | -.1070 | .1501 |
| | SEWA | -.0476 | .04078 | .851 | -.1740 | .0789 |
| EQWA | CEWA | .0045 | .04146 | 1.000 | -.1240 | .1330 |
| | ESWA | -.0080 | .04163 | 1.000 | -.1371 | .1211 |
| | EYWA | .0260 | .04163 | .983 | -.1031 | .1551 |
| | SEWA | -.0431 | .04096 | .893 | -.1701 | .0839 |
| ESWA | CEWA | .0125 | .04146 | .999 | -.1161 | .1410 |
| | EQWA | .0080 | .04163 | 1.000 | -.1211 | .1371 |
| | EYWA | .0340 | .04163 | .955 | -.0951 | .1631 |
| | SEWA | -.0351 | .04096 | .947 | -.1621 | .0919 |
| EYWA | CEWA | -.0215 | .04146 | .992 | -.1501 | .1070 |
| | EQWA | -.0260 | .04163 | .983 | -.1551 | .1031 |
| | ESWA | -.0340 | .04163 | .955 | -.1631 | .0951 |
| | SEWA | -.0691 | .04096 | .585 | -.1961 | .0579 |
| SEWA | CEWA | .0476 | .04078 | .851 | -.0789 | .1740 |
| | EQWA | .0431 | .04096 | .893 | -.0839 | .1701 |
| | ESWA | .0351 | .04096 | .947 | -.0919 | .1621 |
| | EYWA | .0691 | .04096 | .585 | -.0579 | .1961 |

Based on observed means.□ The error term is Mean Square(Error) = .050.

**Carbon_Tetrachloride_ln**

Scheffe

| | | Subset |
|---|---|---|
| Site | N | 1 |
| EYWA | 58 | -2.1627 |
| CEWA | 59 | -2.1411 |
| EQWA | 58 | -2.1366 |
| ESWA | 58 | -2.1287 |
| SEWA | 62 | -2.0936 |
| Sig. | | .592 |

Means for groups in homogeneous subsets are displayed

# Organic Carbon

**Tests of Between-Subjects Effects**

Dependent Variable:Organic_Carbong_ln

| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
|---|---|---|---|---|---|
| Corrected Model | 10.673[a] | 7 | 1.525 | 3.653 | .001 |
| Intercept | 151.798 | 1 | 151.798 | 363.686 | .000 |
| Site | 3.090 | 3 | 1.030 | 2.468 | .063 |
| Season | 5.986 | 1 | 5.986 | 14.341 | .000 |
| Site * Season | 2.413 | 3 | .804 | 1.927 | .126 |
| Error | 108.521 | 260 | .417 |  |  |
| Total | 263.332 | 268 |  |  |  |
| Corrected Total | 119.194 | 267 |  |  |  |

a. R Squared = .090 (Adjusted R Squared = .065)

**Multiple Comparisons**

Organic_Carbong_ln□Scheffe

| (I) Site | (J) Site | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval |  |
|---|---|---|---|---|---|---|
|  |  |  |  |  | Lower Bound | Upper Bound |
| CEWA | EQWA | .0189 | .11999 | .999 | -.3187 | .3565 |
|  | ESWA | .0443 | .11946 | .987 | -.2918 | .3805 |
|  | SEWA | .2342 | .10731 | .193 | -.0678 | .5361 |
| EQWA | CEWA | -.0189 | .11999 | .999 | -.3565 | .3187 |
|  | ESWA | .0254 | .12049 | .998 | -.3136 | .3645 |
|  | SEWA | .2152 | .10846 | .271 | -.0899 | .5204 |
| ESWA | CEWA | -.0443 | .11946 | .987 | -.3805 | .2918 |
|  | EQWA | -.0254 | .12049 | .998 | -.3645 | .3136 |
|  | SEWA | .1898 | .10787 | .379 | -.1137 | .4934 |
| SEWA | CEWA | -.2342 | .10731 | .193 | -.5361 | .0678 |
|  | EQWA | -.2152 | .10846 | .271 | -.5204 | .0899 |
|  | ESWA | -.1898 | .10787 | .379 | -.4934 | .1137 |

Based on observed means.

**Organic_Carbong_ln**

Scheffe[a],b,c

| Site | N | Subset |
|---|---|---|
|  |  | 1 |
| SEWA | 94 | .5950 |
| ESWA | 58 | .7848 |
| EQWA | 57 | .8102 |
| CEWA | 59 | .8291 |
| Sig. |  | .242 |

Means for groups in homogeneous subsets are