



Review of Current Air Monitoring Capabilities near Refineries in the San Francisco Bay Area

Final Report

Prepared for:
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1. INTRODUCTION

This study reviewed and evaluated measurement approaches and methods for assessing the impacts of refinery emissions on ambient concentrations of criteria and air toxic pollutants in nearby communities. Available data for refinery emissions along with ambient air concentrations were reviewed and compared to established levels for acute and chronic health effects to identify the species that should be considered for air monitoring. Various monitoring options were then associated with the following monitoring objectives: short-term characterization of emission fluxes; long-term continuous fence-line monitoring of refinery emission releases to the community; community-scale monitoring with varying time scales to evaluate potential chronic or acute health impacts; and episodic monitoring during catastrophic events. These objectives were reconciled with available air quality data from existing BAAQMD criteria and air toxics pollutant monitoring programs, and air monitoring (both regulatory and voluntary) by the refineries to identify existing gaps in information or useful supplemental data. Published results from relevant applications of the monitoring approaches were reviewed and the specifications for selectivity, sensitivity, precision, accuracy and costs of commercially-available continuous or semi-continuous monitors, and time-integrated sampling and analysis methods were compared for each target pollutant to determine the positive and negative attributes of each monitoring approach and method. Potential augmentations to existing monitoring in the Bay Area are suggested with scalable options. This report is intended to facilitate the evaluations by a panel of monitoring experts from academia, industry, the community and other governmental agencies to provide input to the BAAQMD in developing a community air monitoring program designed to inform the public of the potential air quality and health impacts near refineries and other major industrial facilities in the Bay Area.

1.1 Background

Exposure to toxic air pollutants (toxics) remains a concern in the San Francisco Bay Area and other major metropolitan areas. While air quality data from existing monitoring networks are generally adequate to characterize the spatial variations of secondary pollutants such as ozone, nitrogen dioxide, and nitrate and sulfate particles, they are less useful for determining the range of exposures to directly emitted toxics. Pollutant concentrations may vary in space and time and gradients can be especially sharp near emission sources (e.g., near roadways and adjacent to major industrial facilities). These variations may result in significant differences between the community exposures estimated from annual average ambient concentrations from existing neighborhood-scale air quality monitoring sites and the actual exposures of individuals who spend more time in environments in close proximity to emission sources.

In recognition of the higher pollutant concentrations that may exist near emission sources, the recent revisions to the National Ambient Air Quality Standard (NAAQS) for nitrogen dioxide (NO₂) and sulfur dioxide (SO₂) established new ambient air monitoring and reporting requirements for determining compliance with the new standards. Monitors are required for the first time near major roads as well as in other locations where maximum concentrations are expected. These new monitoring requirements are designed to help protect communities that are susceptible to higher exposure concentrations. This is the latest phase in a trend over recent years toward a greater focus on near-source impacts. In 2004, the U.S. Environmental Protection Agency (EPA) began awarding grants to State and local agencies to conduct short-term, local-scale monitoring projects to augment on-going routine criteria

pollutant and air toxic monitoring programs. These studies addressed a wide range of air toxics issues including near-source impacts.

Paralleling the recent emphasis on local-scale monitoring, the concept of environmental justice (EJ) was developed to address disproportionate impacts that may be experienced by certain communities due to their proximity to pollutant sources. Several programs were initiated in California to evaluate tools for assessing such exposures. The California Air Resources Board (ARB) established the Neighborhood Assessment Program (NAP) in order to develop guidelines for evaluating neighborhood air pollution impacts and reduction strategies. In response to Senate Bill 25 (Children's Environmental Health Protection Act), ARB conducted special studies in six communities around the state including an 18-month (November 2001 through April 2003) special air quality monitoring study in the communities of Crockett in Contra Costa (ARB, 2004) and Fruitvale in Oakland (CARB, 2005) to investigate the impact of traffic and other industrial sources on children's exposure to air pollution. These studies were conducted as part of a larger statewide evaluation of the adequacy of the State's air quality monitoring network as required by SB 25. The California Office of Environmental Health Hazard Assessment (OEHHA) conducted the East Bay Children's Respiratory Health Study to determine whether exposures to traffic-related air pollutants are associated with increased respiratory symptoms and disease in children, such as asthma and bronchitis (Kim et al. 2004).

In addition to near-road measurement studies, a number of community-scale studies have been conducted throughout California, which addressed environmental justice concerns or were conducted as part of a legal settlements arising from planned expansions of existing facilities. The subject of these studies include the Ports of Los Angeles and Long Beach (Fujita et al, 2009; Kozawa et al., 2009; Moore et al., 2009; Mason et al., 2011), Port of Oakland (Fujita et al, 2010) and the Roseville Rail Yard (ARB, 2004; Campbell and Fujita, 2005). A major study of the air quality impacts of operations at the LAX International Airport is currently nearing completion. In the Bay Area, the ARB and the BAAQMD conducted a health risk assessment (HRA) study of the impact of diesel particulate matter (DPM) emissions from the port of Oakland to the community of West Oakland (ARB, 2008). The West Oakland Monitoring Study (WOMS) was conducted in 2009-10 to provide supplemental air quality monitoring that will be used by the BAAQMD to evaluate local-scale dispersion modeling of diesel emissions and other toxic air contaminants for the area within and around the Port of Oakland (Fujita et al., 2010). Monitoring data from WOMS showed spatial patterns of higher pollutant concentrations that were generally consistent with proximity to vehicle traffic. The concentrations of DPM estimated from measured elemental carbon at the WOMS community sampling sites were consistent with the model estimates of DPM from the HRA for 2005 after adjusting the model projections for changes in distributions and volumes of truck traffic provided by a detailed Truck Survey (BAAQMD, 2009) conducted by BAAQMD and projected impact of mitigation measures that have been implementation since 2005. The combined decrease in DPM emissions estimated by BAAQMD of 40 to 60% were consistent with reductions reported in an exhaust plume measurements study made in the port area during implementation of the California drayage truck regulation (Dallman, et al. 2011).

The new near-source monitoring requirements as well as the community monitoring studies that have been conducted in the Bay Area (e.g. WOMS) and elsewhere in California attest to the growing interest in the disproportionate impacts that may exist within communities that are located in close proximity to major emission sources. The fire that erupted at the

Richmond Chevron Refinery on August 6, 2012 heightened public concerns in the Bay Area about such impacts and added impetus for the BAAQMD to consider additions or reconfiguration of existing monitoring programs to inform susceptible communities of the potential impacts of TAC emissions from major industrial sources.

1.2 Study Objectives

1. Identify the primary risk drivers that can be used to determine ambient air health risks associated with living near refineries and chemical plants. While the main focus is on emissions associated with normal facility operations, consider means to capture emissions during facility upsets and accidents.
2. Review and evaluate current air monitoring capabilities.
3. Develop a matrix that lists additional instrumentation, methodologies and/or other exposure assessment tools that could be employed to enhance monitoring capabilities and provide information about emissions from refineries and chemical plants. Include in the matrix potential advantages, disadvantages, and approximate costs associated with each option that accommodate varying scales of the monitoring network.
4. Develop a short report describing the process used and how the matrix was developed.

1.3 Major Emitting Facilities in the Bay Area

The San Francisco Bay Area, the largest urban area in Northern California with approximately 7.15 million people, encompasses the major cities and metropolitan areas of San Francisco, Oakland, and San Jose, along with smaller urban and rural areas. The Bay Area's nine counties are Alameda, Contra Costa, Marin, Napa, San Francisco, San Mateo, Santa Clara, Solano, and Sonoma. The 2008 base year inventory in Table 1-1 shows the contributions of areawide, mobile and stationary sources in the Bay Area. Stationary Sources account for about 15% of the total emission of particulate matter less than 2.5 μm ($\text{PM}_{2.5}$), 28% of reactive organic gases (ROG), 11% of nitrogen oxides (NO_x), 75% of sulfur dioxide (SO_2) and 3% of the carbon monoxide (CO).

Major emitting facilities are subsets of stationary sources that emit more than a total for the facility of 0.05 tons/day of any criteria pollutant. The five refineries in the Bay Area account for about half of the $\text{PM}_{2.5}$, ROG and NO_x emissions from all major emitting facilities and over 90% of the SO_2 emissions. Table 1-1 also shows the subcategories of emissions from petroleum refining and total emissions of the five Bay Area refineries. The refineries are located in Contra Costa and Solano County along the shore of San Pablo Bay and Suisun Bay. A list of the refineries, their location and capacity is shown in Table 1-2. The aggregate emissions for industrial categories other than petroleum refining are relatively small in comparison. The information in this report focuses on refineries due to the greater potential for near-source impact in the Bay Area from this source. However, the measurement method and approaches described in the report are generally applicable to other point sources of toxics.

Table 1-1. Inventory of emissions (annual average tons per day) from petroleum refining in the Bay Area.

	PM10	PM2_5	ROG	NOX	SOX	CO
Areawide	175.51	52.90	87.95	16.92	0.62	161.86
Mobile	20.33	16.27	183.12	380.52	14.93	1541.50
Stationary	16.30	12.14	106.58	50.59	45.95	44.31
Total Emissions	212.14	81.31	377.65	448.03	61.50	1747.66
Petroleum Refining						
Catalytic Cracking	0.37	0.34	0.00	0.00	8.10	0.00
Coking	0.48	0.44	0.02	0.37	16.26	0.00
Cooling Towers	0.06	0.06	1.67	0.00	0.00	0.00
Fixed Roof Tanks	0.00	0.00	0.82	0.00	0.00	0.00
Floating Roof Tanks	0.00	0.00	1.67	0.00	0.00	0.00
Fugitive Losses	0.00	0.00	0.71	0.00	0.00	0.00
Others	0.02	0.02	0.17	0.07	0.04	0.06
Sulfur Plants	0.01	0.01	0.01	0.09	0.88	0.18
Tanks Unspecified	0.00	0.00	0.00	0.00	0.00	0.00
Vacuum Distillation	0.03	0.02	0.13	0.00	0.02	0.00
Vapor Recovery/Flares	0.00	0.00	0.03	0.08	0.33	0.03
Wastewater Treatment	0.00	0.00	0.94	0.00	0.00	0.00
Boilers	0.11	0.11	0.32	5.97	2.39	1.02
I.C. Reciprocating Engines	0.00	0.00	0.01	0.86	0.00	0.15
I.C. Turbine Engines	0.13	0.13	0.01	1.46	0.22	0.90
In-Process Fuel	0.08	0.08	0.43	0.66	4.22	2.61
Process Heaters	1.25	1.23	0.27	6.57	2.32	2.31
Total Petroleum Refining	2.57	2.45	7.20	16.11	34.78	7.26
% of Total Emissions	1.2%	3.0%	1.9%	3.6%	56.6%	0.4%
Major emitting facilities that emit more than 0.05 tons/day of any criteria pollutant.						
All major facilities	8	6	19	33	38	36
Refineries						
Chevron (Richmond)	0.62	0.55	2.80	2.26	4.65	1.50
Tesoro (Martinez)	0.42	0.28	3.14	4.48	7.75	0.88
Shell Oil (Martinez)	0.90	0.84	3.53	3.02	3.19	3.07
Valero (Bencia)	0.71	0.58	0.63	5.33	14.52	1.77
Conoco Phillips (Rodeo)	0.39	0.38	0.45	2.56	4.64	0.84
% of All Major Facilites	38%	44%	56%	53%	91%	22%

Table 1-2. Bay Area Refinery Locations and Capacities (Information as of October, 2012).

Refinery Name	Location	Barrels
		Per Day
Chevron U.S.A. Inc. Richmond Refinery	Richmond	245,271
Tesoro Refining & Marketing, Golden Eagle Refinery	Martinez	166,000
Shell Oil Products US, Martinez Refinery	Martinez	156,400
Valero Bencia Refinery	Benicia	132,000
Phillips 66, Rodeo San Francisco Refinery	Rodeo	78,400

The Richmond Refinery is the largest and oldest (1901) major oil refinery on the West Coast. With a processing capacity of over 350,000 barrels per day, this refinery is among the largest in the United States. It covers 2,900 acres, has 5,000 miles of pipelines, and hundreds of large tanks that can hold up to 15 million barrels of crude, gasoline, jet fuel, diesel, lube oil, wax, and other chemicals produced by the refinery. Chevron is currently implementing an Air Quality Monitoring program in the surrounding neighborhoods of North Richmond, Point Richmond and Atchison Village. This program is part of the Richmond Community Benefits Agreement for the Chevron Energy and Hydrogen Renewal Project. The Air Quality Monitoring Program will sample air quality using testing methods similar to those used by government agencies and publish these results on a community-accessible website.

The Martinez Refinery is the second largest refinery in the Bay Area and was the first American refinery built by the Shell Oil Company in 1915. It is operated by Equilon, a joint partnership of Shell and Texaco. Today it employs 900 people and processes around 165,000 barrels of crude per day. It is connected to oil fields in the Central Valley by a 170 mile long pipeline.

The Golden Eagle Refinery in Martinez, also known as the Avon Refinery has a processing capacity of 166,000 barrels of crude per day, making mostly automotive fuels. It was built in 1913, to process heavy crude from the southern San Joaquin Valley, to which it is connected by pipeline. It is now owned by Tesoro, of San Antonio, TX, and has previously been owned by Tosco and Ultramar Diamond Shamrock.

The Benicia Refinery was built by Exxon from 1966-1969, and has the distinction of receiving the first shipload of crude to be delivered from the Alaskan Pipeline, in 1977. Most of the crude processed here still comes from the pipeline via Valdez, though the refinery is also connected to a crude pipeline that brings oil from the San Joaquin Valley. It employs around 500 people, and is considered an average, large refinery, capable of processing 150,000 barrels of oil per day. Exxon sold the refinery to Valero in 2000. The oil refinery and the surrounding industrial park were built on the grounds of the Benicia Arsenal.

The San Francisco Refinery is an oil refinery located in Rodeo, California and in Arroyo Grande, California, in the San Francisco Bay Area and Santa Maria Valley. These two locations, although more than 200 miles apart are considered one location. The two locations are directly connected by a pipeline. The refinery is currently owned and operated by Phillips 66, a downstream company with midstream and chemical businesses spun-off from ConocoPhillips in 2012. The complex is capable of refining 100,000 barrels (16,000 m³) of crude oil per day.

Refineries can be classified as topping, hydroskimming or complex. Topping refineries are the least sophisticated and contain only the atmospheric distillation tower and possibly a vacuum distillation tower. The topping refiner's ability to produce finished products depends on the quality of the petroleum being processed. A hydroskimming refinery has reforming and desulfurization process units in addition to basic topping units. This allows the refiner to increase the octane levels of motor gasoline and reduce the sulfur content of diesel fuel. Complex refineries are the most sophisticated refinery type and have additional process units to "crack" the heavy gas oils and distillate oils into lighter, more valuable products. Complex refineries have the highest utilization rate at approximately 95 percent. Utilization rate is the ratio of barrels input to the refinery to the operating capacity of the refinery. Complex refineries are able to produce a greater proportion of light products, such as gasoline, and operate near capacity. The five refineries in the Bay Area are all complex refineries.

1.4 Chemical Species of Interest

Refineries emit a wide variety of pollutants including criteria pollutants (SO₂, NO_x, CO, and PM), volatile organic compounds that are photochemically reactive (e.g., ethylbenzene, formaldehyde), carcinogenic hazardous air pollutants (benzene, naphthalene, 1,3-butadiene, polycyclic aromatic hydrocarbons), non-carcinogenic toxics (hydrogen fluoride, hydrogen cyanide), persistent bioaccumulative toxics (mercury), and other pollutants (hydrogen sulfide). Refineries include the following process units with associated air emissions.

- Crude Desalting removes contaminants that can cause corrosion of equipment and processing problems by washing the crude oil with water. Process produces wastewater with contaminants including benzene and other VOCs that can be emitted into the air. Control technology: steam stripper/biotreatment.
- Catalytic Reforming converts naphtha-boiling range molecules into higher octane reformate. Process produces hydrogen as a byproduct that can be used in hydrotreaters or the hydrocracker. Air emissions include CO, NO_x, benzene, toluene, xylene, naphthalene, other VOC and dioxins. Control technology: scrubber.
- Fluid Catalytic Cracking upgrades heavier fractions into lighter, more valuable products. Process uses a fluidized catalyst to contact the feedstock at high temperature and moderate pressure to vaporize long chain molecules and break them into shorter molecules. Largest source of emissions of SO₂, NO_x, CO, PM, and metals at the refinery. Control technology: scrubber and ESP.
- Sulfur Recovery removes and recovers H₂S using an amine treating unit and the Claus process. Air emissions include SO₂, NO_x, CO, carbonyl sulfide, and H₂S. Control technology: Scrubber.
- Thermal Processing converts heavy fractions into lighter products. Types include delay coking, fluid coking (no emissions), visbreaking (no emissions) and flexicoking (no emissions). Heavy residues are thermally cracked in the delayed coking unit in a furnace with multiple parallel passes (semi-batch process), which cracks the heavy, long chain hydrocarbon molecules into gas oil and petroleum coke. Process is potentially a significant source of emissions. Delayed coking unit emits SO₂, NO_x, PM, toxics (metals) and VOC. Control technology: Flares.

Flares are combustion control device used to burn waste gases in both normal and process upset conditions. Flare stacks are primarily used for burning off flammable gas released by pressure relief valves during unplanned over-pressuring of refinery equipment. During facility or partial plant startups and shutdowns, flare stacks are also often used for the planned combustion of gases over relatively short periods. Oil refinery flare stacks may emit methane and other volatile organic compounds as well as sulfur dioxide and other sulfur compounds, and soot particles containing elemental carbon and polycyclic aromatic hydrocarbons (PAH).

Fugitive emissions are emissions of gases or vapors from pressurized equipment due to leaks and other unintended or irregular releases of gases. Fugitive emissions are potentially the largest source of VOC emission within a refinery. Leaks from pressurized process equipment generally occur through valves, pipe connections, mechanical seals, or related equipment. Fugitive emissions also occur from storage tanks. Because of the huge number of potential leak sources and the difficulties in detecting and repairing some leaks, fugitive emissions can be a significant proportion of total emissions. To minimize and control leaks at process facilities operators carry out regular leak detection and repair activities. Routine inspections of process equipment with gas detectors are used to identify leaks and estimate the leak rate in order to decide on appropriate corrective action. Proper routine maintenance of equipment reduces the likelihood of leaks.

1.4.1 Air Toxics Inventory

The Air Toxics "Hot Spots" Information and Assessment Act (AB 2588, Connelly, et. al.1987: in the California Health and Safety Code § 44300,) established a formal regulatory program for site-specific air toxics emissions inventory and health risk quantification that is managed by California air districts. Under this program, a wide variety of industrial, commercial, and public facilities are required to report the types and quantities of toxic substances their facilities routinely release into the air. The goals of the Air Toxics Hot Spots Program are to collect emissions data, to identify facilities with potential for localized health impacts, to ascertain health risks, to notify nearby residents of risks that are determined to warrant such notification, and to reduce significant risks. Table 1-3 gives the annual emission of toxics for the five refineries in the Bay Area for 2009.

The Toxics Release Inventory (TRI) program was established in 1986 by the Emergency Planning and Community Right-to-Know Act (EPCRA, section 313). In 1990, Congress passed the Pollution Prevention Act (PPA), which required that facilities report additional data on waste management and source reduction activities under TRI (Section 6607 of PPA). The Toxics Release Inventory (TRI) is a database that contains detailed information on nearly 650 chemicals and chemical categories collected from over 23,000 industrial facilities. The EPA maintains this information in a national database called the Toxics Release Inventory, which is available to the public via the Internet at www.epa.gov/tri. MyRight-To-Know TRI application (<http://www.epa.gov/tri/myrtk/index.htm>) is a look-up tool on the web site, Table 1-4 summarize the TRI data for the five refineries for the 2011 reporting year.

Table 1-3. Bay Area AQMD inventory of air toxic contaminants for 2009.

Pollutant	Shell	Tesoro	Chevron	Phillip 66	Valero	TOTAL		
	Martinez	Martinez	Richmond	Rodeo	Benicia	lbs/yr	lbs/day	
	Emissions lbs/yr							
Acetaldehyde	702	228	181	76	280	1468	4.0	
Ammonia (NH3) pollutant			292134	124128	265069	681330	1865	
Arsenic (all)	2.8	0.5	1.5	1.4	0.2	6.5	0.0	
Benzene	1864	1131	5524	681	263	9464	25.9	
Butadiene, 1,3-	15		51	274		340	0.9	
Cadmium	0.3	0.2	0.4	6.9	23.1	30.8	0.1	
Chloroform				308		308	0.8	
Chromium (hexavalent)	5.0	0.4	0.8	1.4	0.3	7.9	0.0	
Diesel Engine Exhaust Particul	6.3	29.6	315.3	20.7	75.9	448	1.2	
Diethanolamine	650	675				1325	3.6	
Ethylbenzene	479		900	62		1441	3.9	
Formaldehyde	37772	11904	1664	38239	4224	93803	256.8	
Glutaraldehyde				84		84	0.2	
Hydrogen Sulfide (H2S)	1538		1552		7294	10385	28.4	
Lead (all) pollutant	7.4			16.2		23.6	0.1	
Manganese	47.7	13.2	117.3	11.8	284.7	474.7	1.3	
Mercury (all) pollutant	8.8	1.9	3.0	69.4	31.4	114.4	0.3	
Naphthalene	345			2003		2348	6.4	
Nickel pollutant	5.4	1.6	4.2	47.8	438	497	1.4	
PAH's (benzo[a]pyrene equiv)	61.4	129.8	239.5	30.2	30.1	491	1.3	
Sulfuric Acid mist pollutant		62.4				62.4	0.2	
Perchloroethylene			28.6		36.4	65.0	0.2	
Toluene			19289			19289	52.8	

Source: <http://www.baaqmd.gov/Divisions/Engineering/Air-Toxics/Toxic-Air-Contaminant-Control-Program-Annual-Report.aspx>

Table 1-4. 2011 Toxic Release Inventory (TRI) for refineries in the Bay Area in lbs per year.

Parameter	Chevron, Richmond		Phillips 66, Rodeo		Shell Oil, Martinez		Tesoro, Martinez		Valero, Benicia	
	Fugitive	Point	Fugitive	Point	Fugitive	Point	Fugitive	Point	Fugitive	Point
1,2-DIBROMOETHANE	4	0								
1,3-BUTADIENE	130	2			34	11	17	57	37	98
BENZENE	1600	2100	1954	1424	610	1200	1300	3200	3159	3334
CARBON DISULFIDE	0	1900	0	0	1	5	0	0	0	1472
CARBONYL SULFIDE	0	280	1359	0	5	0	0	0	0	9877
CHROMIUM			0	174	23	12			0	60
COBALT COMPOUNDS	2	4							0	71
CRESOL (MIXED ISOMERS)	40	440			1	11			2	20
CUMENE					100	260	280	170	117	11
CYANIDE COMPOUNDS	0	0			0	48			0	1452
DIETHANOLAMINE	80	0			1100	1	140	0		
ETHYLBENZENE	2400	1400	630	721	1200	2700	830	750	2647	1710
HYDROCHLORIC ACID (1995 AND AFTER AC	0	2600			0	8900			0	0
LEAD COMPOUNDS	10	41	1	27	2	20	4	74	0	99
MERCURY COMPOUNDS	0.7	7.2	0.0	20.0	0.5	21.0	0.7	3.8	0.0	6.0
METHANOL	1700	28000	4715	0	0	22000	500	4100	0	59410
N-HEXANE	3200	10000	249	2295	1400	6700	2300	1500	47	1595
NAPHTHALENE	500	300	74	169	480	500	330	110	635	63
NICKEL COMPOUNDS	18	310			25	25			0	725
PHENOL	210	210	0	104	23	61			21	37
POLYCYCLIC AROMATIC COMPOUNDS	6.8	7.7	0.5	3.2	3.0	15.0	0.6	4.7	0.1	91.0
TETRACHLOROETHYLENE	2600	23			77	0	20000	0	52	2588
TOLUENE	8100	6000	4272	2516	3500	5700	2000	7000	10083	6365
XYLENE (MIXED ISOMERS)	9600	4400	4288	5696	4200	4200	2300	2800	11423	2282

1.4.2 Health Risk Assessments

Table 1-5 shows the health risk values approved by the California Office of Environmental Health Hazard Assessment (OEHHA) as of February 25, 2013 for toxic air contaminants that are commonly associated with refinery emissions. By comparison, the unit risk factor for diesel exhaust is $3.0 \times 10^{-4} \mu\text{g}/\text{m}^3$. The table includes all cancer potency values and non-cancer acute, 8-hour, and chronic Reference Exposure Levels (RELs) that are available for use in the AB 2588 Air Toxics "Hot Spots" Program. The most current acute and chronic health values should be used for the development of a facility health risk assessment.

The BAAQMD conducted a risk assessment for refinery emissions as part of the reformulated gasoline requirements in the 1990s. The results of this assessment are shown in Table 1-6. Health risk results for the maximally exposed individual (MEI) have been adjusted for changes in OEHHA health effects values (as of March 2012). The health risk impact for each TAC calculated specifically for the MEI locations were scaled by the ratios of the current and previous health effect values. A recalculation of the health risk impacts using the updated health risk values for all receptor locations may result in a change in the MEI location and a change in the corresponding maximum risk values. This also doesn't take into account any changes in the facility's operations since the Facility-wide HRA was prepared. TACs of most concern include benzene, PAH, hexavalent chromium and 1,3-butadiene for cancer risk and nickel, H₂S, formaldehyde for acute risk.

Table 1-5. OEHAA health risk values as of February 25, 2013.

TAC	Oral Potency Value (mg/kg/day)-1	Derived Residential Cancer Risk for 0.02 g/s deposition					Derived Residential Chronic HI for 0.02 g/s deposition			AEL ug/m3
		Dermal Unit Risk Factor (ug/m3)-1	Soil Unit Risk Factor (ug/m3)-1	Milk Unit Risk Factor (ug/m3)-1	Inhalation Unit Risk Factor (ug/m3)-1	Total Unit Risk Factor (ug/m3)-1	Chronic Inhalation (ug/m3)	Chronic Oral (mg/kg/day)	Maximum Pathway 1/Chronic HI (ug/m3)	
1, 3- butadiene					1.70E-04		2.00E+01			
Acetaldehyde					2.70E-06		1.40E+02			4.70E+02
Acrolein							3.50E-01			2.50E+00
Ammonia							2.00E+02			3.20E+03
Arsenic	1.50E+00	8.32E-03	4.05E-03	0.00E+00	3.48E-03	1.59E-02	1.50E-02	3.50E-06	3.97E-04	2.00E-01
Benzene					2.90E-05		6.00E+01			1.30E+03
Beryllium	na				2.40E-03		7.00E-03	2.00E-03	6.99E-03	
Bromine	na				na		na			na
Cadmium					4.20E-03		2.00E-02	5.00E-04	1.79E-02	
Chlorine							2.00E-01			2.10E+02
Chlorobenzene							1.00E+03			
Chromium, Hexavalent	na				1.50E-01		2.00E-01	2.00E-02	2.00E-01	
Copper							na			1.00E+02
Cresols							6.00E+02			
Ethylbenzene					2.50E-06		2.00E+03			
Ethylene Dibromide					7.10E-05		8.00E-01			
Ethylene Dichloride					2.10E-05		4.00E+02			
Formaldehyde					6.00E-06		9.00E+00			5.50E+01
Hexane							7.00E+03			
Hydrochloric Acid							9.00E+00			2.10E+03
Hydrogen Cyanide							9.00E+00			3.40E+02
Hydrogen Sulfide							1.00E+01			4.20E+01
Lead	8.50E-03	6.96E-07	2.29E-05	0.00E+00	1.22E-05	3.58E-05	na			na
Manganese							9.00E-02			
Mercury							3.00E-02	1.60E-04	7.09E-03	6.00E-01
Methanol							4.00E+03			2.80E+04
Methyl ethyl ketone							na			1.30E+04
Methyl tertiary butyl ether					2.60E-07		8.00E+03			
Methylene chloride					1.00E-06		4.00E+02			1.40E+04
Naphthalene					3.40E-05		9.00E+00			
Nickel					2.60E-04		1.40E-02	1.10E-02	1.40E-02	2.00E-01
Nickel Carbonyl (must adjust emissions for Ni portion only)					2.60E-04		1.40E-02	1.10E-02	1.40E-02	2.00E-01
Nitrogen Dioxide							4.70E+02			
PAHs (as BaP)	1.15E+01	1.35E-02	2.02E-03	0.00E+00	1.01E-03	1.65E-02	na			
Perchloroethylene					5.90E-06		3.50E+01			2.00E+04
Phenol							2.00E+02			5.80E+03
Selenium							2.00E+01			
Styrene							9.00E+02			2.10E+04
Sulfur Dioxide										6.60E+02
Toluene							3.00E+02			3.70E+04
Xylenes							7.00E+02			2.20E+04
Zinc	na						na			na

Table 1-6. Facility-wide HRA conducted by the BAAQMD for the reformulated gasoline project (BAAQMD, 1993).

Facility	Chevron (1993 HRA MEI)		Shell (1998 HRA MEI)		Valero (Exxon, 1993 HRA MEI)		Phillips 66 (Unocal, 1991 HRA MEI)	
# of TACs reviewed in HRA	29		34		25		15	
Toxic Air Contaminant	Adjusted Cancer Risk	TAC % contribution to Cancer risk	Adjusted Cancer Risk	TAC % contribution to Cancer risk	Adjusted Cancer Risk	TAC % contribution to Cancer risk	Adjusted Cancer Risk	TAC % contribution to Cancer risk
Benzene	5.9E-06	77.3%	5.7E-06	82.3%	8.0E-07	40.6%	2.1E-06	40.4%
PAHs (as BaP)	8.2E-07	10.7%	3.5E-07	5.0%	8.1E-07	41.0%	2.0E-06	38.4%
Chromium, Hexavalent	2.1E-07	2.8%	4.2E-07	6.1%	3.1E-07	15.8%	8.9E-07	17.1%
1, 3- butadiene	3.2E-07	4.2%	2.0E-07	2.9%	1.7E-11	0.0%	NA	
Perchloroethylene	1.6E-07	2.1%	NA		NA		NA	
Arsenic	3.1E-08	0.4%	1.4E-07	2.1%	3.8E-08	2.0%	9.4E-08	1.8%
Cadmium	2.6E-08	0.3%	9.1E-08	1.3%	4.5E-09	0.2%	1.1E-07	2.2%
Remaining TACs	1.6E-07	2.1%	2.6E-08	0.4%	8.5E-09	0.4%	7.2E-09	0.1%
Total	7.6E-06	100.0%	6.9E-06	100.0%	2.0E-06	100.0%	5.2E-06	100.0%
Toxic Air Contaminant	Adjusted Acute HI	TAC % contribution to Acute HI	Adjusted Acute HI	TAC % contribution to Acute HI	Adjusted Acute HI	TAC % contribution to Acute HI	Adjusted Acute HI	TAC % contribution to Acute HI
Nickel	1.6E+00	65%	1.4E-02	2.9%	2.4E-03	1.2%	NA	
Hydrogen Sulfide	6.7E-01	28%	4.6E-01	96.2%	3.3E-03	1.7%	4.0E-03	3.37%
Formaldehyde	3.5E-02	1.4%	1.5E-03	0.3%	2.8E-03	1.4%	1.2E-01	96.6%
Sulfur Dioxide	NA		NA		1.8E-01	90%	NA	
Mercury	1.2E-01	4.9%	3.8E-04	0.1%	2.5E-04	0.1%	NA	
Remaining TACs	3.0E-02	1.2%	2.3E-03	0.5%	1.1E-02	5.6%	0.0E+00	0.0%
Total	2.4E+00	100.0%	4.8E-01	100.0%	2.0E-01	100.0%	1.2E-01	100.0%
Toxic Air Contaminant	Adjusted Chronic HI	TAC % contribution to Chronic HI	Adjusted Chronic HI	TAC % contribution to Chronic HI	Adjusted Chronic HI	TAC % contribution to Chronic HI	Adjusted Chronic HI	TAC % contribution to Chronic HI
Mercury	1.2E-01	60%	6.8E-03	3.9%	1.7E-03	4.7%	3.8E-03	16.4%
Hydrogen Sulfide	5.5E-04	0.3%	4.5E-02	26%	5.5E-05	0.2%	1.9E-06	0.0%
Naphthalene	1.7E-02	8.6%	3.0E-02	17%	8.7E-05	0.2%	NA	
Arsenic	1.4E-02	7.0%	5.5E-02	32%	2.8E-02	76%	1.5E-02	64.2%
Nickel	2.1E-02	11%	6.9E-03	4.0%	4.6E-04	1.3%	7.9E-04	3.4%
Cadmium	6.7E-03	3.4%	1.8E-02	10%	1.9E-03	5.3%	1.5E-03	6.5%
Manganese	1.2E-02	5.8%	2.6E-04	0.2%	1.7E-04	0.5%	5.1E-04	2.2%
Remaining TACs	8.9E-03	4.5%	1.0E-02	6.0%	4.2E-03	11.7%	1.7E-03	7.2%
Total	2.0E-01	100.0%	1.7E-01	100.0%	3.6E-02	100.0%	2.3E-02	100.0%

2. REVIEW OF EXISTING AIR QUALITY MONITORING NEAR REFINERIES

Air quality monitoring at and near the five refineries in the Bay Area include the permanent and special purpose air quality monitoring stations operated by the BAAQMD, and the ground-level monitors (GLM) that the refineries are required to operate as part of their permit to operate. Additionally, the Phillips 66 (formerly Conoco Phillips) Rodeo Refinery and Chevron Richmond Refinery are conducting additional fence line monitoring as part of an agreement with the local government. This section describes and summarizes the data from these measurement programs and evaluates the adequacy of the existing monitoring for determining the impacts of refinery emissions to air quality in nearby residential communities.

2.1 Criteria Pollutant and Air Toxics Monitoring by the BAAQMD

Ambient concentrations of criteria pollutants are routinely monitored in urban areas throughout the country to determine compliance with National Ambient Air Quality Standards. The National Air Monitoring Stations (NAMS) were established to ensure a long term national network for urban area-oriented ambient monitoring and to provide a systematic, consistent database for air quality comparisons and trend analysis. NAMS was replaced by the National Core (NCore) network, which began in January 1, 2011 with 80 sites; 63 urban sites and 17 rural sites. NCore is a multi-pollutant network that integrates several advanced measurement systems for particles, pollutant gases and meteorology.

The State and Local Air Monitoring Stations (SLAMS) allow state and local governments to develop networks tailored to their immediate monitoring needs. Special purpose monitors (SPM) fulfill very specific or short-term monitoring goals and are typically used as source-oriented monitors rather than monitors which reflect the overall urban air quality. Photochemical Assessment Monitoring Stations (PAMS) are a specialized subset of SLAMS sites that collect data on certain volatile organic compounds and carbonyl compounds (aldehydes and ketones) in ozone non-attainment areas. EPA has also developed additional specialized subsets for special purposes, such as the Chemical Speciation Network (CSN) and National Air Toxic Trends Stations (NATTS) discussed below.

Although the Clean Air Act does not require a national air toxics monitoring network, many areas began sampling and analyzing ambient air samples for air toxics. Many of the high-population states and local areas implemented their own air toxic monitoring programs including California and the San Francisco Bay Area. Such a network was put in place by the BAAQMD in 1986. The EPA initiated a technical and laboratory analytical support program in 1988 to support emerging needs for information regarding ambient levels of organic toxic species in ambient air. This urban air toxic monitoring program (UATMP) supports the year-round collection and analysis of a 24-hour canister sample every 12 days. EPA established the NATTS beginning in 1999 to provide long-term monitoring data for certain priority toxics across representative areas of the country in order to establish overall trends for these pollutants. As of 2004, EPA had established 23 NATTS in 22 cities. The national network is a subset of over 300 ambient air toxics monitoring stations that have been established nationwide by State and local agencies. The NCore monitoring station in San Jose (Jackson) is one of the NATTS.

EPA also established the CSN network to monitor and gather data on the chemical makeup of PM_{2.5} (selected ions, metals, carbon species, and organic compounds) and to establish the relationships between PM concentrations and public health impacts. The CSN (formerly the

Speciation Trends Network) was initiated by EPA in 2000. The CSN consists of 54 long-term trends sites and approximately 185 supplemental sites. These sites are existing NCore and SLAMS sites across the Nation. The BAAQMD air monitoring station in San Jose is also a CSN as well as an NCore and NATTS site.

2.1.1 Routine Air Quality Monitoring Programs in the Bay Area

There are 27 air quality monitoring stations in the San Francisco Bay Area, 26 operated by the BAAQMD and one operated by the California Air Resources Board (ARB). Twenty-three of the 27 stations are classified by EPA as SLAMS that are permanently sited. The remaining four are classified as SPM stations in Crockett, Fort Cronkhite, Cupertino and Patterson Pass. The BAAQMD also performs air monitoring as part the NATTS Program, the National Core (NCore) Program, the PAMS Program, and the PM_{2.5} CSN Program. Table 2-1 lists the locations and parameters measured at air quality monitoring stations in the Bay Area. The green highlights in the Table indicate the eight monitoring stations that located within communities that are near the five refineries. Five of the monitoring sites (Martinez, Point Richmond, Richmond 7th, Rodeo and Crockett) are intended to determine source impacts near the refineries. Three sites (Concord, San Pablo, and Vallejo) characterize the pollutant concentrations in nearby urban areas. The map in Figure 2-1 shows the locations of the eight BAAQMD monitoring stations (blue dots) and the refinery GLM sites (yellow circles and triangles). The five refineries are shown on the map in yellow strips and the white crosshatch show the populated urban areas of Contra Costa and Solano Counties. Color-coded bars indicate the parameters measured at each of the BAAQMD monitoring stations.

Figure 2-2 and Figure 2-3 show that, with the exception of Crockett, there are no communities located downwind of the refineries during typical wind patterns.

The BAAQMD operates 18 air toxics monitoring sites. Locations are at existing SLAMS and SPM monitoring stations and are generally in major population centers or downwind of major industrial sources such as refineries. Air samples are collected for a 24 hour period on a 1-in-12 day schedule except at special study sites such as Cupertino and San Jose where sampling is on a 1-in-6 day schedule. Gaseous (VOC) toxics are collected in 6-liter SUMMA stainless steel canisters using Xontech 910 samplers and analyzed by gas chromatography with photoionization and electron capture detectors. Samples taken after January 1, 2012 were analyzed using gas chromatography and mass spectrometry.

2.1.2 Summary of Existing Ambient Air Quality Data

The most extensively monitored pollutant of interest around the refineries is SO₂, which is the largest component of emissions from petroleum processing and is produced predominately by refineries. Hourly measurements are recorded continuously at 9 sites (not including the GLM sites) to track compliance with the NAAQS. As shown in Figure 2-4, although the 99th percentile SO₂ concentrations were higher at sites in communities near refineries than in San Jose, the regulatory values measured were less than 10% of the primary and secondary standards at all sites during 2011 and 2012. Interestingly, the highest mean SO₂ concentrations occurred at the San Pablo site in both years although it is located farther from the Chevron refinery than the Richmond site. Such results illustrate the effect of prevailing wind patterns and the elevation and buoyancy of pollutant emissions on the locations of greatest impact of refinery emissions.

The charts in Figure 2-5 and Figure 2-6 show the long-term trends in concentrations of several gaseous toxics over the last 12 years. The 90th percentile for each year is plotted, to represent the high-end of the concentration range and avoid the influence of outlier and below detection values. A similar decreasing trend is seen for all sites, and the sites in communities near refineries fall within the range observed at other sites in the Bay Area. Other VOC compounds (ethylbenzene, o-xylene) were examined for the same time period, however most of the values were near the limit of detection. Data for toxic metals is much more limited, but Figure 2-7 indicates that concentrations are uniformly low relative to the OEHAA recommended chronic exposure limit (REL). The spatial distribution of formaldehyde and PAH could not be evaluated since there are no sites near the refineries monitoring aldehyde or speciated organic PM concentrations.

2.2 Existing Monitoring by Refineries

Ground Level Monitors (GLM) are air-quality monitoring stations that are required in the permit conditions for certain large industrial facilities such as oil refineries. The facility operates the monitoring equipment but the Bay Area Air Quality Management District audits and validates the data.

In 1997, in response to chemical releases into the neighboring community, Contra Costa County required the installation of a fenceline monitoring system at the Tosco Oil Refinery in Rodeo, CA, USA (now owned by Phillips 66).¹ This network of optical remote sensing devices “is designed to detect and track concentrations of a wide range of hazardous gases, and to provide early warning to the surrounding communities in the event of a chemical emergency.”²

The current monitoring system includes three types of open path monitors: FTIR (Fourier transform infrared), UV (ultra violet), and TDL (tunable diode laser). The monitors sit along both the north and south fencelines. Each of the monitors operates continuously, delivering data at 5-minute intervals, 24 hours a day, 7 days a week. One monitoring station also collects meteorological data, including wind direction. The FTIR measures ammonia, carbon monoxide, carbonyl sulfide, methane, ethylene, 1,3 butadiene, ethanol, mercaptan, MTBE, nitrous oxide, and total hydrocarbons. The UV instrument monitors benzene, toluene, xylene, carbon disulfide, SO₂ and ozone). The TDLs measure hydrogen sulfide (H₂S). Six “organic gas detectors” have also been deployed along the SE and NW perimeter of the refinery property as a warning system for high concentrations of explosive gases. More detail is given in Appendix D. Since these optical systems can be reconfigured to monitor a different suite of compounds, or replaced or upgraded with improved technology at any time, the information given here may not be entirely up to date but serves to illustrate potential applications and provide an example of in-place systems.

Current raw data from the fenceline monitors is posted by the contractor, Argos Scientific, at www.fenceline.org along with messages describing events that resulted in higher than normal level detection and links to data reports for the past few months. During the initial years of operation, Contra Costa County stated that the concentrations reported by the UV and TDL monitors were not sufficiently accurate to post them on their web site. Based on

¹ <http://www.ergweb2.com/fenceline>

² <http://www.fenceline.net/sea>

examination of the limited recent data available online, SO₂ and BTEX are generally below the 5 ppb limit of detection (LOD) and the equipment has been frequently out of service. Occasional concentration spikes were recorded, but most were determined to be due to instrument calibration, weather events (fog), or false detections. Overall, it appears that the system may be useful for early warning and evaluation of high-level releases and provides information to the community about routine operation, but is not adequate for determining emissions flux during normal operations.

At the request of the City of Richmond, Chevron has agreed to implement an Air Quality Monitoring Program in three neighborhoods surrounding the Chevron Richmond Refinery for two years starting the second quarter of 2013. The locations are North Richmond, Point Richmond and Atchison Village. Program will include fence line and community monitoring. Monitoring measurements include: VOC, metals, H₂S, PAH, and PM_{2.5}, black carbon, ammonia, and meteorological data. Fence-line monitors are proposed at the fence lines of each neighborhood (3 total) and will be operated for a minimum of two years. Fence line measurements will cover 1000 yards of fence line and measure benzene, toluene, xylene, SO₂, H₂S and CS₂. Fenceline data are now available online at <http://www.fenceline.org/richmond/data.php>.

Table 2-1. Locations and parameters measured at air quality monitoring stations in the San Francisco Bay Area.

STATION	ADDRESS	City / ZIP	O ₃	NO _x	Noy	SO ₂	CO	HC	PM ₁₀	PM ₁₀		PM _{2.5}		metals & aldehyde	PAH	BC	PM _{2.5} SASS speciation	TSP Lead	Neph light scatter	PAMS GC	UFP Count	
										Continuous	PM _{2.5}	Continuous	TOXICS	H ₂ S								
Hayward	3466 LaMesa Dr.	94542	X-S																			
Livermore	793 Rincon Ave.	94551	X-N	X-S				X				X - F	X				X	X		X	X	X
Oakland	9925 International Blvd.	94603	X	X			X					X - F	X									
Oakland	1100 - 21st Street	94607	X	X		X	X					X	X				X	X				
Pt. Richmond	140 W. Richmond Ave.	94801												X								
Martinez	521 Jones St.	94553				X-S							X									
Crockett	End of Kendall Ave.	94525				X-S							X									
Concord	2956-A Treat Blvd.	94518	X-N	X-N		X-S	X-N		X-N			(2) X-C	X									
Richmond	1065 Seventh St.	94801				X-S							X	X								
Bethel Island	5551 Bethel Is. Rd.	94511	X-S	X-S		X-S	X-S		X-S				X									
Rodeo	326 Third St.	94572												X								
San Pablo	1865-D Rumrill Blvd.	94806	X-S	X-S		X-N	X-S		X				X									X
San Rafael	534 Fourth St.	94901	X-S	X-S			X-S		X-N				X - F	X						X		
Fort Cronkhite	Building 1049	94965											X									
Napa	2552 Jefferson St.	94558	X-S	X-S			X-S		X-S-C				X	X								
San Francisco	10 Arkansas St.	94107	X-S	X-N			X-S		X-N				X - F	X-P		CARB						
Redwood City	897 Barron Ave.	94063	X-S	X-S			X-S						X - F	X						X		X
Los Gatos	306 University Ave.	95030		X-N																		
Gilroy	9th & Princevalle Sts.	95020		X-S									X - F									
San Martin	13030 Murphy Ave.	95046		X-S																		
San Jose	158 E. Jackson St., Ste. B	95112	X-S	X-N	X-N	X	X-S			X	X	X - F	X-P		X-N	X-N	X					
Vallejo	304 Tuolumne St.	94590	X-S	X-S		X-S	X-S						X - F	X			X		X			
Fairfield	1010 Chadbourne Rd.	94534		X-S																		
Santa Rosa	837 Fifth St.	95404	X-S	X-S			X-S						X - F	X								X
Cupertino	22601 Voss Ave.	95014	X	X		X	X	X	X				X	X		X						
Patterson	6500 Patterson Pass Rd	94550	X	X																		X
San Ramon	9885 Alcosta Blvd	94583	X	X																		X
Palo Alto Airport	1925 Embarcadero Road	94303																				X
San Carlos Airport	620 Airport Drive	94070																				(2) X-C
Reid Hillview Airport	2500 Cunningham Ave	95148																				X
TOTAL			21	16	1	10	13	2	7	1	3	12	18	3	3	1	2	4	4	4	3	4

Notes: x = parameter monitored; P = parallel sampling with CARB; N = National Air Monitoring Station (NAMS); S = State and Local Air Monitoring Station (SLAMS); CARB = CARB sampling only; C = collocated; F = FEM BAM.

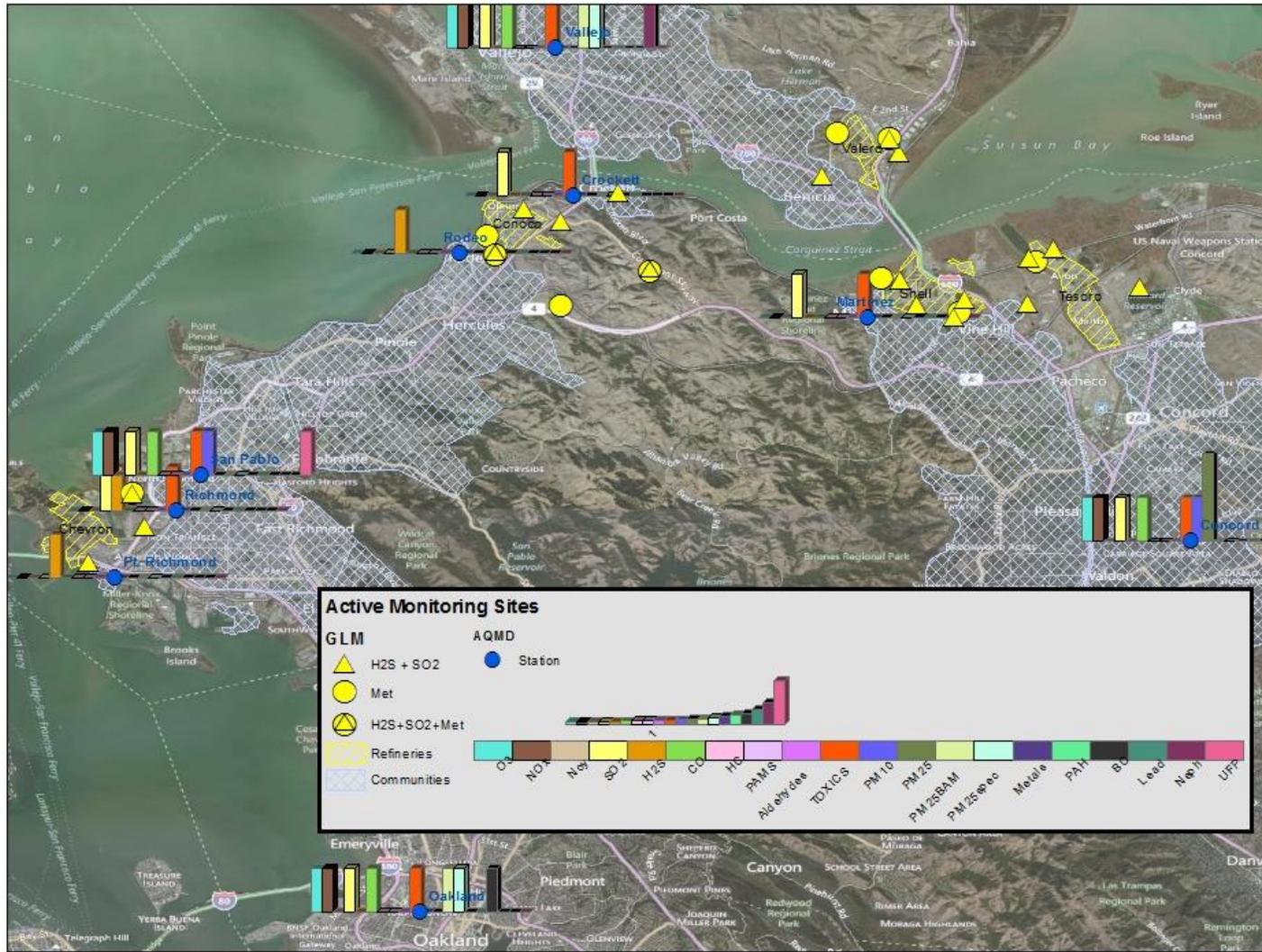


Figure 2-1. Locations of active BAAQMD air monitoring sites and refineries in the Bay Area.

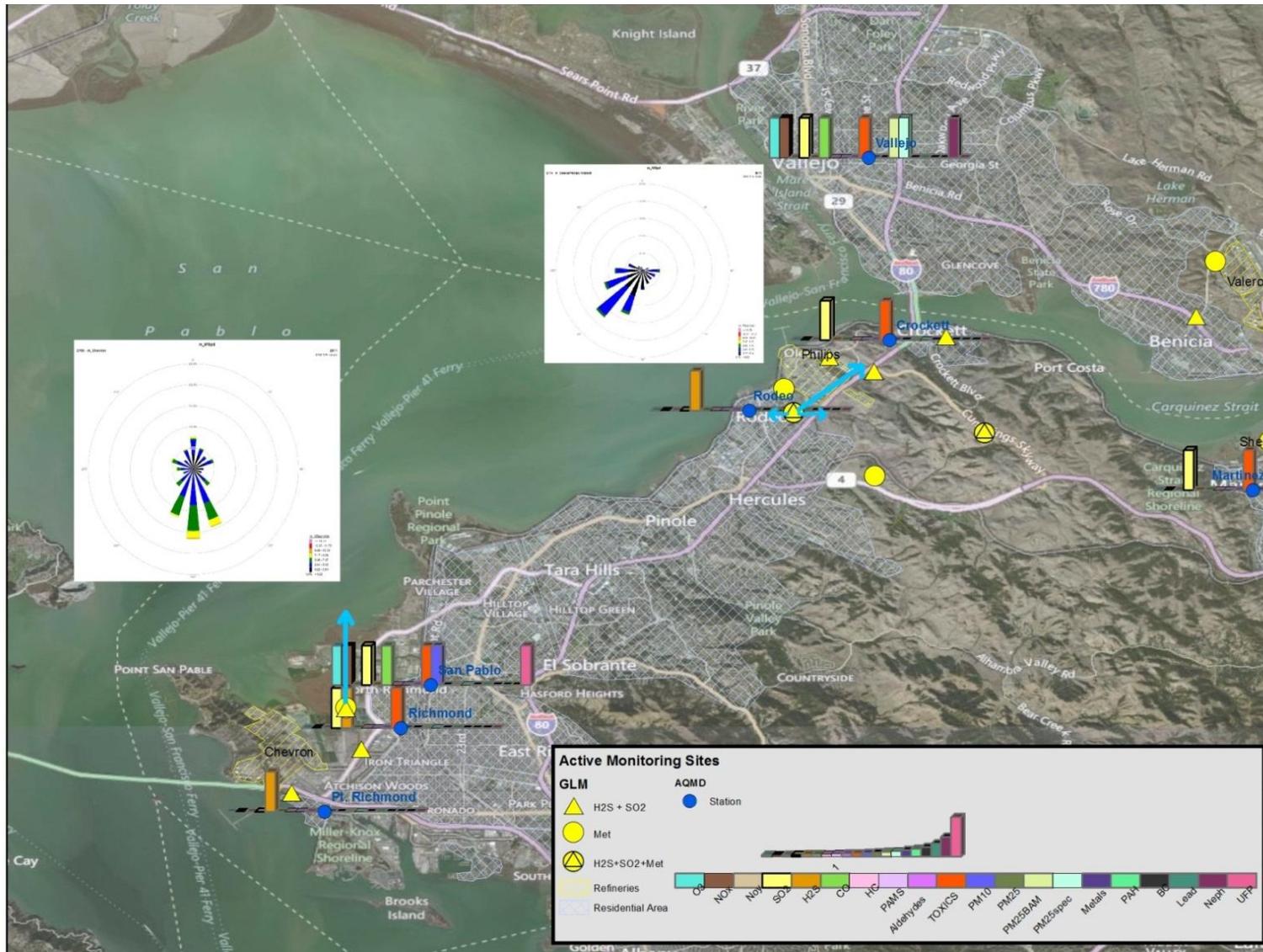


Figure 2-2. Closeup of locations of active air monitoring sites and refineries, showing prevailing wind directions (blue arrows).

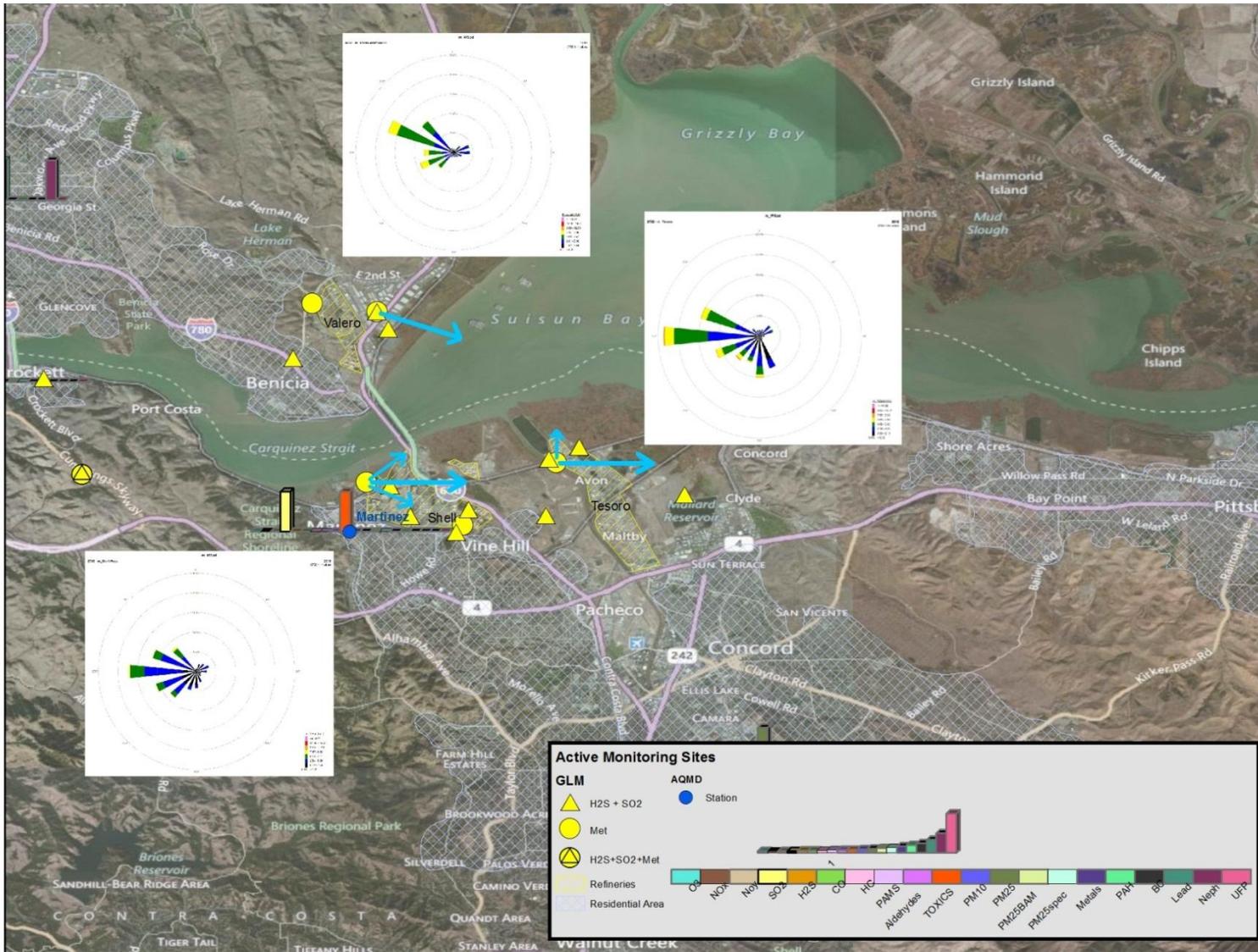


Figure 2-3. Closeup of locations of active air monitoring sites and refineries, showing prevailing wind directions (blue arrows).

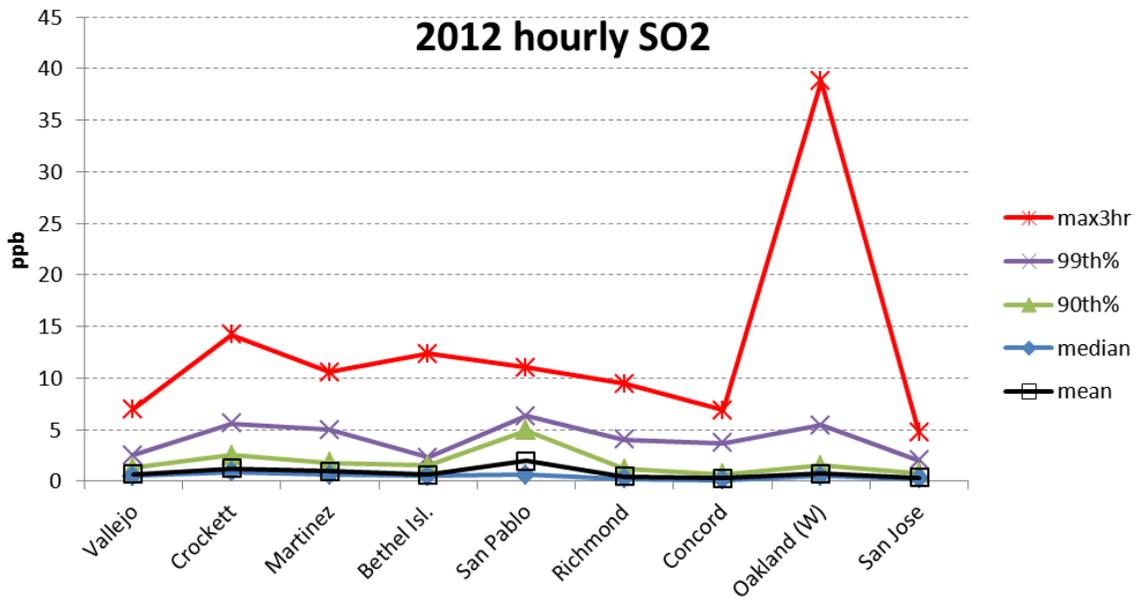
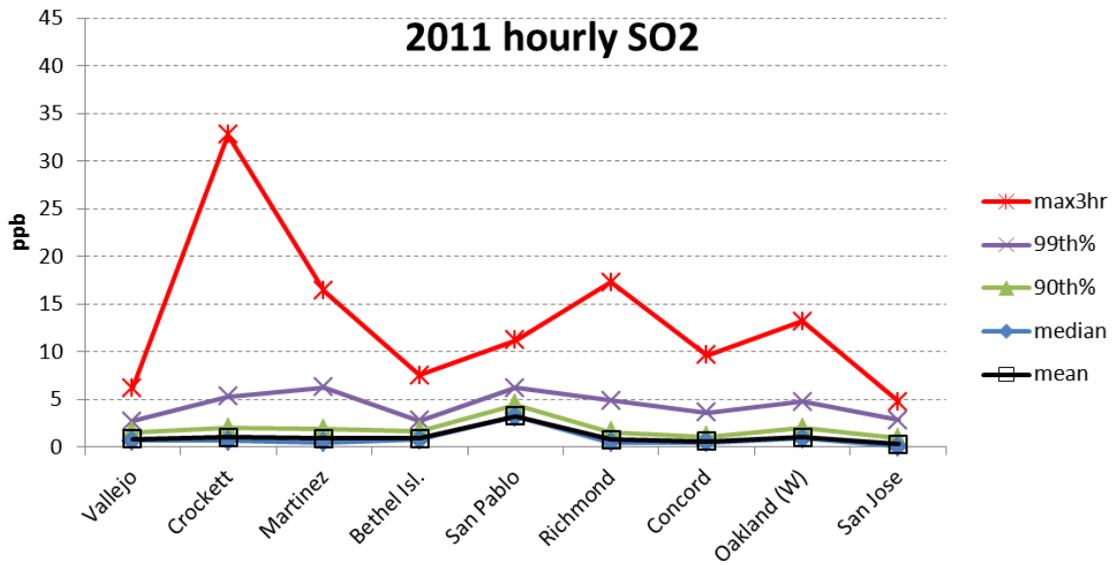


Figure 2-4. Annual statistics for SO₂ sites in the Bay Area. The primary NAAQS is 75ppb (99th percentile) and secondary is 500 ppb (maximum 3hr average).

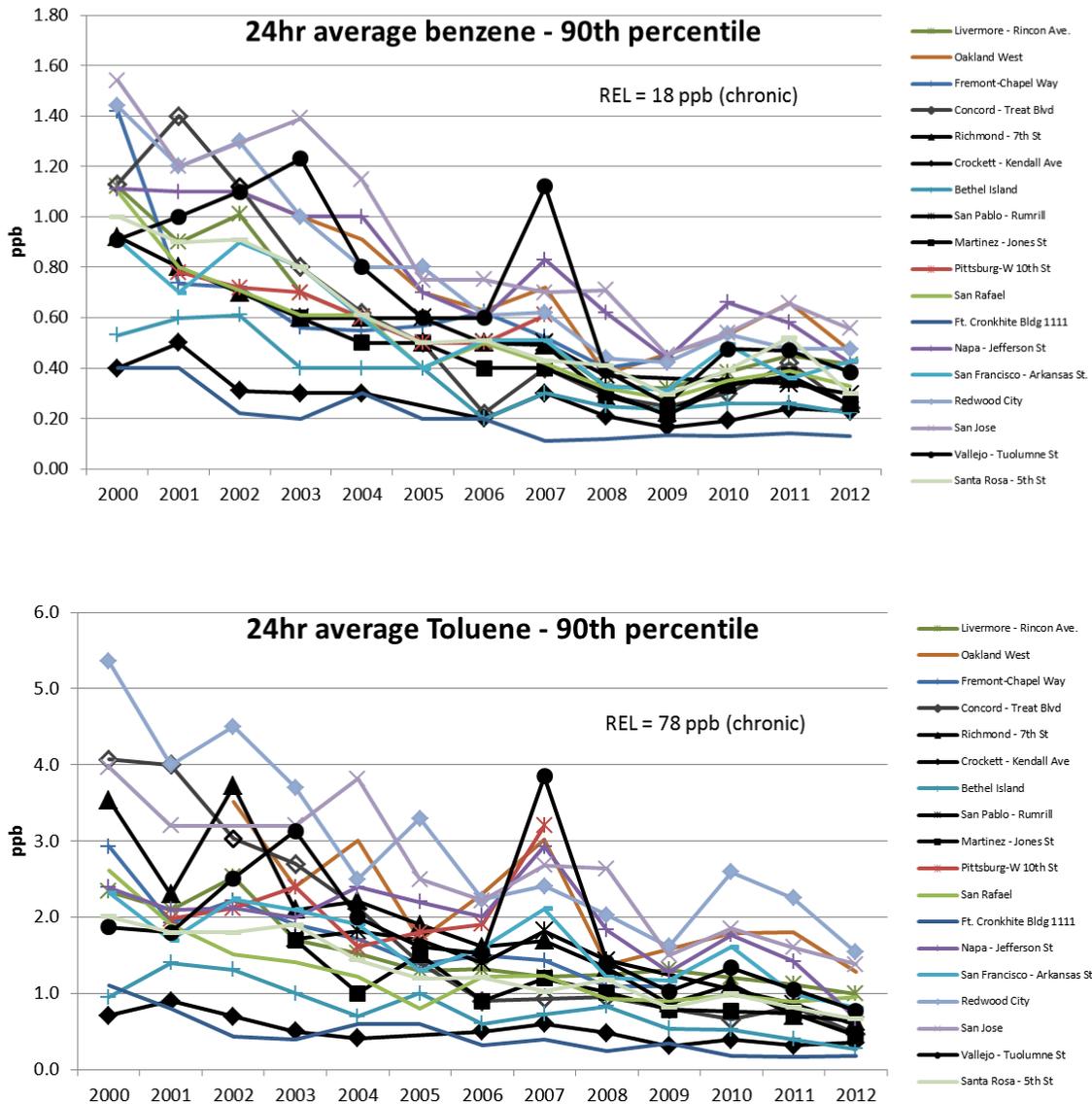


Figure 2-5. Trends in air toxics, 2000 – 2012. Sites near refineries are indicated by bold black lines. Values below LOD are not shown.

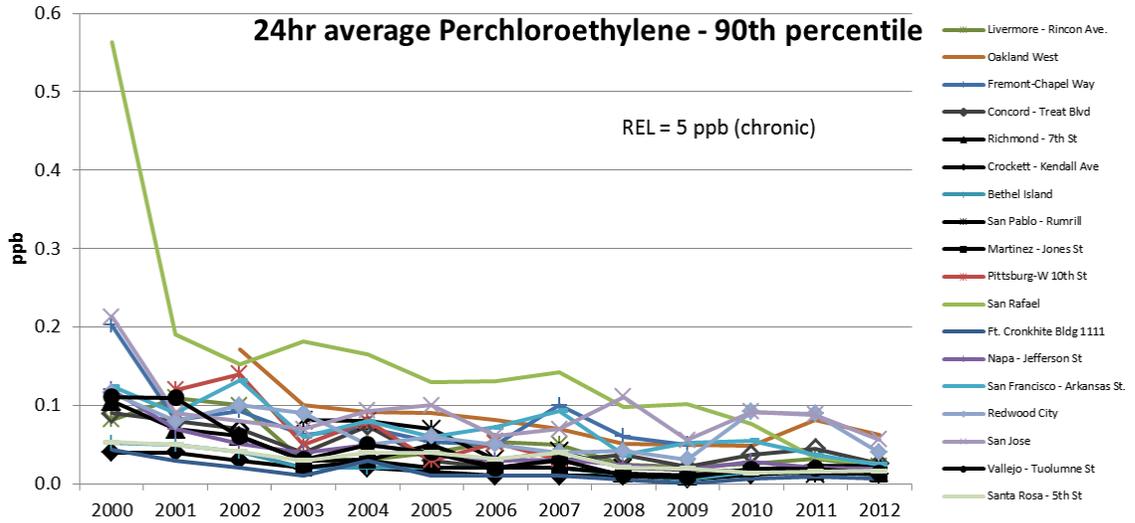
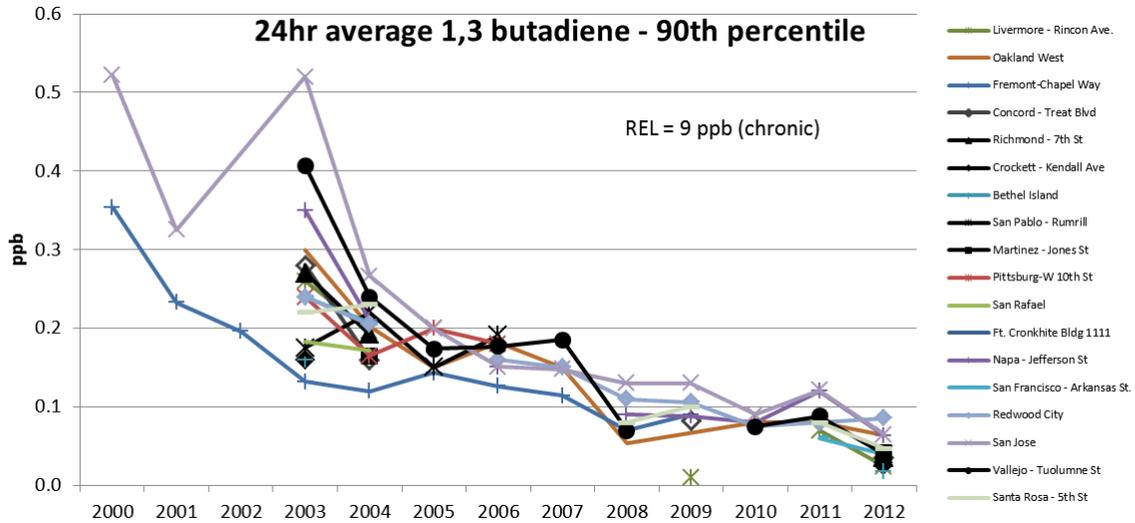


Figure 2-6. Trends in air toxics, 2000 – 2012. Sites near refineries are indicated by bold black lines. Values below LOD are not shown.

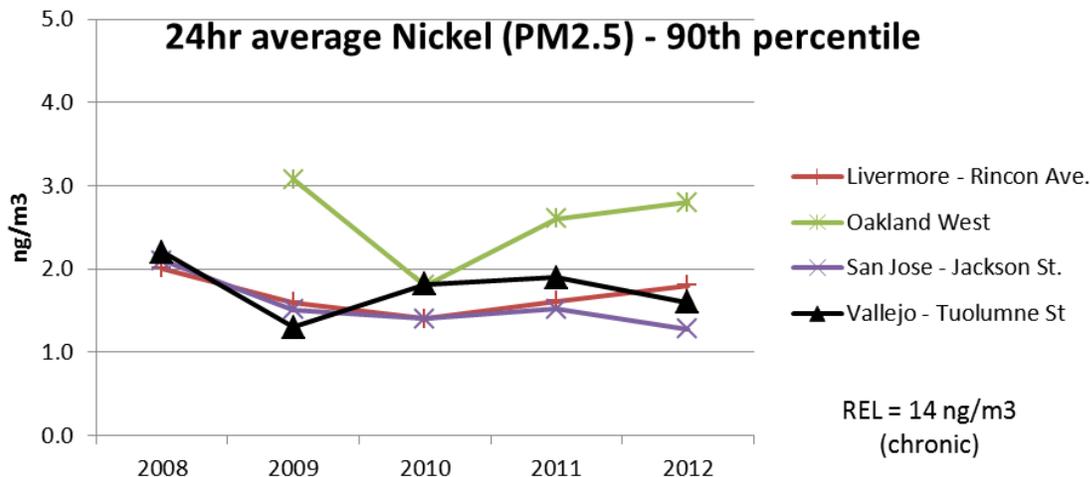


Figure 2-7. Trend in fine particulate nickel, 2000 – 2012. Sites near refineries are indicated by bold black lines. Values below LOD are not shown.

2.3 Incident Response Monitoring

Accidental releases of air contaminants trigger emergency response as specified by state law. While emergency response agencies (state and local law enforcement and fire agencies) have primary responsibility for scene management during an accidental release or emergency incident, air pollution agencies can provide the following supporting resources: air sample collection and analysis, air monitoring, dispersion modeling. The BAAQMD is responsible for taking any enforcement action under its jurisdiction that may be necessary based upon the cause of the accidental release.

Following an accidental release, such as the August 6, 2012 Chevron Refinery fire, the Compliance and Enforcement Division of the BAAQMD prepares an incident report describing the nature and cause of the incident and associated health alerts (available online at <http://www.baaqmd.gov/Divisions/Compliance-and-Enforcement/Incident-Reports.aspx>). The report summarizes the air quality data collected during the incident from nearby BAAQMD air quality monitoring stations and facility GLMs along with air samples collected in downwind areas.

2.4 Special Studies

Special monitoring programs have been conducted in California to characterize the ambient air toxic concentrations and potential exposures to certain susceptible populations and within communities that may experience disproportionate impacts due to their proximity to pollutant sources. The California Air Resources Board (ARB) conducted an 18-month (November 2001 through April 2003) special air quality monitoring study in the communities of Crockett in Contra Costa (ARB, 2004) and Fruitvale in Oakland (CARB, 2005) to investigate the impact of traffic and other industrial sources on children’s exposure to air pollution. The studies were conducted as part of a larger statewide evaluation of the adequacy of the State’s air quality

monitoring network as required by SB 25 (Children's Environmental Health Protection Act). Monitoring in the Crockett community was conducted at John Swett High School from October 2001 to May 2003.

Average levels of criteria air pollutants in Crockett were comparable to measurements from the nearest long-term monitoring sites located in Vallejo and San Pablo. The average PM₁₀ concentration at the Crockett site was 19 µg/m³ from October 2001 to May 2003 with a maximum of 70 µg/m³. The State PM₁₀ standard (50 µg/m³) was exceeded on two occasions. The State carbon monoxide, ozone and nitrogen dioxide standards were not exceeded during the study. Monitoring of TACs included 1,3-butadiene, benzene, formaldehyde, acetaldehyde, several halogenated compounds, polycyclic aromatic hydrocarbons and several metals. The average concentrations of benzene and 1,3-butadiene during the monitoring period were 0.24 and 0.05 ppb, respectively and the corresponding cancer risks are 22 and 21 excess cancer cases in one million people over a 70-year lifetime³, similar to the risks at the nearest long-term toxics site, at Crockett. In general, the risk from toxic pollutants measured at John Swett High School was approximately one-half of what was measured at Fremont.

2.5 Discussion and Conclusions

Exposures to hazardous air pollutants (toxics) within an urban area vary greatly due to varying proximity to emission sources, magnitude and specific mix of emissions, and meteorological conditions. These variations pose significant challenges for air quality monitoring programs and the exposure assessments that rely on the available air quality data. The existing air quality monitoring near the refineries are designed with the following goals.

1. Determine neighborhood or other EPA-defined spatial scale concentration average and range of concentrations for criteria pollutants (SO₂, NO₂, CO) and certain high-priority toxics (benzene, toluene, ethylbenzene, xylenes, 1,3-butadiene, formaldehyde).
2. Provide ambient concentrations of criteria pollutants and/or toxics with appropriate accuracy and representativeness to aid in the determination of exposure of nearby residents.

This section reviews the measurement challenges and limitations of the existing monitoring programs for addressing these objectives.

Five of the eight BAAQMD air quality monitoring stations that are located near or downwind of the refineries are intended for monitoring source impacts. The San Pablo, Vallejo, and Concord air quality monitoring stations are population-oriented monitoring sites, which are designed to characterize air quality over neighborhood scales up to 4 km.

- Point Richmond (H₂S) is a source impact monitoring site located 300 m south of the Chevron Refinery boundary. Although winds in the area are from the south-southwest, occasional northerly winds will transport emission from the refinery over the community.
- Richmond 7th Street (SO₂, H₂S, toxics) is a source impact monitoring site located 0.8 km east of the Chevron Refinery boundary, which is along the secondary prevailing wind

³ Cancer risk estimates in this report did not include diesel particulate matter (diesel PM).

direction. Prevailing northerly winds transport refinery emissions over the Bay to San Pablo.

- Rodeo (H₂S) monitoring is a source impact monitoring site located 1.0 km southwest of the Phillips 66 Refinery. This location is usually upwind of the refinery as the prevailing winds are from the southwest.
- Crockett (SO₂, toxics) is a source impact monitoring site located downwind of the Phillips 66 Refinery about 1.5 km northeast of the Phillips 66 Refinery and 300 m west of I-80.
- Martinez (SO₂, toxics) is a source impact monitoring site located near downtown Martinez and is 0.8 km southwest of the Shell Refinery and 4.0 km west of the Tesoro Refinery. Prevailing winds in the area are easterly, putting the site downwind of the refineries less than 3% of the time.
- Vallejo (O₃, NO_x, SO₂, CO, continuous PM_{2.5}, speciated PM_{2.5}, toxics) is a population-oriented monitoring station in a mixed commercial and residential neighborhood 1.6 km east of downtown Vallejo and 0.8 km west of Interstate 80. The site is about 4.8 km north of the Phillips 66 Refinery and 8 km northwest of the Valero refinery.
- San Pablo (O₃, NO_x, SO₂, CO, PM₁₀, continuous PM_{2.5}, toxics) is a population-oriented monitoring station located 1.9 km northeast of the Chevron Refinery. This area has heavy industry and high traffic volume in addition to the Chevron Refinery, including two major freeways.
- Concord (O₃, NO_x, SO₂, CO, PM₁₀, continuous PM_{2.5}, toxics) is a population-oriented monitoring site in a residential area near the intersection of two major streets. Concord is the largest city in Contra Costa County and is located in Diablo Canyon where locally emitted pollutant can become trapped when wind are light. Large emission sources in the valley include two major freeways and the Chevron and Tesoro Refineries located about 10 km to the north.

Various near-source air monitoring studies show that changes in pollutant concentrations due to dispersion and dilution of emissions are inversely proportional to the square of the distance from the source. This process of dilution can result in sharp gradients in pollutant concentrations near sources of emissions. For example, NO_x, CO and VOC concentrations near major roadways typically drop from 2-4 times urban background levels at roadside to near the surrounding urban background levels within 300 m downwind of the roadway (Zhu et al., 2002; Fujita et al., 2003; Fujita et al., 2008, Fujita et al, 2010). Presence of diesel vehicles may increase the near-road concentrations to as much as a factor of 10 higher than background for NO_x and black carbon (BC) (Fujita et al., 2010; Westerdahl et al. 2005). Even higher ratios have been measured for NO_x, sulfur dioxide (SO₂), BC and ultrafine particles (UFP) near airport runways during jet takeoffs (Westerdahl et al. 2008; Zhu et al., 2011).

With the exception of Pt. Richmond, which is located 300 m upwind of the Chevron Refinery, all other monitoring sites are located 0.8 km or more from any refinery. Furthermore, there are no communities located downwind of the refineries during typical wind patterns with the exception of Crockett. The BAAQMD air toxic monitoring data show that the concentrations of BTEX, 1,3-butadiene and perchloroethylene at the near-refinery monitoring locations are generally lower than elsewhere in the Bay Area with similar long-term declining trends (2000-

2012) at all monitoring stations. These observations indicate that the urban background levels for BTEX and 1,3-butadiene are primarily influenced by other emission sources, such as motor vehicles, that are more evenly distributed throughout the Bay Area and produce greater total emissions. Although SO₂ can be considered a tracer for refinery emissions in the absence of other significant sources in the area, all monitoring stations report similarly low SO₂ concentrations throughout the Bay Area that are well below the NAAQS. Emissions from process units are released from stacks, which result in elevated plumes of SO₂, H₂S and certain VOCs that may travel some distance before reaching the ground. These emissions will add to the regional background pollutant levels in downwind area with little impact to ground-level concentrations near the refinery.

Data from the eight routine criteria and air toxics monitoring stations are generally representative of the pollutant levels in the area and show no evidence of impacts from refinery emissions that differ significantly from other Bay Area monitoring locations. However, for the reasons given above, they do not preclude the possibility of higher concentrations at locations in closer proximity to the refinery and consequential contributions to regional background pollutant levels further downwind (e.g., oxidation of SO₂ to sulfate).

3. REVIEW OF AVAILABLE AIR MONITORING APPROACHES AND MEASUREMENT METHODS

This section describes the air monitoring approaches that can be used to obtain air quality data that can be used to determine the impact of refinery emissions on air quality in nearby communities. The measurement options associated with these approaches are described.

3.1 Monitoring Approaches

Refineries are large facilities with multiple sources of process and fugitive emissions scattered over a wide area. While process units produce emissions continuously from elevated stacks, fugitive emissions (e.g., valves, pumps, connectors, storage tanks) have multiple sources with varying chemical composition and temporal patterns. As a result, the concentrations and mix of pollutants are temporally and spatially irregular with potentially complex vertical variations in pollutant concentrations at the boundaries of refinery. Unlike vehicle emissions, the chemical composition of refinery emissions indicated by the emissions inventory does not exist and cannot be directly measured. Consequently, no single pollutant can serve as a tracer or surrogate for other refinery emissions. Measured ambient concentrations of SO₂ or H₂S alone do not necessarily imply the presence of other emissions from the refinery such as benzene or metals, nor their attribution to refinery emissions. Facility-specific health risk assessments (HRA) are typically performed by applying risk factors to predicted pollutant concentrations obtained from by dispersion modeling. Dispersion modeling results provide useful insight regarding the spatial distributions of pollutant concentrations in downwind areas where monitoring data are not available. However, the reliability of the modeling results depend on the accuracy of the emission inventory estimates. Based upon a review of existing monitoring programs in the previous section, we identify the following measurement approaches that could provide useful data for assessing the impact of refinery emission on air quality in nearby communities.

3.1.1 Emission Flux Measurements

A number of studies in the U.S., Canada and Europe have found that reported emissions of volatile organic compounds (VOCs) at refineries and chemical plants are substantially underestimated. Techniques such as Differential Absorption Light Detection and Ranging (DIAL) and Solar Occultation Flux (SOF) measure the VOC concentrations in a two dimensional vertical plane and calculate VOC flux in pounds per hour. The results determine the total VOC mass released.

DIAL technology was developed in the 1960's and first applied to measure pollutants at petrochemical facilities by National Physical Laboratories in the U.K. DIAL makes use of pulsed lasers which reflect off particles in the air to provide information about pollutant concentration. Typically these lasers are scanned across a vertical plane perpendicular to the wind direction. A two dimensional concentration map is constructed and used in conjunction with the perpendicular wind speed to measure the mass flux of emissions. Since all DIAL vendors who take measurements at petrochemical facilities currently are based in the U.K., the cost of the measurement techniques can easily exceed \$500,000 for a one-month study. Estimates for the construction of a new DIAL system are typically at least \$2-3 million.

SOF technology was developed by Johan Mellqvist at Chalmers University of Technology in Sweden. SOF uses a Fourier Transform Infrared (FTIR) spectrometer mounted in a passenger van. The van has a hole cut in the roof where a solar tracker is mounted designed to always point towards the sun and draw light to the spectrometer. As the van drives past a petrochemical complex on a sunny day, it gathers information about the concentration of chemical species. Readings are also taken before and after approaching the petrochemical facilities to subtract out background signals. When this information is combined with wind direction and speed, it can also be used to calculate the mass flux of pollutants. The SOF technique requires direct sunlight and cannot measure some compounds like benzene directly. However, the developers use other measurement techniques to address these issues. In this case, the method is currently only available from the developers who are in Sweden. The cost for a one-month study can be less than \$200,000. A new SOF unit may be built for \$400,000 - \$500,000; however, issues relating to purchasing or licensing the SOF technology must be resolved with the developer.

3.1.2 Emission Plume Characterization

Optical remote sensing (ORS) utilizes a light source to detect and measure concentrations of chemical compounds along the distance covered by the light signal. Depending on the source of light (wavelength), the following types of ORS instrumentation could be used:

- Open-Path Fourier Transform Infrared Spectrometer (OP-FTIR), IR light, 2 to 20 micrometers wavelength
- Open-Path Tunable Diode Laser Absorption Spectrometer (OP-TDLAS), near-IR light, approximately 1.5 micrometers wavelength
- Ultraviolet Differential Absorption Spectrometer (UV-DOAS), UV light, 245 to 380 nanometers wavelength

Optical remote sensing (ORS) instruments have been used as an alternative to conventional point monitors for measuring air emissions for many years. ORS instruments use infrared (IR), laser, or ultraviolet (UV) light to measure concentrations of chemical compounds of interest along the distance covered by the light signal. A light signal is sent out to mirrors deployed in the field, and the signal is reflected back to the instrument detector. Depending on the instrument and application, typical ORS instrument range varies from 50 to 500 meters. The major advantage of ORS instrumentation over traditional point monitors is their ability to provide greater spatial resolution of the monitored area. The increased resolution reduces the chance of emissions hot spots being undetected over the measured area. It is possible to accomplish increased spatial resolution because of the development of the Radial Plume Mapping method (RPM), which is capable of collecting concentration data along multiple beam paths in the configuration. In this method, multiple retro-reflecting mirrors are deployed in the survey area. The RPM can be applied using any scanning ORS instrument.

3.1.3 Community Air Monitoring

The characterization of a community's exposure to air pollutants is essential in assessing cumulative health impacts. However, the costs of traditional monitoring technologies pose significant limitations on the number of monitoring locations that can be established for exposure studies. A few widely-spaced fixed monitoring stations have limited capacity to characterize localized high concentrations and accompanying sharp pollutant concentration gradients that may exist near emission sources. Yet various measurement and modeling studies and epidemiological evidence indicate that such high concentrations with sharp concentration gradients are critically important to characterize in order to accurately determine human exposures and possible adverse health effects at the individual and sub-community levels.

The term "saturation monitoring" is used in reference to ambient air monitoring for the purpose of establishing more detailed spatial variations in pollutant concentrations at the community scale. The objectives of this type of monitoring in the context of health risk assessments is to determine the seasonal or annual average air toxics concentrations at a sufficient number of locations within the community to: 1) establish the spatial variations in annual average pollutant concentrations; 2) identify the potential influence of hotspots of pollutant emission on the community's exposure; and 3) characterize gradients in pollutant concentrations from these hotspots. Besides the accuracy, precision, selectivity and sensitivity of alternative measurement methods, the range of sampling periods, power requirements, size and portability of sampler or instrument are important considerations in a saturation monitoring study. The Desert Research Institute recently conducted saturation monitoring as part of the Harbor Community Monitoring Study (HCMS) (Fujita et al. 2009) sponsored by the California Air Resources Board and the West Oakland Monitoring Study (WOMS) (Fujita et al. 2010) sponsored by the Bay Area Air Quality Management District, and the Barnett Shale Gas Production Study (Zielinska et al, 2010). The same approach has been applied in on-going LAX International Airport Air Quality and Source Apportionment Study (AQSAS). The core component of the saturation monitoring networks consisted of 7-day time-integrated sampling at multiple sites using a combination of passive diffusive samplers for NO₂, NO_x, SO₂, H₂S, VOC (benzene, toluene, xylenes, ethylbenzene), and carbonyl compounds (formaldehyde, acetaldehyde and acrolein), and mini-volume aerosol sampling for PM_{2.5} mass, elements and organic and elemental carbon and metals. Samples were collected during 28 to 42 consecutive days in 2 or 4 seasons. This approach maximizes the number of sampling sites with the resources available while providing sufficient data to determine valid annual average ambient concentrations of TACs at each site. These time-integrated measurements are supplemented by continuous measurements of CO, NO_x, SO₂, and PM at existing air quality monitoring stations.

Saturation monitoring provides spatial information about cumulative exposure concentrations over an extended period of time. To address possible acute health effects, the saturation monitoring is coupled with a smaller network of air monitoring stations that provide time-resolved gaseous pollutant and PM mass concentrations. A complementary approach is the use of a mobile platform equipped with real-time and near real-time monitoring instruments that provide the necessary time resolution to identify high concentrations and sharp spatial gradients.

3.2 Continuous Monitors

Continuous monitoring methods provide the time resolution necessary to correlate variations in pollutant concentrations with temporal patterns of source activity. They also allow

the flexibility to examine pollutant concentrations averaged over different time scales, which can be useful for evaluating potential acute and chronic health impacts to a community.

3.2.1 Fixed-site Gas Analyzers

This type of monitor is typically used monitoring of criteria gaseous pollutants, and accepted methods have been designated by EPA for regulatory purposes. They are designed to operate continuously for years with minimal maintenance, but require a weatherproof shelter with temperature control and periodic evaluation of the zero level and gain by introduction of clean air and an appropriate gas standard (span gas).

Nitrogen Oxides

Nitric oxide (NO) is continuously measured by the chemiluminescence nitric oxide-ozone method (OCM). This method is based on the gas-phase chemical reaction of NO with ozone. In this method ambient air is mixed with a high concentration of ozone so that any NO in the air sample will react, releasing photons in the process. The resulting light intensity is measured with a photomultiplier and converted into an electronic signal which is proportional to the NO concentration. To measure NO_x concentrations, the sum of NO and NO₂ (nitrogen dioxide), the NO₂ in the air sample is first reduced to NO, either by a heated catalyst (molybdenum or gold in the presence of CO) or chemically using FeSO₄, adding to the NO already present in the sample, then introduced into the reaction chamber for measurement as described above. The NO₂ concentration is derived by subtracting the NO concentration measurement from the NO_x concentration measurements. Monitors typically cycle through the total NO_x and NO modes every 10 seconds.

Standard sensitivity instruments have detection ranges from ≤ 0.5 ppb to 20 ppm and response times < 60 seconds, and are suitable for air quality monitoring in urban and suburban areas. Thermo Environmental Instruments, Inc. (TEI) Model 42i and Ecotech 9841 are examples of this type of instrument. These have been used widely by federal, state, and local agencies for routine monitoring of NO and NO₂.

The reduction of NO₂ to NO by these methods is not specific and a number of other nitrogen-containing species are reduced to NO that can interfere with the measurement of NO₂ (e.g., HNO₃, PAN, N₂O₅, HONO, and NO₃). Since the group is not well defined, it is commonly referred to as NO_x and the species included in the group depend on factors such as inlet and line losses and environmental factors. HNO₃ is most prone to line losses. Placing the converter as close to the sample inlet as possible minimizes these losses. Chemiluminescence analyzers that are configured in this manner are commonly known as NO_y analyzers. NO_y, or reactive nitrogen oxides, consists of a variety of species, the most abundant of which are typically NO, NO₂, PAN and HNO₃. TEI Model 42i-Y and Ecotech 9843 are commercially available NO_y analyzers.

Sulfur Dioxide

Analyzers like the Thermo 450i and Ecotech 9850 use UV fluorescence detection technology to measure SO₂ in ambient air with detection limits and response times similar to the NO_x analyzers. The Thermo 450i can also convert H₂S to SO₂, allowing differential measurement of H₂S in a manner analogous to the NO₂ method described above. Increased sensitivity can be achieved by trace-level analyzers like the Thermo 43i-TLE, which is designed to measure concentrations down to 50 ppt. Since ambient levels of SO₂ are frequently below 1

ppb in many areas, this extra sensitivity may be required to accurately monitor average concentrations.

Carbon Monoxide

CO is typically monitored by absorption of IR light using the gas-filter correlation method, in which a rotating filter wheel containing a known concentration of CO passes in front of the beam at regular intervals. Because infrared absorption is a nonlinear measurement technique, it is necessary for the instrument to use this reference signal to transform the detector signal into a linear output relative to the concentration of CO in the sampled air. Detection limits of 40 ppb are achieved in this manner, with range up to 200 ppm or greater.

VOC

Automated gas chromatographs (GC) can provide speciated analysis of gaseous organic compounds in ambient air over discrete time intervals as short as 15 minutes. The analytical method is analogous to that used to analyze canister samples in a laboratory with a GC/FID (Flame Ionization Detector) system and can detect individual compounds <1 ppb. Although automated, these instruments consume hydrogen gas and zero air and require appropriate span gas blends for calibration standards.

Total HC or VOC concentrations can be continuously monitored using FID or PID (Photo Ionization Detector), but provide no speciation information. The Thermo 55i monitors non-methane hydrocarbons (NMHC) down to 50 ppb with a response time of <90 seconds. PID based monitors such as the Rae Systems ppbRAE 300 can record continuous HC levels down to ppb levels without the requirement for any zero or carrier gas, but the response to different types of compounds varies so the result is only semi-quantitative for air containing a mixture of organic compounds.

3.2.2 Open-Path Gas Monitors

Although fixed site monitors can provide high sensitivity and time resolution, they may be inadequate to monitor pollutant concentrations that vary spatially due to proximity to a source or complex terrain. An alternative that is less sensitive to localized variations in concentration, but can still provide high time resolution, is to use open-path optical methods. These systems measure the attenuation of light of specific frequencies due to absorption by various pollutants. The performance achieved by open-path monitors is highly dependent on configuration of the optical components (path length, alignment), atmospheric conditions (dust, smoke, fog, or turbulence), and interferences from high concentrations of gases other than those of interest. Detailed information on the various technologies for open-path monitoring can be found in the EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux <http://www.epa.gov/ttnemc01/guidlnd/gd-052.pdf> so only a brief description of the relevant features is given here.

OP-FTIR (Fourier Transform Infra-Red)

The most commonly used open path systems employ a long wavelength light source that has characteristic absorption bands for many organic compounds plus CO and SO₂. Since the relationship between concentration and absorption of IR light is a non-linear function, a library of absorption spectra and Fourier transform signal processing are used to produce a linear output

for the compounds of interest. As a result of the intensive data processing required, a subset of the hundreds of possible species is typically reported.

Open path FTIR systems can be installed in 3 basic configurations: Bistatic in which a separate light source is directed at the receiver, Monostatic in which the light source originates at the detector and is reflected back by a mirror, and Passive in which only ambient radiation is received by the detector. The highest sensitivities are achieved by the bistatic configuration, but it requires electric power and operator access at both ends of the path. Monostatic systems give up some sensitivity for a simpler configuration and more flexible siting (e.g. reflector may be mounted on a stack or tower to give a vertical component to the measurement path). Passive systems require less power and can easily be repositioned, but have low sensitivity and can only detect flares or hot plumes at night. Path lengths may be up to 1000 meters with bistatic systems and cryogenically cooled detectors, but 100 meter paths are more typical.

DOAS

Differential Optical Absorption Spectroscopy systems are similar in concept to bistatic OP-FTIR, but may use short wavelength UV light sources to achieve higher sensitivity for NO₂, SO₂, and some organic species such as benzene. As with FTIR, a selected set of species is reported but some systems can store the raw spectra for later reanalysis if additional species are desired.

3.2.3 Imaging systems

A variety of remote sensing techniques exist for identifying and characterizing emissions.

IR Cameras

Video cameras tuned to IR wavelengths that are absorbed by methane and hydrocarbons (HC) (FLIR GF300) can be used to identify the location of emissions in real-time. Spectral imaging devices designed to be deployed at fixed locations for remote identification and characterization of gas plumes are available from Bruker (HI 90, SIGIS 2).

DIAL

Differential Absorption Lidar can create images of the flux of gaseous species across a facility boundary. The technique measures the backscattered intensity of light at different UV-VIS-NIR wavelengths while scanning in a 2-dimensional plane. The resulting data can be used to quantitatively characterize emissions or track plumes.

DIAL systems are large and complex, and require specially trained operators, so they are only suited to short-term studies to characterize emissions rather than routine monitoring.

SOF

A technology similar to DIAL that is used for annual emissions evaluations in parts of Europe is Solar Occultation Flux, in which a spectrometer mounted in a vehicle tracks the sun as it moves across a transect near a facility. SOF can quantify the flux of NO₂, SO₂, or specific VOC compounds (FluxSense AB, Sweden).

3.2.4 PM Mass Monitors

Beta Attenuation

Beta particles are absorbed by matter at a rate that is proportional to the areal mass density. By collecting aerosol particles on a filter tape that passes between a radiation source and beta detector, the accumulated mass of particles can be derived from the increase in attenuation of the beta source. This method is not truly continuous since it calculates mass concentrations from the change in signal relative to a baseline measurement from a clean section of filter tape at regular intervals, typically 1 hour. Although not a direct mass measurement, beta attenuation has been sufficiently validated to be accepted as a Federal Equivalent Method (FEM) and is widely used in regulatory monitoring for the PM_{2.5} and PM₁₀ air quality standards. Since the method calculates aerosol concentrations from the very small increase in density of a spot on a filter tape (typically a glass fiber matrix) over a fixed time period (1 hour), there is a large uncertainty in the individual hourly measurements ($\pm 10 \mu\text{g}/\text{m}^3$), however longer averaging times decrease the uncertainty ($\pm 2 \mu\text{g}/\text{m}^3$ for 24 hrs). As with any on-site mass measurement, humidity can affect the measured concentration so these monitors are generally operated with a heated inlet to maintain sample RH below a predetermined level (typically 45%)

Variations on the standard FEM beta attenuation monitor (e.g. MetOne BAM) may provide better temporal resolution. The Thermo SHARP monitor incorporates a light-scattering sensor along with the beta detector. The light-scattering signal, which is more sensitive but dependent on aerosol composition and morphology is used to track short-term variations in concentration during hourly beta-attenuation measurements. Kimoto makes a monitor that uses Teflon membrane tape, which has a much lower density than glass fiber, to reduce the uncertainty of the beta-attenuation measurement. The Kimoto monitor is also equipped for use with an optional separator tape that protects the sample deposits as they are rolled onto the take-up spool so that they may be preserved for compositional analysis.

The subsequent analysis of tape sampler spots by XRF to determine the elemental composition of aerosol during events of interest has been successfully demonstrated by Watson, et al. (2012) for the FEM type BAM sampler, although reduced sensitivity due to the media thickness and some loss of material due to contact with the back of the adjacent tape roll was noted. Analysis of sample spots from PTFE tape should allow improved analysis results, however the Kimoto instrument is produced in Japan and not widely used in the US limiting the available information about its suitability for routine monitoring. . Modification of the BAM or EBAM to use Teflon tape is available from MetOne on request, and might be a better option if those monitors are already in use in the network.

TEOM

The TEOM utilizes a unique method for measuring aerosol mass concentrations. Particulate matter is actively collected onto a small filter mounted on the tip of a vibrating glass cone. Increases in the mass on the filter change the resonant frequency of the cone, and this variation is detected and translated to mass concentration. This “oscillating microbalance” method is quite sensitive, but requires precise control of the instrument temperature and flow rates making the TEOM more expensive and complex than other continuous mass methods. While the TEOM incorporates a heated inlet to control sample air humidity, it has been our experience that it can

produce highly erratic readings when ambient RH changes rapidly such as during daily fog events, so it is not recommended for this program.

XRF Tape Sampler

A unique type of analyzer that can provide continuous elemental analysis of aerosol particles is marketed by Cooper Environmental. The Xact 625 and related models collect aerosol on a filter tape in a manner similar to a beta-attenuation sampler, however an X-ray fluorescence source and detector provide detailed elemental analysis (K to Pb) of the filter deposit with time resolution as short as 15 minutes. Detection limits below 1 ng/m³ are possible for most metals. As with any filter based analysis method, actual performance will vary with composition and density of the aerosol deposit. The Xact has the potential to characterize the temporal variations of toxic metals for evaluation of potential acute health effects, but the high cost (approx. \$250k) and complexity of the instrument would likely prevent its use at multiple monitoring locations.

Nephelometers

Aerosol mass concentrations can be estimated from the scattering of light by particles. This nephelometry approach is used in a variety of “real-time” monitors, such as the TSI DustTrak or MIE DataRAM. While such monitors can provide good sensitivity and very fast response times, the relationship between light-scattering and mass concentration varies significantly with changes in aerosol composition, size distribution, hydration, and morphology so observed fluctuations in reported mass concentration may be due, all or in part, to other factors. For example, during one prior study mass concentrations reported by the DustTrak were found to exceed gravimetric mass concentrations for mobile ambient samples by a factor of 2.24 with an R² of 0.75. For this reason, we would not recommend relying on light-scattering except as an adjunct to more direct mass measurement methods with less time resolution.

Black Carbon Monitors

Light-absorbing carbon, also referred to as black carbon (BC) and elemental carbon (EC), is a product of fuel combustion and has been used as a viable surrogate for estimating ambient concentrations of “diesel particulate matter” (DPM), in areas where diesel vehicle exhaust is known to be the dominant source of EC. Two commercially available methods that have been used to monitor BC with fast time resolution are the Aethalometer and the photoacoustic aerosol spectrometer.

The Aethalometer collects aerosol particles on a filter tape and measures the decrease in transmittance of light thru the tape as it becomes progressively darkened by the light absorbing particles in the air stream. An empirically developed algorithm is used to convert the measured changes in transmittance over time to concentrations of BC. The technique is quite sensitive, providing detection limits well below 1 µg/m³, and the use of multiple wavelength light sources can provide some information about the composition of the light-absorbing particles. However, the effect of light scattering by particles can cause a well-documented non-linear response^{4,5}

⁴ California Energy Commission (2007), *Evaluating Past and Improving Present and Future Measurements of Black Carbon*.

⁵ Weingartner, et al. (2003), Absorption of Light By Soot Particles: Determination of the Absorption Coefficient by Means of Aethalometers. *Journal of Aerosol Science*, 34:10.

when aerosol concentrations are high, resulting in significant underestimation of BC concentrations.

The photoacoustic instrument was developed at DRI and has been described in several publications (Arnott, Moosmüller et al. 1999; Arnott, Moosmüller et al. 2000). Briefly, light from a 1047 nm laser is power-modulated at the operating frequency of an acoustical resonator. Sample air is continuously drawn through the resonator at a flow rate of 1 – 3 lpm. Light absorbing aerosol (black carbon) will absorb some of the laser power, slightly heating the aerosol (typically much less than 1 C). The heat transfers very rapidly from the aerosol to the surrounding air, and the local pressure increases, contributing to the standing acoustic wave in the resonator. The acoustic wave is measured with a microphone as a measure of the light absorption. For the operating conditions of the resonator, and the laser wavelength used, the light absorption measurement is linearly proportional to the mass concentration of the black carbon aerosol in the sample air. The constant of proportionality has been inferred from correlations of black carbon measurements with elemental carbon as determined by the TOR method, and is used to go from aerosol light absorption to estimated black carbon mass concentration. No filters are needed for the photoacoustic measurement, and the flow rate is not used in the calculation of aerosol mass concentration. The flow rate must only be sufficient to adequately sample the air with minimal particle loss in the instrument and sample lines. The resolution of the instrument for a 3 second averaging time is 0.5 microgram per cubic meter for black carbon mass concentration. The resolution scales as the square root of sampling time, so for example, a resolution of 0.25 micrograms per cubic meter can be obtained for a 9 second averaging time. The photoacoustic measurement does not receive interference from exhaust gases, in our experience so far, and it is a zero-based measurement when no light absorbing aerosols are present. Commercial versions of the instrument, providing measurements of BC and total mass concentrations (estimated from light scattering) at multiple wavelengths, are available from Droplet Measurement Technologies.

PAH monitor

The Ecochem PAS 2000 is a photoelectric aerosol sensor (PAS) for continuous measurement of particle-bound polycyclic aromatic compounds (PAH). According to the manufacturer, it measures 3 or more ringed PAH which are predominantly adsorbed on particles and also pose the maximum health risk. Sensitivity is in the ng/m^3 range and the instrument is portable with a built in pump with flow control, datalogger, and serial output.

The PAS has been characterized and applied during the past couple of decades by various investigators. The PAS response varies for different PAHs and must be calibrated to appropriate mixtures of PAHs if these monitors are to provide more than semi-quantitative screening estimates of PAH exposure. Exposing the PAS to high levels of water vapor or source emissions, such as diesel exhaust, can cause erratic results. PAS results have also been found to vary with inlet temperature. However, the question about what the PAS really measures goes beyond calibration. The morphology of particles emitted from combustion sources changes rapidly due to adsorption of semi-volatile material on the particle surface and due to coagulation. These processes are important to the question of what the PAS measures since only surface composition contributes to the photoemission signal (Niessner et al, Anal. Chem. 1990, 62, 2071-2074). Because of these issues, data from the PAS may only be considered semi-quantitative in most situations. Therefore, its benefit for exposure estimates may be limited to

qualitative source attribution when combined with other compositional data such as BC concentrations.

Ultrafine Particle Counters

Also known as Condensation Particle Counters, CPCs measure particle number concentrations by supersaturating an incoming air stream with a condensing liquid and thereby growing smaller particles to a size at which they can be detected optically. There are a variety of models available from TSI and other vendors, that differ mainly in the condensing liquid used (butanol, isopropanol, or water) and the resulting ability to detect particles below 10 nm size. They typically record particle number concentration data with 1-minute or faster time resolution. Since aerosol size distributions are typically dominated in number by the smallest particle sizes and change rapidly with distance from combustion sources, the low-end sensitivity and accuracy of an individual instrument to these nm sized particles and the can greatly influence the measured particle counts making UFP data difficult to compare between monitors. Since these instruments provide no information about the size distribution or composition of the particles counted it is not possible to convert the measured number concentrations to mass concentration equivalent or estimate potential health effects.

3.3 Time-Integrated Gaseous Speciation Sampling and Analysis

Not all gaseous pollutants can be monitored continuously with sufficient sensitivity to determine average ambient concentrations, so it may be necessary to collect air samples or extract pollutants from the air for analysis in a laboratory. Well defined and characterized methods exist for most air toxics and other regulated pollutants.

3.3.1 Whole Air Samples in Stainless Steel Canisters

Stainless steel SUMMA™-polished canisters of 6-L capacity are customarily employed for volatile hydrocarbon (C₂-C₁₂) collection. These canister samples may be analyzed for speciated hydrocarbons by a method consistent with EPA Method TO-15, as well as for CO, CO₂, methane, and oxygenated species. Prior to sampling, the canisters are cleaned by repeated evacuation and pressurization with humidified zero air, and certified as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215).

The sampling procedure should essentially follow the pressurized sampling method described by EPA Methods TO-12 and TO-15 and the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). A pump constructed of chemically inert materials (e.g., stainless steel, Viton rubbers seals) draws in ambient air from the sampling manifold to fill and pressurize the sample canisters. A flow control device maintains a constant flow into the canisters over the desired sample period. This flow rate is preset to fill the canisters to about 1 atm above ambient pressure at the end of the sampling period (as described by EPA Method TO-15). For automatic operation, the timer starts and stops the pump at the appropriate time. The timer also opens the solenoid valve when the pump starts and closes it when the pump stops. The use of the solenoid manifold valves permits the automatic selection of preloaded canisters. Multiple-event sampling systems, such as the Tisch TE-323 or Xontech 901, allowing unattended collection of up to 16 canister samples are recommended for this study. Highly

portable, single-canister samplers like the Nutech2702 may also be useful for characterizing VOC composition from specific events or near-source locations.

Gas chromatography with mass spectrometry (GC/MS) is the established technique for monitoring volatile hydrocarbons, ozone precursors, in ambient air. The gas chromatographs should be connected to a data acquisition system. The software performs data acquisition, peak integration and identification, hardcopy output, post-run calculations, calibrations, peak re-integration, and user program interfacing. Typically, over 85% of total detectable C₂-C₁₂ hydrocarbon mass is identified and quantified. The detection limit for hydrocarbon VOC is approximately 0.1 ppbC for each compound.

Methane (CH₄), carbon monoxide (CO), and carbon dioxide (CO₂) can also be measured from the canister samples using gas chromatography with flame-ionization detector (GC/FID). Since the FID does not respond to CO and CO₂, these species are to be converted to methane by a methanator, positioned after the GC column, but ahead of the FID. The minimum detection limit for both CO and CH₄ should be < 20 ppbv, whereas for CO₂ < 3 ppmv. The precision of measurements should be generally better than 10%.

3.3.2 Flow-through Sampling on Chemically Active Adsorbents

Formaldehyde and other volatile carbonyl compounds are collected utilizing solid adsorbent cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) reagents, by the method consistent with the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). The method is based on the specific reaction of organic carbonyl compounds with DNPH deposited on silica gel or C₁₈ bonded SepPak cartridges in the presence of an acid to form stable derivatives, hydrazones, which are subsequently analyzed by high performance liquid chromatography (HPLC).

A carbonyl sampling system consists of a diaphragm pump capable of maintaining air flow through the cartridges of 500 - 1500 ml/min, flowmeter, six-port solenoid manifold allowing unattended collection of up to six carbonyl samples, needle valves for flow rate regulation, and check valves to protect cartridges from outside air when air is not being sampled through a given cartridge. For automatic operation, the timer starts and stops the pump at the appropriate time. The timer also opens the six-port solenoid valve when the pump starts and closes it when the pump stops. A charcoal filter is attached to the pump outlet in order to remove traces of acetonitrile from DNPH cartridges. Commercially available samplers of this type can collect from 3 (Tisch TE-423) to 16 (ATEC 8000) samples on a pre-determined schedule.

Carbonyl compounds collected in the cartridges (as hydrazones) are eluted with HPLC grade acetonitrile and analyzed by HPLC with UV detection at 360 nm. A reverse phase HPLC column is used. Identifications are made based on matching the HPLC retention times with those of authentic standards. A three-level calibration curve (plus blank) is constructed for each quantified hydrazone. Carbonyl compounds commonly measured by this method are formaldehyde and acetaldehyde. Other C₁-C₇ compounds that can be quantified include: propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, tolualdehyde, and hexanaldehyde.

3.3.3 Passive Gas Sampling

Passive sampling methods have been used extensively in Europe for ambient pollutant monitoring and more recently in the U.S. Because passive samplers do not require power for sample collection and are compact, they can be placed in locations that may not be accessible using active sampling techniques. Sampling times range from 24 hours up to 2 weeks. The ability of passive samplers to collect analytes over extended periods of time allows for potentially high sensitivity for low concentration pollutants. Sensitivity is limited only by the amount of time for which a sampler can be exposed and the blank value of the analyte on an unexposed adsorbent surface.

The basic principle employed in passive sampling is diffusion of gaseous pollutants across a surface to an adsorbing material on which the pollutant of interest accumulates over time according to Fick's law. The continual adsorption of the pollutant from the air maintains a concentration gradient near the surface that allows uptake of the pollutant to occur without any forced air movement (i.e., no pump or fan is required). After sampling, the collected pollutant is desorbed from the sampling media by thermal or chemical means and analyzed quantitatively. The average concentration of the pollutant in the air to which the sampler was exposed can be calculated from the following relationship:

$$\text{Concentration} = \frac{\text{AnalyteMass}}{\text{SamplingRate} \times \text{Time}}$$

The sampling rate can be determined theoretically or experimentally and is regulated by Fick's Law of Diffusion. Fick's first law, Equation 1, describes the rate of diffusion, J , of a solute across a surface area, A , and following a path length, L .

$$J = DA \times \frac{C}{L} \quad [1]$$

Assuming the blank value of the media is zero, the concentration C is that of the ambient compound of interest. D is the coefficient of diffusion and is dependent on the affinity of the adsorbing material for the analyte. Theoretical calculation of the coefficient of diffusion is possible, but the real world dependencies regulating its value are extensive and ambient tests are required for validation. Therefore, experimental determination of sampling rates in chambers and controlled field studies is usually preferred (Sunesson, 2007).

Several different geometries of passive samplers have been developed to control the diffusion rates according to Fick's first law. Thus sampling rates can be varied depending on the desired exposure time and expected ambient concentrations of the compounds of interest. Since the coefficient of diffusion, D and the concentration, C , are known, the sampling rate is proportional to the diffusive path area, A , and inversely proportional to the path length, L . Figure 2-8 shows three different geometries of passive monitors. The tube geometry is best for low sampling rates, while the shield (e.g., Ogawa) and radial geometry (e.g., Radiello) were developed for applications where higher diffusion rates were desired.

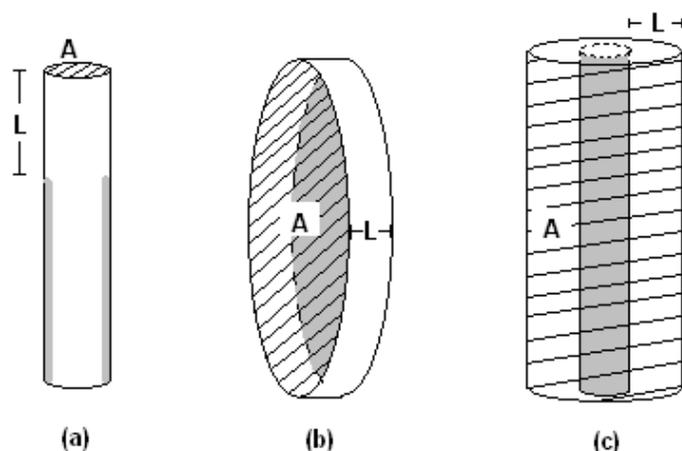


Figure 3-1. Schematics of (a) tube, (b) shield, and (c) radial geometry passive samplers with path length, L; Dashed area represents diffusive path area, A; Grey area represents adsorbent surface.

Six different types of passive samplers each with a unique adsorbent and method of analysis are described below. The NO_x and SO₂ samplers are manufactured by Ogawa and Co. The VOC, Aldehyde, and H₂S samplers are manufactured by Radiello and marketed in the US by Sigma-Aldrich. The analysis methods are listed in the table below:

Manufacturer	Target Pollutant	Analysis Method
Ogawa	NO ₂ /NO _x	Colorimetry for nitrite
Ogawa	SO ₂	Ion Chromatography
Radiello	VOC	Thermal Desorption/GC/MS
Radiello	1,3 butadiene	Thermal Desorption/GC/MS
Radiello	Aldehydes	HPLC/UV
Radiello	H ₂ S	Visible Spectrometry

The sampling rate for every analyte is calculated experimentally since pumps are not used in passive collection. Radiello and Ogawa supply these sampling rates for a number of commonly collected compounds. The reported sampling rates have been validated in chamber experiments at the Desert Research Institute for NO_x, formaldehyde, acrolein, BTEX, 1,3 butadiene, SO₂, and H₂S. Mass of analyte is calculated as the average blank result subtracted from the analytical result. Sampling time is the amount of time that the sampler was exposed. While lengthening the exposure time corresponds to an increase in sensitivity, it should be noted that exposure time is generally limited to 14 days due to the capacity of the adsorbents. Measurement sensitivities for a 7-day integration period are 0.3 ppb for NO_x and NO₂, 0.5 ppb for SO₂, 0.015 ppbv for benzene, 0.002 ppbv for toluene, ethylbenzene, and xylenes, 0.07 ppbv for formaldehyde, 0.05 ppbv for acetaldehyde, and 0.12 ppbv for acrolein. Passive samplers are insensitive to humidity within the range 10-90% RH and wind speeds between 0.1 and 10 m/s. Their sampling rates depend somewhat on ambient temperature, for which adjustment can be made. These passive samplers can be used in indoor environments and for personal sampling as

well. Several other passive samplers have been used extensively for personal exposure studies and are commercially available.

These passive measurements were evaluated by DRI during the Harbor Communities Monitoring Study (HCMS) (Mason et al., 2011). The HCMS was conducted to characterize the spatial variations in concentrations of toxic air contaminants and their co-pollutants within the communities adjacent to the Ports of Los Angeles and Long Beach (Fujita et al., 2009). The passive monitors were also used by DRI investigators in the West Oakland Monitoring Study (WOMS) (Fujita et al., 2010), an exposure assessment study of the Barnett Shale natural gas production area (Zielinska et al., 2010), and the LAX Air Quality Source Apportionment Study (2012).

The precisions of the passive measurements for these prior studies were better than 10 percent for compounds with ambient levels greater than five times the limit of detection, as shown in Table 3-1 to Table 3-3. The passive samples for BTEX were stable for storage times of up to 14 days at -18° C and measured values were generally within ± 15 percent of corresponding samples collected by active sampling methods commonly used in state and local monitoring programs. The experimentally-determined sampling rates (rate of specific pollutant absorption) for toluene and xylenes were within 10 percent of those published by Radiello. DRI's experimentally-determined sampling rates were used for benzene and ethylbenzene of 22.4 and 37.4 ml/min, respectively, rather than 27.8 and 25.7 ml/min values published by Radiello, which result in concentrations that are a factor of 1.24 higher for benzene and 0.69 lower for ethylbenzene. Passive measurements of formaldehyde and acetaldehyde were in good agreement with diluted standards for the laboratory evaluations, however acetaldehyde measured by the passive sampler was 43 percent lower than values obtained by active sampling on DNPH cartridges. The poor accuracy for acetaldehyde was most likely due to low collection efficiencies over extended sampling times, which may also apply to "reference" samples collected actively on DNPH cartridges. The accuracy of passive measurements of acrolein could not be evaluated as the ambient concentrations were typically below the limits of detection.

Table 3-1. Precision of passive NO₂, NO_x, and SO₂ measurements the LAX AQSAS, the West Oakland Monitoring Study (WOMS), and Harbor Communities Monitoring Study (HCMS).

	MDL ¹	Mean ²	<u>Differences of Replicates</u>	
	ppb	ppb	Mean (ppb) ³	%RD ⁴
<u>LAX AQSAS Winter 2012 Summer</u>				
Nitric Oxide (NO)	0.32	30.6	1.3	4.8%
Nitrogen Oxides (NO ₂)	0.32	25.6	0.6	2.5%
Sulfur Dioxide (SO ₂)	0.54	0.07	0.10	142%
<u>LAX AQSAS Summer 2012</u>				
Nitric Oxide (NO)	0.32	7.0	1.5	20.0%
Nitrogen Oxides (NO ₂)	0.32	15.4	1.5	9.0%
Sulfur Dioxide (SO ₂)	0.54	0.8	0.80	85%
<u>WOMS Summer 2009</u>				
Nitrogen Dioxide (NO ₂)	0.32	9.0	1.3	14.0%
Nitrogen Oxides (NO _x)	0.32	17.5	0.7	4.2%
Sulfur Dioxide (SO ₂)	0.54	0.09	0.03	33.9%
<u>WOMS Winter 2009/10</u>				
Nitrogen Dioxide (NO ₂)	0.32	5.7	0.1	1.7%
Nitrogen Oxides (NO _x)	0.32	25.9	0.8	3.1%
Sulfur Dioxide (SO ₂)	0.54	1.0	0.79	81.5%
<u>HCMS Summer 2007</u>				
Nitrogen Dioxide (NO ₂)	0.32	19.5	1.0	4.9%
Nitrogen Oxides (NO _x)	0.32	29.4	0.6	2.2%
Sulfur Dioxide (SO ₂)	0.54	1.0	0.20	19.8%
<u>HCMS Winter 2007</u>				
Nitrogen Dioxide (NO ₂)	0.32	28.5	1.5	5.3%
Nitrogen Oxides (NO _x)	0.32	73.0	2.0	2.8%
Sulfur Dioxide (SO ₂)	0.54	1.1	0.11	9.8%

¹ Minimum detection limits (MDL) are based upon manufacturer's specification for 7-day exposure.

² Seasonal means of six 7-day sampling periods for LAX AQSAS and four 7-day sampling periods for WOMS and HCMS.

³ Mean of the absolute differences between duplicate samples for LAX AQSAS (up to 6 values per season) and mean of the triplicates and individual sample for WOMS and HCMS (up to 12 values per season).

⁴ Mean of the absolute differences normalized to mean of the duplicates or triplicates in percent.

Table 3-2. Precision of passive BTEX measurements during the LAX AQSAS, the West Oakland Monitoring Study (WOMS), and Harbor Communities Monitoring Study (HCMS).

	MDL ¹	4-wk Mean	<u>Differences of Replicates</u>	
	ppb	ppb	Mean (ppb) ²	%RD ³
<u>LAX AQSAS Winter 2012 Summer</u>				
benzene	0.015	1.37	0.18	12.2%
toluene	0.002	1.78	0.24	13.3%
ethylbenzene	0.002	0.20	0.03	16.5%
xylenes	0.002	1.17	0.18	15.2%
<u>LAX AQSAS Summer 2012</u>				
benzene	0.015	0.30	0.15	68.0%
toluene	0.002	0.41	0.11	51.0%
ethylbenzene	0.002	0.04	0.02	58.0%
xylenes	0.002	0.30	0.14	65.0%
<u>WOMS Summer</u>				
benzene	0.015	0.16		
toluene	0.002	0.19	Not Available.	
ethylbenzene	0.002	0.08	See text for explanation.	
xylenes	0.002	0.36		
<u>WOMS Winter</u>				
benzene	0.015	0.26	0.02	7.8%
toluene	0.002	0.78	0.04	5.1%
ethylbenzene	0.002	0.15	0.01	5.1%
xylenes	0.002	0.63	0.03	5.0%
<u>HCMS Summer</u>				
benzene	0.015	0.35	0.03	7.5%
toluene	0.002	1.05	0.04	4.2%
ethylbenzene	0.002	0.21	0.01	6.7%
xylenes	0.002	0.69	0.06	9.2%
<u>HCMS Winter</u>				
benzene	0.015	0.61	0.01	2.3%
toluene	0.002	1.73	0.04	2.3%
ethylbenzene	0.002	0.34	0.01	2.4%
xylenes	0.002	1.41	0.03	2.2%

¹ Minimum detection limits (MDL) are based upon manufacturer's specification for 7-day exposure.

² Seasonal means of six 7-day sampling periods for LAX AQSAS and four 7-day sampling periods for WOMS and HCMS.

³ Mean of the absolute differences between duplicate samples for LAX AQSAS (up to 6 values per season) and mean of the triplicates and individual sample for WOMS and HCMS (up to 12 values per season).

⁴ Mean of the absolute differences normalized to mean of the duplicates or triplicates in percent.

Table 3-3. Precision of passive carbonyl compounds and 1,3-butadiene measurements during the LAX AQSAS, the West Oakland Monitoring Study (WOMS), and Harbor Communities Monitoring Study (HCMS).

	MDL ¹	4-wk Mean	<u>Differences of Replicates</u>	
	ppb	ppb	Mean (ppb) ²	%RD ³
<u>LAX AQSAS Winter 2012 Summer</u>				
Formaldehyde	0.07	2.2	0.13	5.8%
Acetaldehyde	0.05	1.4	0.09	6.5%
Acrolein	0.12	0.31	0.48	170%
1,3-butadiene		0.13	0.01	5.7%
<u>LAX AQSAS Summer 2012</u>				
Formaldehyde	0.07	1.34	0.26	19.0%
Acetaldehyde	0.05	0.43	0.10	24.0%
Acrolein	0.12			
1,3-butadiene		0.015	0.010	80.0%
<u>WOMS Summer</u>				
Formaldehyde	0.07	1.4	0.03	1.8%
Acetaldehyde	0.05	0.55	0.03	4.7%
Acrolein	0.12	0.009	0.005	57.7%
<u>WOMS Winter</u>				
Formaldehyde	0.07	1.3	0.1	5.1%
Acetaldehyde	0.05	0.5	0.1	18.9%
Acrolein	0.12	0.028	0.009	65.5%
<u>HCMS Summer</u>				
Formaldehyde	0.07	1.76	0.12	6.7%
Acetaldehyde	0.05	0.73	0.03	4.7%
Acrolein	0.12	0.010	0.005	47.4%
<u>HCMS Winter</u>				
Formaldehyde	0.07	2.65	0.06	2.2%
Acetaldehyde	0.05	1.88	0.05	2.8%
Acrolein	0.12	0.028	0.015	52.0%

¹ Minimum detection limits (MDL) are based upon manufacturer's specification for 7-day exposure. None provided for 1,3 butadiene.

² Seasonal means of six 7-day sampling periods for LAX AQSAS and four 7-day sampling periods for WOMS and HCMS.

³ Mean of the absolute differences between duplicate samples for LAX AQSAS (up to 6 values per season) and mean of the triplicates and individual sample for WOMS and HCMS (up to 12 values per season).

⁴ Mean of the absolute differences normalized to mean of the duplicates or triplicates in percent.

3.4 Time-Integrated PM Speciation Sampling and Analysis

3.4.1 High and Medium-Volume Aerosol Samplers

Due to the low ambient concentrations of many toxic components of airborne particulate matter, such as trace metals (Ni, Mn, Hg, etc.) and higher-MW PAHs (benzo[*a*]pyrene, benz[*a*]anthracene, chrysene, etc.), it is necessary to concentrate the PM from a large volume of air onto a filter in order to obtain a sufficient mass of material for accurate speciation analysis. High-volume samplers such as the EcoTech HiVol 3000 or Tisch TE-PNY1123, which draw air at approximately 1000 liters/min (lpm) through an 8" x 10" sheet of filter paper in a manner analogous to a vacuum cleaner, have been in use for many years. Size-selective inlets are available to remove particles greater than 10 or 2.5 μm aerodynamic diameter. While they can collect large amounts of particulate matter, they are labor intensive to operate and the large filter sheets result in substantial background lowering the detection limits and increasing analytical uncertainty. Medium volume samplers, which collect aerosol onto smaller Teflon or glass fiber filters (typically 47mm diameter) at flow rates from 16.7 to 113 lpm, depending on the requirements of the size-selective inlet used, have the advantages that they can be pre-weighed and loaded into sealed cassettes resulting in much lower analytical background and can be used in automated sequential sampling systems. Commercially available samplers that meet the Federal Reference Method requirements for PM_{2.5} monitoring (operating at 16.7 lpm) include the Thermo Partisol and BGI PQ-200. Since the acceptance of the beta-attenuation method as an equivalent method by EPA, sequential FRM PM_{2.5} samplers are no longer manufactured by many vendors. At this time only the Thermo 2025i Partisol, which can collect up to 16 filters on a pre-determined schedule, and the Met One SASS which collects up to 8 sequential samples, are available. Although the lower sample volumes may be insufficient for analysis of PAH from typical 24hr duration samples collected with the FRM samplers, the low analytical background allows laboratory compositing of the filter extracts to achieve good results at the cost of reduced time-resolution.

3.4.2 Low-Volume Aerosol Samplers

Because suitable passive sampling methods are not available to monitor the concentrations of aerosol pollutants, portable PM_{2.5} air samplers are used for particle sampling in saturation monitoring programs. These monitors consist of an impactor to remove particles above the cut-point of 1, 2.5 or 10 μm in aerodynamic diameter, a filter holder, pump, 12V power supply, and programmable control timer. A constant air flow rate of 5 L/min is maintained during sampling by a flow controller. Particles can be collected on either 47 mm diameter Teflon filters which can be analyzed gravimetrically for mass and XRF for elements (Na-U), or on pre-fired quartz filters for quantification of organic and elemental carbon (OC and EC) by thermal/optical reflectance (TOR) analysis. These systems are lightweight and operate on less than 100W of AC or 12VDC power, making them much easier to install at temporary sites. Comparable systems are available from Airmetrics (MiniVol), SKC (DCS), and BGI (Omni-FT). Due to the low flow rate, sample durations of 7-days or more may be needed to collect sufficient aerosol for analysis of trace components making them suitable primarily for characterization of the spatial variation in average pollutant concentrations within a study area.

4. MEASUREMENT APPROACHES AND METHODS TO ACHIEVE COMMUNITY MONITORING OBJECTIVES

This section provides general recommendations for community-scale air quality monitoring near refineries. While refineries are the main focus of this report, the methods are also applicable to other industrial sources with fuel combustion emissions or toxics in common with refinery emissions. The recommendations in this section are intended to facilitate further evaluation and discussion by a panel of monitoring experts gathered from academia, industry, the community and other governmental agencies. It is anticipated that the BAAQMD will use this report and the panel's recommendations to develop regulatory requirements for affected facilities to conduct community-scale air monitoring to supplement the ambient air quality data from existing criteria pollutant and air toxics monitoring programs.

The objectives of community-scale monitoring include: long-term monitoring to determine potential chronic and; acute health effects as well as short-term monitoring during major accidental releases of emissions. With the possible exception of SO₂, H₂S, and perchloroethylene, most of the other pollutants associated with refinery emissions, such as benzene and polycyclic aromatic hydrocarbons, are also emitted by motor vehicles and other combustion sources. Therefore, the monitoring data should also provide means for estimating the incremental contributions of refinery emissions to the observed ambient pollutant concentrations, if possible. As mentioned in Section 3, there is no single chemical profile that can be used in receptor modeling of refinery emissions. One method of estimating the source contribution of refinery emissions can be combining fence-line monitoring data with measurements of downwind concentration gradients with appropriate background subtraction. Long-term continuous monitoring at the boundaries of the refinery can also be used to determine trends in emissions and provide indications of seasonal or operational-cycle variations in emissions.

4.1 Community-Scale Monitoring Options

Each of the community-scale monitoring objectives mentioned above is associated with appropriate measurement approaches and methods in Table 4-1. Figure 4-1 shows a conceptual illustration of a monitoring program for a community (blue rectangle) near a refinery (black rectangle) that combines three monitoring approaches: A) continuous fence-line monitoring at edge of the facility closest to community; B) fixed site monitoring within the community at locations closest and further away from the refinery; and C) saturation monitoring to determine pollutant gradients around the facility and within the community. Table 4-2 shows the available continuous monitoring and time-integrated sampling methods and the approximate detection limits for various pollutants of interest. The acute and chronic RELs set by OEHHA are also shown for comparison. Note that the detection limits shown in the table are only estimates provided for comparison. Actual performance may vary significantly due to the presence of interfering pollutants, meteorology, operational conditions, and measurement time scale. Table 4-3 and Table 4-4 compile typical specifications and costs for the various monitoring methods described in this report. The information presented are representative values based on individual examples of each type of monitor, in order to enable comparisons. Actual specifications and costs will vary by manufacturer, model, and options selected.

Table 4-1. Measurement approaches and methods to achieve community monitoring objectives.

Objective	Emissions		Community Exposure		
	Charaterization	Surveillance	Acute Effects Routine Monitoring	Acute Effects Catastrophic Event	Chronic Effects Routine Monitoring
Duration of measurement program	days to weeks	continuous	continuous	days	Minimum of 4 weeks in 2 season
Time-resolution of measurements	minutes	hourly	hourly	varies	7 to 14 days
Measurement Location	refinery boundary	fenceline	representative community sites	Grab sampling, mobile sampling	representative community sites
Number of measurement sites	multiple	downwind edge	1 to 3 sites	multiple	Multiple ("saturation")
Parameters	alkanes, olefins, CO, NH ₃ , HCHO, SO ₂ , NO ₂ ,	benzene, butadiene, HCHO, NO ₂ , H ₂ S	all	determined by event	benze, butadiene, HCHO, NO ₂ , H ₂ S, metals
Recommended Methods	SOF, DIAL flux measurements	OP	photometric, auto-GC or OP, tape samplers, met	monitoring van + canisters, med-vol PM, OP	passive, low-vol PM

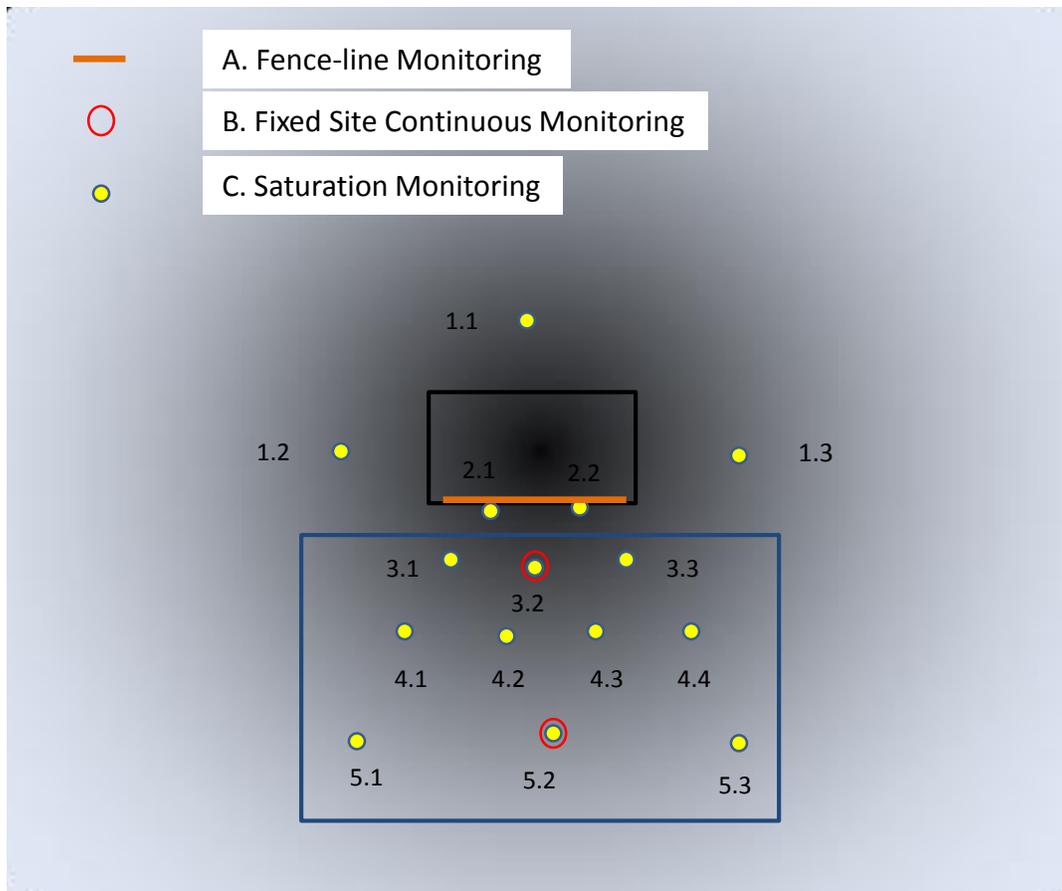


Figure 4-1. Conceptual illustration of a monitoring program for a community (blue rectangle) near a refinery (black rectangle) combining: A) continuous fence-line monitoring; B) fixed site monitoring; and C) multi-site saturation monitoring.

Table 4-2. Minimum detection limits for alternative continuous and time-integrated sampling methods for target compounds.

Target Compound	Major Sources ¹ (>10%)	Risk Exposure Levels (REL)		Continuous						Time-integrated Samping				
		Acute ² (µg/m ³)	Chronic ² (µg/m ³)	Point			Open Path 500m	OpenPath 100m	Area	Time-integrated Point sample (up to 24 hrs)			Saturation Monitoring (7-day)	
				Photo-metric	Auto-GC	XRF tape sampler ⁶	UV-DOAS	OP-FTIR ⁷	DIAL	Canister	Chemically active adsorbent	Filter ¹⁰	Passive	MiniVol
Benzene	M/F/R	1300	60		0.03		3	50	3	0.06			0.3	
1,3 Butadiene	M/R		20		0.02		1	10		0.04			0.02	
Formaldehyde		55	9				10	10			8 µg/m ³ h		0.15	
Acetaldehyde		470	140				20				6 µg/m ³ h		0.05	
Perchloroethylene		20000	35					40					0.02	
Carbon tetrachloride		1900	40					25					?	
Napthalene			9		0.05		2						?	
NO ₂		470	100 ³	0.2			2		25				0.16	
SO ₂	R/I/M			0.8			2	10					1.5	
CO	M/C	23000	g ⁴	35				100		40				
H ₂ S		42	10	0.2			0.2						0.15	
Ni		0.2	0.014			0.0002						0.26 µg/m ³ h		0.001
Mn		0.17	0.019			0.0003						0.35 µg/m ³ h		0.001
Cr VI		0.2												
Hg		0.6	0.03			0.001/ 0.0002 ⁵	?					0.66 µg/m ³ h		0.0008
As		0.2	0.015			0.0001						0.35 µg/m ³ h		0.001

All units are ug/m3 unless otherwise specified.

[1] R = refinery, F = fueling operations, M = motor vehicles, I = industrial processes, S = solvents, C = combustion; [2] <http://www.oehha.ca.gov/air/allrels.htm>; [3] AQS (annual mean 1-hr); [4] AQS (annual mean 8-hr); [5] Vapor/particle; [6] 1-hour average; [7] Det limits from: <http://clu-in.org/programs/21m2/openpath/op-ftir/>; [8] based on FRM PM sampler (16.7 lpm).

Table 4-3. Specifications for alternative continuous instruments.

Continuous Monitors	Vendor	Model	Power	Targets	MDL (1 hr)	Min Averaging Time	Unit Cost	Supplies (\$/yr)	Environment	Form Factor	features
Auto-GC	Peak Laboratories, Chromatotec	PeakPerformer, GC 866	Mean: 150 VA, Peak 360 VA	Speciated VOC <C13	<0.5 ppb (BTEX)	3 to 60 min	\$ 30,000		Climate-Controlled	Rack mount	may require H2 carrier gas and zero air
Beta-attenuation tape sampler	Met-One	BAM 1020	3.4 A max	PM2.5	10 ug/m3	1 hr	\$ 20,000	\$ 200	Indoor	Rack mount	Federal Equivalent Method for PM10 and PM2.5 designed for temporary, outdoor use. Solar power option.
	Met-One	EBAM	<50W 12VDC, Solar	PM2.5	10 ug/m3	1 hr	\$ 10,000	\$ 700	Outdoor	Rack mount	Low density Teflon tape, optional cover tape to preserve spots for analysis
	Kimoto	TE-PM711	AC 100 V, 50/60 Hz, 300 VA	PM2.5	2 ug/m3	1 hr	\$ 15,000	\$ 2,000	Indoor	Rack mount	continuous readings from integral neph
	Thermo	Sharp	300 W	PM2.5	<5 ug/m3	1 min			Indoor	Rack mount	Federal Equivalent Method for PM10 and PM2.5
TEOM auto-XRF tape sampler	Thermo	1405	440 W	PM2.5	<5 ug/m3	10 min	\$ 30,000		Indoor	Rack mount	
	Cooper	Xact 625	20A	Elements K - Pb	<0.5 ng/m3	15 min	\$ 250,000	\$ 1,500	Climate-Controlled	full Rack	
Aethalometer	Magee Sci.	AE-22	40 W	LAC	0.1 ug/m3	5 min	\$ 20,000	\$ 300	Climate-Controlled	Rack mount	
Photo-Acoustic Soot Spectrometer	Droplet Measurement Tech.	PASS-3	500 W	LAC, PM2.5	<0.5 ug/m3	2 sec	\$ 125,000		Climate-Controlled	Rack mount	measures absorption and light scattering at three-wavelengths across visible spectrum
CPC	TSI	Various	< 100 W	UFP	N/A	10 sec	\$ 10,000		Climate-Controlled		
NO/NOx analyzer	Thermo	42i	330 W	NO, NO2, NOx	<0.4 ppb	10 sec	\$ 12,000		Climate-Controlled	Rack mount	
CO analyzer	Thermo	48i	275 W	CO	40 ppb	10 sec	\$ 11,000		Climate-Controlled	Rack mount	
SO2 analyzer	Thermo	450i	300 W	SO2 or H2S or total S	<0.5 ppb	10 sec	\$ 11,000		Climate-Controlled	Rack mount	
UV-DOAS	OP SIS, Cerex			NO2, SO2, H2S, select	<1 - 10 ppb	<10 sec	\$60,000 - 200,000		Outdoor	tripod mount	
OP-FTIR	Kassay, Optra, Bruker			SO2, CO, select VOC	5 - 100 ppb	<10 sec	\$80,000 - 125,000		Outdoor	tripod mount	
DIAL	NPL			NO2, select VOC	25ppb NO2, <10ppb VOC		N/A	\$500k/survey	Mobile	trailer	not commercially available, requires service contract with operators
SOF	FluxSense			H2S, select VOC	>0.5 mg/m2 (flux)		N/A	\$200k/survey	Mobile	van	not commercially available, requires service contract with operators
Remote IR imaging	FLIR, Bruker	GL320, HI 90, SIGIS 2		VOC			\$ 100,000	\$3000/wk rent (FLIR)	Mobile	tripod mount	handheld, real-time imaging of emissions (not quantitative)
Meteorology				WS, WD, T, RH			\$10-15k		Outdoor	tower	

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[1] May require multiple configurations to measure all desired compounds.

Table 4-4. Specifications for alternative time-integrated sampling and analysis.

Time-integrated sample collection	Vendor	Model	Power	Targets	MDL	Min Averaging Time	Unit Cost	Analysis Cost (\$/sample)	Environment	Form Factor	features
portable PM2.5 filter sampler	AirMetrics, SKC, BGI	MiniVol, DCS, Omni-FT	12VDC (rechargeable) or 110VAC	PM2.5 mass, metals	< 1 ng/m3	~7 days	\$ 5,000	N/A	Outdoor	tripod mount	Portable, battery or solar operation
FRM PM2.5 filter sampler	Thermo, MetOne, BGI	Partisol, SASS, PQ-200	330 W	PM2.5 mass, metals, particulate PAH	< 2 ng/m3	24 hrs	\$8k - 14k	\$175 mass & metals, \$180 EC/OC, \$800 PAH	Outdoor	Stand Alone	Sequential sampling models available from Thermo and MetOne.
filter/XAD sampler	EcoTech, Tisch	HiVol 3000, TE-PNY1123	15A 110VAC	semi-volatile PAH		~6 hrs	\$ 4,000	\$ 1,000	Outdoor	Stand Alone	
DNPH cartridge sampler	Tisch, Atec	TE-423, 8000	2A (5A 12VDC)	acetaldehyde, formaldehyde	>0.5 ug/m3	~6 hrs	\$ 13,000	\$ 160	Indoor	Rack mount	
Canister sampler	Tisch, Xontec	TE-323, 901	2A (5A 12VDC)	speciated HC	<0.1 ppb	1 min	\$ 10,000	\$ 400	Indoor	Rack mount	
Radiello passive sampler	Sigma-Aldrich	R141	N/A	butadiene	<0.02 ppb	24 hrs	\$ 110	\$ 160	Outdoor	clip-on	
	Sigma-Aldrich	R145	N/A	BTEX	<0.02 ppb	24 hrs	\$ 110	\$ 160	Outdoor	clip-on	
	Sigma-Aldrich	R165	N/A	acetaldehyde, formaldehyde	>0.1 ppb	24 hrs	\$ 60	\$ 160	Outdoor	clip-on	
	Sigma-Aldrich	R170	N/A	H2S	<1 ppb	24 hrs	\$ 60	\$ 85	Outdoor	clip-on	
Ogawa passive sampler	Ogawa-USA		N/A	SO2, NO2	0.5, 0.3 ppb	24 hrs	\$ 100	\$ 100	Outdoor	clip-on	

4.1.1 Fence-line Monitoring

Fence-line monitoring should include continuous open-path monitors (IR and/or UV) that can detect and record concentrations of major target compounds (e.g., benzene, perchloroethylene, H₂S, SO₂) with sufficient sensitivity to identify pollutant fluxes that could result in exposures above the defined risk levels in the nearby community on an hourly basis or shorter time scale. Since fence-line monitors only detect pollutant fluxes across a linear path, they cannot be used to determine the overall emissions from a facility to the community, so detection limits need not be sufficient to accurately measure long-term ambient concentrations. More than one type of monitor may be required to provide adequate sensitivity for all target compounds. Since emissions may originate from various locations within a facility, the measurement path should be sufficient to cover all likely transport paths between the facility and community at an appropriate height to be determined by the elevation of the source. Large separation between sources within a facility or terrain features that interrupt the desired path may create a need for multiple monitors. Due to the various interferences that can affect open-path measurements, interpretation of raw data by a trained analyst is essential to avoid false indications of high emission events. Considering the high capital cost (about \$100K per unit), operating requirements, and limitations of fence-line monitoring, careful consideration should be given to the level of surveillance required before deploying systems. Detailed evaluation of routine emissions by remote sensing and study of the distribution of operations within a facility to determine potential fugitive emissions should precede fence-line monitoring. Toxic metals cannot be detected by OP methods so, unless a specific point source can be identified, fence-line monitoring for metals is not recommended. In the case where it is appropriate, and emissions are of sufficient concern to warrant the high cost (\$250K), an XRF filter tape monitor would be the only available method that could provide continuous surveillance data.

4.1.2 Fixed-Site Monitoring

Due to the difficulties in locating suitable sites and high operating costs, only a very limited number of fixed monitoring stations can be implemented to monitor the ambient pollutant concentrations in a community on a long-term basis. Therefore, the location of fixed monitors must be chosen with care so that they adequately represent the concentrations of pollutants that community residents are exposed to. Considering that few Bay Area residential areas exist downwind of refineries during typical weather conditions, the highest exposure to emissions is likely to occur either near the facility boundaries if the release is near ground level and atmospheric conditions are stable or at a distance from the facility if emissions are elevated and there is negative stability. In order to record exposure concentrations during either case, two fixed monitoring sites are recommended as shown in Figure 4-1; one located in the community as near the boundary with the facility as possible and another within the more distant half of the community. The latter requirement may be met by existing BAAQMD monitoring sites in several communities. Monitoring at fixed sites should include continuous (hourly) measurement of SO₂, H₂S, speciated VOC, wind speed and direction at a minimum. Adding NO₂, CO, and BC would be useful for distinguishing between sources of air toxics like benzene. Continuous monitoring of PM_{2.5} is likely to have little application for detecting refinery emissions, but operation of tape samplers would provide potential for analysis of metals by XRF during events. Cost of implementing fixed site monitoring could range from as low as \$30K to add speciated VOC to an existing SO₂ + H₂S site up to \$150K for a new, fully instrumented monitoring shelter.

Daily 24-hr canister and filter samples to be analyzed by GC/MS and XRF should be collected at these sites for several days during 2 or more seasons. If possible, parallel samples should be collected at a site without any local source impacts to represent the regional background and along the fence line monitor path to represent refinery emissions.

4.1.3 Saturation Monitoring

The term “saturation monitoring” is used in reference to ambient air monitoring for the purpose of establishing more detailed spatial variations in pollutant concentrations at the community scale. The objectives of this type of monitoring in the context of health risk assessments is to determine the seasonal or annual average air toxics concentrations at a sufficient number of locations within the community to: 1) establish the spatial variations in average concentration of air toxics; 2) identify the potential influence of hotspots of air toxic emissions on the community’s exposure; and 3) characterize the gradients in air toxic concentrations from these hotspots. Besides the accuracy, precision, selectivity and sensitivity of alternative measurement methods, the range of sampling periods, power requirements, size and portability of sampler or instrument are important consideration in a saturation monitoring study.

To verify the representativeness of the fixed monitoring sites, a one-time saturation monitoring study should be performed in each community over a period of at least 4 weeks in both summer and winter. Low-cost, low power or passive samplers can be deployed in a roughly 1 km spaced grid to determine the average spatial pattern of pollutant concentrations. The actual spacing may need to be varied due to topography, location of local sources, or land use patterns. If available resources do not permit saturation coverage of the entire community, or if there is no reason to suspect that significant spatial variations exist within an area, a limited number of sites can be deployed concentrating on the area nearest the refinery border and the fixed monitoring sites, as shown in Figure 4-1. Cost of saturation monitoring for SO₂, H₂S, and speciated VOC (BTEX, aldehydes, and 1,3-butadiene) is estimated to be about \$5000 per site, including materials, sample analysis and data QA. Extending sampling durations from 7 to 14 days could reduce costs by almost 50%, but increases the risk of significant data loss if samplers are damaged or stolen. PM_{2.5} filter sampling and analysis for mass, elements, and EC/OC would add about \$8000 per site. To reduce costs, low-volume portable filter samplers for metals and OC/EC can be added to the base configuration of passive SO₂, H₂S, and speciated VOC at only a subset of the sites. Considering the monitoring configuration shown in Figure 4-1 as an example, total cost to determine pollutant gradients in a community would be approximately \$90K. Standard operating procedures for the collection of passive gas samples are provided in Appendix B (Ogawa samplers) and C (Radiello samplers).

4.2 Incident Monitoring

4.2.1 Dispersion modeling

Dispersion modeling can provide valuable insights regarding the transport and range of impacts of refinery emissions during accidental releases. Using local meteorology (e.g. wind speed and direction) and details of the emission release (e.g. stack height, temperature and quantity), the location and magnitude of maximum concentrations can be predicted. Various release and meteorological scenarios can be simulated to provide predicted pollutant concentrations and likely areas of impacts. Ambient air quality monitoring may be used to verify

these predictions, especially if limit values are predicted to be approached. The modeling results can be used to make deployment choices for mobile monitoring and collection of grab samples.

4.2.2 Mobile Sampling

The existing BAAQMD monitoring van (described in Appendix D) could provide a useful tool for characterizing the spatial variations and composition of emissions during incidents. However, the current instrumentation in the van is designed for detection of mobile source emissions. Addition of an auto-GC for speciated VOC and a continuous H₂S/SO₂ monitor (see Table 4-3) would allow detection of major refinery emissions that could be distinguished from motor vehicle exhaust, allowing measurements to be made at roadsides and with the on-board generator operating. During an event the van could be quickly deployed to multiple locations identified by dispersion modeling as likely to be impacted, where pollutant gradients could be measured and canister and/or filter samples could be collected for additional speciation. For rapid deployment it would be necessary to have staff on call that is familiar with the SOPs for operation of the mobile monitoring system and incident response. When the instruments are not used for mobile sampling, they can be deployed in various residential and other fixed locations to complement the saturation monitoring network and the limited number of sites with supplemental continuous measurements.

Another possibility for mobile emergency response is to partner with EPA Region 9's Emergency Response Program. This program was developed to respond to environmental disasters, hazardous materials releases and inland oil spill that threaten human health and/or the environment. The program is based in San Francisco and includes mobile real-time capabilities to measure VOC's, using a number of different technologies such as Area Rae units, H₂S, chlorine, ammonia and hydrogen cyanide. In addition, EPA has particulate matter measurement capabilities, with some providing real time data. The EPA Emergency Response Program has well developed sampling protocols in the event that samples need to be collected for further laboratory analysis. These services are available around the clock and can include a federal on-scene coordinator that can access additional federal services, if necessary.

4.2.3 Emerging Technology and Cooperative Approaches

The development of new electrochemical and solid-state gas sensors has resulted in a wide variety of highly portable, low cost monitors that have potential to make large scale saturation monitoring much more affordable. Gas Sensitive Semiconductor (GSS) technology is less accurate than traditional methods and more susceptible to bias caused by interferants, but comes with significant cost savings. Electro-chemical sensors are less prone to interference than GSS sensors, but can be adversely affected by changes in temperature and humidity. At this time, none of these methods can provide the sensitivity and accuracy required for regulatory monitoring of ambient air quality, however, we recommended that their development be monitored and evaluated over time.

Another monitoring approach that bears consideration for the future is to involve community volunteers for increased spatial coverage during incidents. Some passive sampling technologies, such as absorbant cartridges and canister grab samples, are easily deployed and require minimal technical know-how and little training to operate, but must be executed in a highly coordinated manner to provide scientifically useful results. If sampling media were distributed in advance to a network of volunteers within communities that might be impacted by

an unplanned chemical release, existing communication technology such as text message alerts or Twitter could be employed by BAAQMD or refinery personnel to coordinate sample collection during events. Once sufficient spatial and temporal data has been collected from the enhanced monitoring networks proposed in this report, it should be used to evaluate the feasibility of such a cooperative incident monitoring plan. This would require significant outreach, training and education of participants and the community to ensure that requirements and limitations of such an approach are understood. It would also require the development of appropriate training programs and easy to understand Standard Operating Procedures (SOPs) to provide uniform sample collection as well as infrastructure and resources to provide appropriate sample media on a timeline to ensure adherence to shelf life requirements.

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Review of Current Air Monitoring Capabilities near Refineries in the San Francisco Bay Area

Appendices to Final Report

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Appendix A

Rodeo Refinery Fenceline Monitoring MOU

MEMORANDUM OF UNDERSTANDING

FENCELINE MONITORING AT RODEO REFINERY

This Memorandum of Understanding ("MOU") is entered into this 16th day of ~~February~~ ^{April} 2012 between ConocoPhillips Company ("ConocoPhillips"), the Crockett Community Foundation, Communities for a Better Environment, and the Community Working Group (collectively referred to herein as the "the Parties").

BACKGROUND

A. The Parties

1. **ConocoPhillips Company** operates a petroleum refinery in Rodeo, California ("the refinery") and is a successor-in-interest to the Tosco Refining Company with respect to ownership and operation of the refinery, which itself was a successor-in-interest to the Union Oil Company of California with respect to ownership and operation of the refinery. ConocoPhillips recently announced its intention to spin-off its downstream operations, which will include ownership and operation of the refinery, to Phillips 66 Company in 2012. For the purposes of this MOU, the term "ConocoPhillips" is meant to designate the ConocoPhillips Company and all of its successors-in-interest with respect to ownership and operation of the refinery, including but not limited to, Phillips 66 Company (after the effective date of any spin-off that may occur).
2. **Communities for a Better Environment** is an original signatory to a Memorandum of Understanding between the Union Oil Company of California, the Crockett/Rodeo Coalition, the Shoreline Environmental Alliance, and Communities for a Better Environment. The Memorandum of Understanding was entered into on November 4, 1996 and pertains to installation and operation of a fenceline monitoring system at the refinery. It was amended on September 5, 1997. The 1996 Memorandum of Understanding as amended is referred to herein as "the 1996 MOU."
3. The **Crockett Community Foundation** is a successor-in-interest to the Shoreline Environmental Alliance, the latter of which is an original signatory to the 1996 MOU.
4. The **Community Working Group** is a group consisting of certain Rodeo, Crockett, and Tormey citizens that negotiated a 14-part agreement with ConocoPhillips that was incorporated into ConocoPhillips' Land Use Permit No. 05-2048 as Condition No. 46, issued by Contra Costa County effective September 25, 2007. The Community Working Group, which represents that it is a community-appointed group of interested persons, meets with ConocoPhillips on a periodic basis to address problems or issues that arise in the design, operation, and maintenance of the refinery's fenceline monitoring system. The Community Working Group is the successor-in-interest to the

Crockett/Rodeo Coalition, an original signatory to the 1996 MOU. The Community Working Group agrees to provide a list of the CWG members and notify ConocoPhillips in writing if the membership on the Community Working Group changes.

B. Purpose of this Memorandum of Understanding

This Memorandum of Understanding has the following two purposes:

1. Fulfill the requirements of Land Use Permit No. 05-2048, Condition 46, paragraph 12 by "describing the equipment, QA/QC and monitoring changes for the fenceline monitoring system"; and
2. Updating and replacing the 1996 MOU (this document supersedes all previous versions and drafts of the Memorandum of Understanding).

It is the Parties' belief and understanding that Contra Costa County will accept ConocoPhillips' compliance with this Memorandum of Understanding to serve as compliance with any refinery Land Use Permit conditions requiring compliance with the 1996 MOU. The Parties agree not to challenge the County's acceptance of this Memorandum of Understanding in lieu of the 1996 MOU.

I. ConocoPhillips agrees to maintain the following fenceline monitoring system (the "System") at the refinery.

- A. The kind, location, and spacing of monitors are shown on Attachment A, which is incorporated by reference herein, and is further described below.
 1. Open-Path Fourier Transform Infrared Spectroscopy (FTIR) Air Monitoring Systems - There are two FTIR systems. One is located as part of the 930 meter open path North Fenceline Monitoring System (N. FLM) and one is located as part of the 820 meter open path South Fenceline Monitoring System (S. FLM). As depicted in Attachment A, the infrared receiver is found in the N. FLM building that is located east of Tank 288 and the infrared light source is located north of Tank 209. The infrared receiver is found in S. FLM building that is located southeast of the SF1 MET Station and the infrared light source is located south of Tank 108.
 2. Open-Path Tunable Diode Laser Systems - There are two Tunable Diode Laser Systems (TDLS) utilized to measure concentrations of hydrogen sulfide (H₂S) at the fenceline. These are co-located with the FTIRs and UVs at the N. FLM and S. FLM as described above. The TDLS transceivers are located in the N. and S. FLM buildings, respectively. The TDLS retroreflectors are co-located with the FTIR and UV light sources at the N. and S. FLM, respectively.

3. Open-Path UV Air Monitoring Systems - There are two UV systems. These are co-located with the FTIRs at the N. FLM and S. FLM as described above.
4. Organic Gas Detectors – A total of six organic gas detectors are located along the eastern and western ends of the refinery as depicted in Attachment A:
 - a) AT-1 located along T Street in Seasonal Storage near Tank 1010;
 - b) AT-2 located along the Main Road in Seasonal Storage near Tank 1004;
 - c) AT-3 located at the N. FLM building;
 - d) AT-4 located near the E-003 Outfall;
 - e) AT-5 located near the Saltwater Pump House; and
 - f) AT-6 located outside the Unit 40 Control Room.
5. Meteorological equipment consisting of wind speed, wind direction, temperature, and relative humidity is co-located with the FTIR, TDL and UV air monitoring systems at the N. FLM building. The Meteorological equipment co-located with the FLM monitors at the North FLM building will be considered part of the Fenceline System and the operational uptime will be reported.
6. Ancillary equipment including organic gas detector wireless radio receiving, onsite data storage work stations, DSL (internet) connection equipment, and electrical interconnection wiring are located at the N. FLM and S. FLM buildings and at Unit 100 Control Room. The organic gas detector data collection and storage as well as the primary DSL (internet) and secondary dial-up connection equipment are located at the Unit 100 Control Room.

B. Description of Equipment

The open-path monitoring systems used as part of the Fenceline Monitoring (FLM) at the refinery are based on the optical principle that when exposed to light, numerous chemicals will absorb various wavelengths of the light at levels that are proportional to amount of gas in the light beam. The FLM monitors use infrared (IR), ultraviolet (UV), and tunable diode laser light to detect gases that cross the fenceline. The fundamental operation of the IR, UV, and tunable diode laser systems are as follows:

1. a lamp produces a beam of light;
2. specially-designed optics focus the beam and project it through the air;
3. at the opposing end a receiver collects the light and focuses it into a spectrometer; and
4. the spectrometer analyzes the wavelengths and magnitudes of received light and determines the presence and concentration of interfering gases.

Data averaging time will be no greater than six minutes and will be minimized by the contractor so long as it can be accomplished without compromising acceptable spectral quality, as determined by the contractor. To this end, these instruments are set to collect data at approximate five minute intervals.

1. Open-Path Fourier Transform Infrared Spectroscopy (FTIR) Air Monitoring Systems - The MIDAC Corporation FTIR air monitoring system is a long-path air survey instrument designed for real-time detection of organic compounds using an IR transmitter and high-resolution spectrometer that collects light and saves the raw spectra at approximately five-minute time intervals. Compounds present in the beam path that are absorbent between 750 and 4200 wavenumbers will be detected and quantified at concentrations proportional to the amount of gas present. The IR system is connected to a computer workstation that calculates and displays gas concentrations in parts-per-billion by volume (ppbv) on a real-time basis using Midac AutoQuant™ software. Data from the spectrometer is stored in approximate five-minute averages in a Microsoft Excel™ (summary.csv) data file that provides the capability to re-analyze the data for the presence of other compounds of interest.
2. Open Path Tunable Diode Laser Systems (TDLS) - The Tunable Diode Laser transmits light emitted from the transceiver unit through the atmosphere to the retroreflector, which returns the beam back to the TDL unit where it is focused onto a photodiode detector. The amount of gas detected in the air is found by measuring the amount of light absorption from the beam and comparing this to a reference concentration. The data is collected at approximate five-minute intervals.
3. Open-Path UV Air Monitoring Systems - The Argos Scientific Incorporated UV air monitor is a portable, fenceline air survey tool designed for real-time detection of organic and inorganic compounds using a UV transmitter (Xenon lamp) and high-resolution spectrometer that collects light and saves the raw spectra. The light beam is transmitted through the ambient air to a receiver. Compounds present in the beam path that are absorbent between 240 and 330 nanometers absorb light at particular wavelengths at levels proportional to the amount of gas present. The UV air monitor is connected to a computer workstation to calculate gas concentrations in parts-per-billion by volume (ppbv) on a real-time basis using Argos UVS Quant software. Data from the spectrometer is stored in approximate five-minute averages in a Microsoft Excel™ (summary.csv) data file that provides the capability to re-analyze the data for the presence of other compounds of interest.
4. Organic Gas Detectors - The fenceline monitoring system has the following two types of organic gas detectors, both of which are digital: (1) the Sensor Electronics model SEC 2000 is a catalytic bead type; and (2) the Sensor Electronics model SEC 3100 is an infrared open path type. Both types of instruments are designed to detect explosive gases in the ambient air and provide an alarm when gas concentrations reach preset levels. As replacement is warranted, the SEC 2000 model may be replaced with the SEC 3100 model.
5. Meteorological Equipment - The meteorological equipment is located at the north fenceline monitoring building. The equipment consists of sensors that measure

wind speed, wind direction, temperature, and relative humidity. The anemometer (used to measure wind speed and direction) is an RM Young Model #81000 3D Anemometer. The temperature and relative humidity sensor is manufactured by TIPTEMP Products, Model # LASREC008 temperature/humidity sensor. The temperature/humidity sensor is used to calculate the dew point using the following formula:

The dew point T_d given the relative humidity RH and the actual temperature T in the air:

$$T_d = \frac{b \gamma(T, RH)}{a - \gamma(T, RH)}$$

Where:

$$\gamma(T, RH) = \frac{a T}{b + T} + \ln(RH/100)$$

where the temperatures are in degrees Celsius and "ln" refers to the natural logarithm.

The constants are:

$$a = 17.271$$

$$b = 237.7 \text{ } ^\circ\text{C}$$

6. Ancillary equipment includes organic gas detector wireless radio receiving, onsite data storage work stations, the primary DSL (internet) and secondary dial-up connection equipment, and electrical interconnection wiring.
- C. The compounds monitored are shown in Attachment B, which is incorporated by reference herein. Data averaging time will be no greater than six minutes. The chemicals listed in Attachment B will be monitored using the equipment specified below.
1. Open Path Tunable Diode Laser Systems (TDLS) - The chemicals and detection limits for the TDLS are depicted in the following table:

Fugitive Chemical	Detection Limits (ppbv)
Hydrogen Sulfide	25

2. Open-Path UV Air Monitoring Systems - The chemicals and detection limits for the Open-path UV systems are depicted in the following table:

Fugitive Chemical	Detection Limits (ppbv)
Benzene	5.0
Carbon Disulfide	5.0
Sulfur Dioxide	5.0
Toluene (including m- and o- Xylene)	5.0
p-Xylene	5.0

Ambient ozone will be included as part of the real-time quantification as a method of real-time Quality Assurance (QA) check.

3. Open-Path Fourier Transform Infrared Spectroscopy (FTIR) Air Monitoring Systems - The chemicals and detection limits for the Open-path FTIR systems are depicted in the following table:

Fugitive Chemical	Detection Limits (ppbv)
1,3 Butadiene	4.5
Carbonyl Sulfide	2.25
Carbon Monoxide	45
Ethanol	11.25
Ethylene	4.5
Total Hydrocarbons (as Hexane)	4.5
Mercaptan	11.25
MTBE	2.5
Ammonia (NH ₃)	15.75

Ambient methane and nitrous oxide (N₂O) will be included as part of the real-time quantification as a real-time quality assurance (QA) check.

4. Organic Gas Detectors (OGDs) - For the combustible gas version of the SEC 2000 (catalytic bead type), the concentration of combustible gas is displayed in terms of a percentage of the lower explosive limit (LEL). 100% LEL represents the minimum concentration of combustible gas in air that will cause an explosion. The sensor has an analog output between 4-20 milliamps (mA). The following table lists the gas concentration scale.

Signal Output (mA)	Percent of LEL
4.0	0
5.6	5
8.0	12.5
12	25
16	37.5
20	50
>20	Out of Range

For the combustible gas version of the SEC 3100 (infrared open path type), the concentration of combustible gas is displayed in terms of a percentage of LEL. The sensor has an analog output between 4-20 milliamps (mA). The following table lists the gas concentration scale for this model.

Signal Output (mA)	Percent of LEL
4.0	0
5.6	10
8.0	25
12	50
16	75
20	100
>20	Out of Range

- D. Alarm levels triggering Contra Costa County Community Warning System (CWS) notifications for Levels II and III conditions are listed in Attachment C.
- E. Method of recording, preserving, and using data will be as follows:
1. ConocoPhillips will require the contractor operating the System to utilize computers with ample storage and operating capacity and reliability for running the System and its software.
 2. ConocoPhillips will require the contractor operating the System to record all data electronically.
 3. ConocoPhillips will require the contractor operating the System to utilize a redundant electronic recording system.
 4. ConocoPhillips will require the contractor operating the System to provide automated notification to ConocoPhillips immediately when levels of pollutants are at or above the CWS response levels set forth in Attachment C to ensure a timely response.
 5. ConocoPhillips will require the contractor operating the System to monitor the compounds found on Attachment B with the equipment as specified in paragraph I.C.1, 2, 3, and 4 at the detection limits listed in I.C.1, 2, 3, and the percent LEL level in 4.
 6. ConocoPhillips will require the contractor operating the System to prepare a monthly report that will summarize the monitoring data and performance of the System. The monthly report will include on-stream efficiency data collection statistics for each technology and monitoring location listed in I.A.1 through 4, the Meteorological Station listed in I.A.5, and the on-stream efficiency for the public website described in I.E.8. below. The monthly report will include both adjusted monthly and adjusted 12-month rolling average data as defined in I.F.3 below, for each technology and monitoring location. Along with the onstream

efficiency statistics, the report will include a full reconciliation of the data that had to be invalidated or was not collected. A corrective action plan will be completed anytime the adjusted 12-month rolling average on-stream efficiency (for each technology and monitoring location) falls below 95%. The corrective action plan will be included in the monthly report following a report of a technology and monitoring location being below the 95% threshold. The Monthly Report or Cover Letter will include a summary of calibrations and maintenance activities completed during the month, provide a summary of audit results completed during the month, and include dates of Quarterly Meetings with the CWG that were held during the month. The cover letter or Monthly Report will also describe problems that occurred during the month, including such things as power failures or system component problems, and their resolution or proposed resolution. The cover letter will also include the planned audit schedule for audits required by the MOU. Monthly Reports will be provided to the County, the BAAQMD, the ConocoPhillips CAP, MOU signatories, and any individual Community Working Group members that make a written request to ConocoPhillips.

7. ConocoPhillips will require the contractor operating the System to develop an automated procedure whereby the system archives all data, including raw spectral data, on a daily basis by posting the data on a third party website site for download. If the system fails to post the daily data the contractor will manually upload the missing data within five working days. One member of the CWG will be given access to download such daily data (which will be available for 30 days after posting). The CWG will designate that individual in writing to ConocoPhillips. Also, upon written request within two years following posting, ConocoPhillips will provide all data, including raw spectral data, to the BAAQMD, County, CAP, and/or MOU signatories. The contractor will provide the requested information as expeditiously as possible with consideration for the amount of data requested, but shall provide the information no later than 15 working days from the date of the request.

8. Real-time, read-only data access to the raw data collected in accordance with I.E.5 and with equipment listed in Section I.A. will be provided to the community by ConocoPhillips via a public website that will be operated and maintained by the contractor. ConocoPhillips will also make the real-time data available to a community-run website, if requested by the CWG. Real-time data values have not undergone quality assurance or quality control review and are subject to change. In addition, information found on the public website is not meant for emergency or health care purposes. In the event of an emergency, ConocoPhillips will activate the CWS.

The public website maintained by ConocoPhillips or its contractor will include methods (color coding) to indicate the following detected chemical conditions:

1. Concentrations of chemicals above the detection limits found in I.C.;

2. Concentrations of chemicals above CWS Level II limits found in Appendix C; and
3. Concentrations of chemicals above CWS Level III limits found in Appendix C.

The public website will include the real-time status of all equipment and will auto update (with a date and time stamp) at the same interval as data is collected by the equipment listed in Section I.A. The public website will include a site map showing the locations of all equipment listed in Section I.A., along with an arrow showing real-time wind direction. The public website will contain a Message Board that will allow the contractor to post date and time-stamped messages of interest, which would include extended equipment outages. ConocoPhillips or its contractor will post notification messages on extended equipment outages within one business day of becoming aware of such outages. The Message Board will be archived with a link to the archive showing the running dialog of all previous messages. The public website will include a notification subscription feature that will notify registered members of the community by e-mail or by mobile phone text message of the following:

1. Contractor posts to public website Message Board.
 2. Equipment problem notifications.
 3. CWS alarm level exceedances measured by the system.
9. The Corrective Action Plan referenced in paragraph I.E.6. above will address the technology and monitoring locations, meteorological station, and/or public website referenced in section I.E.6. The purpose of the Corrective Action Plan is to document the root cause(s), provide action step(s), and provide an implementation timeline to improve on-stream efficiency of the Fenceline System, with the goal of returning to 95 percent or better adjusted on-stream efficiency (based on 12-month rolling average) as soon as practicable. The Corrective Action Plan would consist of the following minimum elements: 1) Analysis of instrument downtime from the immediate previous eighteen months; 2) List of existing action steps (if any) that have already been taken in the past eighteen months to improve on-stream efficiency; 3) New Action Step(s) to improve on-stream efficiency, unless action resolving the problem has already been taken; and 4) an Action Step(s) Implementation schedule.
- F. ConocoPhillips may utilize a qualified contractor or contractors to operate and maintain the System to achieve maximum online performance. Although the MOU contains references to a "contractor" in several places throughout, the Parties agree that ConocoPhillips has sole discretion whether to use a contractor for operation and/or maintenance of the System. It is the intent to ensure that equipment and public website downtime is evaluated to identify and correct reoccurring problems when possible, and improve online performance.

1. ConocoPhillips will contractually obligate the contractor operating the System to develop and maintain an operational program that minimizes instrument downtime. To this end, ConocoPhillips will require the contractor operating the System to develop, and update as necessary, an Operations Guidance Document for the System. The Operations Guidance Document will address items such as: detailed equipment hardware descriptions, data communication, management of system notifications and alarms, instrument maintenance, Quality Assurance/Quality Control (QA/QC), and public website management. The Operations Guidance Document will include a spare parts list dedicated to the operation and maintenance of the system, and those items will be kept as inventory and maintained by the contractor. The Operations Guidance Document will be reviewed, and updated if necessary, at least once per year. The CWG will be provided with an updated copy of the Operations Guidance Document anytime the document has been revised. Notwithstanding the specific actions referenced above, which actions are required as part of this MOU, with respect to the Operations Guidance Document, the Parties agree that the Operations Guidance Document is not part of this Memorandum of Understanding.
2. All instrument and public website downtime will be reconciled and reported in the Monthly Report as set fourth above. All instrument or public website downtime will be evaluated to identify whether improvements can be made to minimize future system downtime.
3. ConocoPhillips will maintain an adjusted on-stream efficiency of 95% based on a 12-month rolling average for each technology and monitoring location listed in sections I.A. 1 through 5, and including the public website. The monthly on-stream efficiency, reported as a percentage, is defined as the total number of data points collected and stored during the calendar month divided by the total data collection intervals in the calendar month assuming that data is collected at five minute intervals. The on-stream efficiency for each technology and monitoring location will be adjusted for atmospheric conditions (fog, rain, dust, sleet, snow, wind). When the 12-month rolling average onstream efficiency for any individual equipment or the internet connection falls below 95% a corrective action plan will be developed in accordance with Conditions I.E.6 and I.E.9. The plan will then be reviewed with the CWG at the next quarterly meeting and documented to completion.
4. ConocoPhillips is allowed to upgrade the System, without prior consultation of the other Parties, only with substantially-equivalent equipment or software (i.e., equipment that does not diminish the sensitivity or reliability of the equipment or the Fenceline System) as necessary to maintain system operability (changes to equipment described in this MOU may trigger a change in the Quality Assurance/Quality Control requirements associated with the updated equipment – any such changes will be communicated to interested members of the community at the quarterly meetings described below). These types of changes will be documented in the Monthly Reports and discussed in the quarterly meetings.

Changes to the system that would adversely affect the sensitivity or reliability of the equipment or system will not be made without advance consultation and agreement with both Contra Costa County and the CWG.

5. Land Use Permit No. 05-2048, Condition 46-14, requires in part that the CWG may annually request that an independent audit of the System be conducted by a mutually-agreeable third party pursuant to the following parameters:

"ConocoPhillips will fund the cost of this audit not to exceed \$5,000 per year. Any funds not expended for such an audit, will carry over to the following years and be added to the \$5,000 per year budget up to a maximum amount of \$20,000."

The Parties agree that the audit scope will include baseline concentrations, algorithms used, methods calculating the real time measurements, as well as methods used for calculating the data included in the monthly report, subject to the limitation in the following sentence. Certain items listed in the audit scope referenced above may be proprietary and business confidential to the contractor operating the System, and therefore, such items will only be included in the audit scope if the audit contractor agrees to the System contractor's confidentiality and intellectual property protection provisions, if any. Such issues and ability for mutual agreement are beyond ConocoPhillips' control however, ConocoPhillips will not limit the scope of the System audit other than as described in this paragraph.

6. ConocoPhillips will hold quarterly meetings with the CWG and invited representatives of the County, if such representatives attend, to provide a forum for ongoing communications and issue resolution. Equipment upgrades, system onstream efficiency, explanation of downtime, planned QA/QC activities, and previous monthly reports will be covered in these meetings. While these meetings will occur on a quarterly basis, ConocoPhillips encourages the members of the CWG to contact refinery representatives whenever questions arise.
7. ConocoPhillips will allow all contractor(s) to operate and maintain the System and make decisions or determinations for which they are responsible under this MOU in a reasonable and scientifically based manner; ConocoPhillips shall not require its own approval prior to contractor(s) undertaking actions that fall within the normal course of the contractor's business regarding the operation and maintenance of the System, subject to the limitations in this MOU and any contract between ConocoPhillips and its contractor(s).

II. Quality Assurance/Quality Control (QA/QC)

The following section addresses quality assurance and quality control for each of the major equipment described in Section I.B. The section outlines the types of tests that will be conducted on a periodic basis.

A. OPEN-PATH FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) AIR MONITORING SYSTEMS

This section presents the QA protocol used for the measurement of broad spectrum Op-FTIR spectra according to the guidelines given by the U.S. Environmental Protection Agency (EPA) and other agencies that certify the calibration, operation, and maintenance of broadband spectroscopy related to the sampling of the atmosphere. The QA document is based on the EPA's Compendium Method TO-16 "Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases." It should be noted TO-16 is a generic document that covers the operation of Op-FTIRs and is not instrument specific. Therefore, the refinery's protocol is based on the key elements of TO-16 as they are applied to the MIDAC Corporation Op-FTIR monitoring system and the application of a long-term fence line monitoring system at the Rodeo Refinery. The following Data Quality Indicators (DQI) will be used to evaluate the performance of the Op-FTIR:

1. detection limits for chemicals of interest;
2. detection of ambient levels of methane and N₂O;
3. measurement signal strength of Infrared beam; and
4. monthly challenge of the system with a QA/QC gas.

For many of the issues identified via the QA/QC process, it is possible to take corrective action to improve instrument performance in the field. Some examples of correctable problems include re-alignment of the instrument mirrors to improve signal strength, or changing the IR source. Some of the problems identified will not affect data quality, but instead will indicate a potential long-term problem with the instrument that will be corrected by an instrument specialist once a problem has been identified. An example of this would be a major degradation of signal strength that could be corrected by realigning the internal optics of the instrument.

1. DQI No. 1 - Detection limits for chemicals of interest

At the end of each month, the real-time data will be reviewed to determine if the system is quantifying the chemicals of interest (i.e., fugitive emission gases) at or below the level specified when the systems were purchased. To pass this test, the detection limits need to be at or below the detection limits listed below:

Fugitive Chemical	Detection Limits (ppbv)
1,3 Butadiene	4.5
Carbonyl Sulfide	2.25
Carbon Monoxide	45
Ethanol	11.25
Ethylene	4.5
Total Hydrocarbons (as Hexane)	4.5
Mercaptan	11.25
MTBE	2.5
Ammonia (NH ₃)	15.75

The following procedure will be used to determine whether the data meets these data quality objectives (DQOs):

- 16 continuous samples will be selected when no fugitive gases are present in the spectra.
- The real-time results will be used to determine an average value and standard deviation.
- The limit for each chemical listed above should be greater than three standard deviations of the average value.

If the chemicals fail this QA test then corrective actions for the Op-FTIR air monitoring system will be taken.

2. DQI No. 2 - Concentration Checks for Ambient Gases

The Open-path FTIR air monitoring systems are currently setup to detect the following ambient gases:

Chemical	QA Limit
Methane	Greater than 1.72 ppmv
Nitrous oxide	Between 280-320 ppbv

At the end of the month the continuous monitoring data will be analyzed to determine if the data is within these limits. If more than 10% of the data points are outside the limits, corrective actions for the Op-FTIR air monitoring system will be taken.

3. DQI No. 3 - Signal Strength of Infrared beam

At the end each month's maintenance activity the signal strength of the IR Beam will be measured at three different wavenumbers:

- 950 cm-1 < 3,000 counts;
- 2,750 cm-1 < 400 counts; and
- 4,100 cm-1 < 100 counts.

If the signal strength drops below the above stated values, ConocoPhillips will perform the following tasks to improve the signal strength:

- clean all optical components of the system;
- perform a realignment of both the source and receiver unit; and
- if necessary, replace the IR source.

4. DQI No. 4 - Challenge of System with Gas

During the monthly maintenance check, ConocoPhillips will challenge the system by introducing a gas (ammonia) in the beam and then check the quantitative result for accuracy.

B. OPEN-PATH UV AIR MONITORING SYSTEMS

This section addresses QA and QC for the new UV equipment.

1. Method Summary

The Argos UV air monitor is a portable, single-point air survey tool designed for real-time detection of organic and inorganic compounds using a UV transmitter (Xenon lamp) and high-resolution spectrometer that collects light and saves the raw spectra. The light beam is transmitted through the ambient air to a receiver. Compounds present in the beam path that are absorbent between 240 and 330 nanometers absorb light at particular wavelengths at levels proportional to the amount of gas present. The UV system is connected to a laptop computer via USB cable to display gas concentrations in parts-per-billion by volume (ppbv) on a real-time basis using Argos UVS Quant software. Data from the spectrometer is stored in five-minute averages in a Microsoft Excel™ (summary.csv) data file that provides the capability to re-analyze the data for the presence other compounds of interest.

2. Quality Assurance Checks

The QA procedure for the Open-path UV air monitors is an automated process that uses a sealed sample cell (the lollipop) containing two of the gases on the target compound list. The QA check will occur on a monthly basis or whenever a UV source is changed. The field check is used to detect compounds across the low, middle, and high areas of the UV absorbance spectrum. This check takes approximately five minutes. Detailed operational methods for the QA/QC check for the UV system are described in the ConocoPhillips, Rodeo Fenceline Monitoring Program, and Quality Assurance Plan Document # 032009a.

During the monthly maintenance on the system ConocoPhillips will re-align the system and measure the signal strength of the UV beam. If the system cannot achieve a signal strength of 3000 counts (max) at a sample integration time of 750 milliseconds, ConocoPhillips will perform the following tasks:

- Clean the optical components of the system
- Realign the source and receiver units
- If necessary, replace the UV light source

3. Signal-to-Noise Ratio Check

A check of the Signal-to-Noise ratio for the Open-path UV air monitors will occur as follows:

- Two back-to-back spectra will be subtracted from each other to create an absorbance spectra.
- The peak-to-peak noise absorbance spectra will be examined in the region of 252.00 to 255.00 nanometers.
- The systems will be within operational specifications if the peak-to-peak noise is less than 0.003 absorbance units (AU) units.
- If the noise level is greater than 0.003 absorbance units, additional actions including aligning the source optics and replacing the light sources will be conducted.

When the additional maintenance items are complete, the systems will be retested to ensure they are back within specification.

4. Selection of Clean Air References

The Argos UVQuant data collection software has a built in algorithm to minimize the baseline drift by automatically updating the background whenever a gas is determined to not be present in the light beam. However, if during the process of data collection it is determined that the light signal has insufficient intensity (such as periods of heavy fog, rain or other times when the beam is partially blocked), then the software disables the automatic background update function. When the signal strength rises to a level where optimal data quantification occurs, the software automatically re-enables the automated background update function.

C. ORGANIC GAS DETECTORS

1. SEC 2000 (catalytic bead type) Model

The SEC 2000 (catalytic bead type) models will be calibrated according to Sensor Electronic supplied procedures at least quarterly. Calibration consists of exposing the SEC 2000 sensor to the known quantity of methane gas (i.e., 10% LEL concentration of methane in air) and adjusting the electronic circuitry to generate a reading equal to the concentration of the calibration gas.

2. SEC 3100 (infrared open path type) Model

The SEC 3100 (infrared open path type) models will be calibrated according to Sensor Electronic supplied procedures at least quarterly. No calibration gas is required for the factory recommended calibration procedure. However, following the calibration, the person performing the calibration will check the response of the cell by injecting a calibration gas (10% LEL concentration of methane in air) and noting the instrument response and the proper operation of the status lamps.

D. OPEN PATH H2S TUNABLE DIODE LASER SYSTEMS (H2S TDLS)

The H2S Tunable Diode Lasers will be challenged on a monthly basis using a calibration cell with a known concentration of gas. The following calibration procedure will be used:

1. Check to see that TDL is in data collection mode.
2. Insert the H2S calibration cell in front of the TDL transmitter/receiver unit.
3. Adjust the reflector to maximum signal strength.
4. Record the output level of the H2S detected by the TDL as the beam enters and exits the calibration cell.
5. Collect seven consecutive data points. The average value of the collected data should be 25 ppbv \pm 2 ppbv.
6. If the concentration value is outside the range in Step 5, contact the vendor for possible service activities.

E. METEOROLOGICAL EQUIPMENT

The RM Young 3D anemometer portion of the meteorological station will be sent to the manufacture on an annual basis for calibration of wind speed and direction

The temperature and relative humidity probe will be challenged on a quarterly basis by comparing the output to TIPTEMP model # COCSEN079, temperature/humidity calibration sensor. The calibration sensor includes an individually serial-numbered Traceable® Certificate is provided from an ISO 17025 calibration.

- III. ConocoPhillips will continue operation of the System for the duration of Land Use Permit Nos. 2038-93 and 05-2048.
- IV. The detailed System descriptions in this MOU, including vendor and equipment names, are included in part for completeness' sake and information purposes. Pursuant to the provisions of Section I.F.4, the Parties agree that ConocoPhillips is allowed to upgrade the System with substantially-equivalent equipment or software as necessary to maintain system operability without prior consultation with the other Parties. Changes to equipment described in this MOU may trigger a change in the Quality Assurance/Quality Control requirements described elsewhere in this MOU. Any such changes will be communicated to interested members of the community at the quarterly meetings described above. Changes to the system that would adversely affect the sensitivity or reliability of the system will not be made without advance consultation and agreement with both Contra Costa County and the CWG.
- V. ConocoPhillips shall make all reasonable efforts to ensure that the Fenceline Monitoring System is operational during refinery turnarounds, i.e., periods of scheduled major maintenance at the Refinery. Specifically, ConocoPhillips shall not schedule major routine maintenance of the System or any of its components that would result in extended downtime during a planned turnaround. Periodic short term calibrations and maintenance required to

maintain system operability will be allowed during turnarounds, but reasonable efforts will be made to minimize instrument downtime.

- VI. The Parties agree to make reasonable efforts to resolve disputes regarding rights and obligations contained in this MOU via informal means prior to invoking any action involving Contra Costa County.
- VII. The signatories below represent that they are authorized to execute this MOU on behalf of the Party for whom they are signing.

Acknowledged by ConocoPhillips, the Crockett Community Foundation, Communities for a Better Environment, the Crockett/Rodeo Coalition, and the Community Working Group by the signatories of their respective representatives and the dates indicated below.

By: Rand H. Swenson 2/22/2012
Rand H. Swenson Date
San Francisco Refinery Manager
ConocoPhillips Company

By: Howard Adams 3/3/12
Howard Adams Date
Crockett/Tormey
Community Working Group Member

By: _____
[Printed Name] Date
~~Crockett/Rodeo Coalition~~

By: Janet Callaghan 3/5/12
Janet Callaghan Date
Rodeo
Community Working Group Member

By: _____
[Printed Name] Date
Communities for a Better Environment

By: Danielle Fugge 3/7/12
[Printed Name] Date
Crockett Community Foundation
Danielle Fugge

By: W.A. Concannon 3/2/2012
WILLIAM CONCANNON
CROCKETT
COMMUNITY WORKING
GROUP

By: Ed Tannenbaum 3/2/12

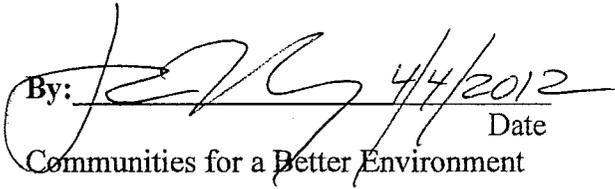
Ed Tannenbaum
CCWG

By: _____
Rand H. Swenson Date
San Francisco Refinery Manager
ConocoPhillips Company

By: _____
Howard Adams Date
Crockett/Tormey
Community Working Group Member

By: _____
Date
Crockett/Rodeo Coalition

By: _____
Date
Janet Callaghan
Rodeo
Community Working Group Member

By:  4/4/2012
Date
Communities for a Better Environment

By: _____
Date
Danielle Fugere
Crockett Community Foundation

Attachment A



Attachment B

Monitored Chemicals List

Ammonia
Benzene
1,3 Butadiene
Carbon Disulfide
Carbon Monoxide
Carbonyl Sulfide
Ethylene
Hexane (Total Hydrocarbons)
Hydrogen Sulfide
Methane
Methyl Mercaptan
MTBE
Sulfur Dioxide
Toluene
Xylene

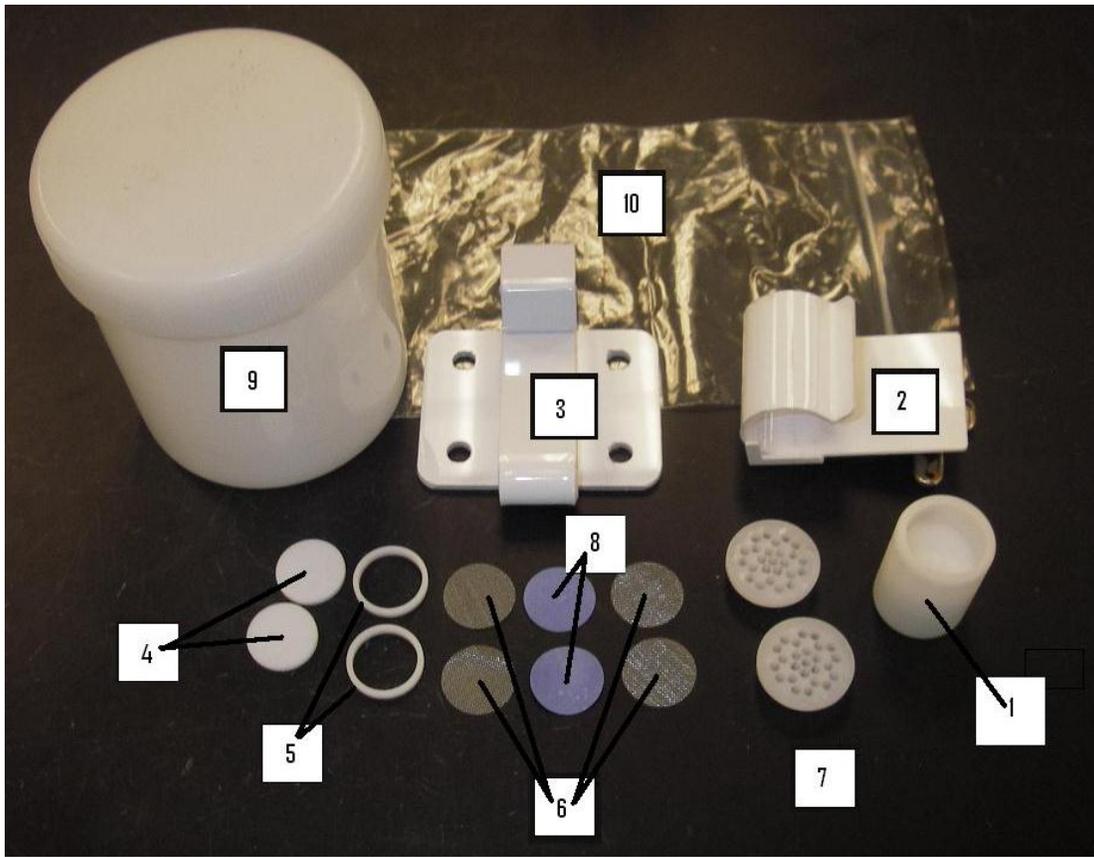
Attachment C

Response Levels from the Fenceline Monitors

CHEMICAL	FENCELINE MONITORING CWS NOTIFICATION LEVELS (ppb)		
	INSTRUMENTATION	CWS Level II	CWS Level III
Ammonia	FTIR	3,000	100,000
Benzene	UV	1,000	5,000
1,3 Butadiene	FTIR	10,000	50,000
Carbon Disulfide	UV	1,000	10,000
Carbon Monoxide	FTIR	20,000	400,000
Carbonyl Sulfide	FTIR	1,000	10,000
Ethylene	FTIR	1,000,000	2,700,000
Hexane (Total Hydrocarbons)	FTIR	50,000	75,000
Hydrogen Sulfide	TDLS	30	15,000
Methane	FTIR	1,000,000	5,000,000
Methyl Mercaptan	FTIR	500	10,000
MTBE	FTIR	40,000	200,000
Sulfur Dioxide	UV	300	3,000
Toluene	UV	50,000	100,000
Xylene	UV	1,000	200,000

Appendix B

Standard Operating Procedure for Ogawa Passive Monitors



Equipment List - Ogawa Passive Sampler

ID #	Description	Quantity
1	Sampler Housing	1
2	Sampler Holder	1
3	Mounting Bracket	1
4	Solid Pad	2
5	Pad Retaining Ring	2
6	Stainless Screen	4
7	Diffuser End Cap	2
8	Pre-Coated Collection Pad	2
9	Shelter/Vial	1
10	Sample Bag	1

The Ogawa *Pre-Coated Collection Pads* come in a few varieties depending on the application. Specific information on the correct parts for each monitoring application can be found at the company website (www.ogawausa.com).

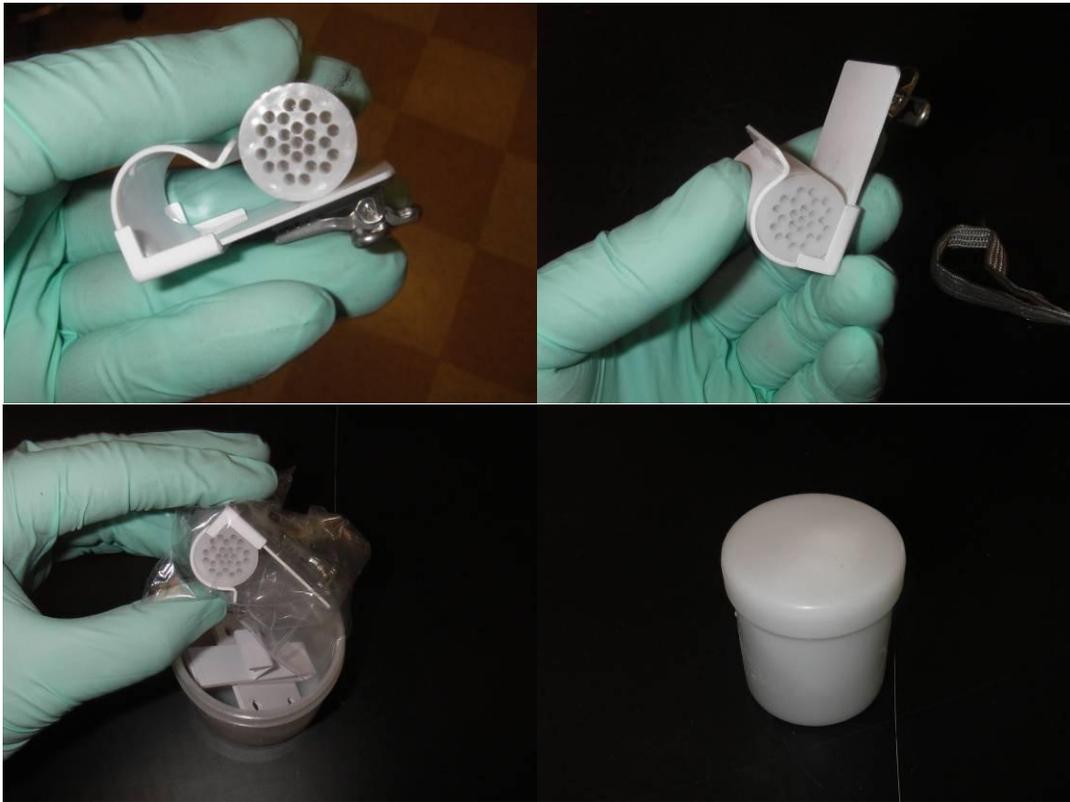
Assembly of the Ogawa Passive Sampler should be completed in a clean, indoor environment devoid of dust and then transported to the sampling site. Dirt and oils from your skin can affect the Ogawa Sampler if contact is made with the *collection pads* so gloves and/or a sterile pair of tweezers should be used for assembly.

To assemble, remove the Ogawa *Sampler Housing* from the *Sampler Holder* and the *Opaque Vial*. Remove the *Diffuser End Cap* from one side of the *Sampler Housing* and remove the two stainless screens behind the *Diffuser End Cap*. The *Solid Pad* and *Pad Retaining Ring* should be visible inside of the sampler and should not be removed. If they come loose, just insert the *Solid Pad* into the *Sampler Housing* first and then slide the *Pad Retaining Ring* above it to hold it in place.

The *Pre-Coated Collection Pads* will come sealed in a vial and a resealable aluminum envelope. Remove one *Collection Pad* from the vial with the tweezers and place it in between the two *Stainless Screens*. Insert this assembly into the *Sampler Housing* taking care that it sits level on top of the *Retaining Ring*. The fit should be loose. If it feels snug, then remove and try again. Then, snap the *Diffusion End Cap* into place. Repeat this process on the other end of the *Sampler Housing* if two measurements are being conducted. See below.



After assembling the *Sampler Housing*, insert it into the *Sampler Holder* as shown below. The assembled sampler should now be sealed into the *Sample Bag*, removing as much as air as possible to prevent contamination. Place the bag inside the *Opaque Vial* with the *Mounting Bracket*, screw on the lid, and transport to the sampling site. See Below.



At the sampling site, remove the Ogawa Sampler from the *Opaque Vial* and *Sample Bag*. Attach the sampler to clothing for personal exposure or to the *Mounting Bracket* for ambient monitoring as shown below.



The *Mounting Bracket* can be easily attached to objects such as fences and poles with zip ties. If sampling outdoors, the *Opaque Vial* should be used as a shelter. It can easily be slipped over the

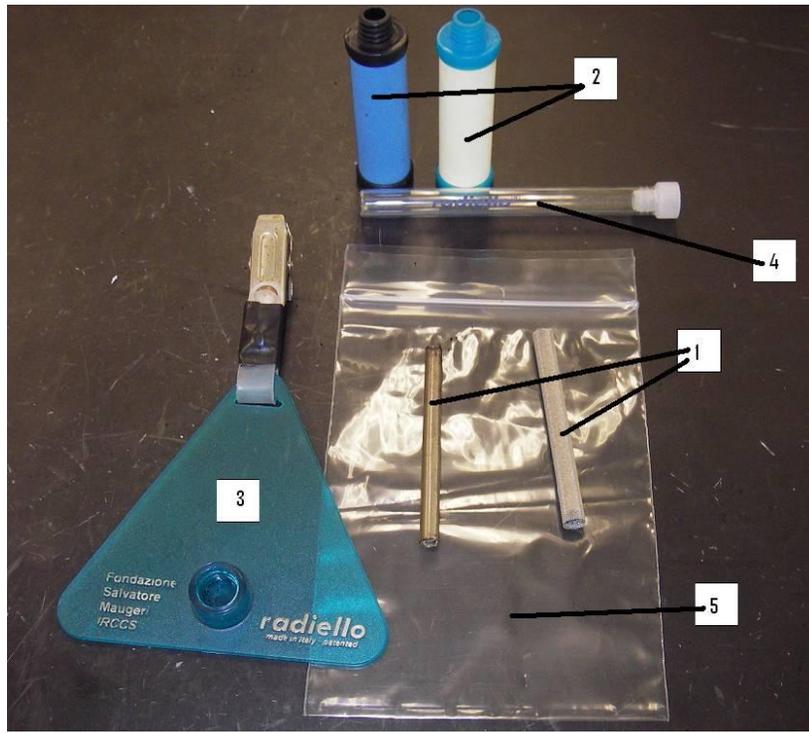
Mounting Bracket and sampler as shown below. Keep the *Opaque Vial* lid and sealed *Sample Bag* for later. Note time and date when sampling begins.



Make sure to note the time and date when sampling ends. After sampling, remove the *Opaque Vial* and sampler from the *Mounting Bracket*. Seal the Ogawa Sampler inside the *Sample Bag* removing as much air as possible and store the *Sample Bag* inside the capped *Opaque Vial*. The Exposed Sampler inside the *Opaque Vial* should be stored in a freezer or in a cooler on blue ice for transportation to a laboratory for analysis.

Appendix C

Standard Operating Procedure for Radiello Passive Monitors



Equipment List - Radiello Passive Sampler

ID #	Description	Quantity
1	Radiello Adsorbing Cartridge	1
2	Diffusive Body	1
3	Supporting Plate	1
4	Glass Vial	1
5	Sample Bag	1

The *Radiello Adsorbing Cartridges* and *Diffusive Bodies* come in a few varieties depending on the application. Specific information on the correct parts for each monitoring application can be found at the company website (www.radiello.com).

Assembly of the Radiello Passive Sampler is simple and should be completed at the location where sampling will take place. Dirt and oils from your skin can affect the Radiello Sampler if contact is made with the porous midsections of the *Diffusive Body* or with the *Adsorbing Cartridge* so gloves should be worn during assembly.

The *Adsorbing Cartridge* will arrive sealed in the *Glass Vial* and may be wrapped in plastic in addition. Remove the plastic wrapper, if necessary, and the cap from the *Glass Vial*. Slide the *Adsorbing Cartridge* into the *Diffusive Body* as shown below. Try to handle the *Diffusive Body* from the hard plastic ends. If the opening of the *Glass Vial* is mated with the opening on the

Diffusive Body, transfer can be made without touching the *Adsorbing Cartridge*. The *Glass Vial* will be used later to store the exposed cartridge so re-cap it to prevent contamination.



Next, screw the *Diffusive Body* into the *Supporting Plate* as shown below. Be careful, to ensure the threads are aligned properly before tightening. The fit should be snug, but do not over-tighten as this can result in breaking the *Supporting Plate* or the *Diffusive body*. Screw the assembly together upside-down to ensure that the *Adsorbing Cartridge* is not protruding from the end of the *Diffusive Body* during tightening.



Assembly of the Radiello Passive Sampler is now complete. Use the metal clip to attach the sampler to clothing for personal exposure monitoring or to another object for ambient

monitoring. If monitoring is being done outside where the sampler may be exposed to rain, care must be taken to attach the sampler under an overhanging feature. Plastic shelters can be fashioned easily from disposable cups or other containers but make sure not to inhibit airflow from reaching the sampler. Note start time and date. See below.



After exposure, note end time and date. Sampler should be taken down by unscrewing the *Diffusive Body* from the *Supporting Plate*. Slide exposed *Adsorbing Cartridge* back into *Glass Vial* by mating the two openings. Recap the *Glass Vial* containing the *Adsorbing Cartridge* and seal it into the *Sample Bag*. Remove as much air as possible from the *Sample Bag* to prevent contamination. Place the *Sample Bag* into a freezer or cooler containing blue ice for transportation to a laboratory for analysis.

Appendix D

Operating procedures for BAAQMD mobile monitoring system

This document describes basic setup and operating procedures for the mobile air quality monitoring system used in the West Oakland Monitoring Study (WOMS) in 2009-2010. The instrument platform is a 2008 Ford E-350 cargo van with raised roof and rear air conditioning modified by E-N-G Mobile Systems, Inc. to include an instrument rack, desk/workbench, calibration gas cylinder rack, and 120VAC and 12VDC power system that can operate off of on-board batteries or line power. The following instruments/measurements are included in the standard setup:

Instrument	Parameters measured
2Btech model 400	NO
2Btech model 202	O3
TEI model 48	CO
ppbRAE 3000	VOC
LiCor	CO2
DRI mini-photoacoustic	BC
TSI model 3007 CPC	Ultrafine particle conc.
TSI DustTrak II model 8530	PM
Garmin GPS-16	Lat, long, elevation, speed, direction
Davis Weather Envoy	T, RH, wind speed, direction

All instruments listed are capable of making real-time measurements of the listed parameters with averaging times as low as 10 seconds.

Ambient air is drawn into the van via an electric fan-driven roof duct into glass or stainless-steel plenum for connecting gas and particle sampling instruments, respectively. The air velocity in the duct can be adjusted via the fan control to minimize anisokinetic sampling effects when making aerosol pollutant measurements while the van is in motion, or if there is a significant cross-wind at a stationary sampling location.

An Environics 6100 gas-diluter/ozone generator connected to cylinders of zero air and a span gas mixture is also included to allow frequent checks of the accuracy of the gaseous pollutant monitors.

Air inlet manifold

There are four ¼” stainless-steel tubes exiting the inlet duct that can be connected to particle sampling instruments via flexible conductive tubing. The connection tubes are curved to avoid impaction losses, and sharp bends in the conductive tubing should be avoided. A ¼” Teflon hose also exits the fan duct and connects to a particle filter cartridge that is followed by a glass plenum with up to 4 connection ports for gaseous pollutant sampling. The output of the gas calibrator should also be attached to this plenum. If additional connections are required it is permissible to install “T” connectors in the lines downstream of the plenum for gas sampling.

Before the start of monitoring each day, check that there are no open ports on either the glass or stainless steel inlet manifolds. Turn on the fan in the inlet duct and adjust to an appropriate setting (12VDC breaker on wall panel must be on). The fan speed should be set to produce air velocity at the intake on the roof that is near the median value of the anticipated ambient wind speed and/or van travel speed. An assistant with a handheld anemometer is recommended for making this adjustment.



Photos of the inlet duct and fan control, stainless steel plenum exiting duct, and glass plenum with particle filter (replaceable paper disk filter is in the orange cartridge).

On-board power system

The on-board power systems are operated from the control panel located on the wall behind the driver's seat:



When operating the equipment with the van connected to an external AC line (aka “shore power”), the toggle switches in the upper left section should be in the ON position, as shown above. If starting up without shore power, flip on AC Circuit switches for inverter, instrument rack, and utility outlets after starting the inverter, as described below.

Before disconnecting from shore power, activate the Inverter by pressing the Enter button on the Xantrex System Control Panel until you see the status screen shown below, then turn on inverter by pressing the ↑ key in the Inverter section so that the soft key label on the LCD screen changes to DsInv. The Inverter On LED should light within a few seconds. *If the Low Battery LED lights and a warning message appears on screen you must continue to charge the batteries or start the engine before disconnecting from shore power.*



INSTRUMENTS

2Btech model 400 Nitric Oxide monitor

Connections:

12VDC power supply must be connected to jack on rear panel of instrument and plugged into 110V power strip on rack.

9-pin RS232 serial cable connected from instrument rear panel to USB port on notebook PC via a serial-USB converter.

¼" Teflon tubing from inlet on rear panel to glass manifold.

Startup:

Press power switch on front panel.

Wait 20 minutes for warm-up cycle to complete, after which display will show NO concentration alternating with flow and ozone supply readings. If logging data to computer the internal datalogging must not be enabled and the averaging time should be set to 10 seconds (default). Otherwise, see instrument manual (pdf file on PC) for internal datalogging and downloading instructions.

2Btech model 202 Ozone monitor

Connections:

12VDC power supply must be connected to jack on rear panel of instrument and plugged into 110V power strip on rack.

9-pin RS232 serial cable connected from rear panel to PC docking station (Com1).

¼" Teflon tubing from inlet on rear panel to glass manifold.

Three voltage inputs for logging analog data output by other instruments are available on the rear of the ozone monitor. Voltages received through these jacks will be recorded and/or transmitted along with ozone concentrations if the ozone monitor is operating.

Startup:

Press power switch on front panel.

If logging data to computer the internal datalogging must not be enabled and the averaging time should be set to 10 seconds (default). Otherwise, see instrument manual (pdf file on PC) for internal datalogging and downloading instructions.

DRI mini-photoacoustic (PA)

Connections:

Universal power cord to 110V outlet.

Conductive tubing (black plastic) from inlet on rear panel to one of the stainless steel manifold tubes exiting from the duct on ceiling.

Flexible mesh-wall tubing from outlet (rear panel) to vacuum pump inlet using quick disconnects.

USB hub connected to front panel USB port.

USB cable to keyboard/touchpad combo or mouse.

Wireless monitor transmitter connected to USB hub. Wireless monitor must be connected to 12VDC power outlet and to receiver via serial cable. Receiver power supply plugged into 110V outlet.

Startup:

Power switch on rear of case On.

Turn computer on by pressing button on front panel (right of monitor). Blue LED will light.

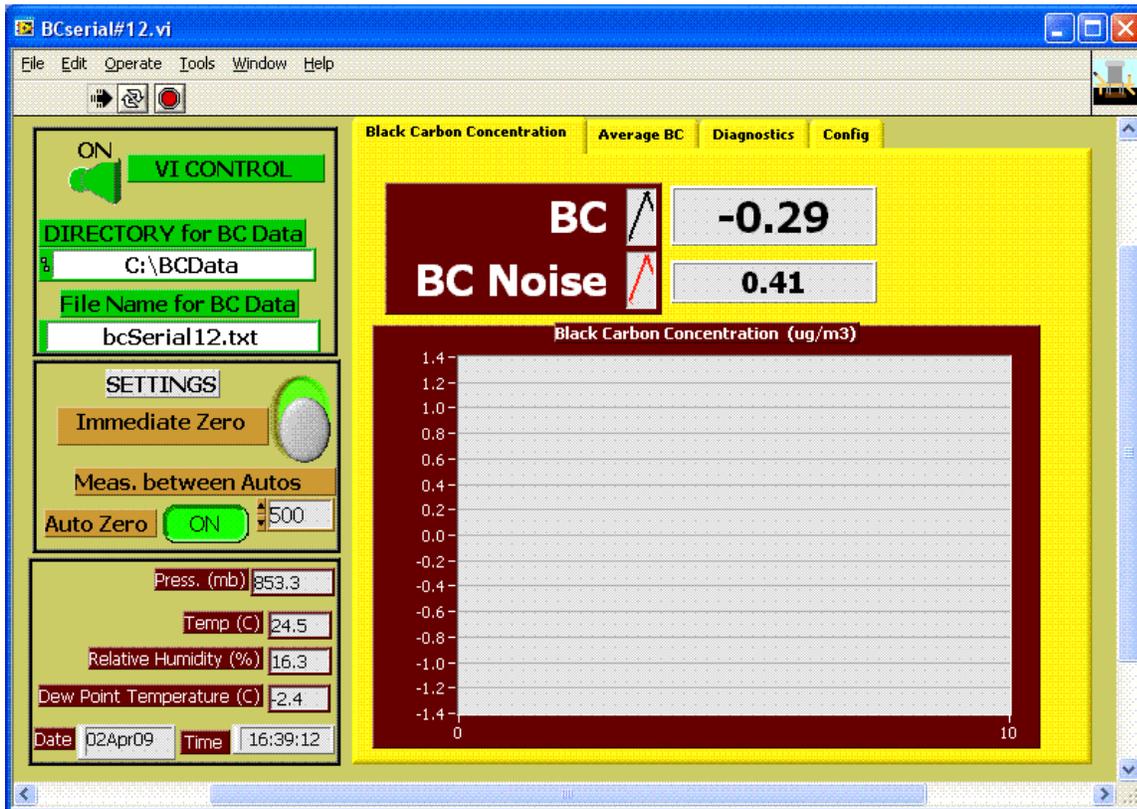
Switch on vacuum pump.

Monitors have power button below screen (should be left on).

LabView application should start up automatically. If not, see PA documentation.

Allow to warm up for at least 30 minutes. Check laser power graph on Diagnostic tab to verify stability before starting data collection.

Once all instruments have completed warmup cycles, go to the “O3 and NO tab” and enable data logging for these instruments. Current values should appear within 10 seconds. Warning: enabling serial data logging when no data is being transmitted by the instruments may cause the program to freeze up.



Initial screen view of photoacoustic instrument LabView program



Diagnostics tab of photoacoustic instrument LabView program. Top graph shows laser power during warmup (not stabilized yet).

Other tabs are included for simultaneous recording of data from other samplers, but are not needed if data is logged to the notebook PC (recommended).

ppbRAE 3000 VOC monitor

connections:

¼" Teflon tubing from inlet probe to glass manifold

For run times greater than 8 hrs, connect 12VDC battery charger to the instrument cradle and plug into 110V outlet. Otherwise, charge the instrument overnight.

USB device cable from jack on left side to USB port on laptop (for downloading stored data).

startup:

press center yellow button and hold until beep. Verify that data is logging (floppy disc icon at bottom of display. Allow 1 minute for warm-up.

DustTrak II aerosol monitor

connections:

Conductive tubing (black plastic) from inlet on rear panel to one of the stainless steel manifold tubes exiting from the duct on ceiling.

For run times greater than 12 hrs, connect 12VDC battery charger to the instrument cradle and plug into 110V outlet. Otherwise, charge the instrument overnight.

(IMPORTANT: the battery only charges while unit is turned on).

USB device cable from jack on left side to USB port on laptop (for downloading stored data).

startup:

press On button above display.

When ready, touch Start on screen. Should start logging data within 1 minute. No warmup needed.

TSI 3007 CPC

connections:

¼" Teflon tubing from inlet to glass manifold.

6VDC power supply, coaxial jack next to inlet.

USB serial cable to laptop for data acquisition.

startup:

Replace the alcohol cartridge with a freshly charged one, if necessary. Cartridges must be refreshed after 5-6 hours of operation.

Press black button to start 10 minute warmup cycle. Warmup can be skipped by pressing the enter key.

Start TSI Aerosol Instrument manager software on laptop. Open new file of type for 3007. When instrument is recognized, press Start to begin data logging.

The logging interval can be adjusted via the Log Mode 1 tab of the dialog box accessed from the Run/Properties menu item. *Make sure the number of samples is set to a large enough value to accommodate the logging interval and run time you wish to use.* Com port assignment and the Instrument Clock can also be changed via the Properties menu.

TEI CO monitor

Connections:

Universal power cable to 110V power strip on back of rack.

Analog output cable to analog input B (stereo mini-plug jack) on back of 2Btech Ozone monitor (data is logged along with ozone data).

¼" Teflon tubing from inlet probe to glass manifold.

Startup:

Press start button on front panel.

Allow to warm up for about 30 minutes prior to data collection. Check rotameter on front panel for stable flow rate (about 0.7 lpm).

If necessary, press Run button until indicator lights under Zero and Span on display are off.



TEI CO analyzer front panel with light indicating instrument is in Span mode circled – this indicator should be off when collecting data.

GPS

Check that GPS USB cable is attached to laptop. Start ‘Spanner’ program from desktop icon. It should indicate that a Garmin GPS-18 is recognized. If not, try reconnecting USB cable, and/or rebooting. Once Spanner is running, data may be logged via various applications that read NMEA standard data streams. A Hyperterm shortcut named ‘Garmin GPS.ht’ on desktop can be used to view the raw data and verify the Com port number.

PC data logger

Serial data streams from the 2Btech NO and ozone monitors can be logged along with GPS data on the notebook PC using the DAQfactory application. Data are logged as running 10 second averages to an Excel readable file stored in the C:\data folder. The program automatically creates a file with the name DAQraw_yymmdd.xls and continuously appends data to that file whenever data logging is enabled.

To begin logging data:

1. if GPS data is desired, first run the Spanner application from the desktop icon.
2. run DAQfactory from the desktop icon labeled “datalogger”.
3. verify that current values from all operating instruments are displayed in the application window and the UTC time from the GPS is advancing (*PM data are indicated on the application front panel, but at present the continuous data output features of the DustTrak are not available due to a design flaw*)

- a. if serial data from the ozone monitor are not being received via Com port 1, you may need to reboot the PC after confirming that the ozone monitor is operating and properly connected.
4. the application should immediately begin logging data. You can suspend logging by clicking on the button labeled “Datalogging ON/OFF”. Current values will still be displayed while datalogging is suspended.
5. it is recommended that you periodically check to confirm that current values for all operating instruments are displayed by the application.

If additional instruments are connected or data cable connections are changed it may be necessary to update the comm. port assignments using the ‘Quick’ menu ‘Device Configuration’ feature of the application (see documentation for details).

Meteorology Package

If met data is desired during operation, the wireless sensor package should be deployed to a suitable location. Plug in the power supply for the met station console/receiver. Confirm communication with the sensor package by moving the wind vane and observing the wind rose on the display. The sensor package should then be mounted on the tripod with the arm of the anemometer pointing due North. Data from the station can be downloaded and/or viewed in real time by connecting the console to a USB port on the laptop and running the WeatherLink software (if installed).



Wireless met station console.

Synchronizing clocks:

Should be done before the start of data collection each day if 10 second average data is being collected. For longer averages, weekly synchronization may be adequate.

Adjust Windows system time on notebook PC to current time (GPS or cell phone are good reference time sources). This system time will be recorded with each data point by the datalogging software.

Adjust Windows system time on PA computer to match laptop (you can do this while the LabView program is running, but it may result in duplicate time signatures in the data logs if you adjust to an earlier time). This will sync all data being logged together (BC, NO, O3, and CO).

For DustTrak, set time via the Setup menu, which is only accessible when sampling is stopped.

For CPC, sync internal clock to laptop when starting AIM software

For ppbRAE, press N/- twice to see system time and date. If needed, sync internal clock by accessing the instrument configuration using ProRAE Suite software on the laptop (see data retrieval instructions).

Data Retrieval

The ppbRAE 3000 does not allow real-time data acquisition, so data from the internal logs must be downloaded. To download:

1. start the ProRAE Suite software on the laptop
2. press the N/- button on the instrument repeatedly until the “Enter PC comm” message appears, then press Y/+
3. select “Receive Data” from software menu and follow prompts
4. to backup data files to laptop, select a test data set on screen and use the “Options\export” menu item.

DustTrak internal data logs can be retrieved using TSI TrakPro software on the laptop. Stop the instrument (but don't turn off), then start the program. The software should detect the instrument if it is connected to a USB port. Click the Retrieve Data button  on the toolbar and follow instructions to download. Data can be backed up to Excel-readable files via the File/Export menu item.

PA data files can be copied from the C:\BCdata directory on the PA computer. This can be done while the LabView program is running or stopped. Two text files in a date-named folder are created each day. One contains complete ‘raw’ data (recorded about every 2 seconds) with lots of diagnostics, and the other contains 1 minute averages and selected BC diagnostics.

Shut down

At the end of data collection:

Switch off the pump for the PA. Stop the PA LabView program by clicking on the green On/Off switch on the left side of the application window. The program should stop after a few seconds. The computer can be shut down via the normal Windows method after data is copied.

Stop the data acquisition program on the PC.

Click the stop button of the AIM application on the laptop to cease acquiring CPC data. After downloading data, press and hold the center yellow button on the ppbRAE for 5 extremely loud beeps until shutdown occurs.

Press the Stop button on the DustTrak screen. Power off by pressing the button above the screen (*this will prevent battery charging and data retrieval*).

Press the black power button on the CPC to shut down. If the instrument will not be used again that day, remove the alcohol cartridge and place it in a recharging tube. Plug the instrument chamber with the cap from the tube.

The 2Btech instruments and TEI CO can be switched off at any time, but if a span check or calibration is planned it may be advisable to leave them running to avoid additional warm-up time.

After backing up all data, close all applications on the laptop and shut down.

Turn off all AC and DC circuits, except Shore Power, via switches on left side of control panel.

If system will be used again soon: Connect van to shore power, if available. Switch the inverter Off from the System Control Panel (press DsInv button). Check that the green AC In/Charge LED is lit (if not, press the EnChg button).

If system will not be used for an extended period: Switch off inverter on control panel. Check battery voltage on display. If fully charged (>12 V), turn off charger with DsChg button on control panel. Otherwise, allow to charge (deep-cycle batteries may be damaged if left in a discharged state for extended periods).

Calibration checks

Periodic zero and span checks are required to ensure the accuracy of the measurements. If time permits, checks should be done prior to and immediately after each period of data collection.

NO and CO can be checked using compressed zero air and a certified gas standard. A gas dilution system like the Environics 6100 will produce known concentrations of the target gases at concentrations ranging from zero to the upper limit of the range of anticipated ambient

concentrations (i.e., the span value). See the manufacturer's instructions for the required line pressures and calculation of dilution settings. If the gas mixer is already set-up with zero air and span gas blend, the procedure is as follows:

- warm up calibrator for at least 30 minutes
- open cylinder valves and adjust pressure to approx. 25 psi.
- select concentration mode (press button under CONC on screen)
- if desired gas is not displayed, press GAS to display a list, move cursor, then press SELECT.
- enter desired span gas and/or ozone concentration and total flow rate (should be greater than combined flow to all running instruments)
- press START
- if using a gas blend, press VIEW to see concentrations of all components
- when instrument readings have stabilized (may take several minutes), record if additional span concentrations are desired, press EDIT, change values, then UPDATE
- when finished, press STOP and close all gas cylinder valves.

With all instruments fully warmed up, zero air should be introduced to the glass inlet manifold at a flow rate in excess of the total intake flows of all instruments connected to the manifold. Wait until readings appear to be stable¹ and record the average value over a period of 5 minutes. If the average reading differs significantly from zero, adjust the offset value via the instrument's setup menu (see manual). Once the zero has been checked and adjusted, introduce gas at the span value concentration and record the average². If desired, the displayed span readings may be adjusted, however significant variations generally indicate some sort of malfunction.

The zero value of the ppBRAE 3000 VOC monitor may also be checked and adjusted during this process. An automated zero adjustment can be made via the setup menu. For maximum low end sensitivity, zeroing with an activated carbon filter tube on the inlet is recommended (see manual for instructions). Span adjustment is also possible, but is of limited value since the response of the PID varies substantially with organic pollutant composition.

The zero reading of the DustTrak aerosol monitor should be checked by attaching a particle filter to the inlet, recording the low reading, then running the automated zeroing cycle. The photoacoustic instrument automatically adjusts the zero value at regular intervals during data collection, but an occasional check with a particle filter on the inlet is still recommended. An inlet filter should also be connected to the CPC periodically, and the reading noted if it is greater than zero. Generation of known concentrations of aerosol particles is beyond the scope of field operations, so no span checks are possible.

¹ *Since the NO monitor measures the difference in ozone concentration before and after titration by ambient NO, the readings at concentrations below 20 ppb are subject to a relatively large amount of electronic noise making them very unstable.*

² Application of extremely low humidity (compressed) air to the 2BTech NO monitor will result in erroneous readings. Span gas should be humidified using a 24" length of Naphion tubing attached to the inlet during calibration checks.

Maintenance

Inlet filters are used on all gas monitors to remove moisture and particles from the incoming air. This is particularly important for the NO monitor. The line filter installed between the ceiling duct and the glass manifold should be inspected periodically and the replaced if dirty or clogged. The frequency will depend on the concentration and nature of aerosols as well as ambient humidity. Operating in extremely dusty conditions such as on unpaved roads or in areas with high concentrations of combustion aerosols will require more frequent filter changes.

The ppbRAE and DustTrak have internal filters that should be checked and replaced periodically. See the manuals for details.

Although the concentrations reported by the continuous monitoring instruments are not a function of the air flow rate, the inlet flows should be checked periodically with a reference meter to assure that they are within the specified range. Significant variations in flow rate are usually symptomatic of internal leaks or pump failure. The entire inlet system should also be checked for leaks by comparing the total flow at the inlet manifold to the sum of the individual instrument flows.

Although all instruments can be operated on line power, it may be desirable at times to reduce power use by running on internal batteries. The batteries also provide backup in the event of a power outage. The DustTrak and ppbRAE have rechargeable internal batteries, but the CPC and weather station use replaceable alkaline or externally rechargeable NIMH batteries.