

Petroleum Refinery Sector Risk and Technology Review

Presentation to the U.S. EPA Science Advisory Board
July 19, 2013

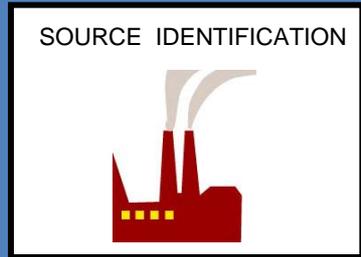
Overview

- ▶ Exposure and Risk Assessment Process
- ▶ Refinery Emissions: Inventories and Emission Sources
- ▶ Monitoring Approaches

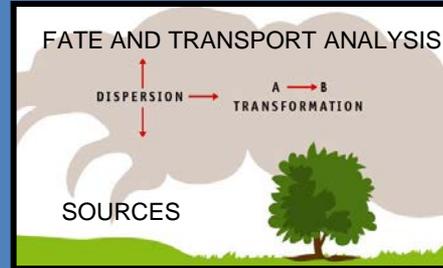
Human Risk Assessment Process

Planning and Scoping

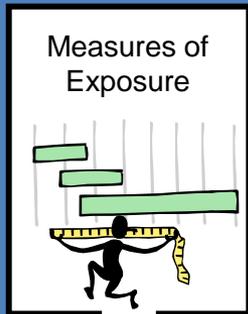
Exposure Assessment



Chemical Release

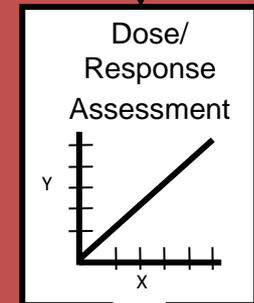


CHEMICAL CONCENTRATIONS
Air, Soil, Water, Food
(monitor/model)



Toxicity Assessment

Hazard Identification



Risk Characterization

EXPOSURE
information

DOSE/RESPONSE
information

Quantitative and Qualitative Expressions of Risk/Uncertainty

Estimating Inhalation Risks under the Risk and Technology Review Program

For the inhalation pathway, the concentration (C) of the chemical in air (in ug/m³) at the point of exposure (called the exposure concentration or EC) can be used as a measure of exposure

For *chronic inhalation exposure*, usually use an estimate of annual arithmetic average concentration at census blocks centroids to represent the long-term EC

For *acute inhalation exposure*, usually use an estimate of highest 1-hour ambient concentrations at or near the facility fenceline to represent the short-term EC

The basic equations for calculating risk from breathing air toxics is:

$$\text{Cancer Risk} = \text{EC} \times \text{URE}$$

$$\text{Noncancer Hazard Quotient} = \text{EC} / \text{RfC}$$

Where:

EC = concentration of the chemical in air at the point of exposure (ug/m³)

URE = Unit Risk Estimate (risk/ug/m³)

RfC = Reference Concentration in (ug/m³)

Developing Exposure Estimates

- ▶ We use the EPA Human Exposure Model (HEM) risk modeling system to estimate exposure, which contains:
 - ▶ AERMOD dispersion model (EPA's approved local-scale model)
 - ▶ 2010 Census data at census block resolution (about 10 households)
 - ▶ Terrain elevation data
 - ▶ Meteorological data
 - Uses historical (2011) data from weather stations nationwide
- ▶ Exposure estimates are conservative
 - ▶ We assume that there is a person at the centroid of census block who is continually exposed for 70 years
 - If the highest concentration is at residence closer to the facility than the centroid, we use that concentration as our exposure estimate
 - ▶ This reflects the Clean Air Act mandate to assess risks to the 'individual most exposed'

Human Health Benchmarks

- RTR assessments includes benchmarks developed from EPA (IRIS) and other peer reviewed sources (ATSDR, CALEPA), and is compiled and maintained by EPA air program toxicologists
<http://www.epa.gov/ttn/atw/toxsource/summary.html>

Table 1. Prioritized Chronic Dose-Response Values (5/21/2012).
Revisions since 04/27/10 are shown in red.
 CAS NO. = Chemical Abstracts Services number for the compound. HAP NO. = Position of the compound on the HAP list in the Clean Air Act (112[b](2)). "999" denotes substances under consideration for listing.
 Sources: IRIS = Integrated Risk Information System; ATSDR = US Agency for Toxic Substances and Disease Registry; D-ATSDR = draft ATSDR; CA = California EPA; P-CAL = Proposed CAL; HEAST = EPA Health Effects Assessment Tables

IARC WOE = weight-of-evidence for carcinogenicity in humans (1 - carcinogenic; 2A - probably carcinogenic; 2B - possibly carcinogenic; 3 - not classifiable; 4 - probably not carcinogenic).

EPA WOE (2005 Guidelines) = weight of evidence for carcinogenicity under 2005 EPA cancer guidelines: CH - carcinogenic to humans; LH - likely to be carcinogenic; SE - suggestive evidence of carcinogenic potential; InI - inadequate information to assess carcinogenic potential; NH - not likely to be carcinogenic).
 EPA MOA (2005 Guidelines) = mode of action for carcinogenicity: Mf - mutagenic and early life data lacking; age-dependent adjustment factors should be applied when assessing risk for ages younger than 16 years per 2005 Supplemental Guidance. [See Table 1 notes.]

EPA WOE (1986 Guidelines) = weight of evidence for carcinogenicity under the 1986 EPA cancer guidelines: A - human carcinogen; B1 - probable carcinogen, limited human evidence; B2 - probable carcinogen, sufficient evidence in animals; C - possible human carcinogen; D - not classifiable E - evidence of noncarcinogenicity.

Table 1. Prioritized Chronic Dose-Response Values for Screening Risk Assessments (5/7/2012)				CHRONIC INHALATION					CHRONIC ORAL						
				NONCANCER		CANCER			NONCANCER		CANCER				
CHEMICAL NAME	CAS NO.	HAP NO.	IARC WOE	mg/m3	SOURCE	EPA WOE	1/(ug/m3)	MOA	SOURCE	mg/kg/d	SOURCE	EPA WOE	1/(mg/kg/d)	MOA	SOURCE
Acetaldehyde	75-07-0	1	2B	0.009	IRIS	B2	0.0000022		IRIS						
Acetamide	60-35-5	2	2B				0.00002		CAL						
Acetonitrile	75-05-8	3		0.06	IRIS	InI									
Acetophenone	98-86-2	4				D									
Acrolein	107-02-8	6	3	0.00002	IRIS	InI									
Acrylamide	79-06-1	7	2A	0.006	IRIS	LH	0.0001	Mf	IRIS						

Table 2. Acute Dose-Response Values for Screening Risk Assessments (12/19/2011). AEBL = Acute exposure guideline levels for mild effects (AEBL-1) and moderate effects (AEBL-2) for 1- and 8-hour exposures. Superscripts indicate the AEBL's status: 1 = final, I = interim, and p = proposed. ERPG = US DOE Emergency Removal Program guidelines for mild or transient effects (ERPG-1) and irreversible or serious effects (ERPG-2) for 1-hour exposures. MRL = ATSDR minimum risk levels for no adverse effects for 1 to 14-day exposures. REL = California EPA reference exposure level for no adverse effects. Most, but not all, RELs are for 1-hour exposures. IDLH/10 = One-tenth of levels determined by NIOSH to be imminently dangerous to life and health, approximately comparable to mild effects levels for 1-hour exposures. TEEL = US DOE Temporary emergency exposure limits for no effects (TEEL-0) and mild, transient effects (TEEL-1) for 1-hour exposures. TEELs are derived according to a fixed formula/the methodology, and do not undergo peer review. They are not recommended as the basis for regulatory decision-making, and are shown here only to inform situations where acute values from other sources are not available.

Table 2. Acute Dose-Response Values for Screening Risk Assessments (12/19/2011)			NEGL-1 (1-h)	NEGL-1 (8-h)	NEGL-2 (1-h)	NEGL-2 (8-h)	ERPG-1	ERPG-2	MRL	REL	IDLH/10	TEEL-0	TEEL-1
CHEMICAL NAME	CAS NO.	HAP NO.	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3
Acetaldehyde	75-07-0	1	81 ¹	81 ¹	450 ¹	200 ¹	18	350		0.47	350		
Acetamide	60-35-5	2										25	75
Acetonitrile	75-05-8	3	22 ¹	22 ¹	540 ¹	140 ¹							
Acetophenone	98-86-2	4										10	30
2-Acetylaminofluorene	53-96-3	5										0.25	0.75

Inhalation Risk Outputs

▶ Chronic

- ▶ Cancer: Maximum Individual Risk (MIR) – highest cancer risk (in a million) at a location where people live (census block centroid or nearest residence)
- ▶ Noncancer: Hazard Index (HI) – highest noncancer risk at a location where people live (census block centroid or nearest residence)
- ▶ Annual cancer incidence (cases/year)
- ▶ Cancer risk bin distributions (>100 in a million, 10 in a million...)
- ▶ Source category and facility wide risks
- ▶ Process level risk contributions

▶ Acute

- ▶ Maximum off-site impact: pollutant-specific highest 1-hour Hazard Quotient (HQ) outside estimated facility fence line
 - Default factor of 10x time the annual emissions rate unless source category specific information is provided
 - Can be refined with site-specific boundary conditions

Development of Emission Inventories

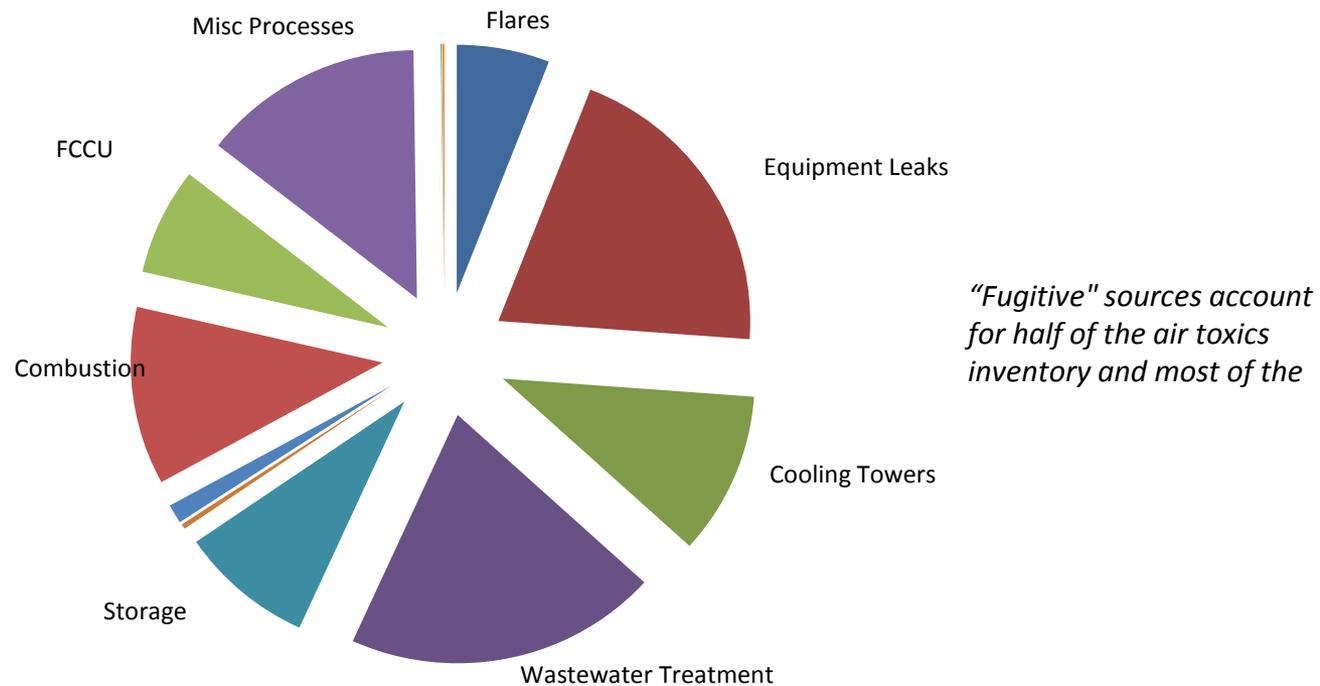
- ▶ The purpose of the risk and technology review is to evaluate the MACT standards to determine if:
 - ▶ It is necessary to tighten the standards to protect human health and the environment with an “ample margin of safety”
 - ▶ There are advancements in practices, processes or technologies that warrant tightening the standards
- ▶ Risk and technology review requires emission inventory data
- ▶ Emission inventories are developed to satisfy state requirements
 - ▶ EPA provides guidance in the form of AP-42 emission factors, but does not mandate their use
 - ▶ Inventories are not consistent among states
 - ▶ Speciation and completeness of data for air toxic pollutants vary
 - ▶ EPA houses state inventories in the Emission Inventory System (EIS)

Refinery Emissions Inventory

- ▶ EPA was petitioned in 2008 under the Data Quality Act to improve emission factors from refineries
 - ▶ In response, EPA developed a refinery emissions estimation protocol, which was put through two rounds of public notice and comment in 2010
 - <http://www.epa.gov/ttn/chief/efpac/protocol/index.htm>
- ▶ Refinery Emissions Estimation Protocol
 - ▶ Provides consistent set of methods for estimating emissions (criteria pollutants and air toxics)
 - ▶ Requires speciation of air toxic pollutants
 - ▶ Describes what refinery emission sources should have pollutant emission estimates
 - ▶ No new sampling is required
 - ▶ Ranking of methodologies depending on available data
 - ▶ More detailed and comprehensive than AP-42 emission factors
- ▶ 2011 Refinery ICR required refiners to use the Refinery Emissions Estimation Protocol to develop their inventory
- ▶ Refinery inventory submitted in response to the ICR will be used to perform the risk and technology review of the MACT standards

Air Toxics Emissions from Refineries

Petroleum Refinery HAP Emissions



Source: 2011 ICR

Refinery Emission Sources

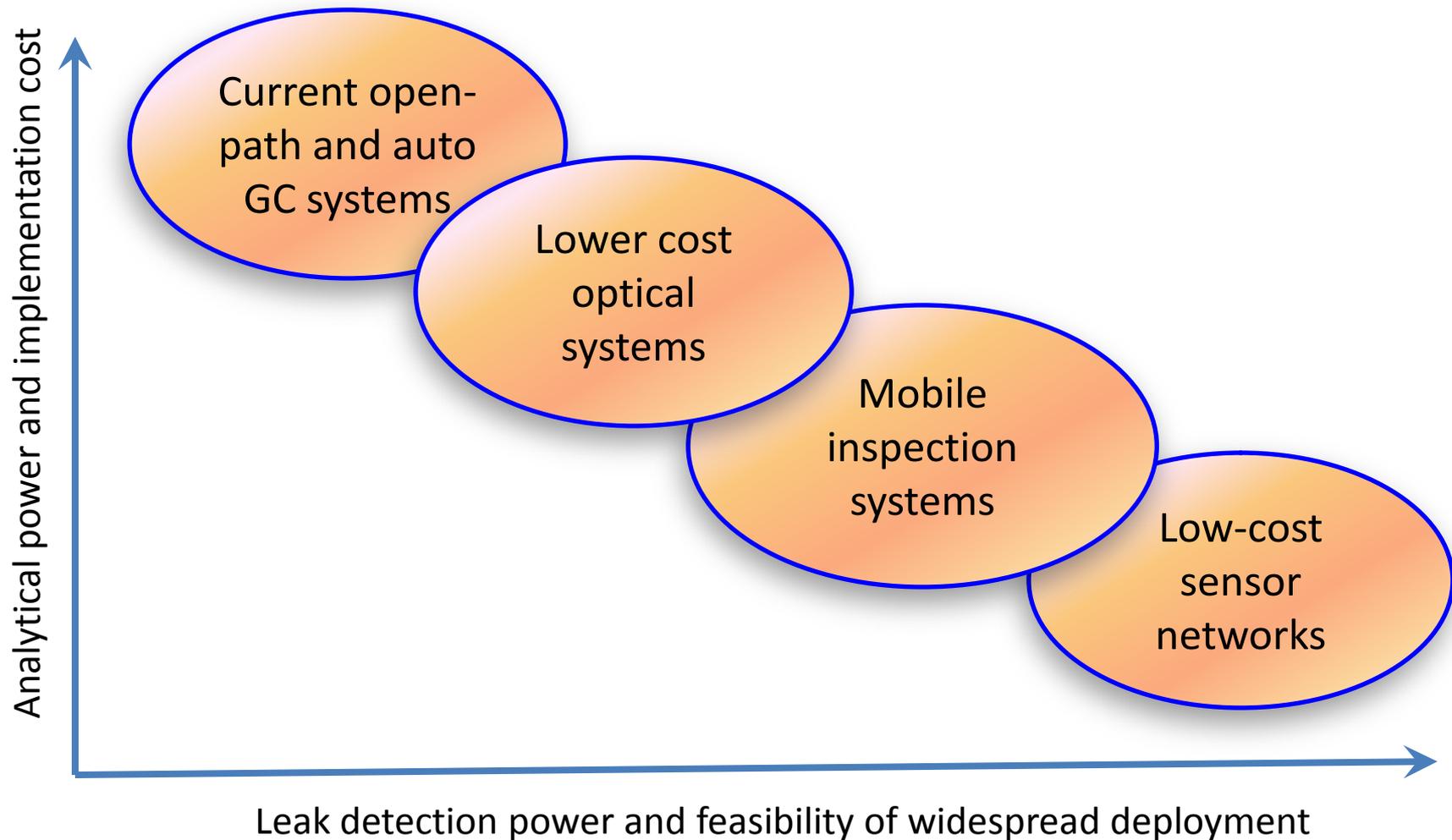
- ▶ Point sources (vents or stacks)
 - ▶ Emissions generally well understood and well characterized, and some test data available where pollutants were directly measured
 - ▶ Examples include vents at catalytic cracking, fluid coking, delayed coking, catalytic reforming, sulfur recovery, hydrogen plants
 - ▶ As part of risk and technology review, EPA is amending rules to require electronic submission of performance test data; will be used to periodically update emission factors
- ▶ Flares
 - ▶ Destruction of pollutants in an open flame
 - ▶ Difficult to directly measure pollutants
 - ▶ Flare studies available to develop correlations for parameters that affect flare destruction efficiencies (2012 peer review)
 - ▶ September 2012 NSPS flare amendments will require all flares to eventually have monitors to measure waste gas flow
 - ▶ Flare operational requirements ensure good combustion and provide information (waste gas composition and flare destruction efficiency) that can be used to estimate emissions from flares
- ▶ Fugitive emission sources
 - ▶ Tend to be open sources or not emitted through a stack or vent, thus difficult to directly measure pollutants
 - ▶ Examples include equipment leaks and pressure relief devices, tanks and transfer operations and wastewater handling and treatment
 - ▶ Emission models and estimates are used to predict pollutant emissions
 - ▶ An emission standard at the fence line can help ensure fugitive emission standards are being met

Fenceline Monitoring

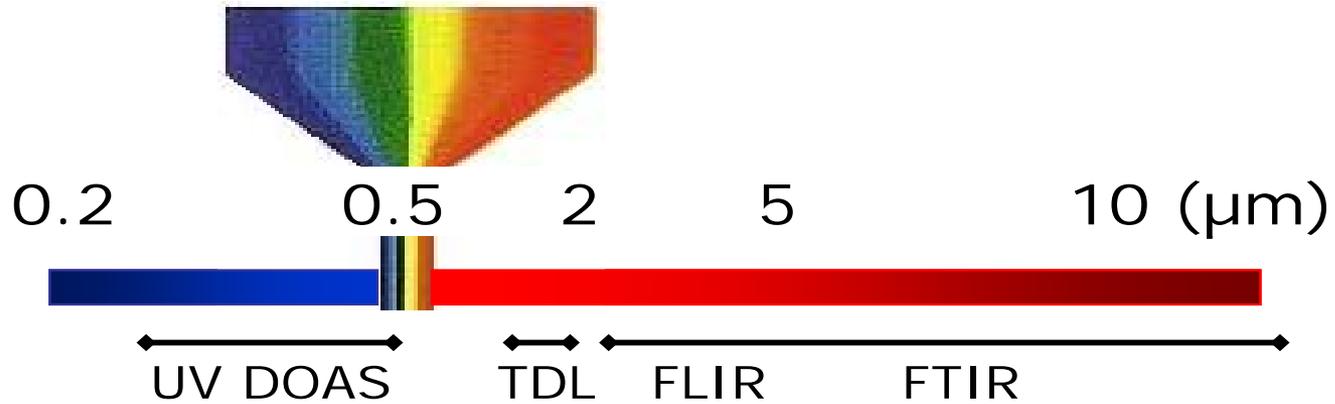
- ▶ Fugitive emission sources may not be well characterized in the inventories but are likely significant contributors to overall emissions
 - Fugitives from process piping
 - Wastewater sources
 - Pressure relief events
 - Tanks
- ▶ Highest concentrations of these fugitive emission sources outside the facility likely occur by the property boundary near ground level
- ▶ Air monitoring at the property boundary can provide a direct measure of the annual average concentrations of air toxics directly surrounding the refinery
- ▶ Benzene is a refinery risk driver and also primarily emitted from fugitive sources; 85% of benzene emissions from refineries is from fugitive, ground-level sources, so reducing emissions of benzene from fugitive sources will reduce emissions of other toxic pollutants
- ▶ Perimeter or fenceline monitoring provides an indicator of the level of emissions at refineries and is a way to ground-truth fugitive emission estimates

Monitoring for Assessment of Fugitives

Different technologies and approaches to detect and measure pollutants over extended areas and time



Open-Path Instruments



UV Diff. Optical
Absorption
Spectroscopy



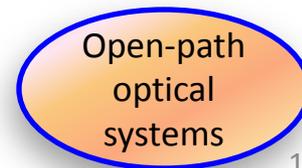
Tunable Diode
Laser (scanning)



Forward-Looking
InfraRed
(leak imaging)

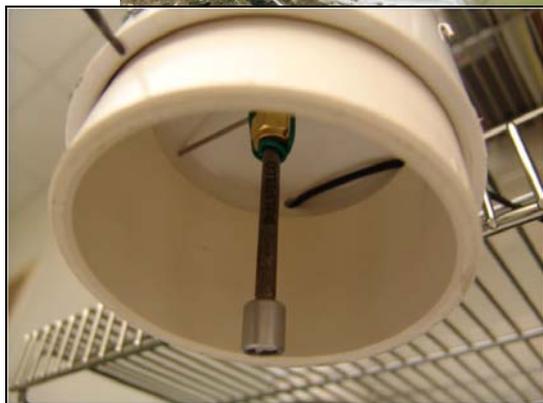


Fourier Transform
InfraRed (scanning)

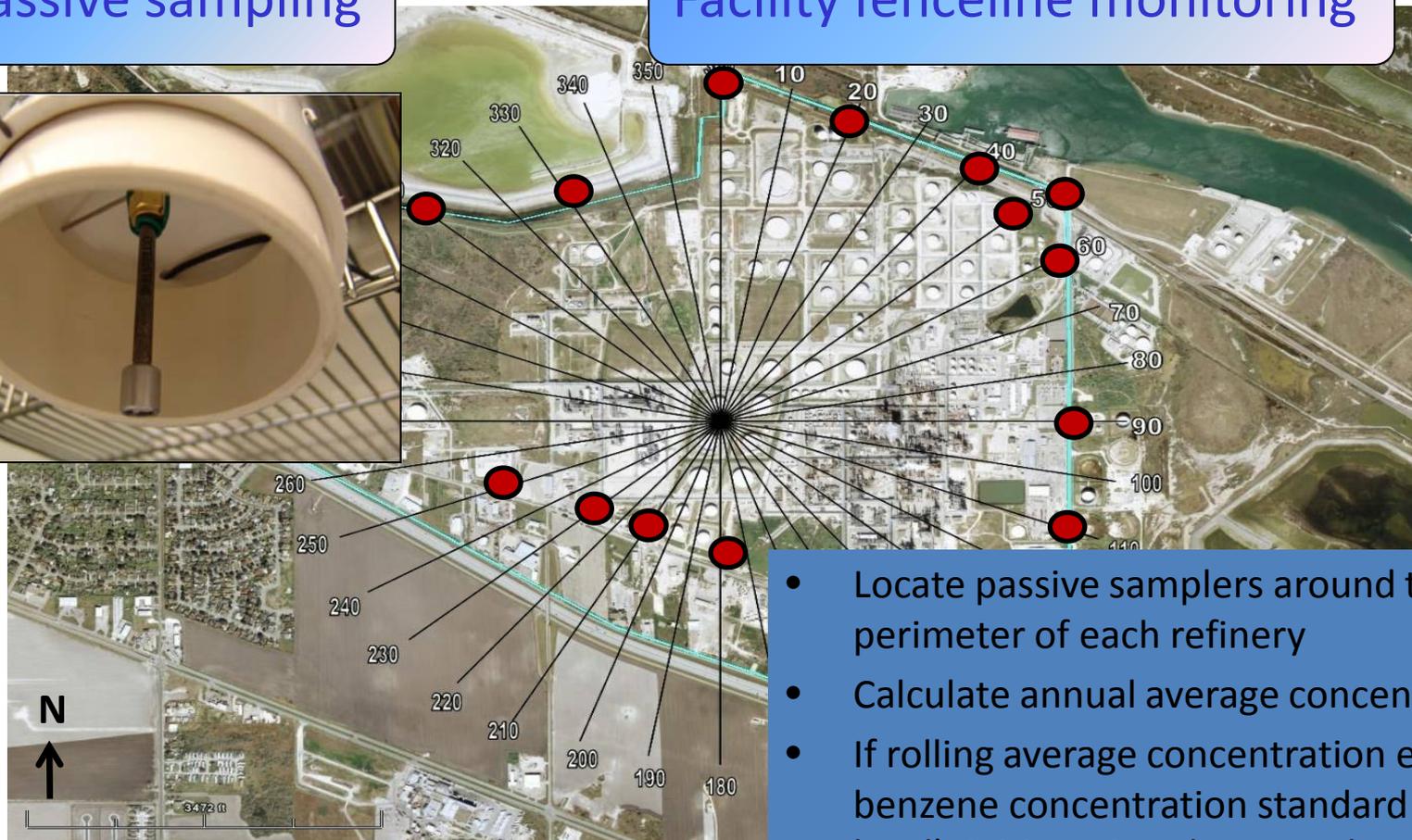


Low-Cost Sensors Can Provide 24-7 Observation and Enable New Regulatory Approaches

Passive sampling



Facility fenceline monitoring

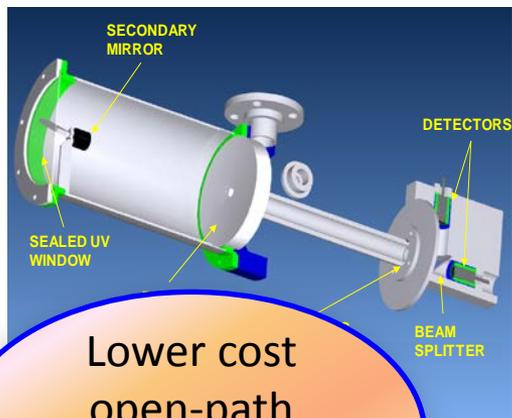


- Locate passive samplers around the perimeter of each refinery
- Calculate annual average concentration
- If rolling average concentration exceeds benzene concentration standard (the action level), initiate tiered approach to positively identify facility contribution and conduct corrective action to reduce emissions

Low-cost
sensor
networks

Developments in Lower-Cost Time-Resolved Monitoring to Support Time-Integrated Passive Sampler Fenceline Measurements

Deep UV optical sensor



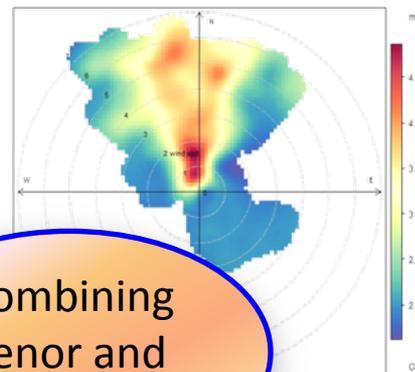
Lower cost open-path optical systems

Drive-by leak inspection



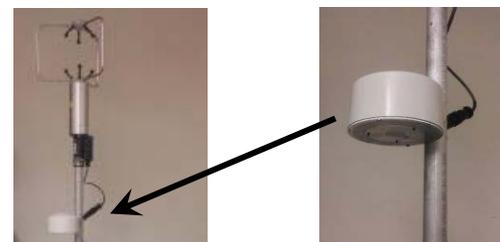
Mobile inspection systems

New leak-location algorithms



Combining sensor and wind data

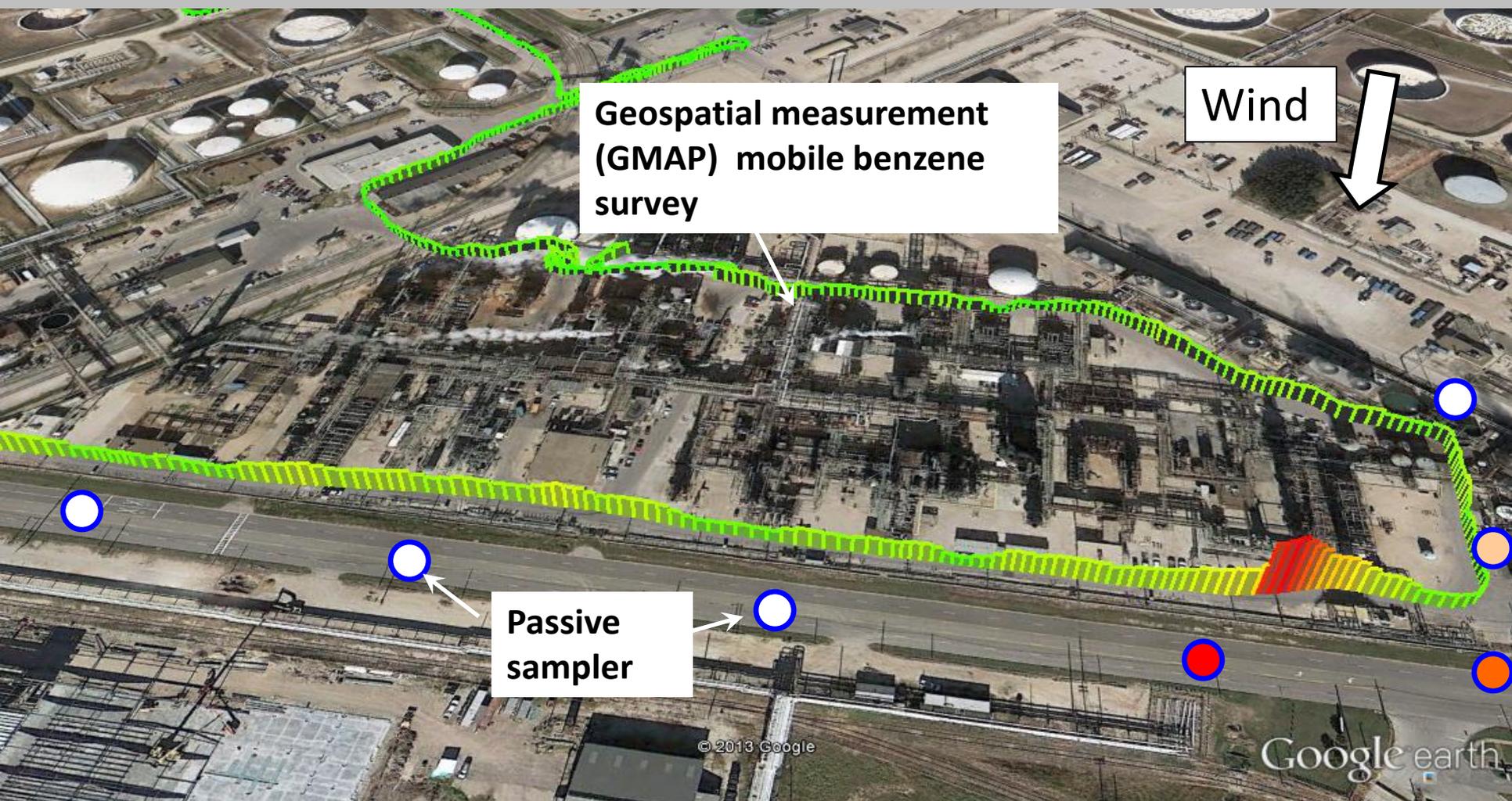
Drop-in-place sensor packages



Prototype PID sensor package (pres. temp., RH., VOC)

Low-cost stand-alone sensors

Passive sampler fenceline and mobile inspection demonstration



April 2013 passive sampler and GMAP demo with a cooperating refinery
Mobile inspection detected benzene leak at location of the highest passive sampler reading