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

Prepared for:

Bay Area Air Quality Management District

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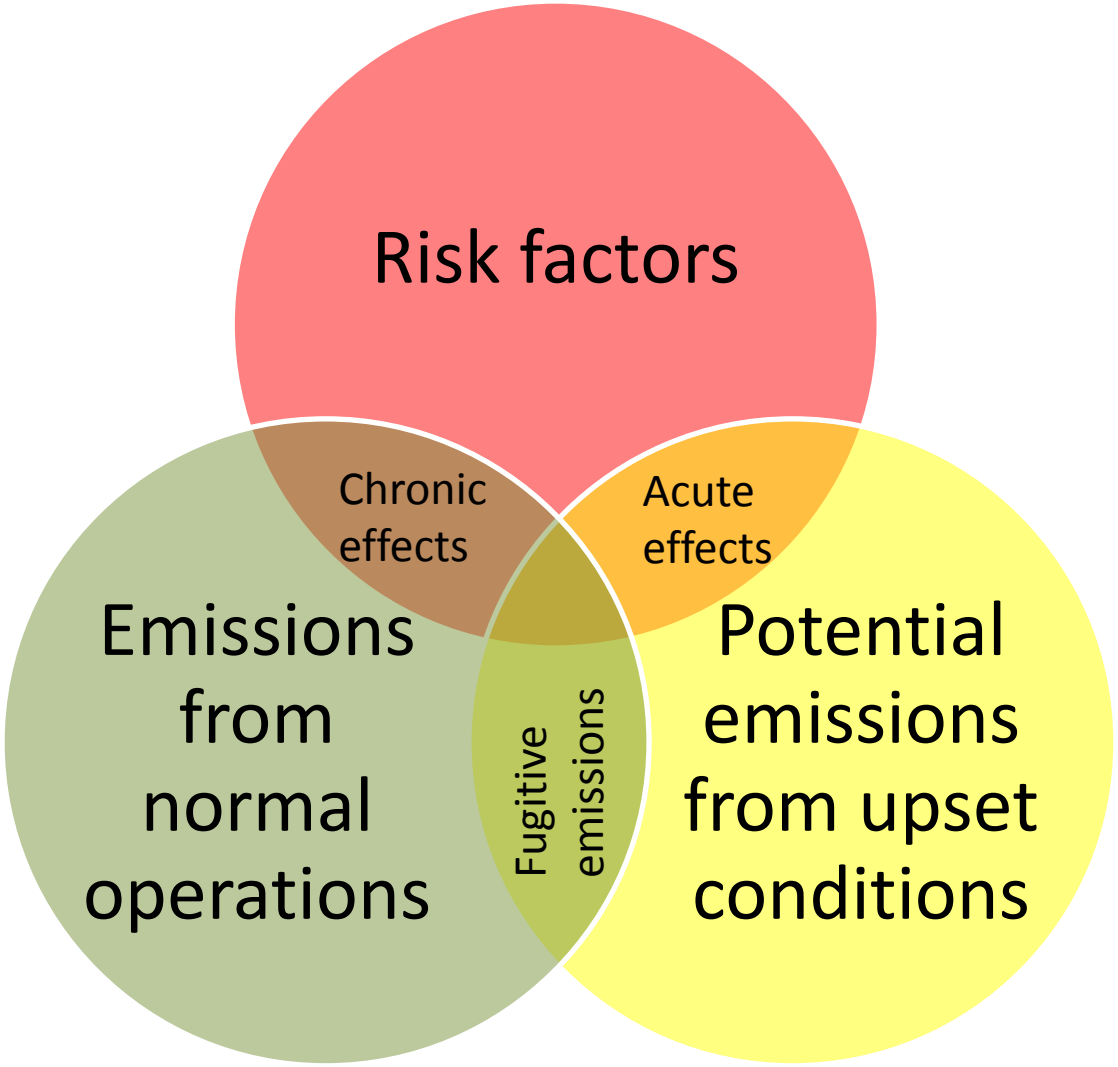
Objectives

- Identify the primary risk drivers
- Review and evaluate current air monitoring capabilities.
- Develop a matrix of instrumentation, methodologies and/or other exposure assessment tools to:
  - enhance monitoring capabilities
  - provide information about emissions
- Prepare a short report describing the process used and how the matrix was developed.

Identifying primary risk drivers



Target compounds, RELs, and monitoring methods

			Continuous						Time-integrated Samping				
	Risk Exposure Levels (REL) [2]		Point			Open Path 500m	OpenPath 100m	Area	Time-integrated Point sample (up to 24 hrs)			Saturation Monitoring (7-day)	
Target Compound	Acute (µg/m3)	Chronic (µg/m3)	Photo-metric	Auto-GC	XRF tape sampler [6]	UV-DOAS	OP-FTIR [7]	DIAL	Canister	Chemically active adsorbent	FRM filter sampler	Passive	5 lpm filter sampler
Benzene	1300	60		0.03		3	50	3	0.06			0.3	
1,3 Butadiene		20		0.02		1	10		0.04			0.03	
Formaldehyde	55	9				10	10			8 µg/m^3 h		0.15	
Acetaldehyde	470	140				20				6 µg/m^3 h		0.05	
Perchloro-ethylene	20000	35					40					0.02	
Napthalene		9		0.05		2						?	
NO_2	470	100 [3]	0.2			2		25				0.16	
SO_2	660		0.8			2	10	25				1.5	
H_2S	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			0.0002						0.66 µg/m^3 h		0.0008
As	0.2	0.015			0.0001						0.35 µg/m^3 h		0.001

Current air monitoring capabilities

- Current Air District network consists of 32 locations with 136 instruments
  - 20 staff in Air Monitoring with greater than $3 million in annual operations and maintenance budget
  - 5 dedicated Quality Assurance staff and 7 laboratory staff support air monitoring activities

Existing air quality monitoring was designed to determine neighborhood or other EPA-defined spatial scale concentration average and range of concentrations for criteria pollutants (O_3, SO_2, NO_2, CO, PM_{10}, $PM_{2.5}$) and certain high-priority toxics (benzene, toluene, ethylbenzene, xylenes, 1,3-butadiene, formaldehyde).

“Traditional” methods: Fixed-site Community Monitoring

Other monitoring activities

Refineries are currently required to measure H_2S and/or SO_2 at their fence lines:

- Enforcement action can be taken on measurements
- Sites are audited and data reviewed by the Air District
- Additional pollutants can be monitored simultaneously

US EPA is moving to more source oriented monitoring

- NO_2/CO/PM near roadway monitoring now required
- SO_2 monitoring may be required near sources, depending on emissions and population
- Lead monitoring required at sources emitting more than 0.5 tons per year

Fenceline monitoring

Phillips 66 Rodeo Refinery - Fenceline Data

Ambient air quality data provided on the Phillips 66 Rodeo Refinery website is raw data at the time of collection – unchecked data that may contain errors.

Message Board

06/12/2013 10:11 - The calibration of the Organic Gas Detectors is complete. The systems are now back on-line.

Document Download Center | Message Archive

FTIR Systems

Chemical (values in PPB)	South Fence Line	North Fence Line
System Status	Online	Online
System Type	IMACC	MIDAC
Data Date	2013-06-17	2013-06-17
Data Time	15:17:49	15:10:58
1,3 Butadiene	ND	ND
Carbonyl Sulfide	ND	ND
Total Hydrocarbons	ND	614.5
Carbon Monoxide	90	45.6
Ethanol	ND	ND
Ethylene	ND	ND
Nitrous Oxide	326.29	290.67
Ammonia (NH3)	ND	ND
Mercaptan	ND	ND
Methane	1836.22	1260.4
MTBE	ND	ND

UV Systems

Chemical (values in PPB)	South Fence Line	North Fence Line
System Status	Online	Online
Signal Strength	2171	1877
Data Date	2013-06-17	2013-06-17
Data Time	15:17:49	15:18:31
Benzene	ND	ND
Carbon Disulfide	ND	ND
Ozone	ND	27.645
Sulfur Dioxide	ND	ND
Toluene	ND	ND
Xylene	ND	ND

TDLs

System Status	Online	Online
Data Date	2013-06-17	2013-06-17
Data Time	15:19:26	15:16:08
Signal Strength	6779	4890
H2S	ND	ND

Organic Gas Detectors

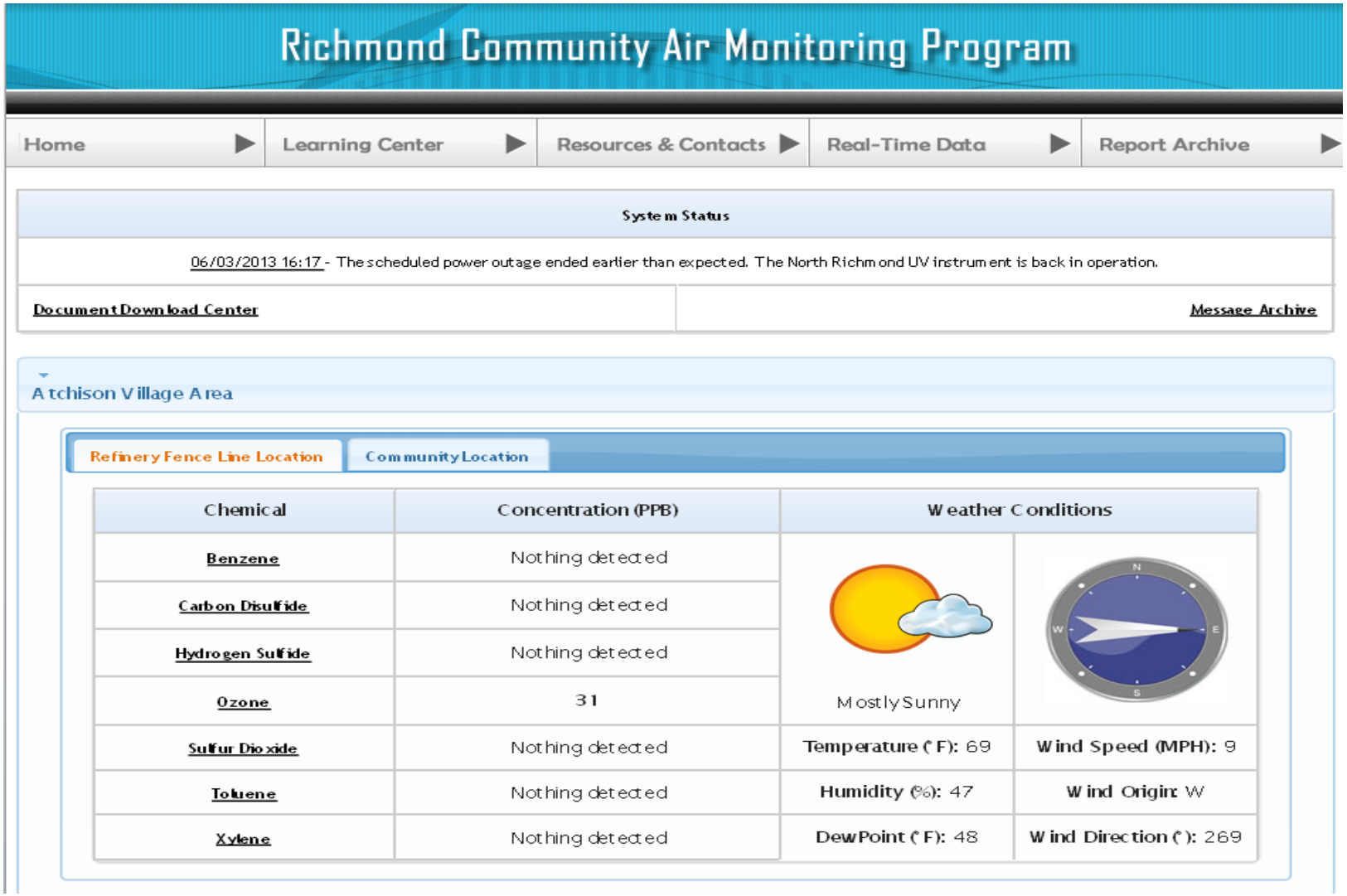
Instrument (values in %LEL)	Value
System Status	Online
Data Date	2013-06-17
Data Time	15:19:50
AT-1	0
AT-2	0
AT-3	0
AT-4	0
AT-5	0
AT-6	0

Weather Conditions

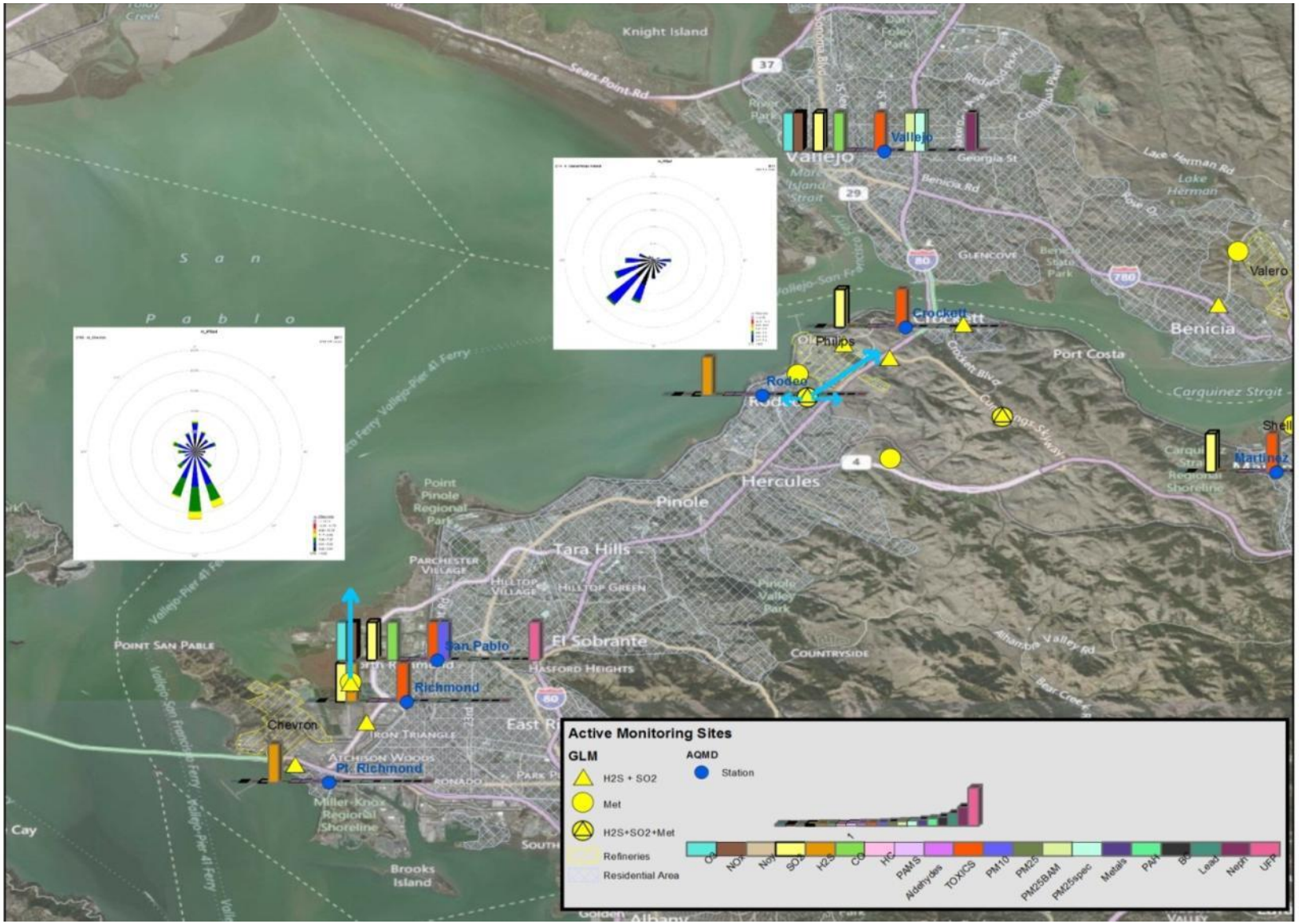
System Status	Online
Date	2013-06-17
Time	15:16:39
Temperature (°F)	71.9
Humidity (%)	54
Dew Point (°F)	54
Wind Speed (MPH)	13

Wind direction from West-Northwest - 283°

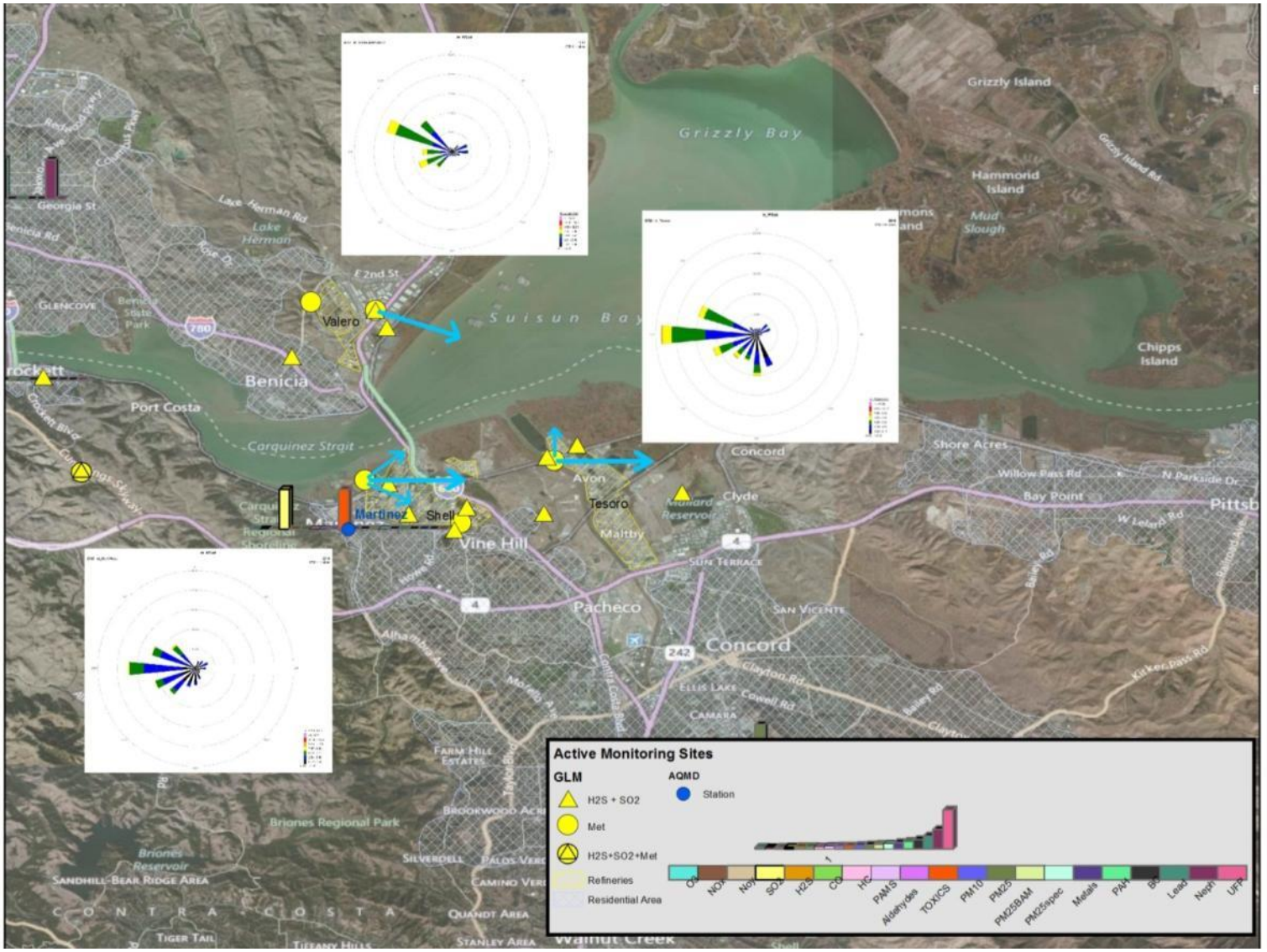
Public access to fenceline monitoring



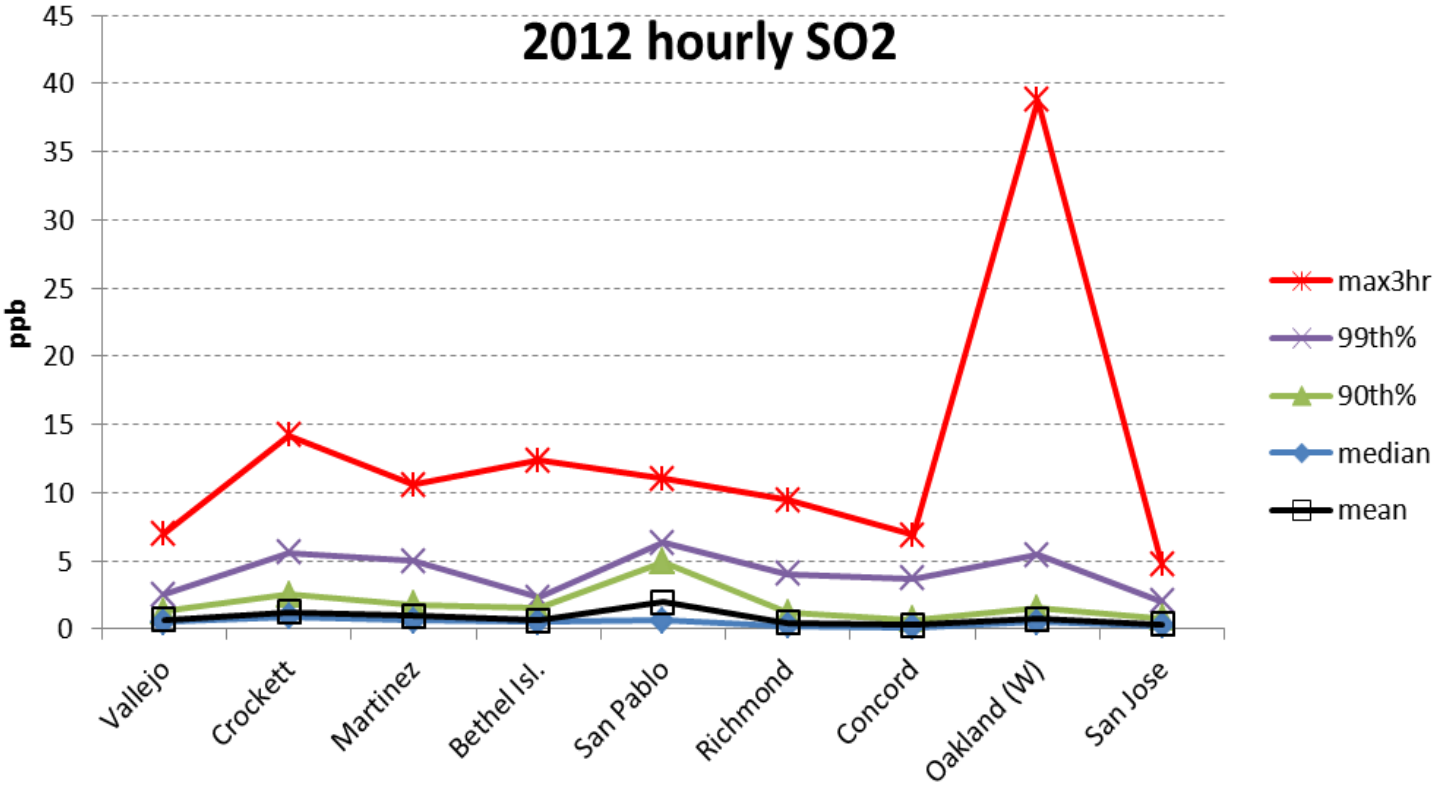
Existing air monitoring with prevailing wind directions (West side)



Existing air monitoring with prevailing wind directions (East side)



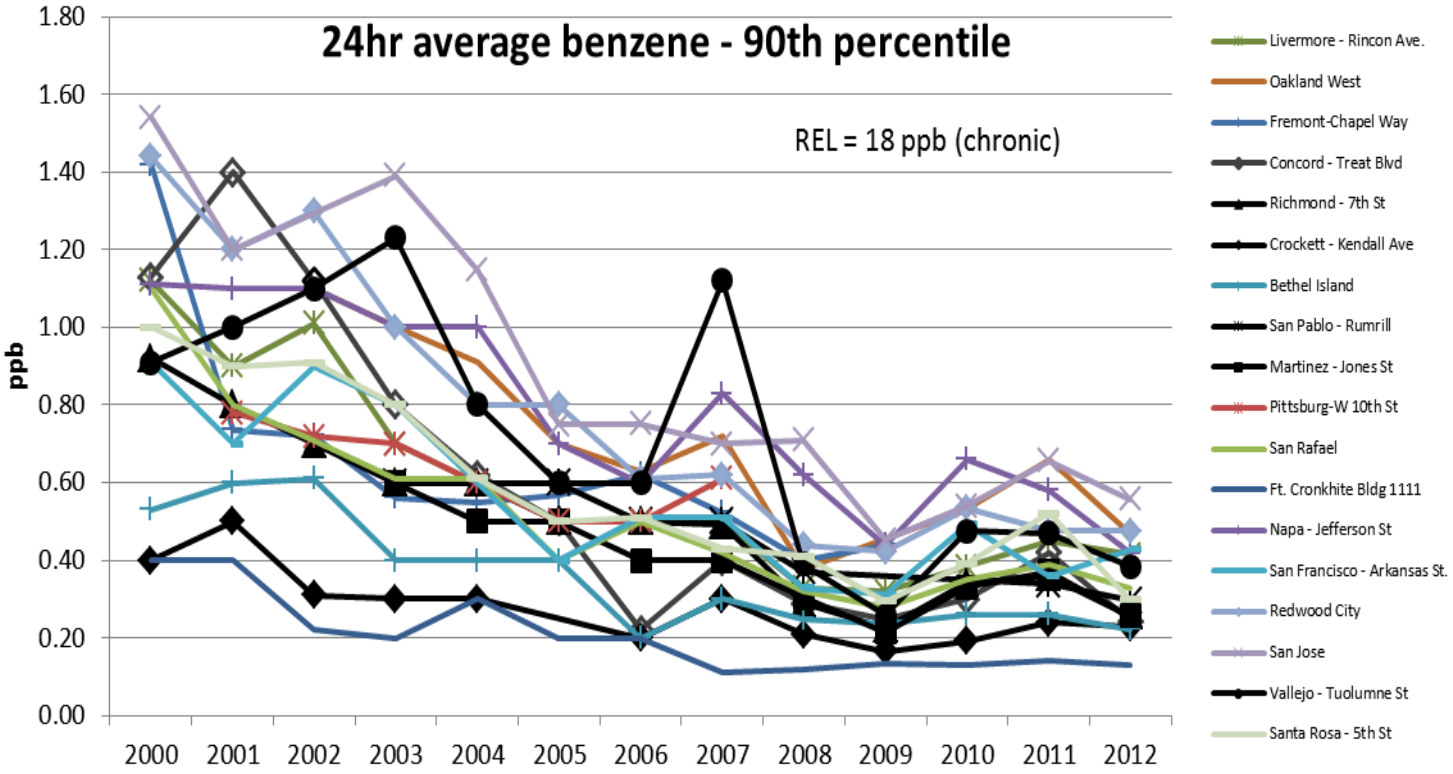
SO_2 monitoring shows concentrations well below standards at area community monitors



Primary NAAQS = 75 ppb (99th percentile)

Secondary NAAQS = 500 ppb (maximum 3hr average)

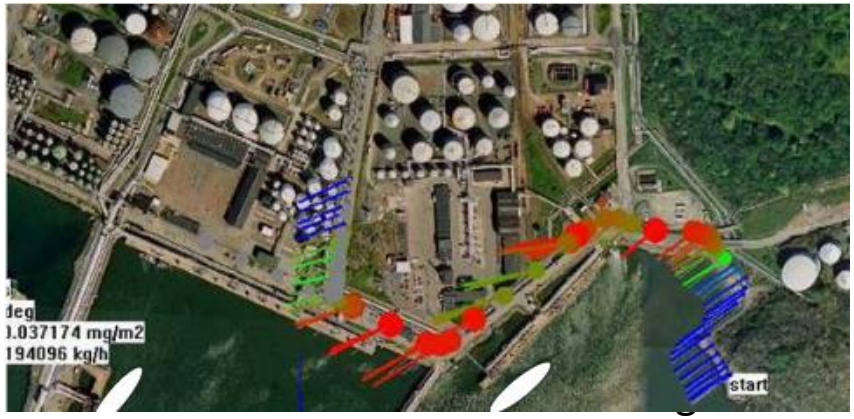
Current air toxics monitoring does not show elevated concentrations near refineries, but may not capture incidental peaks.



Instrumentation, methodologies and/or other exposure assessment tools

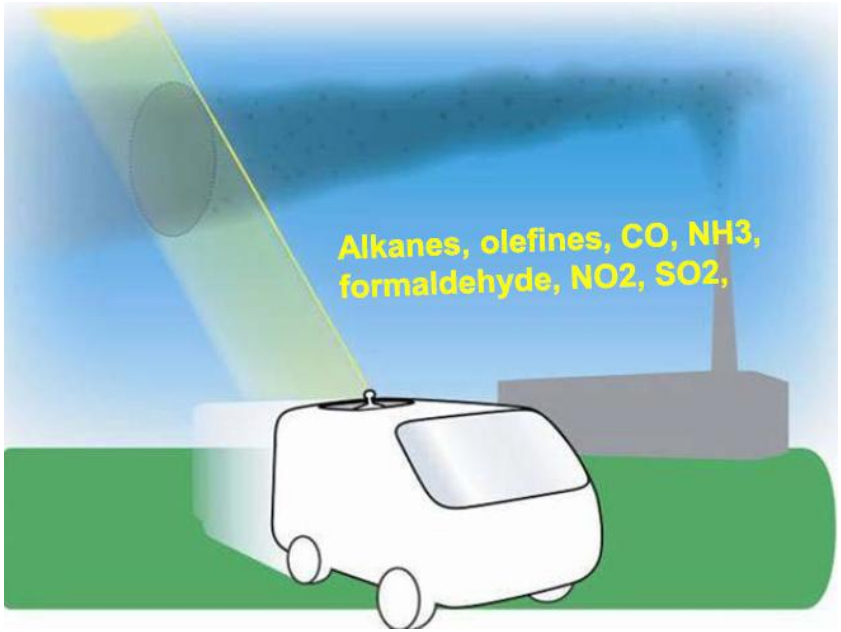
- Monitoring Approaches
  - Emission Flux Measurements
    - Quantitative estimates of routine refinery emissions
  - Emission Plume Characterization
    - Identify location of plumes and leaks
  - Community Air Monitoring
    - Continuous Monitors
      - Fixed-site Gas Analyzers (high sensitivity, good speciation)
      - Open-Path Gas Monitors (lower sensitivity and specificity)
      - PM Mass Monitors
    - Time-Integrated Speciation Sampling and Analysis
      - Active (PM or gas) or passive (gas)
      - short (≤ 24 hours)or long (up to 14 days) term

Emission Flux Measurements and Plume Characterization

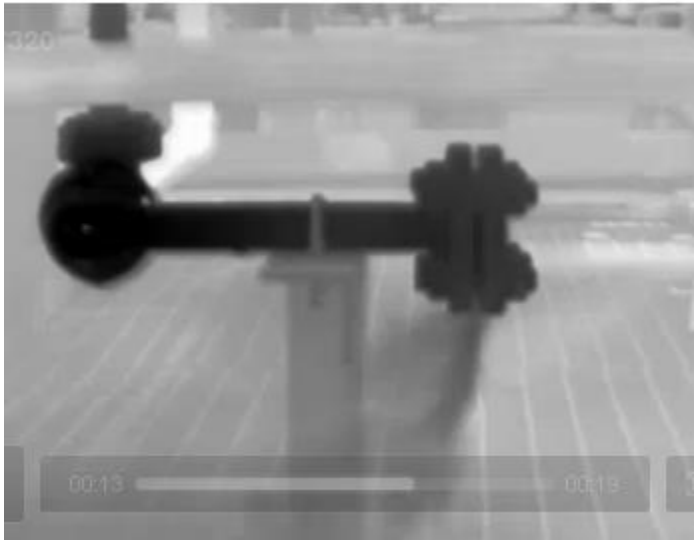


Solar Occultation or Differential LIDAR

IR video cameras can locate plume source and leaks



EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux



www.flir.com

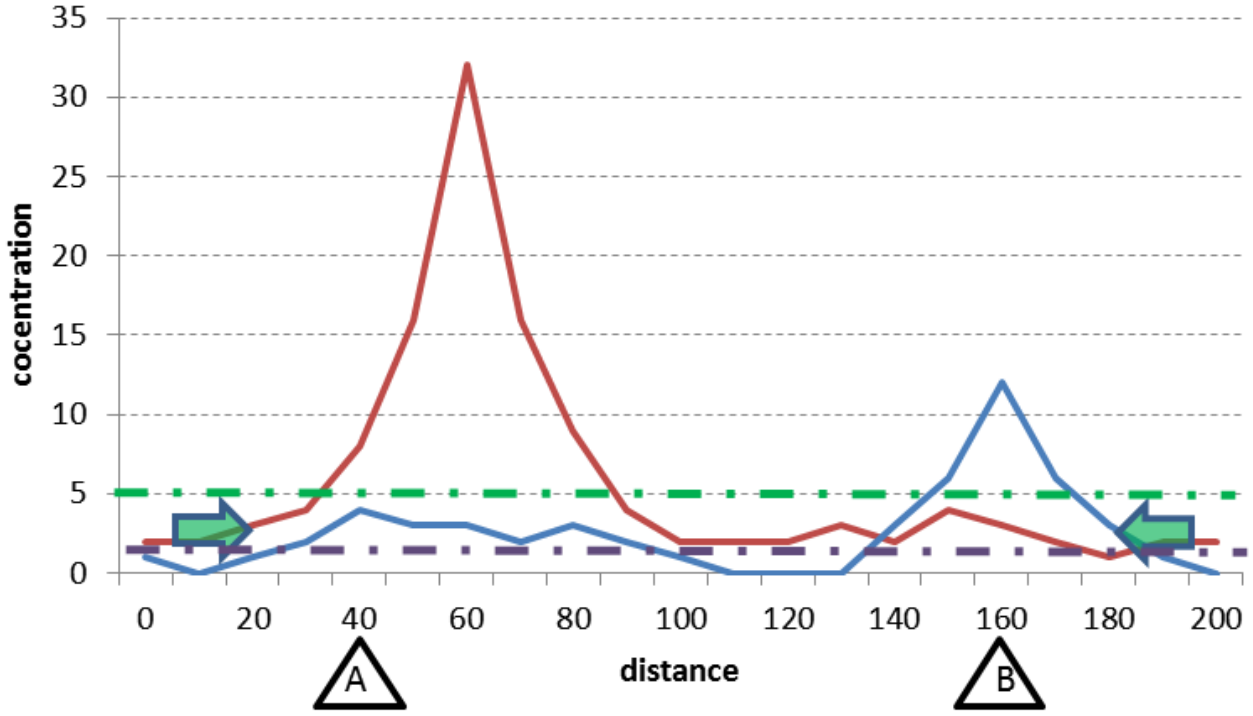
Continuous PM monitors

Continuous Monitors	Targets	MDL (1 hr)	Min Averaging Time	Unit Cost	Environment	features/limitations
Beta-attenuation tape sampler	PM2.5	2 - 10 ug/m3	1 hr	$15 -20k	Indoor	Federal Equivalent Method for PM10 and PM2.5. Options for low-density Teflon tape and integral nephelometer for higher time-resolution.
TEOM	PM2.5	<5 ug/m3	10 min	$ 30,000	Indoor	Federal Equivalent Method for PM10 and PM2.5 / possible interference from ΔRH
auto-XRF tape sampler	Elements K - Pb	<0.5 ng/m3	15 min	$ 250,000	Climate-Controlled	unique capability / high cost and unknown reliability
Aethalometer	BC	0.1 ug/m3	5 min	$ 20,000	Climate-Controlled	high sensitivity but non-linear response at high conc.
Photo-Acoustic Soot Spectrometer	BC, PM2.5	<0.5 ug/m3	2 sec	$ 30,000	Climate-Controlled	absorption and light scattering
CPC	UFP	N/A	10 sec	$ 10,000	Climate-Controlled	high sensitivity and time resolution, but no clear relationship between UFP and other pollutants or health effects

Continuous methods for monitoring gaseous pollutants

Continuous Monitors	Targets	MDL (1 hr)	Min Averaging Time	Unit Cost	Environment	features/limitations
NO/NOx analyzer	NO, NO2, NOx	<0.4 ppb	10 sec	$ 12,000	Climate-Controlled	Federal reference method / NOx produced by all types of fuel combustion
CO analyzer	CO	40 ppb	10 sec	$ 11,000	Climate-Controlled	Federal reference method / CO primarily from motor vehicles
SO2 analyzer	SO2 or H2S or total S	<0.5 ppb	10 sec	$ 11,000	Climate-Controlled	Federal reference method, most relevant criteria pollutant to refinery emissions
Auto-GC	Speciated VOC <C13	<0.5 ppb (BTEX)	3 to 60 min	$30 - 60k	Climate-Controlled	VOC speciation with high sensitivity and specificity / complex data interpretation
UV-DOAS	NO2, SO2, H2S, select VOC	<1 - 10 ppb	<10 sec	$60,000 - 200,000	Outdoor	good for detection of releases / does not easily translate to community exposure
OP-FTIR	SO2, CO, select VOC	5 - 100 ppb	<10 sec	$80,000 - 125,000	Outdoor	good for detection of releases / does not easily translate to community exposure

Hypothetical comparison of reported concentrations from Fixed-site and Open-path continuous monitors



Open Path: 6.2 ppm
Open Path: below LOD

Fixed site A: 8 ppm
Fixed site A: 4 ppm

Fixed site B: 3 ppm
Fixed site B: 12 ppm

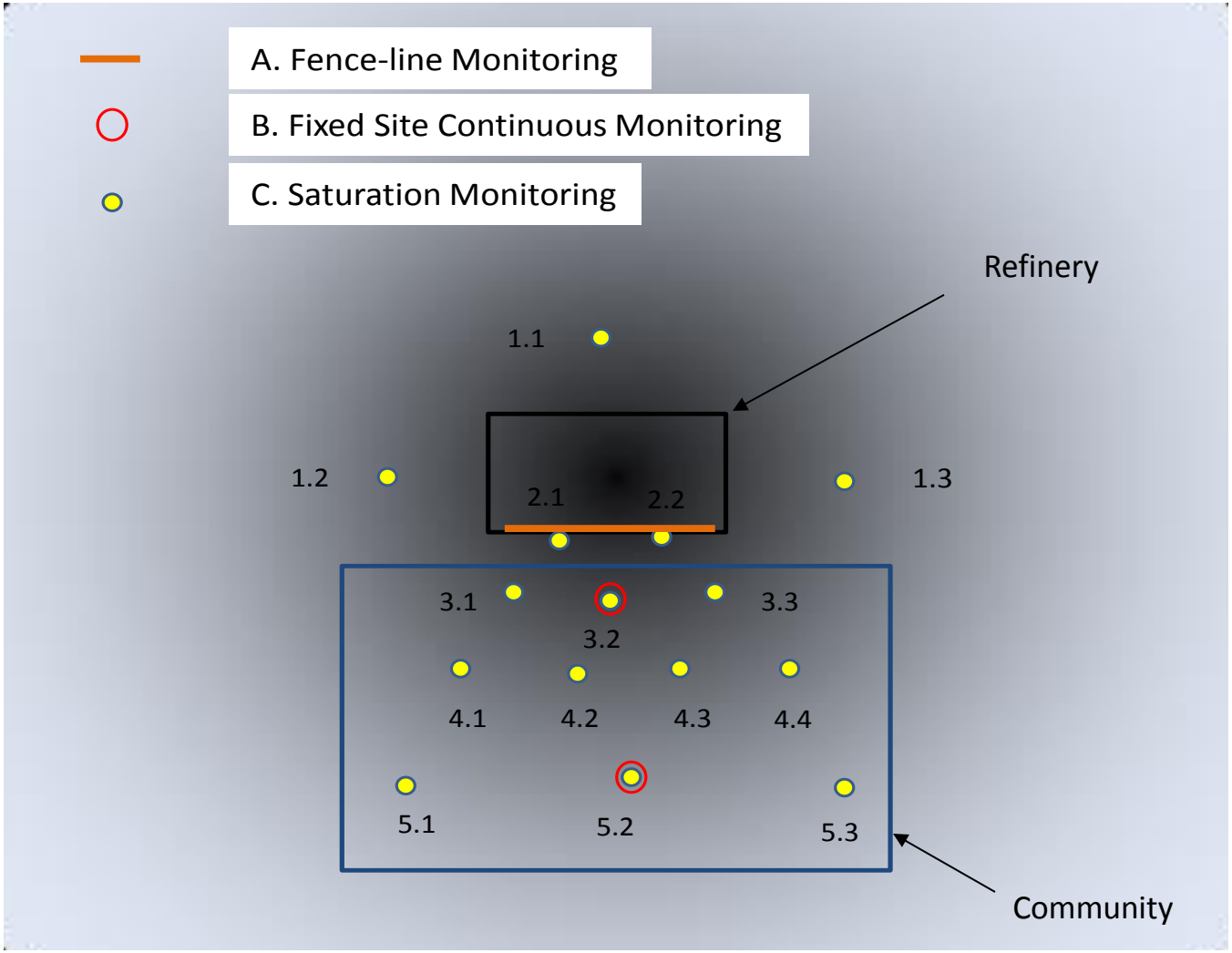
Problem:

- Open-path ‘fenceline’ monitors can detect peaks in emissions, but do not provide quantitative exposure concentrations
- Fixed site continuous monitors can accurately measure ambient concentrations, but these may not reflect higher levels at other locations

Solution:

- A dense array of low cost, portable samplers can be used to determine how well fixed-site continuous monitoring represents ambient concentrations in other locations throughout a community.

Conceptual Illustration of Community Saturation Monitoring Program Near a Refinery



Samplers for Saturation Monitoring

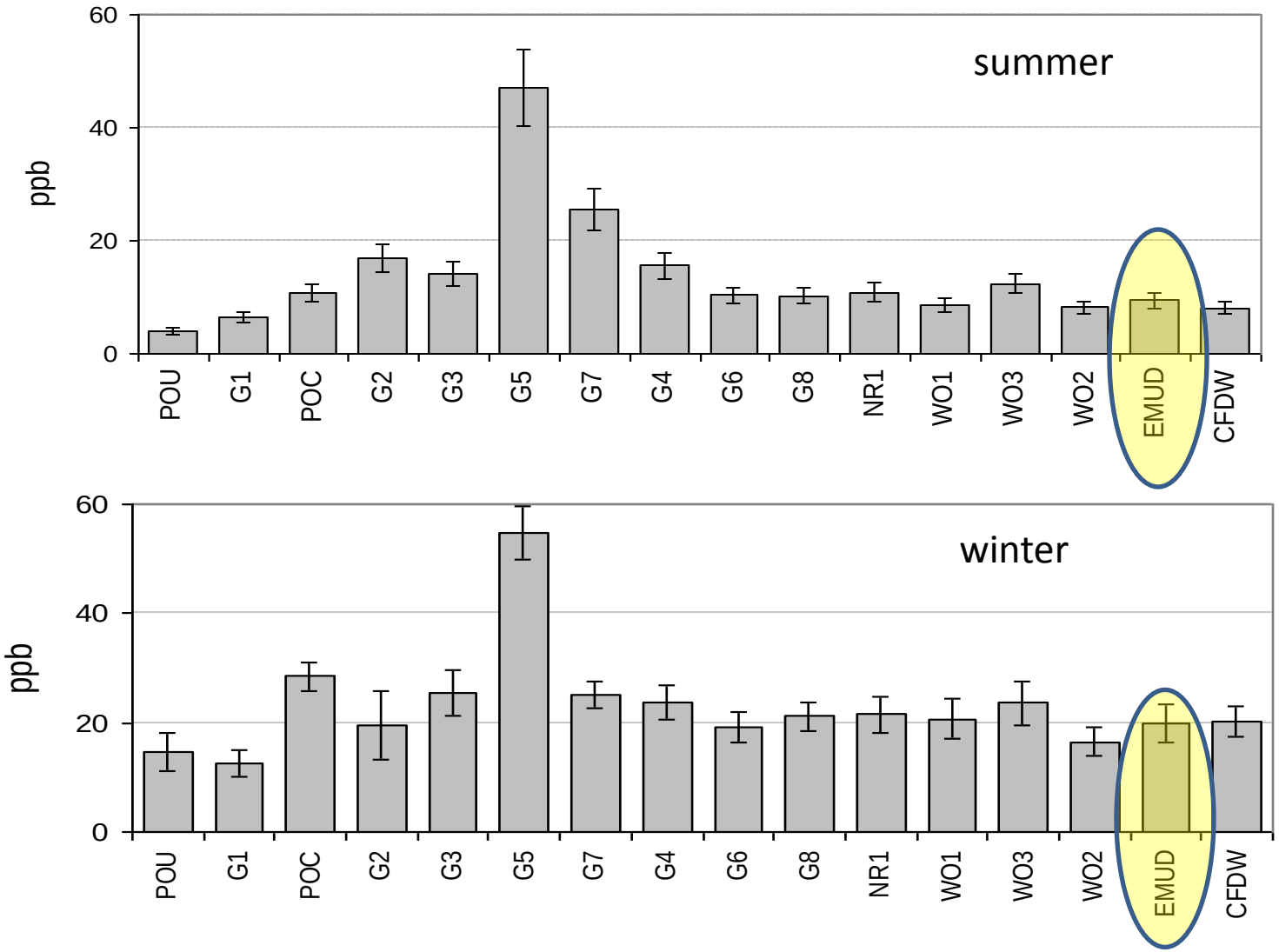
AirMetrics Minivol Aerosol Sampler
(10” diameter x 24” tall)
12V battery or 110VAC

Ogawa passive samplers
for NO_2/NOx and SO_2
(thumb size in cup shield)

Radiello passive samplers for VOC, aldehydes and H_2S
(size of a roll of pennies)

West Oakland Monitoring Study (WOMS)

Seasonal Average NO Concentrations



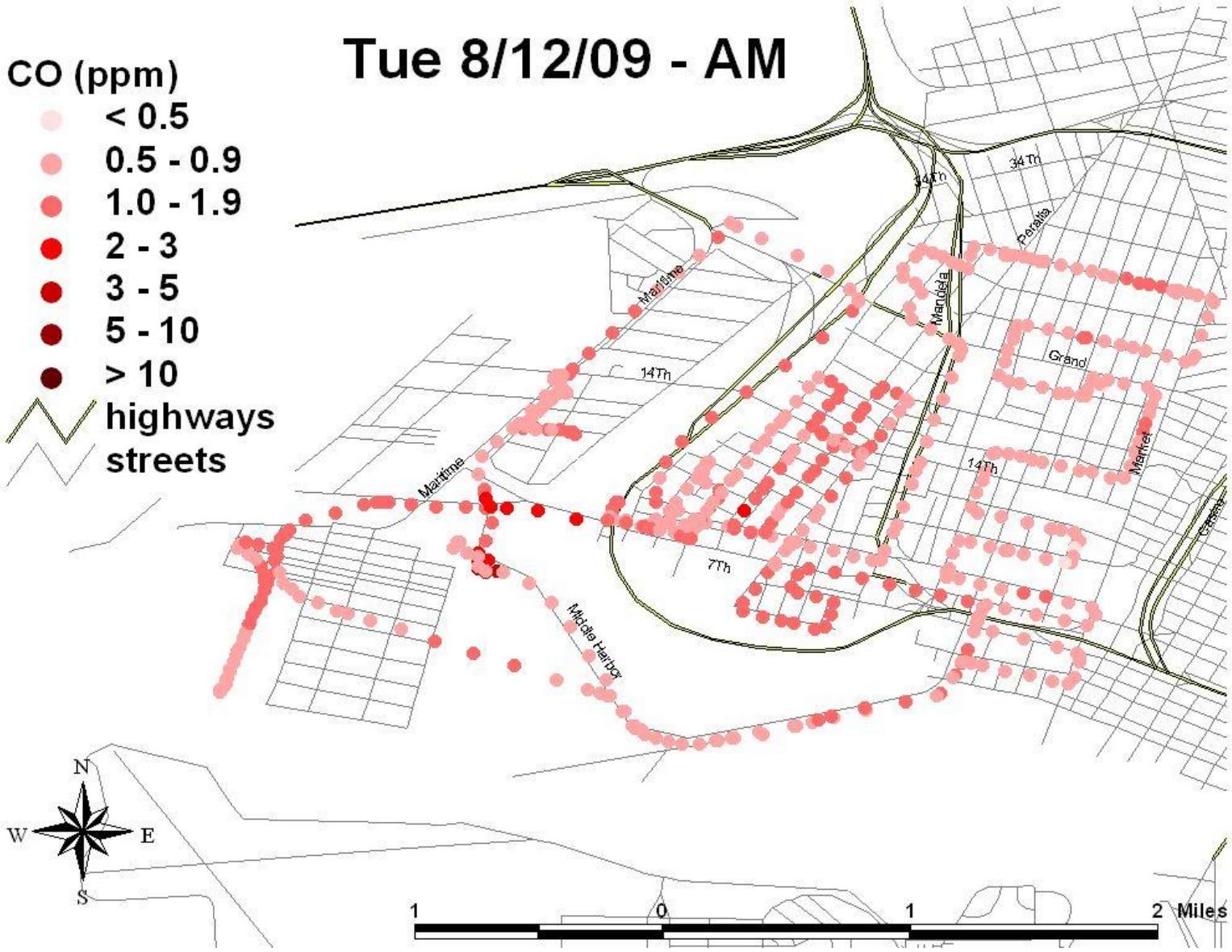
West Oakland Monitoring Study

Incident Monitoring

- Dispersion modeling
  - Predict areas that will experience maximum concentrations for different types of release and weather conditions
- Mobile Sampling
  - BAAQMD and/or EPA Mobile Monitoring Vans can be used to determine areas most impacted and monitor levels
- Emerging Technology and Cooperative Approaches
  - highly portable, low cost monitors have potential to make large scale saturation monitoring affordable
  - involve community volunteers for increased spatial coverage during incidents

BAAQMD Mobile Monitoring Platform

Community Survey using Mobile Monitoring



Summary of Recommendations

- Verify type, location, and quantity of emissions using remote sensing flux methods
  - Work with refinery operators to gather this information
- Track variations in emissions via fenceline monitoring
  - Program already active
- Determine spatial variations in concentrations within communities using mobile and saturation monitoring projects
  - Use results to validate or enhance existing monitoring
- Prepare for unplanned high-level releases with dispersion modeling and fast-response enhanced monitoring protocols
  - Explore cooperative approaches involving community, district, and industry

Recommended methods to achieve monitoring objectives

Objective of measurement program	Emissions		Community Exposure		
	Characterization	**Surveillance**	**Acute Effects Routine Monitoring**	**Acute Effects Catastrophic Event**	**Chronic Effects Routine Monitoring**
Duration	days to weeks	continuous	continuous	days	Minimum of 4 weeks in 2 season
Time-resolution	minutes	hourly	hourly	varies	7 to 14 days
Location	refinery boundary	fenceline	representative community sites	Grab sampling, mobile sampling	representative community sites
Number of 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_2S	all	determined by event	benze, butadiene, HCHO, NO_2, H_2S, metals
Recommended Methods	SOF, DIAL flux measurements	Open-Path	photometric, auto-GC or OP, tape samplers, met	monitoring van + canisters, med-vol PM, OP	passive, low-volume PM