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Air Monitoring Guidelines for Petroleum Refineries

AIR DISTRICT REGULATION 12, RULE 15: PETROLEUM REFINING EMISSIONS TRACKING

Prepared by the staff of the
Bay Area Air Quality Management District

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Air Monitoring Guidelines for Petroleum Refineries

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Executive Summary

On August 6, 2012, a substantial fire occurred due to a hydrocarbon leak at a crude oil processing unit at the Chevron Refinery in Richmond, California. The fire resulted in a large plume of black smoke and visible emissions from a refinery flare. The August 6, 2012 incident prompted the Bay Area Air Quality Management District (Air District) staff and Board of Directors to identify a series of follow-up actions to enhance the Air District's ability to respond to similar incidents (Board of Directors, October 17, 2012). One of these actions was to convene a panel of air monitoring experts (Expert Panel) to recommend technologies, methodologies and tools to enhance air monitoring capabilities near refineries. In order for the Expert Panel to have a uniform starting point for their discussion, the Air District contracted with Desert Research Institute (DRI) to compile a report that provided background on current air monitoring capabilities near refineries and potential air monitoring technologies, methodologies and tools that could be used at refinery fence-lines and in the community to determine impacts from normal refinery operations and episodic incident-based releases. Another related follow-up action was the development of a new Air District Petroleum Refining Emissions Tracking rule, which would include a requirement that Bay Area refineries establish and operate fence-line air monitoring systems consistent with guidelines to be developed by the Air District.

The purpose of these *Air Monitoring Guidelines for Petroleum Refineries* (Guidelines) is to provide a framework on how these fence-line air monitoring systems should be developed and deployed and what metrics the Air District will use to evaluate the ability of those systems to meet the goals outlined below. The Guidelines provides refineries with information to be used to develop an air monitoring plan that the Air District will review, provide feedback and/or recommendations and approve once the monitoring plan meets the goals of the monitoring effort. More specifically, these Guidelines provide guidance for parties preparing air monitoring plans required by Regulation 12, Rule 15, and guidance to Air District staff that evaluates those plans.

Note on Community Monitoring:

Although DRI and the expert panel considered and made recommendations on air monitoring in the communities around Bay Area refineries, and although draft Regulation 12, Rule 15 initially included community monitoring requirements, the Air District has decided to implement community monitoring through a different mechanism. Therefore, this version of the Air Monitoring Guidelines for Petroleum Refineries includes only fence-line monitoring guidelines.

Background

On August 6, 2012, a substantial fire occurred due to a hydrocarbon leak at a crude oil processing unit at the Chevron Refinery in Richmond, California. The fire resulted in a large plume of black smoke and visible emissions from a refinery flare. The Contra Costa County Health Department issued a community warning and ordered a shelter-in-place for approximately five hours in Richmond and San Pablo. Thousands of residents sought medical treatment, with most suffering respiratory and/or eye discomfort.

The August 6, 2012 incident prompted the Bay Area Air Quality Management District (Air District) staff and Board of Directors to identify a series of follow-up actions to enhance the Air District's ability to respond to similar incidents (Board of Directors, October 17, 2012). One of these actions was to convene a panel of air monitoring experts (Expert Panel) to recommend technologies, methodologies and tools to enhance air monitoring capabilities near refineries. Another related follow-up action was to expedite the development of a new Air District Petroleum Refining Emissions Tracking rule, and to include a requirement that Bay Area refineries establish and operate fence-line air monitoring systems consistent with guidelines to be developed by the Air District. This guidance document is intended to provide a framework on how these air monitoring systems would be developed and deployed and what metrics the Air District will use to evaluate the ability of those systems to meet the goals outlined below.

As part of the effort to develop this guidance, the Air District contracted with Desert Research Institute (DRI) to compile a report that provides background on current air monitoring capabilities near refineries and potential air monitoring technologies, methodologies and tools to:

- Provide air quality information for communities near refineries;
- Gather data to evaluate health impacts associated with air quality near refineries;
- Track air quality changes and trends over time near refineries.

The DRI report reviewed and evaluated measurement approaches and methods for assessing the impacts of refinery emissions on ambient concentrations of criteria and air toxics pollutants in nearby communities and is included in Appendix A. 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 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. With these objectives in mind, air quality data from existing Air District criteria and air toxics pollutant monitoring programs, and air monitoring (both regulatory and voluntary) by the refineries were then used 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 were suggested with scalable options. It was the intent of the Air District to utilize the DRI report to provide the Expert Panel with a starting point for further discussion.

The Expert Panel was convened on July 11, 2013 and included monitoring experts from around the nation representing academia, community advocates, industry, and government. The final report of the Expert Panel, including a list of participants is provided in Appendix B. The Expert Panel reviewed the DRI report, received a presentation by one of its authors, Mr. David Campbell, and then addressed questions developed by the Air District to further explore potential air monitoring methodologies and instrumentation that could be developed to provide the public, refineries, and regulators information about exposures to the public near refineries. The Expert Panel addressed the following questions:

- What should the size and spatial orientation of a network of monitors be around refineries?
- What network components should be considered (compounds measured, technology and instrumentation used, methodologies applied, air quality assessment tools utilized, etc.)?
- How should the data be provided to the public?
- What should be considered when developing measurement quality objectives, such as:
    - What type of instrument siting criteria should be used?
    - What should the time resolution of the equipment be?
    - How often should the instrumentation be calibrated?
    - What should the accuracy/precision/completeness requirements of the data be?
    - What other quality control/quality assurance requirements should be put in place?
- What technologies, methodologies and tools could be employed to augment any fixed network to better quantify pollutant variations over space and time, especially during short duration incidents?
- What emerging technologies might be utilized in the future to further enhance community air monitoring capabilities?

The Expert Panel believed that open path monitoring capable of measuring representative compounds at near-ambient background levels of detection likely to be emitted by refineries should be employed at, or near, refinery fence-lines. Measurements of these compounds should be collected at a time resolution of five minutes. Data should be displayed to the public real-time, with appropriate QA/QC parameters defined and context provided so that the public can more easily understand when concentration from refineries reach levels of concern.

The Air District has developed this Guidelines Document for monitoring near refineries based on the DRI report and the input provided by the Expert Panel. This Guidelines Document can be used by the refineries to develop Air Monitoring Plans as described in Air District Regulation 12, Rule 15. The guidance is intended to identify what should be included in the Air Monitoring Plan and what must be provided to the Air District in order to deviate from specific recommendations and satisfy flexible conditions of the guidelines. The Air District recognizes that, in certain circumstances, flexibility must be provided in order to allow for operational or technical limitations of instrumentation or sampling methodologies and has identified where that flexibility may be used as long as acceptable rationale is provided that outlines the operational or technical limitations.

In addition, the Air District will use this Guidelines Document as a basis to evaluate whether Air Monitoring Plans and the monitoring systems contained therein adequately address the monitoring goals of measuring compounds of interest near refineries and reporting them to the public. The Air District encourages the inclusion of the community and other interested parties in the development of Air Monitoring Plans to help ensure that the community's concerns and desires are adequately addressed.

Revisions and updates to this guidance will be required as new instrumentation, methodologies and monitoring strategies are developed. Staff will bring any substantial changes to the Board of Directors for their consideration of approval.

Note on Community Monitoring:

Although DRI and the expert panel considered and made recommendations on air monitoring in the communities around Bay Area refineries, and although draft Regulation 12, Rule 15 initially included community monitoring requirements, the Air District has decided to implement community monitoring through a different mechanism. Therefore, this version of the Air Monitoring Guidelines for Petroleum Refineries includes only fence-line monitoring guidelines.

Section 1: Basic Requirements for an Approvable Air Monitoring Plan

This Section describes the criteria for an approvable Air Monitoring Plan. Plans that meet these criteria will be considered by the Air District and approved if all criteria in this Section are met. However, as part of the approval process, the Air District will consider comments received during the public comment period.

This Guidelines Document provides additional information in later sections that demonstrates pathways to alternatives and outlines processes and considerations for meeting the requirements of developing an Air Monitoring Plan. Where air monitoring requirements described in this Section are not met, subsequent sections outline what a refinery owner/operator should provide as a rationale for why the Air Monitoring Plan should be approved. Such rationale will be evaluated on a case-by-case basis.

1.1 Fence-line Monitoring

Refinery operators must measure **benzene, toluene, ethyl benzene, and xylenes (BTEX)** and **hydrogen sulfide (H_2S)** concentrations at refinery fence-lines with open path technology capable of measuring in the parts per billion range regardless of path length. Open path measurement of **sulfur dioxide (SO_2)**, **alkanes or other organic compound indicators, 1, 3-butadiene**, and **ammonia** concentrations are to be considered in the Air Monitoring Plan. Refinery operators must provide a rationale in the Air Monitoring Plan for not measuring all of the above compounds that addresses: why these compounds are not contained in the compositional matrix of emissions; are not at expected concentrations measured by available equipment; and/or address the technical or other considerations that make specific measurements inappropriate or unavailable.

Fence-line measurements must be continuously measured with a time resolution of five minutes. If this is not the case, refinery operators must provide a rationale in the Air Monitoring Plan for lesser time resolutions based on equipment or other operational limitations. These measurements must be provided to the public on a real-time basis, with appropriate Quality Assurance/Quality Control (QA/QC) measures taken to provide assurance of data accuracy. A Quality Assurance Project Plan (QAPP) that follows EPA guidelines must be developed that outlines the QA/QC parameters. Instrumentation must meet a minimum of 75 percent completeness on an hourly basis, 90 percent of the time based on annual quarters. Atmospheric conditions beyond the control of the refinery that affects accurate measurements, such as dense fog, shall not be counted against data completeness requirements as long as appropriate meteorological measurements document time periods when these conditions exist.

Measurements must cover populated areas within one mile of the refinery fence-line likely to be affected when the annual mean wind direction lies in an arc within 22.5 degrees of a direct line from source to receptors 10 percent of the time, or greater, based on the most representative meteorological measurements for sources likely to emit the compounds listed above at the refinery. If this is not the case and an alternative method, such as dispersion modeling is used to determine fence-line locations, refinery operators must provide a rationale for utilizing any alternative in the Air Monitoring Plan that addresses why receptors would not be affected by emissions from the sources within the refinery.

Refineries that already have open path monitoring capabilities in place need only provide verification those current systems adequately address population requirements.

1.2 Display of Monitoring Information

The data must be displayed to the public as defined above and available to the Air District in an approved format. The refinery operator must include in the Air Monitoring Plan how the data will be displayed and the steps taken to provide context of the measurements to the public, including how background concentrations and/or contributions from non-refinery sources affect measured concentrations. The Air Monitoring Plan must also outline a methodology for the public to provide comments and feedback for improvement of the website. It is hoped that this will be a mechanism to help improve the general understanding by the public of the air quality information presented but does not require refineries to address all comments received.

Comments regarding the website made by the public must be made available to the Air District upon request.

Section 2: Air Monitoring Guidelines Document and Development of Air Monitoring Plans

The Air District is providing this Guidelines Document to enable Air District staff, the community, industry and other interested parties to determine if Air Monitoring Plans submitted by Bay Area refineries adequately collect the data needed to determine air pollutant exposures associated with living or working near Bay Area refineries. Information gathered by the equipment and methodologies outlined in the Air Monitoring Plan will be used to evaluate the need for additional actions to reduce emissions and exposures.

This Guidance Document and the below sections outline where documentation and rationales for decision making must be included in the Air Monitoring Plan. The Air District understands that there is a need for flexibility when designing air monitoring networks. Air Monitoring Plans should document the considerations that were taken, the process involved with determining the proposed course of action and the potential affects the different choices may have on the data produced to support the decisions made.

The Expert Panel was clear that not all measurements need to necessarily utilize high cost instrumentation, provide real-time results or be located on a permanent basis as long as technologies met monitoring goals, long term measurements or demonstrated strong agreement with Health Risk Assessment (HRA) modeling. The Expert Panel stressed the need to leverage all monitoring activities available, be they regulatory or informational. Examples of this type of monitoring strategy are also provided in the DRI report. If alternatives monitoring strategies, such as those outlined in the DRI report or discussed by the Expert Panel, are proposed to replace measurement and/or equipment required in Section 1 for consideration, an acceptable rationale for this substitution must be supplied and approvable in the Air Monitoring Plan.

It is important to note that the Expert Panel generally agreed that information collected outside of refinery fence-lines could not be effectively utilized to take direct enforcement action but could be an effective tool to potentially identify areas where actions could be taken to reduce emissions. However, the Air District believes that there is the potential for fence-line measurements to be used in the Ground Level Monitoring (GLM) regulatory network if data collected correlates well with the current in-place network. In addition, this Guidelines Document is not intended to provide a representation of exposures within refinery property.

The following sections and appendices are intended to provide guidance on specific considerations that should be investigated and thoroughly addressed in the Air Monitoring Plan. It is required that a Quality Assurance Project Plan (QAPP) that follows EPA guidelines be provided with the Air Monitoring Plan that outlines the specific goals of the monitoring networks and instrumentation, the data quality that is required and how that relates to when data generated by the instrumentation is accepted, and how the data will be reviewed and managed by the refineries.

2.1 Data Display and Dissemination

The Expert Panel discussed how measurement results should be displayed to the public. The Air Monitoring Plan must address the measurements of compounds as well as the display and dissemination of this information. This Guidelines Document provides information on this subject in *Section 4: Data Display/Reporting*. Providing context for the measurements is an important consideration when displaying the information. The Air Monitoring Plan submitted by the refinery operators must describe how the refinery will provide the air monitoring data in a way that the public can readily access and understand. This would require involving interested parties in the design of data dissemination. The Air Monitoring Plan must also provide a means for the public to provide input toward improving the way data are displayed in order to aid in understanding. It is hoped that this will be a mechanism to help improve the general understanding by the public of the air quality information presented, but does not require refineries to address all comments received. It should also be noted that there is potential for the current GLM network to be incorporated into this display of data in the future.

Section 3: Considerations for Fence-line Monitoring

As stated above, the main goals of fence-line monitoring are to:

- Provide continuous air quality concentration information on a short enough time scale to address changes in fence-line concentrations of compounds associated with refinery operations;
- Provide data of sufficient accuracy to identify when concentrations of compounds associated with refinery operations are elevated as compared to other monitoring locations throughout the Bay Area;
- Provide context to the data so that the community can determine differences in air quality between their location and other locations in the Bay Area;
- Potentially aid in identifying corrective actions that will lower emissions.

It is expected that the fence-line monitoring will be permanently installed and continually operated.

As pointed out in the DRI report, multiple technologies need to be employed to ensure adequate compound identification at appropriate levels of detection and accuracy. The Expert Panel also agreed that each refinery should identify compounds of interest and define correlations and relationships of compounds prior to choosing measurement technologies and that potential interference(s) should be identified to ensure representative results. Air Monitoring Plans must include which organic and other refinery generated compounds likely to impact the health and wellbeing of people are likely to cross fence-lines and whether or not the proposed equipment is capable of measuring those compounds. If a refinery wishes to utilize a technology other than open path, the rationale for the choice must be outlined in the Air Monitoring Plan. The rationale must include how the proposed technology will be representative of the varying concentrations along the applicable refinery fence-line and how the time resolution goal of five minutes will be met. In addition, it should include how the proposed technology will meet data completeness and quality objectives and how the proposed technology's advantages/disadvantages compared to open path technologies.

Technologies proposed in the Air Monitoring Plan must be able to measure, at a minimum, benzene, toluene, ethyl benzene, and xylenes (BTEX) and hydrogen sulfide (H_2S) and potentially sulfur dioxide (SO_2), alkanes or other organic compound indicators, 1, 3 butadiene and ammonia. Exclusion of any of these compounds by fence-line monitoring must be thoroughly explained in the Air Monitoring Plan.

3.1 Open Path Monitoring

The Expert Panel agreed with the DRI report that open path monitors best addressed the goal of monitoring potential impacts from refineries and also believed that shorter time scale resolution was very desirable. Open path equipment should provide appropriately accurate data on an hourly basis, at a minimum, and the Expert Panel believed that five-minute data resolution was reasonable. The rationale for the technology chosen and the associated time resolution should be included in the Air Monitoring Plan.

Investigation prior to fence-line installation should address areas more likely to emit compounds of interest and identify the appropriate open path distance necessary to accurately and precisely capture those emissions. The results of the investigation must be provided in the Air Monitoring Plan, providing support for the technologies chosen. In addition, the elevation of likely emissions as well as topographical changes should also be incorporated into the evaluation to ensure maximum coverage.

Meteorological measurements should also be used and addressed in the Air Monitoring Plan to ensure proper location of fence-line systems, looking at long term measurements such as annual average wind rose, but also taking into account more seasonal and recurring short term meteorological events. It was also suggested, and is likely in the best interest of the facilities, to locate additional fence-line monitoring in a predominately upwind location to measure contributions from upwind sources that could impact downwind refinery fence-line measurements. The following guidance and metrics will be used by the Air District to evaluate the expected performance of the fence-line monitoring portion of the Air Monitoring Plan.

Refineries that already have open path monitoring capabilities in place need only provide verification those current systems adequately address population requirements.

The EPA has recently proposed a rule requiring monitoring for benzene at refinery fence-lines. The Air District believes that the best methodology for this is the use of open path technologies, and will work to ensure that monitoring systems proposed as part of the Air Monitoring Plan meet all applicable EPA requirements for monitoring of benzene.

A summary of fence-line monitoring considerations appears in Table 1.

Table 1. – Fence-Line Monitoring Considerations

Evaluate	Information Needed	Additional Considerations
Compounds likely to be emitted	Compound relations and correlations within the facility	Likely interferences
Precision, accuracy and minimum levels of detection of equipment	Information that is represented of compounds of interest at concentrations likely to cause concern	Maximum path length allowed to provide precision and accuracy
Time resolution of data produced	Resolution will be adequate to appropriately capture short duration events	Data management
Identify likely emission sources and compounds likely to be emitted from those sources	Compounds potentially unique to emission sources to ensure appropriate technology will be representative	Potential to utilize multiple technologies to capture relevant information
Topography of measurement area and elevation of equipment	Measurements will likely capture emissions from sources of concern	Power and security
Meteorology	Annual average and likely to occur wind patterns	Variations of wind from location to location

3.2 Appropriate Sampling Locations

Air Monitoring Plans must include locations of equipment, elevations of equipment and expected path length and the rationale behind these choices. Potential disruption of airflow and the potential effect on measured concentrations cause by obstacles must also be addressed. Any interferences cause by meteorological or process issues associated with the chosen location must be addressed. For example, an explanation should be included if a chosen measurement area is likely to be affected by fog or process steam. In addition, the Air Monitoring Plan should include how the open path monitoring will effectively provide relevant information for all nearby downwind communities during expected meteorological conditions.

3.3 Appropriate Sampling Methodologies

Air Monitoring Plans must address why a particular measurement method was chosen for a given location based on likely emissions from nearby contributing sources, desires to reach appropriate levels of detection and ability to measure compounds that have potentially unique relationships that apply to the particular facility. Factors that affect measurements, such as path length and potential interferences, should also be addressed. Issues that affect data completeness for the measurement technique proposed should be documented. If time periods when data cannot be collected due to these operational issues are to be excluded from data completeness calculations, methodologies for determining and documenting when the events occur must be addressed. Errors associated with the measurement technologies as well as accuracy, repeatability and precision should be documented and presented and ways to address these issues provided in the Air Monitoring Plan.

3.4 Quality Assurance/Quality Control (QA/QC)

Methodologies for ensuring appropriate levels of QA/QC must be provided in the Air Monitoring Plan to ensure data are of high enough quality and representative and defensible enough to meet the goals described in Section 3.3. The QA/QC plan should set data acceptance levels as well as appropriate levels of data quality. In addition, the QA/QC plan should address data management issues and provide the levels of review that data will go through to determine validity. This should be outlined in a Quality Assurance Project Plan (QAPP) that follows EPA guidelines submitted in the Air Monitoring Plan. It is critical that this portion of the monitoring plan identify a clear and transparent manner when data does not meet quality requirements and should be removed from the data set, to ensure the community understands why data is removed.

Section 4: Data Display/Reporting

The Expert Panel discussed the importance of providing relevant, useful and understandable monitoring information to the public. Monitoring that requires laboratory analysis, or involves time-integrated sampling methods and therefore would not be presented to the community real-time, would also need to be made available to the public, but would most likely require a different display format. It should be noted that use of integrated sampling methods and laboratory analysis would require an explanation in the Air Monitoring Plan of why these methods were chosen over open path technologies as stated in other sections of this Guidance Document. The Expert Panel stressed the need for QA/QC requirements to be stated clearly up front, so that if data removal were required due to failed QA/QC objectives, the rationale for the data removal would be done in a transparent way with proper notation.

Providing context to measurements that the public could readily understand was also stressed, with graphics to allow residents to determine when concentrations were within normal ambient ranges and what constituted concentrations that might indicate potential issues. This included providing information regarding the affects background concentrations as well as non-refinery sources may impact measurements. There was also a realization that more complex data should also be provided, so that residents that had the understanding and ability could perform additional analysis. There was also general agreement by the Expert Panel that any data display should contain a means for residents to provide feedback so that improvements could be made to data display as well as monitoring activities over time.

Air Monitoring Plans must provide an explanation of how data will be provided to the public, how that data will be provided context, and how the public will be able to provide feedback to improve the process. Feedback regarding the website or other data presentation must be made available to the Air District upon request. It should also be noted that there is potential for the current GLM network to be incorporated into this display of data in the future.

4.1 Time Resolution and Data Availability

Air Monitoring Plans should provide information on how real-time data will be distributed to the community and how other data generated by this air monitoring will be made available. It is assumed that this will likely result in data being presented on a website on a real-time basis and many examples of these types of websites exist. Ideally, the websites for all refineries would be similar in nature, so that the public could compare the various data to each other, though this is not a requirement. In addition, the Air Monitoring Plan must contain alternatives for those members of the community who may wish to have access to data while not having computer access at home, such as ensuring that the website can be accessed at a public library. The data must also be made available to the Air District in an approved format.

As stated previously, continuous instrumentation should be capable of producing data on an hourly basis, at a minimum, with data resulting from fence-line instrument measurements available on a shorter time resolution, ideally at five minutes. Data completeness for displayed data (as defined by collected measurement data being successfully displayed) should be upwards of 95 percent, given the reliability of current telecommunications equipment. Members of the Expert Panel representing the community provided input that as long as QA/QC data removal requirements were provided up front and were reasonable, removal of questionable data was not usually an issue. As a result, Air Monitoring Plans must incorporate how data can be displayed real-time, while incorporating necessary QA/QC to ensure representative data. Air Monitoring Plans must also address timeframes that data will be provided and the rationale behind those decisions as well as minimum expected uptime for the website. While QA/QC and data completeness must be addressed in the QAPP, how these will be applied to real-time display must also be provided in the Air Monitoring Plan. It is understood that a balance between providing data as close to real time as possible and providing adequately QA/QC'd data must be struck. It is assumed that data will go through a rudimentary QA/QC screening prior to display, and a more thorough review in which data may need to be removed from display due to data quality issues. Clearly defining the QA/QC parameters that will result in data removal in the QAPP is critical in ensuring a transparent method to data removal.

The Air Monitoring Plans must also include how the refineries will provide context that the community can utilize to understand what the data mean. This must include a mechanism for feedback and improvement of the site and a means for residents to report experiences and provide information regarding potential impacts from the refinery that could be used to improve data display and the monitoring activities themselves.

Air Monitoring Plans should also include how residents can access historical data directly, as websites should not simply provide graphical information about current conditions. The Expert Panel suggested that data should be “layered” so that interested parties with expertise could access more complex and complete datasets and these considerations must be incorporated into the Air Monitoring Plan. It is recognized and expected that this will likely involve appropriate annotation of data to convey limitations and issues associated with these more complex datasets.

Section 5: Siting Considerations

Sampling should be spaced away from certain supporting structures and have an open, unobstructed fetch to the target area. At least 90 percent of the monitoring path for open path, remote sensing instruments, should be at least one meter vertically and/or horizontally away from any supporting structure, and away from dusty or dirty areas. Rationale for siting equipment should be included in the Air Monitoring Plan. Locations where power may not be adequate to ensure proper equipment operation or where substantial security measures must be taken may also be considered while evaluating appropriate sites.

5.1 Nearby Structures

Structures may be present that can significantly impact pollutant concentrations. These structures include sound walls or noise barriers, vegetation, and buildings. Physical barriers affect pollutant concentrations around the structure by blocking initial dispersion and increasing turbulence and initial mixing of the emitted pollutants. While these structures can trap pollutants upwind of the structure, these effects are very localized and likely do not contribute to representative peak exposures for the nearby population. In general, these structures should be avoided when establishing fence-line monitoring systems. Air Monitoring Plans must address how any effects caused by structures were identified and addressed.

5.2 Terrain

As described previously, local topography can greatly influence pollutant transport and dispersion. However, large-scale terrain features may also impact where peak concentrations can occur. Air Monitoring Plans must address how the effects of terrain were taken into consideration and addressed.

5.3 Meteorology

Evaluating historical meteorological data is useful in determining whether certain candidate locations may experience a higher proportion of direct impacts from emissions from a given source or process. Often, peak concentrations occur during stable, low wind speed conditions. Thus, historical wind directions should be a consideration in establishing any monitoring site, but should not be the only considerations. A rationale for how meteorological measurements were used to determine sampling locations should be included in the Air Monitoring Plan.

Section 6: Multi-pollutant Monitoring

Multi-pollutant monitoring is a means to broaden the understanding of air quality conditions and pollutant interactions, furthering capabilities to evaluate air quality models, develop emissions control strategies, and support research, including health studies. The DRI report and the Expert Panel recognized the need to employ a multi-pollutant monitoring strategy at refineries for these reasons and this Guidelines Document provides the following list of compounds for consideration as part of the Air Monitoring Plan. All compounds must be considered and evaluated with rationale for chosen measurements. As stated throughout this Guidelines Document, the Air District would consider adding or deleting compounds in the below list dependent on the rationale provided for inclusion and/or exclusion in the Air Monitoring Plan.

6.1 Hydrogen Sulfide (H_2S)*

H_2S is a colorless gas with a strong “rotten egg” odor and can be smelled at very low concentrations. It is poisonous, discolors paints and can tarnish metals. Although it is produced at sewage treatment plants and through anaerobic processes, it is also produced at oil refineries as a by-product of refining crude oil. As a result, measurement of this compound will help identify potential leaks at refineries.

6.2 Nitrogen Oxides (NO_2)*

Scientific evidence links NO_2 exposures with adverse respiratory effects, making it a compound that is routinely measured in ambient air monitoring networks. NO_2 measurements also typically include measurement of NO and NO_X. It is emitted during combustion and is therefore of interest near refineries, though there are many sources of nitrogen oxides. Measurement of these constituents will help determine if refineries add significant concentrations to nearby urban environments by comparing measurements with other Bay Area locations.

6.3 Particulate Matter (PM) and Constituents

Combustion sources emit significant amounts of PM. Motor vehicles may also contribute to elevated PM concentrations by re-suspending dust present on the road surface. There are regulations that address ambient concentrations of PM less than 10 µm in diameter (PM_{10}) and PM less than 2.5 µm in diameter ($PM_{2.5}$). While both of these PM size fractions are emitted during combustion, the majority will generally be in the $PM_{2.5}$ size fraction. Since combustion-emitted particles typically occur at less than 0.1 µm in diameter, these emissions tend to contribute little to ambient $PM_{2.5}$ mass concentrations, but do contribute significantly to PM number concentrations, and may impact the chemical composition of the $PM_{2.5}$ mass collected relative to urban background conditions. PM emitted through mechanical processes (brake wear, tire wear, re-suspended road dust) will tend to be in the PM_{10} size fraction and can lead to elevated mass concentrations. As a result, $PM_{2.5}$ mass measurements may be useful for estimating potential refinery contributions to nearby urban environments by comparing measurements with other Bay Area locations.

Most PM_{10} and $PM_{2.5}$ mass measurements use filter-based, gravimetric analyses over a 24-hour sample collection period. Diurnal variations in meteorology can have a tremendous impact on air quality that may not be identifiable in 24-hour average measurements. Thus, continuous PM measurements provide useful information for refinery emission measurement applications; however, care must be taken in choosing a sampling method. Optical PM mass samplers typically cannot detect particles less than approximately 0.2-0.5 µm in diameter. Therefore, these measurement devices may not capture a significant amount of the PM mass related to primary combustion emissions. In addition, some continuous PM samplers heat the inlet air prior to analysis. Since PM emissions can contain a significant amount of semi-volatile organic compounds, these samplers can underestimate the PM mass by volatilizing the organic PM prior to collection in the sampler.

6.4 Speciated Hydrocarbons*

Speciated hydrocarbons are pollutants that are made up of hydrogen and carbon and can be associated with adverse health effects. They are emitted by a large number of sources, but many hydrocarbons are associated with fuels and the production of fuels. As a result, measurement of these compounds is critical to determining the impacts refineries have on nearby communities. The following are potential compounds of interest and are separated out based on their measurement and/or analytical techniques. Measurement of hydrocarbons will help determine if refineries add significant concentrations to nearby urban environments and can indicate leaks and emissions from refinery sources by comparing measurements with other Bay Area locations.

6.4.1 Aldehydes*

Aldehydes emitted into ambient air include, but are not limited to, formaldehyde, acetaldehyde, and acrolein. A more detailed listing of aldehydes with potential health concerns is provided by OEHHA. Aldehydes are typically measured using cartridges containing dinitrophenyl hydrazine (DNPH). However, other methods, including evacuated canisters and cartridges containing other compounds, have been used to measure ambient concentrations of some of these compounds. Sample collection periods of 24 hours or more are typically required for assessing ambient aldehyde concentrations, although a few manufacturers advertise semi-continuous analyzers for select compounds.

6.4.2 Polycyclic Aromatic Hydrocarbons (PAH)*

Polycyclic Aromatic Hydrocarbons (PAHs) are hydrocarbons with multiple aromatic rings that have been associated with potential health effects. They are present in fossil fuels and can be formed as part of the combustion process, though there are many sources of PAHs. Sampling and analysis for PAHs requires very specific techniques and methodologies, though there are some non-specific, real-time instruments available. A more detailed listing of PAHs with potential health concerns is provided by OEHHA.

6.4.3 Volatile Organic Compounds (VOCs)*

These air pollutants are found in the gas phase in ambient air. Typical VOCs of concern include, but are not limited to, benzene, toluene, ethylbenzene, xylenes (BTEX), 1, 3 butadiene, acrolein, and styrene. A more detailed listing of potential VOCs of health concern is provided by the OEHHA. VOCs are typically measured by the collection of ambient air using evacuated canister sampling and subsequent analysis on a gas chromatograph (GC). For evacuated canister sampling, the sample collection time can vary from instantaneous grab sample to averaging times of more than 24 hours depending on the collection orifice used. As discussed for PM sampling, shorter averaging times can be important to discern the impacts of varying environmental conditions. Auto-GCs can be used to measure select VOC pollutant concentrations semi-continuously at a monitoring site. A number of manufacturers also advertise semi-continuous analyzers for one or more VOCs of interest using various GC technologies.

6.5 Sulfur Dioxide (SO_2)*

Heating and burning of fossil fuel releases the sulfur present in these materials and result in the formation of SO_2. SO_2 can have direct health impacts as well as cause damage to the environment and, as result, is routinely measured in ambient air monitoring networks. Like H_2S, SO_2 is produced at refineries, though there are other sources. As a result, measurement of this compound will help identify potential leaks and other issues at refineries.

6.6 Surrogate Measurements*

A number of surrogate measurements can also be considered to assist in interpreting emission impacts on air quality and to determine possible causes of adverse health effects. A common surrogate has been the use of CO to represent the impacts of other non-reactive gas emissions that are more difficult to measure from emission sources. While studies do show that CO and other non-reactive VOC concentrations tend to correlate in some near combustion source environments, the magnitude of VOC concentrations relative to CO concentrations may be difficult to discern because of varying impacts from control strategies and emission sources. Regulations that have led to reductions in CO emissions may not equally affect VOC emission rates. In addition, CO is emitted by fuel combustion, whereas VOCs are emitted from both combustion and evaporation processes.

Other surrogate measurements focus on PM constituents that are primarily emitted from motor vehicles and other combustion processes and may pose a public health concern. These surrogate measurements were discussed in the above sections.

If surrogate measurements are proposed in the Air Monitoring Plan, the relationship to compounds of interest must be identified and confirmed for the application desired.

Appendix 1: DRI Report

Appendix 2: Expert Panel Report

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

Final Report

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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 plant 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.

Background

Exposure to hazardous air pollutants (HAP) 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 HAP. 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 (NO_2) and sulfur dioxide (SO_2) 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.

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 plant operations, consider means to capture emissions during plant 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.

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 0-1 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 ($PM_{2.5}$), 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 $PM_{2.5}$, ROG and NOx emissions from all major emitting facilities and over 90% of the SO_2 emissions.

Table 0-1 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 0-2. 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 hazardous air pollutants.

Table 0-1. 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 0-2. 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, Califorina, 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.

Chemical Species of Interest

Refineries emit a wide variety of pollutants including criteria pollutants (SO_2, 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 HAP (hydrogen fluoride, hydrogen cyanide), persistent bioaccumulative HAP (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 naptha-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, NOx, 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 SO_2, NOx, CO, PM, and metals at the refinery. Control technology: scrubber and ESP.
- Sulfur Recovery removes and recovers H_2S using an amine treating unit and the Claus process. Air emissions include SO_2, NO_x, CO, carbonyl sulfide, and H_2S. 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 (semibatch 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 SO_2, NO_x, PM, HAP (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 plant equipment. During plant 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.

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 0-3 gives the annual emission of HAP 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 0-4 summarize the TRI data for the five refineries for the 2011 reporting year.

Table 0-3. Bay Area AQMD inventory of air toxic contaminants for 2009.

	Shell Martinez	Tesoro Martinez	Chevron Richmond	Phillip 66 Rodeo	Valero Benicia	TOTAL	
Pollutant			Emissions lbs/yr			lbs/yr	lbs/day
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 0-4. 2011 Toxic Release Inventory (TRI) for refineries in the Bay Area in lbs per year.

	Chevron, Richmond		Phillips 66, Rodeo		Shell Oil, Martinez		Tesoro, Martinez		Valero, Benicia	
Parameter	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

Health Risk Assessments

Table 0-5 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 E-4 $\mu g/m^3$. The table includes all cancer potency values and noncancer 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 0-6. 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 location 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, H_2S, formaldehyde for acute risk.

Table 0-5. OEHAA health risk values as of February 25, 2013.

	Derived Residential Cancer Risk for 0.02 g/s deposition						Derived Residential Chronic HI for 0.02 g/s deposition			
TAC	Oral Potency Value (mg/kg/day)-1	Dermal Unit Risk Factor (ug/m3)-1	Soil Unit Risk Factor (ug/m3)-1	Mother's 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)	AEL 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 0-6. 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%

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 communities. 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.

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 nonatttainment 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 s 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 HAP 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.

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 0-7 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 0-1 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 0-2 and Figure 0-3 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.

Summary of Existing Ambient Air Quality Data

The most complete extensively monitored pollutant of interest is SO_2, for which hourly measurements are recorded continuously at 9 sites (not including the GLM sites) to track compliance with the NAAQS. As shown in Figure 0-4, although the 99th percentile SO_2 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 SO_2 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 0-5 and Figure 0-6 show the long-term trends in concentrations of several gaseous HAPS 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 0-7 indicates that concentrations are uniformly low relative to the OEHA 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.

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 July of 1997, The Tosco Oil refinery in Rodeo, CA, USA (now owned by Phillips 66) completed the installation of its new "fenceline monitoring system". This new monitoring network, which incorporates ten 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. Installation of the monitors came about as part of an agreement reached between the refinery and local community groups in after a disastrous chemical release which occurred in 1994 (UNOCAL facility at the time). After this incident, Contra Costa County Health Services required additional air monitoring at the refinery in conjunction with the refinery's request for a land use permit. The County required the refinery to work with community members to design and install a monitoring network that could simultaneously measure and report toxic air pollutants at the refinery's fenceline.

The refinery installed 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, butane, carbon monoxide, carbonyl sulfide, formaldehyde, methane, nitrous oxide, and ozone. The UV instrument monitors for BTEX compounds (benzene, ethyl-benzene, toluene, and xylene). The TDL monitors measure for ammonia and hydrogen sulfide. The data are available online at http://www.ergweb2.com/fenceline/default.asp. The measurements at the concentrations reported by the UV and TDL monitors are not sufficiently accurate that Contra Costa County is willing to report them on this Web site. 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. Based on examination of the limited data available from this website, data for SO_2 and BTEX are generally below the 5 ppb 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 useful 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, H_2S, 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, SO_2, H_2S and CS_2. Fenceline data are now available online at http://www.fenceline.org/richmond/data.php.

Table 0-7. Locations and parameters measured at air quality monitoring stations in the San Francisco Bay Area.

STATION	ADDRESS	City / ZIP	O_3	NOx	Noy	SO_2	CO	HC	PM_{10}	PM_{10} Continuous	$PM_{2.5}$	$PM_{2.5}$ Continuous	TOXICS	H_2S	metals & aldehyde	PAH	BC	$PM_{2.5}$ SASS speciation	TSP Lead	Neph light scatter	PAMS GC	UFP Count
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 Cunninghan 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.

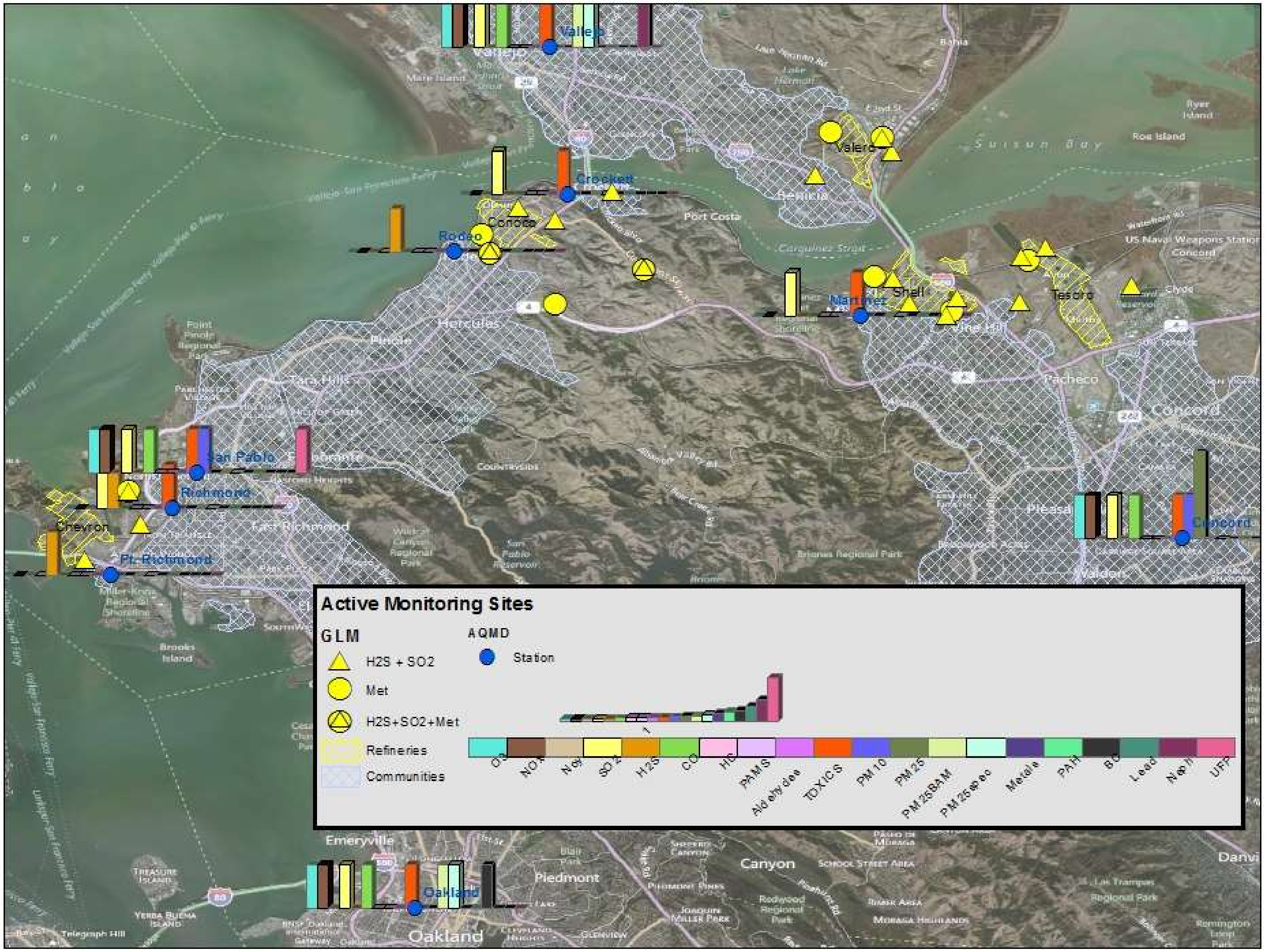


Figure 0-1. Locations of active BAAQMD air monitoring sites and refineries in the Bay Area.

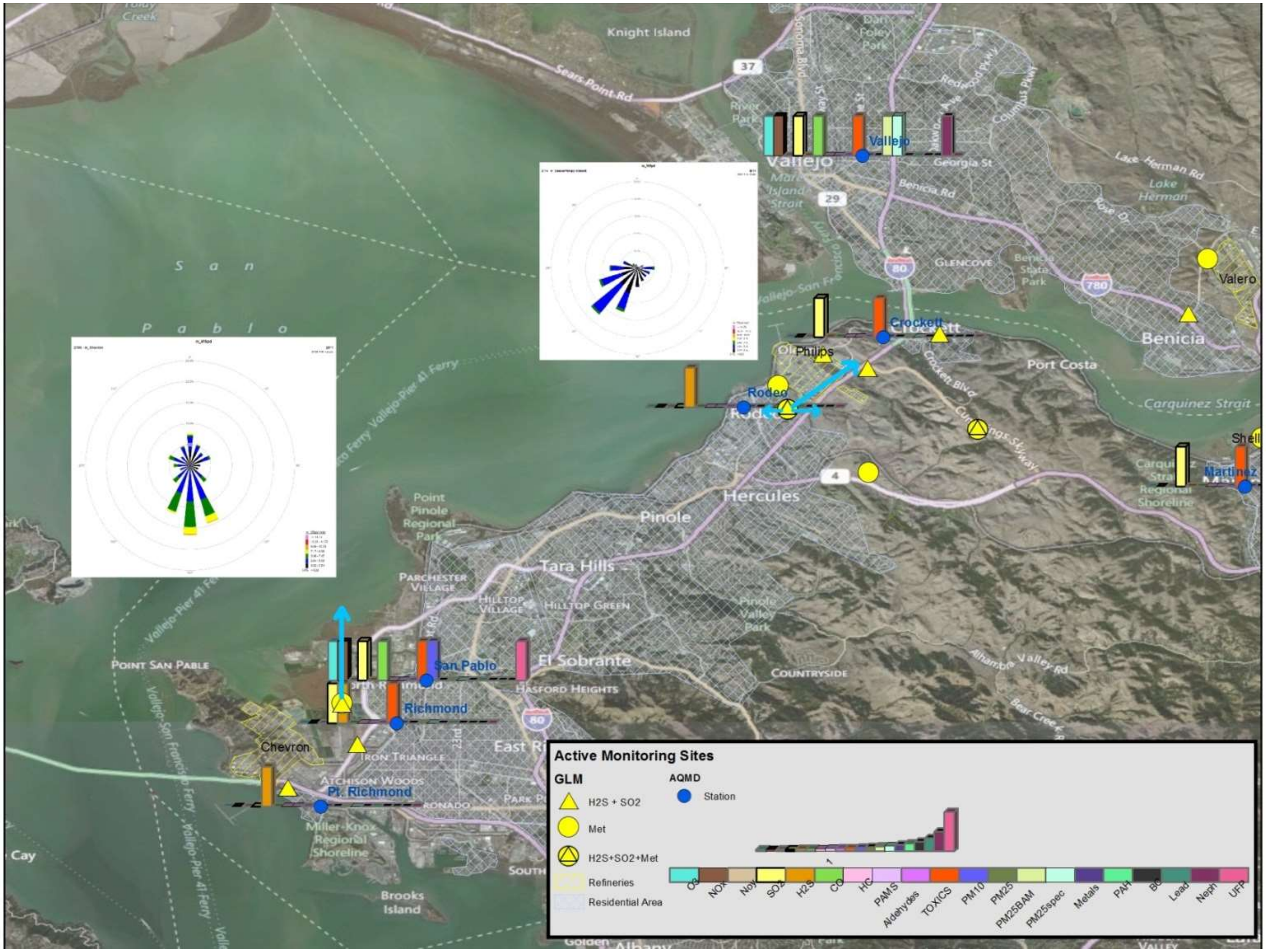


Figure 0-2. Closeup of locations of active air monitoring sites and refineries, showing prevailing wind directions (blue arrows).

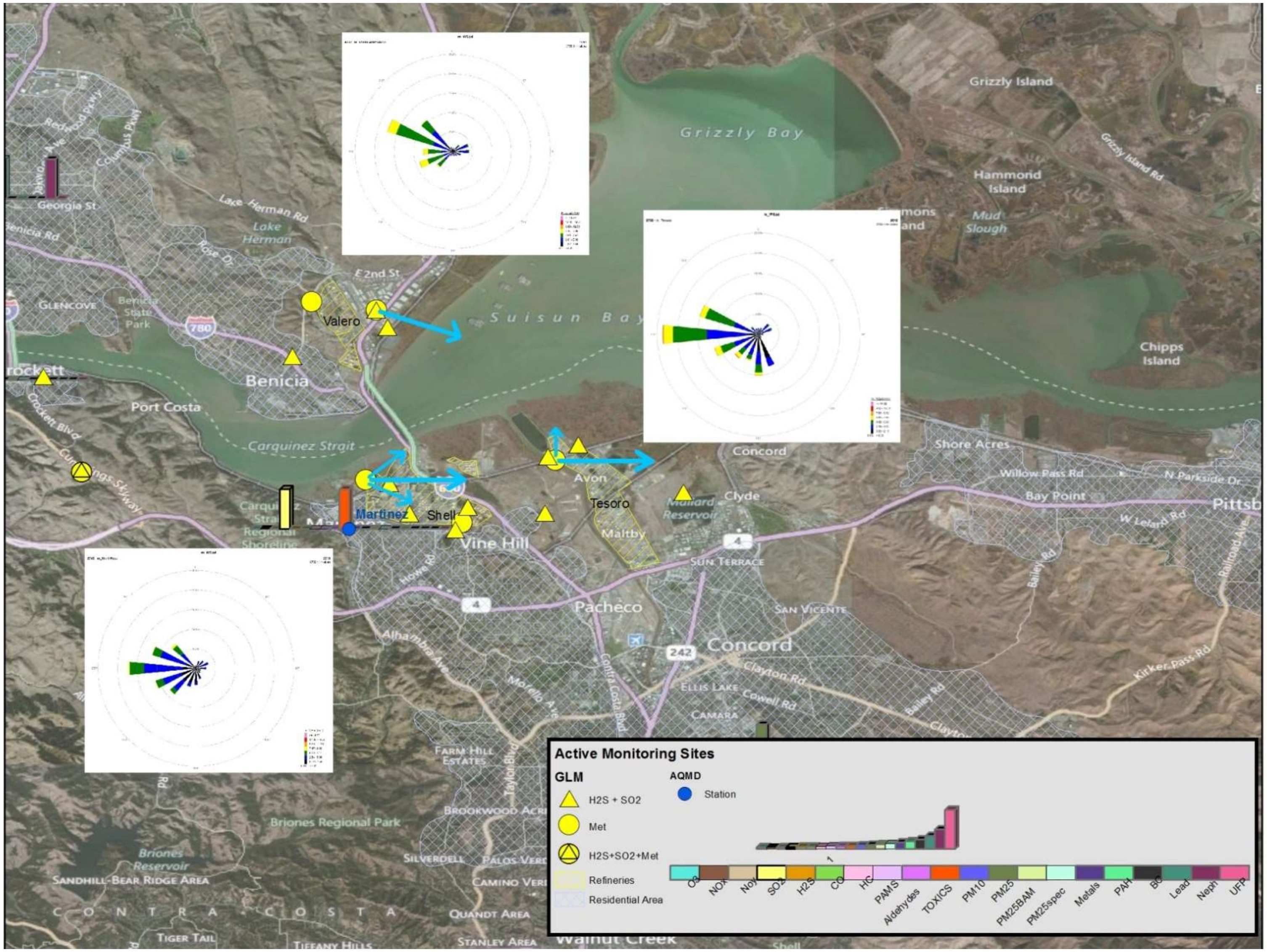


Figure 0-3. Closeup of locations of active air monitoring sites and refineries, showing prevailing wind directions (blue arrows).

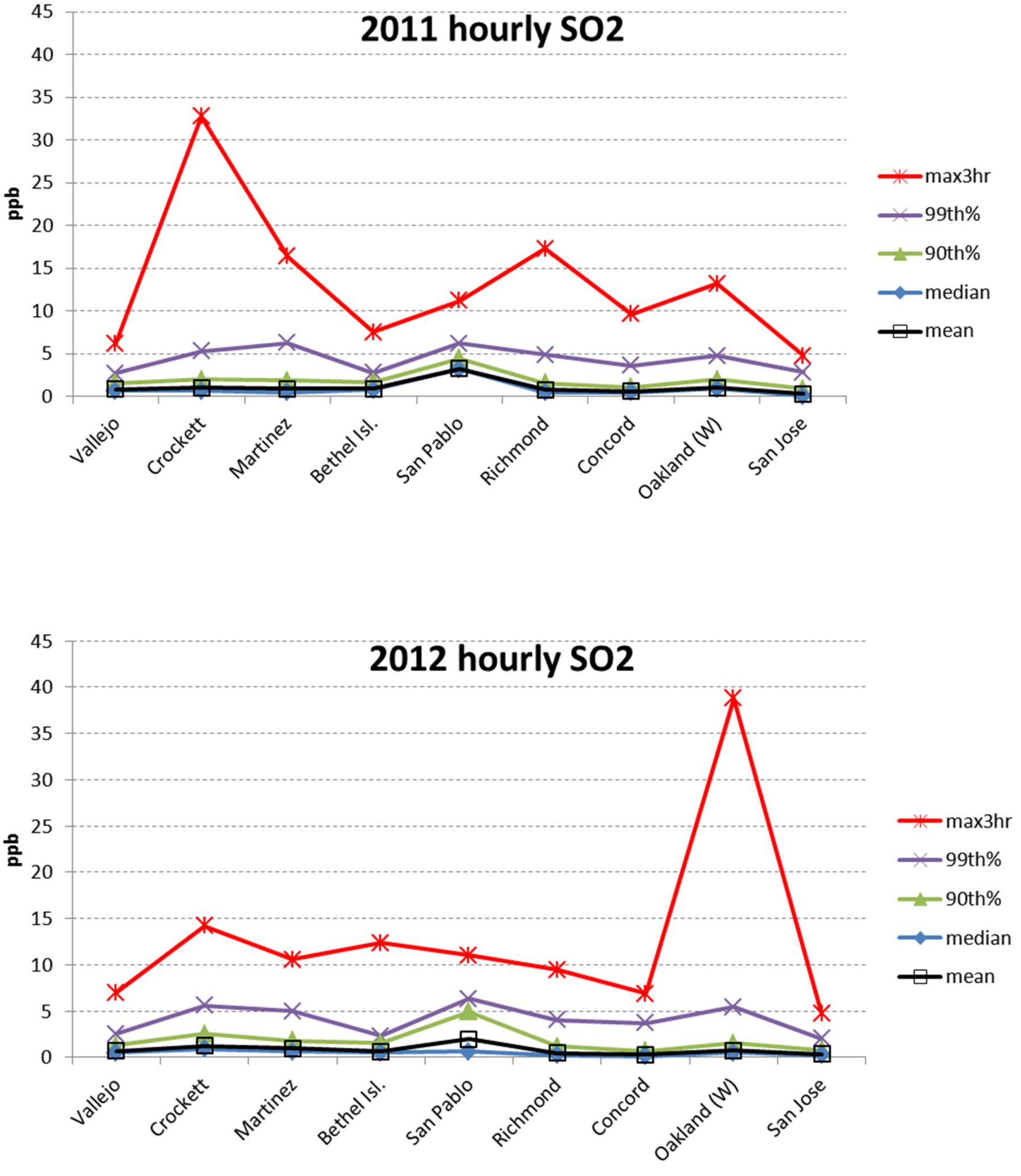


Figure 0-4. Annual statistics for SO_2 sites in the Bay Area. The primary NAAQS is 75ppb (99^{th} percentile) and secondary is 500 ppb (maximum 3hr average).

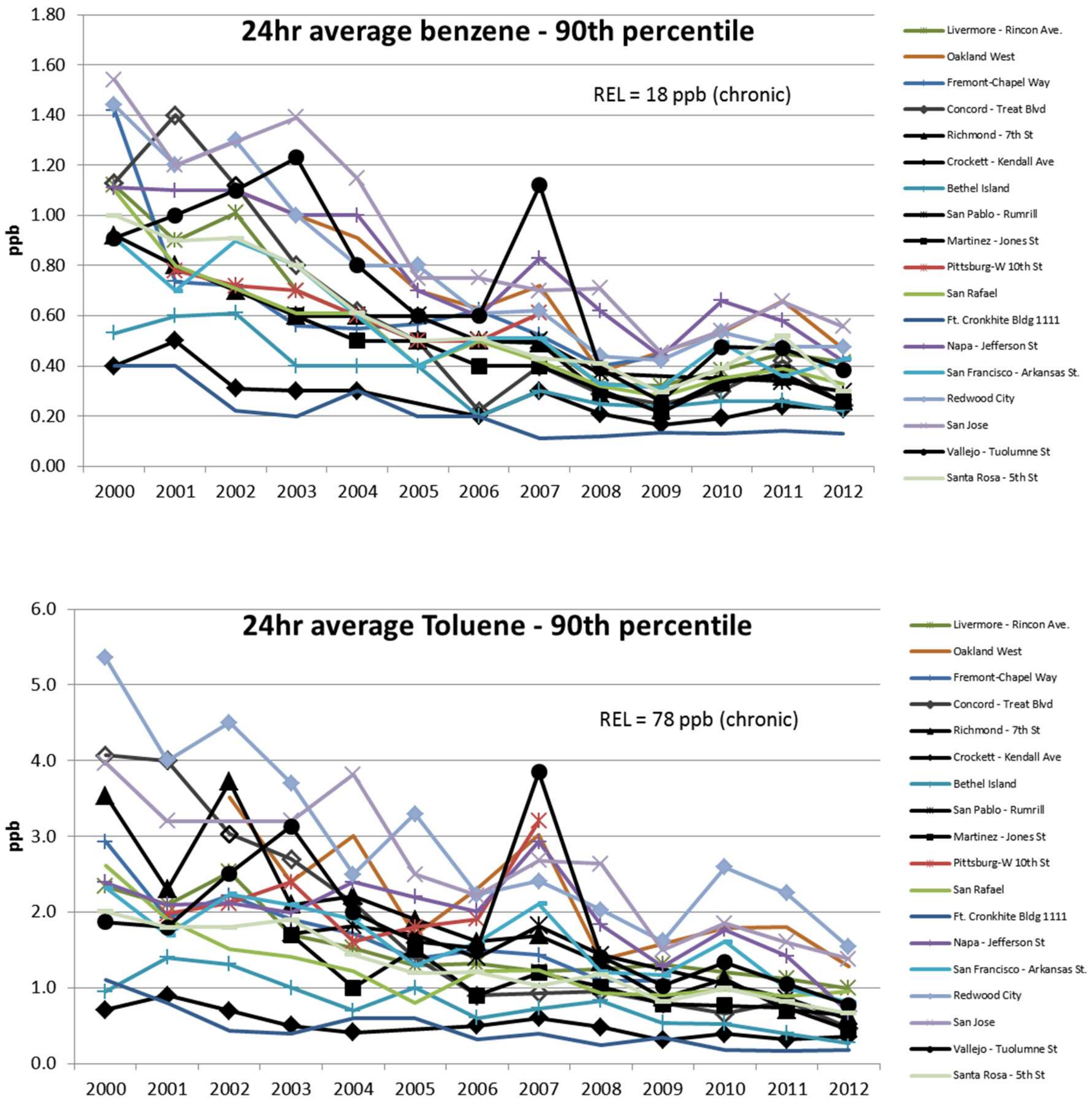
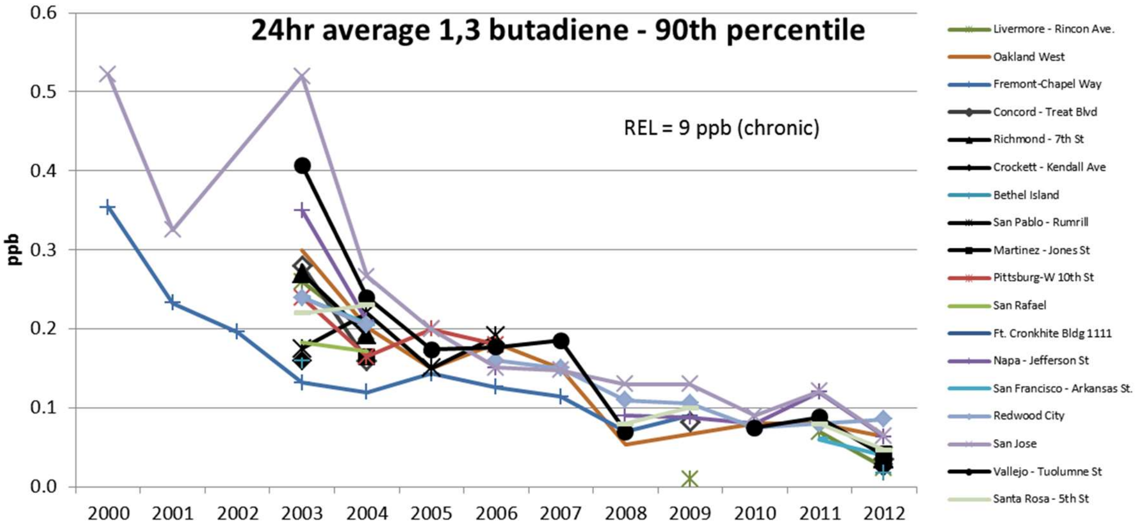


Figure 0-5. Trends in air toxics, 2000 – 2012. Sites near refineries are indicated by bold black lines. Values below LOD are not shown.



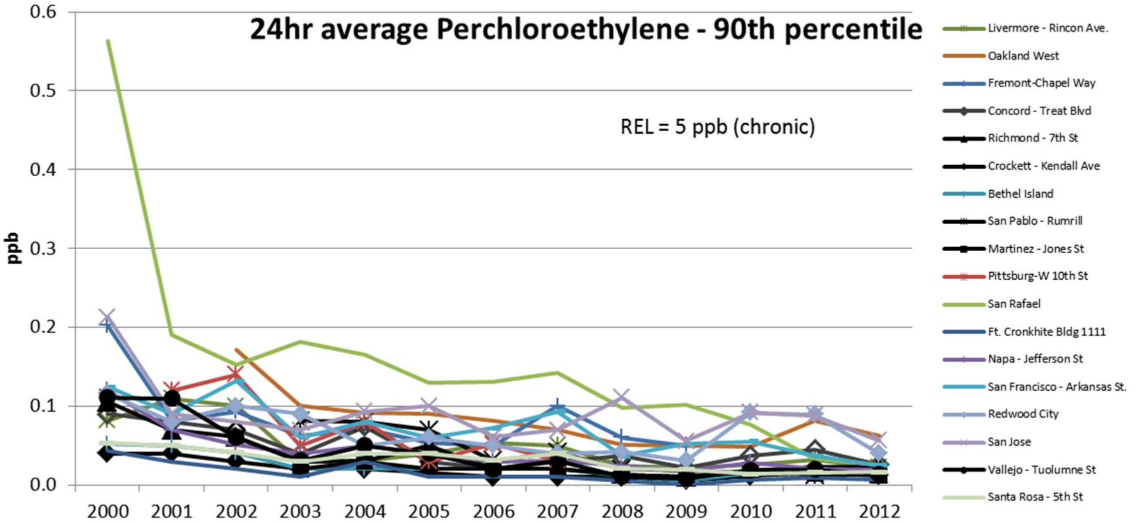


Figure 0-6. Trends in air toxics, 2000 – 2012. Sites near refineries are indicated by bold black lines. Values below LOD are not shown.

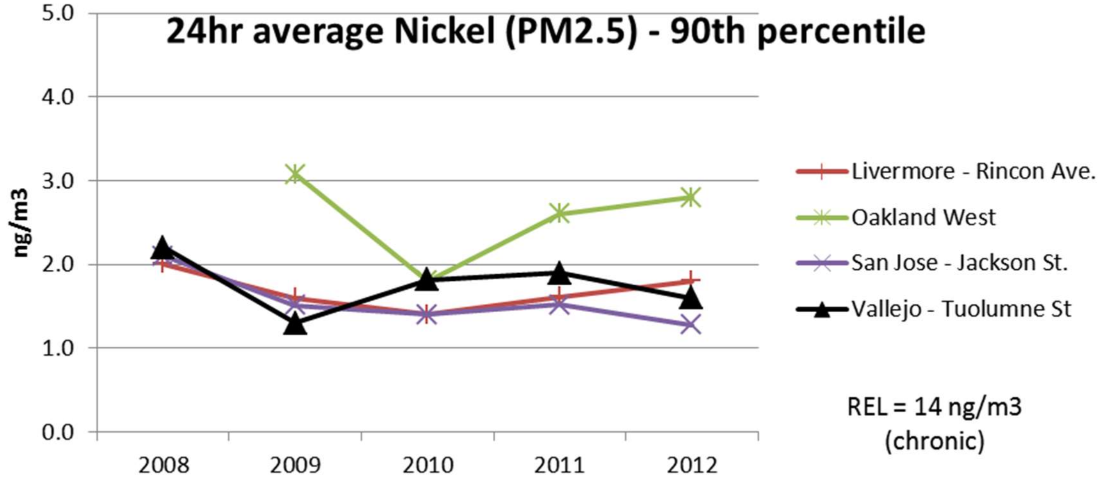


Figure 0-7. Trend in fine particulate nickel, 2000 – 2012. Sites near refineries are indicated by bold black lines. Values below LOD are not shown.

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 assessing the air quality impacts to the community and taking any enforcement action 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. Protocols and procedures during such accidents are outlined in the BAAQMD Incident Response Guidelines.

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 PM_{10} concentration at the Crockett site was 19 $\mu g/m^3$ from October 2001 to May 2003 with a maximum of 70 $\mu g/m^3$. The State PM_{10} standard (50 $\mu g/m^3$) 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 lifetime[1], 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..

Discussion and Conclusions

Exposures to hazardous air pollutants (HAP) 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 objectives.

1. Determine community-scale average and range of concentrations for criteria pollutants (SO_2, NO_2, CO) and certain high-priority HAP (benzene, toluene, ethylbenzene, xylenes, 1.3-butadiene, fomaldehyde).
2. Determine the impacts of routine and unplanned refinery emissions during unhealthy levels of criteria pollutants or HAP.

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 (H_2S) 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 (SO_2, H_2S, toxics) is a source impact monitoring site located 0.8 km east of the Chevron Refinery boundary, which is along the secondary prevailing wind

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[1] 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 (H_2S) 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 (SO_2, 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 (SO_2, 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 (O_3, NO_x, SO_2, 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 (O_3, NO_x, SO_2, CO, PM_{10}, 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 (O_3, NO_x, SO_2, CO, PM_{10}, 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, NOx, 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 NOx and black carbon (BC) (Fujita et al., 2010; Westerdahl et al. 2005). Even higher ratios have been measured for NOx, sulfur dioxide (SO_2), 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 SO_2 can be considered a tracer for refinery emissions in the absence of other significant sources in the area, all monitoring stations report similarly low SO_2 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 SO_2, H_2S 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 disproportionate impacts from refinery emissions. 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 SO_2 to sulfate).

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.

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 SO_2 or H_2S 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.

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 (Cuclis, 2012). 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 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. All DIAL vendors who take measurements at petrochemical facilities currently are based in the U.K. According to recent estimates, the cost of the measurement techniques can easily exceed $500,000 for a one-month study and the cost of a new DIAL system is typically at least $2-3 million (Cuclis, 2012).

SOF uses a Fourier Transform Infrared (FTIR) spectrometer mounted in a passenger van. As the van drives past a petrochemical complex on a sunny day, it gathers information about the concentration of chemical species and a background subtraction is applied using readings taken before and after approaching the petrochemical facilities. This information is combined with wind direction and speed to calculate the mass flux of pollutants. The cost for a one-month study can up to $200,000 and 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 (Cuclis, 2012)..

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.

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 NO_2, NOx, SO_2, H_2S, 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, NOx, SO_2, 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.

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.

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 NOx concentrations, the sum of NO and NO_2 (nitrogen dioxide), the NO_2 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 $FeSO_4$, adding to the NO already present in the sample, then introduced into the reaction chamber for measurement as described above. The NO_2 concentration is derived by subtracting the NO concentration measurement from the NOx concentration measurements. Monitors typically cycle through the total NOx 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 NO_2.

The reduction of NO_2 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 NO_2 (e.g., HNO_3, PAN, N_2O_5, HONO, and NO_3). Since the group is not well defined, it is commonly referred to as NOx and the species included in the group depend on factors such as inlet and line losses and environmental factors. HNO_3 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 NOy analyzers. NOy, or reactive nitrogen oxides, consists of a variety of species, the most abundant of which are typically NO, NO_2, PAN and HNO_3. TEI Model 42i-Y and Ecotech 9843 are commercially available NOy analyzers.

Sulfur Dioxide

Analyzers like the Thermo 450i and Ecotech 9850 use UV fluorescence detection technology to measure SO_2 in ambient air with detection limits and response times similar to the NOx analyzers. The Thermo 450i can also convert H_2S to SO_2, allowing differential measurement of H_2S in a manner analogous to the NO_2 method described above. Increased sensitivity can be achieved by trace-level analyzers like the Thermo 43*i*-TLE, which is designed to measure concentrations down to 50 ppt. Since ambient levels of SO_2 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.

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 SO_2. 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 configuratons: 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, SO_2, 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.

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 NO_2, SO_2, or specific VOC compounds (FluxSense AB, Sweden).

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 PM_{10} 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 (±10 µg/m^3), however longer averaging times decrease the uncertainty (±2 µg/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 R^2 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 $\mu g/m^3$, 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[2,3] 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

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

[3] 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.

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.

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.

Whole Air Samples in Stainless Steel Canisters

Stainless steel SUMMA™-polished canisters of 6-L capacity are customarily employed for volatile hydrocarbon (C_2-C_{12}) collection. These canister samples may be analyzed for speciated hydrocarbons by a method consistent with EPA Method TO-15, as well as for CO, CO_2, 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 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 C_2-C_{12} hydrocarbon mass is identified and quantified. The detection limit for hydrocarbon VOC is approximately 0.1 ppbC for each compound.

Methane (CH_4), carbon monoxide (CO), and carbon dioxide (CO_2) 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 CO_2, 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 CH_4 should be < 20 ppbv, whereas for $CO_2 < 3$ ppmv. The precision of measurements should be generally better than 10%.

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 C_{18} 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 C_1-C_7 compounds that can be quantified include: propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, tolualdehyde, and hexanaldehyde.

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:

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

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.

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

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.

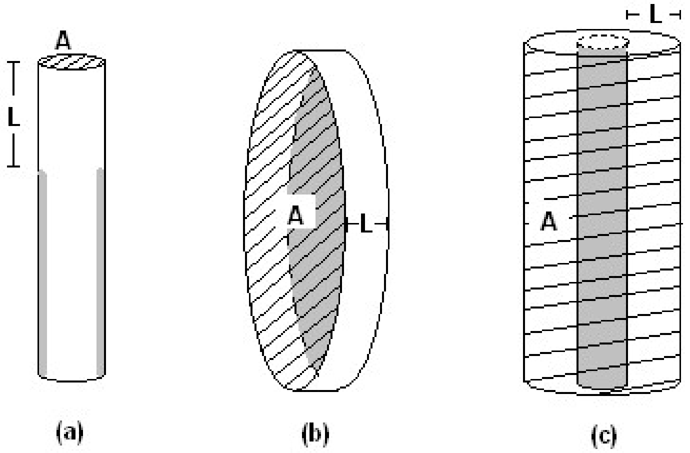

Figure 0-8. Schematics of (a) tube, (b) shield, and (c) radial geometry passive samplers with path length, L; Dashed area represents diffusive path area, A; Grey area represents adsorbent surface.

Six different types of passive samplers each with a unique adsorbent and method of analysis are described below. The NOx and SO_2 samplers are manufactured by Ogawa and Co.

The VOC, Aldehyde, and H_2S 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/NOx	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_2S	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 NOx, formaldehyde, acrolein, BTEX, 1,3 butadiene, SO_2, and H_2S. 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 NOx and NO_2, 0.5 ppb for SO_2, 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 Barnet 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 0-8 to Table 0-10. The passive samples for BTEX were stable for storage times of up to 14 days at -18º 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 0-8. Precision of passive NO_2, NO_x, and SO_2 measurements the LAX AQSAS, the West Oakland Monitoring Study (WOMS), and Harbor Communities Monitoring Study (HCMS).

	MDL [1]	Mean [2]	Differences of Replicates	
	ppb	ppb	Mean (ppb) [3]	%RD [4]
LAX AQSAS Winter 2012 Summer				
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%
LAX AQSAS Summer 2012				
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%
WOMS Summer 2009				
Nitrogen Dioxide (NO_2)	0.32	9.0	1.3	14.0%
Nitrogen Oxides (NOx)	0.32	17.5	0.7	4.2%
Sulfur Dioxide (SO_2)	0.54	0.09	0.03	33.9%
WOMS Winter 2009/10				
Nitrogen Dioxide (NO_2)	0.32	5.7	0.1	1.7%
Nitrogen Oxides (NOx)	0.32	25.9	0.8	3.1%
Sulfur Dioxide (SO_2)	0.54	1.0	0.79	81.5%
HCMS Summer 2007				
Nitrogen Dioxide (NO_2)	0.32	19.5	1.0	4.9%
Nitrogen Oxides (NOx)	0.32	29.4	0.6	2.2%
Sulfur Dioxide (SO_2)	0.54	1.0	0.20	19.8%
HCMS Winter 2007				
Nitrogen Dioxide (NO_2)	0.32	28.5	1.5	5.3%
Nitrogen Oxides (NOx)	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 0-9. Precision of passive BTEX measurements during the LAX AQSAS, the West Oakland Monitoring Study (WOMS), and Harbor Communities Monitoring Study (HCMS).

	MDL [1] ppb	4-wk Mean ppb	Differences of Replicates Mean (ppb) [2]	Differences of Replicates %RD [3]
LAX AQSAS Winter 2012 Summer				
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%
LAX AQSAS Summer 2012				
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%
WOMS Summer				
benzene	0.015	0.16	Not Available. See text for explanation.	
toluene	0.002	0.19		
ethylbenzene	0.002	0.08		
xylenes	0.002	0.36		
WOMS Winter				
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%
HCMS Summer				
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%
HCMS Winter				
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 0-10. 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	Differences of Replicates	
	ppb	ppb	Mean (ppb) [2]	%RD [3]
LAX AQSAS Winter 2012 Summer				
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%
LAX AQSAS Summer 2012				
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%
WOMS Summer				
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%
WOMS Winter				
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%
HCMS Summer				
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%
HCMS Winter				
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.

Time-Integrated PM Speciation Sampling and Analysis

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.

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.

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 HAPs 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 SO_2, H_2S, 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 must also provide means for estimating the incremental contributions of refinery emissions to the observed ambient pollutant concentrations. As mentioned in Section 3, there is no single chemical profile that can be used in receptor modeling of refinery emissions. The source contribution of refinery emissions can be estimated by 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.

Community-Scale Monitoring Options

Each of the community-scale monitoring objectives is associated with appropriate measurement approaches and methods in Table 0-11. Figure 0-9 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 0-12 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 OEHA 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 0-13 and Table 0-14 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 0-11. Measurement approaches and methods to achieve community monitoring objectives.

	Emissions		**Community Exposure**		
Objective	**Charaterization**	**Surveillence**	**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 meaurements	minutes	hourly	hourly	varies	7 to 14 days
Measurement Location	refinery boundary	fenceline	representative community sites	Grab samping, mobile sampling	representative community sites
Number of measurement sites	multiple	downwind edge	1 to 3 sites	multiple	Mulitiple ("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 meaurements	OP	photometric, auto-GC or OP, tape samplers, met	monitoring van + canisters, med-vol PM, OP	passive, low-vol PM

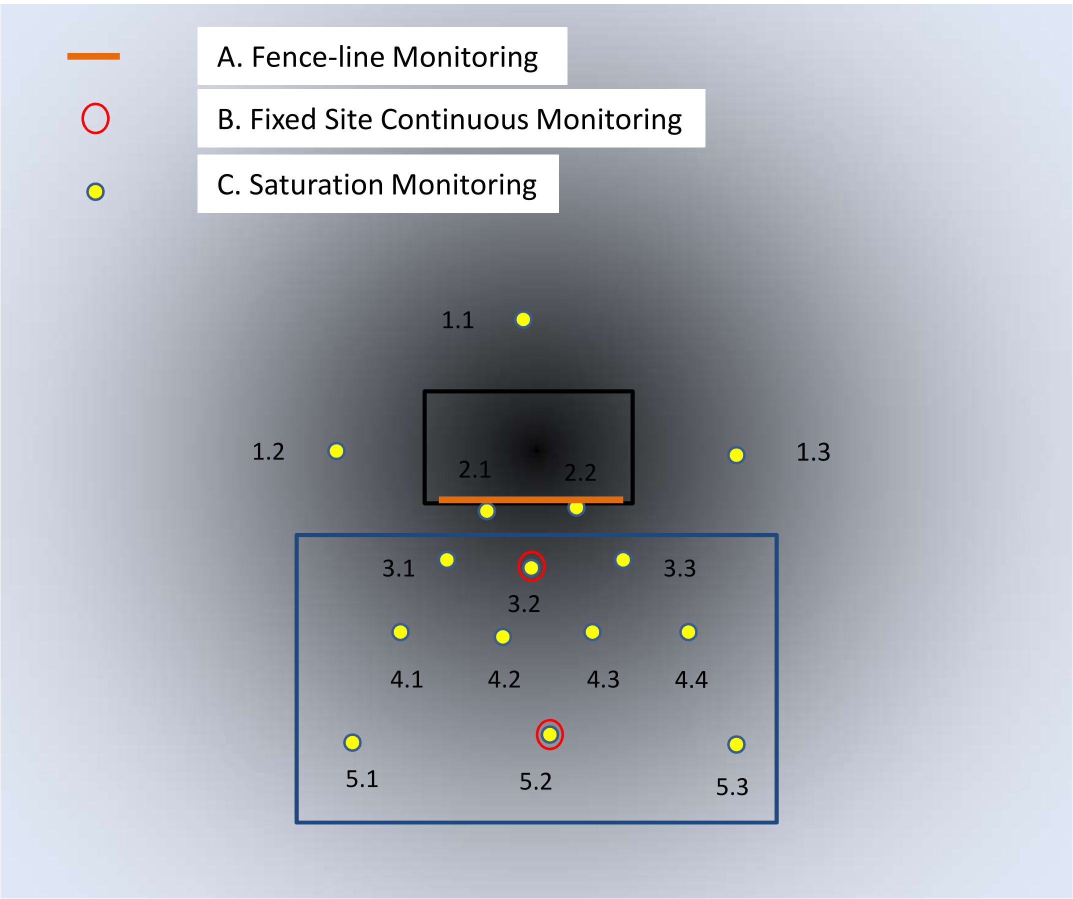

Figure 0-9. Conceptual illustration of a monitoring program for a community (blue rectangle) near a refinery (black rectangle) combining: A) continuous fence-line monitoring; B) fixed site monitoring; and C) multi-site saturation monitoring.

Table 0-12. Minimum detection limits for alternative continuous and time-integrated sampling methods for target compounds.

				Continuous						**Time-integrated Samping**				
		Risk Exposure Levels (REL)		Point			Open Path 500m	OpenPath 100m	Area	Time-integrated Point sample (up to 24 hrs)			Saturation Monitoring (7-day)	
Target Compound	Major Sources[1] (>10%)	Acute[2] (µg/m3)	Chronic[2] (µg/m3)	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	9[4]	35				100		40				
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			0.001/ 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 0-13. 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
	Met-One	EBAM	<50W 12VDC, Solar	PM2.5	10 ug/m3	1 hr	$ 10,000	$ 700	Outdoor	Rack mount	designed for temporary, outdoor use. Solar power option.
	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	Low density Teflon tape, optional cover tape to preserve spots for analysis
	Thermo	Sharp	300 W	PM2.5	<5 ug/m3	1 min			Indoor	Rack mount	continuous readings from integral neph
TEOM	Thermo	1405	440 W	PM2.5	<5 ug/m3	10 min	$ 30,000		Indoor	Rack mount	Federal Equivalent Method for PM10 and PM2.5
auto-XRF tape sampler	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 Measurment 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	OPSIS, 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 commerically available, requires service contract with operators
SOF	FluxSense			H2S, select VOC	>0.5 mg/m2 (flux)		N/A	$200k/ survey	Mobile	van	not commerically 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	

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

Table 0-14. 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 (rechargable) 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	

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, H_2S, SO_2) 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.

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 SO_2, H_2S, speciated VOC, wind speed and direction at a minimum. Adding NO_2, 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 SO_2 + H_2S 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.

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 0-9. Cost of saturation monitoring for SO_2, H_2S, 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 SO_2, H_2S, and speciated VOC at only a subset of the sites. Considering the monitoring configuration shown in Figure 0-9 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 A (Ogawa samplers) and B (Radiello samplers).

Incident Monitoring

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.

Mobile Sampling

The existing BAAQMD monitoring van (described in Appendix C) 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 H_2S/SO_2 monitor (see Table 0-13) 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. Examples of recent application of mobile monitoring in the context of exposure assessment are described in Appendix C along with the applicable measurement methods.

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, H_2S, 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.

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 novel 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 skill 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 Tweets 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 feasiblility of such a cooperative incident monitoring plan.

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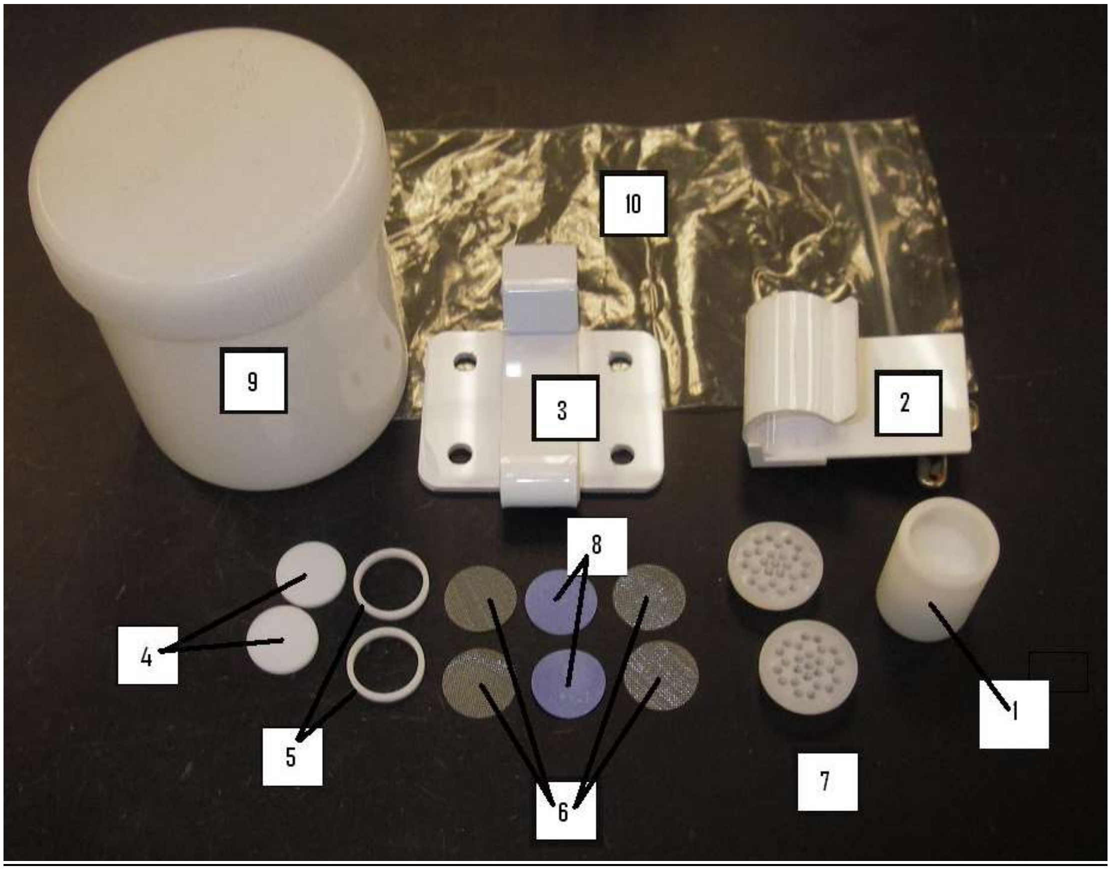
Appendix A

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

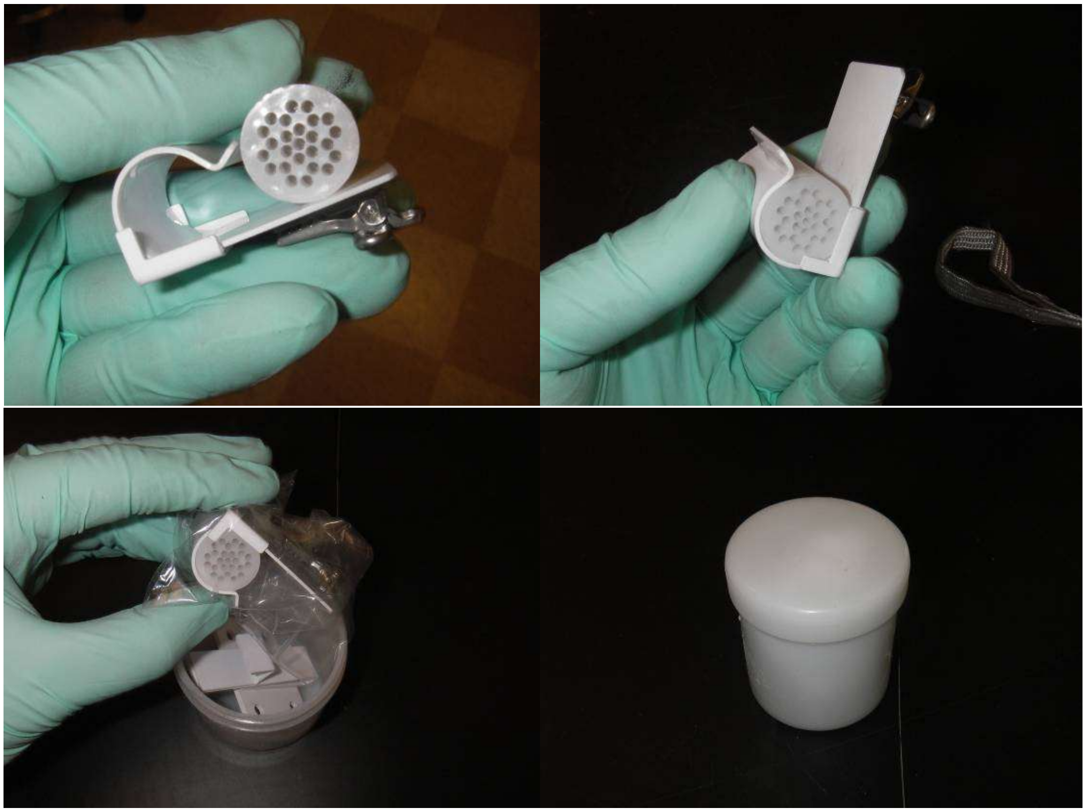
The Ogawa *Pre-Coated Collection Pads* come in a few varieties depending on the application. Specific information on the correct parts for each monitoring application can be found at the company website (www.ogawausa.com).

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 S*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.



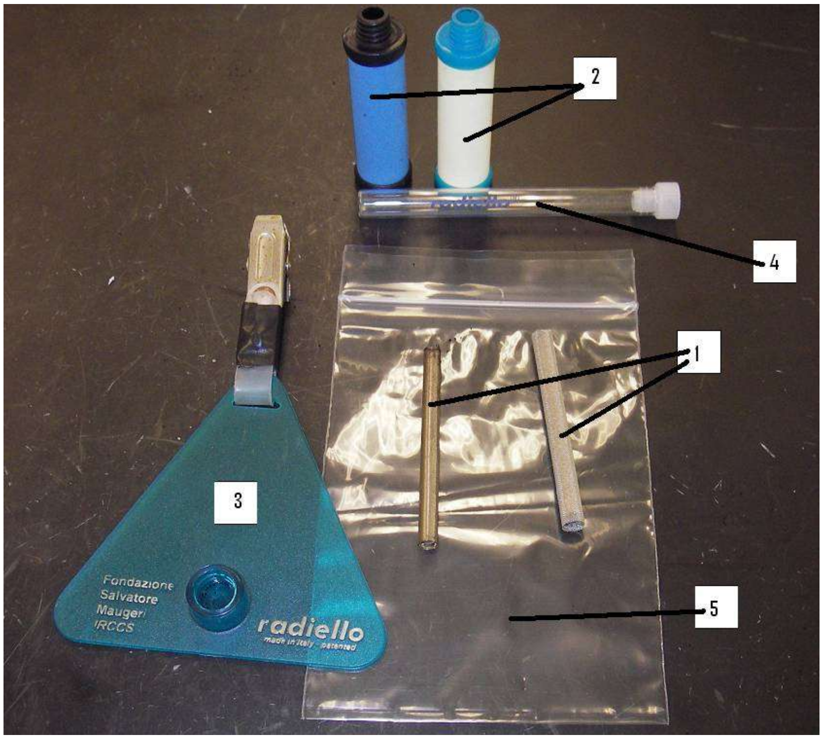
At the sampling site, remove the Ogawa Sampler from the *Opaque Vial* and *Sample Bag*. Attach the sampler to clothing for personal exposure or to the *Mounting Bracket* for ambient monitoring as shown below.

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 B

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 D*iffusive 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 C

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.

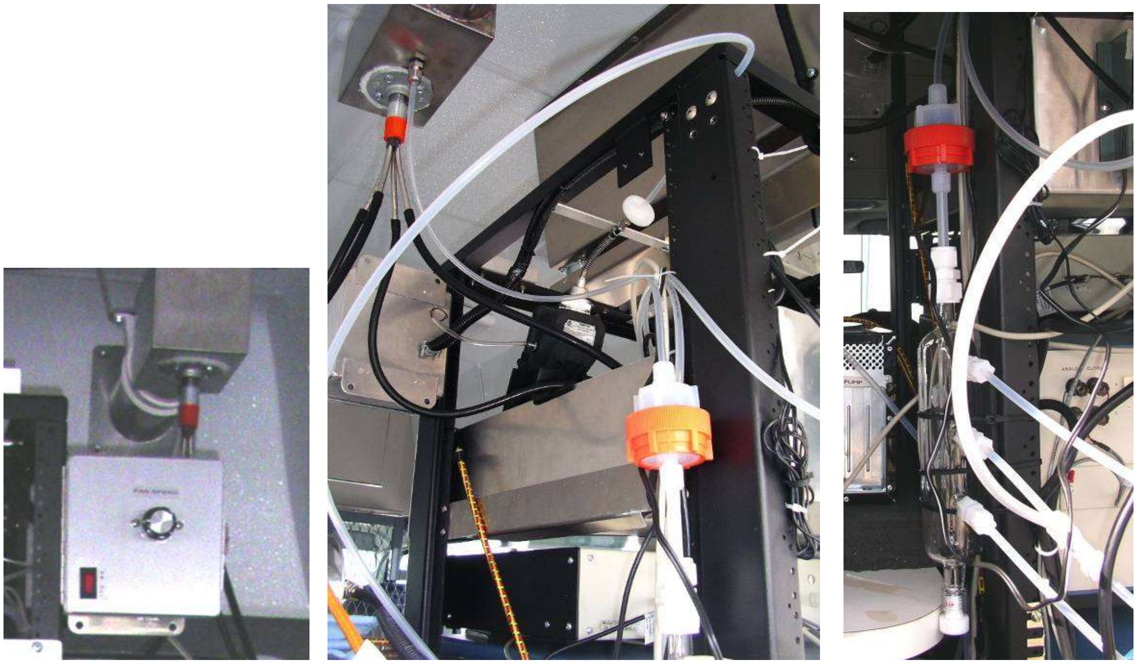
Ambient air is drawn into the van via an electric fan-driven roof duct into glass or stainless-steel plenum for connecting gas and particle sampling instruments, respectively. The air velocity in the duct can be adjusted via the fan control to minimize anisokinetic sampling effects when making aerosol 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.



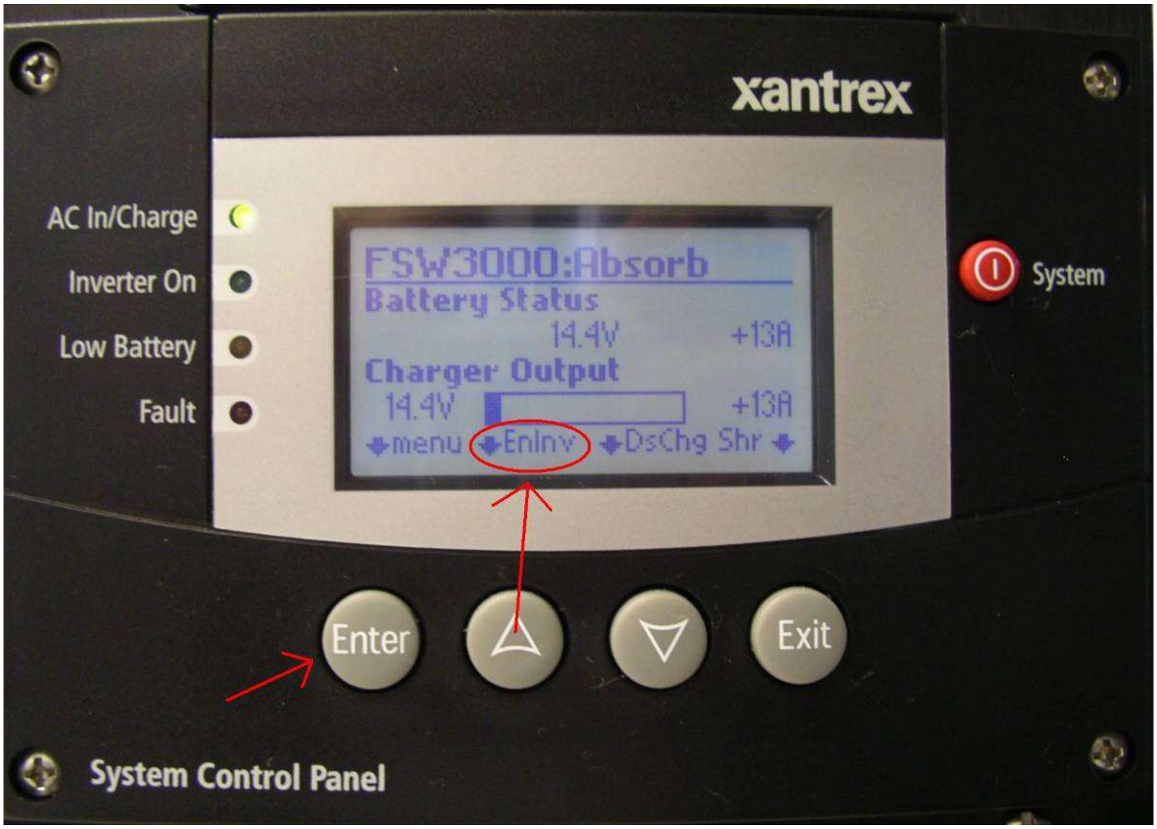
Photos of the inlet duct and fan control, stainless steel plenum exiting duct, and glass plenum with particle filter (replaceable paper disk filter is in the orange cartridge).

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.*



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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.

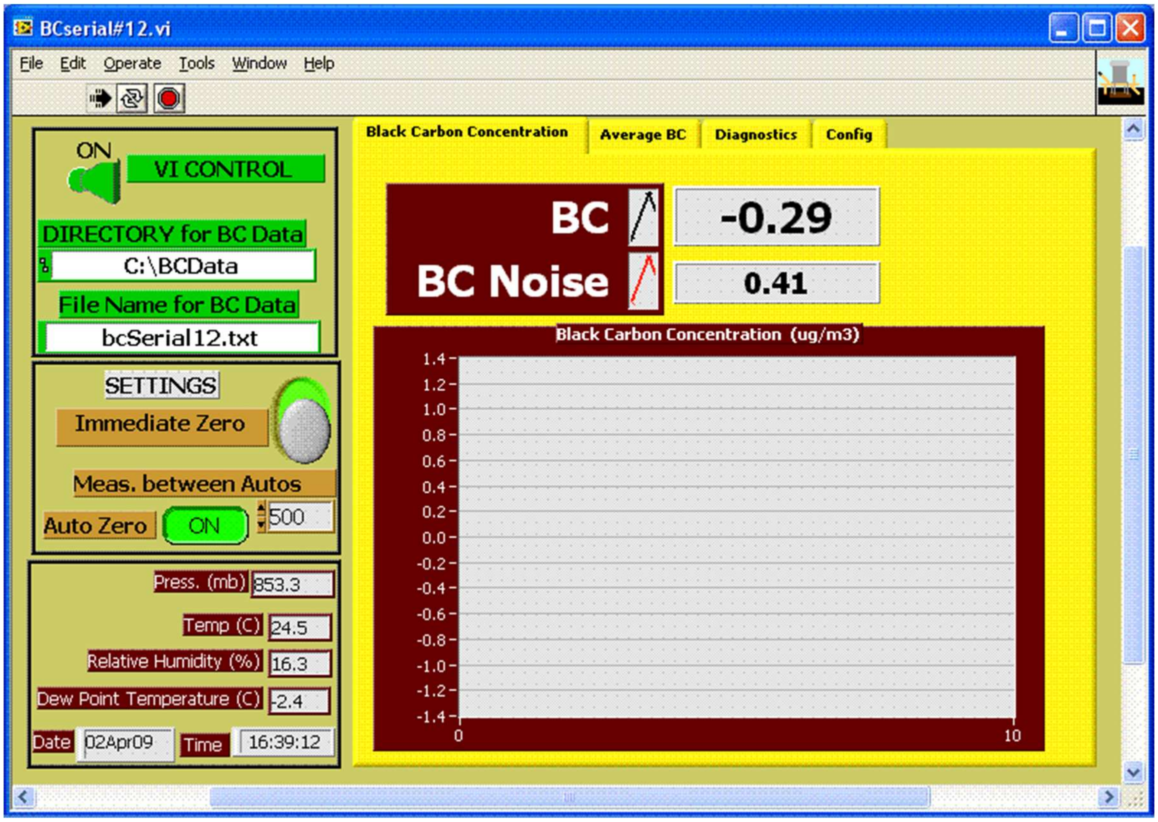
Startup:
Press power switch on front panel.
If logging data to computer the internal datalogging must not be enabled and the averaging time should be set to 10 seconds (default). Otherwise, see instrument manual (pdf file on PC) for internal datalogging and downloading instructions.

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.

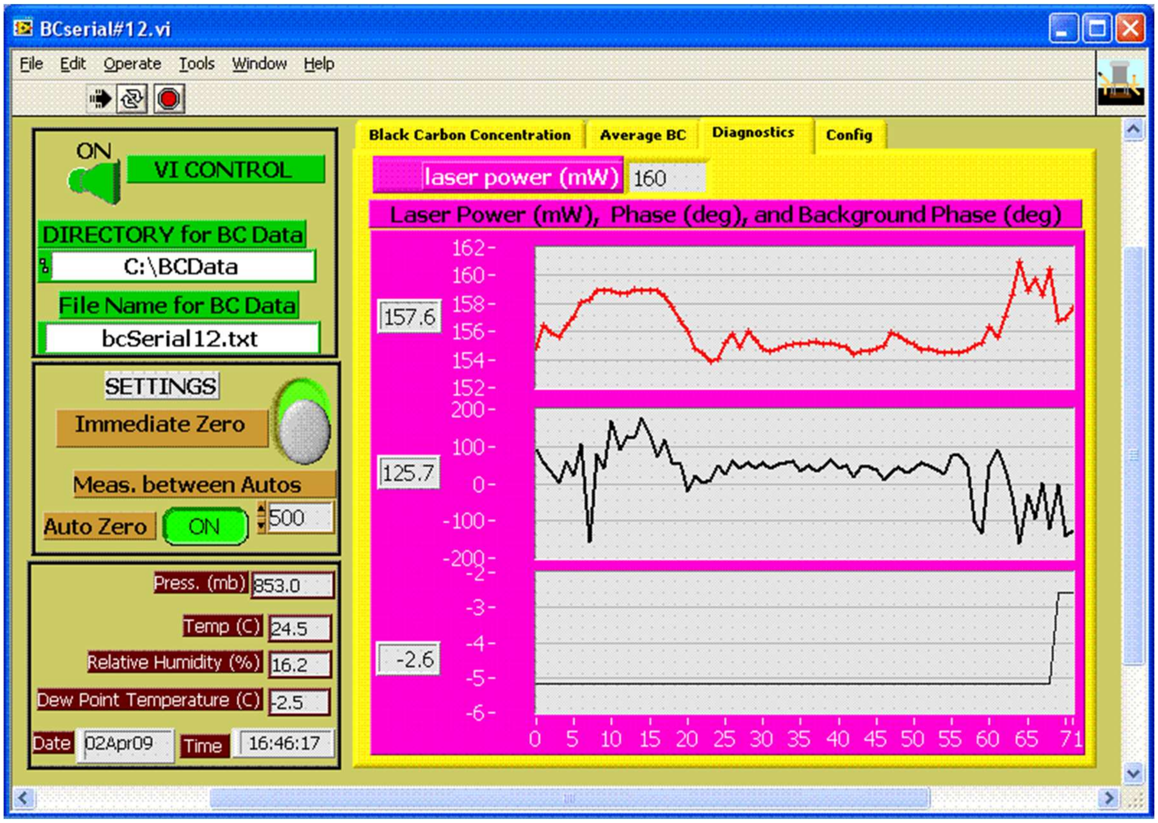
Wireless monitor transmitter connected to USB hub. Wireless monitor must be connected to 12VDC power outlet and to receiver via serial cable. Receiver power supply plugged into 110V outlet.

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.



DIRECTORY for BC Data: C:\BCData
File Name for BC Data: bcSerial12.txt
Meas. between Autos: 500
Auto Zero: ON
Press. (mb) 853.3
Temp (C) 24.5
Relative Humidity (%) 16.3
Dew Point Temperature (C) -2.4
Date 02Apr09 Time 16:39:12
BC -0.29
BC Noise 0.41

Initial screen view of photoacoustic instrument LabView program



ON

DIRECTORY for BC Data: C:\BCData

File Name for BC Data: bcSerial12.txt

Meas. between Autos: 500

Auto Zero: ON

laser power (mW): 160

Press. (mb): 853.0

Temp (C): 24.5

Relative Humidity (%): 16.2

Dew Point Temperature (C): -2.5

Date: 02Apr09

Time: 16:46:17

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.

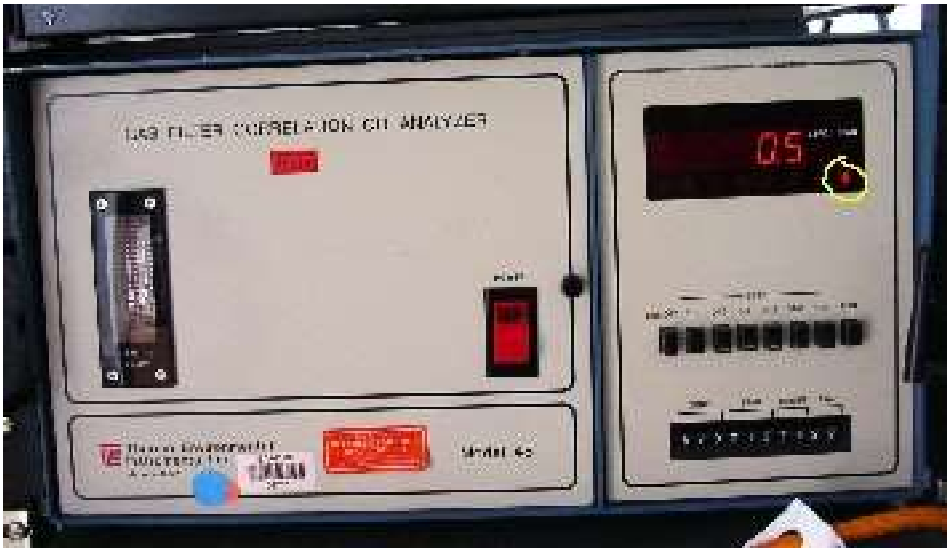
startup:
Replace the alcohol cartridge with a freshly charged one, if necessary. Cartridges must be refreshed after 5-6 hours of operation.
Press black button to start 10 minute warmup cycle. Warmup can be skipped by pressing the enter key.
Start TSI Aerosol Instrument manager software on laptop. Open 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 <u>off</u>.



TEI CO analyzer front panel with light indicating instrument is in Span mode circled – this indicator should be <u>off</u> 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 is 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 stable[4] 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 average[5]. 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.

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[4] *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.*

[5] 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.

AIR MONITORING TECHNOLOGY & METHODOLOGY EXPERT PANEL REPORT & FINDINGS

Convened by

Bay Area Air Quality Management District

July 11, 2013

Acknowledgements –

The Bay Area Air Quality Management District (Air District) wishes to thank both Eric Fujita and David Campbell of the Desert Research Institute (DRI) for their work compiling the *Review of Current Air Monitoring Capabilities near Refineries in the San Francisco Bay Area*. In addition, the Air District wishes to thank members of the Expert Panel listed below for their efforts and time providing input towards the goal of enhancing monitoring efforts at and near Bay Area refineries.

- *George Allen* –Senior Scientist at Northeast States for Coordinated Air Use Management (NESCAUM)
- *Michael Benjamin, Ph.D.* –Chief of the Monitoring and Laboratory Division at the California Air Resources Board (CARB)
- *Kenneth Stroud* (Serving for Dr. Michael Benjamin) –Chief of the Air Quality Surveillance Branch at CARB
- *Philip Fine, Ph.D.* - Assistant Deputy Executive Officer for Science & Technology Advancement at the South Coast Air Quality Management District (SCAQMD)
- *Andrea Polidori Ph.D.* (Serving for Dr. Fine) - Quality Assurance Manager for Science & Technology Advancement at the SCAQMD
- *Jay Gunkelman* – Member of the public and fence line monitoring expert
- *Robert Harley, Ph.D.* –Professor in the Department of Civil and Environmental Engineering at the University of California, Berkeley
- *Thomas Kirchstetter, Ph.D.* - Staff Scientist in the Environmental Energy Technologies Division at Lawrence Berkeley National Laboratory and an Adjunct Professor in the Civil and Environmental Engineering Department at the University of California, Berkeley
- *Denny Larson* – Executive Director, Global Community Monitor
- *Gary Mueller* –Principal Air Quality Consultant with the HSE Services, Environmental Sciences Department of Shell Global Solutions (US) Inc.
- *Jay Turner, Ph.D.* - Associate Professor of Energy, Environmental and Chemical Engineering at Washington University in St. Louis
- *Gwen Yoshimura* –Air Monitoring Lead in the Air Quality Analysis Office with the Environmental Protection Agency (EPA), Region 9

Executive Summary

The Bay Area Air Quality Management District (Air District) contracted with the Desert Research Institute (DRI) to compile a report that provided a background on current air monitoring capabilities near Bay Area refineries and assembled a panel of air monitoring experts from around the country to review and comment on the DRI report. The Panel agreed that the report adequately addressed the issues and complexity involved with monitoring air quality around Bay Area refineries, in general. They also agreed that the report provided a good starting point for developing further guidance. However, the Panel noted that the report did not include the operating and maintenance costs for each monitoring option and should simply be used to compare and evaluate each monitoring option. In addition, the report could not include every available and applicable monitoring technology but was intended to be a starting point for discussion of options and as a way to evaluate options. Finally, the scope of the report did not allow for a complete discussion of meteorological measurement or other methodologies that might be utilized to estimate exposures.

The Panel generally agreed that an approach that utilized a combination of fence line, community, and mobile monitoring would be required to adequately define exposures during normal operations and when upsets and incidents occur. The fence line monitoring would be leveraged primarily to identify non-routine emissions during normal operation, while the community monitoring would be utilized to develop spatial gradients of chronic exposures. Mobile monitoring would be used to supplement on-going monitoring during major upsets and incidents and to help develop information on spatial variability.

The Panel also recommended that compounds of interest should be identified based on the monitoring goals with relationships and correlations between compounds of interest developed to minimize costs. While it was recognized that not all compounds of interest need to be measured, volatile organic compounds (VOC) should be the primary, initial focus.

Panel members generally agreed that information should be provided to the community through a well-designed website that provides appropriate context and allows more sophisticated users to access more complex and complete data. However, alternate methodologies should also be developed to inform members of the public who lack computer access or need additional information. In addition, a means for the public to provide their observations and experiences should be included and that they should be informed of actions taken in response to observations to build trust.

Data quality and time resolution were major topics of discussion, with Panel members again suggesting that different approaches be utilized for different monitoring goals. For example, fence line monitoring should employ higher time resolution than community monitoring, but community monitoring time resolutions should be increased during upsets and incidents when acute exposures are of concern.

Since technologies are rapidly evolving, the Panel recommended that regular review of available instrumentation should occur with a methodology to cost-effectively update the in-place network. Lines of open and honest communication should be established between industry, the community and regulators to ensure appropriate value is provided by the developed network.

Background

On August 6, 2012, a substantial fire occurred due to a hydrocarbon leak at a crude oil processing unit at the Chevron Refinery in Richmond, CA. The fire resulted in a large plume of black smoke and visible emissions from a refinery flare. The Contra Costa County Health Department issued a community warning and ordered a shelter-in-place for about five hours in Richmond, San Pablo and North Richmond. Thousands of residents sought medical treatment, with most suffering respiratory and/or eye discomfort.

The August 6, 2012 incident prompted the Bay Area Air Quality Management District (Air District) staff and Board of Directors to identify a series of follow-up actions to enhance the Air District's response to similar incidents (Board of Directors, October 17, 2012). One of these actions was to convene a panel of air monitoring experts (Expert Panel) to recommend technologies, methodologies and tools to enhance community air monitoring capabilities near refineries. Another related follow-up action was the development of a new Air District Petroleum Refining Emissions Tracking rule, which would include a requirement that Bay Area refineries establish and operate fence line and community air monitoring systems consistent with guidelines to be developed by the Air District.

As part of this effort, the Air District contracted with Desert Research Institute (DRI) to compile a report that provides background on current air monitoring capabilities near Bay Area refineries and potential air monitoring technologies, methodologies and tools to:

- Provide air quality information for communities near refineries
- Gather data to evaluate health impacts associated with air quality near refineries
- Track air quality changes and trends over time near refineries

The DRI report reviewed and evaluated measurement approaches and methods for assessing the impacts of refinery emissions on ambient concentrations of criteria and air toxics 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 plant emission releases to the community; community-scale monitoring with varying time scales to evaluate potential chronic or acute health impacts; and episodic monitoring during upsets and incidents. These objectives were reconciled with available air quality data from existing Air District 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 were suggested with scalable options. It was the intent of the Air District to utilize the DRI report to provide the Panel with a starting point of discussion.

DRI Report

The DRI report, Review of Current Air Monitoring Capabilities near Refineries in the San Francisco Bay Area (October 29, 2013 Revision), was designed to provide the expert panel with a starting point for discussion by:

- Evaluating current air monitoring capabilities
- Developing a matrix of additional technologies, methodologies and tools that could be employed to enhance air monitoring capabilities and provide information about emissions from refineries
- Providing costs associated with the technologies, methodologies and tools
- Outlining the potential advantages and disadvantages of each option
- Providing a short description of the process used and how the matrix was developed

The DRI report is available at:
http://www.baaqmd.gov/~/media/Files/Technical%20Services/DRI_Final_Report_061113.ashx

DRI Report Executive Summary

The DRI report provided historical and emissions information from the five Bay Area refineries, which includes Chevron in Richmond, Shell in Martinez, Tesoro in Martinez, Valero in Benicia and Phillips 66 in Rodeo. The refineries account for approximately half of the PM2.5, reactive organic gases (ROG) and NOx and over 90% of the SO2 from stationary sources in the Bay Area. In addition, the report also provided a review of available toxic air contaminant (TAC) information and health risk assessment information and findings. This information could be used to help develop a list of compounds of interest and appropriate sampling methodologies that could be employed near the refineries.

DRI provided a review of current Air District and facility monitoring throughout the Bay Area to determine if and where enhancements could be made. This evaluation included meteorological, individual compound, and special study data as well as incident response capabilities. While DRI concluded that Air District monitoring sites adequately represent pollutant concentrations throughout the Bay Area in general and within approximately a mile or two of the refineries, in particular, they may not be representative of concentrations near fence lines and during upsets when localized conditions and short duration events may not be adequately captured.

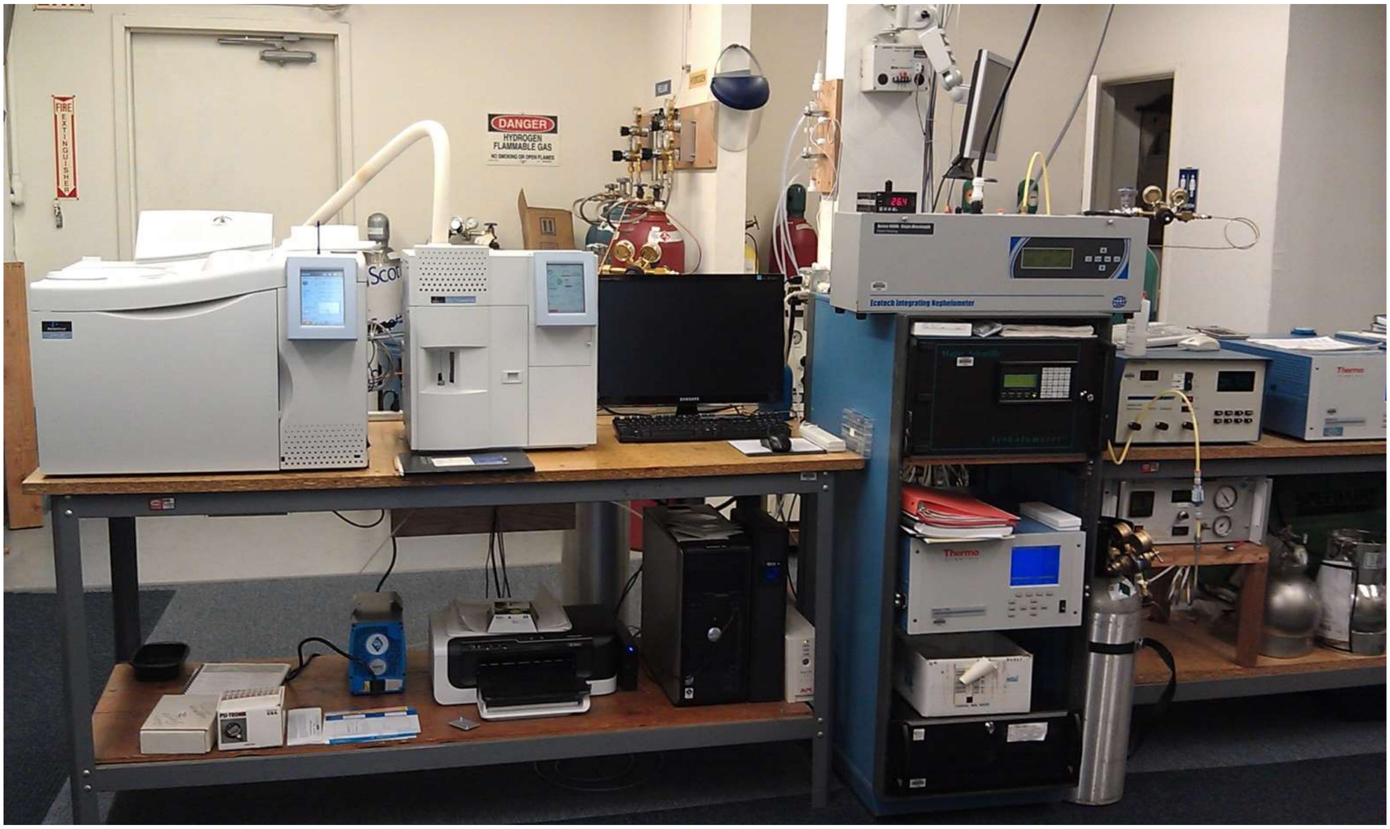
Current commercially available instrumentation was investigated and information and options provided. The instrumentation fell into four major categories:

- Emissions flux measurements that attempt to determine actual emissions rates from facilities

- Optical remote sensing that uses a light source to measure compounds that pass through a light beam and that can be used to determine compound concentrations across a distance
- Saturation monitoring that uses many sampling devices that are usually exposed for longer periods of time to determine more detailed spatial variations in specific compound concentrations
- Continuous monitoring that uses a less instrument “dense” network than saturation monitoring to provide better time resolved information.

The report then provides information on commercially available measurement technologies that fall into these general categories. In addition, it provides examples of individual equipment and methodologies that could be utilized. The report also covers potential measurement technologies and methodologies that could be effectively utilized during short duration upsets and incidents.

The report’s appendices provide operating procedures that could be utilized to perform saturation monitoring and mobile monitoring that could be employed during short duration events and to help determine spatial variability.


FIRE EXTINGUISHER
DANGER
HYDROGEN
FLAMMABLE GAS
NO SMOKING OR OPEN FLAMES
Ecotech Integrating Nephelometer
Thermo
Thermo

The Expert Panel Members

George Allen – George Allen is a Senior Scientist at NESCAUM (Northeast States for Coordinated Air Use Management), an interagency association of the eight Northeastern States. He received a B.S. in Electrical Engineering from Tufts University in 1974. At NESCAUM, Mr. Allen is responsible for monitoring and exposure assessment activities across a range of wide range of air topics, including regional haze, air toxics, on and off-road diesel, near-road, wood smoke, and continuous aerosol measurement technologies. He is the author or co-author of more than 40 peer-reviewed journal papers on development and evaluation of measurement methods, exposure assessment, and air pollution health effects. Before joining NESCAUM in 2002, Mr. Allen was on the professional staff at the Harvard School of Public Health (HSPH) in Boston for more than 20 years, working on a wide range of EPA and NIH funded air pollution studies. While at HSPH, he developed several patented techniques for real-time aerosol measurements.

Mr. Allen serves as the staff lead for the NESCAUM Monitoring and Assessment Committee. He represents states interests to EPA as a member of the National Association of Clean Air Agencies (NACAA) Monitoring Steering Committee and the chartered EPA Clean Air Science Advisory Committee (CASAC).

Michael Benjamin, Ph.D. – As Chief of the California Air Resources Board's Monitoring and Laboratory Division, Dr. Benjamin oversees a staff of approximately 170 scientists, engineers, and field technicians who operate the statewide ambient air quality monitoring network, provide air monitoring capabilities following emergency air releases, conduct chemical analyses of ambient and vehicle exhaust, certify vapor recovery equipment, and develop regulations to reduce evaporative emissions from the gasoline distribution system and off-highway gasoline-fueled equipment. Dr. Benjamin has served in a variety of staff and management positions developing emissions inventories in support of regulations and air quality planning and more recently overseeing the Board's economic analysis and extramural research programs. Prior to beginning his career at the Air Resources Board, Dr. Benjamin worked for five years conducting oceanographic research at Columbia University's Lamont-Doherty Earth Observatory. Dr. Benjamin received his B.S. in Geology from Beloit College, M.S. in Earth Sciences from Dartmouth College, and Ph.D. in Environmental Science and Engineering from the University of California, Los Angeles.

Kenneth Stroud (Serving for Dr. Michael Benjamin) – Mr. Stroud is Chief of the Air Quality Surveillance Branch at the California Air Resources Board. He oversees regulatory air monitoring at more than forty air monitoring locations statewide and has participated in numerous emergency response and community air monitoring studies over the last 26 years with the ARB. Mr. Stroud holds a Bachelor's degree in Chemistry from Cal Poly, San Luis Obispo.

Dave Campbell – Mr. Campbell is an Associate Research Scientist at the Desert Research Institute, whose current research interests are the characterization and apportionment of gaseous and aerosol pollutants and measuring the influence of mobile source contributions and energy production on photochemical processes and human exposure. Prior to joining DRI he spent 13 years working for the NPS/IMPROVE program, monitoring visibility reducing particles impacting protected federal lands. He received MS degrees in Ecology and Engineering from UC Davis and Rensselaer Polytechnic Institute, respectively, and a BS in chemistry from the State University of NY.

Philip Fine, Ph.D. - Dr. Philip Fine is the Assistant Deputy Executive Officer for Science & Technology Advancement at the SCAQMD (South Coast Air Quality Management District). Dr. Fine oversees the SCAQMD ambient network of over 35 air monitoring stations, the SCAQMD laboratory, and numerous special air monitoring projects focusing on air toxics and the local impacts of air pollution. His previous responsibilities at the SCAQMD have included developing the Air Quality Management Plan, strategies for particulate matter control, climate and energy, meteorology and forecasting, air quality evaluation, emissions reporting, and air toxics risk assessment. Dr. Fine serves as SCAQMD's member for the California Air Resources Board legislatively mandated Research Screening Committee. Prior to joining the SCAQMD, Dr. Fine was a Research Assistant Professor at the University of Southern California, Los Angeles where he taught courses and conducted extensive research on particulate pollution and its health effects, resulting in over 45 peer-reviewed scientific publications. Dr. Fine received his Ph.D. from California Institute of Technology in Environmental Engineering Science, and his bachelor's degree in Mechanical Engineering and Materials Science & Engineering from the University of California, Berkeley.

Andrea Polidori Ph.D. (Serving for Dr. Fine) - Dr. Andrea Polidori is the Quality Assurance Manager for Science & Technology Advancement at the SCAQMD (South Coast Air Quality Management District) and is responsible for the development and implementation of quality assurance control methods, plans, procedures, and programs. He is also involved in the analysis of data collected from numerous field activities and air monitoring projects. Prior to joining the SCAQMD, he was a Research Assistant Professor at the University of Southern California (Los Angeles) where he taught courses and conducted extensive research on particulate pollution and its health effects, resulting in over 30 peer-reviewed scientific publications. He received his Ph.D. in Environmental Sciences from Rutgers University (New Brunswick, NJ) and his bachelor's degree, also in Environmental Sciences, from Urbino University (Urbino, Italy).

Jay Gunkelman – Mr. Gunkelman, Quantitative Electroencephalography (QEEG) Diplomate, has served as president of The International Society for Neurofeedback and Research, as well as a board member and treasurer of the Association for Applied Psychophysiology and Biofeedback and is a past-president of the Biofeedback Society of California. Mr. Gunkelman was the first EEG technologist to be certified in QEEG (1996) and was granted Diplomate status in 2002. He co-authored the textbook on EEG artifacting (2001) and has conducted, published or participated in hundreds of research papers, articles, books and international meetings. Mr. Gunkelman is co-founder and Chief Science Officer of Brain Science International and is a popular lecturer at neuroscience meetings worldwide. For the purposes of the BAAQMD panel, Mr. Gunkelman's involvement is related to his community work designing the oldest continuously operated remote sensing fence line system, with internet community reporting, monitoring the Phillips 66 facility between Rodeo and Crockett, CA. This includes FTIR, UV, TDLS and point source monitoring, as well as meteorological data, all with internet tracking. These system's QA/QC documents and on-line efficiency standards as well as community access are relevant to the interests to the panel.

Robert Harley, Ph.D. – Dr. Harley is a Professor in the Department of Civil and Environmental Engineering at the University of California, Berkeley, where he has been on the faculty since 1993. He holds a bachelor's degree in Engineering Science (Chemical Engineering option) from the University of Toronto, and both M.S. and Ph.D. in Environmental Engineering Science from the California Institute of Technology. Dr. Harley's research focuses on air quality and sustainable transportation; he is an author of over 80 papers published in peer-reviewed scientific journals.

Thomas Kirchstetter, Ph.D. - Dr. Kirchstetter is a Staff Scientist in the Environmental Energy Technologies Division at Lawrence Berkeley National Laboratory and an Adjunct Professor in the Civil and Environmental Engineering Department at the University of California, Berkeley. His research focuses on air quality and climate-related implications of particulate matter, including emission trends and evaluation of emission controls. He has authored or co-authored over 50 publications on these topics and serves as an editor for the Aerosol Science & Technology Journal and the Journal of Atmospheric Chemistry and Physics. Dr. Kirchstetter holds a B.S. in atmospheric science and mathematics from the State University of New York, Albany and an M.S. and a Ph.D. in environmental engineering from UC Berkeley.

Denny Larson – Mr. Larson has nearly 30 years of experience as a community organizer and campaigner working with industrial communities fighting for justice. He developed the first national network in the U.S. focused on oil refineries and the corporations that own them as well as innovating the Bucket Brigade community air sampling system. In his work, he has assisted communities in 27 countries and 100 partner groups establish their own air monitoring network. Mr. Larson has published a series of community organizing handbooks and co-authored a variety of environmental legislation and regulation pertaining to air pollution, accident prevention and environmental monitoring policies at the local, regional, state, national and international level. His work as paid off, as he's negotiated two dozen binding agreements with major polluters in conjunction with impacted communities to reduce tons of unnecessary pollution and create direct community oversight.

Gary Mueller – Mr. Mueller is a Principal Air Quality Consultant with the HSE Services, Environmental Sciences Department of Shell Global Solutions (US) Inc. He has a Master's Degree in Environmental Engineering from the University of Missouri-Columbia, and has worked for Shell in a variety of environmental positions for over 32 years. His experience includes work in water and wastewater treatment, groundwater treatment, and the past 15 years in air quality management programs. His job assignments have included both environmental research and technical support to operations. One of his responsibilities within Shell Global Solutions is to insure the development and maintenance of a skill pool that has the necessary tools and competencies to assess and evaluate the impact of air emissions from Shell and other 3rd party customers' operations on the environment and to mitigate any such impacts. During his career at Shell, Mr. Mueller has authored or coauthored over 20 technical papers and presentations on a variety of environmental topics.

Jay Turner, Ph.D. - Dr. Turner is an Associate Professor of Energy, Environmental and Chemical Engineering at Washington University in St. Louis. His research primarily focuses on air quality characterization and control with emphasis on field measurements and data analysis to support a variety of applications in the atmospheric science, regulation and policy, and health studies arenas. Current research projects include estimating lead (Pb) emissions from piston engine aircraft, high time resolution air toxics metals measurements, and long-term fence line monitoring for gaseous air toxics and particulate matter species at an industrial facility. Dr. Turner currently serves on the Ambient Monitoring and Methods Subcommittee (AMMS) of CASAC, the Independent Technical Advisory Committee of the Texas Air Quality Research Program, and the Health Effects Institute (HEI) project panel for the National Particle Components Toxicity Initiative. Dr. Turner holds B.S. and M.S. degrees from UCLA (1987) and a D.Sc. from Washington University (1993), all in Chemical Engineering.

Gwen Yoshimura – Ms. Yoshimura is an air monitoring specialist in the Air Quality Analysis Office with the Environmental Protection Agency (EPA), Region 9, specializing in ambient air monitoring of lead and sulfur dioxide. She previously worked on air planning issues, focusing on lead and air toxics, in EPA's Region 7 office. Ms. Yoshimura has a B.S. in Earth Systems from Stanford University.

The Expert Panel and Comments on the DRI Report

The Air District sought input from experts in the air monitoring field assembled from throughout the nation. Their knowledge and expertise regarding available technologies, methodologies and tools to enhance air monitoring around refineries will assist the Air District in developing improved air monitoring systems at and around refineries. The entire meeting was webcast and is available here: http://baaqmd.granicus.com/MediaPlayer.php?publish_id=052ef9b8-3bd9-1031-92de-7c92654424e8. This input will be used by the Air District to: (1) further evaluate its current air monitoring capabilities, and; (2) develop additional requirements for community monitoring by the Bay Area refineries as part of the Air District's proposed Petroleum Refining Emissions Tracking Rule (Draft Rule and Workshop Report available here: http://www.baaqmd.gov/~/media/Files/Planning%20and%20Research/Rules%20and%20Regs/Workshops/2013/1215_dr_rpt032113.ashx?la=en).

The Panel provided feedback and comments regarding the DRI report during the meeting and these comments are summarized below. The DRI report was intended to be used as a starting point for discussion about the appropriate technologies, methodologies and tools to consider. The Panel's input, along with the responses by the DRI co-author, David Campbell will be used to develop a path forward for monitoring at and around Bay Area refineries.

In general, the Panel and David Campbell discussed and agreed that pricing included in the report may not accurately represent all costs associated with the equipment presented in the report. The information presented was designed to provide a general idea of costs, since many aspects would depend on unique variables to each application. In addition, there was recognition that it would not be possible to include all current technologies and equipment available in the report. Members were encouraged to provide specific examples of equipment that they believed may be useful in applications for fence line, community and incident response monitoring. There was also general agreement that meteorology technologies and alternative measurement techniques may not have been fully addressed in the report, but were generally addressed later in the Panel's discussions.

Individual Panel members also noted that specific quality control/quality assurance (QC/QA) issues were difficult to address in the report without first knowing all the compounds to be measured and the number and type of devices to be used. In addition, siting issues were difficult to address given the highly localized specifics required to deal with various siting issues. In most instances, these issues were later addressed in comments from the Panel in response to the questions posed to the panel (charge questions).

Individual Panel members also suggested that the Chevron incident, as well as other refinery incidents, could have been summarized and retrospectives developed, and that other methods of determining exposures, such as continuous emission monitoring (CEM) and modeling, could be discussed in the report and should be considered for future consideration. There was also some discussion that Health Risk Assessments (HRAs) used in the report did not incorporate the most recent data and methodologies necessary to be applicable to current conditions. One member also suggested that the report should be summarized and made available with content directed at the general public and utilizing appropriate context so that it could be easily understood.

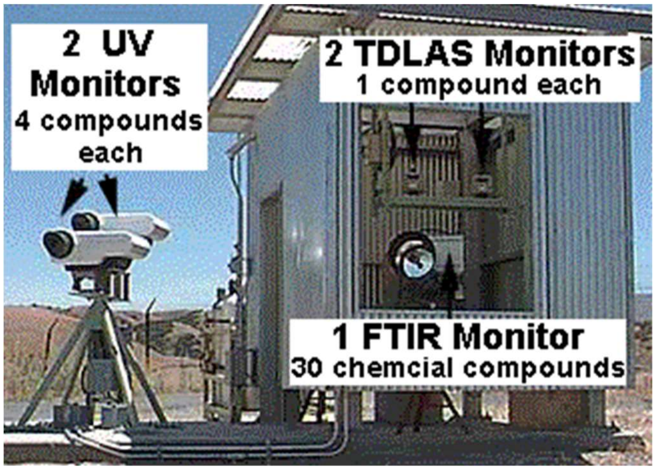
The public was also given an opportunity to comment, and one commenter noted that meteorology technologies were not adequately addressed in the report and that methods of providing information to the public did not adequately address how information might be given context.

A summary of statements made by individual Panel members, and the responses from DRI representative David Campbell, are provided below to provide more information and specifics on the issues discussed. As stated previously, the intent of the DRI report was to foster a conversation among the Panel members so that a more complete and thorough picture of possible monitoring activities could be garnered given the level of expertise and knowledge assembled

Denny Larson - Mr. Larson believed that the costs provided in the report did not represent a hardship to industry given the potential to emit and that typical annual average wind roses should not be used to site community and fence line monitoring since there are large short duration meteorological variations not captured by these annual averages. He also commented that operating culture at refineries was not addressed, that monitoring activities could be a good first step to changing operating culture, and that current and future increased housing density around refineries should be discussed.

Response from David Campbell – Mr. Campbell provided context for the cost information and stated that expected costs of fence line monitoring compared to traditional monitoring are expected to be high. He also pointed out that meteorological measurements used were from the refineries themselves and were not at the elevation of the stacks, so may not be representative of winds at elevation and that modeling would utilize much higher time resolved meteorological data. Mr. Campbell agreed with Mr. Larson regarding the potential that well informed monitoring may have the desired effect of eliciting proactive action on the part of refineries and cause a change in operating culture.

Gary Mueller – Mr. Mueller pointed out that monitoring system design, infrastructure improvement, equipment operating and maintenance and other costs were not included in the report and would be difficult to accurately quantify in a general way. He also believed that inventory emissions, especially for particulate matter (PM) may not be representative, especially given that Bay Area plants are gas fired. As a result, the compounds measured need to be correctly prioritized.



Response from David Campbell – Mr. Campbell agreed that the majority of cost information was associated with capital costs and did not include installation and operational costs, as these costs are specific to the facility and difficult to estimate. He also agreed that HRA and emissions estimates should be updated and validated.

Ken Stroud – Mr. Stroud believed that the report should contain a retrospective of the Chevron incident and that continuous emission monitoring (CEM) and source test emission calculations could be used in modeling to estimate exposure.

Response from Air District staff and Denny Larson – Staff and Mr. Larson discussed the various methods used to characterize the Chevron incident. Staff also stated that CEMs located throughout the refineries could be used in various ways to provide information to the public.

Jay Turner – Professor Turner, pointed out the complexity of emissions associated with Bay Area refineries, believed a discussion of the health risk assessment (HRA) should be included to address changes in methodologies that have occurred over time and potential errors inherent in the HRA process.

Response from David Campbell – Mr. Campbell stated that the HRAs were the latest available. He also pointed out that fugitive emissions, which are extremely difficult to quantify, would greatly affect the compound profiles from each refinery and, hence, the type of monitoring needed.

Jay Gunkelman – Mr. Gunkelman believed that while the cost estimate may not include everything, the refineries ability to pay should be included if cost estimates are revised upward. He also pointed out that long-term data from fence line monitoring is available online, though it may be available on other websites. He believed more traditional point source monitoring locations, such as Ground Level Monitors (GLMs), are important to have as a backup to fence line monitoring and that was not addressed in the report. He stated the importance of including both upwind and downwind measurements and provided examples at various Bay Area refineries to illustrate this point. He also believed it important to include a discussion of path length distance associated with open path measurement systems.

Response from David Campbell – Mr. Campbell agreed that upwind and downwind monitors are critical, though with the complex topography and meteorology in the Bay Area, this can be a difficult task to accomplish. He also mentioned the need for highly trained staff to accomplish the majority of measurements discussed.

George Allen – Mr. Allen pointed out that the report may not have addressed the issues associated with appropriate quality control screening as real-time data are made available to the public.

He believed that many alternative methodologies were not addressed in the report and should be considered, examples provided included:

Flux estimate monitoring (open path monitoring with a vertical component in addition to the horizontal component); adequate meteorological monitoring, including measurements at various elevations; video monitoring; seven-wavelength Aethalometers; total sulfur; short term PM measurement; Condensation Particulate Counter (CPC); ThermoScientific PDR and/or ADR 1500, and; SynSpec Benzene, Toluene, Ethyl Benzene and Xylenes (BTEX). He pointed out that equipment and operational costs have been lowered significantly over time and that there are now many sensors available at low cost, though he could not vouch for the accuracy of these instruments.

In addition, he believed that the following issues involving identified methodologies may not have been adequately addressed:

Uptime of Open Path; the costs and benefits of saturation/community scale monitoring; cheaper "do-it-yourself" measurements being investigated by EPA's Office or Research and Development (ORD). He also cautioned that emissions inventory estimates, especially older ones, tended to underestimate actual emissions, especially those associated with fugitive sources.

Response from David Campbell – Mr. Campbell noted that continuous PM measurements were not covered in-depth in the report and that composition would be needed to determine source. He agreed in general with Mr. Allen's recommendations for particular instrumentation not included in the report.

Gwen Yoshimura – Ms. Yoshimura suggested that the benefits of identifying specific compounds (tracers) associated with refinery operations and performing tracer studies to aid in modeling and equipment location could be included.

Response from David Campbell – Mr. Campbell pointed out that there are no really well defined tracers associated with the particular individual refineries.

Robert Harley – Professor Harley noted that decreasing concentrations of benzene and associated compounds were likely caused by better mobile source controls, that measuring organic compounds other than BTEX is useful, that higher time resolution for PM measurement was important, that odor and smoke on both a chronic and acute scale were critical to consider and he endorsed using flux estimate monitoring at each refinery.

Andrea Polidori – Dr. Polidori suggested that an Executive Summary of the report be produced for the community and noted that a study of flux estimate monitoring was being performed near a Southern California refinery by UCLA. He also suggested that a combination of monitoring techniques could be employed to provide better overall monitoring, such as using total hydrocarbon measurement to trigger canister sampling for laboratory analysis if measurements exceeded a predetermined level, and methods such as this were not addressed in the report.

Response from David Campbell – Mr. Campbell stated that the report contained only commercially available technologies.

Members of the public – Members of the public believed that human monitoring should be addressed in the report, providing a more holistic approach, that data be presented in a way that the public could understand, that meteorological monitoring in four dimensions be addressed for both fixed and mobile equipment, that trajectory modeling capabilities be addressed, that exposure information be provided, that other agencies be included and that satellite evaluation be considered in the report.

Response from David Campbell – Mr. Campbell provided information requested in email for saturation monitoring which were contained in the report.

Gary Mueller – Mr. Mueller pointed out that there are major differences in flux measurements versus direct concentration measurements and, therefore, there are potentially large, unqualified errors that may be associated with flux emissions estimates, particularly regarding the meteorological components. He also stressed that it is important to concentrate on what measurements are of value to both the community and industry, and that overall monitoring goals need to be well defined.

The Expert Panel Addresses Charge Questions

The charge questions the Air District developed for the Panel to consider and member comments are presented below. These comments and input provide a wide range of ideas to consider along with those developed in the DRI report. The Air District intends to use this input to develop guidance for air monitoring activities at Bay Area refineries.

The charge questions considered were:

- *What should the size and spatial orientation of a network of monitors be around refineries*
- *What network components should be considered (compounds measured, technology and instrumentation used, methodologies applied, air quality assessment tools utilized, etc.)*
- *How should the data be provided to the public*
- *What should be considered when developing measurement quality objectives, such as:*
  - *What type of instrument siting criteria should be used*
  - *What should the time resolution of the equipment be*
  - *How often should the instrumentation be calibrated*
  - *What should the accuracy/precision/completeness requirements of the data be*
  - *What other quality control/quality assurance requirements should be put in place*
- *What technologies, methodologies and tools could be employed to augment any fixed network to better quantify pollutant variations over space and time, especially during short duration incidents*
- *What emerging technologies might be utilized in the future to further enhance community air monitoring capabilities*

Summary of Comments

In general, the Panel agreed that a combination of measurements would be required to adequately provide the public with information regarding emissions from refineries in the Bay Area. Members generally agreed that fence line monitoring, particularly open path monitoring that provided information along refinery boundaries, was useful. However, these systems did not provide information about actual community exposures and concentration gradients as distance from fence lines increased. Therefore, monitoring within the community was necessary to capture this information. Members generally agreed that this community monitoring would require a flexible approach with a combination of traditional, fixed-site regulatory air monitoring and more dense, lower cost methods that would allow for better spatial coverage. This coverage should utilize a "layered" gradient approach that focused on near source measurement to help define concentration gradients. During incidents and upsets, it was recognized that a fixed network would likely not adequately characterize localized and highly variable exposures and that mobile monitoring would be the best methodology to capture these emissions. There was also discussion of the usefulness of emission flux measurements to determine the accuracy and variability of emissions inventories. Most Panel members agreed that the DRI report provided appropriate information on the various general techniques available with the appropriate goals and strategies identified in both the report and presentation provided.

The Panel also discussed and generally agreed that compounds of interest should be identified and investigated with relationships and correlations developed to better identify appropriate monitoring goals. It was also generally recognized that not all compounds of interest should be measured, that volatile organic compounds (VOC) should be the primary focus, and that every in-place, available resource should be utilized and/or leveraged to provide information to the public, such as the existing air monitoring network, CEMs and HRAs.

The Panel generally agreed that the data collected should be provided to the public through an easily understood web interface with appropriate context provided. However, alternate methodologies should also be developed to inform members of the public who lack computer access or need additional information. The context should include ways for the public to compare measurements to other locations and to appropriate health indicators and to recognize when values were below instrumentation's level of detection. In addition, there should be ways for more sophisticated users to access and download more complex and/or historical data. Most members of the Panel indicated that the website should employ ways for the public to provide information back to industry and the Air District regarding their experiences and observations. There was much discussion about how to address data quality and the removal/notation of data that did not meet desired quality bench marks. Most members agreed that data completeness was critical, with some members of the Panel representing the community being less concerned about issues arising from data quality.

The Panel generally agreed that higher time resolution was desirable, with the recognition that time resolution and accuracy needed to be appropriately balanced. It was also generally agreed that time resolution depended upon the monitoring goal associated with the measurement and that some flexibility should be developed to address this issue. For example, fence line monitoring should have a higher time resolution, on the order of five minutes, while community monitoring of chronic exposures could have times on the order of hourly, or daily, depending on the monitoring need. However, during incidents or upsets, the community monitoring time resolution should be increased to represent more acute exposures and mobile monitoring should have the highest time resolution possible to address acute exposures and spatial variability. Most Panel members believed the Air District along with instrument manufacturer recommendations would be adequate to determine additional data quality issues.

Members of the Panel generally agreed that periodic review of applicable technologies would be required to ensure that the best techniques were utilized. In addition, Panel members agreed that lines of communication should be fostered to ensure transparency and trust.

- ***What should the size and spatial orientation of a network of monitors be around refineries***

Participants agreed that fence line monitoring in addition to community monitoring be employed. Fence line monitoring should cover the majority of refinery/community interface as possible. They provided the following comments on the community monitoring portion.

Jay Turner – Professor Turner stressed that the appropriate size and spatial orientation of any monitoring network depends on many variables; especially the desired compounds being measured, their relationship to emissions from the refinery and the changes in concentration with increased distance from the source. For example, he noted that particular point sources, such as delayed cokers and catalytic crackers would require a very focused monitoring approach if metals were the targeted compounds, while focusing on hydrocarbons would require a very different approach.

George Allen – Mr. Allen suggested that a “layered” approached should be utilized in which gradients are measured based on a limited number of fixed sites with accurate, stable and continuously operated instrumentation followed by “layers” of more spatially dense measurements that provided better spatial coverage designed to provide more information, potentially sacrificing accuracy or other measurement characteristics to lower costs based on the overall monitoring goal. Panelist’s widely agreed that this was a desirable approach.

Jay Gunkelman – Mr. Gunkelman stressed that each refinery be evaluated separately since each facility has unique characteristics.

Gary Mueller – Mr. Mueller stated that the current air monitoring network for NOx, PM and SO_2 probably does an adequate job. For VOC’s, there is likely room for improvement. So while there are many compounds that may be impacting the community, the focus should be on those that are more known and likely to have impacts, while other, less obvious compounds potentially being the focus of limited investigations prior to a more widely deployed network.

Denny Larson – Mr. Larson agreed with the above approaches and stressed that community involvement would be a good starting point to base investigations of less obvious compounds on, focusing on symptomatic and odor log observations by the community. The involvement of the community in the process should be ongoing to capture changes in refining processes over time.

Robert Harley – Professor Harley stressed that visual and olfactory information collected by the community was important and need not involve expensive equipment or large amounts of technology to accomplish.

Jay Turner – Professor Turner stressed the importance of identifying gradients by measuring in areas that had not been included in the past and relating those measurements back to longer term measurements in the area, providing an idea of scale of impacts and context to measurements. He pointed out that measuring close enough to the sources with appropriate spacing between measurements to fully capture gradients was the key (capturing the "zone of influence"). He also stressed that a representative background site near the refineries was critical to understanding localized concentrations since emissions from refineries mimicked mobile sources in many, surprising ways. He also believed that a gradient/saturation or "layered" approach was appropriate.

Ken Stroud – Mr. Stroud agreed with Professor Turner that a gradient, saturation approach as described by the DRI report was best.

Andrea Polidori – Dr. Polidori stated that budgets need to be defined up front to ensure that adequate sampling is performed prior to funding being exhausted. He also stated that time resolution and capture of seasonal variation was the biggest obstacle to overcome with a gradient approach.

Gwen Yoshimura – Ms. Yoshimura agreed with the above approaches and that a combination of all of the above methods should be employed.

Jay Turner – Professor Turner believed that saturation monitoring could inform the location of more permanent sites and that those site should be located quite near the facilities (within blocks). He believed that no more than three permanent sites should be considered with one of those sites being a "background" site.

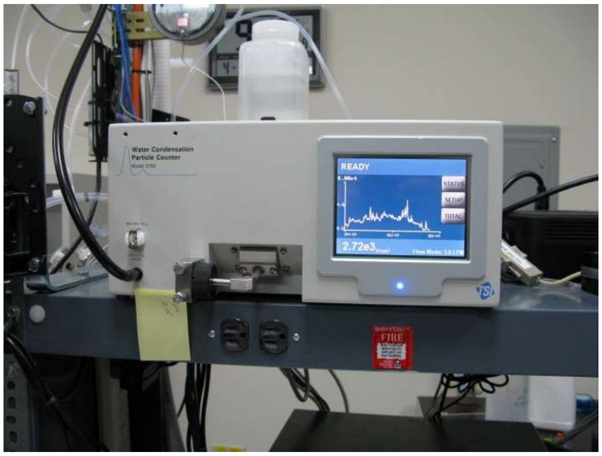
Thomas Kirchstetter – Dr. Kirchstetter cautioned that shorter duration monitoring could be problematic due to seasonal variations in meteorology and that these factors must be considered when shorter term studies are developed.

- ***What network components should be considered (compounds measured, technology and instrumentation used, methodologies applied, air quality assessment tools utilized, etc.)***

Jay Turner – Professor Turner stressed that VOC's are the logical starting point for any study and refinery-to-refinery variation should be identified, if possible. Once VOC relationships and correlations are developed, limiting the number of compounds measured would be a good way to limit costs. He also believed that use of real-time instrumentation was best suited to identify correlations and unique variations. He stressed that speciation of hydrocarbons (such as what field gas chromatographs/SynSpec-like equipment would supply) are well suited for these purposes.

George Allen – Mr. Allen agreed that VOC's should be included and limited to identified "indicators", but also believed sulfur compounds should be used as indicators, especially since most open path equipment respond well to these compounds. He also identified formaldehyde as an example of a risk driver that should be measured, but that it is extremely difficult to measure well. He felt that passive sampling for VOC's, such as canisters, should be triggered by total non-methane hydrocarbon (TNMHC) measurements. He identified ammonia as a compound that is easily measured using passive technologies, but difficult to measure continuously. He used these examples to demonstrate the complexity and difficulty in designing community monitoring networks and the need for a flexible approach.

Gary Mueller – Mr. Mueller pointed out that PM measurements at natural gas fired refineries are not effective during normal operation due to the low amount of PM directly emitted. Measurements of NOx and SOx are performed largely at emission points and probably do not need to be addressed offsite. Identifying the monitoring goal and identifying the impacted areas not addressed by historical monitoring is the first place to start.



Jay Gunkelman – Mr. Gunkelman stressed that upwind and downwind measurements were critical and that specifics and uniqueness of site locations were important to consider, especially during divergent seasons. He believed 10-meter meteorological towers provided the most representative information. He also believed that limiting the number of compounds to include only the most important was necessary, but that at least one compound (for example, carbon tetrachloride) should be used to serve as a background QA/QC check.

Robert Harley – Professor Harley supported the use of radar profilers for meteorological measurements and also believed that flux estimate monitoring was ideal to validate emissions inventory estimates, providing a more realistic estimated community concentration and an ideal starting point for identifying community monitoring needs. He also reminded everyone that PM measurements while potentially not an issue during normal operation, was important during upsets and incidents.

George Allen – Mr. Allen believed that sodar was a good methodology to employ to estimate mixing heights. He also added that if methane and TNMHC measurements were made, that the methane measurements would be a good QA/QC check of the TNMHC data.

Denny Larson – Mr. Larson believed that PM should be included in any network design and that polycyclic organic hydrocarbon compounds (PAHs) should also be considered in the event of fallout from upsets and incidents. He also believed measurements at elevation should be considered to capture buoyant emissions. Mr. Larson also believed analysis of past incidents and upsets were critical to inform future actions.

Jay Turner – Professor Turner stressed again that identification of compound relationships and correlations in conjunction with potential facility uniqueness should be the starting point for VOC measurement. He also agreed that carbonyl measurement is desired, but difficult, and supported the use of UV DOAS instrumentation based on its potential ability to measure carbonyls.

Gwen Yoshimura – Ms. Yoshimura noted that a Beta Attenuation Monitor (BAM) is now in place at the San Pablo air monitoring station as well as other Bay Area locations and these instruments are now producing hourly PM data. She also stated that data quality and presentation to the community must be considered along with everything else.

- ***How should the data be provided to the public***

Denny Larson – Mr. Larson stated that all available air quality data the Air District is responsible for should be provided along with context and a feedback mechanism. He believed that the fence line monitoring systems at Crockett and Rodeo are good models. He also reminded that there are methods other than the internet to provide the information to the public.

Jay Gunkelman – Mr. Gunkelman stressed that feedback to public input must be instantaneous and thorough and that the GLM data need to be posted online. Website graphical interfaces need to be simple and provide general information that is easily understood.

George Allen – Mr. Allen pointed out that data should be web-based along with an alternative, such as a telephone hotline, for those without computers. The web-based data should be “layered”, so that people with rudimentary knowledge have a page and that people who wish more complex data, such as researchers, can get more complex data. He noted that there is a great deal of meteorological data available through other sites, such as Weather Underground. Data should also be tied to risk and/or exposures.

Jay Turner – Professor Turner suggested that context be provided with a baseline reference (either regulatory or “normal” concentration) with comparisons to other Air District/State sites. He stated that AirNow is a good model.

Gwen Yoshimura – Ms. Yoshimura suggested that a feedback loop be developed between the refineries and community so that there are defined actions taken when certain concentrations are reached. These levels and actions should be communicated so that the public knows that there are actions associated with the data. She supported the multilevel approach and reminded that download speeds should be considered.

Ken Stroud – Mr. Stroud suggested that data also be shared with websites that display national data, such as AirNow, and state sites, such as AQMIS, so that the public can get everything they need at one location.

Andrea Polidori – Dr. Polidori suggested that there be consideration for allowing a time period between when the data are collected and when they are displayed to the public to allow for appropriate quality assurance (QA) activities to be completed, if necessary. He provided the example of laboratory analysis that would require additional time. He also suggested that there be a tie-in between measurements and health consequences, if possible, potentially utilizing real time health measurements (though that may not be quite ready yet).

George Allen – Mr. Allen stated that he believed missing data had the potential to raise trust issues and that transparency was the answer to these issues. A mechanism to explain why data are missing should be provided, such as meta data and performance parameters outside of which data are not valid. In addition, clearly identifying what is displayed when values are below the instruments limit of detection (LOD) is important.

Gary Mueller – Mr. Mueller suggested that all data be displayed and labeled to indicate potential issues with data quality, though he was not sure how that might be accomplished.

Denny Larson – Mr. Larson stated that data quality is not an issue as long as real-time results are displayed and available, with QA activities and data reporting that requires additional time achieved quickly. He believed that reliability and up-time were the more critical issues and that 99% data completeness should be the goal. Any corrective action should be taken quickly and feedback mechanisms, such as blogs and bulletin boards, should be employed to provide a venue for sharing information and suggesting improvements.

Thomas Kirchstetter – Dr. Kirchstetter pointed out that web pages should initially provide straightforward information with the ability to get additional, more complex data built in. He believed that the current Air District website was a good starting point, but that it needed to be improved. Having the ability to plot data in graphical format would potentially enhance understanding. Dr. Kirchstetter also believed that displaying data with the correct level of precision was important and that using "<LOD" when concentrations were below instrumentations LOD would be the best method as long as LODs were provided.

Jay Gunkelman – Mr. Gunkelman agreed with Mr. Larson that removal of data that didn't meet quality assurance requirements was not an issue as long as high rates of data completeness were maintained. He supported the use of "<LOD" for values below detection levels. His main concern was the robustness of the website and the defensibility of the data. Traffic to the website could also be used as a means of measuring whether problematic issues were occurring.

Jay Turner – Professor Turner believed that issues around data quality would be addressed quickly if all refineries are performing similar measurements, the data stream is monitored and feedback around missing data or data outliers are addressed.

George Allen – Mr. Allen stated that urban background numbers should be provided to give context to the concentration numbers and associated risk.

- ***What should be considered when developing measurement quality objectives, such as:***
    - ***What type of instrument siting criteria should be used***
    - ***What should the time resolution of the equipment be***
    - ***How often should the instrumentation be calibrated***
    - ***What should the accuracy/precision/completeness requirements of the data be***
    - ***What other quality control/quality assurance requirements should be put in place***

Denny Larson – Mr. Larson stressed the importance of good siting and that elevation, especially for fence line monitoring, is an important consideration. He also stressed that community monitoring should take place in impacted communities, and that compromises for power and security should be less of a consideration than appropriate location within the community.

Jay Gunkelman – Mr. Gunkelman stressed the need for short time resolution, especially at the fence line (5 minute). He stated that the vendor instrument operational recommendations should drive QA requirements. Data completeness for components and the overall system should be 95%.

Robert Harley – Professor Harley agreed that one hour time resolution is the minimum acceptable time frame. Backup power should also be a serious consideration.

Ken Stroud – Mr. Stroud stated that the Air District should have oversight of the QA processes, which the Air District supports.

Jay Turner – Professor Turner made the point that time resolution could be varied according to the major goal of the monitoring. During upsets, for example, time resolution should be increased. This may result in a decrease in accuracy, but this may be an acceptable trade off during short term events when acute exposures are more important. For more chronic exposures, accuracy becomes more of a driving force and time resolution of an hour is more acceptable.

George Allen – Mr. Allen supported the view expressed by Professor Turner, that time resolution and accuracy should be based on the importance of the exposure (chronic versus acute).

Andrea Polidori – Dr. Polidori stated that it was better, in his opinion, to delay posting of data so that quality was ensured and data would not have to be removed at a later date, potentially causing trust issues. He also stressed that co-location of instrumentation would need to be considered to provide information on overall data quality.

Gwen Yoshimura – Ms. Yoshimura stressed that community involvement was critical and that they should be involved in determining how to balance time resolution and accuracy.

- ***What technologies, methodologies and tools could be employed to augment any fixed network to better quantify pollutant variations over space and time, especially during short duration incidents***

Thomas Kirchstetter – Dr. Kirchstetter thought sampling during incidents could be modified to address the shorter duration of incidents, especially those at permanent locations near facilities. For example, canister samples, which are traditionally collected over 24-hours, could be collected every three hours for 24 hours during the event and used to compare to the more traditional sampling. This would provide flexibility and potential cost savings.

Denny Larson – Mr. Larson was not sure if the technique described by Dr. Kirchstetter should be employed. He believed this to be was more of an issue with the goal of the sites (ambient versus incident related). He suggested that monitoring near facilities should follow a different siting criterion. Siting for incidents should be mobile, as opposed to fixed, as this would be the best way to “track” impacts.

George Allen – Mr. Allen supported mobile monitoring during incidents which would augment the fixed network. Time resolution of a minute, maximum, should be employed with the ability to grab canister samples when direct reading instruments indicate high concentrations. He believed this may also be a situation to employ the semi-quantitative Ecochem PAH instrument (fast response and easy to run). This should be tied to real time meteorology and modeling.

Jay Turner – Professor Turner also agreed that mobile monitoring during incidents is likely the best methodology. Characterization of gradients and specific characteristics of individual facilities would also provide context during mobile monitoring. He supported flux measurements and the inclusion of error analysis associated with these types of measurements. He believed there were many good examples of community monitoring outside of California and it would be very valuable to incorporate the lessons learned from these studies and investigations.

Thomas Kirchstetter – Dr. Kirchstetter also supported the use of mobile monitoring during incidents. He noted that there are limitations to mobile measurements, however. He also advocated for use of mobile monitoring resources for gradient and other special studies.

Gary Mueller – Mr. Mueller also supported mobile measurements during incidents. GPS and highly time resolved measurements can provide large amounts of data. He also noted that technology that could be employed for incident response is rapidly changing.

Ken Stroud – Mr. Stroud pointed out that emission profiles don't always exist for any given incident-based release. He advocated for building emission profiles for potential scenarios.

Denny Larson – Mr. Larson supported mobile monitoring and also supported the use of mobile monitoring to aid in gradient determination during more routine operation of the facilities. He believed the use of mobile monitoring during routine operations could help build trust with the community by providing information on daily operations that impact neighbors. He also supported online reporting during incidents by the community and facilities and provided examples of this type of reporting taking place in Texas.

Jay Gunkelman – Mr. Gunkelman supported the use of backup power for fixed sites since power disruptions can cause major upsets at facilities. He again stressed the need for highly time resolved measurements at the fence line. Portability of instrumentation should also be considered so that instrumentation can be moved if experience indicated it.

- ***What emerging technologies might be utilized in the future to further enhance community air monitoring capabilities***

George Allen – Mr. Allen provided information on EPA's ORD activities that were directed toward emerging technologies and also provided information on cutting edge instrumentation being developed by manufacturers (IRIS from ThermoScientific. This product is currently undergoing improvements by the manufacturer and will be re-introduced under another name).

Denny Larson – Mr. Larson stressed the need for periodic review of in-place and emerging technology and the need to investigate how improvements can be brought into operation. He also stressed that communication between government, the facilities and the community is critical to continue over time.

Gary Mueller – Mr. Mueller pointed out that there are numerous technologies that need to be investigated, tracked and potentially installed, but it is important to consider that any technology needs to be tested and evaluated thoroughly prior to use to inform the community.

Members of the Public – Members of the public stressed that it is important that government agencies respond to complaints so that the community knows that their observations are being recognized and investigated. The data needs to be made understandable to the public and context must be provided to ensure that the effort provides value to the community. The public would like to focus on preventative actions. Online information, such as wikis should be considered. Members of the public supported providing an explanation of why data are invalidated. The public also supported the development and dissemination of emission profile information, the use of video monitoring and the investigation of better manufacturing processes that reduce emissions.

- ***The Panel provides their final thoughts***

Robert Harley – Professor Harley stated that whatever actions are taken, they must provide value to the various stakeholders.

Denny Larson – Mr. Larson pointed out that his principals for air monitoring that were provided to the Panel would be a good starting point for any future discussions.

Jay Turner – Professor Turner stressed that the DRI report provided the appropriate five objectives to consider for additional network development and the emphasis of those objectives will be based on policies developed by the Air District through the various inputs, including the Panel and the community.

Gwen Yoshimura – Ms. Yoshimura reminded that the data can have many uses, including uses for the refineries that should use the data to make improvements to their processes proactively.

Gary Mueller – Mr. Mueller stated that continuing communication between all parties is important and should continue to be developed and supported. He also fully supported the use of mobile monitoring during incidents, especially monitoring of PM.

George Allen – Mr. Allen stated that near-field data was of high value, especially to industry. He noted that there have been improvements, but that tools such as video can be quite valuable to both the community and industry.

Jay Gunkelman – Mr. Gunkelman stressed the value of community/government/industry interaction during any process. He was encouraged that monitoring will be taking place at refineries throughout the Bay Area.

Andrea Polidori – Dr. Polidori agreed that good communication is required for any effort to be successful. He suggested that there are practices in place in the South Coast Air District, such as email notifications of planned and unplanned flaring events that could be incorporated in the Bay Area.

Panelists Response to Comments –

Members of the Panel were given an opportunity to provide clarification to comments attributed to them and were incorporated into this report. Panel members were then given another opportunity to provide comments on the DRI report not captured above, and comment on input from other Panel members. All input is provided below.

Mr. Denny Larson provided comment:

"We need to make clear that the process of doing these tasks should model what is done with the GLM monitoring network. That is the District provides a general outline for installing the network and provides specific recommendations for equipment. Then it is up to the refinery to install and contract out the operation of the equipment.

The Air District needs allow the refineries to make available to the public the GLM data that is currently being generated immediately. It costs nothing and provides an immediate public good. Again the key would be to let the refineries make it public, not the air district.

Have each refinery set up a process by which it makes public its data. This should also include input/feedback and participation from local communities. It's better to provide local input as compared to a process where a central authority makes all decisions.

The fence line monitor success for 20+ years in Rodeo at Conoco is due in large part to the local community working group working with the refinery and the relevant agency. The District's policies and rules in this regard should require a local working group of refinery neighbors."

Professor Robert Harley provided comment:

My comments "are all mentioned in the draft report already, but I want to emphasize/elaborate on some key points.

1. That solar occultation or similar open-path techniques be used to survey baseline emissions from each refinery under normal operating conditions (this can be used to check the District's emission inventory; there may be uninventoried fugitive sources of VOC emissions especially).

2. That District monitoring efforts relating to abnormal events/upsets at refineries include measurements of ambient particulate matter using online methods that provide at least hourly updates to the data. Such data on PM mass (measured, for example, by beta attenuation) could be useful in identifying smoke plumes that arise due to fires or large flaring events at the refineries. Fence line and community monitoring efforts seem heavily focused on measuring gaseous pollutants.

3. Earthquakes are a known hazard in the Bay area, and both refinery systems and BAAQMD monitoring capabilities should be assessed for safety and resiliency in the face of extended outages in electric power and other lifeline systems (water supply, transportation, communication, natural gas) that may ensue.

4. Enhancements to meteorological data collection (e.g., from one or a few radar wind profilers operating continuously) may help the District assess the transport and magnitude of air pollution plumes from refineries, as well as impacts on nearby communities. Such data may also serve other District needs such as air quality modeling and planning efforts."

Mr. Ken Stroud provided comment:

"I have reviewed the report, *"Air Monitoring Technology and Methodology Expert Panel Report and Findings,"* and find that it adequately captures my input to the Panel Discussion of July 11, 2013."

Dr. Andrea Polidori provided corrections/clarifications to comments attributed to him which have been incorporated into this report and also provided comments on the DRI Report, which will be forward to the author of that report for editing consideration.

Mr. George Allen provided corrections/clarifications to comments attributed to him and have been incorporated into this report.

***Panelists Written Comments** –*

District staff invited Panelists to provide additional written comments after the meeting to address the charge questions and provide additional insight. These are attached, represent the position of the Panelist, and have not been edited by Air District staff.

Response to Charge Questions to the Air Monitoring Technology and Methodology Expert Panel
DRAFT – George Allen July 17, 2013

Q 1: What should the size and spatial orientation of a network of monitors be around refineries

A network of fixed sites should have multiple layers to meet the multiple objectives needed to properly assess source emissions and population exposures both for routine (normal) operating conditions as well as abnormal emission scenarios.

1. Near-field source characterization measurements. This component of the network is designed to measure pollutants at or near the fenceline (up to ~ 100 m away), and potentially at different heights above the ground. Open path methods are most appropriate here, but not necessarily located on or near the ground. Near-field sampling should be located at heights that are relevant to the structure of the refinery and known or likely emission sources). These measurements would ideally be located both up- and down-wind of the refinery (using prevailing wind directions).

2. Mid to neighborhood-scale fixed sites with full instrumentation. These sites would be the backbone of a long-term network with multiple measurements, including both real-time and integrated sampling. These sites would be between 500 to ~2000 m from the fenceline, and provide detailed and high quality data for routine (non-event) conditions that could be used for assessment of chronic health risks. Depending on resources, this could be a single down-wind site or include several down-wind sites and a single up-wind site. These fixed sites should be located at the most likely high-concentration area, determined by dispersion modeling using appropriate on-site wind fields at multiple elevations if possible. One potential routine use of the data from these sites would be to ground-truth refinery emission inventories. These have been shown to sometimes be substantial under-estimates of true facility emissions due to the potential for a large number of unidentified fugitive emission sources. See:

Henry, R.C., Spiegelman, C.H., Collins, J.F., EunSug Park (1997). "Reported emissions of organic gases are not consistent with observations." Proceedings of the National Academy of Sciences of the United States of America, Vol. 94, 6596–6599.
http://www.pnas.org/content/94/13/6596
and

Ryerson, T. B., et al., Effect of petrochemical industrial emissions of reactive alkenes and NOx on tropospheric ozone formation in Houston, Texas. J. Geophys. Res., 108(D8), 4249, doi:10.1029/2002JD003070, 2003. Report at: http://www.researchgate.net/publication/225089790_Signatures_of_terminal_alkene_oxidation_in_airborne_formaldehyde_measurements_during_TexAQS_2000/file/9fcfd51072f40594aa.pdf

3. Mid to neighborhood-scale fixed sites with limited instrumentation. These sites would be simpler and lower cost, to provide additional spatial information on a limited number of indicator pollutants. Passive or low-cost real-time sensors would be used at these sites. One of these sites should be collocated with a fixed site described in #2 above for QC purposes. One should be up-wind of the refinery.

Q 2: What network components should be considered (compounds measured, technology and instrumentation used, methodologies applied, air quality assessment tools utilized, etc.)

For near-field open path measurements, indicator pollutants are appropriate. These could include methane, benzene or other BTEX VOCs, SO2, or other relevant pollutants. NOx and PM do not need to be measured.

For the larger fixed site monitoring locations (Q1 #2 above), the following measurements should be considered, roughly in order of importance:

Real-time BTEX (Synspec or similar) with 5 to 15-minute resolution

SO2 and total gas-phase sulfur (e.g., reduced S compounds) with 5 to 15-minute resolution

Methane and total non-methane HC with 5 to 15-minute resolution

Optical Black Carbon (BC). The new version of the Magee/TAPI model AE33/633 Aethalometer addresses the limitations of “legacy” Aethalometers, including noisy short-term measurements and “spot-loading” effects. The instrument provides stable data with high time resolution (1-minute or less) over the range of 950 to 370 nm, with 1-minute LOD of ~ 50 ng/m3. Enhanced response at 370 nm relative to 880 or 950 nm is a specific and semi-quantitative indicator of cellulose combustion.

Particle number concentration (PNC or UFP) down to < 10 nm is readily measured with the TSI 3783 CPC (TAPI model 651) with rapid response time and high sensitivity. PNC along with time-resolved and sensitive PM2.5 (pDR-1500) can give an indication of the age of the aerosol; high PNC with relatively low mass is typical of very fresh combustion, while relatively low PNC and high PM2.5 indicates an aged aerosol.

Automated GCs can provide speciated VOCs with high time resolution; these data can be useful to ground-truth total VOC emissions from large facilities as noted in Q1, #2 above).

NH3 (resolution TBD based on method – electro-chemical for higher "event" concentrations ~1 ppm and up)

Meteorology:
10 meter wind with 5 to 15-minute resolution
Ceilometers give a useful measurement of mixing height up to ~ 5 km and are relatively simple and inexpensive compared to radar/profiler systems. Example:
http://www.vaisala.com/en/products/ceilometers/Pages/CL31.aspx

Highly time-resolved (1 to 5-minute) PM2.5 (e.g., optical methods supported by BAM or TEOM measurements that only provide hourly PM data. The Thermo pDR/aDR1500 has been shown to provide useful measurement of PM2.5 at 1-minute or less time resolution:
http://www.thermoscientific.com/ecomm/servlet/productsdetail_11152_L11082_89583_11961321_-1
NO and NO2 (1 to 5-minute resolution)

The EcoTech PAH analyzer provides qualitative highly time-resolved measurement of particle-bound
PAH. While data quality is not high, the method is inexpensive and easy to run.
http://www.ecochem.biz/PAH/PAS2000.htm

Canister measurements of VOCs, both routine (every x days) and possibly event-triggered samples driven by the TNMHC real-time measurements. Similar event grab samples could be taken using the SO2/TS real-time measurements.

The less intensive fixed sites could include passive measurements of VOC, SO2, and possibly NH3; the two major suppliers of passive samplers and related chemistry are noted in the DRI report. PM2.5 could be measured using optical scattering methods such as the self-contained Thermo aDR-1500. Electro-chemical sensors are available for many gases, including CO, H2S, chlorine, ClO2, mercaptans, HCl and others; this technology has dramatically improved over the last decade, with improvements in baseline/temperature drift. One leading manufacturer of high quality electro-chemical cells is City Technology in England:
http://www.citytech.com/

Q 3: How should the data be provided to the public

A web site should be used to provide data to the public. There are several key components of a web site for this purpose:

1. A layered approach to data and interpretation that allows the user to “drill down” to the desired level of detail. The top layer would be simple, non-technical information, using messaging similar to the AQI (colors and descriptors) and indicate if conditions are normal or not. The second layer could include more pollutant-specific information (including health effects). The third layer would provide access to current and historical data and more detailed information on health effects, both chronic and acute. All layers should present information in a spatial context. For example, clicking on a site on a map leads you to the next layer of data.

2. It is critical that data from refinery network monitors be put in context with similar data from urban-scale contemporary measurements, since source-profiles from refineries under normal operating conditions are usually similar to ubiquitous mobile-source air toxics such as benzene. This would require measurements of key real-time pollutants at an urban site not influenced by refinery emissions. Data for all layers of the web site could be presented as “excess” over urban background, either alone or (for the third layer) with the actual concentrations from near-refinery and urban background monitoring sites. This is a health “risk communication” issue, acknowledging that there is some risk even during normal conditions and at urban background concentrations.

3. Data must be “time-relevant”. For routine measurements (and non-event conditions), hourly data is sufficient. But during an event, data must be updated at least every 5-minutes, and ideally every minute when levels are elevated. While instrument uncertainty (LOD, noise, etc) decreases at very short time intervals, the periods when high-time resolution is needed would be when high concentrations of pollution are present. Some degradation in data quality is an acceptable trade-off for high time resolution during these event conditions.

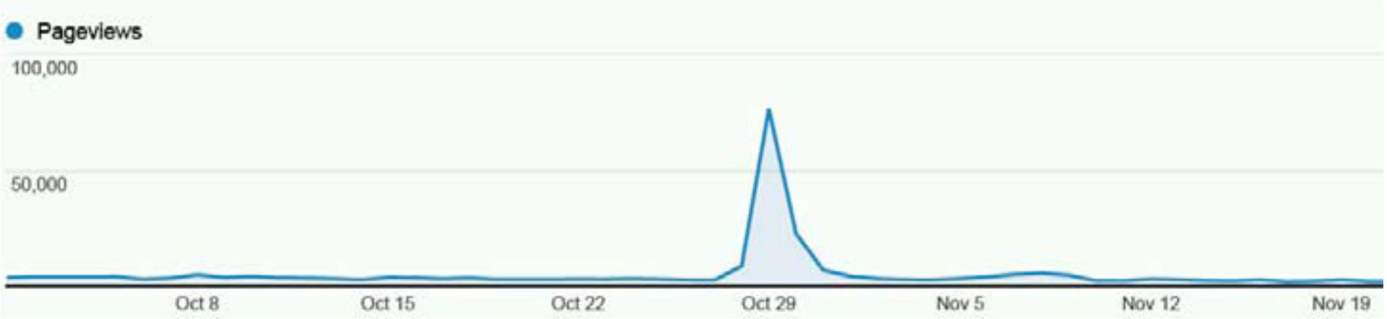
4. “Missing” data must be addressed in a transparent manner. Why it is missing (specific information, not just “invalid data” and (for real-time data) when it is expected to be available again is key information that must be provided.

5. Data quality indicators should be included in some manner at all levels of the web site. For transparency, data below LOD should be shown with suitable data quality indicators. Colors or text size, etc. could be used to mark data of inadequate quality, with the reason noted.

6. To the extent possible, web pages should be ADA-compliant, or an ADA-compliant version of the web site should be provided even if it has limited information relative to the main site. The web site should be designed to be easy to view for those with some vision impairment. This means NO low-contrast layout [e.g., no light blue on darker blue] - information should be black on white wherever possible. Users should be instructed on how to enlarge the page in the browser (View/zoom, or Ctrl +, -, and 0).

7. The web server must be capable of handling very large traffic that would likely occur during a substantial event – when the site is most needed. Below is an example of traffic to hazecam.net

when superstorm Sandy hit the NY/NJ coast on Oct. 29, 2012; this demonstrates the relative traffic during an event of note.



8. Web access can not be assumed. A telephone (toll free?) hotline should be part of the data access system. Information on the hotline would be limited, similar to level 1 of the web site, and presumably limited to a single location unless all locations are "normal". Users could enter a zip code or other geographical locator information such as the name/town of the refinery of interest when conditions are not normal. A telephone contact number for additional information during times when conditions are not normal should also be provided.

Q 4: What should be considered when developing measurement quality objectives, such as:

– What type of instrument siting criteria should be used
This is covered under the first charge question.

– What should the time resolution of the equipment be
This is covered under the second charge question.

– How often should the instrumentation be calibrated
For methods that the US EPA has established QC guidelines for, those guidelines should be followed. For other methods, good laboratory practice should be followed, taking into consideration the level of data quality needed and the stability of the method.

– What should the accuracy/precision/completeness requirements of the data be
Accuracy and precision are most important when normal (non-event) conditions are present and hourly data and data "higher than urban background" are the primary products. As noted above, precision is less important when elevated levels are present and a trade-off between precision and high time-resolution is needed. Completeness is the most important requirement. Routine measurements normally have minimal missing data beyond precision/calibration/maintenance outages. Some methods such as open-path instruments may have substantial missing data due to the complexity of the method. If high data capture is important for these methods, appropriate resources must be made available.

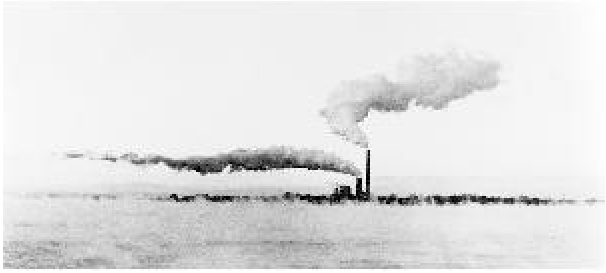
– What other quality control/quality assurance requirements should be put in place

To the extent possible, "buddy-system" checks may provide useful data quality information during routine (non-event) monitoring.

Q 5: What technologies, methodologies and tools could be employed to augment any fixed network to better quantify pollutant variations over space and time, especially during short duration incidents

Rapid deployment of mobile measurements are critical to provide detail on areas of maximum concentrations. The mobile platform must have very highly time-resolved measurements of key indicator pollutants – one minute or less if possible. In addition to methods noted above, portable photo-ionization detectors (PID) instruments may provide useful data for mobile use.

Real-time dispersion modeling along with the real-time fixed monitors could be used to determine the most likely area[s] of maximum concentrations. To maximize the accuracy of the dispersion modeling, wind data at multiple levels at or just down-wind of the refinery are needed, from 10 meters to stack-top elevation, including 30 and possibly 100 meter wind. Multiple elevations are essential since wind direction can change dramatically over several hundred feet as shown in this classic picture by Bruce Egan of the Salem (MA) Harbor coal-fired EGU. The coastal meteorology present at these refineries further complicates estimation of plume impacts using dispersion modeling. These wind measurements should be "3D" sensors that include the vertical wind component. Wind data must be highly time-resolved – 1 minute or less, with vector averaging up to longer time-scales (e.g., 5, 10, 15 minutes or more).



Another source of surface wind data that may be useful during an event is the dense "network" of personal weather stations (PWS) that report to organizations such as the Citizen's Weather Observing Program (CWOP). These data go into the NOAA Meteorological Assimilation and Data Ingestion System (MADIS) where they are QC's using a "buddy-system" approach. The data and related QC parameters are "exposed" by CWOP. See a presentation I gave at the 2009 EPA national monitoring conference:
http://www.epa.gov/ttn/amtic/files/2009conference/AllenFreeMetQC.pdf

Some PWS only report to weather underground and do not receive MADIS QC; all CWOP sites appear on weather underground, identified as APRSWXNET for the data source and with site IDs consisting of M and a single letter ©, D, or E) followed by four digits. Example: MD2257. A list of public stations sending data into MADIS from many different mesonets (CWOP is one of many) is at: http://madis.noaa.gov/public_stntbl.csv
Weather underground provides maps of station locations that link directly to a station's data:
http://www.wunderground.com/wundermap/?lat=37.94056&lon=-122.34944&zoom=12

Data are also available from the MesoWest database:
http://raws.wrh.noaa.gov/cgi-bin/roman/meso_base.cgi?stn=D2257&unit=0&time=LOCAL

Another "measurement" that may be useful is automated photography. Properly sited high resolution cameras (not "web-cams") could be used to track and document plume location, dispersion, and elevation during an event (the pictures from the August 2012 event demonstrate the value of this approach). These cameras could be both visual and infra-red (for night-time use). Ideally each refinery would have three cameras providing views from a few miles away from three angles of view to allow triangulation of any visible plume. A camera network could be part of the web-site (a valuable outreach tool), and could capture smaller events that may not be picked up by the routine monitoring network. A network of "visibility" cameras I run in the northeast US has captured several notable pollution events (including the direction and intensity of the 9/11 NYC plume), and has been used as part of an enforcement action against an EGU in the Boston area by the US EPA. See: www.hazecam.net . Mexico City has a "hazecam" looking at Popocatepétl:
http://148.243.232.113:8080/calidadaire/vigilancia_cam/hazecams.php

Q 6: What emerging technologies might be utilized in the future to further enhance community air monitoring capabilities

There are some key pollutants that are difficult to measure, such as carbonyls, especially HCHO and acetaldehyde. At present, even routine integrated measurement of these carbonyls (using DNPH cartridges) is difficult; optical (open path) methods are the only reliable technique. Carbonyl source profiles may be very different than the more common MSAT-related pollutants, making them important pollutants to measure. There is at least one promising technology under development. Thermo has their "IRIS" system that uses mid-IR spectroscopy to measure methane, CO, CO2, and N2O. As this technology matures, wavelengths are expected to get into the UV range. Conversations with Thermo R&D staff have indicated that measurement of HCHO and other toxic VOCs with high time-resolution should be possible with this technology with the next several years. Information on the IRIS method is at:
http://www.thermoscientific.com/ecomm/servlet/productscatalog_11152__89577_-1_4

The US EPA/ORD has a new program to identify and characterize "next-generation air monitoring" (NGAM) technologies that are in the development stage. Presentations from a meeting earlier this year are at:
http://sites.google.com/site/airsensors2013/final-materials

Another site related to EPA's NGAM efforts but run by Sonoma Technology is:
http://citizenair.net/

Next Steps –

Air District staff will be utilizing the input from the Panel to develop guidance for air monitoring at and near refineries as part of the proposed Petroleum Refining Emissions Tracking rule, and to develop appropriate supplemental monitoring conducted by the Air District (e.g., mobile monitoring during incidents). Additional Expert Panels may be assembled to provide additional input on other topics associated with emissions from refineries to ensure that the best and most effective tools are employed to assess impacts from these sources. Lessons learned during this process may be incorporated in the future.