

**Application for Federal Assistance SF-424**

Version 02

* 1. Type of Submission: <input type="radio"/> Preapplication <input checked="" type="radio"/> Application <input type="radio"/> Changed/Corrected Application	* 2. Type of Application: <input checked="" type="radio"/> New <input type="radio"/> Continuation <input type="radio"/> Revision	* If Revision, select appropriate letter(s): _____ * Other (Specify) _____
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* 3. Date Received: 04/17/2007	4. Applicant Identifier: _____
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5a. Federal Entity Identifier: EPA-R10-WCC-2006	* 5b. Federal Award Identifier: _____
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**State Use Only:**

6. Date Received by State: _____	7. State Application Identifier: _____
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**8. APPLICANT INFORMATION:**

\* a. Legal Name: Puget Sound Clean Air Agency

* b. Employer/Taxpayer Identification Number (EIN/TIN): 91-0823558	* c. Organizational DUNS: 363422374
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**d. Address:**

\* Street1: 1904 Third Avenue, Suite 105  
Street2: \_\_\_\_\_  
\* City: Seattle  
County: King  
\* State: WA: Washington  
Province: \_\_\_\_\_  
\* Country: USA: UNITED STATES  
\* Zip / Postal Code: 98101

**e. Organizational Unit:**

Department Name: Air Resources	Division Name: Operations
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**f. Name and contact information of person to be contacted on matters involving this application:**

Prefix: Mr. \* First Name: Mike  
Middle Name: \_\_\_\_\_  
\* Last Name: Gilroy  
Suffix: \_\_\_\_\_

Title: Manager, Meteorological and Technical Service

**Organizational Affiliation:**

\* Telephone Number: 206-295-5844 Fax Number: 206-343-7522  
\* Email: mikeg@pscleanair.org

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**9. Type of Applicant 1: Select Applicant Type:**

D: Special District Government

Type of Applicant 2: Select Applicant Type:

Type of Applicant 3: Select Applicant Type:

\* Other (specify):

**\* 10. Name of Federal Agency:**

Environmental Protection Agency

**11. Catalog of Federal Domestic Assistance Number:**

66.034

CFDA Title:

Surveys, Studies, Investigations, Demonstrations and Special Purpose Activities Relating to the Clean Air Act

**\* 12. Funding Opportunity Number:**

EPA-OAR-OAQPS-07-01

\* Title:

Community-Scale Air Toxics Ambient Monitoring

**13. Competition Identification Number:**

Title:

**14. Areas Affected by Project (Cities, Counties, States, etc.):**

Washington counties of: King, Kitsap, Pierce and Snohomish

**\* 15. Descriptive Title of Applicant's Project:**

Evaluation of Methods for Air Toxics Source Apportionment Using Real-Time Continuous Monitoring Instruments

Attach supporting documents as specified in agency instructions.

**Application for Federal Assistance SF-424**

Version 02

**16. Congressional Districts Of:**

\* a. Applicant

\* b. Program/Project

Attach an additional list of Program/Project Congressional Districts if needed.

**17. Proposed Project:**

\* a. Start Date:

\* b. End Date:

**18. Estimated Funding (\$):**

* a. Federal	<input type="text" value="361,842.00"/>
* b. Applicant	<input type="text" value="85,000.00"/>
* c. State	<input type="text" value="0.00"/>
* d. Local	<input type="text" value="0.00"/>
* e. Other	<input type="text" value="0.00"/>
* f. Program Income	<input type="text" value="0.00"/>
* g. TOTAL	<input type="text" value="446,842.00"/>

**\* 19. Is Application Subject to Review By State Under Executive Order 12372 Process?**

- a. This application was made available to the State under the Executive Order 12372 Process for review on
- b. Program is subject to E.O. 12372 but has not been selected by the State for review.
- c. Program is not covered by E.O. 12372.

**\* 20. Is the Applicant Delinquent On Any Federal Debt? (If "Yes", provide explanation.)**

- Yes
- No

**21. \*By signing this application, I certify (1) to the statements contained in the list of certifications\*\* and (2) that the statements herein are true, complete and accurate to the best of my knowledge. I also provide the required assurances\*\* and agree to comply with any resulting terms if I accept an award. I am aware that any false, fictitious, or fraudulent statements or claims may subject me to criminal, civil, or administrative penalties. (U.S. Code, Title 218, Section 1001)**

**\*\* I AGREE**

\*\* The list of certifications and assurances, or an internet site where you may obtain this list, is contained in the announcement or agency specific instructions.

**Authorized Representative:**

Prefix:  \* First Name:

Middle Name:

\* Last Name:

Suffix:

\* Title:

\* Telephone Number:  Fax Number:

\* Email:

\* Signature of Authorized Representative:  \* Date Signed:

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Standard Form 424 (Revised 10/2005)

Prescribed by OMB Circular A-102

**BUDGET INFORMATION - Non-Construction Programs**

SECTION A - BUDGET SUMMARY						
Grant Program Function or Activity (a)	Catalog of Federal Domestic Assistance Number (b)	Estimated Unobligated Funds			New or Revised Budget	
		Federal (c)	Non-Federal (d)	Federal (e)	Non-Federal (f)	Total (g)
1. Community-Scale Air Toxics Ambient Monitoring	66.034			\$361,842.00	\$85,000.00	\$446,842.00
2.						\$0.00
3.						\$0.00
4.						\$0.00
5. Totals		\$0.00	\$0.00	\$361,842.00	\$85,000.00	\$446,842.00
SECTION B - BUDGET CATEGORIES						
GRANT PROGRAM, FUNCTION OR ACTIVITY						
6. Object Class Categories	(1) Community-Scale Air Toxics Ambient Monitoring	(2)	(3)	(4)	Total (5)	
a. Personnel	\$27,486.00					\$27,486.00
b. Fringe Benefits	\$6,872.00					\$6,872.00
c. Travel	\$3,500.00					\$3,500.00
d. Equipment	\$73,500.00					\$73,500.00
e. Supplies	\$2,000.00					\$2,000.00
f. Contractual						\$0.00
g. Construction						\$0.00
h. Other	\$322,327.00					\$322,327.00
i. Total Direct Charges (sum of 6a-6h)	\$435,685.00		\$0.00	\$0.00	\$0.00	\$435,685.00
j. Indirect Charges	\$11,156.00					\$11,156.00
k. TOTALS (sum of 6i and 6j)	\$446,841.00		\$0.00	\$0.00	\$0.00	\$446,841.00
7. Program Income						\$0.00

Standard Form 424A (Rev. 7-97)  
Prescribed by OMB Circular A-102

SECTION C - NON-FEDERAL RESOURCES					
(a) Grant Program	(b) Applicant	(c) State	(d) Other Sources	(e) TOTALS	
8. Community-Scale Air Toxics Ambient Monitoring	\$85,000.00				\$85,000.00
9.					\$0.00
10.					\$0.00
11.					\$0.00
12. TOTAL (sum of lines 8-11)	\$85,000.00	\$0.00	\$0.00		\$85,000.00
SECTION D - FORECASTED CASH NEEDS					
Total for 1st Year	1st Quarter	2nd Quarter	3rd Quarter	4th Quarter	
13. Federal	\$152,388.00	\$40,972.00	\$40,972.00		\$40,972.00
14. Non-Federal	\$85,000.00				
15. TOTAL (sum of lines 13 and 14)	\$237,388.00	\$40,972.00	\$40,972.00		\$40,972.00
SECTION E - BUDGET ESTIMATES OF FEDERAL FUNDS NEEDED FOR BALANCE OF THE PROJECT					
FUTURE FUNDING PERIODS (Years)					
(a) Grant Program	(b) First	(c) Second	(d) Third	(e) Fourth	
16. Community-Scale Air Toxics Ambient Monitoring	\$209,454.00				
17.					
18.					
19.					
20. TOTAL (sum of lines 16-19)	\$209,454.00	\$0.00	\$0.00		\$0.00
SECTION F - OTHER BUDGET INFORMATION					
21. Direct Charges:					
22. Indirect Charges:					
23. Remarks:					

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- a. Project Title:** Evaluation of Methods for Air Toxics Source Apportionment Using Real-Time Continuous Monitoring Instruments
- b. Category:** Methods Development / Evaluation
- c. Applicant Information:**

Puget Sound Clean Air Agency  
1904 3<sup>rd</sup> Ave, Suite 105  
Seattle, Washington 98101

Katherine Himes (kathyh@pscleanair.org), (206) 689-4095  
Mike Gilroy (mikeg@pscleanair.org), (206) 295-5844

The Agency is an air pollution control organization as defined in Section 302(b) of the Clean Air Act. The Agency currently receives federal assistance funding and is eligible to receive grant funds under both Sections 105 and 103 of the Act.

<http://www.pscleanair.org/about/default.aspx> , <http://apps.leg.wa.gov/RCW/default.aspx?cite=70.94.143>

**d. Funding Requested:** A total of \$346,841.00 for a period of 24 months after receipt of grant funds

**e. Total Project Cost:** \$449,841.00

The Agency considers this project critical and is contributing a significant amount of its own resources to offset the cost to EPA. These contributions include Agency funding for capital equipment and in-kind staff time. Project partners are contributing significant amounts of staff and technical assistance expertise over and above those amounts requiring federal funding assistance. Additionally, the University of Washington is contributing a suite of state-of-the-art equipment at no charge or at minimal cost. These actions show our combined resolve to the success of the project while maximizing EPA's investment.

**f. Project Period:** December 1, 2007 – November 30, 2009

## **g. Project Description**

### **1. Background and Rationale**

The Puget Sound Clean Air Agency is a local air quality agency serving more than 3.5 million residents. The Agency is recognized for its technical and policy leadership activities, air monitoring skill, fiscal accountability and successful implementation of innovative air quality products. The Agency prioritizes diesel exhaust, especially diesel particulate matter (DPM), as the top air toxic of concern. The Agency works to reduce emissions from public fleets, marine-related diesel sources, railroad sources, and plans to move increasingly into the private fleet.

The Agency and partners have invested effort in estimating diesel concentrations in the Puget Sound area, using fine particulate (PM<sub>2.5</sub>) speciation data, and receptor modeling. The Puget Sound area currently has four speciation (STN) monitoring sites, in addition to an STN and Interagency Monitoring of Protected Visual Environments (IMPROVE) speciation site at the Seattle Beacon Hill national air toxics trends site (NATTS) location. Augmenting the existing federal investment, the Agency maintains a suite of fine particle continuous samplers including Aethalometers at supplemental STN sites to better understand the black carbon components of fine particulate.

These efforts help the Agency to prioritize air toxics of concern, as well as estimate risk and possibly track emission reductions. A 2003 risk evaluation highlighted diesel particulate matter as an air toxic of concern, with over 75% of the potential cancer risk from all air toxics monitored attributed to diesel particulate matter.<sup>1</sup> Estimates of ambient DPM exposures have been based primarily on receptor modeling results data taken at the Beacon Hill site, a population-based site in the middle of Seattle. As shown in Table 1, these estimates vary depending upon the type of speciation data (IMPROVE vs STN), the sample period of interest, and the specific algorithm used in the positive matrix factorization (PMF) model. Table 1 also gives estimates of "gasoline" derived particles and nickel and vanadium-rich particles derived from combustion of low grade residual oil. Annual average DPM estimates range from 1.9 µg/m<sup>3</sup> to as low as 0.7 or even 0.2 µg/m<sup>3</sup>. These estimates by Hopke et al. were part of a larger analysis that included multiple STN sites in addition to Beacon Hill.<sup>2</sup> Known site characteristics would indicate higher expected diesel particulate concentrations at the Duwamish STN (site is located in an industrial and port area). Similarly, high gasoline particulate concentrations are expected at the Olive Street STN site, located adjacent to Interstate 5. Instead, Hopke and coworkers reported that Beacon Hill, a "neighborhood scale" site – has higher gasoline concentrations than any other site, while diesel particulate matter is higher at the interstate site than the industrial site. The inconsistent apportionment results indicate the diesel and gasoline aerosol fractions are poorly understood, underscoring the inadequacies of relying on the Beacon Hill site (actually an urban scale site) to drive our understanding of air toxics in areas where impacts likely are higher. This project intends to address this critical flaw and provide monitoring results to build confidence in developing DPM-related air toxic reduction policies.

**Table 1: Various DPM Concentration Estimates at Beacon Hill ( $\mu\text{g}/\text{m}^3$ )**

PMF Algorithm	PMF-2 <sup>3</sup>	ME-2 <sup>4</sup>	Extended ME-2 w/size and mass <sup>5</sup>	Mass Constrained ME-2 <sup>6</sup>	PMF-2 <sup>2</sup>		Constrained ME-2 w/bootstrap <sup>7</sup>	
Speciation Data Set	IMPROVE	IMPROVE	IMPROVE	STN	IMPROVE	STN	IMPROVE	STN
Period	96-1999	96-2000	2000-2003	2000-2004	2000-2004		2000-2003	
"Gasoline"	0.4	0.8	0.6	0.3	0.9	2.5	0.2 [0.9, 0.1]	0.2 [1.2, 0.1]
"Diesel"	1.6	1.9	1.4	0.7	0.2	0.2	0.9 [1.1, 0.4]	1.8 [2.6, 0.1]
Residual Oil	0.9	0.2	0.7	0.4	0.6	0.4	0.5 [0.7, 0.4]	0.6 [0.8, 0.4]

<sup>2</sup>Hopke et al. 2006, <sup>3</sup>Maykut et al. 2003, <sup>4</sup>Rim et al. 2004, <sup>5</sup>Larson et al. 2005, <sup>6</sup>Wu et al. 2006, <sup>7</sup>Larson 2006 [95% C.I.] estimated via a non-parametric blocked bootstrap with 300 runs and non-overlapping, 3 day blocks.

The fact that the current PMF analyses based upon traditional speciation data cannot distinguish the contributions from these various mobile combustion sources could be due to several factors.

- The species concentrations used in these analyses are daily averages instead of more highly time resolved measurements that could be more readily related to the temporal variation in nearby traffic.
- The species used do not include fuel specific organic markers that could capture, for example, blow-by emissions of lubricating oils from both diesel engines as well as poorly operated gasoline engines.
- Diesel tailpipe emissions at idle or low load are qualitatively different from those at higher loads, and can readily be confused with gasoline tailpipe emissions.<sup>8</sup>

The majority of the studies in Table 1 show standard errors for the contribution estimates were computed using an early version of PMF that does not capture the full range of model uncertainty. Specifically, standard errors were calculated for the source contributions assuming the feature profiles were fixed and known. Reliable comparison of these earlier results is flawed and therefore the confidence limits for these model predictions are not shown here. EPA's recent version of PMF (Ver1.1) uses a time series bootstrap statistical method to better capture model uncertainties in both the feature profiles and their contributions. Larson (2006) used the bootstrap method to estimate uncertainties associated with source contributions at Beacon Hill with the IMPROVE and the STN data. This relatively high uncertainty may also be the case at the Olive Street and Duwamish sites given that the estimates reported by Hopke and co-workers did not incorporate the bootstrap method. Although PMF-derived estimates of DPM at this site remain somewhat uncertain, the potential cancer risk from DPM remains high even if the ambient concentration is only  $0.1\mu\text{g}/\text{m}^3$ , due to its high toxicity. Given the large ambiguity in the current apportionment of diesel and gasoline sources and the significant contribution of diesel exhaust (DE) to risk assessments, it is essential to correctly account for the impact of DE sources.

This project intends to develop an alternative method of apportioning the gasoline and diesel contributions to air toxics that could be applied in the Puget Sound region and across the nation. To accomplish this, the project's approach will be to supplement existing STN speciation data and Aethalometer monitoring with:

- Gas-phase hydrocarbons measured with gas chromatography (GC) or FTIR instruments.
- Aerosol 1-nitropyrene measurements on 24 hour filter samples.

A new apportionment model using these data sources will be developed and applied to sites impacted primarily by gasoline and diesel vehicle traffic. This model will then be validated in part by comparing the model apportionment with meteorological, particulate matter (STN, PM<sub>2.5</sub>, and BC) data, plus traffic data from an innovative automated video data collection traffic system that provides a precise and verifiable car/truck apportioned count at the monitoring sites.

### 1.1 Special Concerns Regarding Marine Emissions

The cities of Seattle and Tacoma operate large seaports. Real concern exists in understanding the areas in the Puget Sound region that are impacted by Port activities and direct maritime DE emissions. For these areas, it is necessary to distinguish meteorological conditions when maritime sources have significant impact. We propose to use LIDAR (light radar) to directly monitor DE emissions from maritime sources, and track the emissions' plume back to landfall. By making these observations under a variety of wind conditions, and combining these observations with global positioning systems (GPS) data on ship traffic and modeling, we can determine when these sources impact population regions. We anticipate these results will become immediately useful in informing health

officials, policy makers, and the public on likely impacts from air toxics related to diesel sources associated with the ports.

## 1.2 Need for New Assessment Methods

Mobile source emissions are a complex mixture with both particle and vapor phase components designated as air toxics. DE typically is distinguishable from other sources of particulate matter based on relatively high contributions from EC and some OC. Using these markers for characterization is inadequate to resolve diesel exhaust contributions from those of other particulates in the Puget Sound region. Also, these markers derived from speciation data have poor temporal resolution (1 in 6 days), which does not provide sufficient information to account for daily source variations due to traffic flows and maritime traffic, or for meteorological variations that can enhance impacts from maritime sources.

Therefore, innovative approaches to assessment of diesel exhaust are required that provide more reliable estimates of the contribution of DE to ambient air toxics. We propose to supplement current DE apportionment with measurements of 1-nitropyrene on 24 hour filter samples, an OP-FTIR model of DE/gas fraction, traffic data on short/long vehicles, and hourly measurements of a suite of non-methane hydrocarbons (NMHC) at the Duwamish site in Seattle. The rationale for using these specific analytical approaches is described below in Section 3.

## 2. Project Objectives

- 1) Develop a method for continuous monitoring of gas phase hydrocarbon air emissions at existing monitoring sites with GC-FID and OP-FTIR instruments.
- 2) Develop apportionment models for these sites using UNMIX and PMF analysis tools that combine continuous gas-phase and continuous monitoring aerosol data.
- 3) Evaluate the use of 1-nitropyrene as a specific marker of diesel exhaust particulates.
- 4) Evaluate the use of LIDAR combined with GPS data on ship traffic and wind conditions to assess the impacts of maritime DE emissions on populated regions.
- 5) Evaluate the revised apportionment models at an industrial site near the Port of Seattle, where anticipated DE emissions from gasoline and diesel vehicles combine with diesel maritime sources.
- 6) Validate the modeled apportioned contribution of gasoline and DE sources against traffic count data at a site adjacent to a major interstate.

## 3. Work Plan: Alternative Markers for Diesel Exhaust

This project will seek to identify, measure, and establish a dependable marker for diesel PM that will strengthen apportioning tools and improve risk characterization.

### 3.1 1-nitropyrene as a diesel particulate matter (DPM) marker

A variety of metrics have been used to measure diesel particulate matter (DPM) in ambient samples, including measurements of ultra fine particles, elemental carbon (EC), polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes.<sup>9,10,11</sup> Indeed the NIOSH method for assessing diesel exposures prescribes measurement of EC. However, these methods are not specific for DPM, and may be confounded by non-diesel sources. Some PAHs (e.g., BghiP) are enriched in DPM relative to other combustion sources, and ratios of PAHs (e.g., BghiP/iP, BghiP/BaA) have been proposed as markers for DE. Hopanes and steranes are present in engine lubricating oil, which comprises a significant component of the particle mass emitted from both gasoline and diesel vehicles.<sup>9,11</sup> EC is enriched in diesel relative to gasoline exhaust; therefore the abundance of hopanes and steranes relative to EC may differentiate gasoline from diesel emissions.<sup>12,9</sup> Nitroarenes also are enriched in DPM and some isomers appear to be highly specific markers for DPM.<sup>13</sup> They also correlate well with the mutagenicity of DE particle extracts.<sup>14</sup> 1-nitropyrene (1-NP) is one of the most abundant particle-phase PAHs in DPM, at a concentration of ~10-40 ppm.<sup>15</sup> Photochemical nitration of pyrene in the atmosphere forms specifically 2- and 4-nitropyrene, and other combustion sources produce minimal amounts of 1-nitropyrene. Therefore, 1-nitropyrene has been proposed as a unique marker for DPM in ambient PM. Murahasi et al. reported that >99% of 1-NP in PM collected in Kanazawa Japan was attributable to diesel exhaust.<sup>16</sup> Levels of this compound are relatively low in ambient air (1-100 pg/m<sup>3</sup>).<sup>17,13</sup> However, analytical methods based on HPLC with tandem MS detection,<sup>13,18</sup> have sensitivities of ~ 300 fg/sample, which would certainly be sufficient to measure 1-NP in low volume ambient samples. We propose to measure 1-NP in filter samples in our study and evaluate it as a specific marker of DPM in apportioned samples. If successful, this effort will provide a new tool for assessing DPM that can be applied in the existing sampling network.

### 3.2 Non-Methane Hydrocarbons (NMHC)

Following the initial work of Scheff et al.<sup>19</sup> in Chicago, numerous urban receptor modeling studies have apportioned the sources of non-methane hydrocarbons in urban air to distinguish mobile source contributions. Watson<sup>20</sup> provides a comprehensive review of the studies done prior to 2001. A number of the more recent studies have used EPA's chemical mass balance (CMB) model to distinguish vehicle exhaust contributions from other

VOC sources like gasoline evaporative losses and stationary sources.<sup>21,22,23,24,25,26,27,28,29</sup> Some more recent studies also have employed multivariate receptor models to obtain both source-related features and associated source contributions.<sup>27,28,30,31,32,33,34,35,36,37,38,39</sup> Many studies have reported separate contribution estimates to total measured VOCs from heavy-duty and light-duty vehicle exhaust, using PMF<sup>27,29</sup> Unmix,<sup>28</sup> CMB,<sup>23,24,26,27,28</sup> other multivariate receptor models,<sup>30</sup> or by direct correlation with traffic information.<sup>40,41</sup> PMF and Unmix are statistical algorithms that solve the chemical mass balance model as a factor analysis problem without requiring source profiles as the input variable.<sup>34</sup> We will use an "on-line ozone precursor analyzer" manufactured by Perkin Elmer Ltd. to sample and automatically analyze a suite of NMHC with hourly resolution. The analyzer consists of a gas chromatograph interfaced with a thermal desorption unit and provides fully automated monitoring of C<sub>2</sub>-C<sub>12</sub> VOCs. This device has been used by the EPA at a number of ambient air monitoring sites<sup>42</sup>; if successful mobile source apportionment models can be developed and validated with this monitoring tool, it will provide greatly improved temporal resolution in evaluating DE and gasoline vehicle impacts.

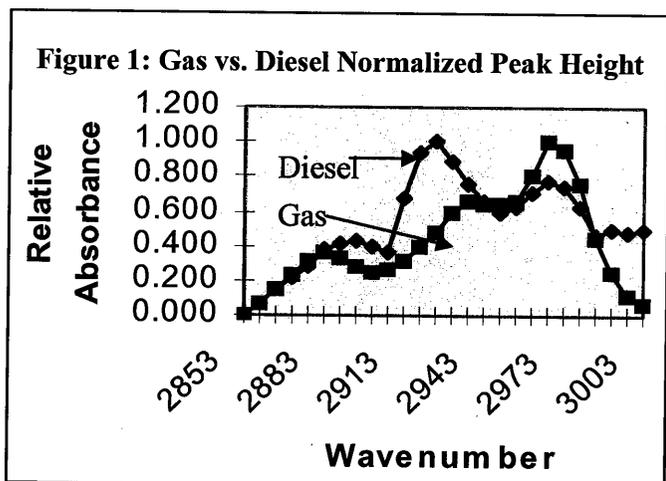
### 3.3 Traffic Measurements

Traffic volumes change significantly over time and location. Traffic sensors are needed to capture real-time traffic variations. Inductance loop detectors have been widely deployed in the central Puget Sound region. There is a loop detector station about every half mile on mainline lanes and freeway ramps in the Greater Seattle area.<sup>43</sup> About half of these are dual-loop detectors, measuring speed and classified vehicle volume data. Vehicles are classified based on their lengths, and assigned to one of the following four bins: (a) Bin 1, passenger cars and other smaller vehicles (length <26 ft); (b) Bin 2, single-unit trucks and vehicles pulling trailers (26 ft to 39 ft); (c) Bin 3, combination trucks and buses (39 ft to 65 ft); and (d) Bin 4, multi-trailer trucks (length greater than 65 ft). Archived loop-detector data of 20-second intervals can be downloaded from the Traffic Data Acquisition and Distribution (TDAD) website to support this project.

For the two selected study locations, the Olive Street site and the Duwamish site, classified traffic volumes can be collected from existing nearby loop detector stations. The algorithms developed can be applied to estimate long vehicle volumes (Bins 3 & 4) from single-loop measurements at this site.<sup>44,45</sup> Loop detectors are subject to various malfunctions; a different method is needed to support air quality considerations.<sup>46,47,48</sup> We will use the Video-based Vehicle Detection and Classification (VVDC) system developed by the Smart Transportation Applications and Research Laboratory (STAR Lab) at the University of Washington. The system will be applied to extract bin volumes from video images. The VVDC system was tested at three test locations under different traffic and environmental conditions. The system achieved exceptional results in both vehicle detection and classification: the accuracy for vehicle detection was above 97% and the total truck count error was lower than 9%.<sup>49</sup> The traffic data resulting from this effort will be relatively precise and verifiable. Therefore, this innovative traffic data collection effort enhances the quality of diesel truck volume data which are critical inputs to evaluate the air toxics models to be developed in this study.

### 3.4 OP-FTIR Source Fingerprinting for Diesel Exhaust

Open Path Fourier Transform Infrared spectroscopy has proven to be useful for quantification of numerous gaseous species including many air toxics. EPA's *FT-IR Open Path Guidance document* provides a rigorous description of this technique. The IR spectrum captures all detectable contaminants over the beam path having a dipole moment. As described in *EPA compendium method TO-16*, quantification of multiple VOC species is possible using Beers Law and multivariate techniques.

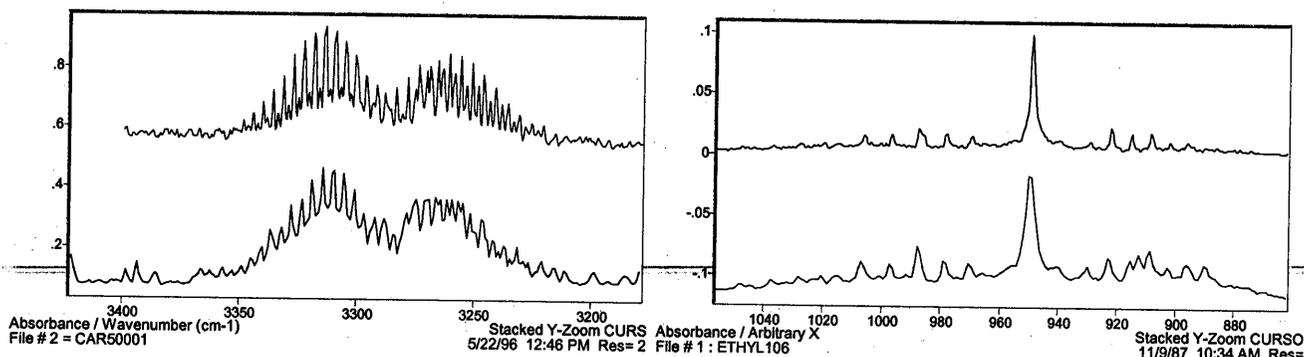


A preliminary method has been developed to apportion hydrocarbon emissions observed with OP-FTIR due to diesel fuel or gasoline fuel vehicles. An OP-FTIR collected 400 spectra from 15 vehicles, five powered by diesel engine and the others by gasoline. The hydrocarbon C-H band from 2850 cm<sup>-1</sup> to 3000 cm<sup>-1</sup> was analyzed to distinguish the two classes of engines. The C-H region was divided into 30 sub-bands of 6 cm<sup>-1</sup> resolution for analyses. The discriminate function correctly classified 100% of the training set spectra (n=200) and 98% of the validation set (n=200). Altering the band resolution or signal-to-noise did not significantly decrease the model prediction ability; the model still correctly classified vehicles until the noise was approximately equal to the peak signal. Successful classification of the 2 vehicle groups depends on hydrocarbon signatures from each type. The basis of

the classification is shown graphically in a peak height normalized plot (Fig. 1-left) of all vehicles by fuel type. Figure 1 shows significant differences in the C-H bands of emissions from vehicles in the different fuel classes. The

diesel peak falls at 2925cm<sup>-1</sup> and the gasoline peak around 2967cm<sup>-1</sup>. Each point on the X axis of this plot represents a variable in the classification model. The weighted model score gives a probability of classification into either diesel or gasoline vehicle for a spectrum. An ensemble of spectra over many vehicles may be interpreted as the proportion of diesel or gasoline vehicle contribution to the hydrocarbon signature.

**Figure 2: Acetylene Ref. vs. CAR 50001 (left panel): Ethylene Ref. vs. CAR 50015 (right panel)**

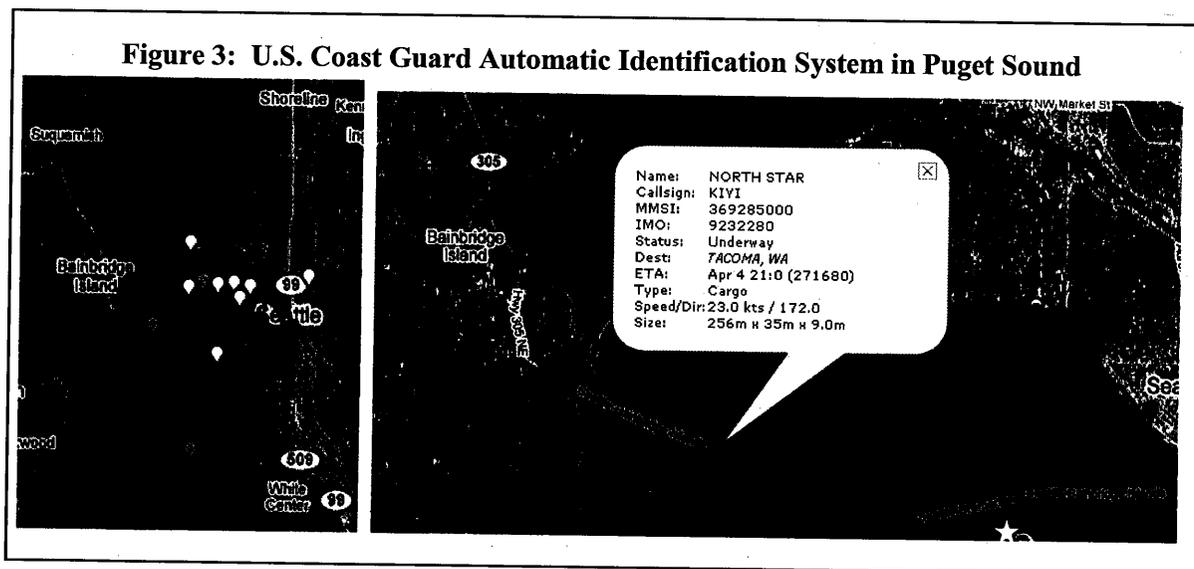


OP-FTIR also can be used to identify specific gas phase compounds for speciation and source fingerprinting. All spectra from vehicles were examined for specific species in addition to the general C-H stretch region above. Computer matching with reference data revealed gases such as methane, ethylene, and acetylene. Figure 2 shows two car spectra compared to reference spectra for matching compounds.

We note the OP-FTIR diesel apportionment method described above depends only on the relative shape of C-H profiles, without speciation of individual compounds. The average spectral properties of each vehicle class are used, not the spectra of individual components. At least 30 hydrocarbon compounds contribute to features in the C-H region that is examined. The advantage of this approach is that it avoids many of the problems with detection limits and missing data that may be found in models using individual chemical species. If this C-H band monitoring approach was successful and validated, it could provide the basis for a low cost alternative method to apportion DE or gasoline hydrocarbon emissions for continuous air monitoring.

### 3.5 Monitoring of Maritime Emissions

We propose to assess maritime emissions using a combination of data sources, including real-time shipping traffic, LIDAR (light radar) aerosol monitoring, and meteorology. These data sources provide a rich and comprehensive view of maritime emissions and their contribution to air quality in the region. The U.S. Coast Guard in 2004 required all ships (> 65 ft) and towing vessels (> 26 ft) in the Puget Sound to be equipped with a vessel Automatic Identification System (AIS). The AIS provides voiceless navigation information exchange between vessels and onshore traffic centers in near real-time. This data is available for public access using a dedicated transponder or via the internet. Figure 3 is an example of AIS data for Seattle: the left side shows ship traffic as individual dots on a photo-map; the right side shows an enlarged image of the port of Seattle, with a detailed listing for one of the vessels.

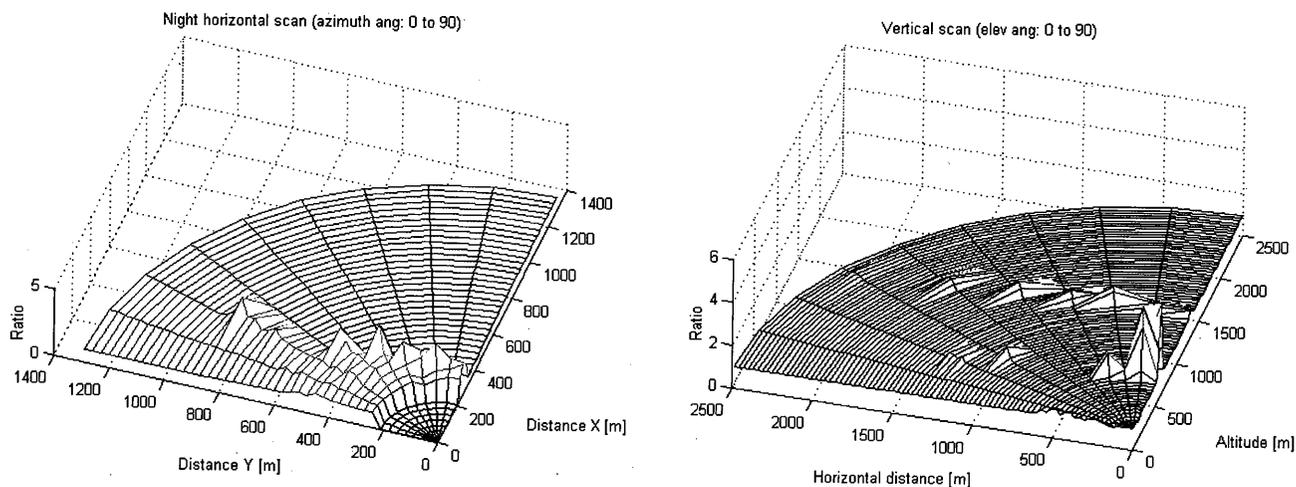


Much like a highway, shipping lanes on waterways can be viewed as transport corridors and emission factors can be applied for the shipping traffic. The AIS provides vessel identifying data such as call sign, name, "IMO" identification number, dimensions, draft, cargo type, destination, and accurate navigation information such as latitude/longitude position, course, and speed. In particular the IMO number can be linked to detailed information on ship size, tonnage, age, and engine hp and propulsion system. The AIS data will be used to estimate air emissions based on the engine size, speed cargo load, and other factors. We will assess the frequency of vessel traffic over shipping lanes by sampling data over monthly intervals during the year, and construct base maps of annual and seasonal emissions for shipping routes.

Monitoring of ship aerosol emissions at the source will use a LIDAR (light radar) provided by the University of Washington's Optical Remote Sensing Lab. LIDAR uses laser light pulses that are backscattered by aerosols in the atmosphere along the beam path and detected with a telescope and sensitive detector. The round-trip travel time for the pulse measures the distance to the aerosols; the intensity of the backscatter is proportional to the particle number density and the optical cross section. Scanning the light beam over azimuth and elevation maps the aerosol density over a relatively large region of sky. The UW-LIDAR is an Orca photonics LRS-50 instrument mounted on a 2-axis computer-scanner and retrofitted with an Nd:YAG laser operated at 355nm. The UW-LIDAR produces 6 ns light pulses at 15Hz with a peak power of 1.6 MW sampled in 30m pixels. By operating in the UV, the LIDAR has high sensitivity for detecting fine aerosols ( $>0.2 \mu\text{m}$ ), and is eye-safe at all ranges.

This LIDAR instrument has been used successfully on several field campaigns. The LIDAR mapped sea-salt aerosols (MMAD  $\sim 7 \mu\text{m}$ ,  $\text{PM}_{2.5} \sim 3 \mu\text{g}/\text{m}^3$ ) from wave action for a study at Westport WA. Figure 4 shows examples of full  $90^\circ$  horizontal (left panel) and vertical (right panel) scans on a clear evening. The horizontal plot shows aerosols downwind from a breakwater about 400 m offshore (along x-axis); the vertical scan shows the top of the boundary layer at  $\sim 1.5 \text{ km}$  height. The UW-LIDAR system currently can map aerosols up to a range of  $\sim 2.5 \text{ km}$ ; for the proposed study this range can be increased by a factor of 3 with a more sensitive detector.

**Figure 4: LIDAR scans of sea salt aerosol at Westport, WA**



The LIDAR will be placed to observe harbor traffic into the port of Seattle and ships passing south to the port of Tacoma. Particle emissions from ships will be measured in 2 one-month long seasonal campaigns to assess the particle density and plume direction during routine operations. The backscatter cross-section and backscatter-extinction ratio for LIDAR data processing will be calibrated using a backscatter nephelometer to measure ship emissions from vessels while in the port. Particle emissions observed for vessels of different sizes will be correlated with AIS data to scale relative emission factor estimates for modeling, based on engine displacement, horsepower, weight, or other factors. Dispersion modeling will be used with ship traffic frequency data and AIS to estimate patterns of emission landfall and impact regions under different seasonal conditions.

### 3.6 Source Apportionment Models

We will apply positive matrix factorization (PMF) to data consisting of: (a) hourly concentrations of selected NMHC from  $\text{C}_2$  to  $\text{C}_{12}$  and OP-FTIR hourly data; and (b) daily averages of particulates from the STN speciation data, the NMHC data, and the OP-FTIR data combined using a single PMF model. The results of this analysis will be a set of source-related profiles and associated contributions to total measured NMHC. This analysis will provide

new insights into the sources of these VOCs. Combined with black carbon measurements using a multi-wavelength Aethalometer, this data should provide robust estimates of the sources of black carbon, including both diesel and gasoline vehicle exhaust. We will perform multiple linear regressions using the PMF-derived feature scores mentioned above as independent variables and the black carbon measurements as the dependent variable. This will provide an estimate of the relative black carbon source contributions. This is particularly important given that black carbon is measured at numerous sites throughout the Puget Sound region. Table 2 summarizes measurements at the Duwamish site.

### 3.6.1 Analysis of Hourly Data

PMF will be applied to a data set consisting of hourly concentrations of selected NMHC from C<sub>2</sub> to C<sub>12</sub> taken at three sites in Seattle, employing the multi-linear engine algorithm (ME-2) to implement the PMF analysis. To generate this data, we will use a continuous gas chromatograph equipped with a thermal desorber (Section 3.2). We expect to have large data sets, given that we plan to measure NMHCs on an hourly basis for between a month and a year, depending upon the site (see Table 2 below). The results of this PMF analysis will be a set of source-related profiles and their associated contributions to total measured NMHC. This analysis will provide new insights into the sources of these VOCs.

In addition, we will redo the PMF analysis including the NMHC species, and the corresponding hourly average peak areas as measured by the OP-FTIR during its operation period. Although this data set will not be as large as that for NMHCs, it will still be a large data set. We plan to operate the OP-FTIR at all three sites during an entire month at the high and low traffic sites, and for the entire year at the Duwamish site. The multivariate features will be extracted from the data via PMF, and the subsequent feature scores will be regressed against total measured mass. For the NMHC data, scores will be regressed against the total measured NMHC for each hour. For the FTIR data, scores will be regressed against the total peak area over all measured peaks. For each PMF-derived feature, we will then be able to examine not only the NMHC abundances to compare with the results of Model 1, but also the corresponding abundances of the FTIR absorption spectrum. Given the promising results outlined above in Sections 3.2 and 3.4, we are confident that this model will provide a good separation of diesel versus gasoline exhaust. Finally, the PMF-based hourly estimates of the gasoline and diesel related features would be correlated with the observed long- and short-vehicle traffic volumes obtained from the nearby roadway. (see Section 3.3)

**Table 2: Summary of Current and Proposed Measurements Study Sites**

<i>Measurements</i>	<i>Method</i>	<i>Averaging Time</i>	<i>Sample Frequency</i>	<i>Sample Locations<sup>a</sup></i>	<i>Sample Period per site</i>	<i>Responsible Party</i>
PM <sub>2.5</sub> Species <sup>b</sup>	STN protocol	24-hour	1 in 6	High, Low	1 month	WDOE
		24-hour	1 in 6	Duwamish	1 year	
1-Nitropyrene	HPLC-tandem MS	24-hour	1 in 6	Duwamish	1 year	UW
NMHC	GC-FID	1-hour	continuous	High, Low	1 month	UW
				Duwamish	1 year	
Total Gaseous Hydrocarbons	OP-FTIR	1-hour	continuous	High, Low	1 month	UW
				Duwamish	1 year	
Traffic Volumes <sup>c</sup>	Loop & Video	1-hour	continuous	High, Low	1 year	UW
				Duwamish	1 year	
Black Carbon <sup>d</sup>	Aethalometer	1-hour	continuous	High, Low	1 year	PSCAA
				Duwamish	1 year	
Particle Backscatter	LIDAR	1-hour	select periods	Duwamish	1 month	UW

<sup>a</sup>High, Low = high and low traffic sites, respectively (high traffic = Olive St site).

<sup>b</sup>PM<sub>2.5</sub> species data are available for the Olive St. site and the Duwamish site.

<sup>c</sup>Traffic counts sorted into 2 categories, Bins 1+2 and Bins 3+4 respectively.

<sup>d</sup>Black carbon measurements are available for Olive St and Duwamish site.

### 3.6.2 Analysis of Daily Data

To improve understanding of the previous apportionments of DPM, we will simultaneously analyze a year's worth of STN speciation data obtained at the Duwamish site along with the NMHC data and the OP-FTIR data. First we will compute daily averages of the gaseous measurements to correspond in time with the STN data. On 1 in 6 days when the STN site is operating, we will have STN particulate species, 1-nitropyrene, and gaseous data inputs; on the other days we will have only the gaseous inputs. We will therefore extend the particle data by including all the previous STN measurements at this site (approximately 4 years). At the end of the study period we should have about an equal number of days of particulate and gaseous species concentration data, with about 60 overlap days.

### **3.6.3 Incorporation of Traffic Data and Meteorological Data**

We will extend the ME-2 algorithm analysis to include hourly traffic counts of both large and small vehicles on major roads near these sites as well as hourly values of local wind speed and direction. Traffic data will be obtained as discussed in Section 3.3 above. These additional variables will be included as categorical variables in the same way that has been previously reported by Paatero and co-workers.<sup>50</sup> For the traffic data, we treat counts in Bins 1 & 2 separately from those in Bins 3 & 4 and establish categorical count levels for each bin group. Output from this extended PMF model will not only include feature scores and loadings, but also accompanying information on the relative importance of traffic type by count category and local meteorology for each PMF-derived feature. These additional hourly measurements of traffic and local meteorology will provide additional, logical constraints on the factorization, thereby reducing overall uncertainty as estimated via bootstrapping methods.

### **3.7 Data Collection and Evaluation**

Analytical data for the NMHC (TO-11) obtained from the automated GC-FID will be continuously logged and downloaded weekly back to the Agency's data repository. Routine quality assurance screening will be applied to check for appropriate zero and span calibrations. Post processing will be used to obtain 1-hour and 24-hour averages for use in modeling and reporting. OP-FTIR spectra will be logged continuously and reported to the data repository on a weekly basis. FTIR monitoring will follow TO-16 guidance document procedures for quality assurance screening and evaluation of method noise. LIDAR data will be stored as time and date stamped scan profiles and archived daily during monitoring campaigns. Due to the large size of these data sets, selected periods corresponding to ship observations (typically 5-to-15 minutes) will be post processed and summarized as the averaged volume backscatter values over a 500 m<sup>3</sup> region directly downstream above the ship's stack in the emission plume. Nitropyrene filter samples will follow standard chain of custody and tracking procedures specified in the quality assurance plan created at the start of the project. Analytical results will be converted to concentration values ( $\mu\text{g}/\text{m}^3$ ) using data obtained from field sampler flow rates and quality assurance/quality control activities.

### **3.8 Data Reduction, QA/QC, and Management**

Data reduction and management will largely consist of archiving and averaging the data collected from the continuous monitoring instruments in the study. The Agency has a great deal of experience in using real-time data in this form. Although most of the routine data collection will be automated, manual inspection of instrument operation and routine site checks will still be conducted by members of this study team or by personnel servicing the sampling network. Data reduction for filter samples will be adapted from existing procedures followed for the STN sample collection sites.

The Agency is committed to providing the highest degree of data quality in order to meet the monitoring objectives of this project. Upon initiating this project, we will develop data quality objectives for each component of the monitoring data, and implement these objectives in a Quality Assurance Project Plan (QAPP) to be written before the start of data collection. Routine quality control checks will be applied to all incoming data that is placed in the data repository. Technical procedures for the quality assurance program will be described in the QAPP and will include routine calibrations, annual system audits, standard checks, system blanks, record keeping checks, and exception logging. All reviewed and validated data will be summarized and submitted to EPA in both presentation form and in a final report at the end of the project.

## **4. Environmental Output/Outcomes**

The method development studies proposed here are motivated by a need to resolve the ambiguity of DE contribution to high impact areas for mobile sources. These studies will develop and test innovative methods for continuous monitoring of gas phase hydrocarbon air emissions at the existing monitoring sites, using either GC-FID or OP-FTIR instruments. The results, combined with site apportionment models will provide new assessments of DE or gasoline emissions with high temporal resolution (~hourly) that combine continuous gas-phase and continuous monitoring aerosol data (black carbon). Further, the evaluation and validation of 1-nitropyrene as a specific marker of diesel exhaust particulates will provide a new analysis tool that can be applied to the existing filter samples from the monitoring network. These metrics and the model-apportioned contribution of gasoline and DE mobile sources will be validated against accurate traffic count data obtained at test sites adjacent to major traffic corridors.

The method development studies proposed here also are motivated by a need to resolve DE contributions from maritime and port emissions as well as vehicle traffic. Maritime emissions are particularly challenging, because it is difficult or impossible to monitor emissions directly at the source and to define meaningful emission factors. We will evaluate LIDAR as a way to observe maritime emissions near the source and describe routine emission factors. When combined with GPS data on ship traffic and wind conditions, this emission data can form the basis of a systematic approach to assess the impacts of maritime DE emissions on populated regions. In conjunction with this monitoring of shipping traffic, we will apply the revised apportionment models at an industrial site near the Port of

Seattle, where mobile source emissions from gasoline and diesel vehicles combine with diesel maritime sources.

#### **5. Roles and Qualifications of the Applicant and Partners**

**Contract Manager** - Mike Gilroy will be responsible for the successful execution of the contract. Mr. Gilroy will regularly interact with team members, including Agency and University of Washington staff. Mr. Gilroy will regularly interface with EPA's contract officer regarding project-related issues and the Agency's team performance to ensure that all work performed adheres to the approved budget and schedule, while meeting expectations of the project.

**Project Operations Coordinator**- Kathy Himes will be responsible for operational oversight of the projects routine activities ensuring that milestones are being met and that required reports are generated and submitted promptly. As Ops Coordinator, along with the Contract Manager she 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.

**Monitoring Supervisor**- Matt Harper will oversee Agency monitoring-related matters and personnel, including set-up and operation of the fixed sites, trouble-shooting challenges that arise, and coordinating monitoring personnel schedules.

**Quality Assurance/Quality Control Manager** - Erik Saganic will ensure quality assurance and control, per the Washington State Quality Assurance Plan.

#### **6. Biographical Information for Key Personnel**

**Mike Gilroy, Puget Sound Clean Air Agency** - Mr. Gilroy is a Meteorologist and Manager of Technical Services. He has more than 35 years of meteorological experience and nearly 12 years of experience in ambient air monitoring network design and new technology implementation. He has been an active partner on a number of EPA national air monitoring and air toxics monitoring committees.

**Kathy Himes, Puget Sound Clean Air Agency** - Ms. Himes holds a Bachelor of Science in Engineering from the University of Michigan as well as a Master's in Environmental Health from the University of Washington, and is a Professional Engineer in Washington State (#41906, Environmental). Ms. Himes brings 3 years of air quality management experience, as well as 8 years environmental consulting and outreach experience.

**Matt Harper, Puget Sound Clean Air Agency** - Mr. Harper holds a Master's in Business Administration from the University of New Haven, CT as well as a Bachelor of Science in Manufacturing Engineering from Boston University, MA. In his current role, he is in charge of the team that operates and maintains 20 monitoring sites, and over 80 monitoring and meteorological monitoring instruments throughout the Puget Sound. He brings 4 years of ambient air monitoring experience as well as 7 years of professional engineering, management, and training experience in his service with the United States Navy.

**Erik Saganic, Puget Sound Clean Air Agency** - Mr. Saganic has a B.S. in Chemistry from Brown University and an M.S. in Chemistry from the University of Washington. He has over 7 years of data analysis and research experience from the private sector and academia, and has published a number of papers. He has worked in the field of environmental science for over 3 years. He currently co-manages quality assurance responsibilities and assists air monitoring projects.

**Dr. Michael Yost, University of Washington** - Dr. Yost is a professor and the director of the Industrial Hygiene and Safety program at UW. He received his Ph.D. from the UC Berkeley in Environmental Health Sciences with a minor in Electrical Engineering and Biostatistics. He founded and directs the optical remote sensing lab at UW and has published widely on remote sensing measurements of chemical and aerosol contaminants.

**Dr. Timothy Larson, University of Washington** - Dr. Larson is the Alan and Inger Osberg Professor of Civil and Environmental Engineering at the University of Washington and holds an adjunct appointment in the Department of Occupational and Environmental Health Sciences. His expertise is in characterization of urban air pollution, exposure assessment of airborne particles and gases, and source/receptor relationships of ambient air pollutants.

**Dr. Chris Simpson, University of Washington** - Dr. Simpson is a Professor in the Department of Environmental and Occupational Health Sciences. He received his Ph.D. from the University of British Columbia in Chemistry, and has a Master's and Bachelor's in Chemistry and Biochemistry, respectively. Dr. Simpson's expertise is developing sensitive analytical methods for measuring exposure to airborne contaminants, including chemicals derived from diesel exhaust and wood smoke.

**Dr. Yinhai Wang, University of Washington** is the Thomas and Marilyn Nielson Professor of Civil and Environmental Engineering at the UW. Dr. Wang has a Ph.D. in Transportation Engineering from the University of Tokyo and a Master's in Computer Science from the UW. Dr. Wang is the founder and lead of the Smart Transportation Applications and Research Laboratory (STAR Lab) at the UW. His areas of expertise include traffic detection systems, traffic sensor data management and analysis, traffic operations, and traffic simulation.

**h. Detailed Itemized Budget:**

Category	Amount	Notes
1. Personnel	\$ 27,486	Appropriate .02FTE
2. Fringe Benefits	\$ 6,871	
3. Contractual Costs – Contract Lab	0	No contractual cost
4. Travel	\$ 3,500	Travel as required by RFP
5. Equipment	\$73,500	
6. Supplies	\$5,000	Monitoring supplies
7. Other (sub-award)	\$322,327	U of Washington services (direct and indirect)
8. Total Direct Costs	\$438,685	
9. Total Indirect Costs	\$11,156	
<b>10. Total Cost</b>	<b>\$449,841</b>	
<b>11. Total Cost after Agency Contribution</b>	<b>\$361,841</b>	Agency to contribute up to \$85,000

**i. Environmental Results Past Performance:** The Puget Sound Clean Air Agency has been the recipient of several, recent EPA grants awards. The Agency has accounting procedures in place that are compliant with federal auditing and reporting requirements, including on-time submittal of required, quarterly progress reports. During the past three years, the Puget Sound Clean Air Agency has received the following federal grants. Progress and results under these agreements were achieved according to established goals and timelines.

<u>Grantor Agency</u>	<u>Program Name</u>	<u>Federal CFDA #</u>	<u>Current Year Expenditures</u>
U.S. EPA	Outdoor Burning Communication & Education	66.034	\$ 14,900
U.S. EPA	Air Quality Forecasting & Special Air Quality Studies	66.034	\$ 24,562
U.S. EPA	Biowatch-Homeland Security	66.034	\$ 329,931
U.S. EPA	Western Washington Clean Buses, Healthy Kids	66.034	\$ 45,297
	Total FY 2006		\$ 414,690
U.S. EPA	Clean Diesel School Bus	66.606	\$ 88,977
U.S. EPA	Air Quality Forecasting & Special Air Quality Studies	66.034	\$ 45,642
U.S. EPA	Biowatch-Homeland Security	66.500	\$ 252,931
U.S. EPA	Western Washington Clean Buses, Healthy Kids	66.034	\$ 172,342
	Total FY 2005		\$ 559,892
U.S. EPA	Clean Diesel School Bus	66.606	\$ 157,380
U.S. EPA	Air Quality Forecasting & Special Air Quality Studies	66.034	\$ 27,842
U.S. EPA	Biowatch-Homeland Security	66.500	\$ 147,601
U.S. EPA	Collaborative Process for Puget Sound Air Quality Management & Energy Efficiency	66.034	\$ 30,000
	Total FY 2004		\$ 362,823
	<b>3-Year Total</b>		<b>\$1,337,405</b>

**j. Programmatic Capability:** The Puget Sound Clean Air Agency has successfully completed or is continuing work on the three projects listed below. These projects are similar in size, scope, and relevance to the proposed project.

<u>Grantor Agency</u>	<u>Program Name</u>	<u>Federal CFDA #</u>	<u>Expenditures</u>
U.S. EPA	Biowatch-Homeland Security	66.500	\$ 748,563
U.S. EPA	Clean Diesel School Bus	66.606	\$ 281,812
U.S. EPA	Air Quality Forecasting & Special Air Quality Studies	66.034	\$ 98,046

For these three projects, the Agency is meeting, or has met, all technical and reporting requirements including submission of periodic and final technical reports. As a frequent recipient of federal funds, our Agency has developed an experienced finance and technical staff with proven ability to manage grants efficiently and effectively. Our staff is regularly trained in contracts management and our Agency is audited annually. Our technical project officers have years of experience directing technical studies and managing projects, including a state-funded diesel retrofit grant program of nearly \$2 million annually.

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