FINAL PROJECT REPORT

THE PORT OF LOS ANGELES

COMMUNITY-BASED AIR TOXICS EXPOSURE STUDY

Prepared for

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U.S. Environmental Protection Agency

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Acronyms

AQS	Air Quality System
ARB	California Air Resources Board
BC	Black carbon
CDX	Central Data Exchange
CE-CERT	Chemical Engineering - Center for Environmental Research and Technology
CFR	Code of Federal Regulations
CO	carbon monoxide
DPM	diesel particulate matter
EC	elemental carbon
EPA	United States Environmental Protection Agency
GC-MS	gas chromatography-mass spectrometry
HAPs	hazardous air pollutants
Hi-Vol	high volume sampler
HPLC	high performance liquid chromatography
ID	inner diameter
MATES	Multiple Air Toxics Exposure study
NO	nitrogen oxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
O_3	ozone
OC	organic carbon
OD	outer diameter
OEHHA	Office of Environmental Health Hazard Assessment
P	atmospheric pressure
PAH	polycyclic aromatic hydrocarbon
PAS	photoelectric aerosol sensor
PCAC	Port Community Advisory Committee
PM	particulate matter
PM_{10}	particulate matter with an aerodynamic diameter of less than 10 microns
$PM_{2.5}$	particulate matter with an aerodynamic diameter of less than 2.5 microns
PST	Pacific Standard Time
QAPjP	quality assurance project plan
RH	relative humidity
ROI	region of influence
SCAQMD	South Coast Air Quality Management District
SO_2	Sulfur dioxide
SPPS	Saints Peter and Paul School
SR	solar radiation
T	ambient temperature
TEOM	Tapered Element Oscillating Microbalance
TEU	twenty-foot equivalent unit

TITP	Terminal Island Treatment Plant
UFP	ultrafine particle
UTM	Universal Transverse Mercator
UV-F	ultra-violet fluorescence
WD	wind direction
WS	wind speed
XRF	x-ray fluorescence

Executive Summary

The Port of Los Angeles (Port) is one of the busiest commercial ports in the United States handling approximately 8.5 million twenty-foot equivalent units of containerized goods and 180 million metric tons of cargo in 2006 and 2007, with a slight decline in 2008 due to the recent worldwide economic downturn. The Port's operation supports a robust regional economy. However, air pollution associated with the Port's operation has become a health concern to local communities and regulatory agencies. The Port has developed a comprehensive plan to mitigate Port-related air pollution. Because the Port and the terminals operate a large population of equipment, the majority powered by diesel, diesel exhaust, particularly diesel particulate matter, may impact neighboring communities. Normally, elemental carbon is used as a surrogate to estimate diesel particulate matter emissions and in health risk analyses.

To understand the potential air quality impacts from Port activities, the Port implemented a four-station particulate matter and elemental carbon monitoring network in 2005. This network was upgraded in 2007 to include real-time analyzers for criteria air pollutants such as nitrogen oxide, sulfur dioxide, and carbon monoxide. Meteorological data is also collected at each site. As part of this grant award, the monitoring capability of this network was further enhanced by installing EcoChem PAS 2000 - real-time polycyclic aromatic hydrocarbon (PAH) analyzers. This instrument can measure airborne PAHs that adhere to the surfaces of particles by a photo-electrification process to excite particle-bound PAHs. The change in electric current can be measured and converted into PAH concentrations. The objectives of operating PAH analyzers are two-fold: to understand the PAH levels in the areas on a real-time basis and to more accurately estimate health risk using direct PAH measurements instead of a surrogate.

The real-time PAH monitoring network is housed in the same shelters of the Port's four-station network. The network consists of a coastal boundary station (Berth 47), a source-dominant station (Terminal Island Treatment Plant or TITP), and two community stations, with one located in the San Pedro (Promenade) and the other in the Wilmington (Saints Peter and Paul School or SPPS). These four stations began monitoring for PAHs in late 2007 and early 2008 and are still in continuous operation. The first year of hourly monitoring data, collected through April 2009, were uploaded to the U.S. Environmental Protection Agency Air Quality System (AQS) database. This report discusses trends of real-time PAH monitoring data and correlations with other parameters measured such as meteorological data, nitrogen oxides, elemental carbon, black carbon, particulate matter, and speciated PAHs.

Diurnal and seasonal trend analyses show that three sites – Berth 47, TITP and Promenade – have a bimodal pattern; one peak appears at morning hours around 7:00 AM and the second peak appears in the evening hours around 8:00 PM. However, SPPS only has one peak that appears in the morning. The bimodal trend is most likely caused by a combination of Port activity, mixing heights, and wind speeds. In general, the trends also show relationships among source, background, and community locations. The lowest concentrations are observed at the background site, the second lowest by the two community sites and the highest concentrations are observed at the source site.

The trend at SPPS is difficult to explain, as it may be caused by local meteorology such as air recirculation. One notable observation is the change in predominant wind patterns recorded between 2005 to 2006 and 2008 to 2009. It is not clear if this shift of wind pattern has any impact on the ambient PAH concentration trend at this site.

As expected, real-time PAH data has a strong correlation ($R^2>0.9$) with nitrogen oxides and elemental carbon ($R^2>0.8$) at all four sites. However, there was a weak correlation between real-time PAH and black carbon at SPPS. Black carbon and elemental carbon are normally used by researchers interchangeably; however, from an analytical chemistry standpoint, they are totally different in measurement techniques. It is not clear whether this difference in measurement techniques is the cause of the weak correlation at this site. Additionally, no significant correlations between real-time PAH and ultrafine particle, $PM_{2.5}$, and speciated PAHs were observed.

The co-located analysis with a transfer standard in the laboratory and at the sites showed that the real-time PAH analyzers were operating normally and data quality was considered satisfactory.

It is recommended that future work include the following:

- Collect activity data near the monitoring sites to facilitate in-depth analysis of real-time PAH data to provide better spatial and temporal trends;
- Require improvements in speciated PAH analysis, for accuracy and better reproducibility. If necessary, a reference aerosol standard should be included; and
- Conduct source-apportionment using real-time PAH data and analytical tools such as non-parametric back trajectory method to elucidate port’s “fair-share” of pollution, particularly PAHs, and the potential health risk to the local communities.

1. INTRODUCTION

The Port of Los Angeles (Port) is one of the busiest container ports in the United States. The Port is located in San Pedro Bay, approximately twenty miles south of downtown Los Angeles. The Port is situated on 7,500 acres of property with 43 miles of waterfront and 27 cargo terminals. Marine terminals include dry and liquid bulk, container, break bulk, automobile and Omni facilities. Established under the California State Tidelands Trust in 1911 to promote harbor commerce, navigation and fisheries and the amendment in 1970 to expand the purposes of all the Port trust lands, the Port has grown into a major international marine port with more than 2,000 vessel calls and more than $100 billion worth of goods annually. The infrastructure that is required for moving goods throughout the region and to other areas in the nation includes many diesel-powered mobile sources. The Port's activity has increased significantly in the last decades due to the tremendous economic growth and trade in the Pacific Rim areas. However, the recent domestic and global economic downturn has reduced marine trade volumes across the Pacific and impacts overall cargo handled by the Port. The Port's records showed that between Fiscal Years 2008 and 2009, there was a 10 % reduction (e.g. 8 million down to 7.3 million) of annual container twenty-foot equivalent units (TEUs) handled.

The California Air Resources Board (ARB) has identified diesel particulate matter (DPM) as a toxic air contaminant because of its known carcinogenic properties. The United States Environmental Protection Agency (EPA) also listed diesel exhaust as a mobile source air toxic among 33 air pollutants in the National-Scale Air Toxics Assessments. The South Coast Air Quality Management District (SCAQMD) conducted three urban air toxics monitoring programs in the South Coast Air Basin in the last two decades, the Multiple Air Toxics Exposure Study-I (or MATES-I) in 1986, MATES-II in 1998 and MATES-III in 2004, to assess potential adverse health effects by exposure to air toxics, including DPM. DPM health risks were estimated using the California EPA risk factors for DPM and elemental carbon (EC) as a surrogate for estimating DPM concentrations. Results from the MATES-III study showed that DPM continued to be the dominant toxic air pollutant based on cancer risk in the air basin, and goods movement was a significant source of diesel emissions. Additionally, the study identified areas near the Port as having a higher estimated air toxics risk due to an increase in cargo throughput and associated goods movement. Finally, the study recommended that improved methodology for measuring ambient levels of DPM or its surrogates will be required to provide a better estimation of risk from DPM.

EC is normally used as a surrogate for estimating DPM concentrations for risk assessment purposes. From a chemistry standpoint, DPM contains numerous individual chemical species, both organic and inorganic, on the surface of the particle. One group of chemical species in DPM that has significant health implication is polycyclic aromatic hydrocarbons (PAHs). PAHs are byproducts of the combustion of organic matter. Many of them are considered potent carcinogens or mutagens, such as benz[a]anthrcene, benzo[b]fluoranthene, benzo[k]fluoranthene and they are also considered as hazardous air pollutants (HAPs). Table 1 provides a list of selected

PAHs and DPM, and their unit risk factors by the California Office of Environmental Health Hazard Assessment (OEHHA).

Table 1.1 Unit Risk Factors for Selected PAH Pollutants and DPM.

Selected PAH Pollutants and DPM	Unit Risk Factor
Benzo[a]anthracene	1.10E-04
Benzo[b]fluoranthene	1.10E-04
Benzo[k]flouranthene	1.10E-04
Benzo[a]pyrene	1.10E-03
Chrysene	1.10E-05
Dibenz[a,h]anthracene	1.20E-03
Indeno[1,2,3-cd]pyrene	1.10E-04
Diesel particulate matter (CARB)	3.00E-04

The Port has implemented a Port-wide air quality monitoring program to measure ambient particulate matter (PM) levels, including DPM, in the Port's vicinity and the adjacent communities. The purposes of this network are to measure ambient air quality, to validate health risk assessments, observe the effects of adopted mitigation measures, and to document air quality improvement as a result of the 2006 San Pedro Bay Ports Clean Air Action Plan (CAAP). The network has collected representative ambient PM and meteorological data within the Port's region of influence (ROI) since February 2005. PM collected included both particulates less than 10 microns in diameter (PM_{10}) and particulates less than 2.5 microns in diameter ($PM_{2.5}$) using filter-based samplers. Selected samples were also analyzed for their carbon content, including EC and organic carbon (OC) by thermal/optical reflectance method, elemental analysis by x-ray fluorescence, and ionic species by water extraction and ion chromatography.

Traditionally, a 24-hour composite sample of airborne PAHs is collected using a combination of filter and adsorbent foam sampling media, to trap both particle-bound and vapor-phase PAHs using a high-volume (Hi-Vol) sampler. The analysis of PAH involves solvent extraction of the sampling media and analysis using gas chromatography-mass spectrometry (GC-MS) or high performance liquid chromatography with ultra-violet and fluorescence (HPLC-UVF) detection. The advantage of the composite samples with GC-MS or HPLC-UVF analysis is to provide a complete specification of total PAHs collected, both particle-bound and vapor-phase, in the sample and with a relatively low method detection limit (e.g., in nanogram [10^{-9} gram] to picogram [10^{-12} gram] range using GC-MS). However, the sampling method is labor-intensive and costly and the sample preparation and analytical processes are complex. Additionally, the composite sample does not provide information on temporal trend or variation during the 24-hour sampling period because air pollutant levels are averaged over the entire sampling period.

Ambient PAH levels from mobile sources are highly activity- (e.g., traffic pattern) and time-dependent. Better temporal resolution can provide insight on emission patterns, particularly the diurnal patterns, for better assessment of health impacts. In this study, quasi-real time photoelectric aerosol sensors (PAS) are used to obtain the concentration of particle-bound PAHs at four ambient monitoring sites from 2007/2008 to 2009. PAH monitoring data and other relevant parameters, such as EC concentration and meteorological data, are analyzed to elucidate the potential sources and their contribution to diesel particulates.

In 1997, the EPA conducted a study to evaluate the PAS in the field and laboratory. The results showed that temperature and humidity did not affect the response of the PAH to aerosols that were equilibrated at the test temperature (1). PAS has been used to measure particle-bound PAHs in ambient air, diesel emissions and indoor air environment (2, 3, 4, 5, 6). The recently completed Wilmington Measurement Study showed that the PAH measurement by PAS correlated well with a real-time absorption method that uses the Magee Scientific Aethelometer to measure BC (7).

To better assess air quality impacts by port-related activities, the Port upgraded the PM network in 2007 to a fully-equipped ambient air quality network including both gaseous and particulate air pollutant measurements. As part of this grant, this network was further enhanced with the real-time PAH monitors to measure real-time particle-bound PAHs.

The main objective of this project was to augment the existing Port-wide ambient air quality monitoring program to include the capability of monitoring air toxics, especially particle-bound PAHs. The monitoring network utilizes real-time PAH analyzers such as the EcoChem Analytics PAS 2000 to measure particle-bound PAHs in the ambient air on a quasi-real time basis. The real-time PAH monitoring provides better temporal resolution for activity-related analysis. Results from the real-time PAH measurements coupled with meteorological data, and particulate mass and chemical measurements obtained from the existing Port-wide air monitoring network can be used to characterize emission sources and potential air quality impacts from the Port’s operations, particularly, diesel exhaust particulates. The results of this study provide an understanding of the following parameters:

- Diurnal and seasonal variability of PAH concentrations
- Correlation between PAHs and other ambient constituents
- Correlation between speciated and real-time PAH concentrations

The study was successful in developing the above understandings, which will assist the Port in future potential studies (source apportionment, health effects, etc.). This report describes operation, data collection and analysis of the enhanced PAH monitoring network.

2. Ambient Monitoring Methodology

2.1 Sampling Location and Monitoring Parameters

The Port completed the basic design of the monitoring network in 2003, selecting monitoring locations that are truly representative of ambient air quality conditions within the areas of interest. Working with ARB, the Port Community Advisory Committee (PCAC) technical consultants and SCAQMD, a work plan for air quality monitoring for the Port was prepared. Short-term validation studies were conducted in 2004 to ensure that the best available monitoring sites were selected. Factors considered in the site selection included meeting siting criteria for unobstructed sample air flow as described in the 40 CFR Part 58 – Ambient Air Quality Surveillance, Appendix E – Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring, site availability and security. The site locations are centrally located within the section of the communities closest to Port operations. Furthermore, the Wilmington site is located at an elementary school which is considered as a sensitive receptor for health risk assessment.

As discussed earlier, the Port installed and operated four PM monitoring sites within the Port's ROI since February 2005. Prior to installing monitoring stations, a site selection study, lasting approximately three months, was conducted to validate the exact locations for two community sites – Wilmington and San Pedro *(8)*. In addition to two community sites, the network also included coastal boundary and source-dominated monitoring sites. This PM monitoring network included the collection of "inhalable" or coarse PM (PM_{10}) and "respirable" or fine PM ($PM_{2.5}$). In addition, a surface meteorological tower was also installed at each of the four stations. All filter samples were analyzed for mass concentration and carbon analysis including EC and OC. Selected filter samples also were analyzed for their chemical compositions, including metals by x-ray fluorescence (XRF), soluble ions (nitrate, sulfate, ammonium, sodium and potassium) by automatic colorimetry, ion chromatography and atomic absorption. Additionally, a ground-level (10-meter) meteorological station was installed at each of the four monitoring sites to measure wind speed, wind direction, and ambient temperature. The Wilmington station also measured atmospheric pressure, solar radiation and relative humidity.

In 2007, the Port upgraded the existing PM network to include real-time monitoring of ultrafine particulates (UFP), $PM_{2.5}$, PM_{10}, and gaseous criteria pollutants (i.e., nitrogen oxides [NO_x], sulfur dioxide [SO_2], carbon monoxide [CO] and ozone [O_3]). These analyzers were housed in weather-controlled semi-permanent shelters. Due to shelter space and weight requirements, two stations – San Pedro and TITP had to be relocated to nearby available property. The selection of the new station locations followed the aforementioned EPA monitoring station siting criteria. Furthermore, a site validation study using $PM_{2.5}$ samplers was conducted in March 2008 at these two sites, to assure that the relocation had no adverse effect on the site representativeness, monitoring capability and data integrity *(9)*.

The expanded monitoring network consists of four stations, all at ground level, including one source-dominant station, one coastal boundary station, and two community monitoring stations - Wilmington and San Pedro. Locations and parameters measured for the Port air quality monitoring network stations are listed in Table 2.1. Geographical locations and meteorological conditions for the four stations are shown in Figure 2.1.

The Wilmington and San Pedro community monitoring stations are designed to collect air quality levels that are representative of the residential areas of the Wilmington and San Pedro communities. The Wilmington station is located at the Saints Peter and Paul School (SPPS) in the City of Wilmington and is centrally located approximately 0.5 miles north of Port operations. The San Pedro station (also known as Berth 87, or the Promenade station) is located at 100 South Harbor Boulevard, near the Promenade walkway at Berth 87 along Harbor Drive, across the street from the intersection of Harbor Boulevard and West 3rd Street and is centrally located approximately 0.1 miles west of the main ship channel. The coastal boundary station, or Berth 47 station, is located at Berth 47 in the Port Outer Harbor at the south end of Miner Street. This location has the least direct impact by emissions from Port operations and, therefore, is designed to collect background air quality levels. The source-dominant station is located at the TITP at 455 Ferry Street, San Pedro. This station is in direct proximity to terminal operations which involve heavy traffic of diesel trucks, trains, ships and operation of cargo handling equipment, therefore, is designed as the source-dominant station, representing direct air impacts by Port's operations from the use of diesel-powered on-road and off-road mobile sources.

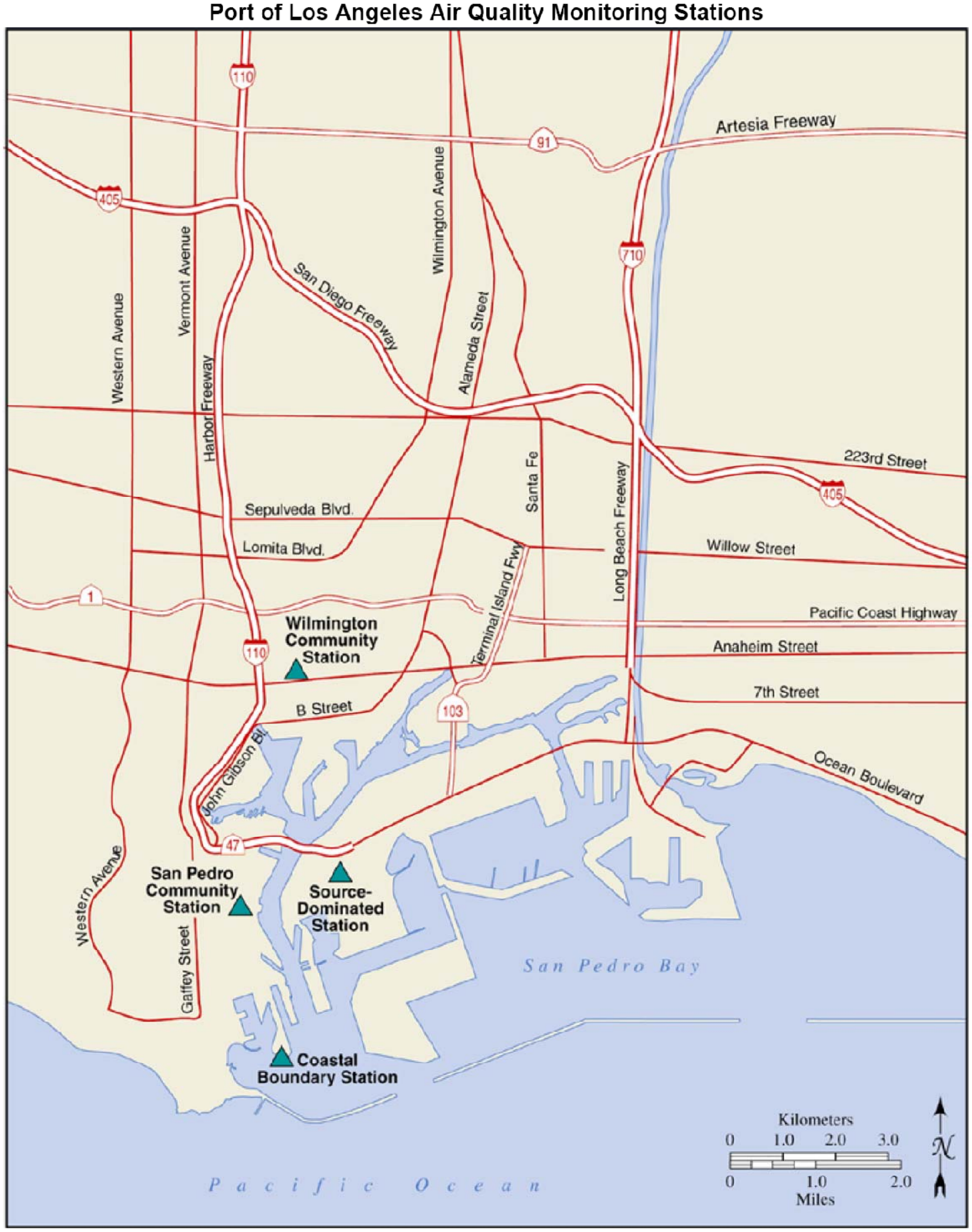
Meteorological data such as wind speed and wind direction are commonly used parameters to determine air pollutant dispersion and downwind receptor locations. Frequency of occurrence of wind speed and wind direction at the monitoring site can be expressed as wind roses to illustrate prevailing wind direction and speed during a given monitoring period at that site. This information is very useful in analyzing air monitoring data and potential ground level air impacts. Figure 2.2 shows wind rose plots for all four stations from May 2005 to April 2006. It should be noted that at that time, the San Pedro community station was located on the rooftop of the Liberty Hill Plaza, across the street from the current location.

Table 2.1. The Port of Los Angeles Air Quality Monitoring Stations and Measured Parameters.

Station Name	**Location**	**Parameter Measured**											
		Air Pollutants						**Meteorological Parameters**					
		CO	**O_3**	**NO_x**	**SO_2**	**PM**	**PAH**	**WS**	**WD**	**T**	**SR**	**P**	**RH**
Coastal Boundary Station (Berth 47)	Berth 47 in the port's outer harbor	V	V	V	V	A,B, C,D	V	V	V	V	-	-	-
San Pedro Community Station (Promenade)	Promenade walkway at 100 South Harbor Blvd.	V	V	V	V	A,B,C	V	V	V	V	-	-	-
Wilmington Community Station (SPPS)	Saints Peter and Paul Elementary School, 706 Bay View Ave., Wilmington, CA	V	V	V	V	A,B, C,D	V	V	V	V	V	V	V
Source- Dominant Station (TITP)	Terminal Island Treatment Plant, 455 Ferry Street, San Pedro	V	V	V	V	A,B,C	V	V	V	V	-	-	-

Note:
A: $PM_{2.5}$ Sequential filter sampler
B: $PM_{2.5}$ DustTrak sampler
C: $PM_{2.5}$ Beta-attenuation monitor (BAM) sampler
D: PM_{10} Beta-attenuation monitor (BAM) sampler
PM: Particulate Matter Monitors
PAH: PAH Analyzers (PAS-2000)
WS: Wind Speed
WD: Wind Direction
T: Ambient Temperature
S.R.: Solar Radiation
P: Atmospheric Pressure
R.H.: Relative Humidity
V: Analyzer installed

Figure 2.1 The Port of Los Angeles Air Quality Monitoring Network Stations.

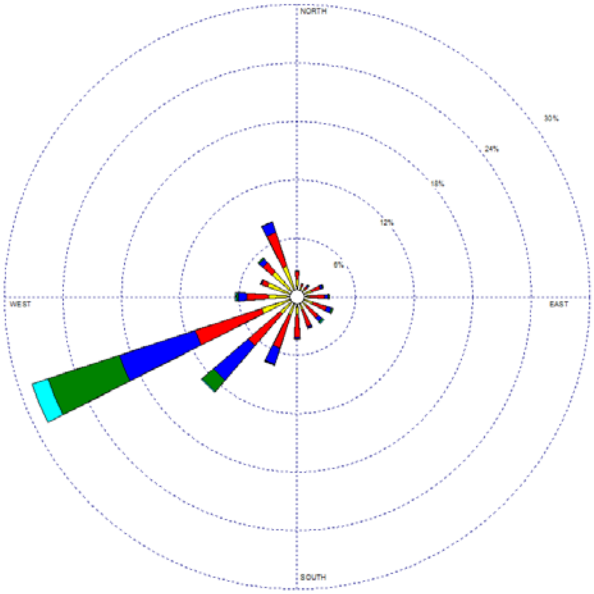


(Source:. "Air Quality Monitoring Program at the Port of Los Angeles, Annual Report – May 2005–April 2006" Port of Los Angeles, April 2007(10)).

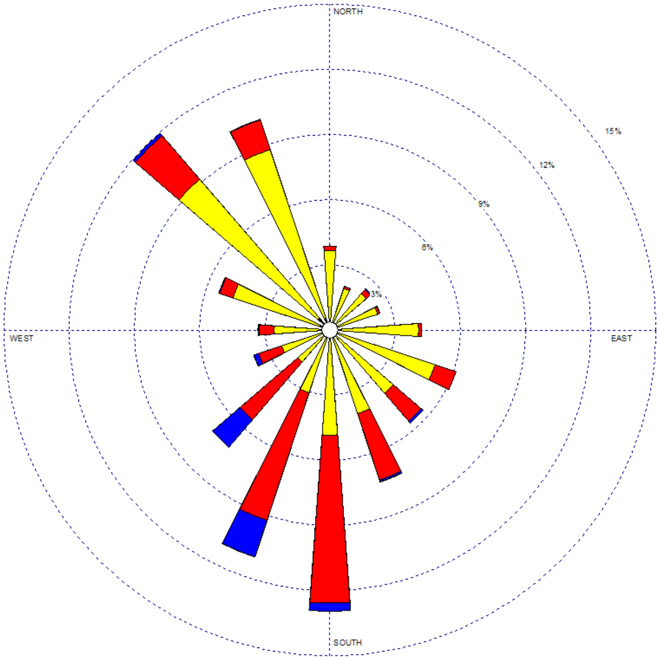
Figure 2.2 Wind Rose Plots for the Port of Los Angeles Air Monitoring Stations.

May 2004-April 2005

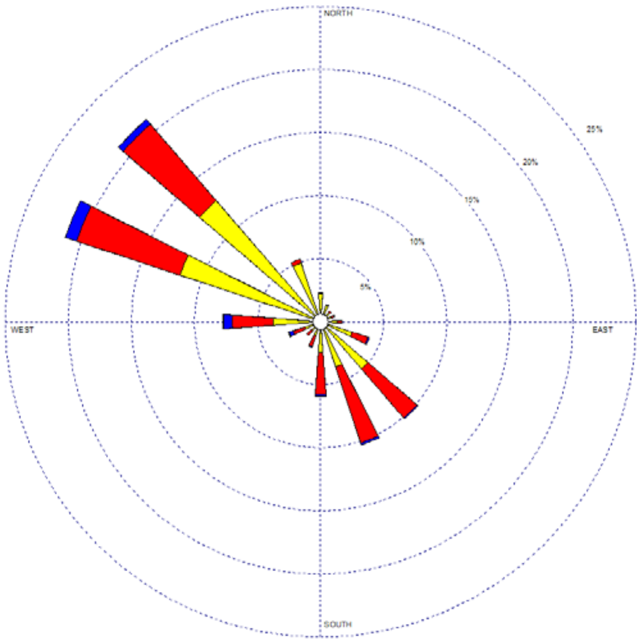
Berth 47



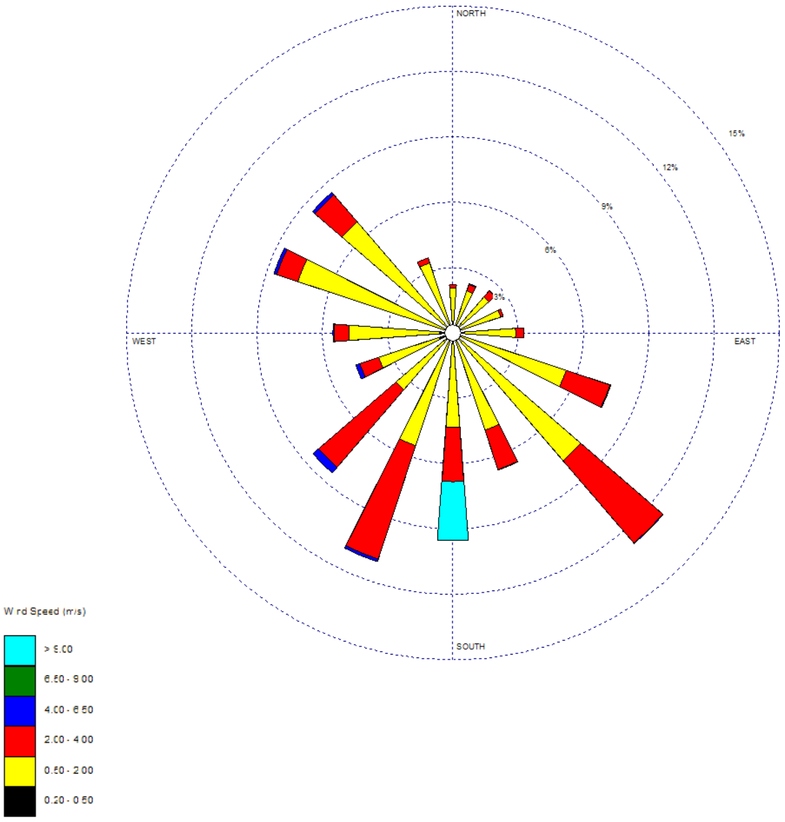
Terminal Island Treatment Plant



Liberty Hill Plaza (Rooftop Station)



Saints Peter and Paul School



Due to its geographical location, the Los Angeles and Long Beach Harbor area has a typical Mediterranean climate pattern. The weather is relatively warm and dry throughout the year with most of the precipitation occurring in the winter months. The predominant wind directions are northwesterly and southerly flows for all three land-side stations – SPPS, TITP and Promenade. However, the Berth 47 station, which is situated at the coastal boundary in the outer harbor, is impacted by the Palos Verdes Hills. Surface air flow over the Pacific is generally from the northwest. However, as the airflows encounter the Palos Verdes Hills, the airflows split around the obstruction of land mass and cause southerly winds on the east side of the hills. The southerly wind is reinforced during the day by sea-breeze. This southerly wind encounters the westerly wind flow from the north of the hills and converges on the northeast side of the hills and expresses a southwesterly wind pattern as observed at Berth 47 station (11).

2.2 Methodology, Sampling Frequency and Monitoring Period

An EcoChem PAS 2000 was used to measure ambient particle-bound PAH concentrations on a real-time basis. The EcoChem Analytics PAS 2000 analyzer is a photoelectric aerosol sensor, which uses an UV excimer lamp to ionize PAH-coated aerosols and measures changes in charge with an electrometer. The lamp radiation occurs at 222 nanometer (nm). PAHs on the surface of the particles are charged by the excimer lamp and negatively charged particles are removed by applying a small voltage in the flow tube. The charged particles are collected on a filter element, which is mounted in a Faraday cage. The electric current associated with the ion current is recorded by an electrometer. The change in the electric current is proportional to the concentration of particle-bound PAHs in the air sample (12). The PAS has a sample air flow of two liters per minute (L/min) and a nominal detection limit of three nanograms per cubic meter (ng/m^3) total particle-bound PAH. Sampling of ambient particle-bound PAHs is performed on a continuous basis. Real-time data outputs are collected by the station data-logger along with other real-time gaseous pollutant analyzers. Hourly data can then be retrieved from the data logger for analysis.

Due to the time required for site preparation and logistics such as power supply and security issues, all four PAH monitoring sites could not begin measurement simultaneously. Therefore, monitoring starting dates for the four stations were slightly different. Both Berth 47 and TITP stations started sampling for PAHs on December 1, 2007. The SPPS and Promenade stations started sampling on April 1, 2008 and May 1, 2008, respectively. Data reporting for this project ended on April 30, 2009 for all four stations.

Selected filter samples were also analyzed by in-injection port thermal desorption and subsequent gas chromatography/mass spectrometry analysis of non-polar organic species, including PAHs, in aerosol filter samples. The quality assurance project plan in the Appendix section describes details of sample preparation and analytical procedures developed by the Desert Research Institute, Reno, Nevada.

3. Development of Work Plan and Quality Assurance Project Plan and Approval

Prior to implementing field monitoring of particle-bound PAHs in ambient air in the areas in and around the Port, a detailed work plan was developed and a Quality Assurance Project Plan was also prepared.

The work plan titled “EPA Local Scale Air Toxics Ambient Air Monitoring Program –Work Plan for Port of Los Angeles Community-Based Air Toxics Exposure Study” was prepared in November 28, 2006 and revised on April 25, 2007. The revised work plan includes the following chapters:

- Introduction including project objective and scope of work
- Project organization and responsibility
- Technical approach including site selection, planning, installation, field monitoring, data management, analysis and reporting
- Quality assurance objectives and corrective action
- Quality control and quality assurance audit including PAH analyzer, data logging equipment
- Data Reduction, Validation and Reporting including data handling, data records, data processing and reporting
- Project schedule
- References

Additionally, a project-specific quality assurance project plan (QAPjP) was required by the EPA before field monitoring could begin. Detailed requirements and key elements for the QAPjP are described in the “EPA Requirements for Quality Assurance Project Plans, EPA QA/R-5” (EPA/240/B-01/003, March 2001), including project management, data generation and acquisition, assessment and oversight and data validation and usability.

The QAPjP was prepared on November 28, 2006, following the EPA guidelines and requirements. The Plan was revised on April 25, 2007 and submitted for EPA’s review and final approval. The QAPjP was approved by the EPA Region 9 Quality Assurance Manager on May 15 and the Quality Assurance Officer on May 16, 2007.

Key elements of the QAPjP include:

- Project Management
    - QA Project Plan Identification and Approval
    - Table of Contents
    - Distribution List
    - Project Organization/ Roles and Responsibilities
    - Background
        - Project Background
        - List of Pollutants

    - Project Description
        - Project Scope
        - Field Activities
        - Project Schedule
    - Quality Objectives and Criteria for Measurement Data
        - Data Quality Objectives
        - Measurement Quality Objectives
    - Documentation and Records
- Measurement / Data Acquisition
    - Site Selection
    - Sampling Methods
    - Quality Control Requirements
        - Quality Control
        - Weekly Check
        - Quality Assurance Audit
    - Instrument Inspection, Testing and Maintenance
        - Instrument Inspection
        - Instrument Testing
        - Instrument Maintenance
    - Instrument Calibration and Frequency
        - PAH Analyzer
    - Data Acquisition
    - Data Management
        - Data Recording
        - Data Processing and Reporting
        - Data Reduction
        - Data Validation
        - Data Storage and Retrieval
- Assessment and Corrective Action
    - Assessment
        - Assessment
        - Corrective Actions
    - Report to Management
    - Reconciliation with Data Quality Objectives
    - Appendix

Copies of the final work plan and the QAPjP are included in the Appendix.

4. Monitoring Data Upload to Air Quality System (AQS) Database

After the completion of the PAH monitoring period, all PAH monitoring data were uploaded to the EPA’s AQS database as part of the project requirements.

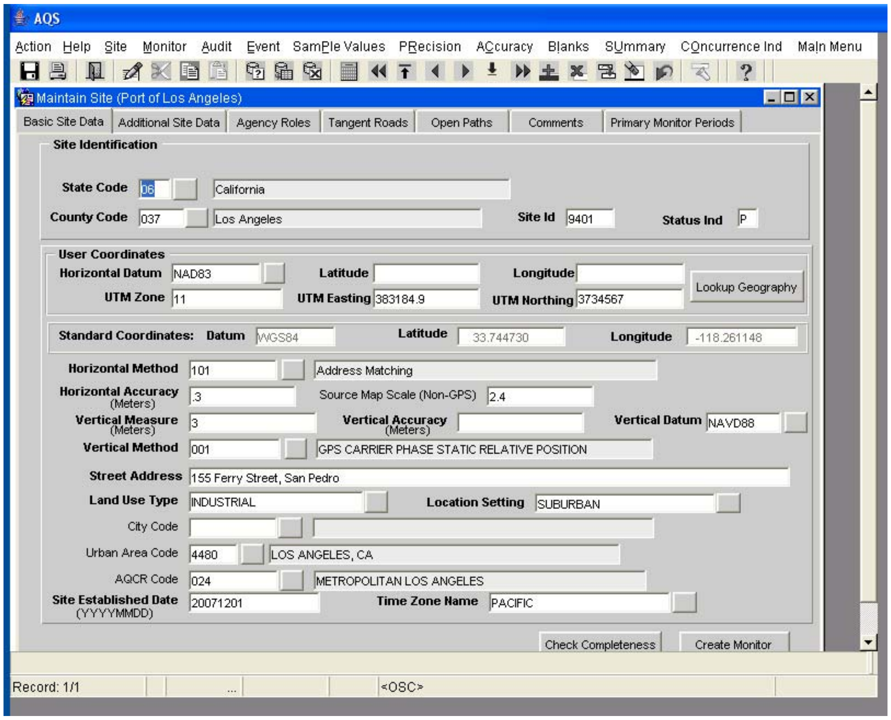
4.1 Create Site and Monitor

Prior to uploading PAH monitoring data to the AQS database, the four Port monitoring sites first had to be created and PAH monitors added into the system. Table 4.1 lists information provided for the four Port stations. Figure 4.1 shows an example of the station information table in AQS database.

Table 4.1 The Port of Los Angeles PAH Monitoring Network Station Information.

Station ID	Station Name	Street Address	X	Y	Elevation (m)
9401	TITP	455 Ferry St., San Pedro	383184.9	3734567	1.9
9403	Berth 47	South end of Miner St., San Pedro	381935.1	3731179.9	0.2
9405	Promenade	100 S. Harbor Blvd., San Pedro	381427	3734173.1	5.9
9407	SPPS	705 Bay View, Wilmington	382448.5	3738357.8	7.8
X attribute is UTM East, Y is UTM North. Datum is UTM Zone 11 North NAD 1983.					

Figure 4.1 Example of AQS Site Maintenance Table.



Site Identification

State Code	06	California		
County Code	037	Los Angeles	**Site Id** 9401	**Status Ind** P

User Coordinates

Horizontal Datum	NAD83	**Latitude**		**Longitude**	
UTM Zone	11	**UTM Easting**	383184.9	**UTM Northing**	3734567

Standard Coordinates: **Datum** WGS84 **Latitude** 33.744730 **Longitude** -118.261148

Horizontal Method	101	Address Matching	
Horizontal Accuracy (Meters)	.3	Source Map Scale (Non-GPS)	2.4
Vertical Measure (Meters)	3	**Vertical Accuracy** (Meters)	**Vertical Datum** NAVD88
Vertical Method	001	GPS CARRIER PHASE STATIC RELATIVE POSITION	
Street Address	155 Ferry Street, San Pedro		
Land Use Type	INDUSTRIAL	**Location Setting**	SUBURBAN
City Code			
Urban Area Code	4480	LOS ANGELES, CA	
AQCR Code	024	METROPOLITAN LOS ANGELES	
Site Established Date (YYYYMMDD)	20071201	**Time Zone Name**	PACIFIC

4.2 Data Formatting and Uploading

After the stations and PAH monitors were created in the AQS database, hourly PAH monitoring data in text format were retrieved from the station data logger. The data were first organized according to the AQS raw data format using MS Excel. Proper flags were then used to identify invalid data. For example, BF was used to flag instrument calibration or daily zero/span checks and AZ was used for other calibration and instrument downtime. Pollutant concentration fields were left blank for flagged invalid data. Finally, formatted data were converted into text file ready for uploading. An example of the AQS raw data format is listed below:

RD|I|06|037|9401|17202|1|1|003|013|20081201|00:00|35.20||||||||||||||||

RD: Raw data
I: Insert
06: Station code
037: County code
9401: Station ID
17202: Pollutant code (PAHs)
1: POC code
1: Sampling duration (1-hour)
003: Unit code (ng/m^3 at 25^{o}C)
013: Method code (instrument by photo-ionization)
20081201: Year and date
00:00: Hour:minute
35.20: Pollutant concentration

Formatted monitoring data in text files were loaded onto the EPA’s Central Data Exchange (CDX) first and then onto AQS. Data file uploads were conducted by refreshing the “CDX” tab and clicking “Load” on the AQS screen. After the data files were uploaded in the CDX, the “Submit Correct Data” tab was selected to start uploading. When uploading was completed, “Stats CR” was clicked to move data files to the CRST. To verify that data files were uploaded correctly the “Post” button was selected, and the report was printed using “Post Data to Production.”

If any error in file uploading was identified, the incorrect data was deleted from the AQS by using the “Maintenance” to review “raw” data and remove incorrect data. The raw data inventory report for all uploaded PAH hourly data in the AQS database is attached in the Appendix.

5. Results and Discussion

5.1 Quality Assurance

5.1.1 Methodology

The PAS 2000 analyzer estimates the amount of particle-borne PAHs by irradiating particles (using a wavelength of 222 nm) which ionizes the PAH bound on particles. Under these conditions, PAHs are the dominant class of compounds found in polluted air that are ionized. The instrument measures the current of the ionized particles, and, using a calibration factor based on comparisons with chemical speciation of the PAH, calculates the concentration of particle-bound PAH. Since there is no standard reference material for calibrating these instruments, the accuracy of the data can only be estimated by the operating conditions (lamp intensity and flow rate) and by comparison with a transfer standard. The lamp intensity is controlled by regulating the frequency. A properly working analyzer should have intensity near 100% and the frequency, which rises as the lamp ages and should be below 21 kHz. The flow rate should be maintained close to 2.0 L/min.

Prior to installation and near the end of the monitoring period, all four instruments used in the monitoring program were allowed to sample ambient air from a single manifold. A fifth PAS 2000, owned by the University of California, Riverside (UCR), was also included in this comparison. This instrument was used as a transfer standard. The data were collected as one-minute averages and the four instruments were plotted versus the transfer standard (on the abscissa). A least squares regression analysis was then performed.

Routine quality control was conducted at approximately 6-month intervals. Quality control activities included observation of the lamp intensity, lamp frequency, and flow rate to assure that these parameters were within the manufacturer’s tolerances. The response of the instrument was then compared to the response of a transfer standard, serial number 140. Since ambient concentrations were often near the detection limit of the instrument, the comparison was performed using an artificial source. Both instruments were configured to measure at the fast time constant available. Antistatic 3/16 inch inner diameter (I.D.) tubing and a ¼-inch outer diameter (O.D.) metal tubing “Tee” were used to connect the inlets of both instruments to a single air sampling line. The artificial source was made of a 32-gallon, one-mil thickness polyethylene plastic bag. The bag was first opened to fill with ambient air and a lighted match was then placed in the bag and extinguished. The sampling line to the instruments was then inserted into the bag and sealed in place with a twist tie wrapped around the plastic film and the tubing. This approach generated high concentrations of particle-bound PAH (typically starting two orders of magnitude above ambient concentrations) and allowed a concurrent measurement of pollutants by two instruments simultaneously from one identical source. The concentrations were then recorded at 1-minute intervals for 10-30 minutes as the concentrations followed an exponential decay. Data from the two instruments were then compared by plotting the results of one versus the other (the data from the transfer standard on the abscissa), and then performing a least squares regression analysis to evaluate the correlation between the two instruments.

5.1.2 Results

Initial and Final Comparisons With All Analyzers Co-Located

Two quality control/quality assurance comparison studies were performed during the course of the project. The initial and the final comparisons were performed from July 11 to 25, 2007 and from May 28 to June 2, 2009, respectively. Both comparisons were conducted at the UCR, CE-CERT facility at 1086 Columbia Avenue in Riverside, California. The co-located comparison study results are summarized in Table 5.1.

Table 5.1. Comparison of the PAS-2000 Analyzers Used in the Study with the Transfer Standard Conducted Co-Located All at One Location.

Instrument	July 11 - 25, 2007			May 28 - June 2, 2009		
	Slope	Intercept	R^2	Slope	Intercept	R^2
SPPS	1.20	0.1	0.988	0.73	0.4	0.924
Berth 47	1.20	0.1	0.991	0.89	0.7	0.940
Promenade	1.22	0.1	0.986	0.79	-0.9	0.929
TITP	1.23	0.0	0.988	0.80	0.9	0.939

The initial comparison showed a nearly identical slope of 1.2 for all four instruments, negligible intercept (e.g., <0.1), and very high correlation coefficients (e.g., R^2 >0.98). However, the slopes (ranged from 0.73 to 0.89) were lower during the final comparison when compared to the transfer standard but still agreed with each other to within approximately 10 %. The intercepts were low (ranged from -0.9 to 0.9), but somewhat higher than in the initial comparison study. Although the correlations were generally good they were somewhat lower (e.g., R^2 >0.92). It is likely that the sensitivity of the four analyzers decreased during the over a year of continuous sampling of ambient air as compared to the transfer standard, which was rarely used. The precision of these four instruments may also have declined slightly during this period resulting in the lower correlation coefficients.

Routine Comparisons With The Transfer Standard

Three calibration checks were performed on June 18, 2008, December 4, 2008, and May 27, 2009. The results are shown in Table 5.2. Although the correlation coefficient values were generally good, the slopes varied for the instruments located at SPPS and Berth 47 sites by approximately a factor of two during the three comparisons. Furthermore, the final comparison showed similar slopes for all four instruments. The PAH concentrations in the artificial source were decaying fairly rapidly when the comparisons were conducted relative to the normal operating cycle of the instrument, therefore, greater noise levels would be expected than when the data from them all sampling at the same site were compared. For this reason greater variability was expected when using this PAH source. These routine checks are therefore most useful to determine if there is a response variability indicating an instrumental malfunction, while the collocated sampling simultaneously with all the instruments is a better indicator of the calibration of the instrument.

Table 5.2 Comparison of the PAH Analyzers Used in the Study with the Transfer Standard Conducted Co-Located at the Monitoring Site Where the Analyzer was Used.

Site	June 18, 2008			December 4, 2008			May 27, 2009		
	Slope	Inter	R^2	Slope	Inter	R^2	Slope	Inter	R^2
SPPS	0.50	9.0	0.986	1.38	-2.5	0.995	0.71	-8.2	0.998
Berth 47	1.41	1.5	0.948	0.84	0.5	0.991	0.76	3.0	0.999
Promenade	0.62	-0.4	0.922	0.63	7.5	0.985	0.83	-13.6	0.997
TITP	1.09	-6.0	0.948	0.87	2.3	0.999	0.84	-0.8	0.993

5.2 Diurnal and Seasonal Trends

To analyze potential diurnal and seasonal variations of ambient particle-bound PAHs in the Port's vicinity, hourly-average PAH concentrations were composited and calculated. For example, 00 hour represents the monitoring time period of 0000 to 0100 hour. Please note that all time are in Pacific Standard Time (PST). PAH monitoring data for the time period were averaged to obtain hourly average data. It should be noted that daily zero-span check for other instruments occurred from 0200 hour to 0300 hour (02 hour data). During this time, the sample air intake manifold was flooded with either zero air or calibration gas. Since neither of these gases contains particles, no responses from the PAHs were observed. Consequently, PAH monitoring data for this particular time period in a day were considered as invalid and excluded from the subsequent data analysis.

5.2.1 Diurnal Variability

Figure 5.1 shows the composited PAH concentrations by hour for the entire study period from April 2008 to April 2009. As expected, the highest PAH concentrations were observed at TITP, a source-dominant site, which was heavily impacted by the Port's operation involving a large number of emission sources powered by diesel engines such as on-road trucks, cargo handling equipment, marine vessels and rail. The lowest PAH concentrations were observed at the background station at Berth 47. Except for the SPPS station, PAH concentrations show a similar pattern. The PAH concentrations rose in the early morning hours, peaking at approximately 7:00 AM, and decreased gradually during the day. The rise of PAH concentrations in the early morning hours is likely due to a combination of increased Port activity, low mixing heights, and low wind speeds. Whereas the fact that the PAH concentrations decrease in the late morning and afternoon hours is mostly likely due to increased mixing heights and greater wind velocities that enhance pollutants dispersion.

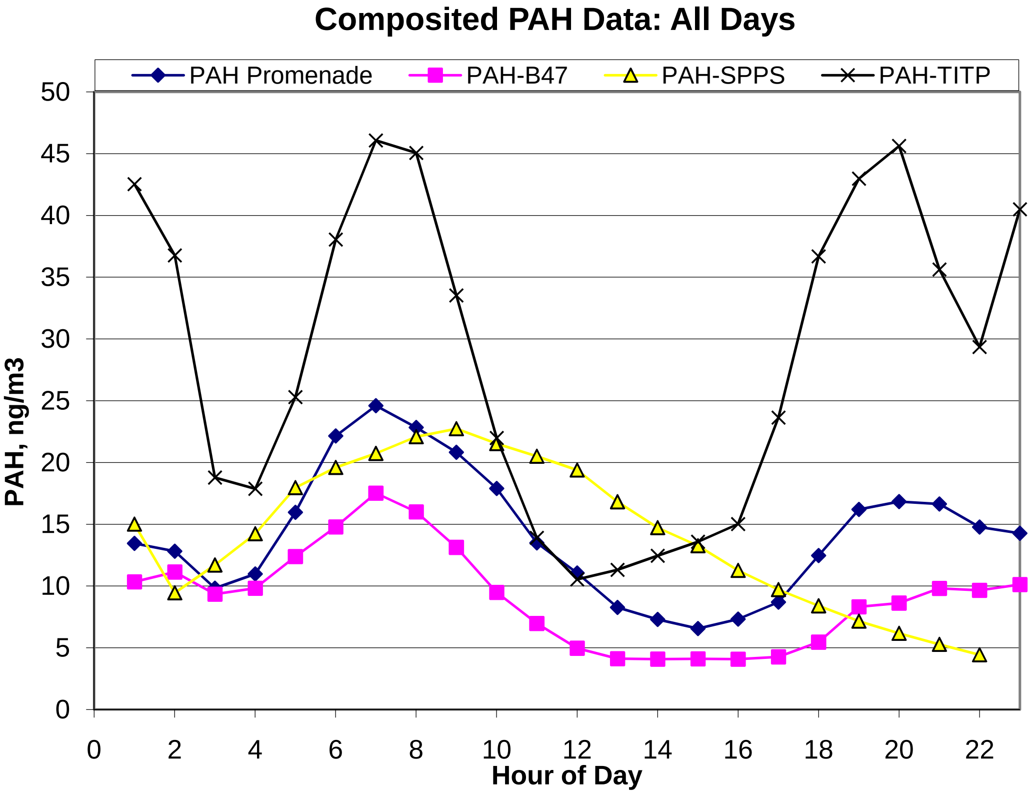
The PAH concentrations then started rising again during the early evening hours and peaking near 8:00 PM. One possible explanation for this concentration increase in the evening hours could be due to marine terminals implementing an "Off-Peak" program that provides incentives for cargo owners to move cargo at night (from 6:00 PM to 3:00 AM) and on weekends (8:00 AM to 5:00 PM) to reduce truck traffic and pollution during peak daytime traffic hours and to alleviate Port congestion. The other possible cause is the meteorological factors such as low mixing height in evening hours, low wind speeds and predominant wind directions shifting from southwesterly to northwesterly wind in the evening hours. This change of wind direction could reduce the inflow of the cleaner sea breeze to dilute the pollution, and, in turn, increase the flow of residual concentrations on the landside to increase pollutant concentration. However, the cause of the unusual behavior of the PAH concentrations at the SPPS station, reaching peak at 9:00 AM and dropping for the rest of the day, is unknown. It may also be caused by the aforementioned meteorological factors. Detailed hourly wind rose plots for all four stations are provided in the Appendix and summarized in Table 5.3. The diurnal wind patterns at three stations (Promenade, Berth 47 and TITP) are similar – mostly northerly and southerly winds, depending on the hour of the day. The SPPS station shows a totally different wind pattern – mostly southerly winds regardless of the hour of the day.

The most significant observation is that the PAH concentrations varied by over a factor of five between source-dominant and community stations at two peak hours – 7:00 AM and 8:00 PM. The results indicated that ambient PAH levels are site dependent, and it is most likely a result of increased activity levels and local meteorology.

Table 5.3 Hourly Wind Patterns at Monitoring Stations.

Hour	**Predominant Wind Direction at Monitoring Sites**			
	Berth 47	**Promenade**	**TITP**	**SPPS**
0000	WSW	WNW	NW	WSW
0100	WSW	NW	NW	WSW
0200	NNW	NW	NW	WSW
0300	NNW	NW	NW	WSW
0400	NNW	NW	NW	WSW
0500	NNW	NW-SE	NW	WSW
0600	NNW	NW-SE	NW	WSW
0700	NNW	NW-SE	NW	WSW
0800	SW variable*	SE	S	ESE
0900	SW variable	SE	S	ESE
1000	SW variable	SE	S	SE
1100	SW variable	SSW	S	SE
1200	WSW	SSW	S	SE
1300	WSW	SSW	SSW	WSW
1400	WSW	SSW	SSW	WSW
1500	WSW	SW	SSW	WSW
1600	WSW	SW	SSW	WSW
1700	WSW	SW	NNW variable	WSW
1800	WSW	SW variable	NNW variable	WSW
1900	WSW	SW variable	NNW variable	WSW
2000	WSW	SSE variable	NNW variable	WSW
2100	WSW	SE variable	NW variable	WSW
2200	WSW	NW	NW	WSW
2300	WSW	NW	NW	WSW
*: Variable – variable wind directions with similar frequencies				

Figure 5.1 Composited PAH Concentrations for All Sites: Entire Measurement Period.



5.2.2 Seasonal Variability

Figures 5.2 to 5.4 illustrate composited PAH concentrations for all sites during the summer, fall and winter starting in 2008. Spring was not included as only partial data were available from spring 2008 and 2009. Note that similar trends are observed for all seasons and sites, although concentrations are significantly lower in the summer. Table 5.4 summarizes the overall averaged PAH concentration by season.

Table 5.4 Summary of PAH Concentrations Averaged by Season, ng/m^3.

Station	Overall	Spring 2008*	Summer 2008	Fall 2008	Winter 2008-09	Spring 2009*
Promenade	14.1	4.0	7.1	19.4	19.2	12.0
Berth 47	9.1	3.3	4.4	13.7	13.5	5.9
SPPS	13.7	4.2	6.0	19.3	20.7	8.7
TITP	28.6	12.2	17.6	47.2	36.3	14.7
*: Insufficient data for Spring season; not included in graphic comparisons.						

Similarly, detailed monthly wind rose plots for all four stations for three seasons are provided in the Appendix and summarized in Table 5.5. The seasonal wind patterns at three sites (Promenade, Berth 47 and TITP) are similar – mostly southerly winds in summer and northwesterly winds for winter season. Again, the SPPS site has a different wind pattern – mostly southerly winds regardless of the month of the year.

Table 5.5 Monthly Wind Patterns at Monitoring Sites.

Month	**Predominant Monthly Wind Direction at Monitoring Sites**			
	Berth 47	**Promenade**	**TITP**	**SPPS**
January	NNW	NW	NW	WSW
February	NNW-WSW	NW variable*	NW	WSW
March	WSW	SW variable	NW-SSW	WSW
April	WSW	SW variable	SSW	WSW
May	WSW	SW-SE	S	WSW-SE
June	WSW	SSE	S	WSW-SE
July	WSW	SE	S	WSW
August	WSW	SSW	S	WSW
September	WSW	SE	S	WSW
October	WSW	SE	WSW	WSW
November	WSW	NW	NW	WSW
December	NNW	NW	NW	WSW
*: Variable – variable wind directions with similar frequencies				

Figure 5.2 Composited PAH Concentrations for All Sites: Summer.

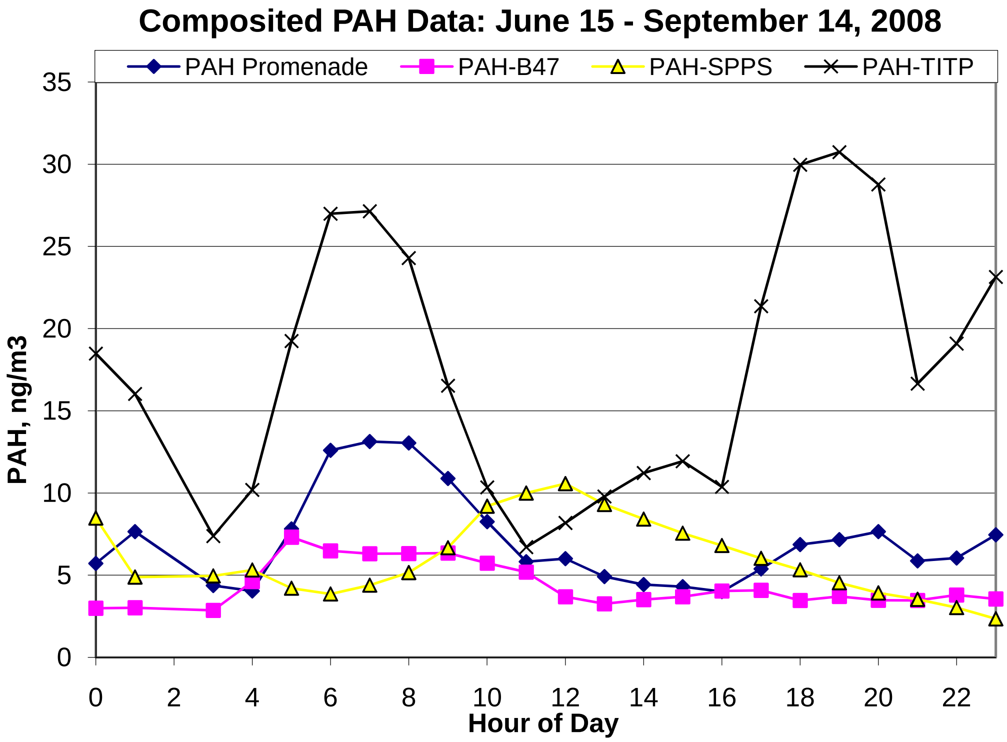


Figure 5.3 Composited PAH Concentrations for All Sites: Fall.

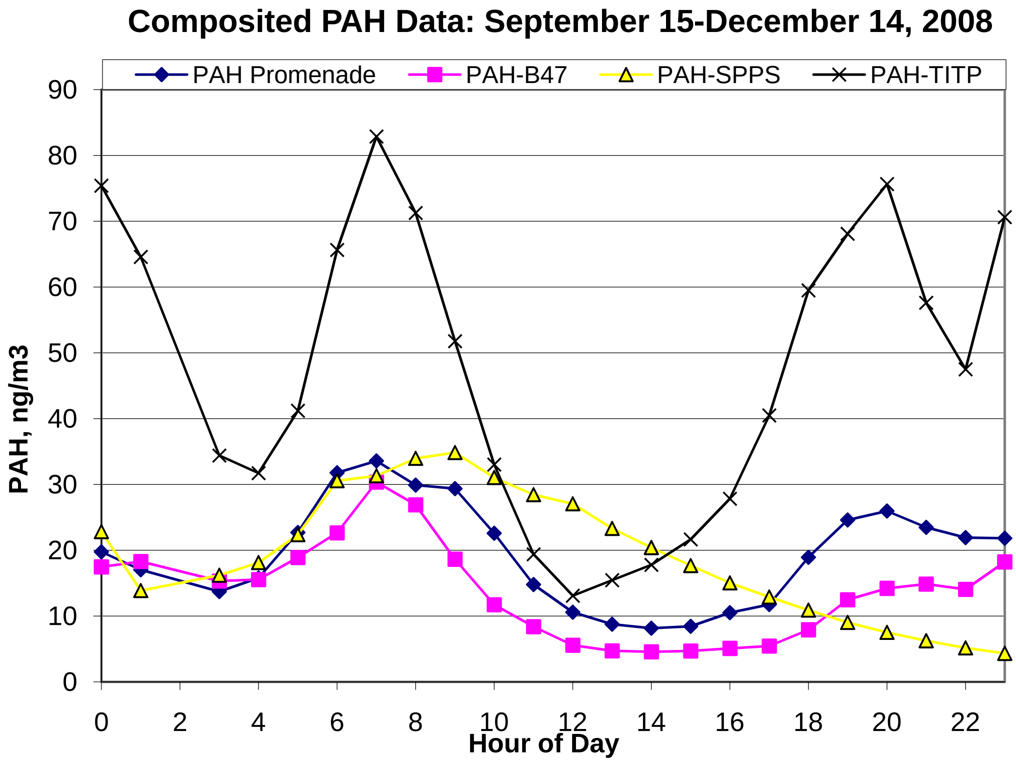
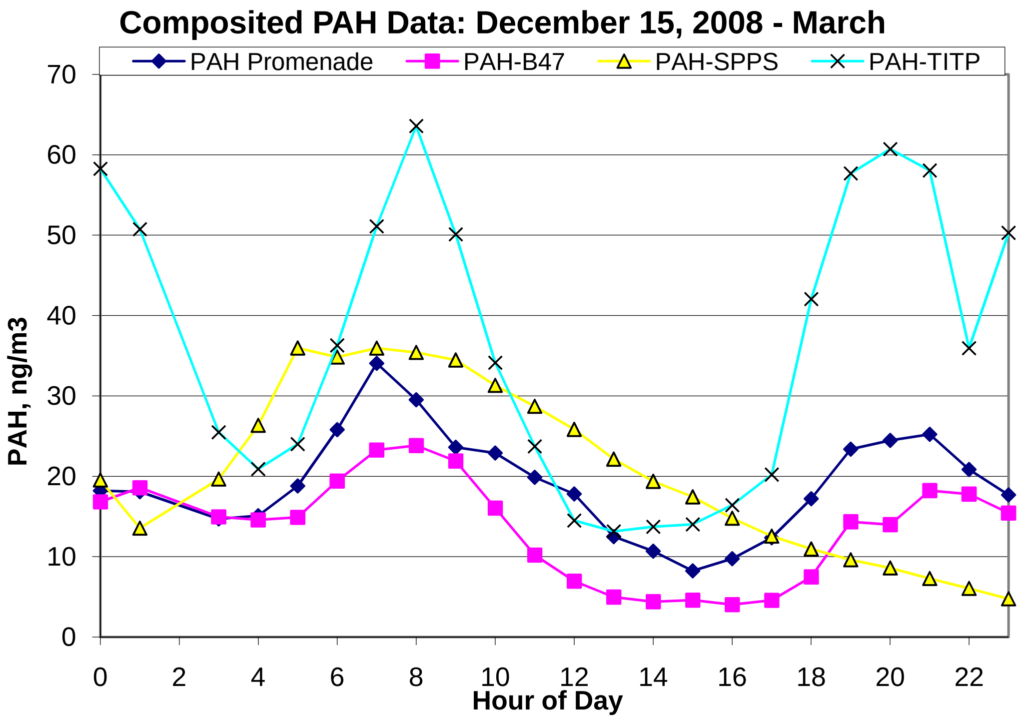


Figure 5.4 Composited PAH Concentrations for All Sites: Winter.

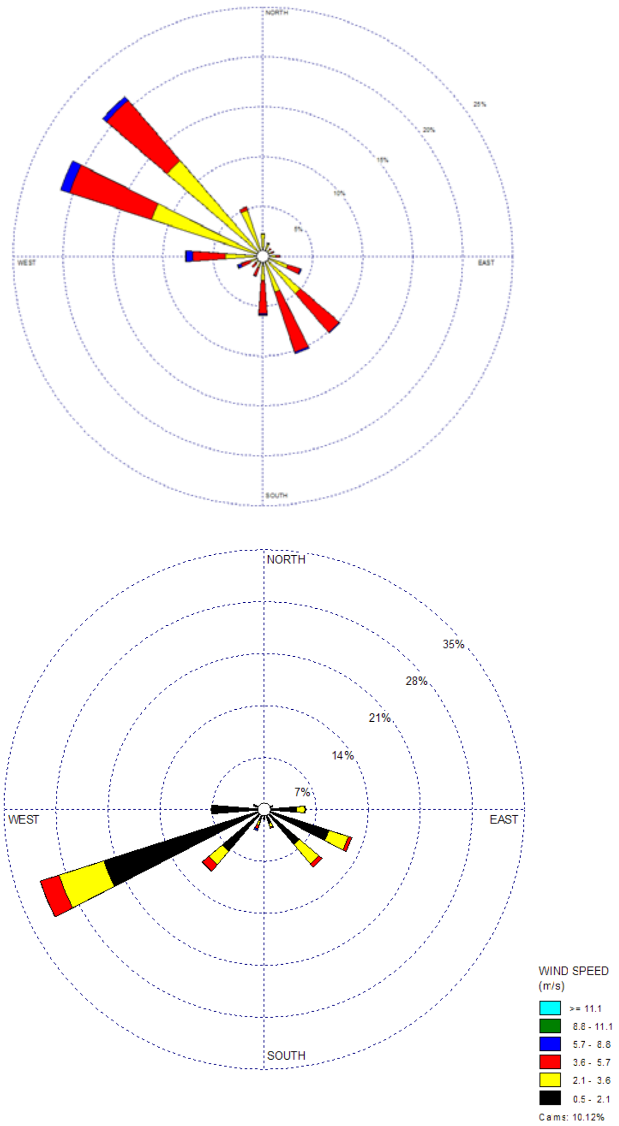


5.2.3 Meteorological Variability at SPPS

In an attempt to understand the unique PAH concentration trends at the SPPS, reviews of meteorological patterns for 2005-2006 and 2008-2009 were conducted. Figure 5.5 shows a significant change in wind patterns, from the northwesterly to southwesterly direction, between these two time periods at this site. The cause of this shift in predominant wind pattern is unknown and is under investigation by the station operator. Furthermore, it is not clear whether the shift of predominant wind patterns has any significant impact on the ambient PAH concentration trends at this location.

Figure 5.5 Change of Predominant Wind Patterns at SPPS.

(Top: 2005-2006; Bottom: 2008-2009)



5.3 Correlation of PAH Concentrations with Other Parameters

5.3.1 Meteorology

To understand influences from meteorological conditions to ambient PAH levels at four monitoring sites, hourly composited wind speed and direction were plotted with the hourly composited PAH concentration. The correlations of hourly composited wind speed and direction and PAH concentrations are illustrated in Figures 5.6 – 5.9. Note that the diurnal wind speed and direction patterns are similar for each site and do not vary more than 50 degrees in either direction from about 200 degrees. There does not appear to be any relationship between PAH concentrations and wind direction when composited wind direction data are used.

The PAH concentration and wind speed data were plotted as shown in Figures 5.10 – 5.13. It appears that there is an inverse-type relationship between PAH concentrations and wind speeds at each site. The plots for Promenade and SPPS showed a similar pattern with two types of correlations depending on the time of day. The plots for Berth 47 and TITP showed a significant relationship that was best described by the exponential equations as shown in the plots.

Figure 5.6 Hourly-Composited PAH, Wind Speed and Wind Direction at Promenade for the Measurement Period.

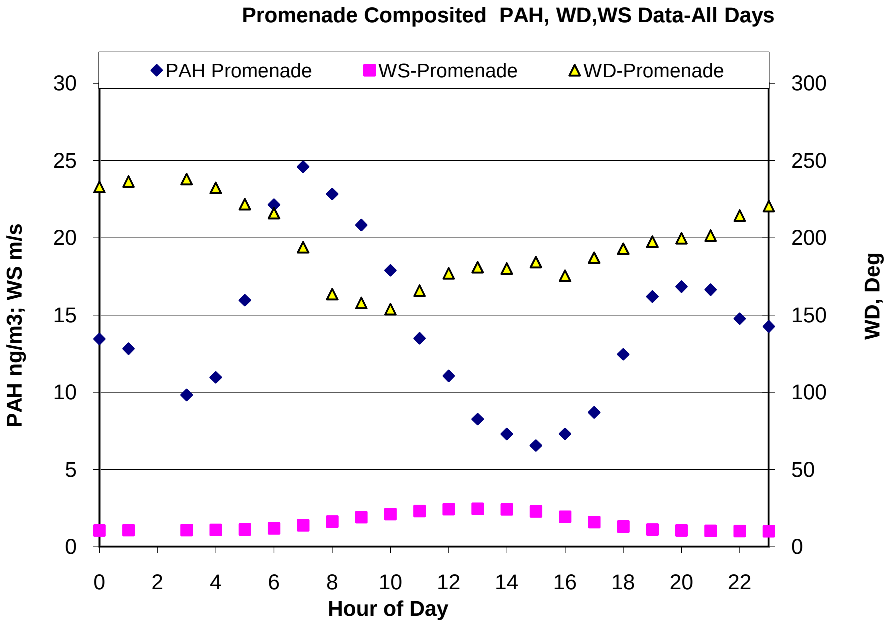


Figure 5.7 Hourly-Composited PAH, Wind Speed and Wind Direction at Berth 47 for the Measurement Period.

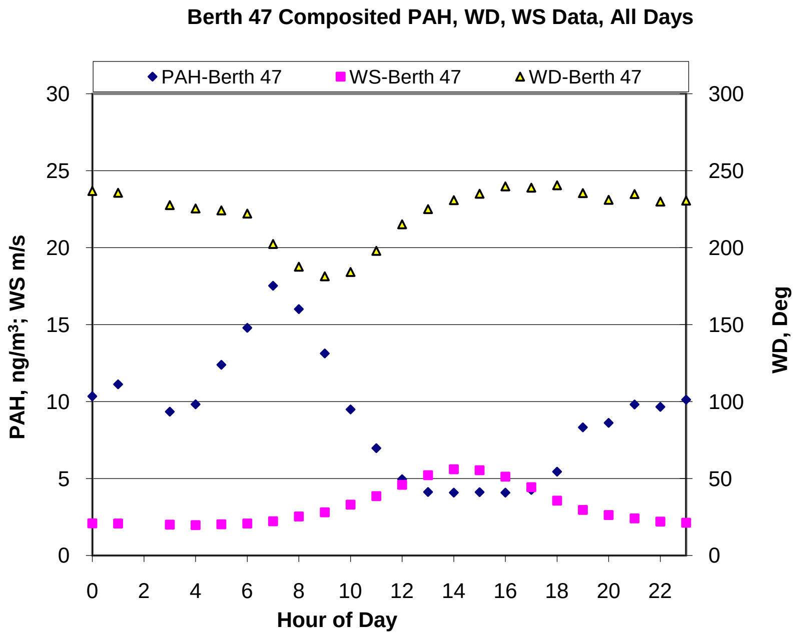


Figure 5.8 Hourly-Composited PAH, Wind Speed and Wind Direction at SPPS for the Measurement Period.

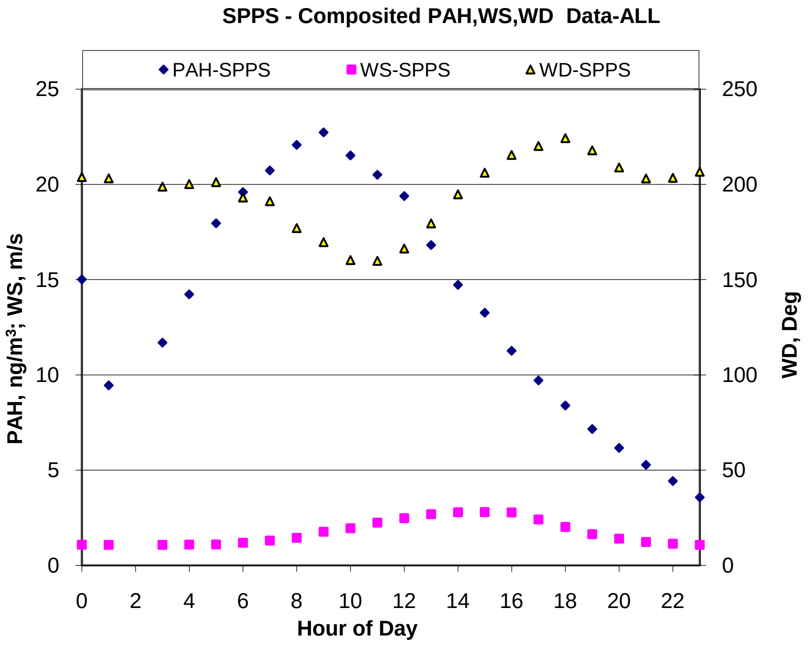


Figure 5.9 Hourly-Composited PAH, Wind Speed and Wind Direction at Berth 87 for the Measurement Period.

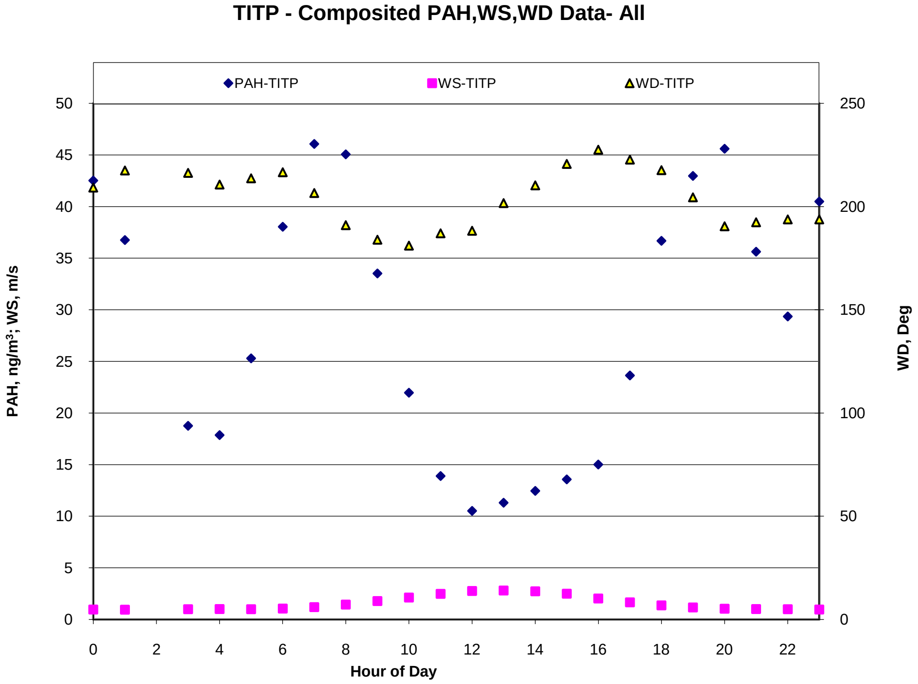


Figure 5.10 Hourly-Composited Wind Speed Plotted Against PAH Concentration at Promenade for the Measurement Period.

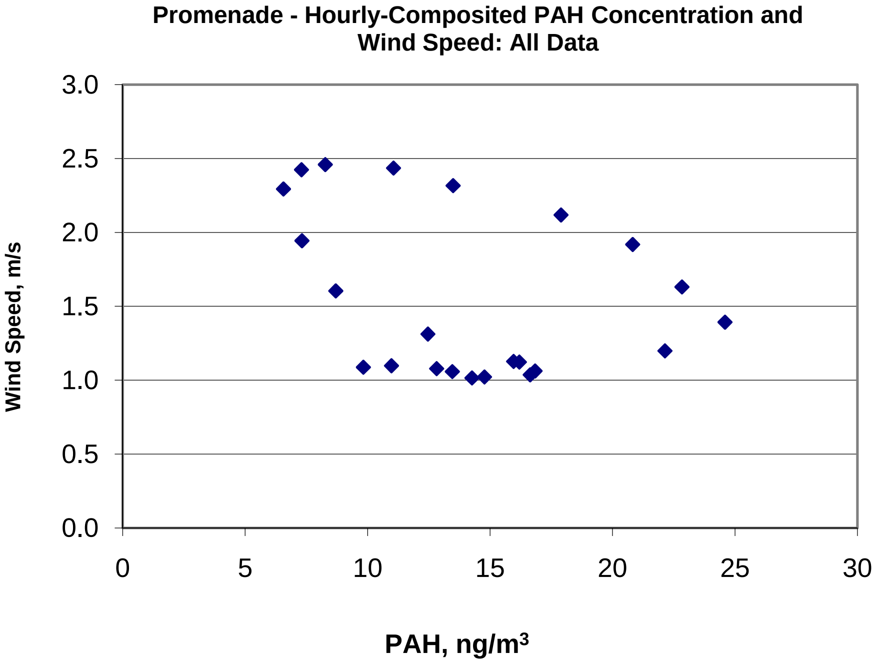


Figure 5.11 Hourly-Composited Wind Speed Plotted Against PAH Concentration at Berth 47 for the Measurement Period.

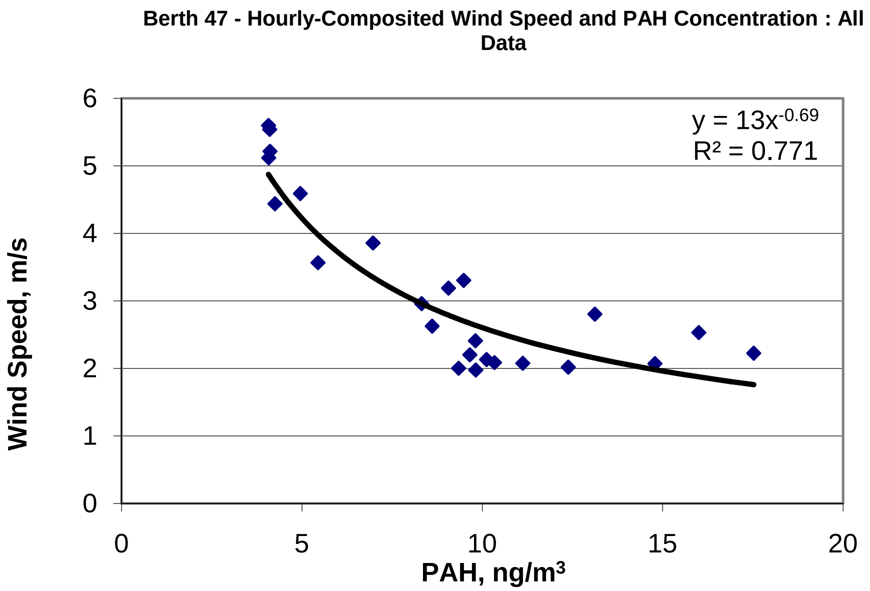


Figure 5.12 Hourly-Composited Wind Speed Plotted Against PAH Concentration at SPPS for the Measurement Period.

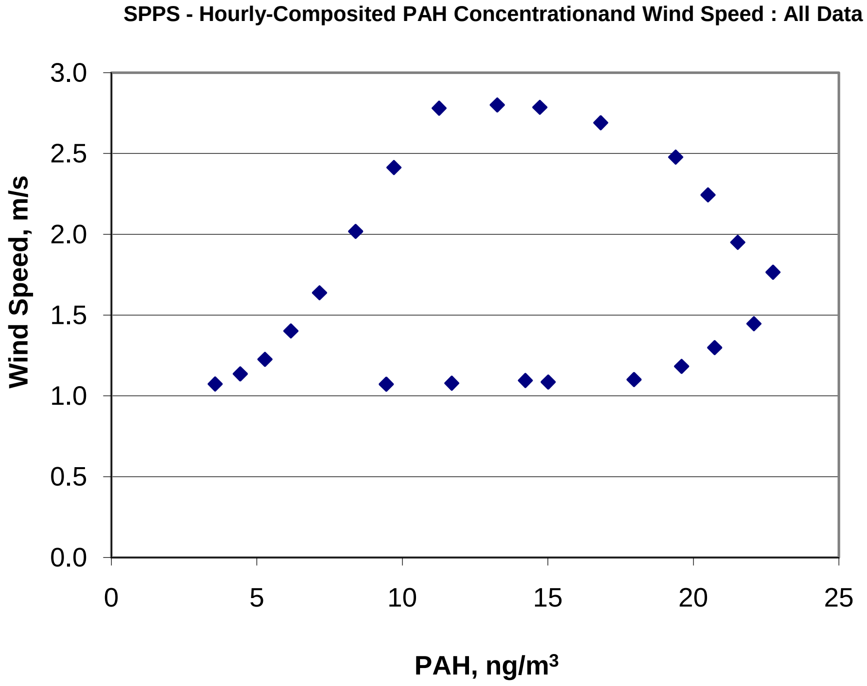
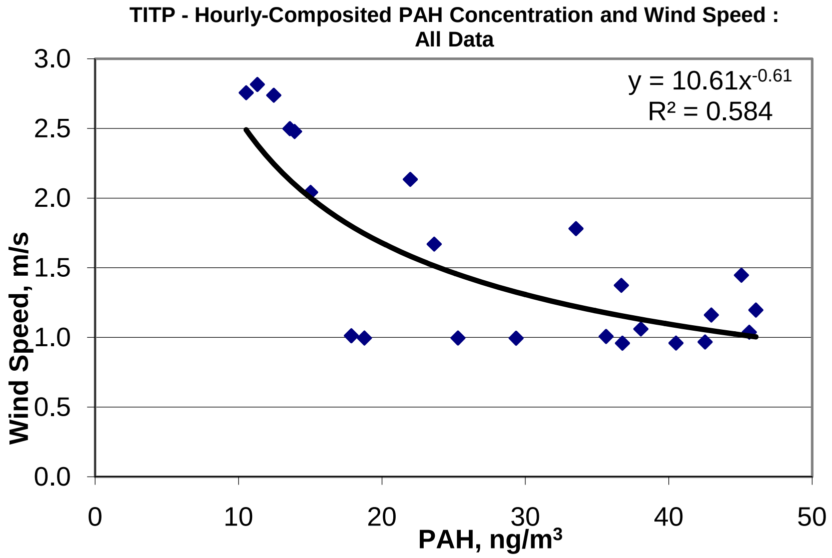


Figure 5.13 Hourly-Composited Wind Speed Plotted Against PAH Concentration at TITP for the Measurement Period.



5.3.2 Nitrogen Oxides

In order to determine the correlation of PAH concentrations with parameters other than meteorological data, the average daily concentrations were plotted against one another. NO_x was chosen since diesel vehicles emit primarily NO, but this may react with ambient ozone to form NO_2, especially later in the days during photochemical smog episodes. Figures 5.14 through 5.17 show the results from these plots for all four stations for the period between June 2008 and November 2008. These results show a very strong correlation, with an R^2 averaging 0.90. Similar correlations were found for the hourly data plotted over a month.

5.3.3 Ultra Fine Particulate Count and Mass

Particle count and $PM_{2.5}$ mass were compared in the same manner and for the same period as NO_x. Particle counts were obtained using a condensation nucleus counter and $PM_{2.5}$ was measured in real-time with a Tapered Element Oscillating Microbalance (TEOM). The particle counts were measured only at Berth 47 and TITP. The results are shown in Table 5.6. While similar magnitudes of slopes are shown when PAH concentration is compared with either particle count or $PM_{2.5}$, the correlation is very low and not meaningful. The highest degrees of correlation were observed at the TITP site, which was most likely impacted by local diesel traffic.

Table 5.6 Linear Regression of Comparing PAH with Ultra Fine Particle Counts and $PM_{2.5}$.

Site	**Ultra Fine Particle Count**		**$PM_{2.5}$**	
	Slope	**R^2**	**Slope**	**R^2**
Promenade	-	-	0.21	0.08
Berth 47	173	0.09	0.39	0.21
SPPS	-	-	0.22	0.06
TITP	62	0.28	0.16	0.24

Figure 5.14 Comparison of PAH and NO_x concentrations at Promenade, June – November 2008.

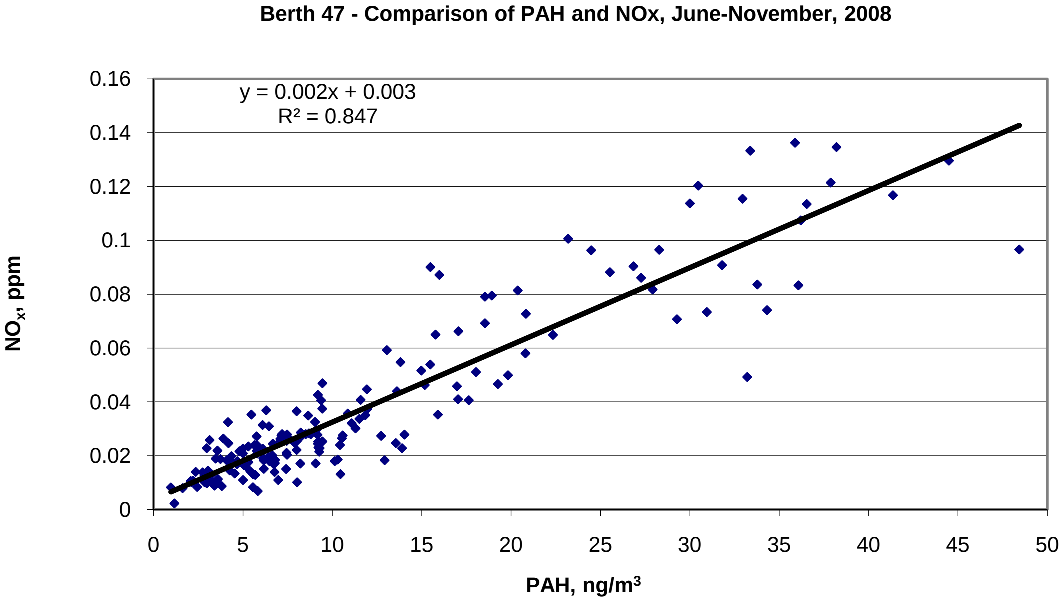


Figure 5.15 Comparison of PAH and NO_x concentrations at Berth 47, June – November 2008.

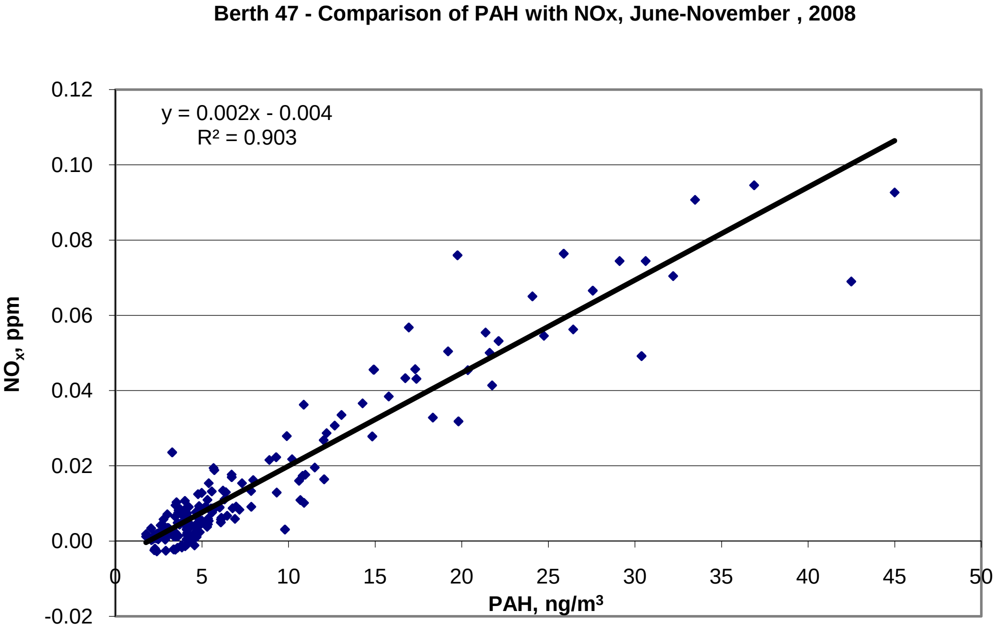


Figure 5.16 Comparison of PAH and NO_x concentrations at SPPS, June – November 2008.

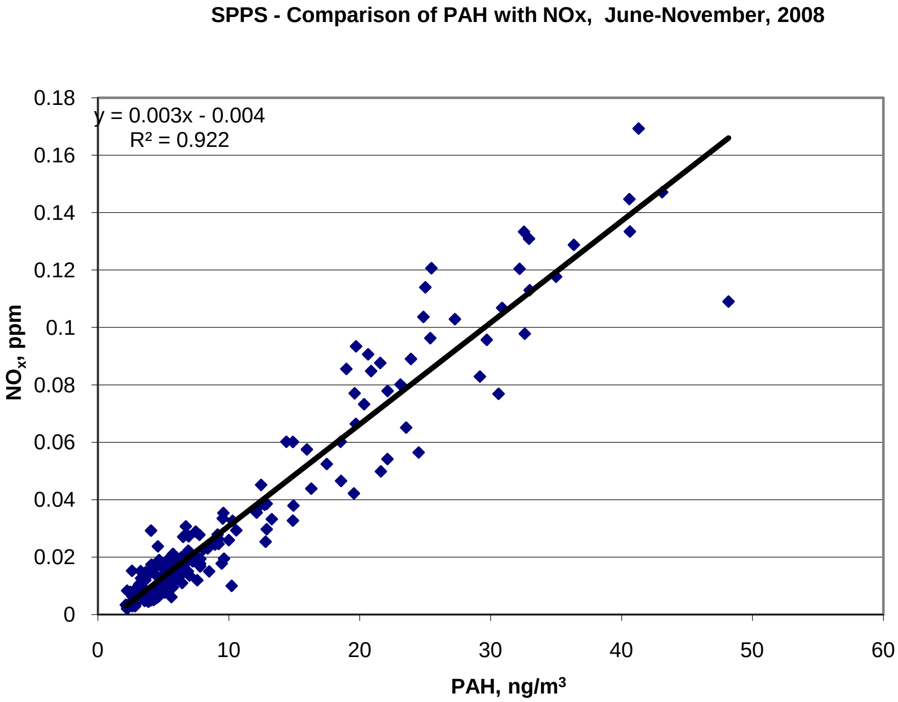
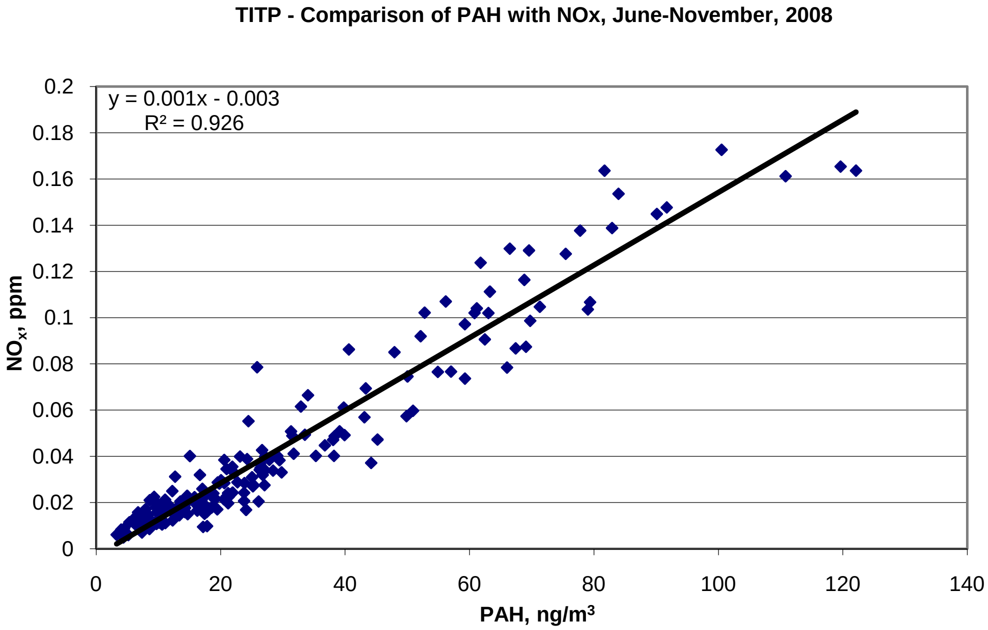


Figure 5.17 Comparison of PAH and NO_x concentrations at TITP, June – November 2008.



5.3.4 Chemical Composition

Black Carbon

Black Carbon (BC) was measured in real time with an Aethelometer at the SPPS station by the SCAQMD. Since these data had not been validated, the results presented here are considered as preliminary. The correlation between BC and PAH hourly concentrations for the period from June 1, 2008 to January 31, 2009 is shown in Figure 5.18. The results show that BC and PAH are weakly correlated with an R^2 value of 0.51.

Elemental Carbon

Twenty-four hour quartz filter samples were collected at all four stations on a one-in-three day schedule. Filter samples from May 2008 through March 2009 were analyzed for EC by thermal desorption. EC is measured by differential thermal method to first convert OC fraction by pyrolytic reaction and then elevating the temperature to convert EC. The resulting carbon dioxide is converted to methane and measured by a detector such as flame ionization detector or non-dispersive infrared detector.

The real-time PAH data were averaged for the 24-hour periods during which the filters were collected and compared to EC concentrations. The results are shown in Figures 5.19 through 5.22 for all four stations over the entire measurement period. The parameters are highly correlated, with an average R^2 value of 0.80. Figure 5.23 shows a comparison of BC with EC for the SPPS site for the period from June 2008 through January 2009. These data are also highly correlated with an R^2 value of 0.86.

BC, EC and diesel soot are often used by researchers to designate incomplete combustion byproducts that contain randomly oriented graphitic structures interspersed with other compounds*(13)*. However, it should be noted that the measurement methodologies are different. BC is normally measured by an Aethelometer using a continuous filtration and optical transmission technique.

Although EC is most often used as a tracer for diesel exhaust, with the recent advancements in diesel technology it becomes more difficult to use EC alone as the marker for DPM. Since other sources of EC such as emissions from wood burning, cooking, forest fire, gasoline engines and power plants become more significant when emissions from the diesel fleet decrease. Nevertheless, results from the correlation indicate that both the PAH and EC measurements are equally good tracers for diesel exhaust.

Figure 5.18 Comparison of PAH and BC concentrations at SPPS, June 2008 – January 2009.

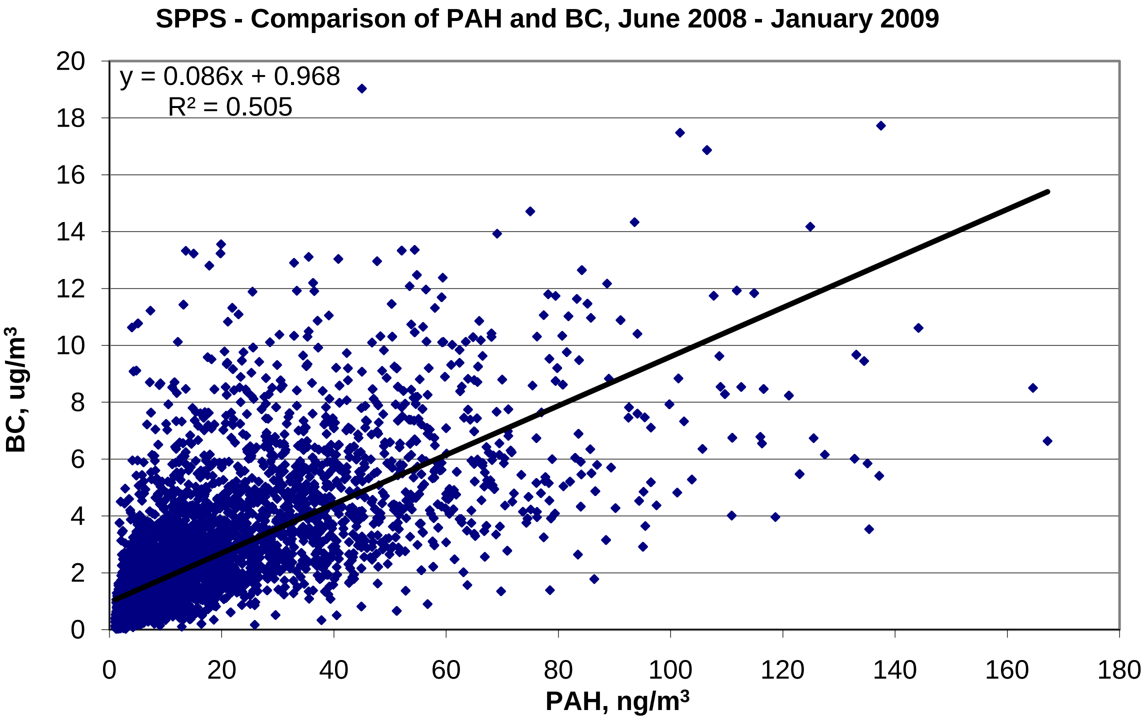


Figure 5.19 Comparison of PAH and EC concentrations at Promenade, May 2008 to March 2009.

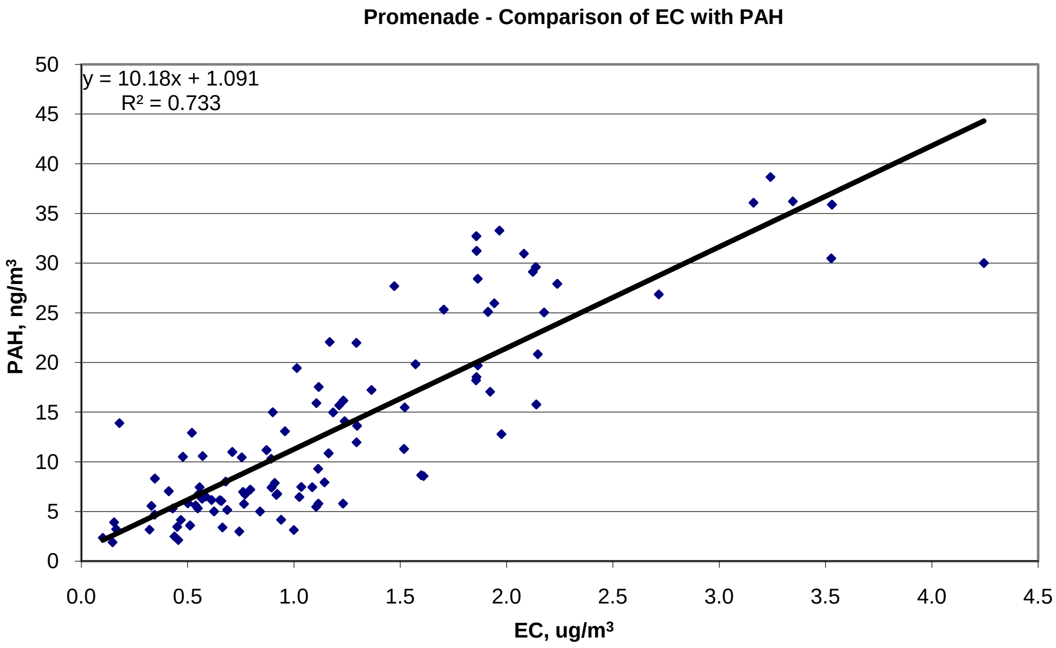


Figure 5.20 Comparison of PAH and EC concentrations at Berth 47, May 2008 to March 2009.

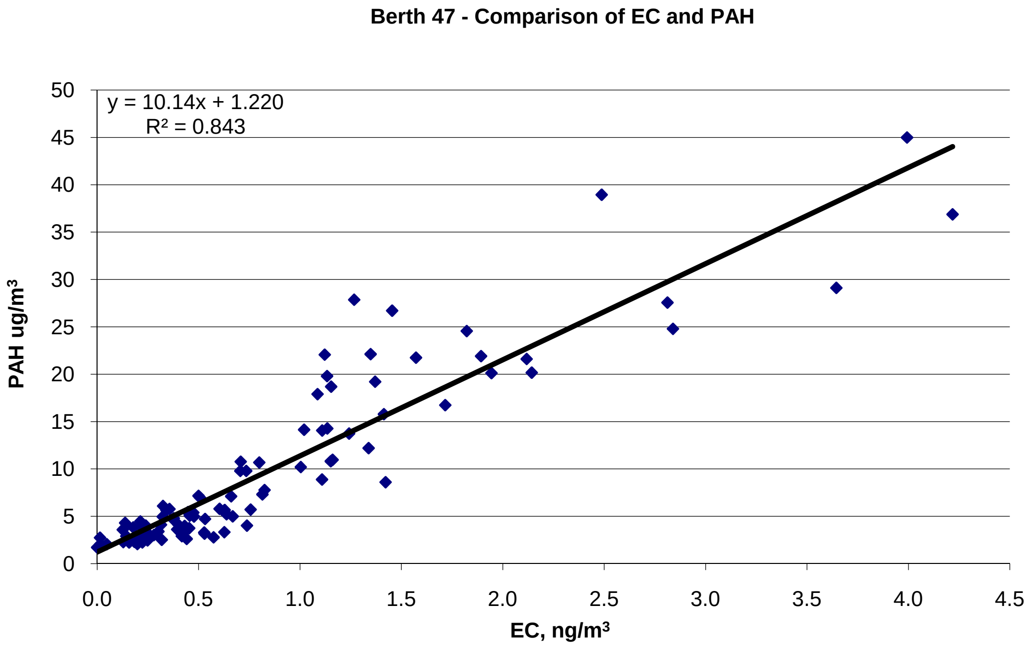


Figure 5.21 Comparison of PAH and EC concentrations at SPPS, May 2008 to March 2009.

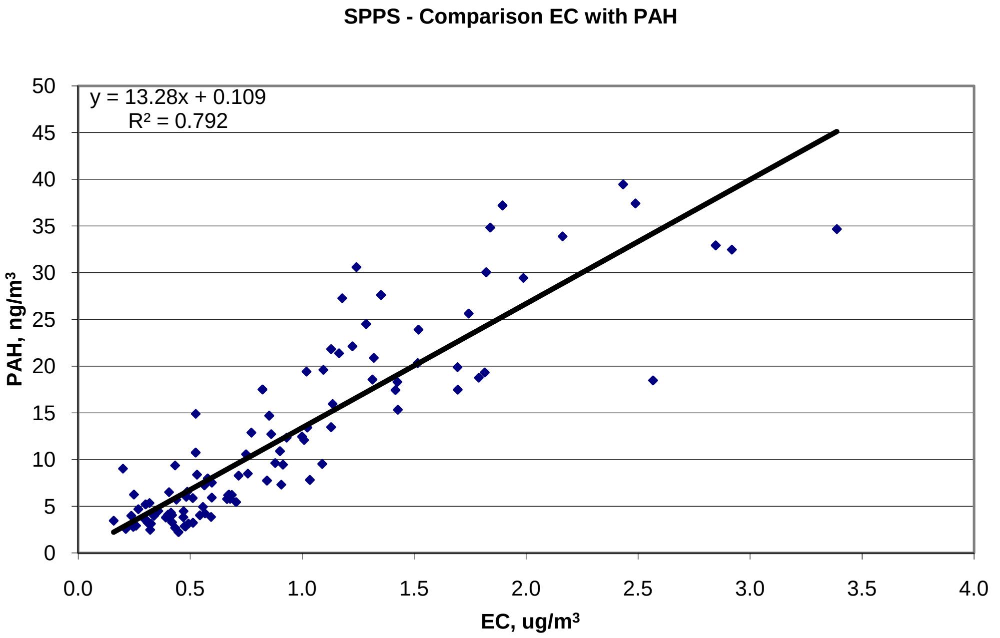


Figure 5.22 Comparison of PAH and EC concentrations at TITP, May 2008 to March 2009.

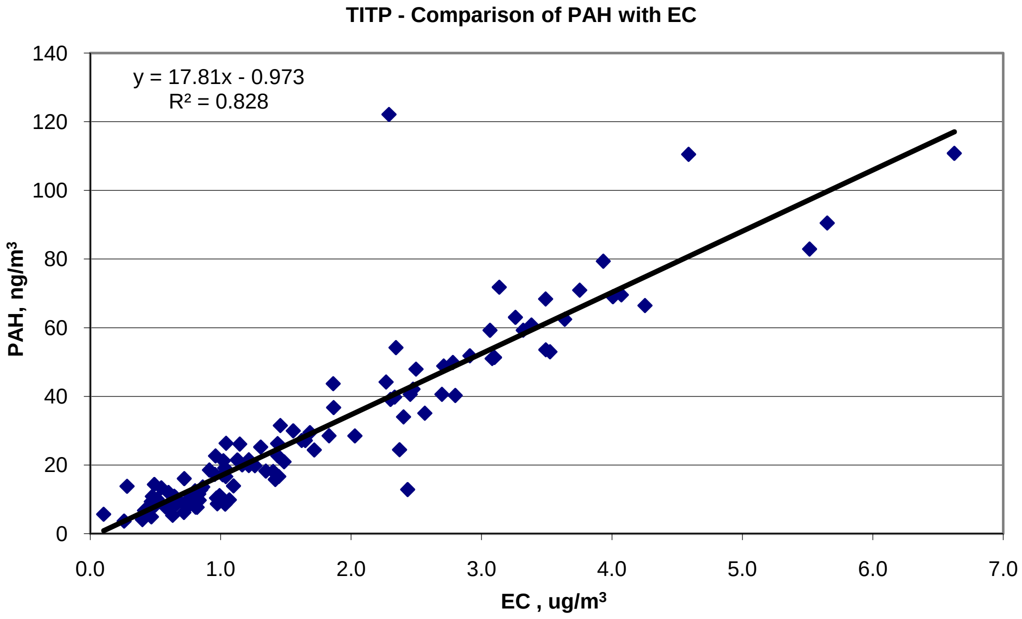
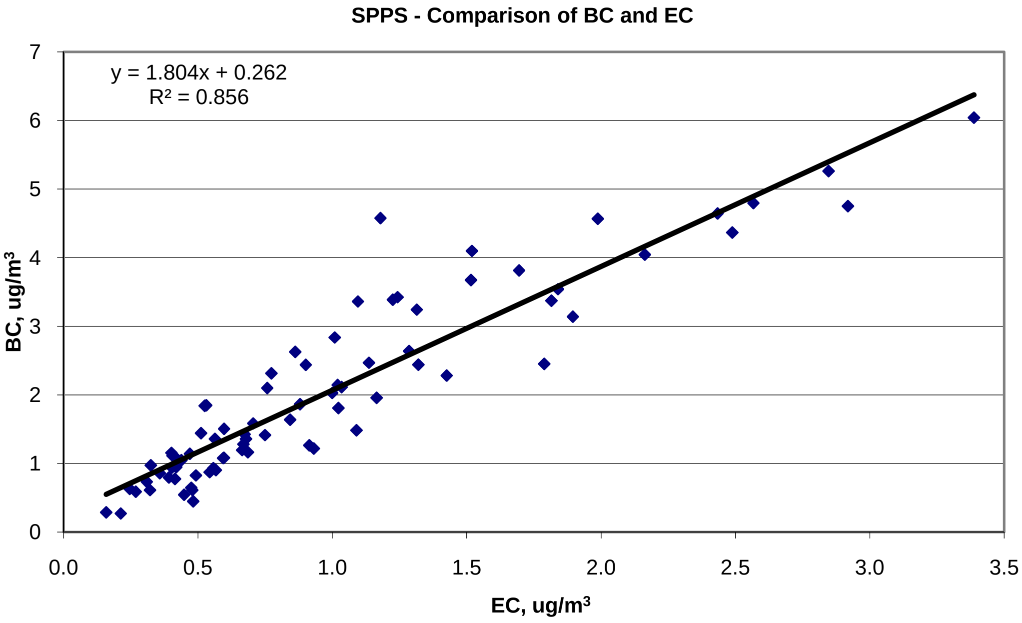


Figure 5.23 Comparison of BC and EC Concentrations at SPPS, June 2008 to January 2009.



Speciated PAH

Filter samples for PAH analysis were collected on a one-in-three day schedule with all of the other particulate samples. A subset of 16 filter sets were selected for speciated PAH analysis based on the daily average real-time PAH concentrations. The analysis was conducted by Desert Research Institute (DRI) using the aforementioned in-injector thermal desorption/GC-MS method. Table 5.7 shows the PAH compounds for which concentration data was reported.

Table 5.7 PAH Compounds Reported.

acenaphthylene	benzo[e]pyrene	3,6 dimethyl phenanthrene
acenaphthene	benzo[a]pyrene	methylfluoranthene
fluorene	perylene	retene
phenanthrene	indeno[1,2,3-cd]pyrene	benzo(ghi)fluoranthene
anthracene	dibenzo[a,h]anthracene	benzo(c)phenanthrene
fluoranthene	benzo[ghi]perylene	benzo(b)naphtho[1,2-d]thiophene
pyrene	coronene	cyclopenta[cd]pyrene
benzo[a]anthracene	dibenzo[a,e]pyrene	benz[a]anthracene-7,12-dione
chrysene	9-fluorenone	methylchrysene
benzo[b]fluoranthene	dibenzothiophene	benzo(b)chrysene
benzo[j+k]fluoranthene	1 methyl phenanthrene	picene
benzo[a]fluoranthene	2 methyl phenanthrene	anthanthrene

The original plan was to select roughly the same number for each season, choosing one from the days highest 10% of average real-time PAH concentrations, one between 75-90%, one from the third quartile (50-75%) and one from the second quartile (25-50%) of average real-time PAH concentration. This could not be followed precisely since not all the required filters were available from all four stations on any given day. The unavailability of selected filter samples somewhat reduces the robustness of original sampling scheme. Nevertheless, samples selected for analysis did cover a wide variety of seasons and PAH concentrations. Two batches of filter samples were subject to detailed analysis for speciated PAHs in March and May 2009.

The average of the real-time PAH concentrations was calculated for each day a filter was analyzed for PAH content. The averaged real-time PAH concentrations were then plotted against the sum of all PAH compound reported, the sum of the seven compounds at highest concentration, and chrysene. Chrysene was chosen because is generally found in high concentrations in diesel exhaust (14). Table 5.8 shows the slopes and correlation coefficients obtained. The results indicate that there are no significant correlations between real-time PAH concentrations and speciated PAH concentrations. Correlation plots for the sum of all PAHs reported and the sum of the seven PAHs versus real-time PAH analyzer are shown in Figures 5.24 and 5.25, respectively.

Table 5.8 Slopes and Linear Regression Coefficients when Comparing Speciated and Real-Time PAH Concentrations.

Site	Promenade		Berth 47		SPPS		TITP	
PAH	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2
Sum All	0.06	0.06	-0.03	0.01	0.13	0.29	0.02	0.04
Sum 7 Highest	0.02	0.03	-0.02	0.12	0.03	0.12	0.01	0.01
Chrysene	0.00	0.01	0.00	0.05	0.00	0.00	0.00	0.01

Figure 5.24 Plot of Sum of DRI PAHs versus Real-Tim PAH Analyzer (PAS 2000).

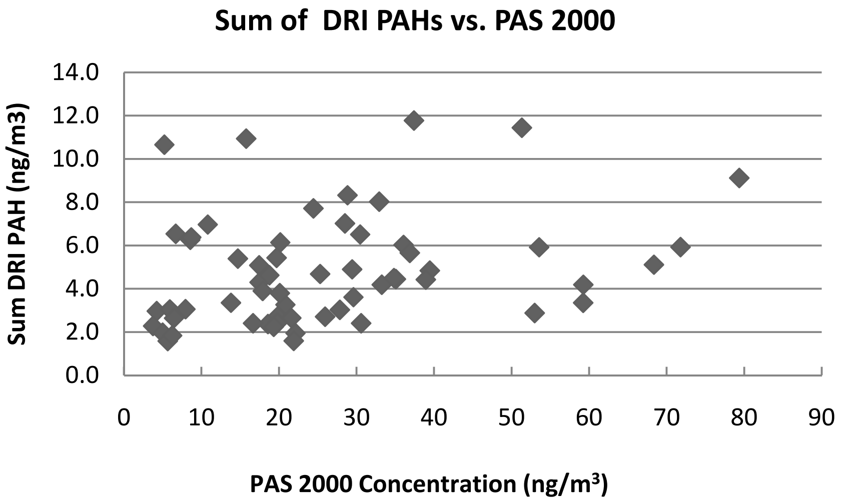
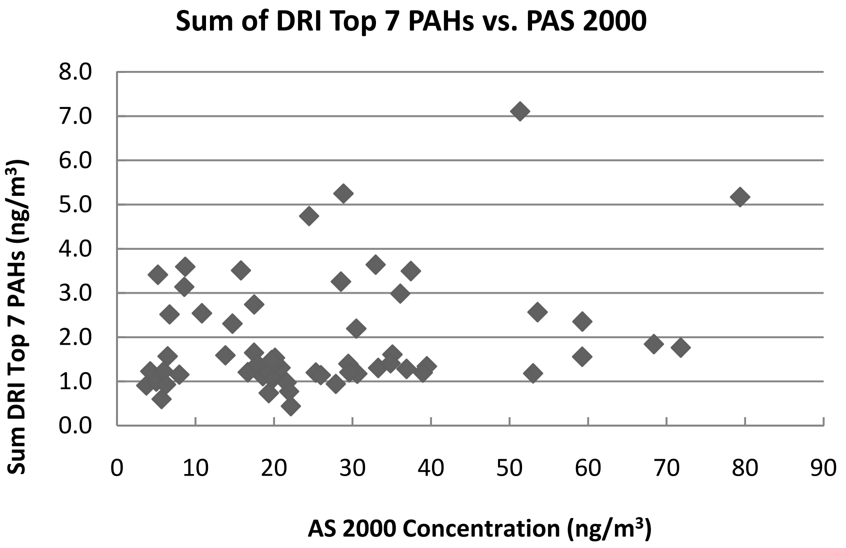


Figure 5.25 Plot of Sum of DRI Top 7 PAHs versus Real-Tim PAH Analyzer (PAS 2000).



The cause for the weak correlation is not clear. Normally, the analytical method for speciated PAH is expected to have a reproducibility of 90% between two runs. One possibility for the low correlations between real-time PAH and laboratory analysis is the particle loading on the filter media was not homogeneous during the sampling phase. Consequently, when a small strip of the filter is removed for analysis and the results can easily vary by more than 10% *(15)*.

A comparison of the seven predominant species in two separate dates of filter analysis reveals a very different PAH profile. Table 5.9 lists predominant PAH species in two separate analyses. The major component in the first analysis is flouranthene, whereas benzo[a]pyrene is the dominant species in the second analysis. Although flouranthene and benzo[a]pyrene are commonly found in diesel exhaust *(16,17)*, it is not clear as to why the PAH profiles from two analyses are significantly different.

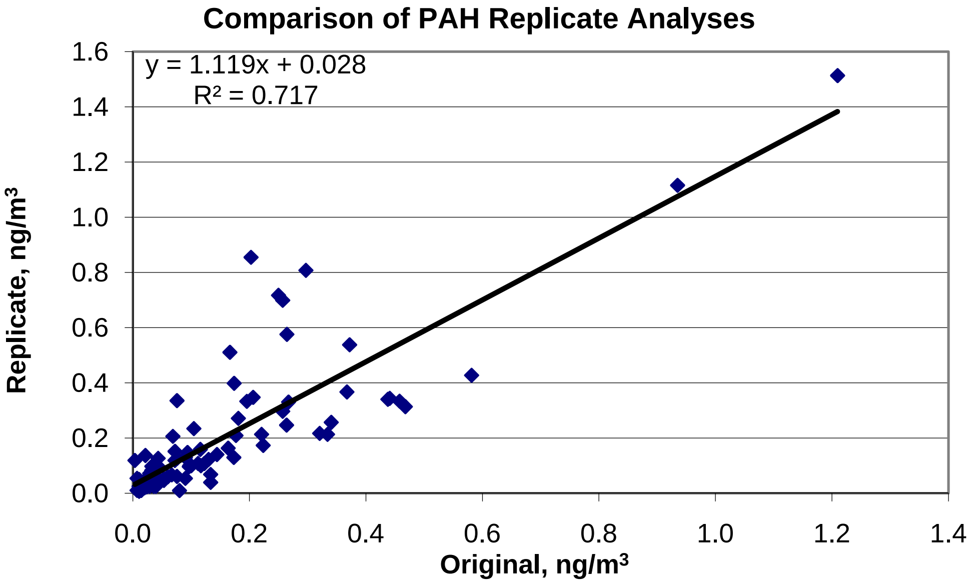
Table 5.9 Predominant PAH Species in Two Separate Analyses.

Predominant PAH Species	**1st**	**2nd**
acenaphthylene	v	v
phenanthrene	v	n.d.
anthracene	v	v
fluoranthene	M	n.d.
chrysene	v	n.d.
benzo[j+k]fluoranthene	v	n.d.
benzo[a]pyrene	n.d.	M
perylene	n.d.	v
benzo[ghi]perylene	v	v
cyclopenta[cd]pyrene	n.d.	v
anthanthrene	n.d.	v
v: detected. M: major species. n.d.: Not detected		

Analytical Reproducibility for Speciated PAHs

To partially assess speciated PAH measurement uncertainty, a single sample was analyzed twice. Figure 5.26 shows a plot of the original versus duplicate analysis. Note that there is considerable uncertainty as the R^2 factor is only 0.72. This analysis is for assessing reproducibility of an analytical method and does not take into account the uncertainties that may be caused by filter sampling and handling.

Figure 5.26 Comparison of a Duplicate Speciated PAH Analysis



6. Conclusion and Recommendations

6.1 Conclusion

The Port has operated a four-station ambient air monitoring network since 2005. The original network was designed to measure ambient PM to assess potential air quality impacts by diesel-powered equipment in Port operations to adjacent residential communities. This network was upgraded in 2007 to include real-time gaseous pollutant and PM analyzers. Through a grant from the EPA, the network was further expanded to include EcoChem PAS 2000, a real-time PAH analyzer, to measure ambient particle-bound PAHs. One of the advantages of using a real-time PAH analyzer is to provide better temporal resolution of pollutants compared to the traditional Hi-Vol 24-hour composite sampling strategy.

The expanded network has been in operation successfully since 2007 and accumulated more than one year of real-time PAH monitoring data. Results from quality control checks and quality assurance audits indicated that the four real-time PAH analyzers used had good precision and instrumental sensitivity when compared to a collocated transfer standard. Also, on-site audits with a transfer standard showed good correlations for all four analyzers, indicating that the overall data quality was satisfactory.

Analysis of potential diurnal and seasonal variability of ambient PAHs showed that three stations, TITP, Promenade, and Berth 47, had a bimodal, or twin-peak, distribution pattern. This pattern may be a result of local activities and meteorological conditions. This bimodal pattern could be the result of several factors including mixing heights, wind speeds, and port operations. Ambient PAH concentration trends at the SPPS station had only one peak during morning hours. The cause of this difference in trend is unknown. A close examination of meteorological data at SPPS revealed that significant wind pattern change occurred in 2008/2009 when the predominant wind pattern changed from northwesterly to southwesterly direction. The other three stations all showed typical wind patterns for coastal sites with predominantly northwesterly and southwesterly winds, depending on the time of the day and the season of the year.

Other correlation analyses included real-time PAH data with meteorology (wind speed and wind direction), ambient NO_x levels, UFP, BC, EC and speciated PAHs. As expected, on average, the source-dominant site (TITP) had the highest concentrations, which could be five times higher than the one background and two community sites.

The correlation between composited wind speed and wind direction and real-time PAH data was moderate. Nevertheless, Berth 47 and TITP showed an exponential decay curve between wind speed and PAH concentrations. The implication of this exponential curve may be that higher wind speeds result in stronger air dispersion and, consequently, lower PAH concentrations.

Results from correlation analyses between various chemical parameters and real-time PAH concentrations showed strong correlations between NO_x, EC and hourly real-time PAH data. Good correlations between these parameters are expected due to the fact that they are all combustion-related emissions (18). Surprisingly, the correlation between BC and EC at SPPS site was relatively weak. The cause for this weak correlation is not clear. One possible explanation is the difference in measurement principles. Additionally, no significant correlations were observed between PAH and both UFP counts and $PM_{2.5}$ levels.

Lastly, the results of correlations between speciated PAHs, either the sum of all speciated PAH or the sum of top seven PAHs, and real-time PAH concentrations were relatively not significant. Additionally, the two batches of filters analyzed for speciated PAH showed different PAH profiles. The possible cause for this lack of correlation and discrepancy in PAH profiles could be the non-homogeneous particle loading on the filter media. A brief evaluation of reproducibility for speciated PAHs analysis showed a correlation of 0.72 between two sample analyses.

6.2 Recommendations

Generally speaking, the data quality of real-time PAH monitoring is considered relatively good and reliable and we recommend that these measurements be continued. However, data interpretation can be improved with additional information. The following are recommendations to enhance future data interpretation and possible future work to utilize PAH monitoring data.

6.2.1 Activity Data

It is recommended that traffic counts or activity data at each site are collected in the future. Activity data such as drayage truck trips and idling, operating hours of cargo handling, vessel calls, etc., are useful in analyzing possible relationships of ambient PAH concentrations with various equipment and activities. It is also useful in analyzing diurnal and seasonal trends.

6.2.2 Improvement in Speciated PAH Analysis

Using in-injector thermal desorption GC/MS to analyze aerosols deposited on filter medium for speciated PAH may be a useful screening tool to avoid the laborious process of sample preparation by solvent extraction. However, the analysis is semi-quantitative. Future improvements in reproducibility and accuracy of analysis are required. As a minimum, a reference aerosol standard should be included in the analysis as a surrogate to assess precision and accuracy of the analytical procedure.

6.2.3 Source Apportionment Study and Health Risk Assessment

Real-time PAH data have high time resolution, (e.g., hour or minute time interval), and will be ideal for a source apportionment study using techniques such as non-parametric back trajectory analysis that requires time resolution of minute-intervals for both pollutant and meteorological data. The results from the source apportionment study can then potentially be used to assess the “fair-share” of pollution, particularly PAHs, from Port-related activities, and the potential health risk to the local communities. From a health risk and cytotoxicology perspective, using PAH data will be preferable to using EC which is normally used as a surrogate for DPM in diesel exhaust.

7. References

1. U.S. EPA. “Field and Laboratory Evaluations of a Real-time PAH Analyzer”, National Exposure Research Laboratory, Research Triangle Park, NC 27711. EPA/600/SR-97/034. 1997.
2. Matter, U., H.C. Siegmann and H. Burtsher. “Dynamic Field Measurements of Submicron Particles from Diesel Engines”. Environ. Sci. Technol. 1999, 33;1946-1952.
3. Tang, Shida, R. Johnson, T. Lanni, W. Webster, T. Tagliaferro, J. Munn, C. Barnes, D. Barnes, K. Kewkirk, D. Rivenburgh and D. Guerrieri. ”Monitoring of PM-bound Polycyclic Aromatic Hydrocarbons from Diesel Vehicles by Photoelectric Aerosol Sensor (PAS)”, Automotive Emission Laboratory, Bureau of Mobile Sources, Division of Air Resources, New York State Department of Environmental Conservation. March 22, 2001.
4. Przybilla, K. W. Berkhahn, H. Burtscher, D. Dahmann, U. Matter and P. Eietschel. “Monitoring Diesel Particulates in Working Areas with the Photoelectric Aerosol Sensor”. Gefahrstoffe-Reinhaltung der Luft 2002: 62 (6) 279-284.
5. Anderson, R. R., D. Martello, C. M. White and D. J. Eatough. “NETL’s Ambient Air Fine-Particulate Characterization Program – First Year Results”. Fuel Chemistry Division Reprints 2002, 47(2): 622-623.
6. Sapkota, A. and T. Buckley. “The Mobile Source Effect on Curbside 1,3-Butadiene, Benzene, and Particle-bound Polycyclic Aromatic Hydrocarbons Assessed at a Tollbooth”. J. Air & Waste Manage. Assoc. 2003. 53:740-748.
7. Fitz, D. Personal Communication. September 2005.
8. Bertolin, G.E., C. Patton, S. Marashi and C. Crabtree. “Development of an Air Toxics Monitoring Program at the Port of Los Angeles”. Paper 1121, presented at Air and Waste Management Meeting, 2005 (Need to confirm with Gary).
9. The Port of Los Angeles. “Evaluation of Alternate Sites for the San Pedro Community Monitoring Station”. April 2007.
10. The Port of Los Angeles. “Air Quality Monitoring Program at the Port of Los Angeles, Annual Report May 2005 –April 2007”, April 2007.
11. Air Resources Board. “Harbor Communities Monitoring Study – Meteorological Summary”. September 12, 2008. (http://www.arb.ca.gov/research/mobile/hcm/met_summary.pdf)
12. EcoChem Analytics. “User Guide – Real time PAH Monitor, PAS 2000 (version 2.0) .” October 1998.
13. Air Resources Board. “Elemental Carbon in Wilmington”. April 28, 2003. (http://www.arb.ca.gov/ch/aq_result/wilminton.wm_ec.htm)
14. Shah, S.D., T.A. Ogunyoku, J.W. Miller and D.R. Cocker. “On-Road Emission Rates of PAH and n-Alkane Compounds from Heavy-Duty Diesel Vehicles”. Environ. Sci. Technol., 2005. 39:5276-5284.
15. Desert Research Institute. “Standard Operating Procedure for In-Injector Port Thermal Desorption and Subsequent Gas Chromatography/Mass Spectrometry

Analysis of Non-Polar Organic Species in Aerosol Filter Samples”. DRI SOP#2-219.1 June 19, 2006.

16. Suro, J., Q, Chen, I.M. Kennedy, T.A. Cahill and P.B. Kelly. “Characterization of Chemical Composition and Size of Diesel Exhaust Particulate Matter by LDITOF/MS”. An International State of Science Workshop on Organic Speciation in Atmospheric Aerosol Research. April 5-7, 2004. Las Vegas, Nevada.
17. Marr, L.C., T.W. Kirchstetter, R.A. Harley, S.V. Hering, S.K. Hammond. “Characterization of Polycyclic Aromatic Hydrocarbons in Motor Vehicle Fuels and Exhaust Emissions”. Environ. Sci. Technol. 1999. 33(18): 3091-3099.
18. Marr. L.C., L.A. Grogan, H. Wohrnschimmel, L. Molina, M. J. Molina, T. J. Smith and E. Garshick. “Vehicle Traffic as a Source of Particulate Polycyclic Hydrocarbon Exposure in the Mexico City Metropolitan Area”, Environ. Sci. Technol. 2004. 38(9):2584:2592.

APPENDIX

- Work Plan
- QAPjP
- AQS Raw Data Upload Records
- Hourly Wind Rose Plots
- Monthly Wind Rose Plots

WORK PLAN

THE PORT OF LOS ANGELES

EPA Local Scale Air Toxics Ambient Monitoring Program

Revised Work Plan
For
Port of Los Angeles Community-Based Air Toxics Exposure Study

Prepared for

Office of Air and Radiation
U.S. Environmental Protection Agency

Contract No.: XA-969631010-0

Prepared by

Environmental Management Division
Port of Los Angeles
Harbor Department
City of Los Angeles

November 28, 2006
Revised: April 25, 2007

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Table of Contents

1. INTRODUCTION

The Port of Los Angeles (POLA) is currently operating an ambient air monitoring network to collect filter samples of particulate matter (PM) to determine impacts of emissions from port-related activities. The network is operated by Science Applications International Corporation (SAIC) under a contract to the POLA. The network also measures chemical compositions of selected filter samples for source apportionment study by a subcontract to Desert Research Institute (DRI). The POLA is in the process of expanding the monitoring capabilities of the existing network to include measurements of gaseous criteria pollutants, such as sulfur dioxide, nitrogen oxides, carbon monoxide and ozone; and, real-time PM ($PM_{2.5}$ and PM_{10}). With a *Community-based Air Toxics Exposure Study* grant provided by the U.S. Environmental Protection Agency (EPA), this project will install and operate real-time poly-aromatic hydrocarbons (PAH) analyzers at the expanded network to measure particle-bound PAHs to provide chemical class specificity to enhance source identification and validation of health risk assessment.

Project Objective

The main objective of this project is to enhance the Port-wide ambient air quality monitoring program currently in progress in the Port to include the capability of monitoring air toxics, especially PAHs. This study will utilize real-time PAH analyzers (EcoChem Analytics PAS 2000) to measure particle-bound PAHs in the ambient air on a quasi-real time basis to provide better temporal resolution. This enhancement expands the capability of the existing ambient air quality monitoring network to include ambient PAH measurements, and upgrade to become a community-scale air toxics exposure monitoring program. Results from real-time PAH measurements coupled with meteorological data, and particulate mass and chemical measurements obtained from the existing Port-wide air monitoring network will be used to characterize emission sources and potential ambient air quality impacts by air emission from the Port's operations, particularly, diesel exhaust particulates. Furthermore, the direct measurement of particle-bound PAH will provide better insight into potential health effects; the chemical class-specific PAH measurements may be considered a better indicator than elemental carbon as a surrogate for diesel particulate matter in estimating diesel particulate matter concentration for health risk assessment purposes.

Scope of Work

Scope of work of the POLA Community-Based Air Toxics Exposure Study includes:

(1) Preparation of Work Plan describing the monitoring program

(2) Procurement of PAH Analyzers

(3) Installation and Start-up

(4) Field Monitoring

(5) Data Reduction and Management

(6) Data Analysis and Reporting

2. PROJECT ORGANIZATION AND RESPONSIBILITY

The proposed POLA team organization is shown in Figure 1, including the specialties for key technical personnel and service areas anticipated from the subcontractors.

Mr. Paul Johansen, Assistant Director of Environmental Management, will be responsible for the successful execution of this project, both technically and financially. He will represent the Port and provide technical and regulatory liaison. Mr. Johansen will regularly interface with the U.S. EPA Contract Administrator regarding all project-related issues and the Port's team performance to ensure that all work performed adheres to the approved schedule and budget while meeting the EPA's highest expectations. Mr. Johansen will be assisted by the Environmental Management Officer - Mr. Christopher Patton to provide daily guidance to Project and Task Managers.

Environmental Affair Officer: Mr. Christopher Patton, Officer of Environmental Management (EM), will be responsible for the day-to-day project supervision, overseeing Project and Task Managers, and ensuring project quality. Mr. Patton will provide guidance to the Project Manager on all project-related activities.

Project Manager: The Project Manager (PM), Lisa Wunder, Environmental Specialist of Environmental Management, will be responsible for the day-to-day planning and execution of project activities, performing cost estimates and budget control for assigned tasks, overseeing Task Managers, and ensuring quality and timeliness of all assignments. Ms. Wunder will maintain close communications with the EPA Contract Administrator on all project activities through routine project meetings and monthly progress reports.

Scientific Advisor: Tetra Tech, Inc. and the University of Riverside-Center for Environmental Research and Technology (UCR-CERT) will provide technical support for this project. Specifically, Mr. Dennis Fitz of UCR-CERT, will serve as the Scientific Advisor. Mr. Fitz brings 27 years of experience directing air quality improvement and research programs nationwide. He is presently serving as Manager of the Air Monitoring Group at the University of California, Riverside.

3. TECHNICAL APPROACH

Site Selection

The existing Air Quality Monitoring Program has five stations, one primary station and four satellite stations, located within the Port's operational region of influence (ROI). The Wilmington station serves two purposes: (1) a satellite station and (2) a primary station, because it is located just north of the Port, the wind flow patterns, and because its proximity to the Port community, this area may experience elevated pollutant concentrations from Port emissions. The first two satellite stations are located in the two adjacent communities, one in Wilmington to the north (at the Saints Peter and Paul Elementary School, or SPPS) and the second one in San Pedro (on the Liberty Hill Plaza building or LHP). The third satellite station, a "coastal boundary" station is located at Berth 47 of the Port and the last satellite station, a "source-dominated" station is located on Terminal Island, near the center of Port operations during onshore wind flows. Figure 2 depicts locations of POLA ambient air monitoring stations.

Air monitoring site selection and development of the air monitoring protocol were a result of the collaborative efforts among the Port staff, their consultants, community groups and regulatory agencies. The Port conducted surveys, evaluations and pilot studies prior to initiating the actual monitoring study.

The existing program collected representative ambient particulate matter (PM) and meteorological data within the Port ROI for an initial period of one year (starting February 2005). This special study program collected PM less than 10 microns in diameter (PM_{10}) and PM less than 2.5 microns in diameter ($PM_{2.5}$) to determine ambient levels and chemical composition of these pollutants within the Port ROI.

Chemical analysis included elemental analysis by X-ray diffraction, ionic species by water extraction and ion chromatography, elemental carbon (EC) and organic carbon (OC) by thermal/optical reflectance method.

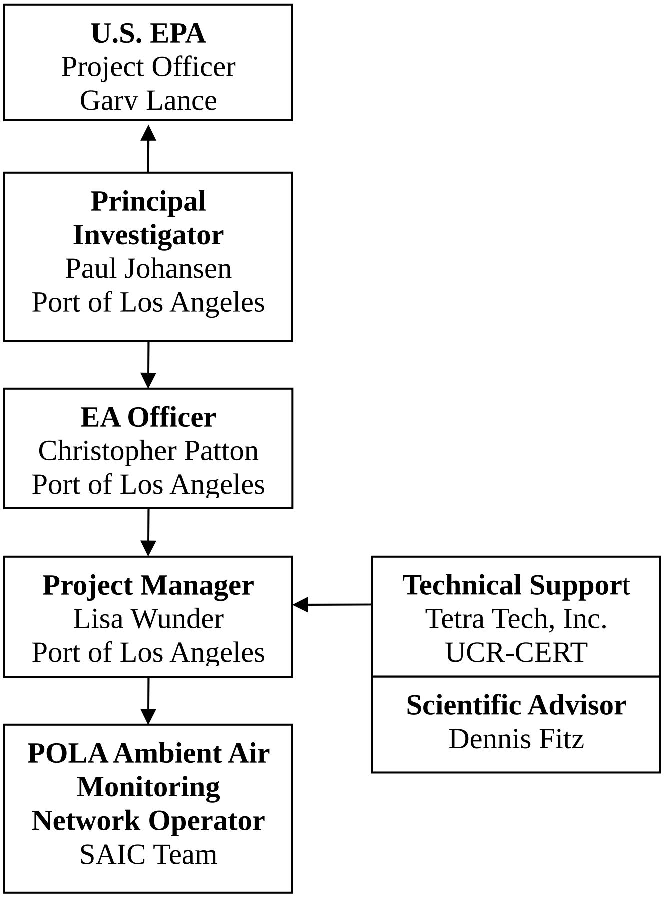


Figure 1. Project organization for Port of Los Angeles Community-Based Air Toxics Exposure Study

As discussed earlier, the Port is in the process of expanding the existing network to include real time monitoring of ultrafine particulates, $PM_{2.5}$ and PM_{10}, gaseous criteria pollutants (i.e., NO_x, SO_2, CO, O_3). Gas analyzers will be housed in a weather-controlled semi-permanent shelter at the existing PM monitoring station.

For this U.S. EPA funded air toxics monitoring, the newly expanded ambient station shelter and data logger will be used to house the PAH analyzer and to collect monitoring data. The PAH data will be analyzed along with data collected at the ambient air and meteorological monitoring network, and from chemical analysis of the filter samples to identify port emission sources and to validate health risk assessment.

Planning

(1) Coordination with the Existing Network Operator

Since the PAH analyzer will be installed inside the weather-controlled station shelter of the expanded network, careful planning and coordination with the existing network operator will be commenced immediately after this Work Plan is approved.

The project team will work with the existing network operator to resolve space requirement and availability of instrument rack, installation, initial set-up, test runs, configuration of data logger and routine operation and data collection.

(2) Procurement of PAH Analyzers

The project team will procure four sets of PAH analyzers, one for each of the network station. Functional check will be performed on the procured equipment prior to installation.

Installation

PAH analyzers will be installed only after the expanded network is completed. The procured equipment will be installed on the 19-inch instrument rack inside the shelter. Ambient air samples for the PAH analyzer will be introduced from the existing sample manifold for gaseous pollutant measurement. Instrument output will be fed into spare channels of data logger for data collection and storage. The data logger will be configured to receive measurement data from the PAH analyzer. After installation, the instrument and data logger will be checked to assure that the system is operating properly.

Field Monitoring

EcoChem Model PAS 2000 analyzers will be used to measure the concentrations of particle-bound PAHs. The instrument uses the principle of photoionization of total particle-bound PAH by means of an ultraviolet lamp. The wavelength of the light is selected such that only the PAH absorbed on aerosols are ionized, while gas molecules and non-carbon aerosols remain neutral. The aerosol particles that have PAH molecules adsorbed on the surface emit electrons, which are subsequently removed when an electric field was applied. Remaining positively charged particles are collected on a filter inside an electrometer where the charge is measured. The resulting electric current established a signal that is proportional to the concentration of total particle-bound PAH. The specifications state that the lower threshold of this method is about 3 ng/m^3 total particle-bound PAH and the response time is less than ten seconds. The operation is a real-time measurement depending on cycle time interval selected (i.e., in seconds), then the data is processed internally and can be displayed as minute-average values.

The field operation of PAH analyzer is rather straight-forward and requires minimal supervision and maintenance because the instrument has very few moving parts. However, manual inspection of instrument operation and routine check will still be conducted by the field personnel currently servicing the existing network. Monitoring data will be collected and temporarily stored by the data logger and transmitted via wireless connection to the network operator headquarter. Monitoring data will be archived.

For the diesel particulate matter (DPM) correlation study, integrated filter samples collected at the existing air quality monitoring stations for the same time period will be retrieved from the storage and analyzed for PAH contents upon request by the POLA. Analysis of PAH in filter samples will be performed by DRI following traditional sample preparation by solvent extraction and analysis by gas chromatography and mass spectrometry or by high performance liquid chromatography and fluorescence detection (CARB MLD-028). Table 1 lists monitoring parameters of the expanded air monitoring network.

The field monitoring period will coincide with the existing network for a period of 12 months and can be extended if required.

Data Management, Analysis and Reporting

(1) Data Reduction and Management

Real-time PAH concentration will be collected and processed for each minute, hour and 24-hour average data using spreadsheet program after downloading from the station data acquisition system.

Analytical data from PAH analysis of filter samples using the DRI's Thermal Desorption and Gas Chromatography-Mass Spectrometry (TD/GC-MS) method will be provided by the analytical laboratory following standard sample custody and tracking procedures. Analytical results will be converted to concentration (i.e., milligram per cubic meter or mg/m^3) using data obtained from field samplers.

(2) Data Analysis and Reporting

Real-time PAH data will be used along with detailed chemical analysis, elemental carbon/organic carbon (EC/OC) and mass data of filter sample and meteorological data to elucidate the potential sources and their contributions of diesel particulates, especially for the periods that prevailing wind carries air emissions from the Port's operation to the downwind locations.

All reviewed and validated PAH monitoring data in this enhancement study and also data collected from the Port-wide air quality monitoring network will be submitted to the U.S. EPA, to be incorporated as part of the National Air Toxic Assessment Database.

Furthermore, ambient ground-level concentrations of PAHs at monitoring stations located at the Port and adjacent community area as well as ambient background level will be used to evaluate and validate the results of health risk assessment from regional air toxics study currently underway by the local agency.

Table 1. Components of the Expanded Port-wide Air Monitoring Program

Monitoring Station	Parameter Measured	Monitoring Method	Sampling Frequency	Analysis
Primary Station (Wilmington)	$PM_{2.5}$	Federal reference method (Rupprecht & Patashnick [R&P] Partisol 2000 Sampler)	24-hr average, every third day	Mass
	PM_{10}	Federal reference method (R&P Partisol 2000 Sampler)		Mass
	Meteorological Parameters	Meteorological Stations	Continuous	None
	Particle-Bound PAH Analyzer	EcoChem PAS 2000	Continuous	Concentration
	SO_2, NO_x, CO, O_3	TEI Analyzers	Continuous	Concentration
Satellite Stations (Wilmington, San Pedro, Berth 47 and Terminal Island)	$PM_{2.5}$	Desert Research Institute (DRI) Sequential Filter Sampler (SFS)	Onshore and offshore flows	Mass, EC/OC, elemental and ionic species
	$PM_{2.5}$	DRI SFS	24-hr average, every third day	Mass, EC/OC, elemental and ionic species
	$PM_{2.5}$	TSI 8520 - Dust Trak Monitor	5-min, coincide with SFS 24-hr sampling frequency	Mass
	Meteorological Parameters (Wind speed, wind direction, temperature)	Meteorological Stations	Continuous	None
	Particle-Bound PAH Analyzer	EcoChem PAS 2000	Continuous	Concentration
	SO_2, NO_x, CO, O_3	TEI Analyzers	Continuous	Concentration

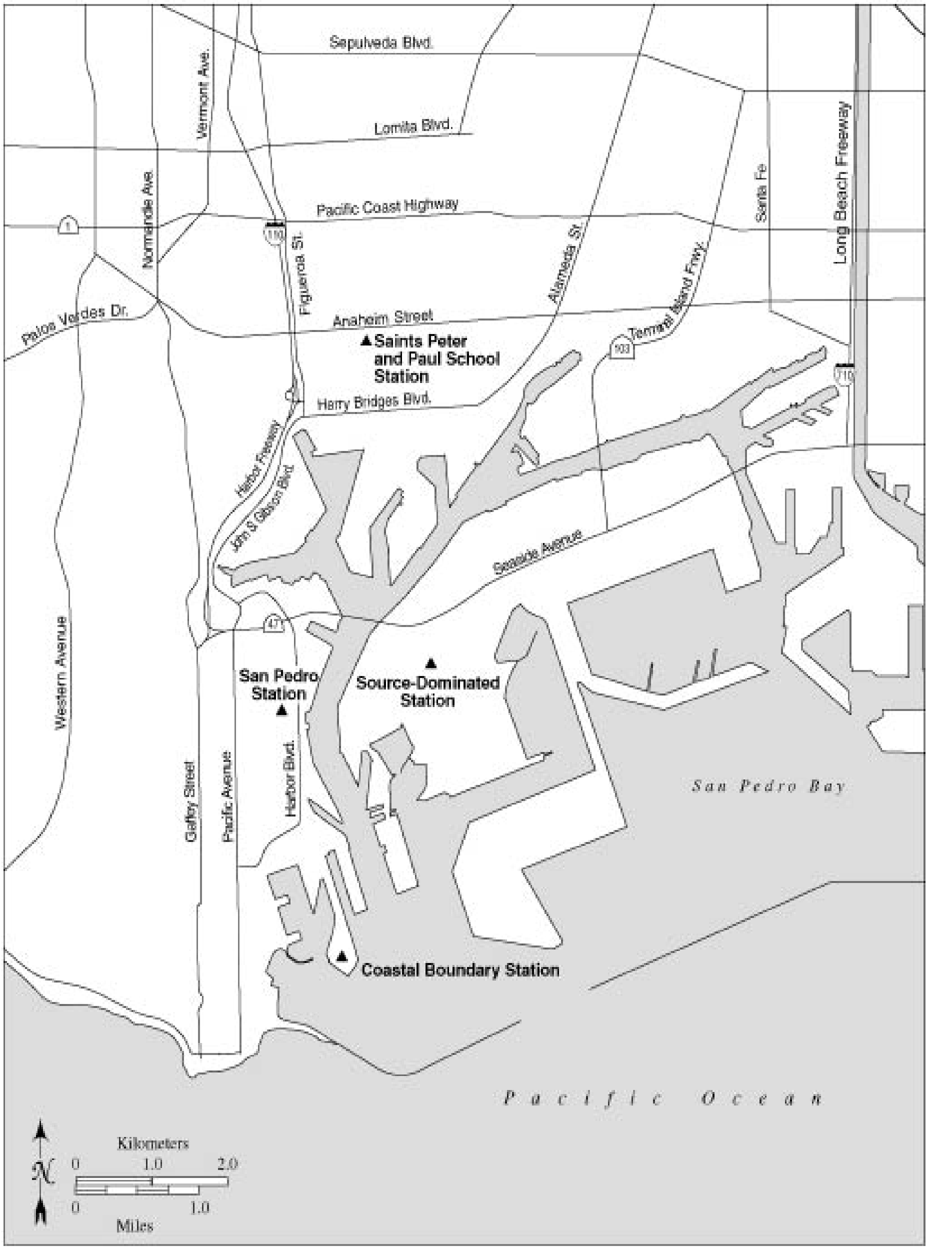


Figure 2. Locations of POLA Air Monitoring Stations

4. QUALITY ASSURANCE OBJECTIVES AND CORRECTIVE ACTION

This section defines the data quality goals for the project and the quality control activities necessary to obtain them. These goals are stated in terms of precision, accuracy and completeness.

Quality Assurance Objectives for Measurement Data

Table 2 shows the data quality objectives and acceptance criteria for the measurements to be made in this project.

Table 2. Data quality objectives.

Measurement	Concentration Range Expected	Completeness	Accuracy	Precision	Detection Limit*
PAH	0-100 ng/m3	90%	±10%	10%	3 ng/m3

* One-minute time constant

Completeness will be calculated based on the number of hours of data planned. Accuracy will be determined by comparison with a transfer standard (a separate PAH analyzer), similar to the process of comparing the ozone transfer standard with a station ozone analyzer. Precision will be determined from collocated measurements.

Corrective Action

Corrective action will be initiated whenever a problem is identified, which may occur during daily data review or weekly site checks. The goal of corrective action is to remedy any problem before the project or equipment and/or parameters drop below the desired accuracy, precision, or completeness.

To minimize the need to take corrective action, all equipment to be used on this program will be serviced prior to field use. Once a problem has been identified, the person who found it will either fix it on-site or request the project manager's assistance.

5. QUALITY CONTROL AND QUALITY ASSURANCE AUDIT

Since calibration standards do not exist for the PAH analyzers the comparability of the analyzers will be determined before and after field deployment by collocated sampling of ambient air. This will be done for a week or more before and after field deployment to evaluate the analyzers. The one-minute data will be plotted and a least squares regression will be performed to determine bias from the slope. If less than 10% of the measurements are less than ten times the detection limit the site will be relocated and additional collocated sampling will be performed. Since accuracy cannot be established, bias will be used as the accuracy goal. If the bias exceeds the accuracy goal presented in Table 2, the least squares regression will be used to normalize the data to an instrument to be designated as a reference.

PAH Analyzer

The response of this analyzer is calibrated at the factory. The instrument is not designed to be directly calibrated in the field and no calibration standards are available. To ensure acceptable operation, instrument flow rates and zero air response will be checked on a weekly basis. The instruments will also be operated during collocation runs to assess their bias as described above. This collocation test will also be considered a key factor in acceptance testing of the PAH analyzers that will be purchased by project funds. Precision will be determined from the weekly zero check. Lamp intensity and analyzer frequency will be checked weekly. Accuracy will be determined using a transfer standard on a quarterly basis. If the discrepancy, i.e., 20%, is observed over an hour of measurements between the transfer standard and the on-site analyzer, a more comprehensive evaluation will be conducted to investigate probable causes of the discrepancy, corrective action will be taken.

Data Logging

A EMC data logger, as part of the expanded network, will be used to collect all data. The data logger will collect data once per second and store data as one-minute averages. This was chosen as the analyzers used operate on time constants of approximately one minute. Data will be downloaded to a PC as one-minute averages and converted to EXCEL spreadsheets. This PC will be backed up on a regular basis. The time of the individual instruments, if recorded, will be compared with data logger time as a part of the weekly site checks.

Quality Assurance Audit

Quality assurance audit of PAH analyzers will be performed within the first two weeks of sampling by UCR-CERT. The flows of the PAH analyzers will be audited. A final audit will also be conducted at the conclusion of monitoring period to assure the accuracy of the analyzers.

6. DATA REDUCTION, VALIDATION AND REPORTING

The objective of the data processing and validation effort is to obtain a quality assured database containing the particle-bound PAH monitoring data in a consistent format. The procedures that project team will use for data processing and validation ensure that reported data are valid and comparable, as much as possible, to those collected by federal, state, and local air pollution agencies. These procedures meet the requirements and guidelines of the U.S. EPA; e.g., Appendices A and B of 40 CFR 58; Quality Assurance Handbook for Air Pollution Measurement Systems, Volumes I and II (1984, 1987). Data processing procedures for this program are discussed below.

Data Handling

Data validation will follow guidelines described by the U.S. EPA documents - Screening Procedures for Ambient Air Quality Data (1978) and Validation of Air Monitoring Data (1980). The validity of the data will be checked as follows: data will not be removed unless there is a good reason or the measurement is physically impossible. All data will be screened for outliers that are not within the physically reasonable (normal) ranges. The following steps will be taken:

(1) Flagging data when significant deviations from measurement assumptions have occurred.
(2) Verifying computer file entries.
(3) Eliminating values for measurements that are known to be invalid because of instrument malfunctions.
(4) Adjustment of measurement values for quantifiable interference biases.

Data Records

(1) Logbook

A logbook will be maintained specifically for this project; all relevant calibrations, experimental procedures and observations will be recorded. If necessary and after transferring the data to a spreadsheet maintained on a PC, calibration factors may be applied to data. A checklist will be maintained to record all relevant QC functions data and observations. Table 3 is the preliminary weekly checklist.

(2) Data Logger Files

Data will be automatically collected and stored digitally on an Environmental Monitoring Company, Inc. (EMC) Station Manager data logger residing in the shelter. The stored data will be transmitted wirelessly to the network operator headquarter. An electronic copy of the transmitted data will be provided to the project team on a regular basis for review and analysis. The “raw” data files from these instruments will be saved “as is.” Copies of the raw data files will be used for subsequent processing steps to obtain “preliminary” and “final” data (i.e., the “original” data will be preserved for potential future use and reference should there be any questions regarding the final data or for use should either the preliminary or final data files become lost or corrupted). All PCs for data processing will be automatically backed up at a minimum of once per week.

Data Processing

As presented earlier, data validation will follow guidelines described by the U.S. EPA. All data will be screened for outliers that are not within the physically reasonable (normal) ranges. Next, the following steps will be taken:

1. Data will be flagged when deviations from measurement assumptions have occurred.
2. Computer file entries will be checked for proper date and time.
3. Measurement data resulting from instrument malfunctions will be invalidated.
4. Data will be corrected or normalized for biases.

PAH monitoring data will be reviewed as time series plots. Rapidly changing, anomalous or otherwise suspect data will be examined with respect to other available data.

Data processing consists of following steps:

1. Describe measurement scenarios
2. Tabulate information from the logbook and checklists
3. Identify data files, data rates and missing data
4. Add columns/rows to item #3 table to reflect data set time synchronization correction
5. Create merged data files for the tests that include the time synchronization corrections
6. Convert to engineering units and apply calibration factors
7. Level Zero Outlier Screening
8. Compile data at desired averaging interval

Table 3. Weekly Check List

Weekly Checklist - Port of Los Angeles Community-Based Air Toxics Exposure Study				
Site(number or description):				
Date:				
Sampler# (1- 4)				
Technician:				
Time: Data logger: Instrument (if recorded)				
Site Secure (y/n)				
Sampling Lines Located Properly? (y/n)				
PAH Analyzer Flow Rate (1.5-2.5 lpm):				
PAH analyzer Intensity.(>98)				
PAH Analyzer Frequency (<15)				
5min PAH Zero Check on/off Time (hh/mm PST)	/	/	/	/
Comments				

Flags will be applied at step eight based on outliers and logbook information in step 3. The data reporting forms will contain a column for flagging and indicating data validity. All problematic and missing data points will be highlighted in the form through the insertion of an appropriate coded flag. Invalidated data will not be placed in the reporting form in order to avoid their possible inadvertent use. Data flags will include the following:

- Valid value
- Valid but comprised wholly or partially of below-MDL data
- Valid but interpolated (value is above the maximum of the instrument)
- Valid despite failing a statistical outlier test
- Valid but qualified because of possible contamination or interference
- Valid but qualified due to non-standard sampling conditions
- Missing value because no data are available
- Missing value because the data were invalidated by the operator

The data will be checked for internal consistency, consistency with operator logbooks, and instrument precision checks. Internal consistency requires that data fall within normal operating ranges and do not exhibit excessive and rapid variations that are inconsistent with expected variations. Consistency with operator logbooks requires that all data acquired during operation, maintenance, instrument versus datalogger time, and outage periods be flagged appropriately. All verified data that have been subjected to these tests will be designated as validated data.

Reporting

The project team will prepare a comprehensive report for the field program. This report will include a description of the measurements and data accuracy, precision and completeness. The report will include the validated program data. The report will include a description of measurement problems and applicability and changes to the protocols for future studies.

In addition to the final project report, the Port Project Manager will communicate regularly with the EPA personnel regarding project status and work progress. On a monthly basis, the Port Project Manager will inform EPA of current progress and submit a monthly update memo. On a quarterly basis, the Port Project Manager will submit a quarterly report to the EPA. In addition, budget control is accomplished by closely monitoring labor and direct expenses for each work assignment. Work reports are completed for each individual, with the Project Manager approving labor hours. Similarly, the Project Manager must approve expense reports and other direct expenses. The Port Project Manager will include budget summaries in quarterly reports to the EPA personnel that detail percentage of the budget used, work anticipated and accomplished.

7. PROJECT SCHEDULE

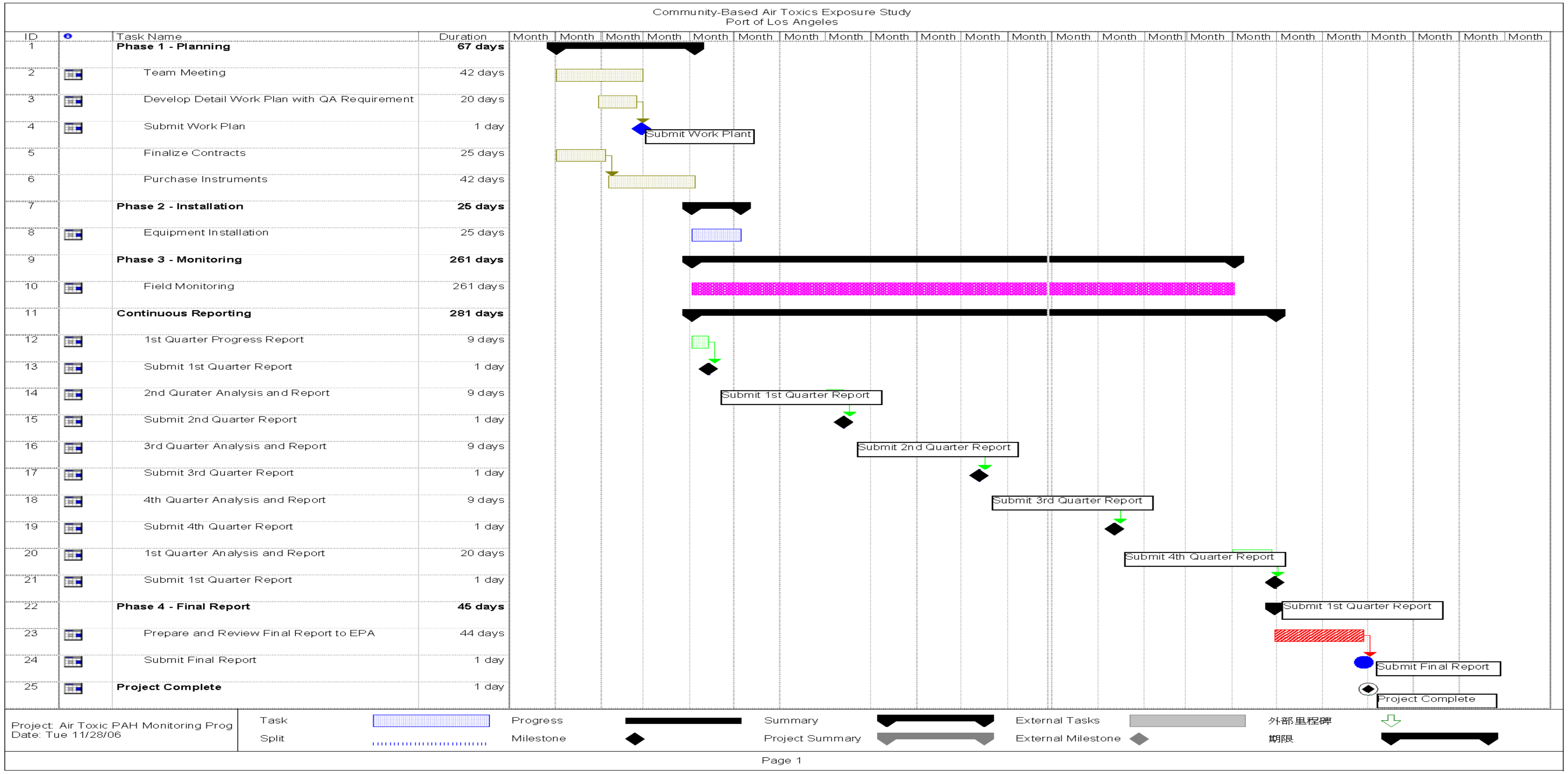
The proposed work schedule can be found in Table 4.

Figure 3 is a Gantt chart showing individual task duration and start and completion dates, milestones and deliverables in the project.

Table 4. Work Plan Overview

Phase	Milestone Time Period	Activities	Frequency
Phase 1- Planning	2 months after grant is awarded	Team meetings	Weekly
		Development of detailed work plan including QA requirements	
		Finalize contracts	
		Purchase instruments from manufacturer	
		Monitoring sites upgrade with tested, calibrated and operational equipment	
Phase 2- Installation	1 month after the shelter are erected *	Prepare and submit quarterly report to EPA	Quarterly
Phase 3- Monitoring	For the following 12 months after monitoring locations are in operation	Data analysis and reporting	
		Prepare and submit final report to EPA	
Phase 4- QA/QC & Reporting	Last 3 months of the program		
Project Total	18 months		

*: Since PAH analyzer will be installed inside the station shelter of the expanded network, therefore, the actual field monitoring starting date will depend on the progress of the expanded network, which is currently under the review by the Port staff.



Community-Based Air Toxics Exposure Study
Port of Los Angeles

ID	ⓘ	Task Name	Duration
1		**Phase 1 - Planning**	**67 days**
2	▦	Team Meeting	42 days
3	▦	Develop Detail Work Plan with QA Requirement	20 days
4	▦	Submit Work Plan	1 day
5		Finalize Contracts	25 days
6		Purchase Instruments	42 days
7		**Phase 2 - Installation**	**25 days**
8	▦	Equipment Installation	25 days
9		**Phase 3 - Monitoring**	**261 days**
10	▦	Field Monitoring	261 days
11		**Continuous Reporting**	**281 days**
12	▦	1st Quarter Progress Report	9 days
13	▦	Submit 1st Quarter Report	1 day
14	▦	2nd Qurater Analysis and Report	9 days
15	▦	Submit 2nd Quarter Report	1 day
16	▦	3rd Quarter Analysis and Report	9 days
17	▦	Submit 3rd Quarter Report	1 day
18	▦	4th Quarter Analysis and Report	9 days
19	▦	Submit 4th Quarter Report	1 day
20	▦	1st Quarter Analysis and Report	20 days
21	▦	Submit 1st Quarter Report	1 day
22		**Phase 4 - Final Report**	**45 days**
23	▦	Prepare and Review Final Report to EPA	44 days
24	▦	Submit Final Report	1 day
25	▦	**Project Complete**	1 day

Project: Air Toxic PAH Monitoring Prog
Date: Tue 11/28/06

Task	Progress	Summary	External Tasks
Split	Milestone ◆	Project Summary	External Milestone ◆

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期限

Page 1

Figure 3. Project Schedule Gantt Chart

8. REFERENCES

Desert Research Institute (2006) Standard Operating Procedures for In-Injection Port Thermal Desorption and Subsequent Gas Chromatography/Mass Spectrometry Analysis of Non-Polar Organic Species in Aerosol Filter Samples. DRI-SOP-#2-219.1, June 19, 2006.

Fitz, D.R. (2004) Measurement of Toxic Air Pollutants Coordinated with Tracer Studies: Wilmington Study. Final Report to the California Air Resources Board Under Contract 00-720, August 2004.

Fitz, D. R., A.M. Winer and S. Colome (2004) Characterizing the Range of Children's Exposure During School Bus Commutes. Report to the California Air Resources Board under Contract 00-322, April 2004.

Port of Los Angeles, (2005) Port of Los Angeles Air Quality Monitoring Program Monitoring Protocol, prepared by SAIC.

U.S. Environmental Protection Agency (1978) Screening Procedures for Ambient Air Quality Data. Document EPA-450/2-78-037. Office of Air Quality Planning and Standards, Research Triangle Park NC 27711.

U.S. Environmental Protection Agency (1980) Validation of Air Monitoring Data. Document EPA-600/4-80-030. Environmental Monitoring and Support Laboratory, Research Triangle Park, NC.

U.S. Environmental Protection Agency (1984): Quality Assurance Handbook for Air Pollution Monitoring Systems: Volume I, Principles, Document EPA-600/9-76-005, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.

U.S. Environmental Protection Agency (1987): Quality Assurance Handbook for Air Pollution Monitoring Systems: Volume II, Ambient Air Specific Methods, Document EPA-600/4-77-027a, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.

U.S. Environmental Protection Agency (2001): Quality Assurance Guidance Document – Quality Assurance Project Plan for the Air Toxics Monitoring Program. Document EPA-454/R-01-007, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

User's Guide – Real-Time PAH Monitor PAS-2000, EcoChem Analytics, Version 2. 1998.

QUALITY ASSURANCE PROJECT PLAN

THE PORT OF LOS ANGELES

Quality Assurance Project Plan
for
The Port of Los Angeles Community-Based Air Toxics Exposure Study

Contract No.: XA-96963101-0

City of Los Angeles
Harbor Department
Environmental Management Division
The Port of Los Angeles
November 28, 2006
Revised April 25, 2007

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1.0 QA Project Plan Identification and Approval

Title: *Port of Los Angeles Community-Based Air Toxics Exposure Study*

The attached QAPP for the Air Toxics Exposure Study is hereby recommended for approval and commits the Division to follow the elements described within.

Environmental Management Division

1) Signature: Paul ______ Date: 4/30/07
Mr. Paul Johansen – Assistant Director, Principle Investigator

2) Signature: ______ Date: 4/30/07
Mr. Christopher Patton, Environmental Affairs Officer

3) Signature: ______ Date: 4/30/2007
Ms. Lisa Wunder – Environmental Specialist, Project Manager

U.S. Environmental Protection Agency, Region 9

4) Signature: ______ Date: 5/15/2007
Mr. Sean Hogan – Air Division/Technical Support Office, Manager

5) Signature: Eugenia McNaughton Date: 5/16/07
Dr. Eugenia McNaughton, - Management and Technical Services Division
/Quality Assurance Office, Manager

2.0 Table of Contents

C. Assessment and Corrective Action

3.0 Distribution

A hardcopy of this QAPP has been distributed to the individuals in Table 3-1.

Table 3-1. Distribution List

Name	**Title**	**Organization**
	Port of Los Angeles	
Paul Johansen	Assistant Director	Environmental Management
Christopher Patton	Environmental Affair Officer	Environmental Management
Lisa Wunder	Environmental Specialist	Environmental Management
	Tetra Tech, Inc.	
Dr. Eddy Huang	Director	Air Quality Group
Dr. Charng-Ching Lin	Principal Scientist	Air Quality Group
	University of California Riverside / College of Engineering - Center for Environmental Research and Technology	
Dennis Fitz	Manager	Atmospheric Processes
	Science Application International Corporation (SAIC)	
Dr. Gary E. Bertolin	Senior Air Quality Specialist	

4. Project Organization/ Roles and Responsibilities

The proposed POLA team organization is shown in Figure 4-1, including the specialties for key technical personnel and service areas anticipated from the subcontractors.

Mr. Paul Johansen, Assistant Director of Environmental Management, will be responsible for the successful execution of this project, both technically and financially. He will represent the Port and provide technical and regulatory liaison. Mr. Johansen will regularly interface with the U.S. Environmental Protection Agency's (EPA) Contract Administrator regarding all project-related issues and the Port's team performance to ensure that all work performed adheres to the approved schedule and budget while meeting the EPA's highest expectations.

Environmental Affair Officer: Mr. Christopher Patton, Officer of Environmental Management (EM), will be responsible for the day-to-day project supervision, overseeing Project and Task Managers, and ensuring project quality. Mr. Patton will provide guidance to the Project Manager on all project-related activities.

Project Manager: The Project Manager (PM), Lisa Wunder, Environmental Specialist of Environmental Management, will be responsible for the day-to-day planning and execution of project activities, performing cost estimates and budget control for assigned tasks, overseeing Task Managers, and ensuring quality and timeliness of all assignments. Ms. Wunder will maintain close communications with the EPA Contract Administrator on all project activities through routine project meetings and monthly progress reports.

Scientific Advisor: Tetra Tech, Inc. and the University of Riverside, College of Engineering - Center for Environmental Research and Technology (UCR CE-CERT) will provide technical support for this project. Specifically, Mr. Dennis Fitz of UCR-CERT, will serve as the Scientific Advisor. Mr. Fitz brings 27 years of experience directing air quality improvement and research programs nationwide. He is presently serving as Manager of the Air Monitoring Group at the University of California, Riverside.

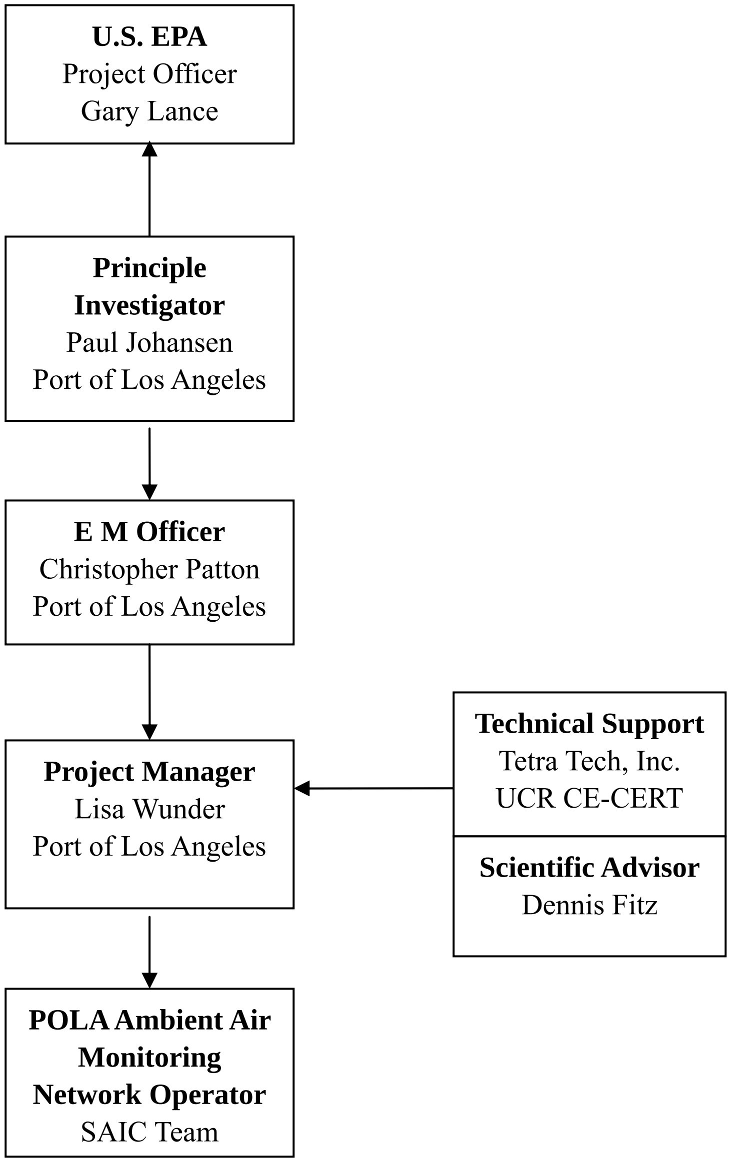

Figure 4-1. Project organization for Port of Los Angeles Community-Based Air Toxics Exposure Study

5. Background

5.1 Project Background

The Port is one of the busiest seaports on the west coast of the United States. The Port has more than 3,000 vessel calls and moves more than $100 billion dollars worth of goods annually. The infrastructure that requires moving goods throughout the region and to other areas in the nation includes many diesel-powered mobile sources. The Port's activity has increased significantly in recent years due to the tremendous economic growth and trade in the Pacific Rim areas. As a result, air emissions from Port's predominately diesel-powered equipment has also increased.

California Air Resources Board (ARB) has identified diesel particulate matter (DPM) as a toxic air contaminant because of its known carcinogenic properties. U.S. Environmental Protection Agency (EPA) also lists diesel exhaust as a mobile source air toxic among 33 air pollutants in the National-Scale Air Toxics Assessment. South Coast Air Quality Management District (SCAQMD) conducted three urban air toxics monitoring programs in the South Coast Air Basin in the last two decades, the Multiple Air Toxics Exposure Study-I (or MATES-I) in 1986, MATES-II in 1998 and MATES-III in 2004 (on going) to assess potential adverse health effects by exposure to air toxics (including DPM). DPM health risks were estimated using California EPA risk factors for DPM and elemental carbon (EC) as a surrogate for estimating DPM concentrations.

DPM is a parameter commonly used by regulatory and scientific communities, the general public and various industries to represent particulate emissions from diesel engines. Although DMP cannot be measured specifically in ambient air, EC may be a good surrogate for estimating DPM concentrations, but other sources in addition to diesel exhausts can also contribute to EC concentrations in ambient samples. As a result, the DPM estimation could be biased. Furthermore, from a chemistry standpoint, DPM contains numerous individual chemical species, both organic and inorganic, on the surface of the particle. One group of chemical species in DPM that has significant health implication is poly aromatic hydrocarbons (PAHs). PAHs are byproducts of the combustion of organic matters, such as benz[a]anthrcene, benzo[b]fluoranthene, benzo[k]fluoranthene and chrysene are considered as hazardous air pollutants (HAPs). Many of them are potent carcinogens or mutagens that can be metabolized and become bioactive to attack cell DNA. Table 5-1 provides a list of selected PAHs and DPM, and their unit risk factors.

The Port has taken initiatives to investigate and mitigate air emissions from Port's activities. One of the benchmark studies was the 2001 Port-wide Baseline Air Emission Inventory, in which five major emission categories were identified: ocean going vessels, harbor craft, cargo handling equipment, heavy duty trucks and locomotives. Control measures were proposed for each category to reduce air emissions.

In a continuing effort, the Port implemented the Port-wide Air Quality Monitoring Program to: (1) measure ambient DPM levels in the Port vicinity and adjacent communities; (2) measure the effect of mitigation activities; and (3) validate health risk assessments.

Table 5-1. Selected PAH Pollutants, DPM and Unit Risk Factors

Selected PAH Pollutants and DPM	Unit Risk Factor
Benzo[a]anthracene	1.10E-04
Benzo[b]fluoranthene	1.10E-04
Benzo[k]flouranthene	1.10E-04
Benzo[a]pyrene	1.10E-03
Chryscene	1.10E-05
Dibenz[a,h]anthracene	1.20E-03
Indeno[1,2,3-cd]pyrene	1.10E-04
Diesel particulate matter (CARB)	3.00E-04

The existing Air Quality Monitoring Program has four stations located within the Port's operational region of influence (ROI). The Wilmington station (at the Saints Peter and Paul Elementary School, or SPPS) serves two purposes: (1) a satellite station, and (2) a primary station, because it is located just north of the Port, the wind flow patterns, and because its proximity to the Port community, this area may experience elevated pollutant concentrations from Port emissions. The first two satellite stations are located in the two adjacent communities, one in Wilmington (SPPS) to the north and the second one in San Pedro (on the Liberty Hill Plaza building or LHP). The third satellite station, a "coastal boundary" station is located at Berth 47 of the Port and the last satellite station, a "source-dominated" station is located on Terminal Island, near the center of Port operations during onshore wind flows.

Air monitoring site selection and development of the air monitoring protocol were developed by the Port staff and their consultants. In consideration of public and regulatory interest in the air quality issues in the Port, concurrence was obtained from SCAQMD and ARB on the protocols and parameters to be measured. In addition, the Port staff also worked with the air quality subcommittee of the Port Community Advisory Committee (PCAC), in the protocol development process to address local community concerns. This unique approach provides an opportunity to address concerns and incorporate input from regulatory agencies and local communities during the development process, and to validate the creditability of the monitoring program. The Port conducted surveys, evaluations and pilot studies prior to initiating the actual monitoring study.

The existing program collects representative ambient particulate matter (PM) and meteorological data within the Port ROI for an initial period of one year (starting February 2005). This special study program collects filter samples of PM less than 10 microns in diameter (PM_{10}) and PM less than 2.5 microns in diameter ($PM_{2.5}$) to determine ambient levels and chemical composition of these pollutants within the Port ROI [1]. Chemical analyses of filters include elemental analysis by X-ray diffraction, ionic species by water extraction and ion chromatography, elemental carbon (EC) and organic carbon (OC) by

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[1] Port of Los Angeles, (2005) Port of Los Angeles Air Quality Monitoring Program Monitoring Protocol, prepared by SAIC.

thermal/optical reflectance method. Table 5-2 lists the parameters measured and sampling frequency at each station.

The network is operated by Science Applications International Corporation (SAIC) under a contract to the POLA. The network also measures chemical compositions of selected filter samples for source apportionment study by a subcontract to Desert Research Institute (DRI). The POLA is in the process of expanding the monitoring capabilities of the existing network to include measurements of gaseous criteria pollutants, such as sulfur dioxide, nitrogen oxides, carbon monoxide and ozone; and, real-time PM ($PM_{2.5}$ and PM_{10}). With a *Community-based Air Toxics Exposure Study* grant provided by the U.S. EPA, the Port will enhance the existing Port-wide air quality monitoring study by deploying real-time PAH analyzers to measure particle-bound PAHs on a quasi-real time basis. This enhancement will provide chemical class specificity in the collected sample as well as better temporal resolution. The measurement results will be used to characterize emission sources and potential ambient air quality impacts by diesel particulate emissions from the Port's operations. From a health risk assessment perspective, direct measurement of particle-bound PAH will provide a better understanding of potential health effects from diesel exhaust than using elemental carbon as a surrogate for estimating DPM concentration in health risk assessment. If needed, selective filter samples will be analyzed for individual PAHs and the data will be used to investigate the potential correlation with real-time PAH data for the same monitoring time period.

A good example of the application of a PAH analyzer occurred in a study of Children's Pollutant Exposure During School Bus Commutes[2], where the researchers measured concentrations of diesel vehicle-related pollutants, such as black carbon and particulate bound PAHs using an EcoChem Analytics PAS 2000 analyzer to measure real-time PAHs. The real-time PAH analyzer uses an ultra violet (UV) lamp to ionize PAH-coated aerosols and measures charge change with an electrometer. Furthermore, the result from the recent completed Wilmington Measurement Study showed that the PAH measurement by real-time analyzer correlated well with a real time absorption method that uses the Magee Scientific Aethelometer to measure EC. Table 5-2 shows the components of the expanded Port-wide Air Monitoring Program (including air toxics monitoring). Figure 5-1 illustrates locations of the Port air monitoring stations.

Normally, PAH in an air sample is analyzed by extraction of 24-hour integrated filter sample and identified by liquid or gas chromatography/mass spectrometry analysis. It is a time-consuming, elaborate and expensive process. Therefore, very few PAH samplings and analyses were performed in large-scale air toxics monitoring programs except for special studies. On the other hand, although only gross particle-bound PAH could be measured by the PAH analyzer, the direct PAH and real time measurement does provide unique insights of emission characteristics as compared to traditional analytical scheme. This enhancement also will complement monitoring data collected at MATES-III stations near the Port to validate health risk assessment results.

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[2] Fitz, D. R. (2004) Measurement of Toxic Air Pollutants Coordinated with Tracer Studies: Wilmington Study. Final Report to the California Air Resources Board under Contract 00-720, August 2004; and, Fitz, D.M., A.M. Winer and S. Colome (2004) Characterizing the Range of Children's Exposure During School Bus Commutes. Report to the California Air Resources Board under Contract 00-322, April 2004.

In summary, in this project selected filter samples will be analyzed using the DRI's Thermal Desorption and Gas Chromatography-Mass Spectrometry (TD/GC-MS)[3] method for their chemical compositions in addition to the real-time PAH measurements for comparison study.

5.2 List of Pollutant

The air toxic pollutants to be monitored in the program are particle-bound PAHs. The real-time PAH analyzer can measure photo-electrically ionized PAHs absorbed on the surface of aerosol particle. The PAH analyzer will not be able to differentiate individual PAHs, only gross particle-bounded PAHs will be measured.

Table 5-2. Components of the Expanded Port-wide Air Monitoring Program Including Air Toxics (PAHs) Monitoring

Monitoring Station	Parameter Measured	Monitoring Method	Sampling Frequency	Analysis
Primary Station (Wilmington-SPPS)	$PM_{2.5}$	Federal reference method (Rupprecht & Patashnick [R&P] Partisol 2000 Sampler)	24-hr average, every third day	Mass
	PM_{10}	Federal reference method (R&P Partisol 2000 Sampler)		Mass
	Meteorological Parameters	Meteorological Stations	Continuous	None
	Particle-Bound PAH Analyzer	EcoChem PAS 2000	Continuous	Concentration
	SO_2, NO_x, CO, O_3	TEI Analyzers	Continuous	Concentration
Satellite Stations (Wilmington-SPSS, San Pedro-LHP, Berth 47 and Terminal Island)	$PM_{2.5}$	Desert Research Institute (DRI) Sequential Filter Sampler (SFS)	Onshore and offshore flows	Mass, EC/OC, elemental and ionic species
	$PM_{2.5}$	DRI SFS	24-hr average, every third day	Mass, EC/OC, elemental and ionic species
	$PM_{2.5}$	TSI 8520 - Dust Trak Monitor	5-min, coincide with SFS 24-hr sampling frequency	Mass
	Meteorological Parameters (Wind speed, wind direction, temperature)	Meteorological Stations	Continuous	None
	Particle-Bound PAH Analyzer	EcoChem PAS 2000	Continuous	Concentration
	SO_2, NO_x, CO, O_3	TEI Analyzers	Continuous	Concentration

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[3] Desert Research Institute (2006) Standard Operating Procedures for In-Injection Port Thermal Desorption and Subsequent Gas Chromatography/Mass Spectrometry Analysis of Non-Polar Organic Species in Aerosol Filter Samples. DRI-SOP-#2-219.1, June 19, 2006.

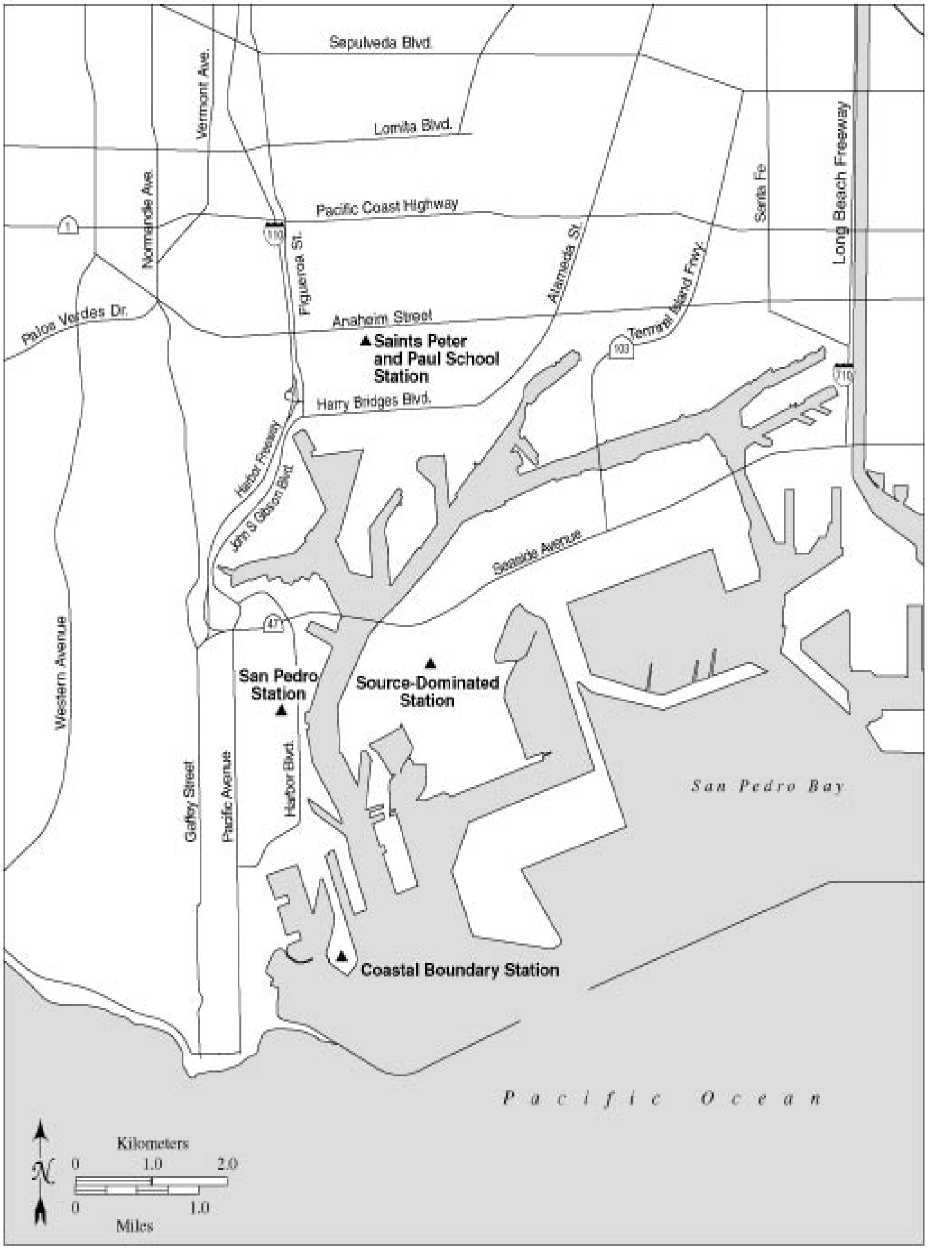


Figure 5-1. Locations of POLA Air Monitoring Stations.

6. Project Description

The addition of PAH analyzers to the four existing air monitoring stations to measure real-time particle-bound PAHs will elevate the effectiveness of the existing Port-wide Air Quality Monitoring Network Program to a Community-based Air Toxics Exposure Program. Data from real-time PAH measurements along with meteorological data, and particulate mass and chemical measurements obtained from the existing Port-wide air monitoring network will be used to:

(1) characterize emission sources,
(2) to determine potential ambient air quality impacts by air emissions from the Port's operations, and
(3) to validate health risk assessments using results from direct ambient PAH measurements.

Since the parameter of the monitored area is limited to community scale, results from the program will impose direct benefits to the local communities.

As previously presented, the Port initiated a Port-wide monitoring study and built a network consisting of four ambient air quality monitoring stations in response to regulatory agency and local community concerns about potential adverse environmental and health impacts from air emissions generated from the Port's daily operations. However, the existing stations do not have the capability of directly monitoring PAHs.

The Community-based Air Toxic Exposure Study will enhance the existing network by expanding the measurement capability of its monitoring stations. All four stations will be upgraded with the PAS analyzers. The real time PAH data will be used with meteorological data and measurement data from existing stations to facilitate the assessment of ambient air quality impacts, to characterize and identify emission sources, and to improve and validate results of health risk assessment.

6.1 Project Scope

Scope of work of the POLA Community-Based Air Toxics Exposure Study includes:

(1) Procurement of PAH Analyzers
(2) Installation and Start-up
(3) Field Monitoring
(4) Data Reduction and Management
(5) Data Analysis and Reporting

6.2 Field Activities

The field operation of PAH analyzer is rather straight-forward and requires minimal supervision and maintenance because the instrument has very few moving parts. Field measurement is continuous throughout the project period.

6.3 Project Schedule

Table 6-1 lists the critical activities required to plan, implement, and assess the air toxics program.

Table 6-1. Schedule of Critical Air Toxics Activities

Phase	**Activities**	**Due Date**	**Comments**
Planning	Team meetings	2 months after grant is awarded	Kick off meeting Coordination with the existing network operator
	Development of detailed work plan including QA requirements		
	Purchase instruments from manufacturer		
	Monitoring sites are upgraded with tested, calibrated and operational gaseous pollutant analyzers		
Installation	Install PAS analyzers at four stations	1 month after the shelter are erected *	
Monitoring	Routine sampling begins	For the following 12 months after monitoring locations are in operation	Routine field activity starts
*: Since PAH analyzer will be installed inside the station shelter of the expanded network, therefore, the actual field monitoring starting date will depend on the progress of the expanded network, which is currently under the review by the Port staff.			

7. Quality Objectives and Criteria for Measurement Data

7.1 Data Quality Objectives

Table 7-1 shows the data quality objectives and acceptance criteria for the measurements to be made in this project.

Table 7-1. Data quality objectives.

Measurement	Concentration Range Expected	Completeness	Accuracy	Precision	Detection Limit*
PAH	0-100 ng/m^3	90%	±10%	10%	3 ng/m^3

* One-minute time constant

7.2 Measurement Quality Objectives

Completeness will be calculated based on the number of hours of data planned.

Precision will be determined from collocated measurements.

Accuracy will be determined by comparison with a transfer standard (a separate PAH analyzer), similar to the process of comparing the ozone transfer standard with a station ozone analyzer.

8. Documentation and Records

The project team will establish and maintain procedures for the timely preparation, review, approval, use, control, revision, and maintenance of documents and records.

Critical documents and records for this project are listed in Table 8-1.

Table 8-1. Critical Documents and Records.

Categories	Record/Document Types
Management and Organization	Project Organizational Structure
Site Information	Existing PM Network Description
	Expanded Air Monitoring Network Description
	Site Selection Procedures
	Site Maps and Pictures
Environmental Data Operations	Quality Assurance Project Plan
	Field Logbooks
	Weekly Check Records
	Inspection and Maintenance Records
Raw Data	Original Data Entry (Including QC data)
	Electronic Deliveries of Summary Measurement Results
Data Reporting	Monitoring Data and Summary Reports
Data Management	Data Algorithms
	Data Management Procedures
	Air Toxics (i.e., Ambient Particle-bound PAHs) Data
Quality Assurance	Data Quality Assessments
	QA Audit Reports (i.e., Flow Checks)
	Response or Corrective Action Reports

B. Measurement / Data Acquisition

9. Site Selection

This project is to expand the existing POLA air monitoring network capability by installing real-time PAH analyzer (EcoChem PAS 2000) at existing stations. No site selection for PAH monitoring is performed.

Please refer to Section 5 – Background for details of the existing air monitoring station locations and measurement parameters.

10. Sampling Method

EcoChem Model PAS 2000 analyzers (EcoChem Analytics, League City, Texas) will be used to measure the concentrations of particle-bound PAHs. The instrument uses the principle of photoionization of total particle-bound PAH by means of an ultraviolet lamp. The wavelength of the light is selected such that only the PAH absorbed on aerosols are ionized, while gas molecules and non-carbon aerosols remain neutral. The aerosol particles that have PAH molecules adsorbed on the surface emit electrons, which are subsequently removed when an electric field was applied. Remaining positively charged particles are collected on a filter inside an electrometer where the charge is measured. The resulting electric current established a signal that is proportional to the concentration of total particle-bound PAH. The specifications state that the lower threshold of this method is about 3 ng/m^3 total particle-bound PAH and the response time is less than ten seconds. The operation is a real-time measurement depending on cycle time interval selected (i.e., in seconds), then the data is processed internally and can be displayed as minute-average values. Process schematic for the Photoelectric Aerosol Sensor (PAS) is illustrated in Figure 10-1.

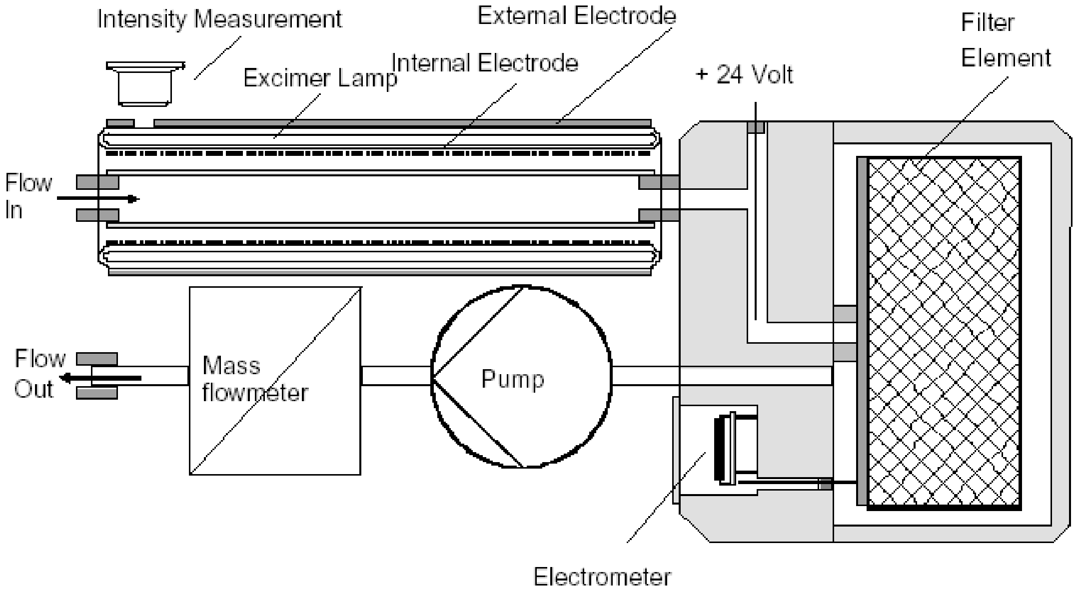


Figure 10-1. Process Schematic for the Photoelectric Aerosol Sensor. (source: PAS 2000 User's Guide)

11. Quality Control Requirements

11.1 Quality Control

Since calibration standards do not exist for the PAH analyzers the comparability of the analyzers will be determined before and after field deployment by collocated sampling of ambient air. This will be done for a week or more before and after field deployment to evaluate the analyzers. The one-minute data will be plotted and a least squares regression will be performed to determine bias from the slope. If less than 10% of the measurements are less than ten times the detection limit the site will be relocated and additional collocated sampling will be performed. Since accuracy cannot be established, bias will be used as the accuracy goal. Accuracy will be determined using a transfer standard on a quarterly basis. If the discrepancy, i.e., 20%, is observed over an hour of measurements between the transfer standard and the on-site analyzer, a more comprehensive evaluation will be conducted to investigate probable causes of the discrepancy, corrective action will be taken. If the bias exceeds the accuracy goal presented in Table 7-1 Data Quality Objectives, the least squares regression will be used to normalize the data to an instrument to be designated as a reference.

11.2 Weekly Check

Weekly check of the analyzers will be performed to assure the instrument is operating according to specifications. Lamp intensity and analyzer frequency will be checked weekly. The time of the individual instruments, if recorded, will be compared with data logger time as a part of the weekly site checks. Table 11-1 lists the example of weekly check record.

11.3 Quality Assurance Audit

Quality assurance audit of PAH analyzers will be performed within the first two weeks of sampling by UCR-CERT. The flows of the PAH analyzers will be audited. A final audit will also be conducted at the conclusion of monitoring period to assure the accuracy of the analyzers.

Table 11-1. Weekly Check List

Weekly Checklist - Port of Los Angeles Community-Based Air Toxics Exposure Study				
Site(number or description):				
Date:				
Sampler# (1-4)				
Technician:				
Time: Data logger: Instrument (if recorded)				
Site Secure (y/n)				
Sampling Lines Located Properly? (y/n)				
PAH Analyzer Flow Rate (1.5-2.5 lpm):				
PAH analyzer Intensity.(>98)				
PAH Analyzer Frequency (<15)				
5min PAH Zero Check on/off Time (hh/mm PST)	/	/	/	/
Comments				

12. Instrument Inspection, Testing and Maintenance

12.1 Instrument Inspection

After the receipt of the procured equipment, an inspection will be performed to assure the instrument integrity not damaged by the shipping.

12.2 Instrument Testing

The instrument will be tested for functionality according to the recommended procedures as stated in the user's manual. The testing will be performed after the power supply and gas inlet connections are completed. Testing will be observed using the front control panel. The control panel is a manual-driven screen where operating parameters such as sampling time intervals, operating mode, etc. will be keyed in and the instrument responses will be observed.

12.3 Maintenance

The PAS analyzer is a low maintenance instrument. However, when the exciter lamp intensity falls below manufacturer's recommended value, the old lamp will be removed and a new lamp will be installed.

13. Instrument Calibration and Frequency

13.1 PAH Analyzer

The response of PAH analyzer is calibrated at the factory. The instrument is not designed to be directly calibrated in the field and no calibration standards are available. To ensure acceptable operation, instrument flow rates and zero air response will be checked on a weekly basis. The instruments will also be operated during collocation runs to assess their bias as described above. This collocation test will also be considered a key factor in acceptance testing of the PAH analyzers that will be purchased by project funds. Lamp intensity and analyzer frequency will be checked weekly. The time of the individual instruments, if recorded, will be compared with data logger time as a part of the weekly site checks. Precision will be determined from the weekly zero check.

14. Data Acquisition

Measurement data will be automatically collected and stored digitally on an Environmental Monitoring Company, Inc. (EMC) Station Manager data logger, as part of the expanded network, residing in the shelter. The data logger will collect data once per second and store data as one-minute averages. This was chosen as the analyzers used operate on time constants of approximately one minute. The stored data will be transmitted wirelessly to the network operator headquarter. An electronic copy of the transmitted data will be provided to the project team on a regular basis for review and analysis. Data will be downloaded to a PC as one-minute averages and converted to EXCEL spreadsheets for data reduction and analysis.

15. Data Management, Review and Validation

This section addresses data management procedures used in support of the Air Quality Program. Specific details of data recording, processing, validation, assessment, transmittal, reporting, archiving and retrieval are discussed in the following sections.

15.1 Data Recording

Air monitoring station reports will be prepared by the Station Operators and revised when changes in the instrumentation or surrounding area occur. These reports will identify the station name, station number, date, time, operator, instrument identification, parameter, scale and units. Additionally, the report will document the station location, address, and probe location. These reports will be sent to the project team for review, processing and archiving.

Air monitoring equipment check reports will be prepared and archived by the project team.

The Station Operators will maintain station logbooks documenting operational and maintenance activities at the monitoring site. The logbook will be identified with the station name, station number, date, time, operator, instrument identification, parameter, scale and units. The log book will be used to document quality control checks (time, zero response, sample flow, shelter temperature, pressure, etc.), maintenance, audits, equipment changes, and missing or invalid data. The logbooks will be reviewed and archived by the project team.

15.2 Data Processing and Reporting

Data from all PAH analyzers are collected, processed and stored by the station data management computer; and wirelessly transmitted to the operators' headquarter computer. Electronic files from the instrumental data systems are typically transferred to Excel Spreadsheets for tabulation and report preparation.

A final report with all measured data will be submitted to Project Officer for review.

15.3 Data Reduction

Data reduction processes involve aggregating and summarizing results so that they can be understood and interpreted in different ways. The project requires summary data to be computed and reported regularly to U.S. EPA as part of the community air toxics monitoring database.

15.4 Data Validation

Data validation will follow guidelines described by the U.S. EPA documents - Screening Procedures for Ambient Air Quality Data (1978) and Validation of Air Monitoring Data (1980). The validity of the data will be checked as follows: data will not be removed unless there is a good reason or the measurement is physically impossible. All data will be screened for outliers that are not within the physically reasonable (normal) ranges. Next, the following steps will be taken:

1. Data will be flagged when deviations from measurement assumptions have occurred.
2. Computer file entries will be checked for proper date and time.
3. Measurement data resulting from instrument malfunctions will be invalidated.
4. Data will be corrected or normalized for calibrations or biases.

PAH monitoring data will be reviewed as time series plots. Rapidly changing, anomalous or otherwise suspect data will be examined with respect to other available data.

Data processing consists of following steps:

1. Describe measurement scenarios
2. Tabulate information from the logbook and checklists
3. Identify data files, data rates and missing data
4. Add columns/rows to item #3 table to reflect data set time synchronization correction
5. Create merged data files for the tests that include the time synchronization corrections
6. Convert to engineering units and apply calibration factors
7. Level Zero Outlier Screening
8. Compile data at desired averaging interval

Flags will be applied at step eight based on outliers and logbook information in step 3. The data reporting forms will contain a column for flagging and indicating data validity. All problematic and missing data points will be highlighted in the form through the insertion of an appropriate coded flag. Invalidated data will not be placed in the reporting form in order to avoid their possible inadvertent use. Data flags will include the following:

- Valid value
- Valid but comprised wholly or partially of below-MDL data
- Valid but interpolated (value is above the maximum of the instrument)
- Valid despite failing a statistical outlier test
- Valid but qualified because of possible contamination or interference
- Valid but qualified due to non-standard sampling conditions
- Missing value because no data are available
- Missing value because the data were invalidated by the operator

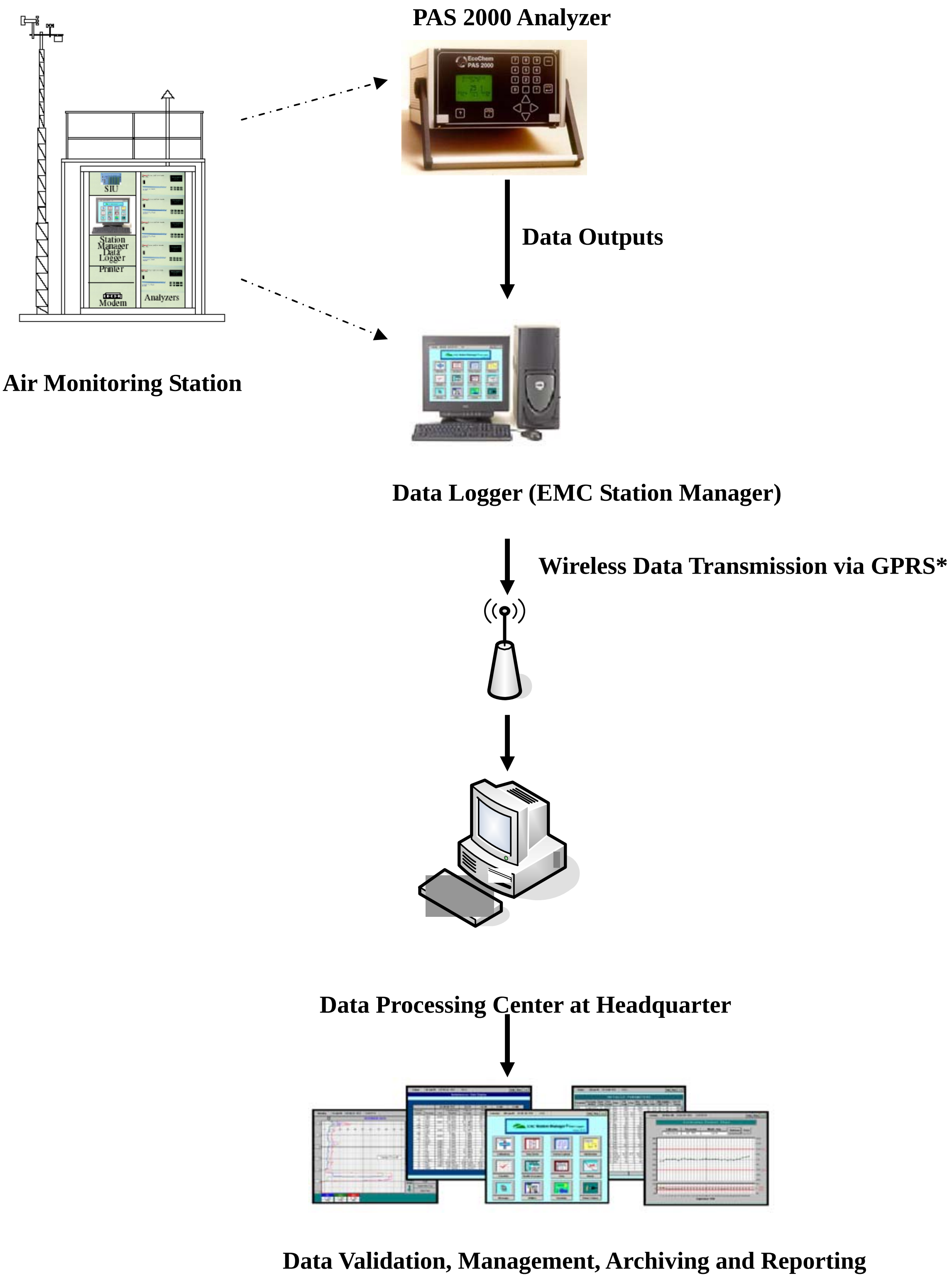
The data will be checked for internal consistency, consistency with operator logbooks, and consistency with calibration zero and span checks, and instrument precision checks. Internal consistency requires that data fall within normal operating ranges and do not exhibit excessive and rapid variations that are inconsistent with expected variations. Consistency with operator logbooks requires that all data acquired during operation, maintenance, instrument versus data logger time, and outage periods be flagged appropriately. All verified data that have been subjected to these tests will be designated as validated data.

15.5 Data Storage and Retrieval

The “raw” data files from these instruments will be saved “as is.” Copies of the raw data files will be used for subsequent processing steps to obtain “preliminary” and “final” data (i.e., the “original” data will be preserved for potential future use and reference should there be any questions regarding the final data or for use should either the preliminary or final data files become lost or corrupted). All PCs for data processing will be automatically backed up at a minimum of once per week.

This PC will be backed up on a regular basis, i.e., monthly. The time of the individual instruments, if recorded, will be compared with data logger time as a part of the weekly site checks.

Figure 15-1 illustrates monitoring data flow.



(*: GPRS - General Packet Radio Service, a wireless data service)

C. Assessment and Corrective Actions

16. Assessment and Corrective Actions

16.1 Assessment

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

The assessment of analyzer performance will be conducted by performing weekly check, sample flow audit, and collocated analyzer comparison study.

16.2 Corrective Actions

Corrective action will be initiated whenever a problem is identified, which may occur during daily data review or weekly site checks. The goal of corrective action is to remedy any problem before the project or equipment and/or parameters drop below the desired accuracy, precision, or completeness.

To minimize the need to take corrective action, all equipment to be used on this program will be serviced prior to field use. Once a problem has been identified, the person who found it will either fix it on-site or request the project manager’s assistance.

17. Report to Management

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.

Quality assessment, including the evaluation of the technical systems, the measurement of performance, and the assessment of data, is conducted to help insure that measurement results meet program objectives and to insure that necessary corrective actions are taken early, when they will be most effective.

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

(1) Adherence to scheduled delivery of data and reports;
(2) Documentation of deviations from approved QA and test plans, and the impact of these deviations on data quality; and
(3) Analysis of the potential uncertainties in decisions based on the data.

Weekly check records and station inspection log book will be reviewed on a regular basis by the project team to assure the quality assurance activities are implemented.

Monthly reports and quarterly reports containing monitoring activity, data summary and related quality control and quality assurance records will be compiled and submitted to the Project Officer.

18. Reconciliation with Data Quality Objectives

As discussed earlier, since accuracy of the instrument cannot be physically established, bias will be used as the accuracy goal. If the bias exceeds the accuracy goal presented in Table 7-1, the least squares regression will be used to normalize the data to an instrument to be designated as a reference.

1. ***Desert Research Institute (2006) Standard Operating Procedures for In-Injection Port Thermal Desorption and Subsequent Gas Chromatography/Mass Spectrometry Analysis of Non-Polar Organic Species in Aerosol Filter Samples. DRI-SOP-#2-219.1, June 19, 2006***

2. ***Port of Los Angeles, (2005) Port of Los Angeles Air Quality Monitoring Program Monitoring Protocol***

DRI STANDARD OPERATING PROCEDURE

In-Injection Port Thermal Desorption and Subsequent Gas Chromatography/Mass Spectrometry Analysis of Non-Polar Organic Species in Aerosol Filter Samples

DRI SOP #2-219.1
Revised 19th June 2006

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1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This standard operating procedure is intended to:

- Provide a basic understanding of the principles of in-injection port thermal desorption (TD)- Gas Chromatography/Mass Spectrometry (GC/MS) analysis and GC/MS operation;
- Describe routine determination of non-polar organic compounds using GC/MS system; and
- Detail the concerns and procedures which will ensure a state-of-the-art organic speciation measurement process.

This procedure will be followed by all analysts at the Environmental Analysis Facility of the Division of Atmospheric Sciences of the Desert Research Institute (DRI), Reno, Nevada, USA.

1.2 Measurement Principle

This method describes the qualitative and quantitative analysis of non-polar organic compounds on aerosol loaded filters. The target compounds include *n*-alkanes, iso/anteiso-alkanes, hopanes, steranes, phthalates, other alkanes, alkenes, cyclohexanes, and polycyclic aromatic hydrocarbons (PAHs). Small strips of aerosol-laden filter materials are packed into a gas chromatography (GC) split/splitless injector liner. The organic compounds on the filter are thermally desorbed in the injection port and focused onto the head of a GC column for subsequent separation and mass spectrometric detection. No instrument modification is necessary to accommodate the introduction of the aerosol organics into the GC/MS system. In comparison with the traditional solvent extraction method, this in-injection port TD has the unique advantages of reduced labor and time by avoiding sample pretreatment and requiring less filter material for analysis (Ho and Yu, 2004).

1.3 Measurement Interferences and Their Minimization

The TD-GC/MS method minimizes the use of solvents for extraction of organic compounds on the filters.

Thus it avoids impurities introduced from solvents. Less time-intensive and simple sample preparation steps also lower the probability to have contamination and analytes loss.

Possible trace amount of organic compounds would be thermally decomposed and desorbed from the injector materials after used for a period of time, i.e. septa and O-ring. These consumables must be replaced according to the maintenance schedule. All tools and apparatus used to handle, transfer, and store the samples must be kept clean. The highest grade of materials and reagents should be used. All glassware used in the experiment must be baked at 550 ^{o}C before use.

1.4 Ranges and Typical Values of Measurements

The sample loading of the TD method is limited by the column capacity and the acceptance level of the MS detector. Hays et al. (2003) found the optimum sample loading is in a range of 7 to 283 µg. Overloading may cause poor separation that directly affects the quantification of peak areas, especially for compounds with similar physical and chemical properties (i.e., molecular isomers) that have similar retention times (RT) in the chromatogram. Too many analytes passing through the ion source may lead over-charge the filaments during ionization and cause the malfunction of the MS detector.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The Lower Quantifiable Limits (LQLs) of the method are defined as the minimum amounts of non-polar organic compounds that generate the minimum distinguishable signals plus three times the standard deviation of the blank signals. No peaks were detected for the target compounds in the blank calibration samples. As a result, we approximate the mean blank signal with the calibration line intercept and the blank signal standard deviation with the standard error for the y (peak area ratio) estimate (Miller and Miller, 1993). By this approach, the LQLs in nanograms per sample were calculated (Tables 1-1).

The method accuracy and precision are described in Section 3.3 and Section 6.2, respectively.

Table 1-1. The Lower Quantifiable Limits (LQLs) of PAHs, Phthalates, Alkanes, Alkenes, Hopanes, and Steranes Using the Thermal Desorption Method.

Compounds	LQL (ng)	LQL (ng/m^3)[a]	Compounds	LQL (ng)	LQL (ng/m^3)[a]
PAHs			**Alkanes**		
acenaphthylene	2.34	0.083	***n*-Alkanes (*n*-C14 to *n*-C44)**		
acenapthene	1.82	0.065	tetradecane (*n*-C14)	1.43	0.051
fluorene	0.88	0.031	pentadecane (*n*-C15)	0.86	0.031
phenanthrene	0.42	0.015	hexadecane (*n*-C16)	0.89	0.032
anthracene	0.17	0.006	heptadecane (*n*-C17)	0.76	0.027
fluoranthene	0.25	0.009	octadecane (*n*-C18)	0.66	0.024
pyrene	0.40	0.014	nonadecane (*n*-C19)	0.51	0.018
chrysene	0.40	0.014	icosane (*n*-C20)	0.51	0.018
benzo[b]fluoranthene	0.82	0.029	heneicosane (*n*-C21)	0.85	0.030
benzo[k]fluoranthene	0.28	0.010	docosane (*n*-C22)	0.64	0.023
benzo[a]pyrene	0.90	0.032	tricosane (*n*-C23)	0.74	0.026
perylene	0.97	0.034	tetracosane (*n*-C24)	0.55	0.020
indeno[1,2,3-cd]pyrene	0.42	0.015	pentacosane (*n*-C25)	0.59	0.021
dibenzo[a,h]anthracene	0.94	0.033	hexacosane (*n*-C26)	0.59	0.021
benzo[ghi]perylene	0.62	0.022	heptacosane (*n*-C27)	0.29	0.010
coronene	0.73	0.026	octacosane (*n*-C28)	0.73	0.026
dibenzo[a,e]pyrene	0.28	0.010	triacontane (*n*-C30)	0.96	0.034
			hentriacotane (*n*-C31)	0.78	0.028
1-methylnaphthalene	0.45	0.016	dotriacontane (*n*-C32)	0.90	0.032
2-methylnaphthalene	0.15	0.005	tritriactotane (*n*-C33)	0.57	0.020
2,6-dimethylnaphthalene	0.87	0.031	tetratriactoane (*n*-C34)	0.67	0.024
9-fluorenone	0.98	0.035	hexatriacontane (*n*-C36)	0.86	0.031
9-methylanthracene	0.91	0.032	tetracontane (*n*-C40)	0.84	0.030
anthroquinone	0.48	0.017	**Methyl-alkanes**		
1,8-napthalic anhydride	0.86	0.031	2-methylnonadecane	0.88	0.031
methylfluoranthene	0.28	0.010	3-methylnonadecane	0.94	0.034
retene	1.21	0.043	**Branched-alkanes**		

cyclopenta[cd]pyrene	0.28	0.010	pristine	0.99	0.035
benz[a]anthracene-7,12-dione	1.02	0.036	phytane	0.99	0.035
methylchrysene	0.42	0.015	squalane	1.00	0.035
			Cyclohexanes		
Phthalates			octylcyclohexane	0.94	0.033
dimethylphthalate	0.57	0.020	decylcyclohexane	0.70	0.025
diethyl phthalate	0.87	0.031	tridecylcyclohexane	1.32	0.047
di-n-butyl phthalate	0.46	0.016	*n*-heptadecylcyclohexane	0.84	0.030
butyl benzyl phthalate	0.86	0.031	nonadecylcyclohexane	0.70	0.025
bis(2-ethylhexyl)phthalate	0.75	0.027			
di-n-octyl phthalate	0.85	0.030	**Alkenes**		
			squalene	0.57	0.020
			1-octadecene	0.80	0.028

Table 1-1. (Con't) The Lower Quantifiable Limits (LQLs) of PAHs, Phthalates, Alkanes, Alkenes, Hopanes, and Steranes Using the Thermal Desorption Method.

Compounds	LQL (ng)	LQL (ng/m^3) [a]	Compounds	LQL (ng)	LQL (ng/m^3) [a]
Hopanes			**Steranes**		
22,29,30-trisnorphopane (Tm)	0.51	0.018	ααα 20R-Cholestane	0.25	0.009
αβ-norhopane (C29αβ-hopane)	0.32	0.011	αββ 20R-Cholestane	0.66	0.024
βα -norhopane (C29βα -hopane)	1.38	0.049	αββ 20S 24S-Methylcholestane	0.80	0.028
αβ-hopane (C30αβ-hopane)	1.06	0.038	ααα 20R 24R-Methylcholestane	0.58	0.020
βα-hopane (C30βα-hopane)	1.17	0.041	ααα 20S 24R/S-Ethylcholestane	0.78	0.028
αβS-homohopane (C31αβS-hopane)	0.84	0.030	αββ 20R 24R-Ethylcholestane	0.35	0.012
αβR-homohopane (C31αβR-hopane)	0.83	0.030	ααα 20R 24R-Ethylcholestane	0.37	0.013

[a] Assume a sampled air volume $28.1m^3$; i.e. 24 hr sampling at $0.113m^3$, and $3cm^2$ used in TD-GC/MS analysis

1.6 Personnel Responsibilities

Before performing TD-GC/MS analysis, all analysts in the laboratory should read and understand the entire Standard Operating Procedure (SOP), including routine system calibration, actual analysis, and immediate review of the data as it is produced, in order to correct system problems.

The responsibilities of the laboratory manager or supervisor are: to ensure that the carbon analyses procedures are properly followed; to examine and document all replicate, standard, and blank performance test data; to designate samples for reanalysis; to arrange for maintenance and repair; to maintain the supplies and gases necessary to ensure uninterrupted analysis; and to deliver the analysis results in database format to the project manager within the specified time period.

The quality assurance (QA) officer of DRI's Division of Atmospheric Sciences is responsible for determining the extent and methods of quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, to update this procedure periodically, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Related Procedures

SOPs, related TD-GC/MS analysis activities, and other manuals that should be reviewed in conjunction with this document are:

DRI SOP #6-001.1	Shipping and Mailing Procedures.
DRI SOP #6-009.1	Field and Laboratory Safety Procedures. Any SOPs dealing with filter handling and shipping in conjunction with the specific sampling method used.
DRI SOP #2-106.1	Pre-Firing of Quartz Filters for Carbon Analysis.
-	Agilent GC/MSD Hardware Manuals.

2.0 APPARATUS, INSTRUMENTATION, REAGENT, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The TD analysis is performed by a typical Agilent 6890 GC with a 5973 or 5975 MSD system (Figure 2-1) consists of (1) an splitless/spilt injector port for a Pyrex glass liner with 78 mm long, 4mm I.D., and 6mm O.D.; (2) a temperate-programmed oven for holding stationary phase column; (3) a mass spectrometric detector (MSD) operating at 70eV for electron ionization (EI) mode; (4) foreline and diffusion pumps allowing the system to be operated at a vacuum environment.

2.1.2 Instrument Characterization

The TD step is an integrated part of the analysis. It takes place in the injector port of an Agilent 6890 GC/5793 or 5975 MSD system. The sample-loaded tube is exchanged with the injector liner after the injector temperature is lowered to 50^{o}C. Once the tube is in place inside the injector port, the injector is immediately closed with a septum cap and its temperature is set to 275^{o}C manually. It takes 10.5 minutes for the injector temperature to reach the new setting. During this period, the GC oven temperature is kept at 30^{o}C. Such a temperature condition would focus the aerosol organic analytes released from the injector port on the head of the GC column in a narrow band. The oven temperature program is then started as soon as the injector temperature achieves 275^{o}C. The injector is kept at 275^{o}C and set in the splitless mode throughout the analysis. The GC oven program is initially set at 30°C, held at this temperature for 2 min, programmed at a rate of 10°C min^{-1} to 120°C and 7°C min^{-1} to 310°C, and then held at the final temperature of 310°C for 18 min. An DB-5MS (5% diphenyl / 95 % dimethylsiloxane, 30 m × 0.25 mm × 0.25 μm) is used. The carrier gas is helium held at a constant flow of 1.0 cc min^{-1}. The GC/MS interface temperature is set at 280 ^{o}C. The MSD is operated at 230^{o}C and 70 eV for EI. The mass scan range was from 50 to 650 amu. A new TD tube was used for each analysis, therefore avoiding any potential contamination carry-over to the next analysis. The TD tubes were reused after cleaning of the content and baking.

2.1.3 Maintenance

Common maintenance tasks are listed in Table 2-1. Performing these tasks when scheduled can reduce operating problems, prolong system life, and reduce overall operating costs. Keep a record of maintenance operations performed. This makes it easier to identify variations from normal operation and to take corrective action.

Proper actions should be taken if the GC/MS system indicates any problems. General troubleshooting is listed in Table 2-2. For other unidentified errors, instrument operators should refer to Agilent GC/MS Hardware Manual or contact with the Agilent Technology Service Support. All actions taken or maintenance work must be marked in the instrument logbook and reported to the laboratory manager.

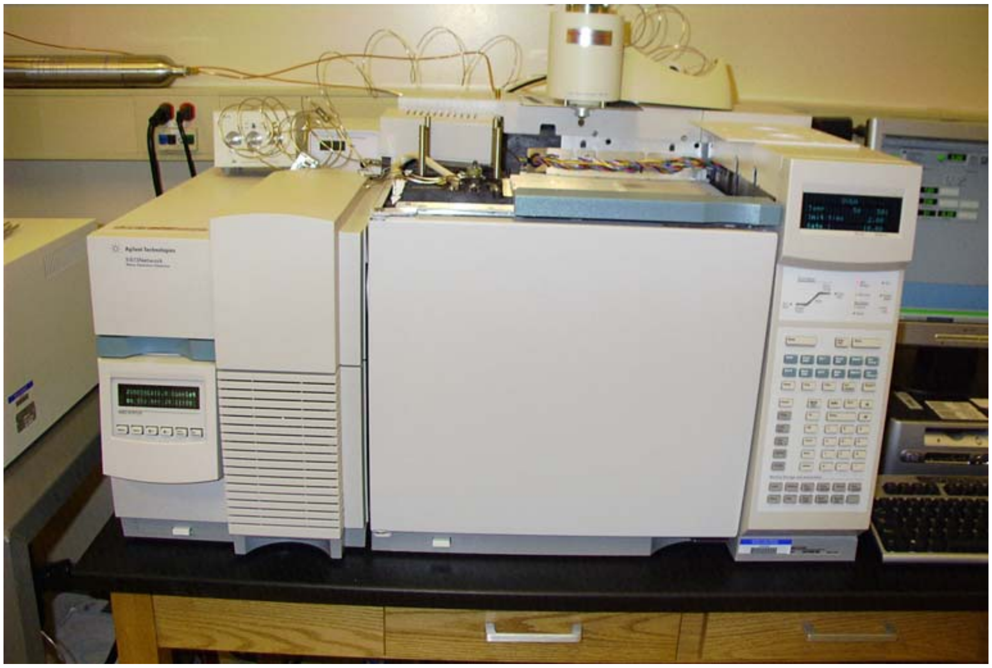


Figure 2-1. Agilent 6890 gas chromatography/ 5973 mass spectrometry System.

Table 2-1. Maintenance Schedule for GC/MS System.

	Every Week	Every 6 months	Every Year	As Needed
Gas Chromatography				
Replace injector septum and O-ring (Section 2.1.3.1)	√			
Replace a GC capillary column (Section 2.1.3.2)				√
Replace injector gold seal and washer (Section 2.1.3.3)				√
Mass Spectrometry				
Check the foreline pump oil level (Section 2.1.3.4)	√			
Replace the foreline pump oil (Section 2.1.3.4)		√		
Check the calibration vial (Section 2.1.3.5)		√		
Replace the diffusion pump fluid (Section 2.1.3.6)			√	
Clean the ion source (Section 2.1.3.7)				√
Tune the MSD (Section 6.1.2)				√

Table 2-2. General Troubleshooting for the GC/MS System.

Problems	Possible Reasons	Actions
No communication between GC/MS and the computer	No power supply to GC/MS	Check electricity
	Server connecting the GCMS with computer is down	Check the server connection Restart the modem and computer
Poor or asymmetric peak shapes	GC column heads are not evenly cut and residues on the column heads	Cut the column heads and reinstall the column (Section 2.1.3.2)
	Separation efficiency of GC column decrease	Change a new GC column (Section 2.1.3.2)
Incorrect mass assignment	Incorrect tuning	Check tune file, retune, check sample
Excessive background and high impurity peaks	Residues retained in the injector port	Change new GC injector O-ring and septum (Section 2.1.3.1) Change golden seal and washer in the injector (Section 2.1.3.3)
	High bleeding or high impurity eluted from the column	Change a new GC column (Section 2.1.3.2)
	Dirty ion source	Clean ion source (Section 2.1.3.7)
	Contaminations from foreline and diffusion pump oils	Change new foreline and diffusion pump oils (Section 2.1.3.4 and 2.1.3.6)
Low or no response during autotune or air and water check	Calibration standard in MSD is low or empty	Fill the calibration vial with standard in the MSD (Section 2.1.3.5)

Large peak widths	Incorrect tuning	Do autotune (Section 6.1.2), check flow rate, and temperature stability
Low signals	Poor vacuum status	Check air and water ratios (Section 6.1.1) Check the foreline and diffusion pumps Check and tighten interface nut, leak test GC injection port
	Dirty ion source	Clean ion source (Section 2.1.3.7)
Fail in air and water check	Poor vacuum status	Check the foreline and diffusion pumps Check and tighten interface nut, leak test GC injection port
	Efficiency of air and water trap decrease	Replace a new air and water trap
Unstable peak areas for calibration standards or IS	Poor GC/MS status	Take all actions listed in above
Fail in autotune	Poor vacuum status	Check the foreline and diffusion pumps Check and tighten interface nut, leak test GC injection port

2.1.3.1 Replace injector septum and O-ring

- Replace injector septum
  - Turn the oven and detector off.
  - Cool the oven and inlet to room temperature.
  - Turn the inlet pressure off.
  - Remove the septum retainer nut, using the wrench if the nut is hot or sticks. Remove the old septum. If the septum sticks, use a sharp tool to remove it. Be sure to get all of it. Take care to avoid gouging or scratching the interior of the septum head.
  - If pieces of the septum are sticking, use a small piece of rolled-up steel wool and forceps or tweezers to scrub the residue from the retainer nut and septum holder. Use compressed air or nitrogen to blow away the pieces of steel wool and septum.
  - Use forceps to insert a new septum. Press it into the fitting firmly. Avoid over-tightening.
  - Restore the GC to normal operating conditions.
- Replace injector O-ring
  - Turn the oven and detector off.
  - Cool the oven and inlet to room temperature.
  - Turn the inlet pressure off.
  - Locate the split/splitless insert nut and loosen it using the wrench if necessary.

  - Lift it straight up to avoid chipping or breaking the liner.

  - Remove the old O-ring and slide a new one onto the liner.

  - Use the forceps to return the liner to the inlet. Replace the insert assembly nut and use the wrench to tighten the nut just to snugness.

  - Restore the GC to normal operating conditions.

2.1.3.2 Replace a GC capillary column

- If the system is on, vent the GC/MS system (see Section 5.5) and allow the automatic venting routine to run its full course. Improper venting may cause diffusion pump fluid to be deposited into the analyzer (backstreaming). It can also reduce the life of the multiplier, or other sensitive MS parts.

- Turn off the oven and detector off.

- Cool the oven and inlet to room temperature.

- Turn the inlet pressure off.

- Open the GC oven front door.

- If an old column is installed, remove the column from the inlet and MSD. Cap the open ends of the column and mark down the information of the old column in the box.

- Before cutting column, place a capillary column nut and ferrule on the column.

- Using a kimwipe moistened with acetone or *iso*-propanol, wipe clean the last 10 cm of the column to remove fingerprints and dust.

- Unwind approximately 30 cm of the column from the column basket.

- Use a GC column cutter with a diamond blade to cut 3 – 5 cm of the column.

- For the end to inlet,

    - Position the column so it extends 4 to 6 mm above the end of the ferrule. Mark the column with typewriter correction fluid at a point even with the column nut.

    - Insert the column in the inlet and slide the nut and ferrule up the column to the inlet base. Finger tightens the column nut until it starts to grab the column.

    - Adjust the column position so that the correction fluid mark on the column is even with the bottom of the column nut.

    - Tighten the column nut an additional 1/4 to 1/2 turn so that the column cannot be pulled from the fitting with gentle pressure.

    - After the column is installed at both inlet and detector, establish a flow of carrier gas through the inlet. Heat the oven, inlet, and detector to operating temperature. Allow them to cool, and then retighten the fittings.

- For the end to GC/MS interface,

    - Adjust the column so it projects 1 to 2 mm past the end of the GC/MSD interface. Use the flashlight and hand lens if necessary to see the end of the column inside the analyzer chamber.

    - Make sure the position of the column does not change by hand tightening the nut.

    - Tighten the nut 1/4 to 1/2 turn and check the tightness after one or two heat cycles.

- Pump down the system (see Section 5.1).

2.1.3.3 Replace gold seal and washer in the injection port

- Vent the GC/MS system (see Section 5.5) and allow the automatic venting routine to run its full course. Improper venting may cause diffusion pump fluid to be deposited into the analyzer (backstreaming). It can also reduce the life of the multiplier, or other sensitive MS parts.

- Turn the oven and detector off.

- Cool the oven and inlet to room temperature.

- Turn the inlet pressure off.

- Open the GC oven front door.

- Remove the column from the inlet. Cap the open end of the column to prevent contamination. If an insulation cup is installed around the base of the inlet, remove it.

- Use the 1/2-inch wrench to loosen the reducing nut, and then remove it. The washer and seal are inside the reducing nut. Remove them. Replace the washer when replace the inlet seal.

- Put on the gloves to protect the inlet base seal and washer from contamination. Place the washer in the reducing nut. Place the new inlet base seal on top of it.

- Replace the reducing nut. Use the 1/2-inch wrench to tighten the nut. Replacing the column and the insulation cup. Install the column into the injector as Section 5.4.2.

- Pump down the system (see Section 5.1).

2.1.3.4 Check and replace foreline pump oil

A slow loss of oil is normal for the foreline pump. Therefore, it is especially important to check the oil level regularly.

- Examine the oil level window. The oil level should be above the lower line. The foreline pump oil should be almost clear. If the oil level is near or below the lower line, add foreline pump oil.
- Vent the GC/MS system (see Section 5.5) and allow the automatic venting routine to run its full course. Improper venting may cause diffusion pump fluid to be deposited into the analyzer (backstreaming). It can also reduce the life of the multiplier, or other sensitive MS parts.
- If necessary, slide the foreline pump out from under the analyzer chamber. The foreline pump may be located on the floor, on the lab bench next to or behind the MSD, or under the analyzer chamber at the back of the MSD.
- Place a book or other object under the pump motor to tilt it up slightly.
- Remove the fill cap.
- Place a container under the drain plug.
- Remove the drain plug. Allow the pump oil to drain out. The oil drains faster if it is still warm.
- Reinstall the drain plug. If the old O-ring appears worn or damaged, replace it.
- Remove the propping object from under the pump motor.
- Add foreline pump oil until the oil level in the window is near, but not above, the upper line. The foreline pump requires approximately 0.28 liters of oil.
- Wait a few minutes for the oil to settle. If the oil level drops, add oil to bring the oil level to

near the upper line.

- Reinstall the fill cap.
- If necessary, slide the foreline pump back under the analyzer chamber. The foreline pump may be located on the floor, on the lab bench next to or behind the MSD, or under the analyzer chamber at the back of the MSD.
- Pump down the system (see Section 5.1).

Note:

If an oil trap on the exhaust port of the foreline pump is used, replace the trap whenever the white filter element turns brown. The trap can be replaced without turning off the MSD as well.

2.1.3.5 Check and refill the MSD calibration valve

- Stop any tuning or data acquisition.
- Turn off the analyzer. Select **View,** and then **Tune and Vacuum Control** on **Instrument #1 - Method Control** window. This directs into **Instrument#1 Tune** page.
- In the **Instrument#1 Tune** view, select **MS OFF** from the **Diagnostics** menu.
- Remove the MSD cover.
- Loosen the calibration vial collar by turning it counterclockwise. Counterclockwise as viewed from the bottom (vial side) of the collar. Do not remove the collar.
- Check the level of calibration solution in the vial.
- Pull the calibration vial out. Some resistance is due to residual vacuum.

- Pour PFTBA into the vial, or use a pipette. Leave the top 6-mm of the vial unfilled.
- Push the calibration vial into the valve as far as possible.
- Withdraw the vial 1 mm. This prevents damage when you tighten the collar.
- Turn the collar clockwise to tighten it. Clockwise as viewed from the bottom (vial side) of the collar. The collar should be snug but not overly tight. Do *not* use a tool to tighten the collar. It does not require that much force.
- Reinstall the analyzer cover.
- Select **Purge Cal Valve** from the **Vacuum** menu in the **Instrument#1 Tune** view**.**

2.1.3.6 Replace the diffusion pump fluid

- Vent the GC/MS system (see Section 5.5) and allow the automatic venting routine to run its full course. Improper venting may cause diffusion pump fluid to be deposited into the analyzer (backstreaming). It can also reduce the life of the multiplier, or other sensitive MS parts.
- Remove the capillary column from the GC/MS interface.
- Move the MSD away from the GC until access to the GC/MS interface cable.
- Place a column nut with a blank ferrule on the end of the interface. This will help prevent contamination out of the MSD.
- Disconnect the GC/MS interface cable. Disconnecting the cable with the GC on can cause a fault condition.
- Continue to move the MSD until access to the part requiring maintenance.

- Disconnect the foreline gauge assembly from the diffusion pump outlet. The foreline gauge cable can be disconnected or can remain connected to the foreline gauge.

- Disconnect the diffusion pump temperature sensor wires from the wiring harness. These are on the side of the diffusion pump not shown in the illustration.

- Disconnect high vacuum power (HIVAC POWER) cable from the back panel of the MSD. This is the thick black cable that emerges near the bottom of the pump.

- Support the diffusion pump with one hand.

- Remove the KF50 clamp.

- Lower the diffusion pump.

- Remove the diffusion pump from the MSD. Make sure you remove the O-ring assembly from the top of the diffusion pump.

- Cover the top of the diffusion pump with aluminum foil (shiny side up).

- Heat the diffusion pump at 60°C for 15 minutes in your GC oven.

- Pour the old diffusion pump fluid out the top of the pump. Even after heating, the pump fluid pours very slowly.

- Wipe clean the diffusion pump flange on the analyzer chamber. Follow the instructions on the bottle for pre-heating the diffusion pump fluid.

- Pour new diffusion pump fluid into diffusion pump until the fluid level is within the FULL COLD range. The recommended charge for this pump is 30 ml. It will require approximately 1.5 of the bottles (18.5 ml each) of diffusion pump fluid. Pour the fluid between the center stack and the side wall. Watch the sight glass while pouring. Do not overfill.

- Reinstall the diffusion pump and reconnect the MSD to the GC.

- Pump down the system (see Section 5.1).

2.1.3.7 Clean ion source

The ion source should be cleaned based on instrument performance (e.g. deteriorated performance over time). The frequency of cleaning is determined by the number of samples run (throughput), the type of samples, and unique, established laboratory protocol.

- Vent the GC/MS system (see Section 5.5) and allow the automatic venting routine to run its full course. Improper venting may cause diffusion pump fluid to be deposited into the analyzer (backstreaming). It can also reduce the life of the multiplier, or other sensitive MS parts.

- Wait the heated zones are less than 100 ^{o}C. The diffusion pump is off and cool. The foreline pump is off and not spinning.

- Open the analyzer chamber. Make sure to use an anti-static wrist strap and take other anti-static precautions before touching analyzer components.

- Disconnect the seven wires from the ion source. Do not bend the wires any more than necessary.

- Disconnect the wires for the ion source heater and temperature sensor from the feedthrough board.

- Remove the thumbscrews that hold the ion source in place.

- Pull the ion source out of the source radiator.

- Remove the filaments. Separate the repeller assembly from the source body. The repeller assembly includes the source heater assembly, repeller, and related parts.
- Remove the repeller.
- Unscrew the interface socket. A 10-mm open-end wrench fits on the flats on the interface socket.
- Remove the setscrew for the lenses.
- Push the lenses out of the source body.

  Note:

  - These are the parts that contact the sample or ion beam. The other parts normally should not require cleaning. If insulators are dirty, clean them with a cotton swab dampened with reagent-grade methanol. If that does not clean the insulators, replace them. Do not abrasively or ultrasonically clean the insulators.
  - In the event of a diffusion pump backstream or other major contamination, the other source components must be cleaned (ultrasonically but not abrasively) or replaced.
  - The filaments, source heater assembly, and insulators cannot be cleaned ultrasonically. Replace these components if major contamination occurs.
- Abrasively clean the surfaces that contact the sample or ion beam. Use an abrasive slurry of alumina powder and reagent-grade methanol on a cotton swab. Use enough force to remove all discolorations. Polishing the parts is not necessary; small scratches will not harm performance. Also abrasively clean the discolorations where electrons from the filaments enter the source body.
- Rinse away all abrasive residues with reagent-grade methanol. Make sure all abrasive

residues is rinsed way before ultrasonic cleaning. If the methanol becomes cloudy or contains visible particles, rinse again.

- Separate the parts that were abrasively cleaned from the parts that were not abrasively cleaned.
- Ultrasonically clean the parts for 15 minutes in each of the following solvents: Ultrasonically clean each group of parts separately: methanol, acetone, and DCM.
- Place the parts in a clean beaker. Loosely cover the beaker with clean aluminum foil (dull side down).
- Dry the cleaned parts in an oven at 100° C to 150 °C for 30 minutes.
- Reassemble the ion source and reinstall the ion source into the MSD chamber.
- Pump down the system (see Section 5.1).

2.1.4 Spare Parts

- GC Capillary Column

  An 5% diphenyl / 95 % dimethylsiloxane (DB-5MS) capillary column. Typical column length is 30 m. The film thickness is 0.25 nm and the internal diameter is 0.25 mm. (Agilent Technology, Part No. 122-5532)

- GC/MS Consumables
  - Gold-plated seal (Agilent Technology, Part No. 18740-20885)
  - Washer, 0.375 in. O.D. (Agilent Technology, Part No. 5061-5869)
  - Fluorocarbon O-ring (Agilent Technology, Part No. 5180-4182)

- General purpose graphite ferrules (Agilent Technology, Part No. 500-2114)
- Preconditioned 85 % Vespel, 15 % graphite ferrules (Agilent Technology, Part No. 5062-3508)
- Advanced green Septa, 11 mm for 6890 GCs (Agilent Technology, Part No. 5183-4759)
- Filaments, 5973 (EI) (Agilent Technology, Part No. 0592-60053)
- PFTBA sample kit, 0.5 mL (Agilent Technology, Part No. 05971-60571)
- Foreline pump oil (Agilent Technology, Part No. 6040-0798)
- Diffusion pump fluid: SantoVac Ultra 5P, 18.5 mL (Agilent Technology, Part No. 6040-0809)
- Abrasive sheets (Agilent Technology, Part No. 5061-5896)
- Electron multiplier replacement horn (Agilent Technology, Part No. 05971-80103)
- MS interface column nut (Agilent Technology, Part No. 05988-20066)
- Universal column nut, 1/16 in. hex (Agilent Technology, Part No. 5181-8830)

2.2 Reagents

- Chemical Standards: *n*-alkanes, iso/anteiso-alkanes, hopanes, steranes, other alkanes, alkenes, cyclohexanes, phthalates, and PAHs.

  They are prepared and stored in amber ampoules for calibration purpose. They are kept in freezer at -4 ^{o}C to minimize degradation.

- Organic Solvents: methanol, acetone, dichloromethane (DCM), benzene, and iso-propanol (GC or highest purity grade available).

  Further purification by distillation is required. They must be stored in clean bottles or vials.

- Deuterated Alkanes and PAHs.

  They are used as internal standard (IS) for quantification of the suite of target organic compounds.

2.3 Gases

- Helium, Ultra-High Purity (UHP) grade, for a carrier gas, regulated to at least 50 psi with a metal diaphragm regulator.

2.4 Other Materials and Apparatus

- Filters Materials.

  Quartz or Teflon-impregnated glass fiber filters (TIGF) are pre-baked to collect aerosols in atmosphere and TD calibrations.

- Furnace

  It is used for baking all glassware, glass wools, aluminum foils, and blank filters at 550°C.

- Aerosol Samples

  Aerosol samples intended for the TD analysis need to be collected onto quartz or glass fiber materials. Teflon coated quartz or fiber materials can be used for aerosol collection substrates as well.

- TD Glass Liners

The TD glass liners are home-fabricated from Pyrex glass tubes. The dimensions are 78 mm long, 4mm I.D., and 6 mm O.D. (the length and the outside diameter are identical to those of an HP 5890 or Agilent 6890 GC injector liner).

- Silicate-Treated Glass Wools

  They are available from Alltech Associate and need to be pre-baked before use. They are used as plugs for holding the filter parts in position and help to retain heavy and polar compounds that, if desorbed from the filter, would contaminate the GC column.

- Volumetric Flasks, various sizes, 5-250 mL

  They are used for preparation of stock chemical standard solutions.

- Disposal Droppers

  They are used to transfer chemical standard solutions or organic solvents.

- Stainless Steel Punches

  They are used to remove a filter punch from a bigger parent filter. Either a rectangle or a circular punch is suitable. A different size punch could work as long as the filter material removed can be accommodated by the TD tube. Calibration of the punch area is required every three months.

- Razor Blades

  They are used to divide filter piece into smaller portions to facilitate the loading of the filter punch into the TD tube.

- Aluminum Foils

  They need to be pre-baked and are used to provide a clean working platform for holding the filters.

- Amber Ampoules

  They are pre-baked and used to store standard solutions.

- Test Tubes with Teflon-Lined Caps

  They are used to store prepared TD glass liners before analysis.

- Forceps

  They are used to handle the sample filters and TD glass liners for avoiding any contamination to the outer portion of the tubes.

- Disposal Gloves

  They are worn by analysts to avoid any contamination to the samples.

- Glass Syringes, 0-10 μL

  They are used for spiking IS or calibration standard solutions onto the filters.

- Glass Plates, 10 x 10 cm^2

  They are used to serve a working platform for punching and dividing the filters.

- Glass Vials with Teflon Teflon-Lined Caps, 2 or 4 mL in volume

  They are used to store the calibration standards, IS, solvents, and waste.

- Kimwipe

  To be used for clean the tools and glass plates after sample preparation.

- GC Column Cutter with Diamond Blade, Magnifier, and Wrenches

  They are used to install and replace GC and MSD parts.

- Labels

  They are used to mark the sample id on the capped test tube.

- Glass Bottles, Beakers, and Other Glassware

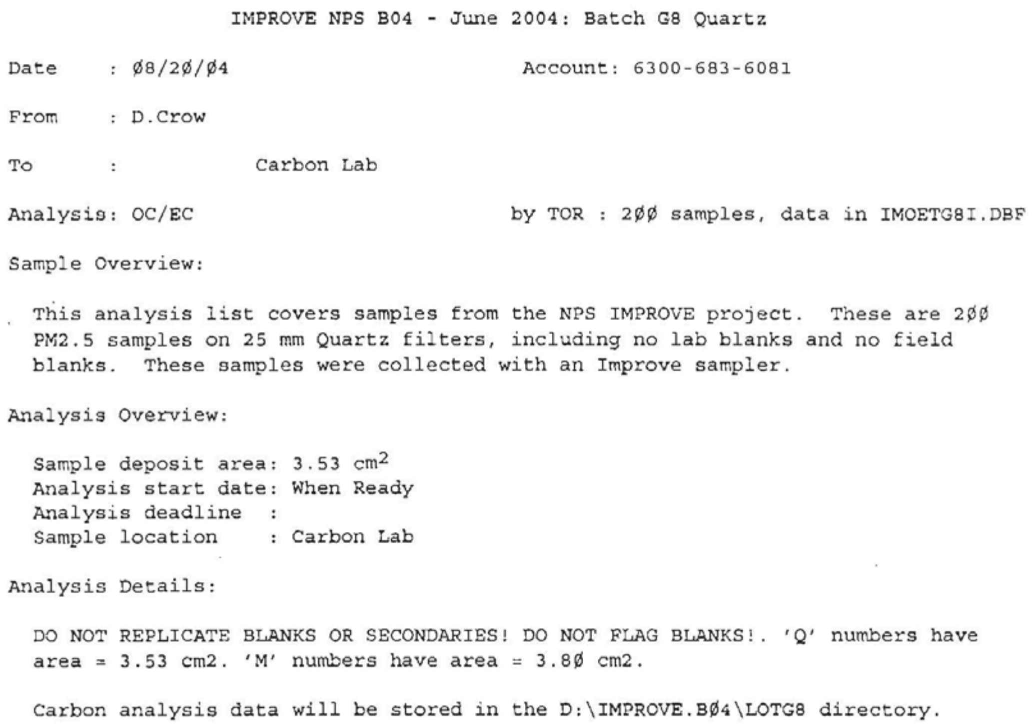
  They are used for various purposes in TD sample preparation.

- CD or DVD Blank Discs

  They are used for data file back-up.

2.5 Forms and Paperwork

All samples ate logged into a receiving book and into a computerized database login file upon receipt at the laboratory. A sample analysis list will be prepared by the laboratory supervisor indicating which samples will be analyzed and any special instructions. Figure 2-1 provides an example of the sample analysis list. As individual samples are analyzed, entries are made in the “GCMS Instrument Logbook”. As each analysis run is completed, the sample analysis is marked with the date and analyzer number.



IMPROVE NPS B04 - June 2004: Batch G8 Quartz

Date : 08/20/04 Account: 6300-683-6081

From : D.Crow

To : Carbon Lab

Analysis: OC/EC by TOR : 200 samples, data in IMOETG8I.DBF

Sample Overview:

This analysis list covers samples from the NPS IMPROVE project. These are 200 PM2.5 samples on 25 mm Quartz filters, including no lab blanks and no field blanks. These samples were collected with an Improve sampler.

Analysis Overview:

Sample deposit area: 3.53 cm^2
Analysis start date: When Ready
Analysis deadline :
Sample location : Carbon Lab

Analysis Details:

DO NOT REPLICATE BLANKS OR SECONDARIES! DO NOT FLAG BLANKS!. 'Q' numbers have area = 3.53 cm2. 'M' numbers have area = 3.80 cm2.

Carbon analysis data will be stored in the D:\IMPROVE.B04\LOTG8 directory.

Figure 2-1. DRI carbon sample analysis run list.

3.0 CALIBRATION STANDARDS

3.1 Preparation, Ranges, and Traceability of Standards

The highest purity chemical stocks, including alkanes, hopanes, steranes, alkenes, cyclohexanes, phthalates, and PAHs, are purchased and properly stored according to the instructions. They are individually weighed with a calibrated micro-balance and mixed into diluted solutions. The ranges of standards prepared are based on the real concentrations of the organic compounds in the samples, usually from 1 μg mL^{-1} to 30 μg mL^{-1}. A solvent mixture of distilled benzene and iso-propanol (50:50) is used to prepare the standards that would be frozen in solid form when they are kept at -4 °C. This minimizes degradation of organic compounds rather than in liquid. The standard solutions are also sealed into amber ampoules that prevent evaporation and light decomposition of the compounds. The weights of chemicals used and their concentrations should be filed and documented. Proper label with the name of standard and the data of preparation should be posted on each ampoule.

3.2 Use of Standards

The chemical standards are used for plotting calibration curves to quantify the amount of organic compounds in the samples. The use of calibration standards are described in Section 5.1.

3.3 Typical Accuracy of Calibration Standards

Method accuracy has been evaluated for a select group of eleven PAH compounds using the National Institute of Standards and Technology (NIST) urban dust standard reference material (SRM) 1649a. Calibration curves were first established by analyzing different amounts of SRM 1649a. The calibration curves derived from SRM 1649a were then used to calculate the concentrations of the standards, which are called concentrations traceable to the NIST-certified values. Figure 3-1 plots the ratio between our nominal concentrations, derived from gravimetric measurements of single standards given by in Jianzhen Yu's or James Schauer's groups, and the concentrations traceable to the NIST-certified values. The agreement for individual PAHs ranged from -5% to 20%.

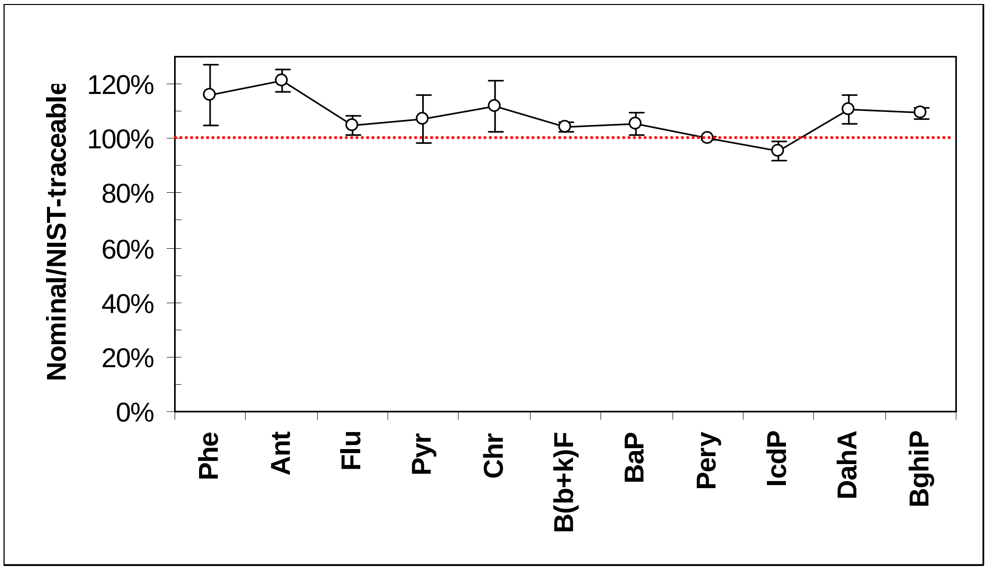


Figure 3-1. The ratio between the nominal concentrations and those traceable to the NIST certified values. (The nominal concentrations refer to those determined from gravimetric measurements of single standards given by Jianzhen Yu's and James Schauer's groups. The concentrations traceable to the NIST certified values were obtained using calibration curves that were established by analyzing different amounts of NIST urban dust SRM 1649a.)

4.0 PROCEDURES

4.1 Analyzer Start-Up

The GC/MS system is not shut down every day unless for maintenance. It is important to keep the system in a good vacuum status.

- Check to see if all instrument components are properly connected.
- Open helium carrier gas cylinder and adjust the outlet pressure of the regulator to at least 50 psi.
- Switch on the power of GC, MSD, and computer in order.
- Start Windows XP with password "**3000hanover**".
- Double click **Instrument #1** icon on desktop. Two windows, **Instrument #1-MS Top** and **Instrument #1 – Method Control**, are shown.
- Select **View,** and then **Tune and Vacuum Control** on **Instrument #1 - Method Control** window. This directs into **Instrument#1 Tune** page.
- Select **Vacuum**, and then **Pump Down**. A new window will be popped up and shows the current pump down status, foreline pressure, and its temperature.
- The foreline pump will be automatically turned on. After the pressure drops below 300 mTorr, the diffusion pump will be turned on and heated up. If the pressure could not lower to 300 mTorr in few minutes, check any possible leak in the GC/MS system (see Section 2.1.3).
- Wait the system to be stable for at least 2 hours.
- Select **View,** and then **Instrument Control** to return method control page.
- Increase the injector, oven, and GC/MS interface temperatures on GC panel or from the software.

4.2 Routine Operation

4.2.1 Check Carrier Gas Supply

- Check the helium gas supply from the regulator and record the reading on the log book.
- If it is below 400 bar, vent the GC/MS system (see Section 4.4) and change a new gas tank.
- Pump down the system (see Section 4.1) and wait for at least 2 hours before use.

4.2.2 Check Vacuum Pressure, MSD and Ion Source Temperatures

- The ion source should be at 150 ^{o}C and the MSD is operated at 230^{o}C.
- Obtain the readings of vacuum pressure, MSD and ion source temperatures from the block diagrams on the software. Mark down the values in the log book.
- Normal foreline pressure should be below 100 mTorr. If the foreline pressure is higher than 100 mTorr or foreline or diffusion pump is off, check to see if there is a leak in the GC/MS system (see Section 2.1.3).

4.2.3 Column and System Blank

System and column blank must be done at the beginning of every single operation day to prevent any carryover or impurities accumulated in the system. Proper actions should be taken if a high impurity level is found in the gas chromatogram.

4.2.3.1 Acquire Data from Software

- Select **<u>Method</u>** on **Instrument #1 - Method Control** window to load TD_BAKEOVEN_01_X.M from the C:\MSDChem\1\METHODS directory, where X is the instrument number.

- Check the injector temperature, pressure, column information, oven temperature program, GC/MS interface temperature, and other MSD parameters from software block diagrams.

- A typical oven temperature program is suggested as the following for an HP-5MS equipped with a 5 % diphenyl / 95 % dimethylsiloxane, 30 m × 0.25 mm × 0.25 µm column: an initial temperature of 50 °C for 2 min, programmed at a rate of 20 °C min^{-1} to 310 °C, and then held at the final temperature of 310 °C for 15 min. The total analysis time is 25 min. The carrier gas is helium held at a constant flow of 1.0 cc min^{-1}. The GCMS interface, so-called AUX, temperature is 280 ^{o}C. The ion source is kept at 150 ^{o}C. The MSD is operated at 230^{o}C and 70 eV for electron ionization. The mass scan range is from 50 to 650 amu.

- Avoid making any changes on the method. Save as other method if any change made. Mark down development of the methods and their history on log book.

- All of the parameters are sent to GC/MS. **“NOT READY”** red light on GC panel is on if the settings do not achieve.

- When the red light turns off and “**READY**” green light is on, click on **Data Acquire** block diagram.

- Enter operator name, sample information, data file directory and name, and miscellaneous information, and select **[Start Run]**. The data file directory is TD_X_COLUMNBLANK and the data file should be named as TD_X_SBYYYYMMDD_Z.D, where X is the instrument number, YYYY is the year, MM is the month, DD is the day, and Z is the run number start from 1.

- Press **[Yes]** on the pop-up window when the program reminds you to save the method.

- After another pop-up window “Waiting for Injection” is shown, press **“PRE-RUN”** button on the GC Panel.

- Once the green light turns off, press “**START**” button on the panel of GC. The oven temperature program will be finished in 25 min.

- Mark down the data file directory and name on the log book.

4.2.3.2 Inspection of System and Column Blank Level

- Double click **Instrument #1 Data Analysis** on desktop to open a new window of **Enhanced Data Analysis**.

- Select **File**, and then **Load** to get target data file or **Take Snapshot** to observe the running sample.

- Check the baseline abundance should not exceed 300,000 counts and that no significant impurity peak, other than any minor peaks desorbed from the injector spectra and O-ring, shows on the chromatogram.

- If high system blank is found, repeat the step of Section 4.2.3.1. Check Section 2.1.3 if the high impurity and background levels in the second run.

4.2.4 Routine TD-GC/MS Analysis

4.2.4.1 Materials Preparation

- TD glass liners, glass test tubes, blank quartz fiber filters, and other glassware
    - Wash TD glass liners, glass test tubes, and other glassware with water.
    - Cover the glassware and blank quartz fiber filters with aluminum foil and bake in a furnace at 550°C for at least 6 hours.
    - After cooling, wear gloves and take out all baked items.

  - Keep baked items in a clean environment to prevent any possible contamination.

- Glass wool
  - Transfer silicate-treated glass wool into a clean glass bottle and cover the opening with aluminum foil.
  - Bake in a furnace at 550°C for at least 6 hours.
  - After cooling, remove the covering aluminum foil and cap the bottle.
  - Keep the bottle in a clean environment to prevent any possible contamination.

- Working platform
  - Cover working platform with kimwipe and pre-baked aluminum foils in a clean fumehood.

- Tools
  - Wear gloves to handle tools during the sample preparation steps. Transfer the sample filters and TD glass liners by forceps.
  - Clean all stainless steel punch, forceps, and glass plates with kimwipe before use.

- Teflon-lined caps for test tubes
  - Wash the Teflon-lined caps with DI water and allow them to air dry before use.

4.2.4.2 Sample Preparation

- Remove a filter punch of 1 cm^2 in size from a parent filter using stainless steel punch over a clean glass plate surface. Transfer the filter punch onto another clean glass plate.

- [Note: More or less filter area can be used for the analysis, subjective to aerosol loading on the samples. Maximum capacity of the glass liner is 5.0 cm^2.]

- Clean stainless steel punches, forceps, and glass plates with kimwipe before the first sample and after every sample thereafter.

- Wash a ten-µL glass syringe with distilled DCM at least twice and discard the waste into a vial.

- Unplug the ampoules containing IS and transfer the solutions into clean vials. Label the vial with the date and name.

- Spike 2 µL of each of the two IS solutions (Table 4.1) onto the filter punch.

- Keep the IS solutions in the freezer at -4 ^{o}C for next sample preparation. The IS solution can be reused for at least 3 months.

- After air-drying for a few seconds to allow evaporation of the organic solvent from the application of the internal standards, each filter piece is divided into 4 (depend on the punch size) roughly equal portions with a clean razor blade to facilitate the loading of the filter pieces.

- Insert the pieces into a pre-baked TD glass liner. Use small amount of pre-baked glass wool (*ca.* 1 cm in length) as plugs for holding the filter parts in position from two ends.

- Clean stainless steel punch, forceps, and glass plates with kimwipe.

Table 4-1. Concentrations and Spiked Amounts for Internal Standards (IS)

IS solution	IS name	MW	Quant. ion	Conc. (ng/μL)	Spiked amount Vol (μL)	Spiked amount Quantity (ng)
TDIS#1	phenanthrene-d10	188	188	5.0	2	10.0
	chrysene-d12	240	240	5.0		10.0
TDIS#2	1-phenyldodecane	246	92	25.7	2	51.4
	tetracosane-d50	388	66	25.0		50.0

4.2.4.3 Sample Storage

- Store the sample loaded glass liners inside capped test tubes before analysis.
- Label the sample id and date of preparation on the tube immediately.
- Place the tubes into a tray and store in a clean environment at room temperature.
- The analysis of the sample filters should be carried out within 24 hours after their preparation.

4.2.4.4 Acquire Data

- Select **<u>Method</u>** on **Instrument #1 - Method Control** window to load TD_STDMETHOD_01_X.M from the C:\MSDChem\1\METHODS directory, where X is the instrument number.
- Check the injector temperature, pressure, column information, oven temperature program, GC/MS interface temperature, and other MSD parameters from software block diagrams.

- A typical oven temperature program is suggested as the following for an DB-5MS equipped with a 5 % diphenyl / 95 % dimethylsiloxane, 30 m × 0.25 mm × 0.25 µm column: an initial temperature of 30 °C for 2 min, programmed at a rate of 10 °C min^{-1} to 120 °C and 7 °C min^{-1} to 310 °C, and then held at the final temperature of 310 °C for 15 min. The total analysis time is 56.14 min. The carrier gas is helium held at a constant flow of 1.0 cc min^{-1}. The GCMS interface, so-called AUX, temperature is 280 ^{o}C. The ion source is kept at 150 ^{o}C. The MSD is operated at 230^{o}C and 70 eV for electron ionization. The mass scan range is from 50 to 650 amu.

- Avoid making any changes to the method. Save as other method if any other changes are made. Record the development of methods and their history in log book.

- All of the parameters are sent to GC/MS. "**NOT READY**" red light is illuminated on GC panel if the parameters have not achieved their set points.

- Lower the injector temperature to 50^{o}C manually on the GC panel or from the software.

- When the red light turns off and "**READY**" green light is on, click on the **Data Acquire** block diagram.

- Enter operator name, sample information, data file directory and name, and miscellaneous information, and select **Start Run**. The data file directory should be entered just as it is written on the runlist. The data file should be named as TD_X_SAMPLE ID_Z.D, where X is the instrument number, SAMPLE ID is the sample id on the runlist and Z is the run number starting from 1.

- Press **[Yes]** on the pop-up window when the program reminds you to save the method.

- After another pop-up window "Waiting for Injection" is shown, press the **"PRE-RUN"** button on the GC Panel.

4.2.4.5 Loading TD Sample Liner

- Wear gloves during the sample loading process and ensure nothing blocks the GC injector area.

- Open the injector carefully with the wrench provided with the GC/MS system. Do not touch the inner part of the injector cover.

- Use two pairs of clean forceps to take out the old glass liner with the O-ring from the injection port.

- Remove the O-ring from the old tube and put it back into the position in the injection port.

- Pick up the test tube containing a sample-loaded glass liner and check that the correct sample is loaded according to the runlist and the sample id entered in the software. Uncap the test tube and transfer the new TD glass liner into the injection port passing through the O-ring carefully.

- Close the injector cover immediately once the tube is in place inside the injector port. This minimizes any air and water entering into the system.

- Set the injector temperature manually to 275^{o}C on the GC panel. It takes 10 minutes for the injector temperature to reach the new setting. During this period, the GC oven temperature is kept at 30^{o}C. Such temperature conditions focus the aerosol organic analytes released from the injector port on the head of the GC column in a narrow band.

- Mark down the data file directory and sample id in the log book.

- Start the oven temperature program by pushing the "**START**" button on the GC panel as soon as the injector temperature achieves 275^{o}C.

- Keep the injector at 275^{o}C throughout the analysis and set it in the splitless mode.

4.2.4.6 Post-Analysis

- After the oven temperature program finished, lower the injector temperature to 50°C manually on the GC panel or from the software. The oven temperature will automatically return to initial temperature. The system will be ready for next analysis after the initial injector and oven temperatures reach.

- Check that there is a data.ms file in the data file folder of TD_X_SAMPLE ID_Z.D

4.3 End of Operation Day

4.3.1 Removal of Old Sample Liner

- Lower the injector temperature to 50°C manually on the GC panel or from the software.

- Wear gloves during the sample loading and unloading processes and ensure nothing blocks the GC injector area.

- Open the injector with a default screw-driver carefully. Do not touch the inner part of the injector cover.

- Use two pairs of clean forceps to take out the old glass liner with an O-ring from the injection port.

- Remove the O-ring from the tube and put it back in the position of injection port.

- Insert a blank pre-baked glass liner into the injection port passing through the O-ring carefully.

- Close the injector cover immediately once the tube is in place inside the injector port. This minimizes any air and water entering into the system.

4.3.2 Set Injector and Oven Temperature

- Set the injector and oven temperature manually to 250 °C and 50 °C, respectively, on the GC panel.

4.3.3 Keep GC/MS, Computer, and Software Running

- It is not necessary to turn off the GC/MS, computer, and MS software in the end of operation day.
- Switch off the monitor to save energy.

4.4 Shut Down Procedures

The GC/MS must be pumped down when you want to: (1) change or disconnect column; (2) change new carrier gas tank; (3) clean the ion source; and (4) perform any maintenance work on the system. It is important to turn off the pump before open the system. This prevents air and impurities entering the capillary column or MS detector.

- Select **View,** and then **Tune and Vacuum Control** on **Instrument #1 - Method Control** window. This directs into **Instrument#1 Tune** page.
- Select **Vacuum**, and then **Vent**. A new window will be popped up and shows the current pump down status, foreline pressure, and temperature.
- Allow the automatic venting routine to run its full course. Improper venting may cause diffusion pump fluid to be deposited into the analyzer (backstreaming). It can also reduce the life of the multiplier, or other sensitive MS parts.
- Switch off the injector, GC/MS interface and oven temperatures on the GC panel or from the software.

5.0 QUALIFICATION

5.1 Calibration Procedures

5.1.1 Calibration Filters Preparation

- Remove filter punches of 1 cm^2 in size from a parent blank filter using stainless steel punch over a clean glass plate surface. Transfer the filter punch on different clean glass plates.

- Wash a ten-µL glass syringe with distilled DCM at least twice and discard the waste into a vial.

- Unplug the ampoules containing chemical standards and IS and transfer the solutions into clean vials respectively. Label the vials with the date and name.

- Prepare calibration standards at four levels by spiking 1, 2, 5, and 10 µL of pre-mixed liquid standards onto four separate pre-baked filter strips. [The amounts of calibration standards can be adjusted according to the levels in real samples.] A list of target organic compounds is shown in Table 5-1. Two µL of the two IS are then spiked onto each calibration filter strip (Table 4-1).

- Keep both IS and chemical standard solution in the freezer at -4 ^oC for next calibration sample preparation. The IS and chemical standard solutions can be used at least 3 months.

- After air-drying for a few seconds to allow evaporation of the organic solvent from the application of the internal standards, each filter piece is divided into 4 roughly equal portions with a clean razor blade to facilitate the loading of the filter pieces.

- Insert the pieces into a pre-baked TD glass liner. Use small amount of pre-baked glass wool (~1 cm in length) as plugs for holding the filter parts in position from two ends.

- Calibration curves are constructed by plotting the peak area ratios between the analytes and the respective IS (i.e., tetracosane-d50 for alkanes and phenanthrene-d10 for PAHs) versus the amounts of the analytes (Section 6).

- Clean stainless steel punch, forceps, and glass plates with kimwipe.

5.1.2 Sample Storage

- Store the sample loaded glass liners stored inside capped test tubes before analysis.

- Label the sample id and date of preparation on the tube immediately.

- Place the tubes into a tray and store in a clean environment at room temperature.

- The analysis of the calibration filters should be carried out within 24 hours after their preparation.

5.1.3 Acquire Data

- Select **Method** on **Instrument #1 - Method Control** window to load TD_STDMETHOD_01_X.M from the C:\MSDChem\1\METHODS directory, where X is the instrument number.

- Check the injector temperature, pressure, column information, oven temperature program, GC/MS interface temperature, and other MSD parameters from software block diagrams.

- A typical oven temperature program is suggested as the following for an DB-5MS equipped with a 5 % diphenyl / 95 % dimethylsiloxane, 30 m × 0.25 mm × 0.25 µm column: an initial temperature of 30 °C for 2 min, programmed at a rate of 10 °C min^{-1} to 120 °C and 7 °C min^{-1} to 310 °C, and then held at the final temperature of 310 °C for 15 min. The total analysis time is 56.14 min. The carrier gas is helium held at a constant flow of 1.0 cc min^{-1}. The GCMS interface, so-called AUX, temperature is 280 ^{o}C. The ion source is kept at 150 ^{o}C. The MSD is operated at 230°C and 70 eV for electron ionization. The mass scan range is from 50 to 650 amu.

- Avoid making any changes on the method. Save as other method if any change made. Mark down development of the methods and their history on log book.
- All of the parameters are sent to GC/MS. "**NOT READY**" red light on GC panel is on if the settings do not achieve.
- Lower the injector temperature to 50°C manually on the GC panel or from the software.
- When the red light turns off and "**READY**" green light is on, click on **Data Acquire** block diagram.
- Enter operator name, sample information, data file directory and name, and miscellaneous information, and select **Start Run**. The data file directory should be the same as the runlist. The data file should be named as TD_X_YYYYMMDD_LEVEL_N_Z.D, where X is the instrument number, YYYY is the year, MM is the month, DD is the day, N is the amount of chemical standard spiked, and Z is the run number start from 1.
- Press **[Yes]** on the pop-up window when the program reminds you to save the method.
- After another pop-up window "Waiting for Injection" is shown, press **"PRE-RUN"** button on the GC Panel.

5.1.4 Loading Calibration TD liner

- Wear gloves during the sample loading process and ensure nothing blocks the GC injector area.
- Open the injector with a default screw-driver carefully. Do not touch the inner part of the injector cover.

- Use two pairs of clean forceps to take out the old glass liner with the O-ring from the injection port.

- Remove the O-ring from the old tube and put it back in the position of injection port.

- Pick up the test tube containing a sample loaded glass liner and check the sample id labeled according to runlist. Uncap the test tube and transfer the new TD glass liner into the injection port passing through the O-ring carefully.

- Close the injector cover immediately once the tube is in place inside the injector port. This minimizes any air and water entering into the system.

- Set the injector temperature manually to 275^{o}C on the GC panel. It takes 10 minutes for the injector temperature to reach the new setting. During this period, the GC oven temperature is kept at 30^{o}C. Such a temperature condition would focus the aerosol organic analytes released from the injector port on the head of the GC column in a narrow band.

- Mark down the data file directory and name on the log book.

- Start the oven temperature program by push the "**START**" button on the GC panel as soon as the injector temperature achieves 275^{o}C.

- Keep the injector at 275^{o}C throughout the analysis and set it in the splitless mode.

5.1.5 Post-Analysis

- After the oven temperature program finished, lower the injector temperature to 50^{o}C manually on the GC panel or from the software. The oven temperature will automatically return to initial temperature. The system will be ready for next analysis after the temperatures achieved.

- Check there is a data.ms file in the data file folder of TD_X_YYYYMMDD_LEVEL_N_Z.D.

5.2 Calculations

5.2.1 Integration of Peak Area

- Double click **Instrument #1 Data Analysis** on desktop to open a new window of **Enhanced Data Analysis**.
- Select **File**, and then **Load** to get target data file, either calibration standards or real samples, or **Take Snapshot** to observe the running sample.
- Right click the mouse at any point on the chromatogram to get its mass spectrum, or left click with holding and dragging to enlarge the chromatogram or mass spectrum.
- Select **Chromatogram,** then **Extracted Ion Chromatograms** to extract target ions of IS, i.e. m/z = 66 (tetracosane-d50), m/z=92 (1-phenyldodecane), m/z =188 (phenanthrene-d10), and m/z =240 (chrysene-d12).
- Select **Chromatogram,** then **Extracted Ion Chromatograms** to extract target ions of other organic species according to Table 7.1.
- Select **Chromatogram,** then **Integrate** or **AutoIntegrate** to integrate the peaks automatically. If manual integration is required, select **Tool** then **Options** to activate **Manual Integration**.
- Select **Chromatogram,** then **Integration Results** to list the peak areas. Copy the peak areas and export into an excel data file. The excel file should be named according to the sample project name with batch number. Save the excel file occasionally during the data analysis process.

5.2.2 Calibration Curves

- Calibration curve of an individual compound should be constructed by plotting the peak area ratios between the between the analyte and the respective IS (i.e., tetracosane-d50 for alkanes and phenanthrene-d10 for PAHs). The peak area for a given compound is the peak area for the quantification ion, not the total ion current. The ions used for quantification are listed in Table 5-1.

- There must be at least 3 calibration points for each curve. The equation is

  $$y = sx + b$$

  where *s* and *b* are the slope and the intercept for the calibration linear curve, *y* and *x* are the peak area ratios and the mass of analyte in nanogram (ng).

- All sample information and sampling parameters must be input into the excel data file.

- Quantification of an individual compound is also based on the peak area ratio between the analyte and the respective IS (i.e., tetracosane-d50 for alkanes and phenanthrene-d10 for PAHs). The peak area for a given compound is the peak area for the quantification ion, not the total ion current. The ions used for quantification are listed in Table 5-1.

- The formula below is used for calculation of the concentration in ng/sample of target compound X.

  $$ng / sample = \frac{(\frac{PA_x}{PA_{IS}}) - b}{s},$$

  where PA is peak area.

- The concentration in ng/sample is compared with the LQLs of the method (Table 1-1). The data below the LQLs is marked as “bd”.

- The air concentration of X in ng/m^3 is calculated as follows:

  $$ng / m^3 = \frac{(ng / sample)}{V_{air}} \times \frac{A_{whole\_filter}}{A_{filter\_TD}},$$

where V_{air} is the sampled air volume, A_{whole_filter} is the entire filter area, and A_{filter_TD} is the area of the filter portion used for TD analysis.

Table 5-1. Individual Standard Compounds: Molecular Weights and Ions for Quantification, for the TD-GC/MS Analysis.

Compounds	**Molecular Weight**	**Quantification Ion**	**Compounds**	**Molecular Weight**	**Quantification Ion**
PAHs			**Alkanes**		
naphthalene	128	128	***n*-Alkane (*n*-C14 to *n*-C44)**		
acenaphthylene	152	152	tetradecane (*n*-C14)	198	57
acenapthene	154	154	pentadecane (*n*-C15)	212	57
fluorene	166	166	hexadecane (*n*-C16)	226	57
phenanthrene	178	178	heptadecane (*n*-C17)	240	57
anthracene	178	178	octadecane (*n*-C18)	254	57
fluoranthene	202	202	nonadecane (*n*-C19)	268	57
pyrene	202	202	icosane (*n*-C20)	282	57
benzo[a]anthracene	228	228	heneicosane (*n*-C21)	296	57
chrysene	228	228	docosane (*n*-C22)	310	57
benzo[b]fluoranthene	252	252	tricosane (*n*-C23)	324	57
benzo[k]fluoranthene	252	252	tetracosane (*n*-C24)	338	57
benzo[a]fluoranthene	252	252	pentacosane (*n*-C25)	352	57
benzo[e]pyrene	252	252	hexacosane (*n*-C26)	366	57
benzo[a]pyrene	252	252	heptacosane (*n*-C27)	380	57
perylene	252	252	octacosane (*n*-C28)	394	57
indeno[1,2,3-cd]pyrene	276	276	nonacosane (*n*-C29)	408	57
dibenzo[a,h]anthracene	278	278	triacontane (*n*-C30)	422	57
benzo[ghi]perylene	276	276	hentriacotane (*n*-C31)	436	57
coronene	300	300	dotriacontane (*n*-C32)	450	57
dibenzo[a,e]pyrene	302	302	tritriactotane (*n*-C33)	464	57
			tetratriactoane (*n*-C34)	492	57
1-methylnaphthalene	142	142	hexatriacontane (*n*-C36)	506	57
2-methylnaphthalene	142	142	heptatriacontane (*n*-C37)	521	57
2,6-dimethylnaphthalene	156	156	octatriacontane (*n*-C38)	535	57
9-fluorenone	180	180	nonatriacontane (*n*-C39)	549	57
9-methylanthracene	192	192	tetracontane (*n*-C40)	563	57

anthroquinone	208	208
1,8-napthalic anhydride	198	154
methylfluoranthene	216	216
retene	234	219
cyclopenta[cd]pyrene	226	226
benz[a]anthracene-7,12-dione	258	258
methylchrysene	242	242
picene	278	278
hentetracontane (*n*-C41)	577	57
dotetracontane (*n*-C42)	591	57
tritetracontane (*n*-C43)	605	57
tetratetracontane (*n*-C44)	619	57
Methyl-alkanes		
2-methylnonadecane	282	57
3-methylnonadecane	282	57

Table5-1. (Con't) Individual Standard Compounds: Molecular Weights and Ions for Quantification, for the TD-GC/MS Analysis.

Compounds	Molecular Weight	Quantification Ion	Compounds	Molecular Weight	Quantification Ion
Iso/Anteiso alkanes[a]			**Hopanes**		
iso-C29	408	57	22,29,30-trisnorneophopane (Ts)[a]	370	191
anteiso-C29	408	57	22,29,30-trisnorphopane (Tm)	370	191
iso-C30	422	57	αβ-norhopane (C29αβ-hopane)	398	191
anteiso-C30	422	57	C29Ts[a]	398	191
iso-C31	436	57	βα-norhopane (C29βα -hopane)	398	191
anteiso-C31	436	57	αβ-hopane (C30αβ -hopane)	412	191
iso-C32	450	57	C30αα-hopane[a]	412	191
anteiso-C32	450	57	βα-hopane (C30βα -hopane)	412	191
iso-C33	464	57	αβS-homohopane (C31αβS-hopane)	426	191
anteiso-C33	464	57	αβR-homohopane (C31αβR-hopane)	426	191
iso-C34	478	57	αβS-bishomohopane[a](C32αβS-hopane)	440	191
anteiso-C34	478	57	αβR-bishomohopane[a] (C32αβR-hopane)	440	191
iso-C35	492	57	22S-trishomohopane (C33)[a]	454	191
anteiso-C35	492	57	22R-trishomohopane (C33)[a]	454	191
Branched-alkanes			22S-tretrahomohopane (C34)[a]	468	191
pristane	268	57	22R-tetrashomohopane (C34)[a]	468	191
phytane	282	57	22S-pentashomohopane(C35)[a]	482	191
squalane	422	57	22R-pentashomohopane(C35)[a]	482	191
Cyclohexanes					
octylcyclohexane	196	83	**Steranes**		
decylcyclohexane	224	83	ααα 20S-cholestane	372	217
tridecylcyclohexane	266	82	ααα 20R-cholestane	372	217
n-heptadecylcyclohexane	322	82	αββ 20R-cholestane	372	218
nonadecylcyclohexane	350	82	αββ 20S-cholestane	372	218
			ααα 20S 24S-methylcholestane[a]	386	217
Alkenes			13α(H),17α(H)-24-ethyldiacholestane	400	217
squalene	410	69	αββ 20R 24S-methylcholestane	386	218

1-octadecene	252	55
Phthalates		
dimethylphthalate	194	163
diethyl phthalate	222	177
di-n-butyl phthalate	278	149
butyl benzyl phthalate	312	149
bis(2-ethylhexyl)phthalate	390	149
di-n-octyl phthalate	390	149
αββ 20S 24S-methylcholestane[a]	386	218
ααα 20R 24R-methylcholestane[a]	386	217
ααα 20S 24R/S-ethylcholestane	400	217
αββ 20R 24R-ethylcholestane	400	218
αββ 20S 24R-ethylcholestane[a]	400	218
ααα 20R 24R-ethylcholestane	400	217

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[a] Due to a lack of authentic standards (for iso-/anteiso-alkanes and a few hopanes and steranes), the organic compound concentrations are estimated by assuming the same response as the respective isomers or the respective *n*-alkanes of the same carbon number.

6.0 QUALITY CONTROL

6.1 Performance Testing

System and column blanks (Section 4.2.3) are performed at the beginning of each day to confirm the system is not introducing bias in the analytical results. Contamination is potentially due to:

- Bleeding from capillary column.
- Contamination from injector septum, O-ring, and golden seal.
- Foreline pump oils.
- Diffusion pump fluids.
- Injector or column nut leakage.

As described in Section 2.1.3, the GC/MS system should be maintained according to the suggest time schedule. This minimizes the uncertainty in the analysis and errors in instrumental operation.

Other regular performance checks should be performed as described as below.

6.1.1 Air & water check

- It should be done if the system has been vented before, i.e. changing of column and after cleaning of ion sources. It is also recommended that the air and water check is performed at least once per week.

- Select **<u>View</u>,** and then **<u>Tune and Vacuum Control</u>** on **Instrument #1 - Method Control** window. This directs into **Instrument#1 Tune** page.

- Select **<u>Vacuum</u>**, and then **<u>Air and Water Check</u>**. The software will automatically check the air and water level in the MS detector. A final report will be printed out and shown on the screen.

- Both ratios of *m/z* =18 (water), *m/z*=28 (nitrogen), *m/z* =32 (oxygen), and *m/z* =44 (carbon dioxide) to *m/z* =69 should be lower than 5%. The abundance of *m/z* =28 should be less than *m/z* =18 (0% or over 100% in ratio). Check for possible leaks if these parameters are not met (See Section 2.1.3).

- Keep the air and water check report print out in the folder and mark down the parameters in the log book.

6.1.2 MSD Autotune

- The MSD should be auto-tuned (1) at least once a week if it is pumped down; (2) every time the instrument has been pumped down; (3) before you are going to run a new batch of samples and calibration standards; and (4) if the MSD performance is changing between the analyses.

  [Notes: The auto-tune will NOT damage the instrument.]

- Select **View,** and then **Tune and Vacuum Control** on **Instrument #1 - Method Control** window. This directs into **Instrument#1 Tune** page.

- Select **Tune**, and then **Autotune (Atune.U)**. The software will automatically tune the MS detector. A final report will be printed out and shown on the screen.

- Check parameters for the three major fragment peaks, *m/z*=69, 209, and 502, which belong to an internal calibration standard perfluorotributylamine (PFTBA).

- PW (peak width) should be between 0.50 and 0.70.

- Isotope ratios for 69, 219, and 502 should be around 1, 5, and 10, respectively.

- Other MS conditions, i.e. the absolute abundance for the three ions, should not be largely varied from previous tune sessions.

- Check Section 2.1.3 if any problems are encountered in the autotune.

- Save the autotune file. Keep the new autotune report print out in the folder and record the parameters in the log book.

6.2 Reproducibility Testing

Method precision can be assessed by replicate analysis of a calibration sample or a high-volume aerosol filter sample. Ten replicate analysis of an ambient aerosol sample collected in Hong Kong showed that the relative standard deviations were 2.7-4.0 %. Five replicate analysis of a calibration sample showed that the relative standard deviations were 0.2-4.2 %.

Replicates of analyzed samples are performed at the rate of one per group of ten samples. The replicate is selected randomly and run immediately after a group of ten is completed. It is run on a randomly selected analyzer (it can be the same or a separate analyzer as the original). This practice provides a better indication of potential differences if samples are analyzed by different laboratories. The ng cm^{-2} or ng/m^3 value for each targeted organic compound is compared with the original run. The difference should be less than 10 % of average of the 2 values.

Replicates which do not fall within the criteria must be investigated for analyzer or sample anomalies. Typical sample anomalies include inhomogeneous deposits or contamination during analysis or from the field sampling location. Inconsistent replicates for which a reason cannot be found must be rerun again.

6.3 Control Charts and Procedures

Control charts are updated at the beginning of each month. These charts include a month of calibration data and are posted in the carbon room until the end of the month, after which they are filed with the raw analysis results.

The control chart gives a plot of IS peak areas as percent deviation from a historical mean versus date. Instances where the calibration peak area deviates by more than 10% from the historical mean must be investigated and the cause must be corrected. The historical mean covers results from the previous three months and is updated either quarterly, when the IS concentrations are changed or when the repair of MSD are performed.

6.4 Analysis Flags

During Level I validation (see Section 6.5), unusual conditions of the deposit or analysis problems are noted on the analysis printouts. Errors in pre-analysis data entry (e.g., in filter ID, punch size, deposit area) are corrected.

Flags are applied to the Access file created from the analysis results (see Section 6.5). The analysis flags commonly used are presented in Table 6-1. Note that all results flagged with "v" must include a description of the reason for invalidating the sample in the remarks field.

Table 6-1. Common DRI Analysis Flags

Flag	Description
b1	Field blank
b2	Lab blank
b3	Blank of undetermined type
b6	Transport blank
f1	Filter damaged, outside of analysis area
f2	Filter damaged, inside analysis area
i1	Inhomogeneous filter deposit
i3	Deposit falling off (usually occurs on heavily loaded samples)
i4	Abnormal deposit area, possible air leakage during sampling
m2	Non-white sample punch after analysis
j	Possible air leakage during sampling
r1	First replicate on same analyzer
r2	Second replicate on same analyzer
r3	Third replicate on same analyzer
r5	Replicate on different analyzer
v	Sample void

6.5 Data Validation and Feedback

Level I validation is performed by manually checking the IS peak area and data file information with the GC/MS software after the analysis is performed. The laboratory supervisor or a designated technician is responsible for checking the data.

6.5.1 Date File Information

The following items are checked on the data file information:

- The filter ID, as known as data file name, and run number are correct.
- The analysis date and time is correct.
- The punch area entered is correct.

Items which have problems are marked on the runlist and reported to the laboratory supervisor.

6.5.2 IS Peak Areas

The IS peak areas are checked to make sure the MSD are operating at required level.

- Double click **Instrument #1 Data Analysis** on desktop to open a new window of **Enhanced Data Analysis**.
- Select **File**, and then **Load** to get target data file or **Take Snapshot** to observe the running sample.
- Right click the mouse at any point on the chromatogram to get its mass spectrum, or left click with holding and dragging to enlarge the chromatogram or mass spectrum.
- Select **Chromatogram,** then **Extracted Ion Chromatograms** to extract target ions of IS, i.e. m/z = 66 (tetracosane-d50), m/z=92 (1-phenyldodecane), m/z =188 (phenanthrene-d10), and m/z =240 (chrysene-d12).
- Select **Chromatogram,** then **Integrate** or **AutoIntegrate** to integrate the peaks automatically. If manual integration is required, select **Tool** then **Options** to activate **Manual Integration**.

- Select **Chromatogram,** then **Integration Results** to list the peak areas. Compares the peaks of IS with the calibration standard and sample runs.

The values for the sample and calibration standard runs should be within 10% of the current mean values. If there is more than 10 % difference from the mean values, flag sample and rerun the sample.

7.0 DATA MANAGEMENT

A data CD or DVD is created for each batch of samples. The following data files should be included on each data CD or DVD: (1) raw GC/MS data files for each aerosol sample and each calibration sample; (2) Excel spreadsheets listing RTs, peak areas, and calculation results.

8.0 REFERENCE

Hays, M.D., Smith, N.D., Kinsey, J., Dong, Y., Kariher, P., 2003. Polycyclic aromatic hydrocarbon size distributions in aerosols from appliances of residential wood combustion as determined by direct thermal desorption - GC/MS. J. Aerosol Sci. 34(8), 1061-1084.

Ho, S.S.H., Yu, J.Z., 2004. In-injection port thermal desorption and subsequent gas chromatography-mass spectrometric analysis of polycyclic aromatic hydrocarbons and *n*-alkanes in atmospheric aerosol samples. J. Chromatogr. A 1059(1-2), 121-129.

Miller, J.C., Miller, J.N., 1993. Statistics for Analytical Chemistry, 3rd ed., Ellis Horwood, New York, p. 46&115.

APPENDIX I ABBREVIATIONS

DCM	Dichloromethane
DRI	Desert Research Institute
EI	Electron Ionization
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometer
I.D.	Inner Diameter
IS	Internal Standards
LQL	Lower Quantifiable Limits
MSD	Mass Spectrometric Detector
NIST	National Institute of Standards and Technology
O.D.	Outer Diameter
PA	Peak Area
PAHs	Polycyclic Aromatic Hydrocarbons
PFTBA	Perfluorotributylamine
PW	Peak Width

QA	Quality Assurance
RT	Retention Time
SOP	Standard Operating Procedure
SRM	Standard Reference Material
TD	Thermal Desorption
TIGF	Teflon-Impregnated Glass Filter

PORT OF LOS ANGELES AIR QUALITY MONITORING PROGRAM MONITORING PROTOCOL

1.0 INTRODUCTION

The Port of Los Angeles (Port) is conducting an air quality monitoring program within the Port operational region of influence (ROI) for an initial period of one year. This special study program will monitor ambient particulate matter (PM) and meteorological parameters during the period of operation, as presented below and documented in the *Final Air Quality Monitoring Work Plan for the Port of Los Angeles and Addendum* (Port 2004 and 2005).

This document describes the approach used to implement this program, including data collection, processing and quality assurance (QA) procedures incorporated within the program.

2.0 General Project Description

The program has established one primary monitoring station and two satellite stations. There are two community monitoring stations, located in Wilmington and San Pedro, and one coastal boundary station located at Berth 47 in the Port. In addition, the Port is evaluating suitable locations for a potential fourth site on Terminal Island, and when a site is identified it will be integrated into the ongoing monitoring program. The locations of the current stations and the surrounding environment are shown in Figure 1. All three stations are permanent installations supplied with AC power.

2.1 Primary Ambient Air Quality Monitoring Station

The primary monitoring station is located in the residential community of Wilmington, on the rooftop of a building at the Saints Peter & Paul Elementary School (SPPS).

Primary Station Components

The primary station will consist of the following sampling components:

1. One federal reference method (FRM) PM less then 10 microns in diameter (PM_{10}) mass sampler: Rupprecht & Patashnick Partisol Model 2000 PM_{10} Air Sampler.
2. One FRM PM less then 2.5 microns in diameter ($PM_{2.5}$) mass sampler: Rupprecht & Patashnick Partisol Model 2000 $PM_{2.5}$ Air Sampler.
3. One Desert Research Institute (DRI) sequential filter sampler (SFS) to collect 24-hour $PM_{2.5}$ samples for mass concentration and carbon analysis (elemental carbon [EC] and organic carbon [OC]).
4. One DRI SFS to collect $PM_{2.5}$ samples for mass concentration, carbon analysis, and elemental and ion analysis during periods of onshore and offshore flow events.
5. One DRI SFS to collect 24-hour PM_{10} samples for carbon analysis.

6. A continuous $PM_{2.5}$ monitor (TSI Model 8520 DustTrak) with data averaging times of five minutes, to evaluate shorter time resolutions of $PM_{2.5}$ concentrations.
7. A Met One meteorological monitoring station to measure wind speed, wind direction, ambient temperature, relative humidity, and solar radiation.

2.2 Satellite Monitoring Program

The two satellite stations are located on the rooftop of the Liberty Hill Plaza (LHP) building in San Pedro and at Berth 47.

Satellite Station Components

Each satellite station will consist of the following sampling components:

1. One DRI SFS to collect 24-hour $PM_{2.5}$ samples for mass concentration and carbon analysis.
2. One DRI SFS to collect $PM_{2.5}$ samples for mass concentration, carbon analysis, and elemental and ion analysis during periods of onshore and offshore flow events.
3. A continuous $PM_{2.5}$ monitor (TSI Model 8520 DustTrak) with data averaging times of five minutes, to evaluate shorter time resolutions of $PM_{2.5}$ concentrations.
4. A Met One meteorological monitoring station to measure wind speed, wind direction, and ambient temperature.

2.3 Summary of Monitoring Instrumentation

The monitoring systems deployed in this program can be divided into two general types:

1. Real-time monitors – these instruments include the meteorological monitoring stations and the DustTrak instruments. The meteorological data are averaged over fifteen- minute and hourly periods, and the DustTrak data are averaged over five-minute periods. These data are collected for 365 days per year and stored on internal dataloggers within the instruments, for later retrieval, review, and analysis.
2. Integrated monitors – these instruments include the FRM and SFS monitors. Filters placed in these instruments collect particulates from the ambient air drawn into the monitor for 24-hour or shorter periods designated as “onshore” or “offshore” flow events.

The integrated monitors initially will collect samples every 3 days for a 90-day trial period. The sampling schedule for the integrated monitors will match EPA’s nationwide third-day sampling schedule. Table 1 summarizes the air quality and meteorological monitoring instrumentation deployed at the primary and satellite monitoring stations.

Table 1. Instrumentation Used in the Port-Wide Air Monitoring Network

Monitoring Parameter	***Primary Station*** **(Wilmington)**	***Satellite Stations*** **San Pedro & Berth 47**
FRM $PM_{2.5}$ Monitor	**X**	
FRM PM_{10} Monitor	**X**	
SFS PM_{10} Monitor (24-Hour Average)	**X**	
SFS $PM_{2.5}$ Monitor (Onshore/Offshore Flows)	**X**	**X**
SFS $PM_{2.5}$ Monitor (24-Hour Average)	**X**	**X**
Continuous $PM_{2.5}$ Monitor	**X**	**X**
Meteorological Station	**X**	**X**

2.4 Project Staff Responsibilities

The successful operation of this program requires clearly defined responsibilities and lines of communication. The following discussion summarizes these responsibilities.

Port of Los Angeles Project Manager – Dr. Shokoufe Marashi (310) 732-3091

- Primary point of contact at the Port
- Coordinates decisions made by Port with respect to the monitoring program
- Works with SAIC project manager and technical project manager to resolve project issues.

SAIC Project Manager – Mr. Chris Crabtree (805) 564-6122

- Responsible for overall management of project, including budget and schedule
- Works with SAIC technical project manager to resolve technical and project issues.

SAIC Technical Project Manager – Dr. Gary Bertolin (858) 826-2725

- Overall responsibility for operation of monitoring program
- Works with SAIC project manager to meet project objectives

- Works with other SAIC team members (staff from SAIC, Worldwide Environmental Corporation (WECo), DRI and Terry A. Hayes Associates [TAHA]) to ensure the success of the monitoring program.

SAIC Project Scientist – Mr. Joel Torcolini (858) 826-2732

- Responsible for day-to-day operations of the monitoring program
- Works closely with TAHA technicians to ensure proper operation of monitoring stations
- Responsible for remotely downloading project meteorological data on a routine basis to ensure high data capture rate
- Works with technical project manager to resolve any project-related technical issues.

WECo Principals – Dr. Judy Chow (775) 674-7040 & Dr. John Watson (775) 674-7046

- Provide support in program design, evaluation, and implementation
- Conduct specialized analyses of data collected by program
- Purchase specialized instrumentation on behalf of the program

DRI Analytical Laboratory Manager – Mr. Steve Kohl (775) 674-7056

- Coordinate laboratory support and analyses of filter samples
- Conduct audit of monitoring program

TAHA Senior Technician – Ms. Vivian Bianchi (310) 337-7900

- Responsible for coordinating TAHA technicians to service and maintain project instrumentation
- Responsible for maintaining contact with SAIC project scientist, to alert him to potential problems and maintain high data capture
- Responsible for shipments of samples to DRI laboratory.

The project organization is shown in Figure 2.

The Port has used an informal working group to provide reviews, comments and feedback in a very timely manner during the development of this monitoring program. This informal working group has included Port EMD staff, SAIC staff, the WECo principals, and the PCAC air quality consultants.

In addition to this working group, comments on the monitoring program were provided by the South Coast Air Quality Management District (SCAQMD) and the California Air Resources Board (CARB) following a meeting in July, 2003. After startup of the monitoring program, the Port will conduct quarterly meetings to review the progress of the program with a formal technical steering group, which includes members of the informal working group, the SCAQMD, and the CARB. Staff of the regulatory agencies can attend these meetings in person or by conference call.

3.0 PROJECT SCHEDULE

During the first 90 days of the monitoring program, each of the integrated samplers (the SFS and the FRMs) at all three sites will be programmed to run on an every third-day schedule matching the EPA nationwide sampling schedule. The 2005 EPA schedule is available at http://www.epa.gov/ttn/amtic/calendar.html.

After the end of the first quarter, initial data and preliminary analysis from the first 30 days of sampling will be available. Upon review of these data, the working group will determine if it is reasonable to reduce the sampling frequency to an every sixth-day schedule.

The monitoring project will begin in January 2005. The following is a preliminary schedule of program activities, although additional reviews, analyses, or changes may occur to the project if warranted. Any program changes will be agreed upon by the Port air monitoring working group.

January 2005

- Complete installation of instrumentation at all monitoring sites
- Test out all instrumentation to ensure proper operation prior to beginning the monitoring program.
- The SAIC team will conduct a 1-day training program for TAHA technicians before the monitoring program begins. The training will include the following:
    - An introduction to each type of monitoring instrumentation, including routine operation and maintenance requirements of the equipment,
    - Procedures for the technicians to implement at each monitoring site, including completion of the monitoring checklists,
    - An outline of communication procedures to follow during routine and emergency operations of the monitoring program.
    - A project-specific training manual will be provided to each technician, which will include the instrument checklists (presented in a later section of this protocol document), detailed instructions on the maintenance of each instrument, sample shipping instructions, and contact information for other members of the SAIC team.
- Senior members of the SAIC team (Gary Bertolin and Joel Torcolini) will accompany the TAHA technicians during the first few sampling days to complete the instruction process.

- The DRI laboratory manager (Steven Kohl) will be present during the installation of the equipment (now expected in late January, 2005) to provide support and to help in troubleshooting if there are instrumentation problems, since DRI has supplied a significant amount of the instrumentation (all SFS monitors and the FRMs). In addition, Mr. Kohl will conduct an audit of the monitoring program after startup. Being responsible for the operation of many field programs including EPA's Fresno SuperSite, he is very familiar with monitoring protocols and procedures.

February 2005

- Filters collected after the first 30 days of sampling will be sent to the DRI laboratory for analysis.

March 2005

- After the 30 days of sampling, conduct a project review. The objective of this project review is to assess data recovery, address any sampling or instrumentation issues, and determine if any changes need to be made in the operation of the monitoring program. If any changes are indicated, discuss the findings with the informal working group.
- Filters collected between sampling days 30–60 sent to DRI laboratory for analysis.

April 2005

- Results from the initial 30-day sampling period received from DRI laboratory (the laboratory requires 4-6 weeks to analyze samples for analyses)
- DRI laboratory results from the first month of sampling are shared with the informal working group at the end of April. Efforts will be made to get faster laboratory analysis of the filters collected during sampling days 30-60, so that this review can also include results from the second month of sampling. Discussions regarding monitoring on a sixth-day vs. third-day sampling frequency will be initiated at this time.
- Filters collected between sampling days 60–90 sent to DRI laboratory for analysis.

May 2005

- Conduct initial quarterly meeting with the technical steering group

June 2005

- Results from first quarter sampling program received from DRI laboratory.
- Results from first quarter shared with the informal working group.
- First quarterly progress review with informal working group

July 2005

- Filters collected during the second sampling quarter sent to DRI laboratory for analysis.

August 2005

- Conduct quarterly meeting with the technical steering group

September 2005

- Results from second quarter sampling program received from DRI laboratory.
- Results from second quarter shared with the working group.
- Second quarterly progress review with working group

October 2005

- Filters collected during the third sampling quarter sent to DRI laboratory for analysis.

November 2005

- Conduct quarterly meeting with the technical steering group

December 2005

- Results from third quarter sampling program received from DRI laboratory.
- Results from third quarter shared with the working group.
- Third quarterly progress review with working group

January 2006

- DRI conducts second audit
- One-year monitoring program is completed
- Fourth quarter of data sent to DRI laboratory
- Analysis of full year of data is initiated.

4.0 MONITORING PROCEDURES

4.1 Summary of Routine Onsite Monitoring Procedures

Each time the TAHA technicians visit a monitoring station they will perform the following tasks:

- Check the operation of the meteorological monitoring station. The technicians will verify the operation by completing the real-time monitors checklist (Figure 3).
- Check the operation of the DustTrak monitor. The technicians will verify the operation by completing the real-time monitors checklist (Figure 3).
- Perform routine support/maintenance on the SFS units. A flow diagram (Figure 4) and step-by-step procedure (Figure 5) are provided to illustrate the daily maintenance steps required on the SFS units. Figure 6 gives an example of the field data sheets or FDS (provided by DRI with every filter set) that needs to be completed and returned to DRI with the exposed filters. Figure 7 provides an SFS checklist that is an integral part of this task.
- Perform routine support/maintenance on the FRM units (located only at the SPPS primary station. This includes recovering the exposed $PM_{10}/PM_{2.5}$ filters and installing new filters. The technicians will complete an FDS (similar to the example in Figure 6) that will be provided by DRI with each filter. They will also complete an FRM checklist (Figure 8) for each sample.
- After every site visit, the TAHA technicians will complete a "Master Monitoring Checklist" (Figure 9) which summarizes the status of the instruments in the monitoring program. Upon completion, this checklist will be sent to SAIC by fax or email to document the status of the monitoring program. In addition, if there are any problems or issues with the monitoring program, the technicians will call Joel Torcolini or Gary Bertolin (SAIC Point of Contact [POC)] to provide a more detailed update and discussion of the monitoring program status. Any necessary corrective action will be documented by the SAIC POC on a corrective action form.

4.2 Summary of Routine Download Procedures for Real-Time Instruments

SAIC staff will routinely download data from the real-time instruments, based upon the following schedule:

- Meteorological Monitoring Station – Each station will be equipped with a cellular telephone system that will allow the data collected on the station datalogger to be downloaded remotely by SAIC team members, Port staff, or other authorized program participants. SAIC staff in San Diego will routinely download the data from each station twice per week, in order to maximize data recovery.

- DustTrak Instruments – Each DustTrak has the capability of storing approximately 200 days of data, when the instrument is set up to record data at the initial setting of five-minute intervals. SAIC staff will download the data from the DustTrak instruments onto a portable laptop computer during each site visit to the Port or at intervals of 2-3 weeks, whichever is shorter.

4.3 Non-Routine Maintenance Procedures

Many of the instruments require periodic maintenance. For example, the SFS instruments should have a leak test, makeup air performance test, and replacement of the pump exhaust filters on a quarterly basis. The SAIC team will strictly follow applicable guidance documents for periodic instrument maintenance. The following documents are incorporated in this protocol document by reference:

- DRI Operating Procedure for Sequential Filter Sampler: Operation, Maintenance, and Field Calibration, Revision 10, November 29, 1990.
- TSI Model 8520 DustTrak Aerosol Monitor Operation and Service manual, Revision N, October 2003.
- State of California Air Resources Board Air Monitoring Quality Assurance, Volume II, Standard Operating Procedures for Air Quality Monitoring, Appendix AJ. Rupprecht & Patashnick Partisol-FRM Model 2000 $PM_{2.5}$ Air Sampler, Monitoring and Laboratory Division, May 1999.
- Met One Instruments Meteorological Monitoring System Operation Manual, July 2004.
- Meteorological Monitoring Guidance for Regulatory Modeling Applications, EPA Office of Air Quality Planning and Standards (EPA-454/R-99-005, February 2000).

4.4 Data Review and Analysis

- Filter-based data – All filters will be analyzed and reviewed by the DRI laboratory, using DRI standard laboratory protocols. They will have the first opportunity to check for outliers, data inconsistencies, etc. In addition, SAIC will conduct a second, overlapping review to check for monitor operation and calibrations, filter integrity, as well as outliers and data inconsistencies. The SAIC and DRI teams will work closely together to ensure the highest level of data integrity.
- Meteorological Data – SAIC will review the meteorological data with the help of a scanning program. This program is based on guidance for quality assurance/quality control and data validation procedures provided in EPA's *Meteorological Monitoring Guidance for Regulatory Modeling Applications*, which was produced by the Office of Air Quality Planning and Standards (EPA-454/R-99-005, February 2000). If the scanning program identifies any potential problems, the SAIC team will initiate discussions with the TAHA technicians immediately to determine the

status of the monitoring instrumentation. If the problem cannot be resolved quickly by telephone, members of the SAIC team will be dispatched directly to the Port to resolve the problem.

- DustTrak Data – SAIC will review the DustTrak data using the users' guide for the instrument, comparisons with the integrated data collected by the FRM and SFS instruments, and with support from the DRI team.

4.5 Quality Assurance and Quality Control

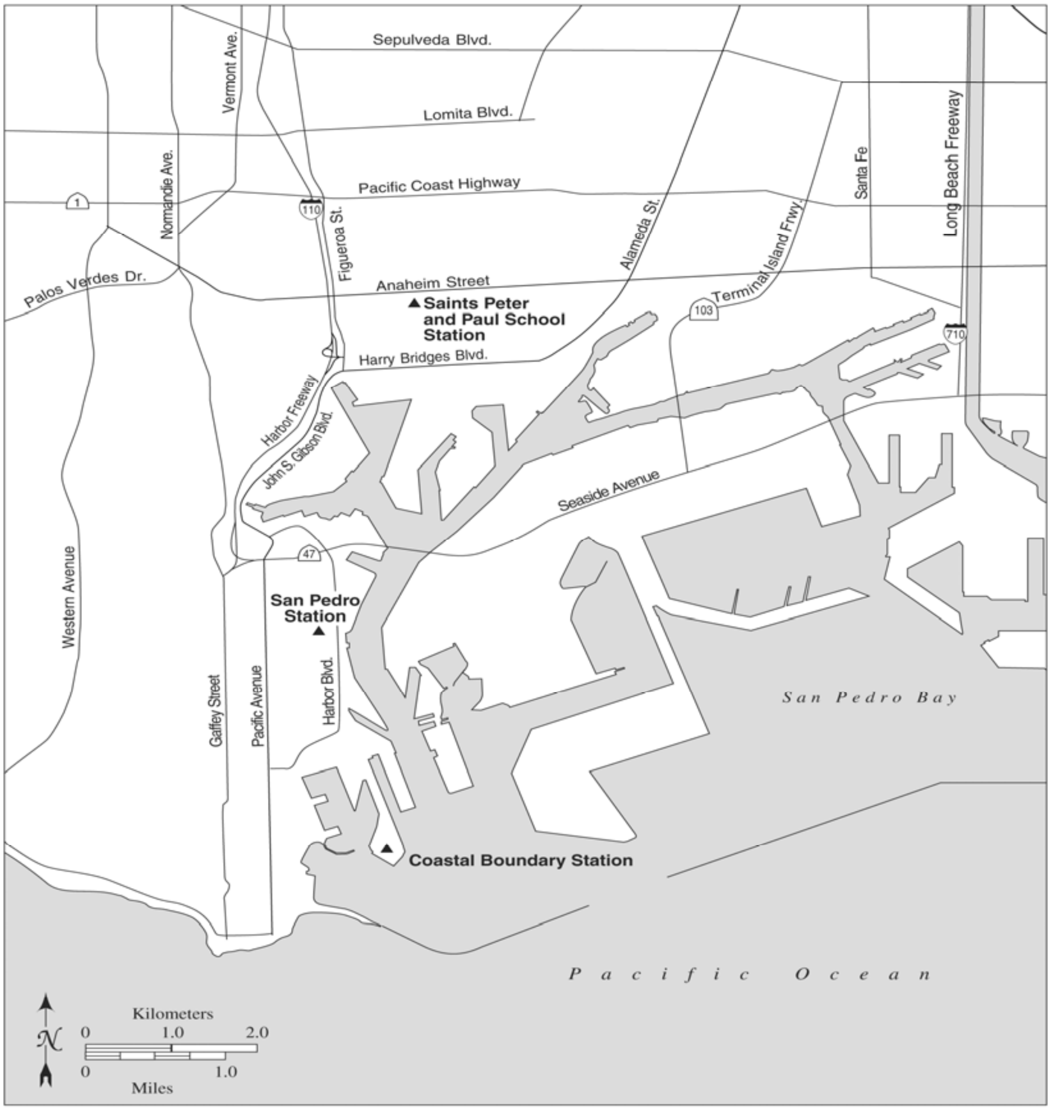
Data quality is maintained for this program by the use of instrument checklists completed for each sampling day, routine project communications between the site technicians and SAIC, and procedures and the data review procedures employed during this program. In addition, data quality will be maintained by periodic audits conducted on the monitoring program.

DRI's laboratory manager, Steven Kohl, will conduct two audits of the monitoring program, one at the start of the program and one near the end of the first year of monitoring. Mr. Kohl has considerable experience in working on and reviewing air quality monitoring programs, and will provide an independent perspective on the operation of this monitoring program. He will review the routine procedures used to operate and maintain the instruments, and write a report detailing his findings and recommendations.

In addition, the Port EMD staff will also request that the SCAQMD or CARB conduct an external audit on this program.

FIGURES

Figure 1. Locations of POLA Air Monitoring Stations



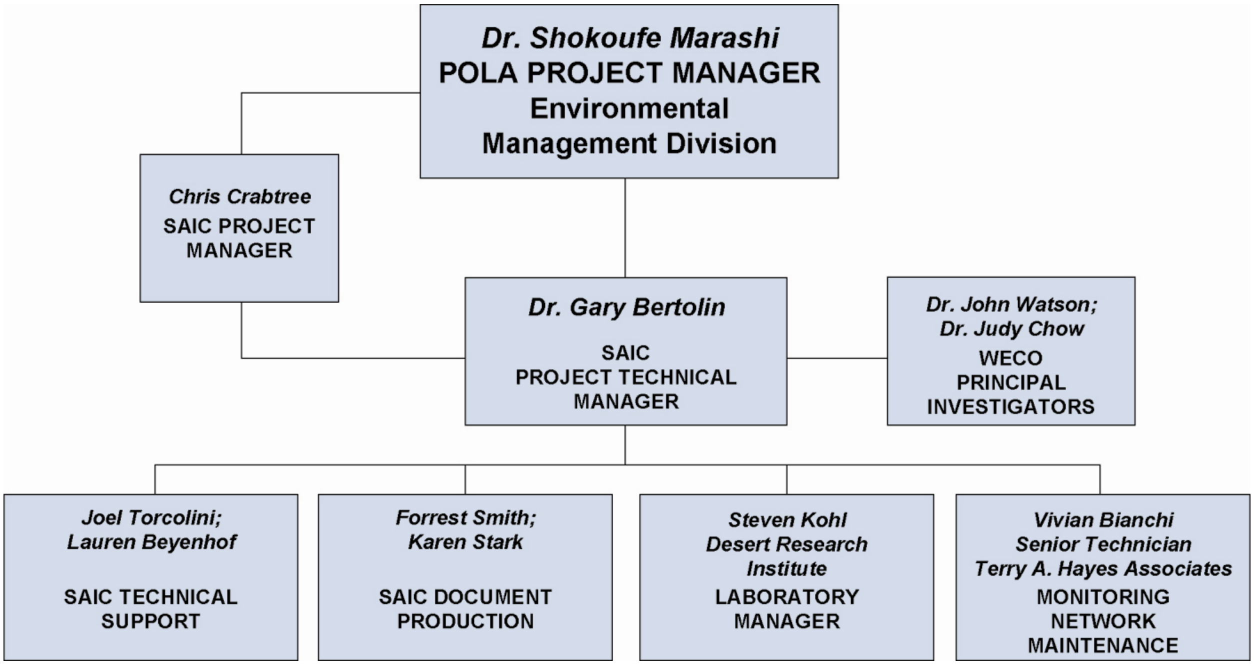

Dr. Shokoufe Marashi
POLA PROJECT MANAGER
Environmental Management Division
Chris Crabtree
SAIC PROJECT MANAGER
Dr. Gary Bertolin
SAIC PROJECT TECHNICAL MANAGER
Dr. John Watson;
Dr. Judy Chow
WECO PRINCIPAL INVESTIGATORS
Joel Torcolini;
Lauren Beyenhof
SAIC TECHNICAL SUPPORT
Forrest Smith;
Karen Stark
SAIC DOCUMENT PRODUCTION
Steven Kohl
Desert Research Institute
LABORATORY MANAGER
Vivian Bianchi
Senior Technician
Terry A. Hayes Associates
MONITORING NETWORK MAINTENANCE

Figure 3. POLA Air Quality Monitoring Program Real-Time Monitors Checklist

Meteorological Monitoring Station & Dusttrak Monitor

Field Tech ______________________________ Date __________________

Site Arrival Time ________ Site ID _________

Unless a specific question is asked, please answer with a "Yes" or "No."	*Status or Response*	*Comments/Time of Data Reading*
1. Datalogger		
A. Is there power to the datalogger?		
B. Enter time and date from display		
2. Meteorological Equipment		
A. Wind Speed		
(1) WS output from datalogger (m/s)		
(2) Does indicated WS seem reasonable?		
(3) Are signal cables visibly free from damage?		
B. Wind Direction		
(1) WD output from datalogger (^{o})		
(2) Does indicated WD seem reasonable?		
(3) Are signal cables visibly free from damage?		
C. Wind Variance		
(1) Enter last hourly sigma theta value from datalogger.		
D. Temperature of Air		
(1) Temperature reading from datalogger (^{o}C)		
(2) Are radiation shields & cables visibly free from damage?		
E. Relative Humidity		
(1) Output from datalogger (%)		

Figure 3 (cont.) POLA Air Quality Monitoring Program Real-Time Monitors Checklist

Meteorological Monitoring Station & Dusttrak Monitor

Field Tech ______________________________ Date __________________

Site Arrival Time ________ Site ID _________

Unless a specific question is asked, please answer with a "Yes" or "No."	*Status or Response*	*Comments/Time of Data Reading*
(2) Does this value seem reasonable, given existing current weather conditions ?		
F. Solar Radiation		
(1) Output from datalogger (mw/cm^2)		
(2) Is signal cable visibly secure and free from damage?		
(3) Is glass hemisphere dirty or damaged?		
(4) Does the sensor appear to be level – any damage to the sensor mount?		
4. General Station Checks		
A. External structures visibly free from vandalism?		
5. DustTrak Monitor		
(1) Is flash lamp and pump operating properly?		
(2) Is display indicating reasonable concentrations and is datalogger		

storing data?		
(3) enter time, date and $PM_{2.5}$ concentration from display		

Field Technician's Signature

Figure 4. Diagram of Routine Maintenance Steps for SFS Monitors During Site Visit

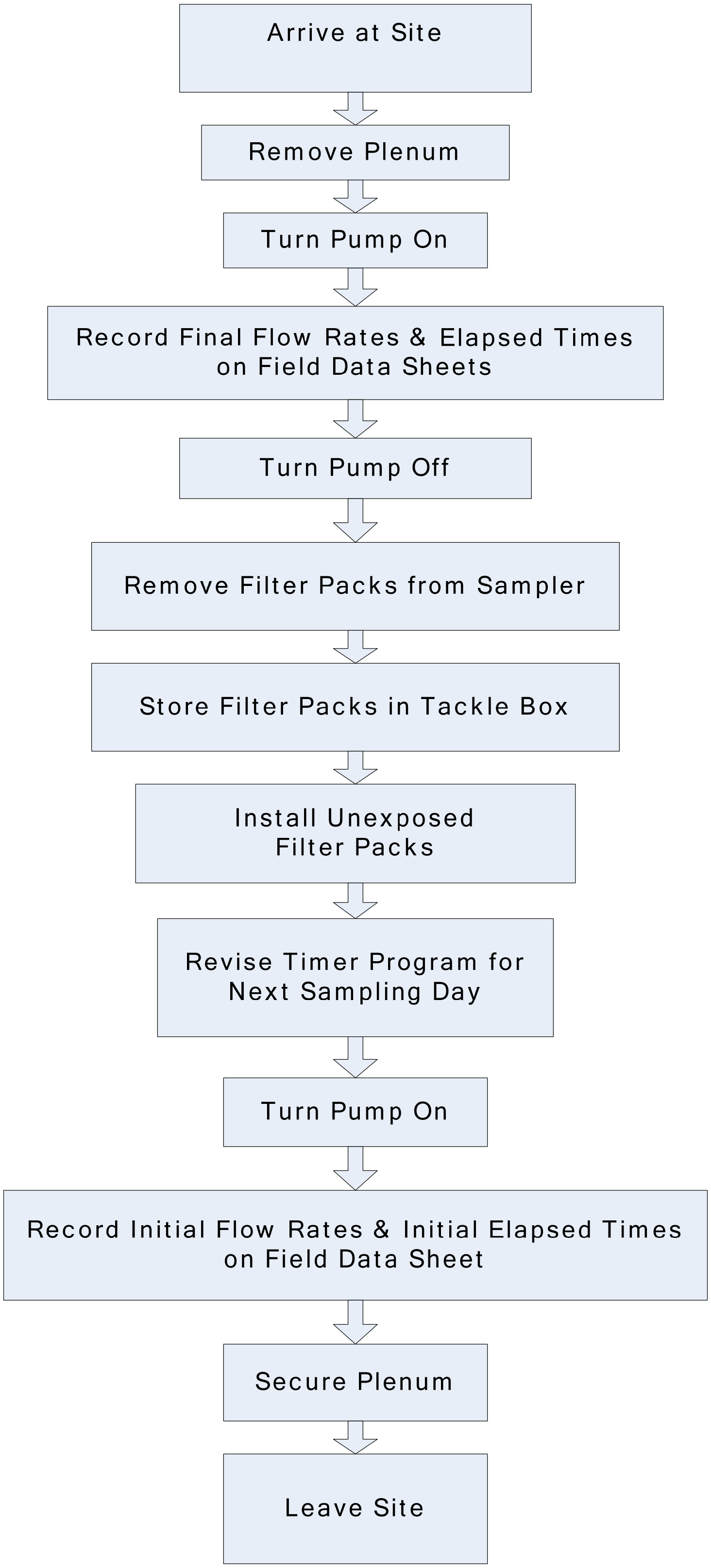


Figure 5. Step-By-Step Checklist for SFS Monitors

1. Remove plenum from SFS monitor.
2. Push Channel 1 override to turn pump on.
3. Verify that the correct sampling ports were used during the last sampling run.
4. Record elapsed time on DRI-supplied field data sheet (FDS) and SAIC SFS checklist form.
5. After instrument has run for approximately one minute to equilibrate, measure flow rates through all samples using DRI-supplied flow calibrator and record on FDS and checklist form. In addition, record the ID No. of the DRI flow calibrator used in measurement.
6. Calculate elapsed time.
7. Place top caps on exposed filter samples.
8. Remove exposed samples and put into Ziplock bag with FDS.
9. Remove bottom caps and place unexposed filter samples on SFS units. Remove top cap. Look at data sheet to match each filter pack to the proper port.
10. Measure flow rates through all filter packs with the flow calibrator and record on FDS and checklist form.
11. Record beginning time for next sampling run on FDS and checklist form.
12. Assure that proper port is on for the next sampling day.
13. Cycle through timer program and modify it as necessary for the next sampling day.
14. Assure that Channel 2 is on "OFF."
15. Secure the plenum.
16. DOUBLE CHECK THE FOLLOWING:

    Power switch is "ON."

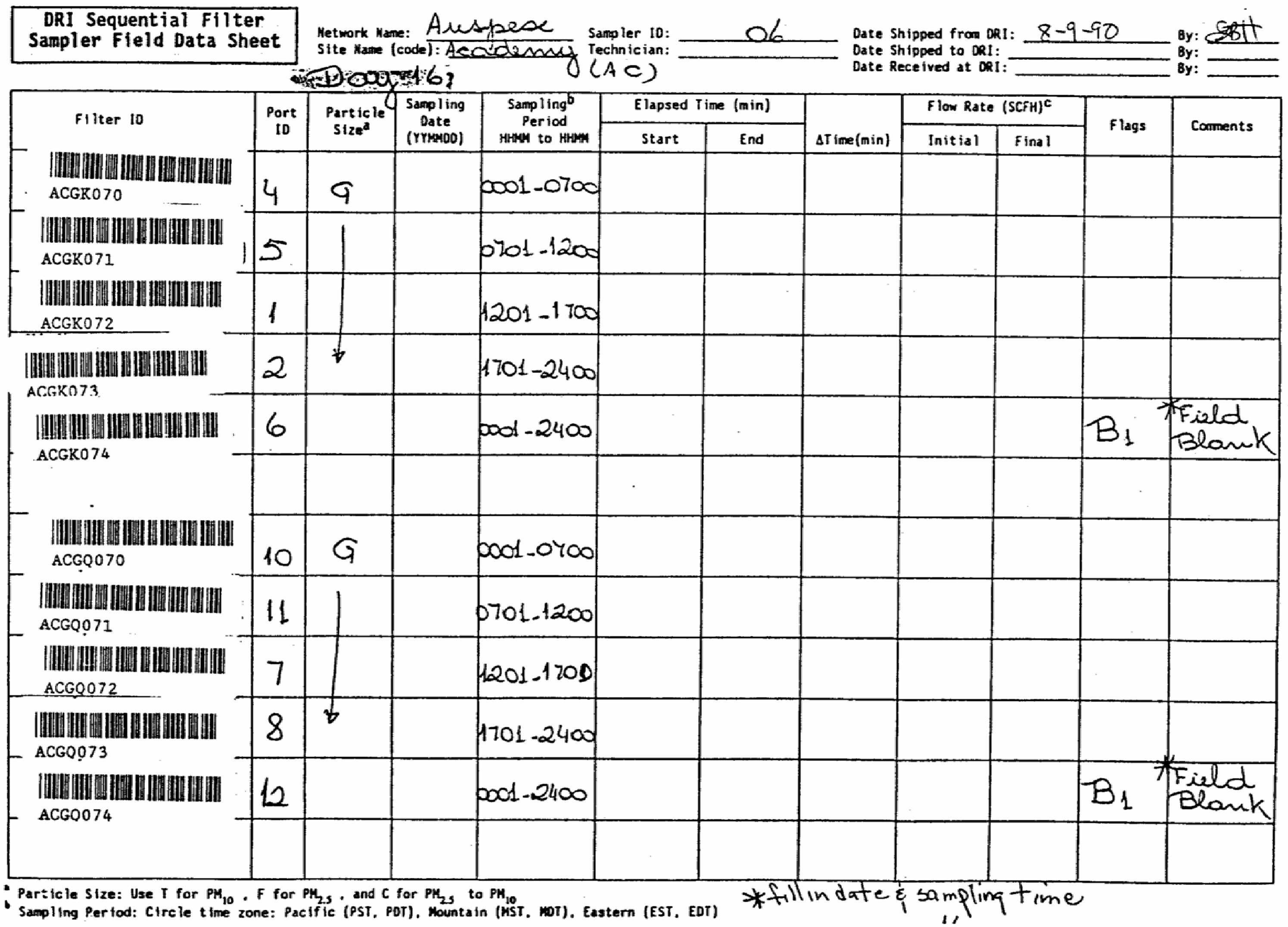
    Current port POSITION is correct.

    Timer has been reset correctly for next sampling day.

    Channel 2 is "OFF."

    Plenum is secured.

Figure 6. Example of DRI Field Data Sheet



DRI Sequential Filter Sampler Field Data Sheet

Network Name: Auspex
Site Name (code): Academy (AC)
Day 16?
Sampler ID: 06
Technician:
Date Shipped from DRI: 8-9-90 By: SBH
Date Shipped to DRI: By:
Date Received at DRI: By:

Filter ID	Port ID	Particle Size[a]	Sampling Date (YYMMDD)	Sampling[b] Period HHMM to HHMM	Elapsed Time (min) Start	Elapsed Time (min) End	ΔTime(min)	Flow Rate (SCFH)[c] Initial	Flow Rate (SCFH)[c] Final	Flags	Comments
ACGK070	4	G		0001-0700							
ACGK071	5	↓		0701-1200							
ACGK072	1	↓		1201-1700							
ACGK073	2	↓		1701-2400							
ACGK074	6			0001-2400						B1	*Field Blank
ACGQ070	10	G		0001-0700							
ACGQ071	11	↓		0701-1200							
ACGQ072	7	↓		1201-1700							
ACGQ073	8	↓		1701-2400							
ACGQ074	12			0001-2400						B1	*Field Blank

[a] Particle Size: Use T for PM_{10}, F for $PM_{2.5}$, and C for $PM_{2.5}$ to PM_{10}

[b] Sampling Period: Circle time zone: Pacific (PST, PDT), Mountain (MST, MDT), Eastern (EST, EDT)

*fill in date & sampling time

Figure 7. POLA Air Quality Monitoring Program – SFS Monitors Checklist

Field Tech ________________________ Date ______________Site Arrival Time __________ Site ID ______

SFS Monitor Identification Number: ____

Filter Installed: ______________/___________/______________________________

Month Day Year Time (local)

Filter Removed: ______________/___________/______________________________

Month Day Year Time (local)

Scheduled Sampling Day: ____________/_________/_______________________

Month Day Year

Elapsed Time Meter Reading:

	Initial Reading	Final Reading	Elapsed Time
Port 1	____________	____________	____________
Port 7	____________	____________	____________
Port 2 (if appropriate)	____________	____________	____________
Port 8 (if appropriate)	____________	____________	____________

Sampler Flow Rate (CFH/hr):

	Initial Flow	Final Flow
Port 1	____________	____________
Port 7	____________	____________
Port 2 (if appropriate)	____________	____________
Port 8 (if appropriate)	____________	____________

ID No. of DRI Flow Calibrator _________________________

Verify the Following:

______________________ Gaskets are in good condition.

______________________ PM_{10} head is secure.

Comments: ____

____

Field Technician's Signature

Figure 8. POLA Air Quality Monitoring Program FRM Monitor Checklist

SAIC 24-Hour - FIELD SAMPLE REPORT
Rupprecht and Patashnick FRM Model 2000 PM2.5/PM10 Sampler

Bar Code:

LIMS Sample ID:

Site Name: ____________________
Site Number: ____________________
Field Technician: ____________________
Particle Size: ____________________

Cassette I. D. Number: ____________________
Scheduled Sampling Date: ____________________
Sampler Property #: ____________________

SAMPLE SUMMARY

☐ Check if data electronically submitted to Laboratory

Start Date / Time: __________ / __________
Total Elapsed Time: __________ Hr:min
Volume: __________ M^3
Flow CV: __________ %

	MIN	AVG	MAX
Ambient Temp(□C):			
Filter Temp (□C):			
Pressure (mmHg):			
Flow :			

Local Condition Codes: ________________

A.	No Unusual Conditions	E.	Fire Nearby
B.	Wind/Blown Sand/Dust	F.	Sampler Malfunction
C.	Construction Nearby	G.	Rain
D.	Farming Operation Nearby	H.	Other (See Comments)

Sampler Flag Codes: ________________

OK	Good	T.	Filter Temp.
F.	Flow Rate	I.	Inst. Elec. Temp
X.	Flow Cutoff	V.	Power Outage
S.	Ambient Temp.	E.	Elapsed Sample Time
P.	Ambient Pressure	C.	Percent CV

Operator Comments ____

____

Figure 9. POLA Air Quality Program - Master Monitoring Checklist

Field Tech ______________________________________ Date_______________ Time of Completion:_____________ Site ID______

4. Notify SAIC of any identified problems (time/date);

	INSTRUMENT STATUS				
	Operation Normal	*Instrument Malfunction*	*Power Loss*	*Other*	*Comments*
1. Saints Peter & Paul School					
A. FRM - PM$_{10}$ Sampler?	☐	☐	☐	☐	
B. FRM - PM$_{2.5}$ Sampler?	☐	☐	☐	☐	
C. SFS - PM$_{2.5}$ 24-Hour Average	☐	☐	☐	☐	
D. SFS - PM$_{2.5}$ Onshore/Offshore?	☐	☐	☐	☐	
E. DustTrak?	☐	☐	☐	☐	
F. Met Station Operation?	☐	☐	☐	☐	
2. Liberty Hill Plaza					
A. SFS - PM$_{2.5}$ 24-Hour Average?	☐	☐	☐	☐	
B. SFS - PM$_{2.5}$ Onshore/Offshore?	☐	☐	☐	☐	
C. DustTrak?	☐	☐	☐	☐	
D. Met Station Operation?	☐	☐	☐	☐	
3. Berth 47					
A. SFS - PM$_{2.5}$ 24-Hour Average?	☐	☐	☐	☐	
B. SFS - PM$_{2.5}$ Onshore/Offshore?	☐	☐	☐	☐	
C. DustTrak?	☐	☐	☐	☐	
D. Met Station Operation?	☐	☐	☐	☐	

____

Field Technician’s Signature

AIR QUALITY SYSTEM UPLOAD RECORD

U.S. ENVIRONMENTAL PROTECTION AGENCY

AIRS-AQS

Report : RAW DATA INVENTORY REPORT

Filename : R252MARK.RDF

Version : 1.7

Run by : HNJ

Report Date: Jul. 20, 2009 20:28

United States
Environmental Protection Agency

Air Quality Subsystem

Raw Data Inventory Report

Jul. 20, 2009

Screening Group: Port of Los Angeles

Monitor Id	*Duration*	*Year-Mon*	*Inserts*	*Updates*	*Deletes*
06-037-9401-17202-1	1 HOUR	2007-12	744	0	0
06-037-9401-17202-1	1 HOUR	2008-1	744	0	0
06-037-9401-17202-1	1 HOUR	2008-2	696	0	0
06-037-9401-17202-1	1 HOUR	2008-3	744	0	0
06-037-9401-17202-1	1 HOUR	2008-4	720	0	0
06-037-9401-17202-1	1 HOUR	2008-5	744	0	0
06-037-9401-17202-1	1 HOUR	2008-6	720	0	0
06-037-9401-17202-1	1 HOUR	2008-7	744	0	0
06-037-9401-17202-1	1 HOUR	2008-8	744	0	0
06-037-9401-17202-1	1 HOUR	2008-9	720	0	0
06-037-9401-17202-1	1 HOUR	2008-10	744	0	0
06-037-9401-17202-1	1 HOUR	2008-11	720	0	0
06-037-9401-17202-1	1 HOUR	2008-12	744	0	0
06-037-9401-17202-1	1 HOUR	2009-1	744	0	0
06-037-9401-17202-1	1 HOUR	2009-2	672	0	0
06-037-9401-17202-1	1 HOUR	2009-3	744	0	0
06-037-9401-17202-1	1 HOUR	2009-4	720	0	0
06-037-9403-17202-1	1 HOUR	2007-12	744	0	0
06-037-9403-17202-1	1 HOUR	2008-1	744	0	0
06-037-9403-17202-1	1 HOUR	2008-2	696	0	0
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06-037-9403-17202-1	1 HOUR	2008-8	744	0	0
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06-037-9403-17202-1	1 HOUR	2008-10	744	0	0
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06-037-9403-17202-1	1 HOUR	2008-12	744	0	0
06-037-9403-17202-1	1 HOUR	2009-1	744	0	0
06-037-9403-17202-1	1 HOUR	2009-2	672	0	0
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06-037-9405-17202-1	1 HOUR	2008-11	720	0	0
06-037-9405-17202-1	1 HOUR	2008-12	744	0	0
06-037-9405-17202-1	1 HOUR	2009-1	744	0	0
06-037-9405-17202-1	1 HOUR	2009-2	672	0	0

Air Quality Subsystem

Raw Data Inventory Report

Jul. 20, 2009

Screening Group: Port of Los Angeles

Monitor Id	*Duration*	*Year-Mon*	*Inserts*	*Updates*	*Deletes*
06-037-9405-17202-1	1 HOUR	2009-3	744	0	0
06-037-9405-17202-1	1 HOUR	2009-4	720	0	0
06-037-9407-17202-1	1 HOUR	2008-4	720	0	0
06-037-9407-17202-1	1 HOUR	2008-5	744	0	0
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06-037-9407-17202-1	1 HOUR	2008-7	744	0	0
06-037-9407-17202-1	1 HOUR	2008-8	744	0	0
06-037-9407-17202-1	1 HOUR	2008-9	720	0	0
06-037-9407-17202-1	1 HOUR	2008-10	744	0	0
06-037-9407-17202-1	1 HOUR	2008-11	720	0	0
06-037-9407-17202-1	1 HOUR	2008-12	744	0	0
06-037-9407-17202-1	1 HOUR	2009-1	744	0	0
06-037-9407-17202-1	1 HOUR	2009-2	672	0	0
06-037-9407-17202-1	1 HOUR	2009-3	744	0	0
06-037-9407-17202-1	1 HOUR	2009-4	720	0	0

Total Inserts: 43056 ***Total Updates:*** 0 ***Total Deletes:*** 0

U.S. ENVIRONMENTAL PROTECTION AGENCY

AIRS-AQS

RAW DATA INVENTORY

HOURLY WIND ROSE PLOTS

Berth 47 Hourly Wind Rose Plots (January – December)

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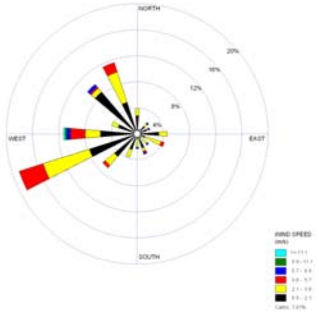	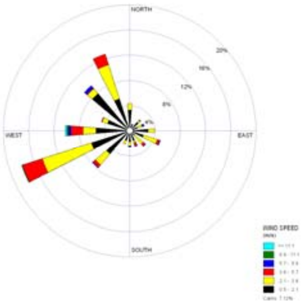	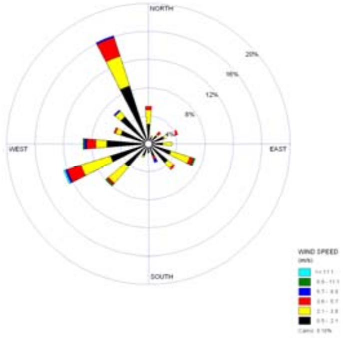	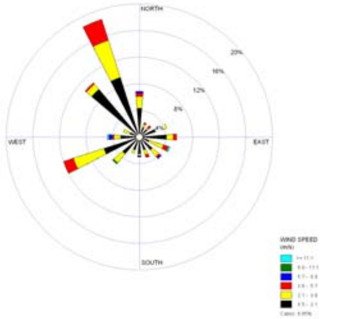
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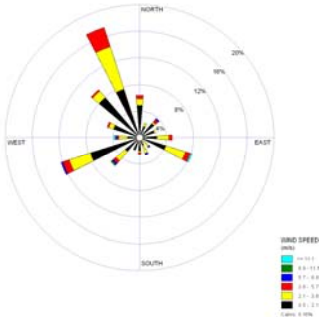	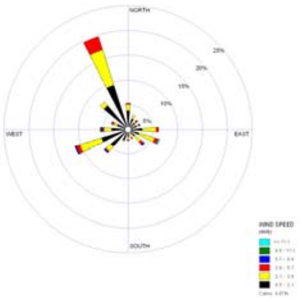	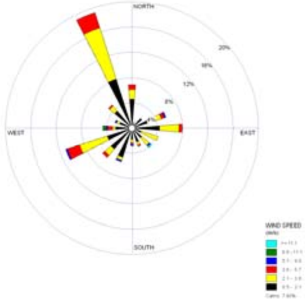	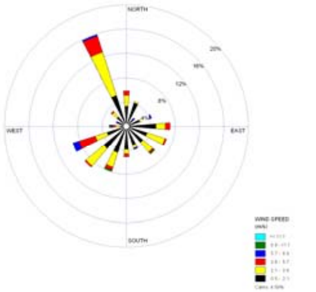
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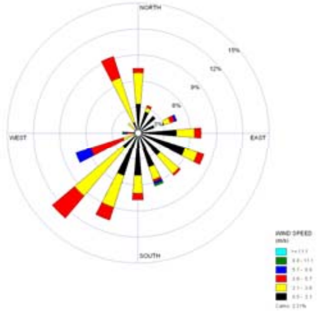	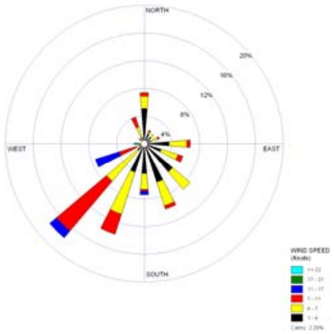	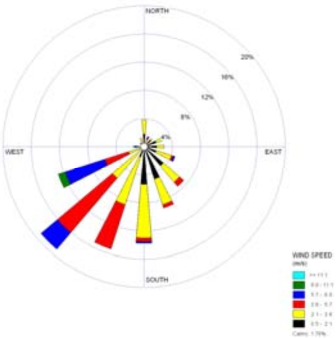	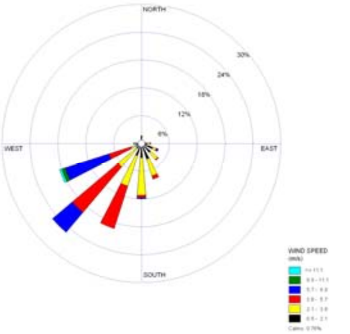

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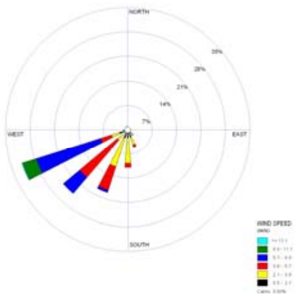	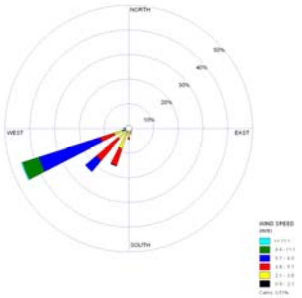	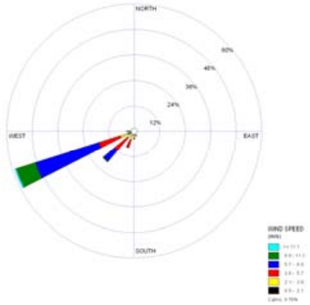	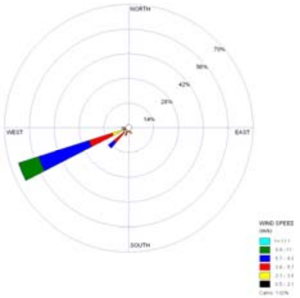
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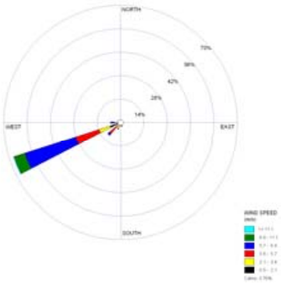	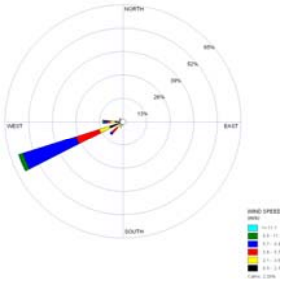	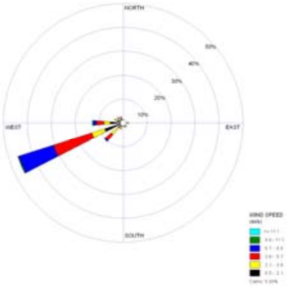	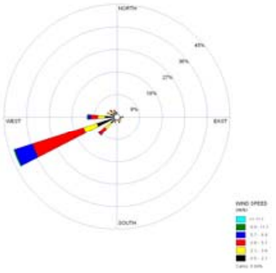
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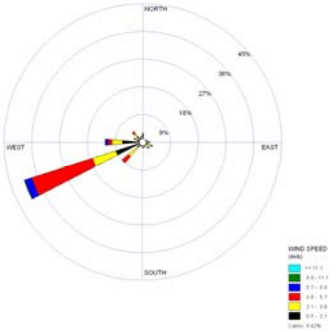	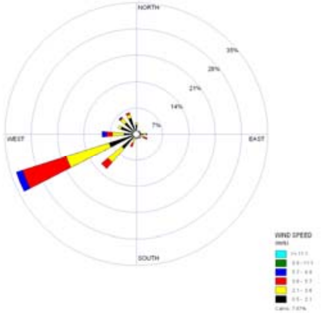	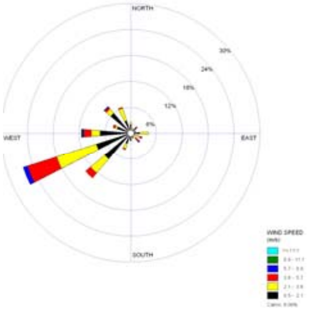	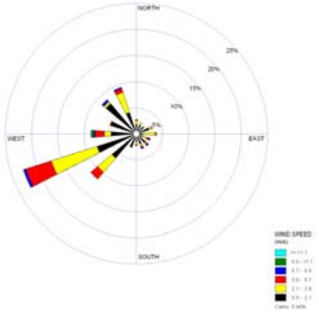

Promenade Hourly Wind Rose Plots (January – December)

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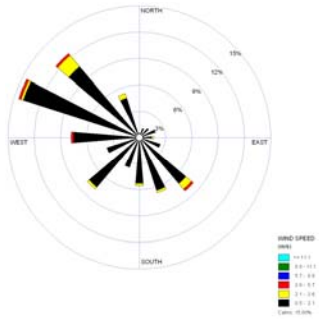	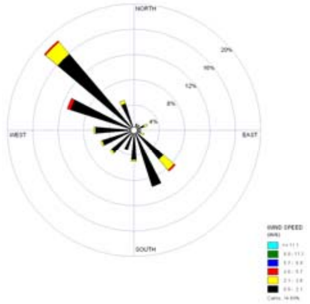	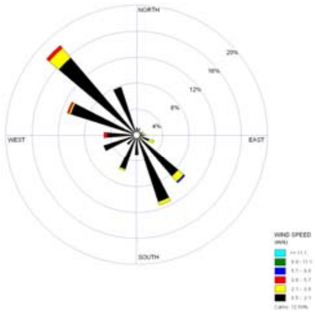	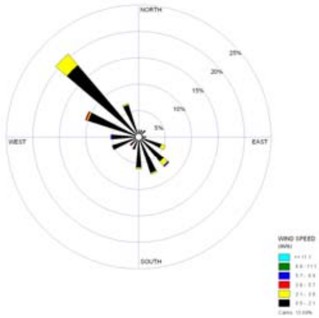
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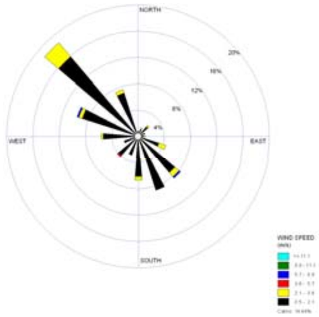	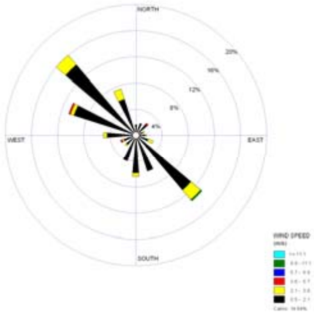	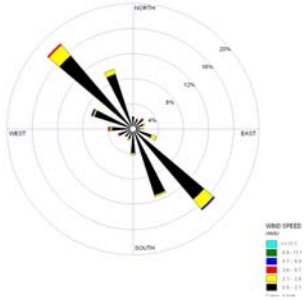	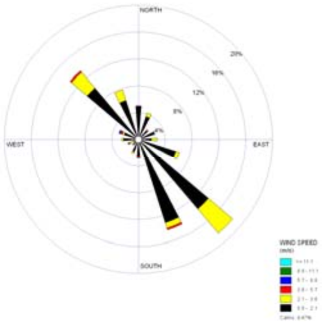
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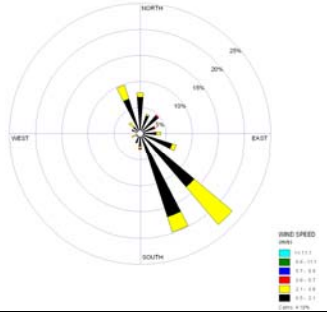	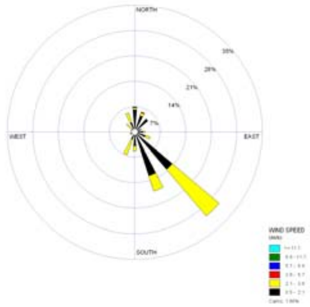	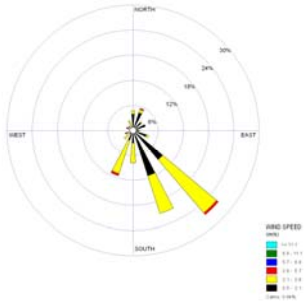	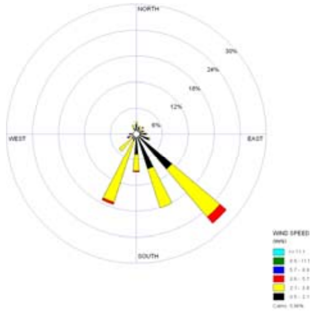

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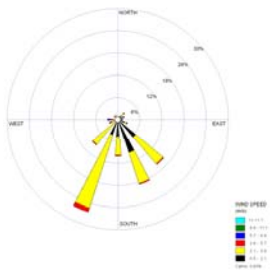	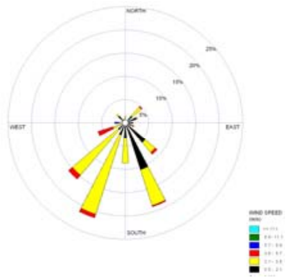	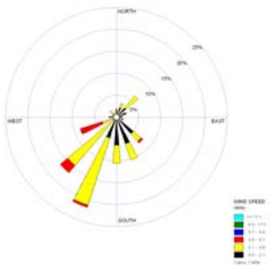	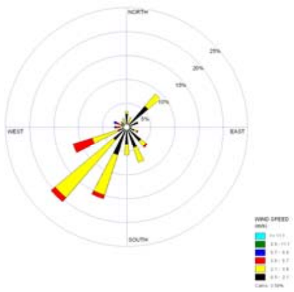
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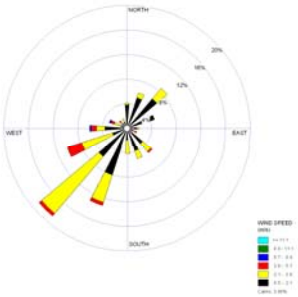	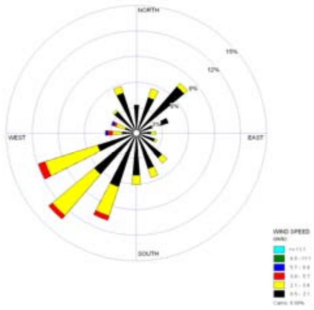	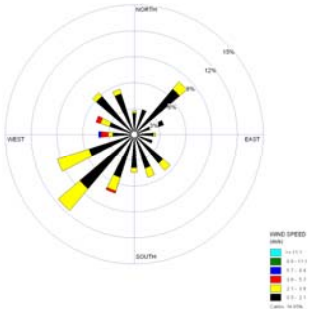	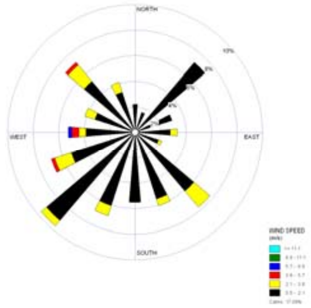
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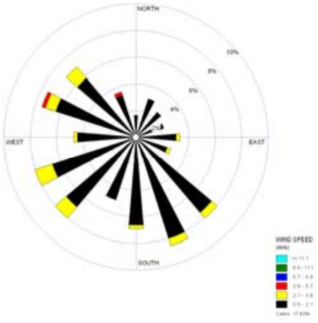	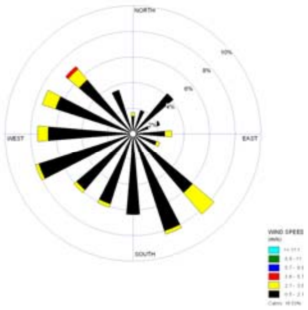	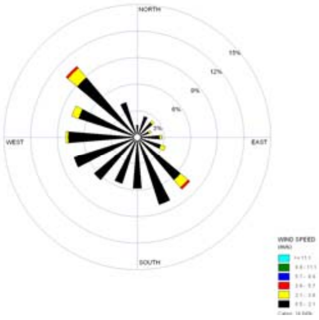	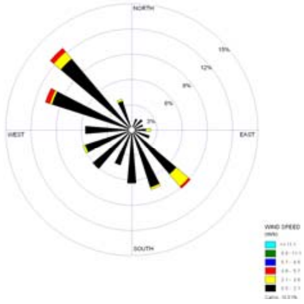

TITP Hourly Wind Rose Plots (January – December)

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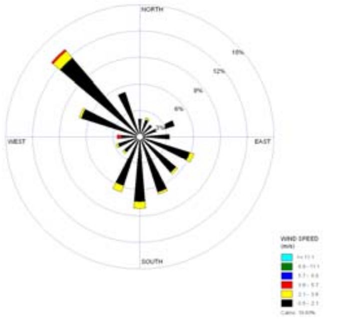

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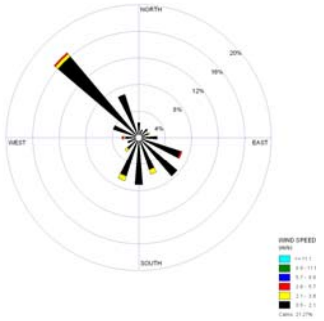

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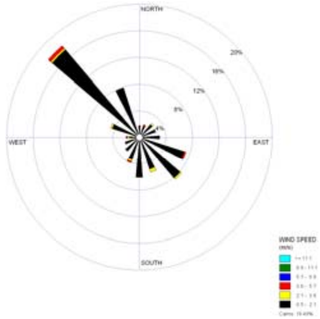

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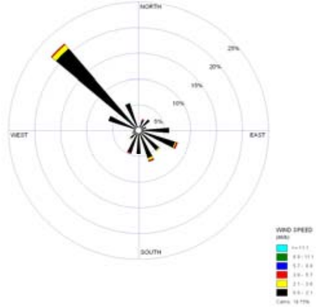

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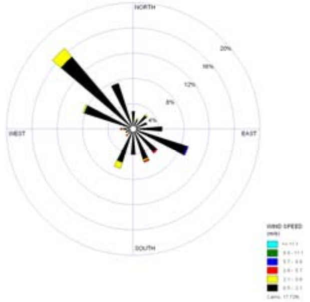

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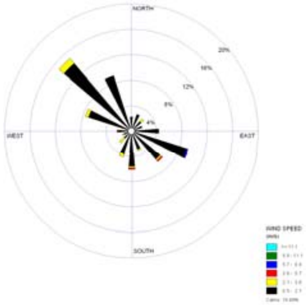

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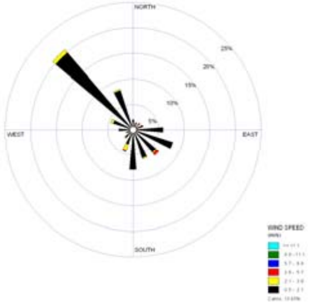

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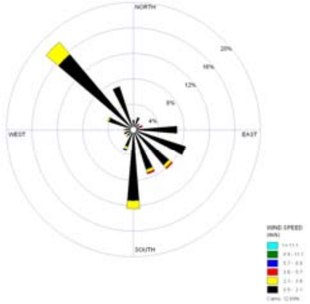

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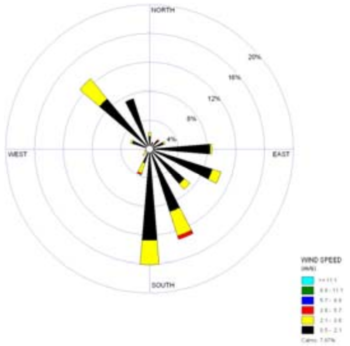

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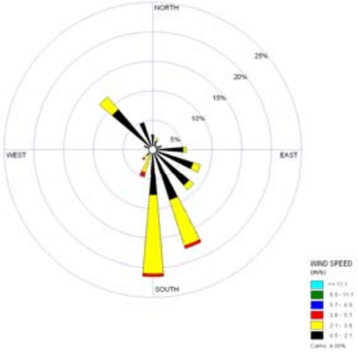

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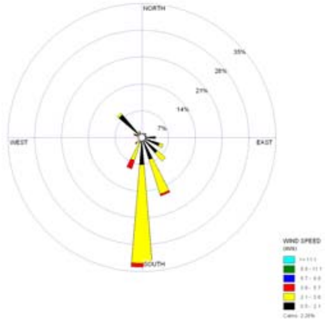

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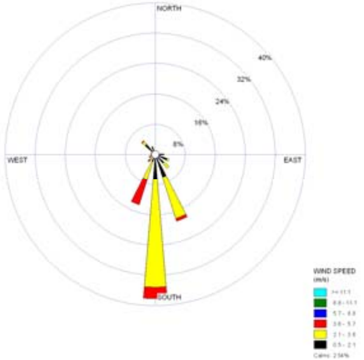

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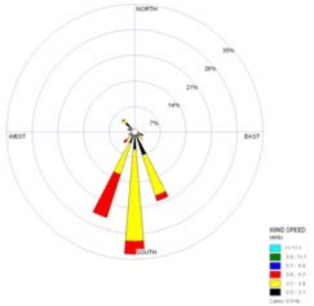	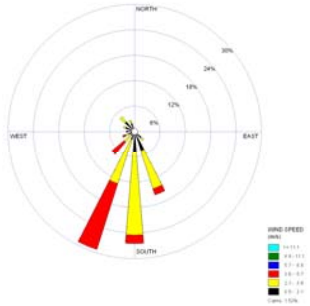	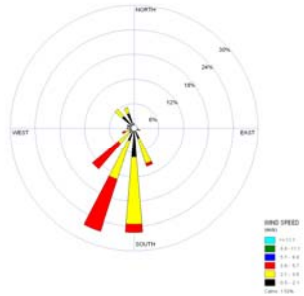	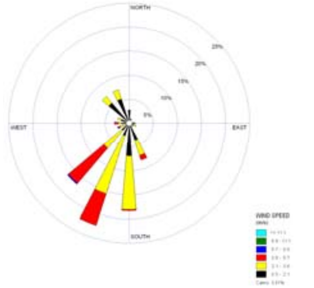
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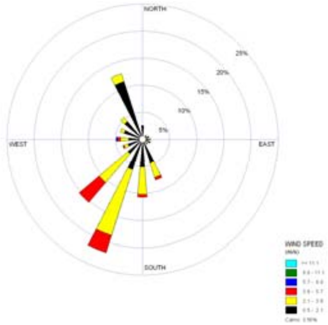	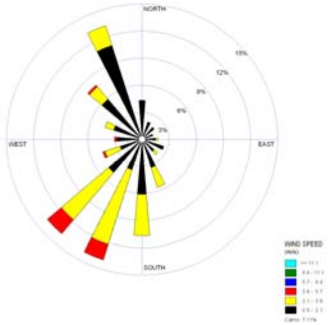	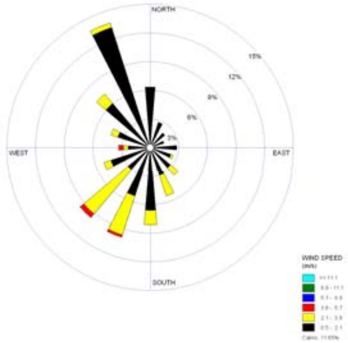	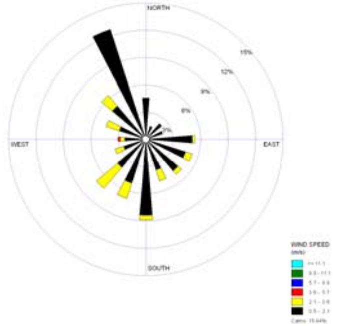
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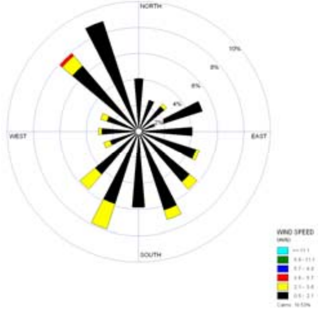	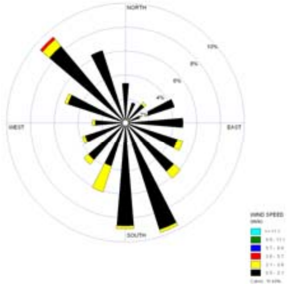	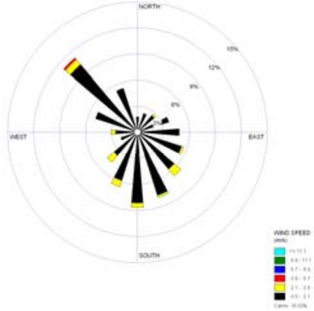	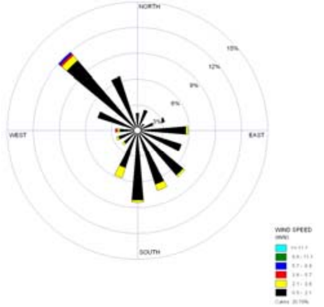

SPPS Hourly Wind Rose Plots (January – December)

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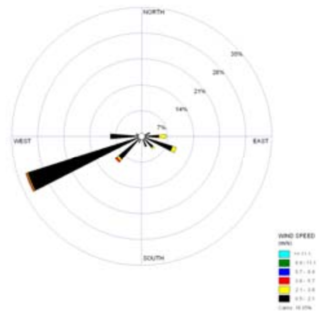	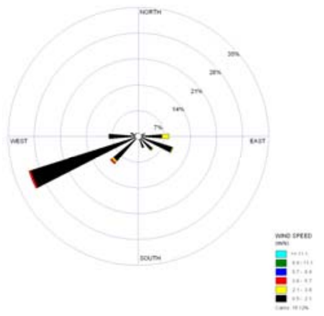	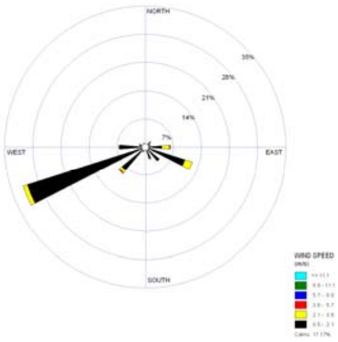	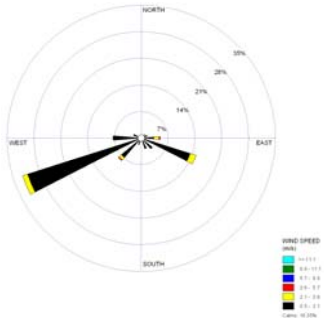
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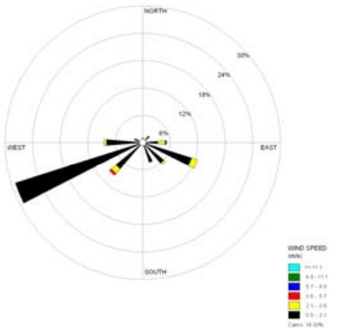	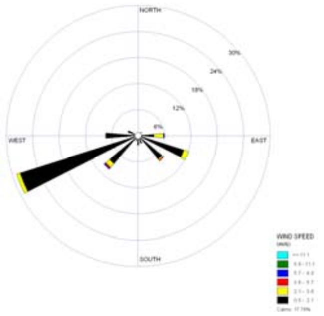	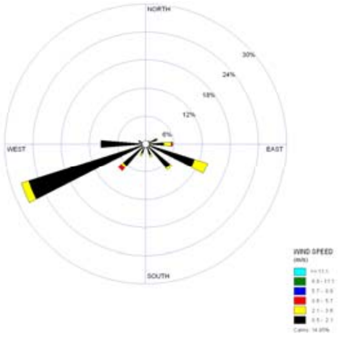	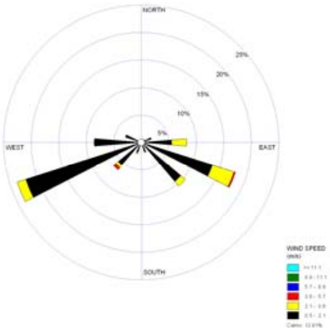
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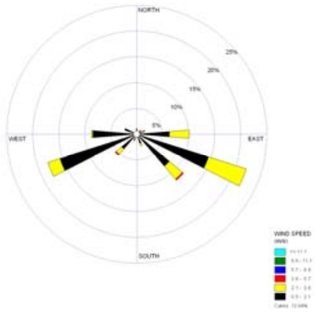	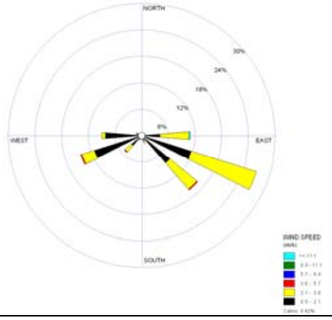	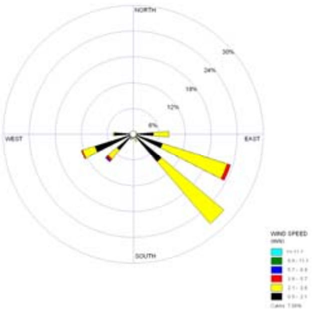	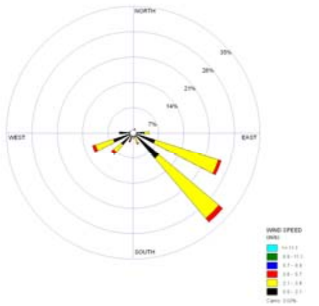

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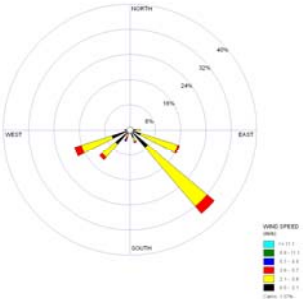	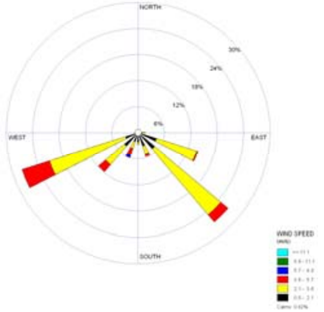	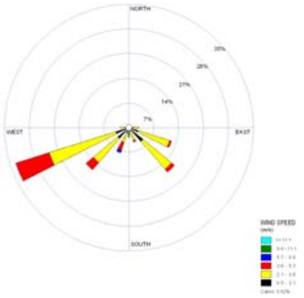	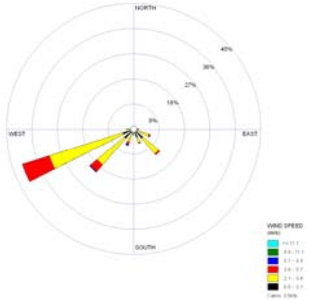
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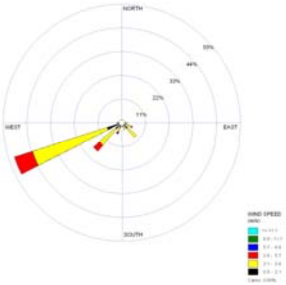	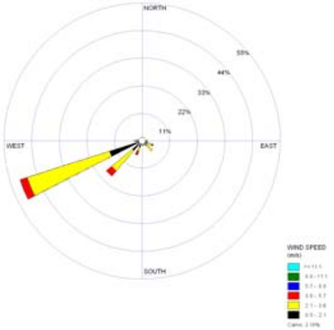	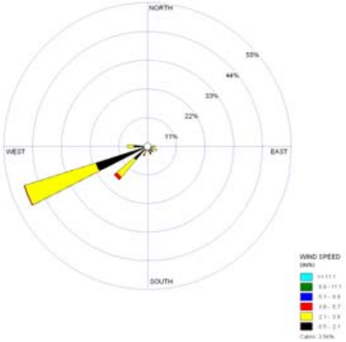	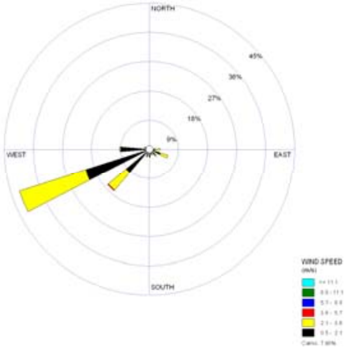
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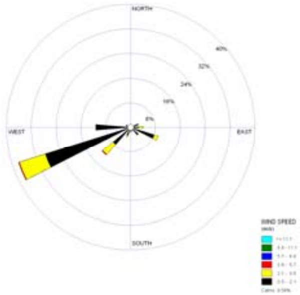
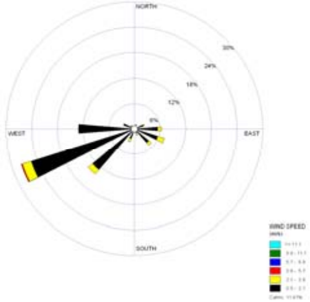
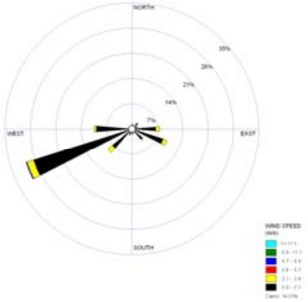
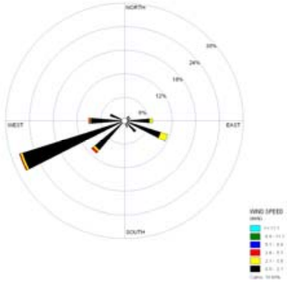
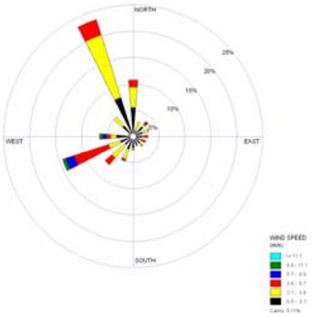
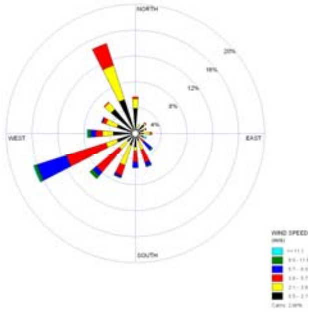
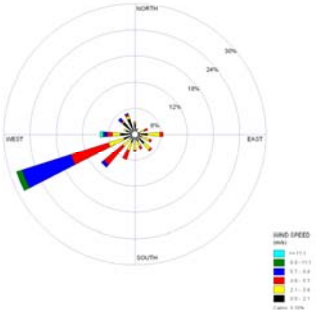
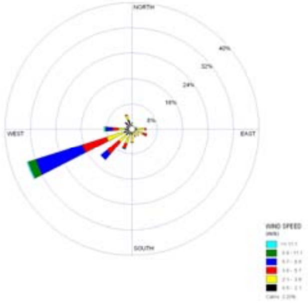
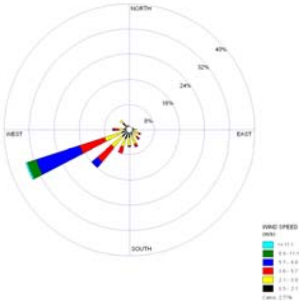
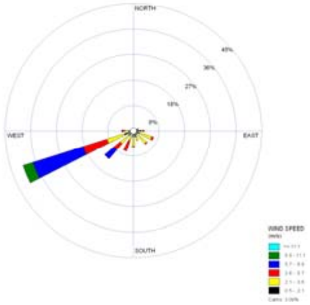
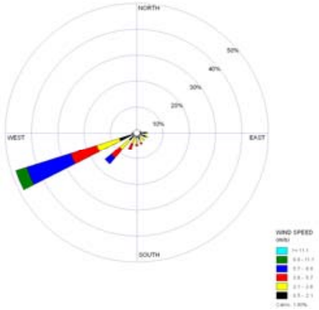
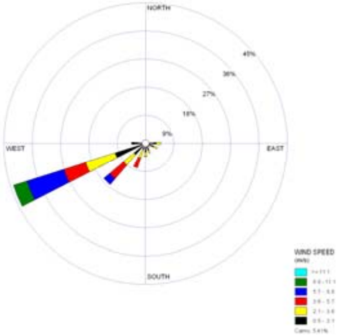
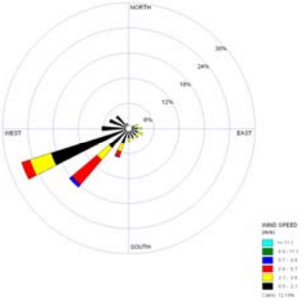
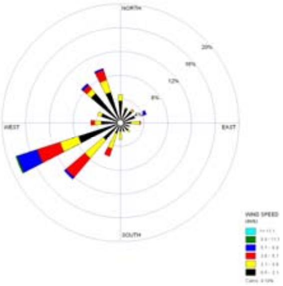
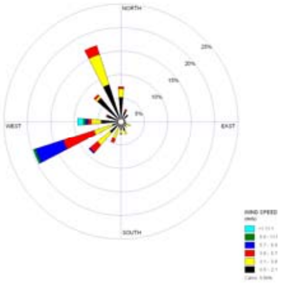
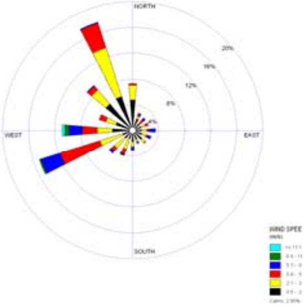
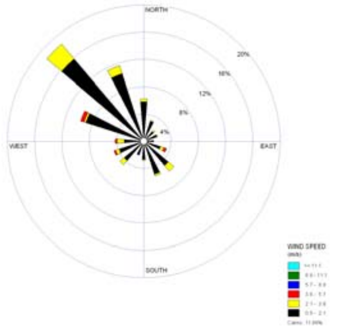
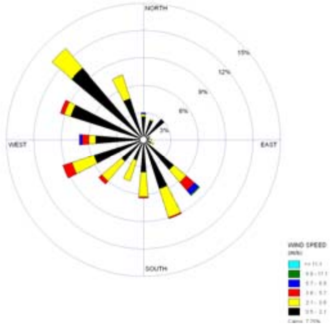
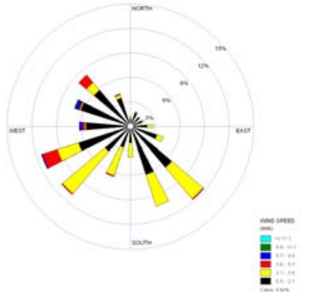
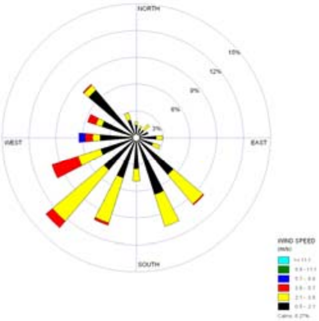
			

MONTHLY WIND ROSE PLOTS

Berth 47 Monthly Wind Rose Plots (January – December)

Jan	Feb	Mar	Apr
			
May	Jun	Jul	Aug
			
Sep	Oct	Nov	Dec
			

Promenade Monthly Wind Rose Plots (January – December)

Jan	Feb	Mar	Apr
			
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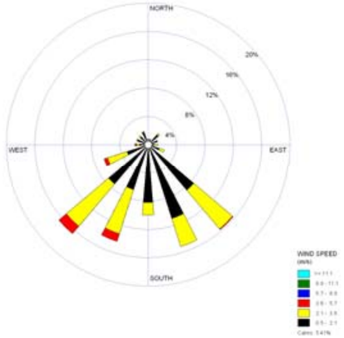
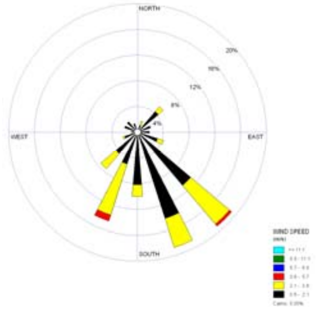
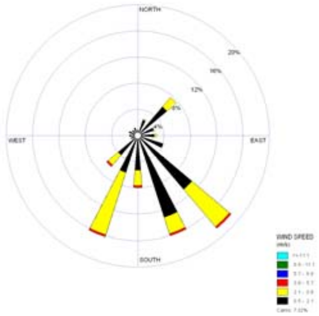
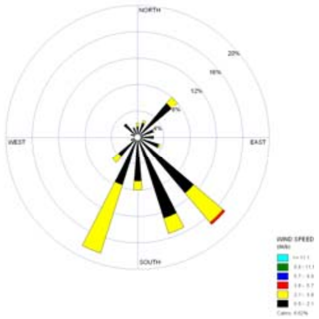
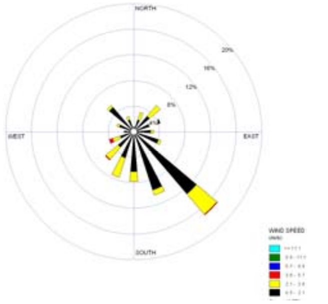
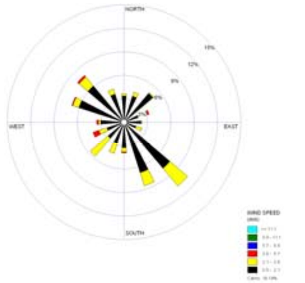
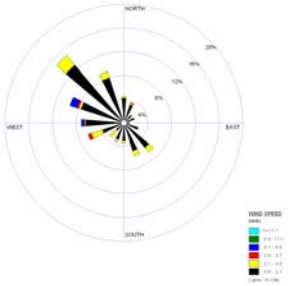
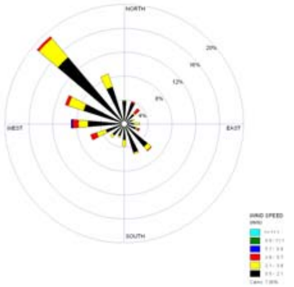
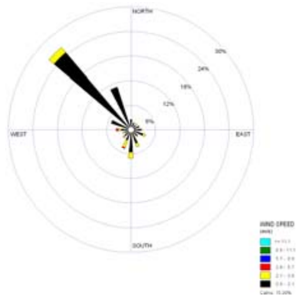
			
Sep	**Oct**	**Nov**	**Dec**
			

TITP Monthly Wind Rose Plots (January – December)

Jan



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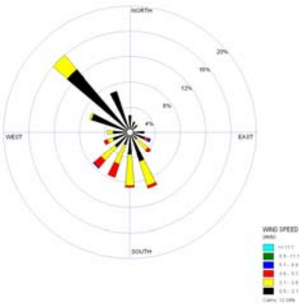

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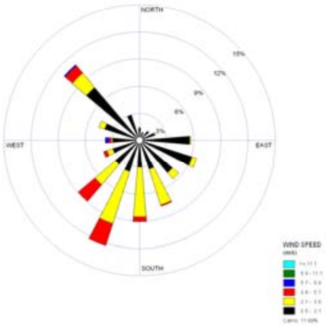

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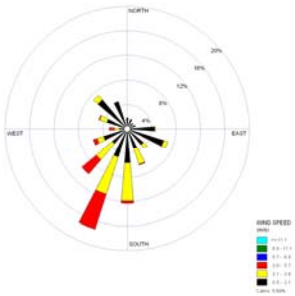

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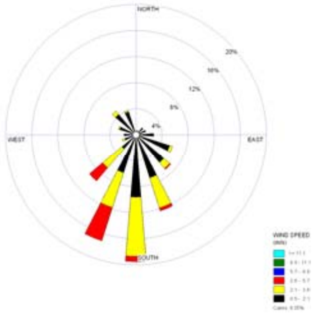

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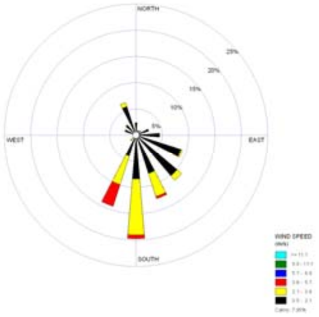

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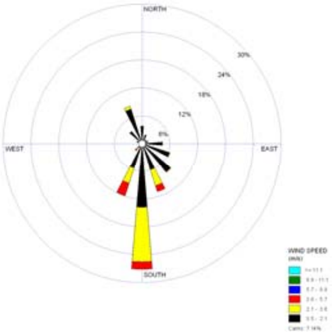

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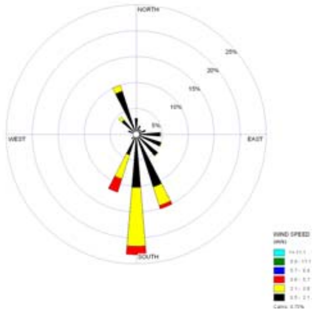

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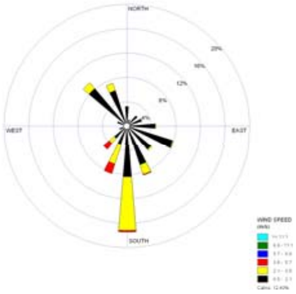

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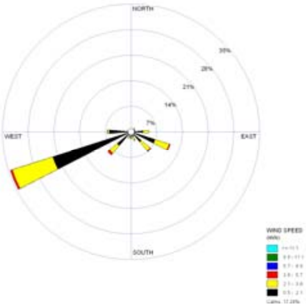

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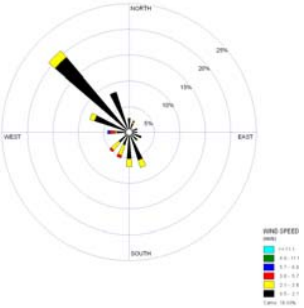

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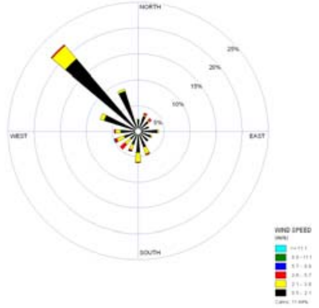
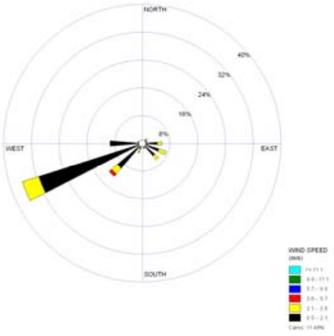
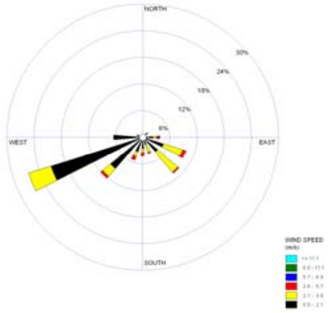
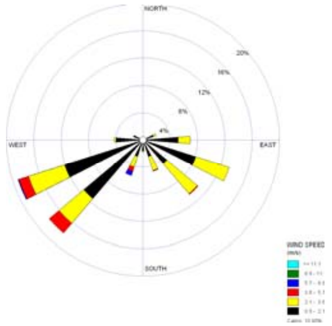
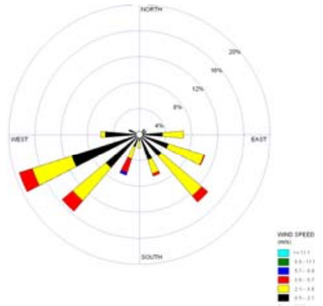
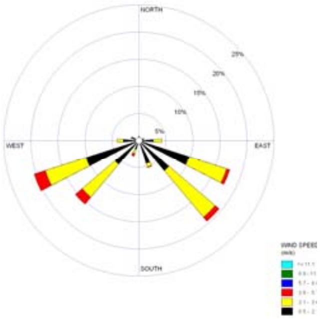
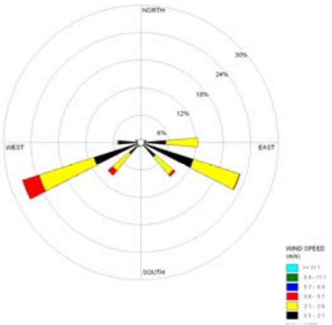
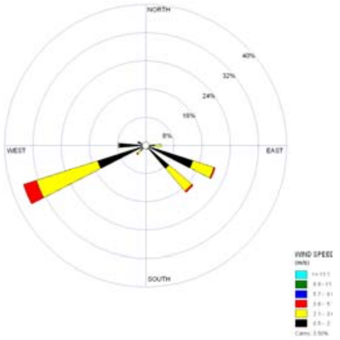
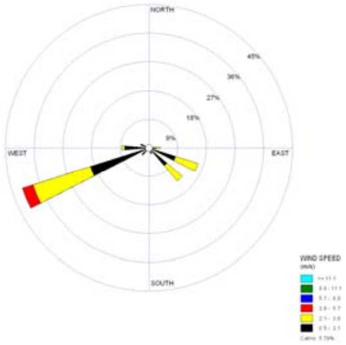


SPPS Monthly Wind Rose Plots (January – December)

Jan	Feb	Mar	Apr
			
May	Jun	Jul	Aug
			
Sep	Oct	Nov	Dec