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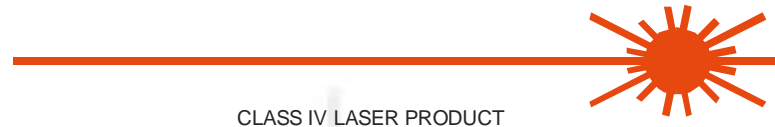
# Reflections on 20 Years of DIAL VOC Measurements in the Oil and Gas Industries



[www.spectrasyne.ltd.uk](http://www.spectrasyne.ltd.uk)

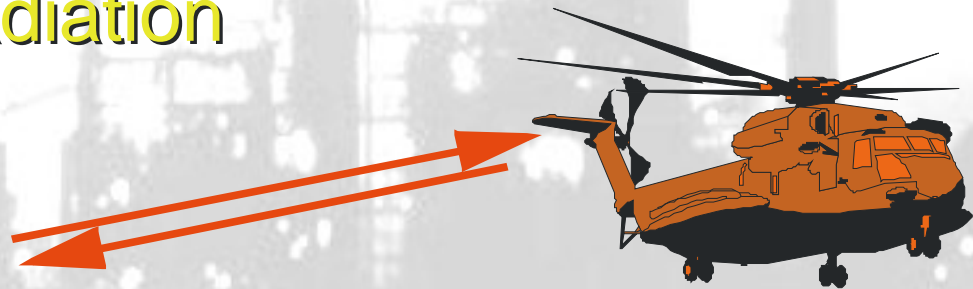
# Acronyms

## LASER



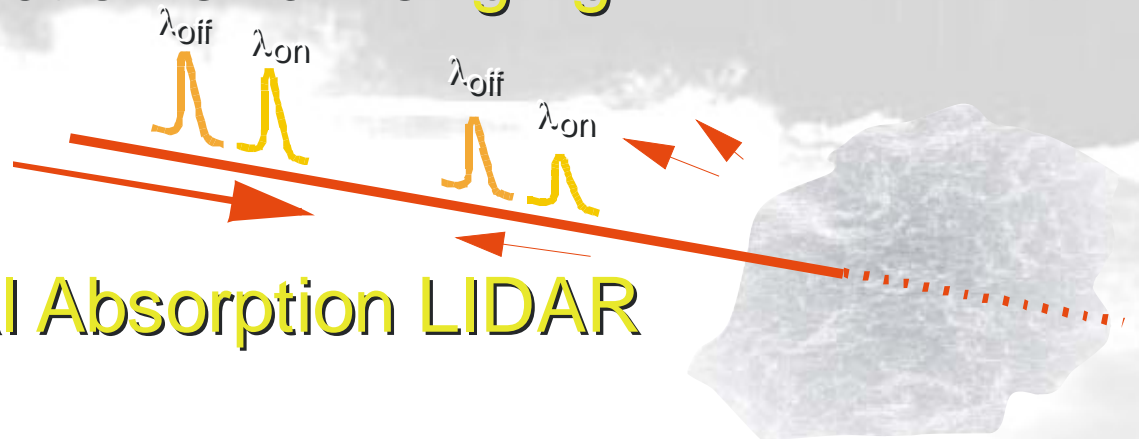
- ◆ Light Amplification by Stimulated Emission of Radiation

## LIDAR



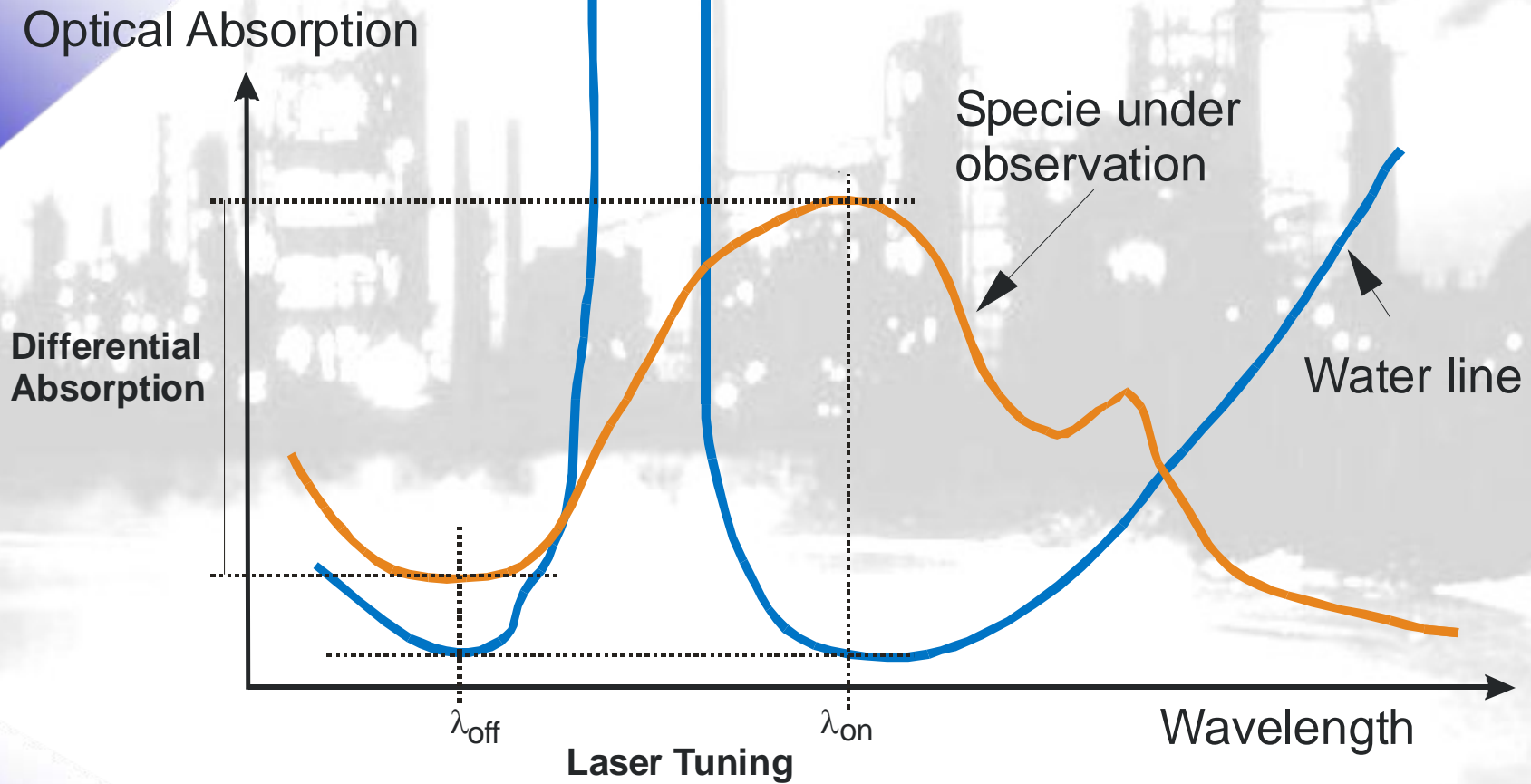
- ◆ Light Detection and Ranging

## DIAL

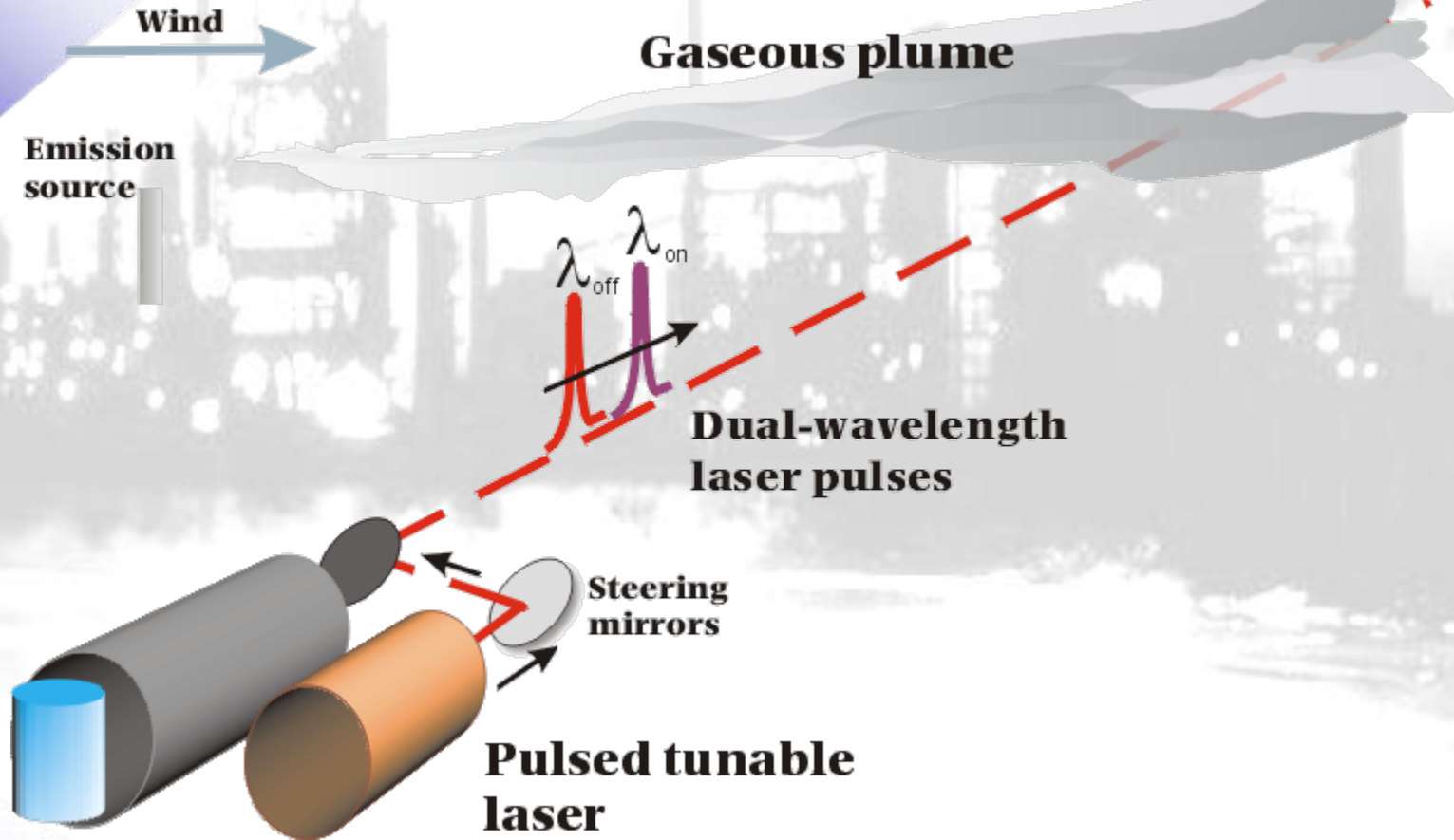


- ◆ Differential Absorption LIDAR

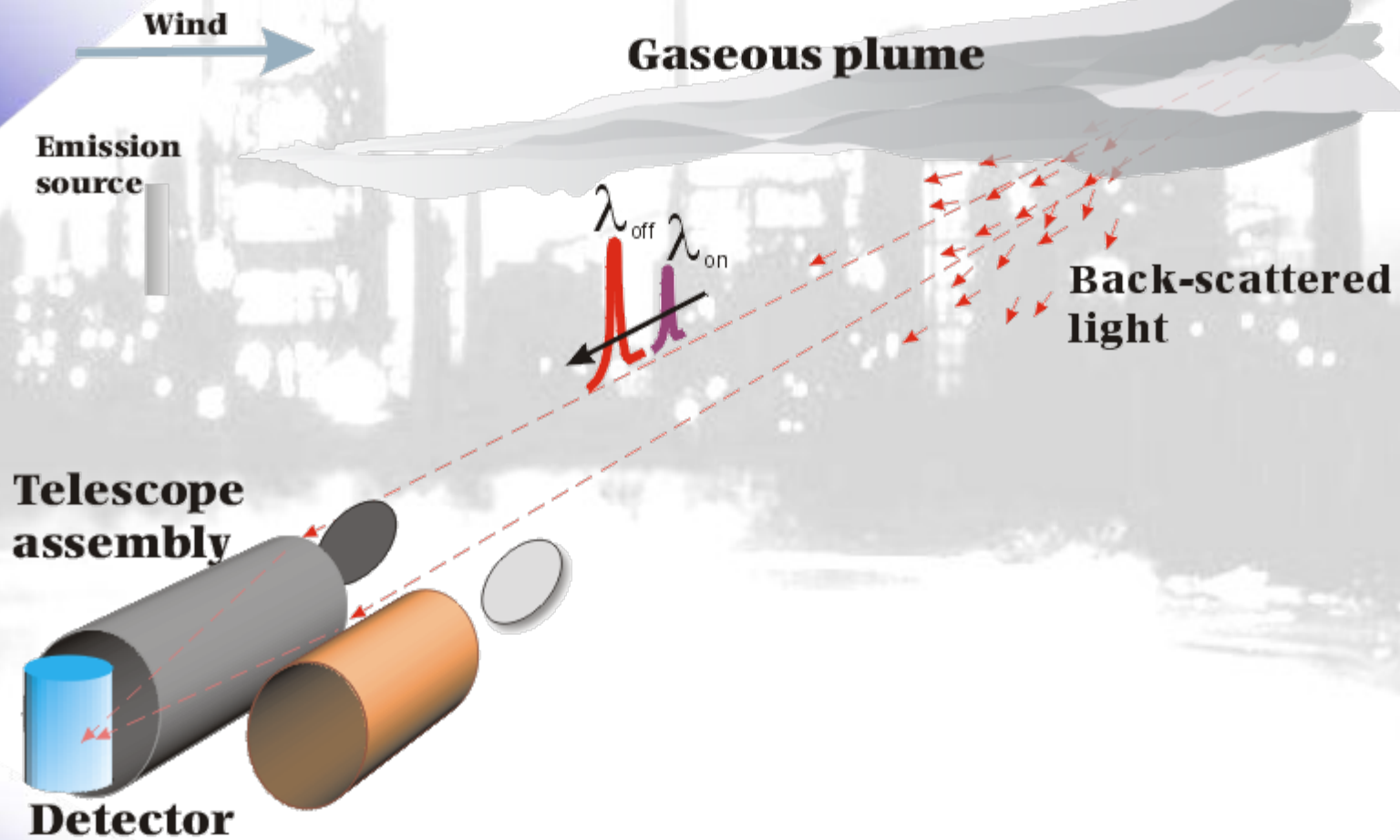
# DIAL Spectroscopic Principle



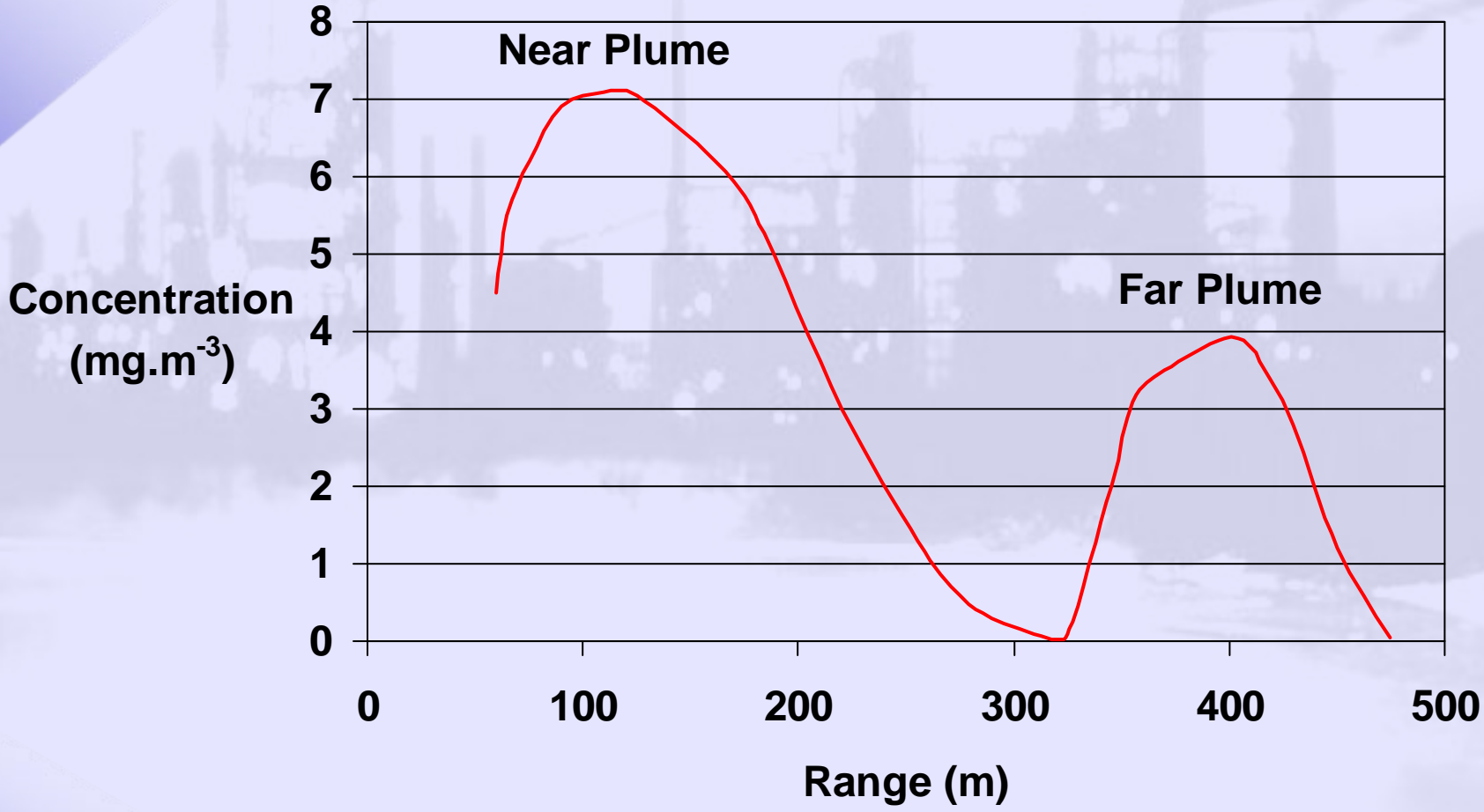
# DIAL Method – Output Signals



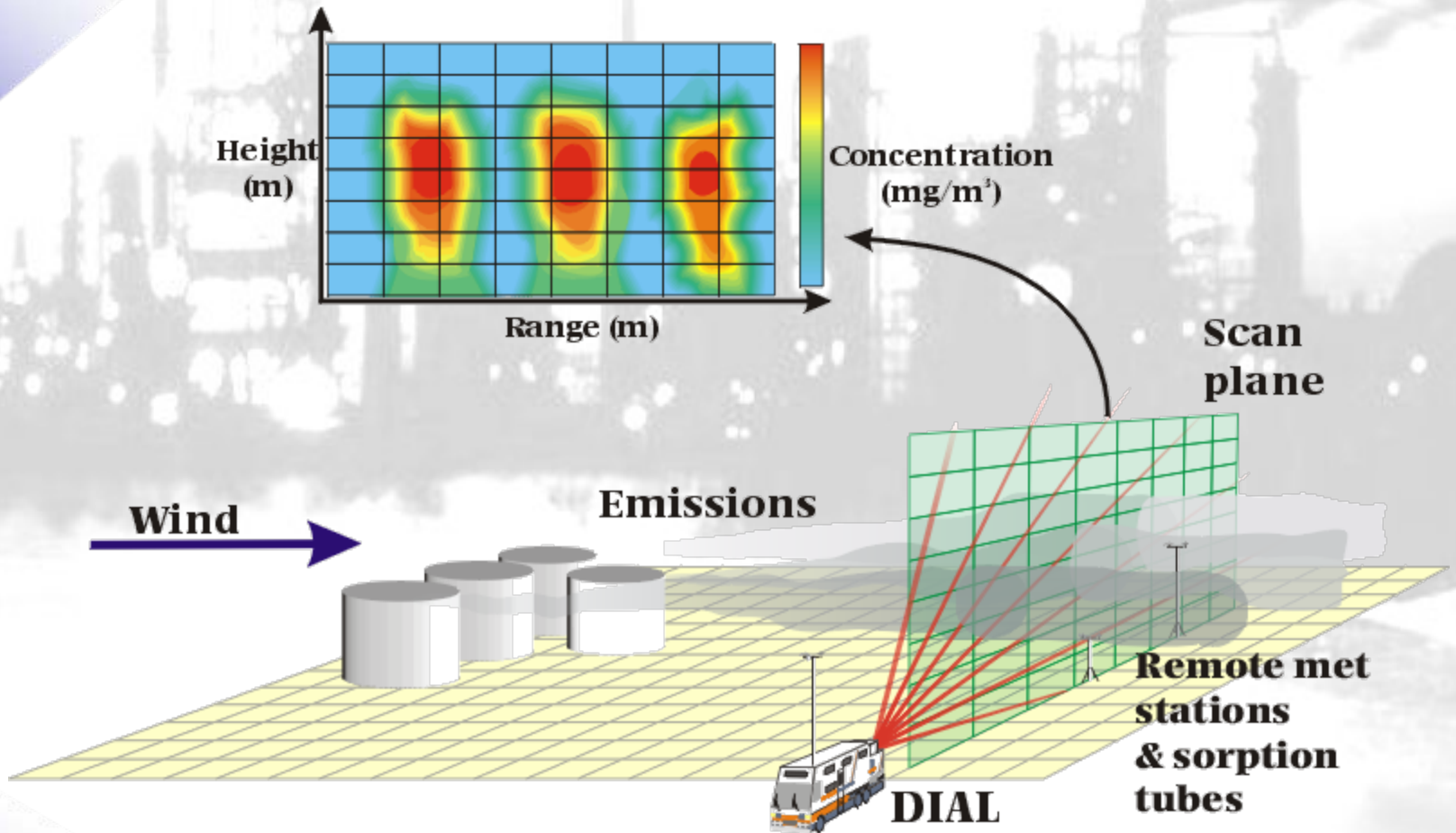
# DIAL Method – Return Signals



# Range Resolved Concentrations



# Spectrasyne DIAL Site Measurement





# Spectrasyne DIAL Vehicle



# Advantages of DIAL

- Single ended  
(no external mirrors)
- Mass emission and area concentration measurement  
(not just a single point or line concentration)
- Simultaneous multi-specie mass emissions.
- High sensitivity and range resolution  
(Emission positioning)
- Hemispherical coverage
- Mobile

# Technique Comparisons

Technique	Sorption Tubes	Point Analysers	LPM*	DIAL
TWM or single concentration (mg.m-3)	✓	✓	✗	✓
Column Content (ppm.m)	✗	✗	✓	✓
Range Resolved Concentration	✗	✗	✗	✓
2D concentration	✗	✗	✗	✓
Mass emission	✗	✗	✗	✓

\*Radial Plume mapping gives Mass Emission

# Spectrasyne DIAL Survey Experience



Type of Survey	Plant / Equipment	Number of separate measurement surveys
Refinery	Process plant, Tankage, Water treatment	30
Chemical works	Process plant, Tankage	10
Oil product terminal	Tankage, Road tanker loading	6
Crude oil terminal (excl'd. refinery sites)	Storage, Pumping, Stabilisation	11
Rail loading terminal	LPG & liquid product loading	2
Shipping terminal	Barges, Product carriers, Crude carriers	17
Oil field gathering station	Process plant, Water treatment	1
Oil production	Well head pumps, sites	3
Natural gas plant	Processing, Storage	21
Flare study	High & ground flares	20
Tank study	Individual / group tanks	8
Process cycle study	Refinery process plant	3
Plume tracking	Gas terminal complex	5
Aero engine emission studies		2
Airport study	Taxiways & runway	1
Other (non-oil, gas and petrochemical) industries	Various	5
<b>TOTAL SPECTRASYNE DIAL SURVEYS SINCE 1990</b>		<b>145</b>

*\* In addition, between 1982 and 1989, the Spectrasyne DIAL team members supervised and reported a further 9 major proving surveys at refinery/terminal sites with the prototype system.*

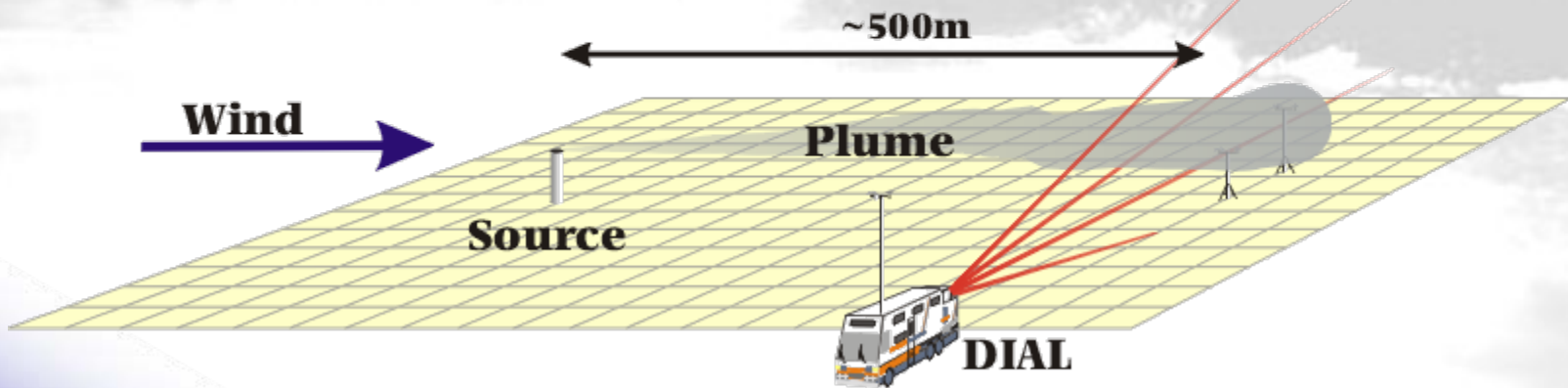
# Spectrasyne DIAL Validation

**Venue** - MOD site at Spadeadam, Cumbria, UK

## Programme

- **Controlled releases** of 10% methane in nitrogen (standardised)
- **DIAL concentration measurements** in plume >500m downwind of source
- **Integrated** plume columns combined with **wind speed and direction** measurements to give **mass** methane emission levels

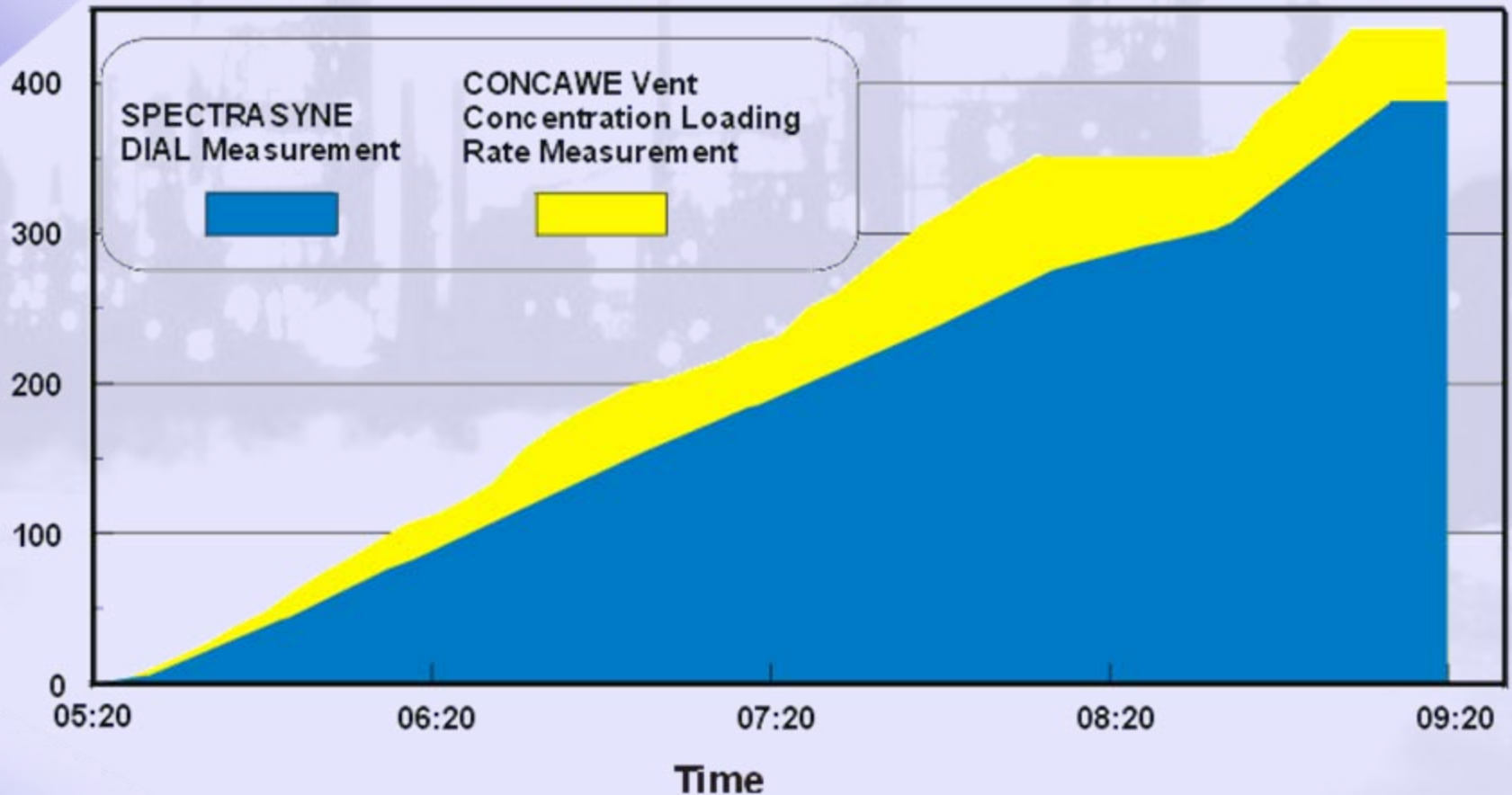
$$\frac{\sum^n \left[ \frac{\text{Measured release} - \text{DIAL measurement}}{\text{Measured release}} \right] \times 100}{\text{Number of releases (n)}} = 10\%$$



# Spectrasyne Barge Loading Correlation

## Measured VOC Emission Comparison

Cumulative Hydrocarbon Loss (kg)



# Spectrasyne – Correlation / Validation Data

## Species

Δ | Analyser/Tube --> DIAL |

### 1. Concentration

HCs (Refinery Water Treatment) 0 - 8%

NO 4%

HCs (Truck Loading Gaso / Diesel) 8 - 11%

HCs (Heavy Hydrocarbon Storage) 3%

Toluene 3 - 18%

Benzene (DOAS) 5%

Benzene (BTX Storage) 7%

### 2. Mass Emission

Methane (CH<sub>4</sub>) 10%

HCs (Gasoline Tanks- small, good cond) 10% (API calc - DIAL)

HCs (Truck Loading Gaso / Diesel) 8 - 11%

HCs (Heavy Hydrocarbon Storage) 3%

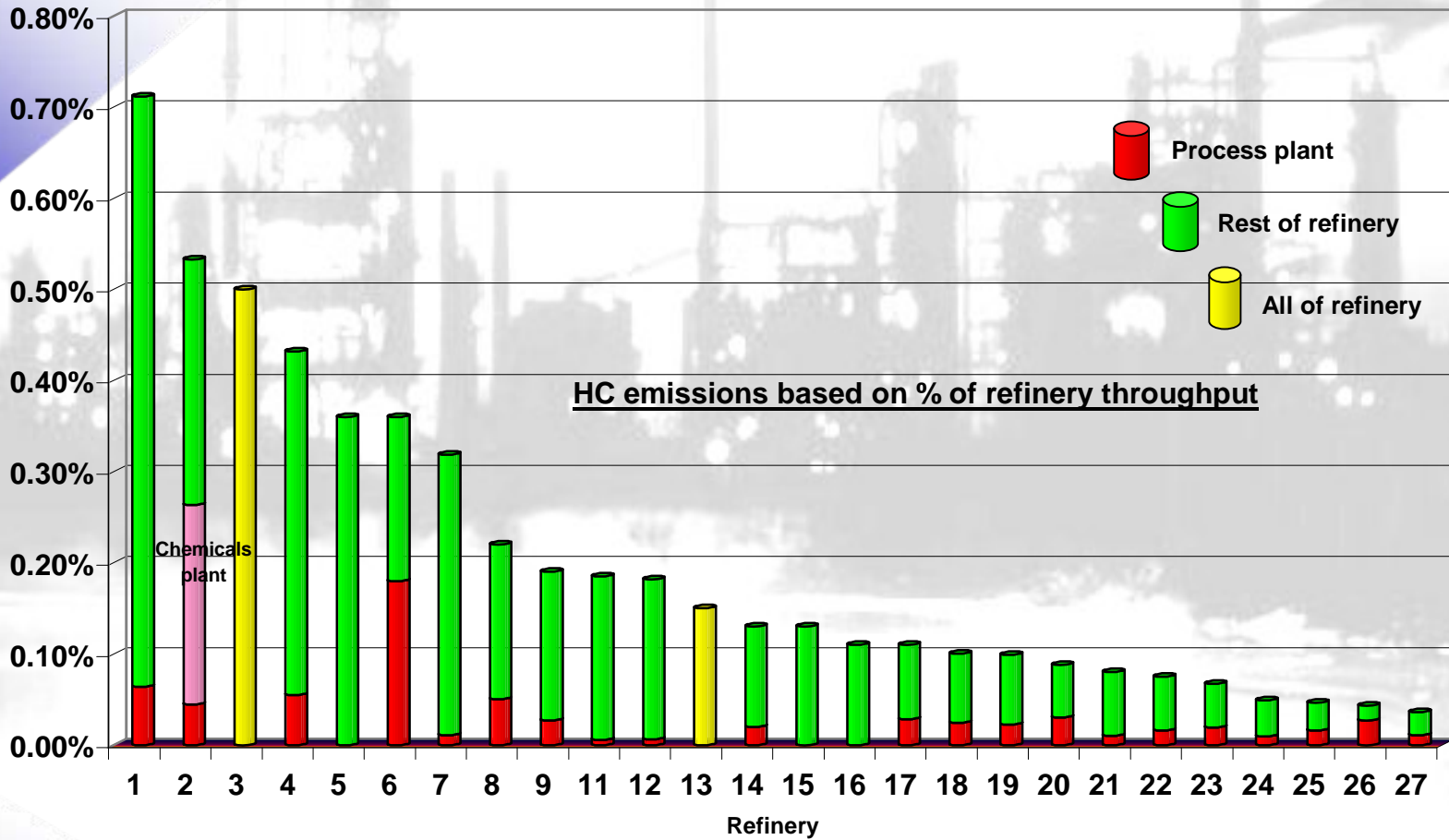
HCs (Gasoline Barge Loading) 10 - 12%

HCs (Crude Ship Loading) 12%

NO & NO<sub>2</sub> (Incinerator Stack) 0%

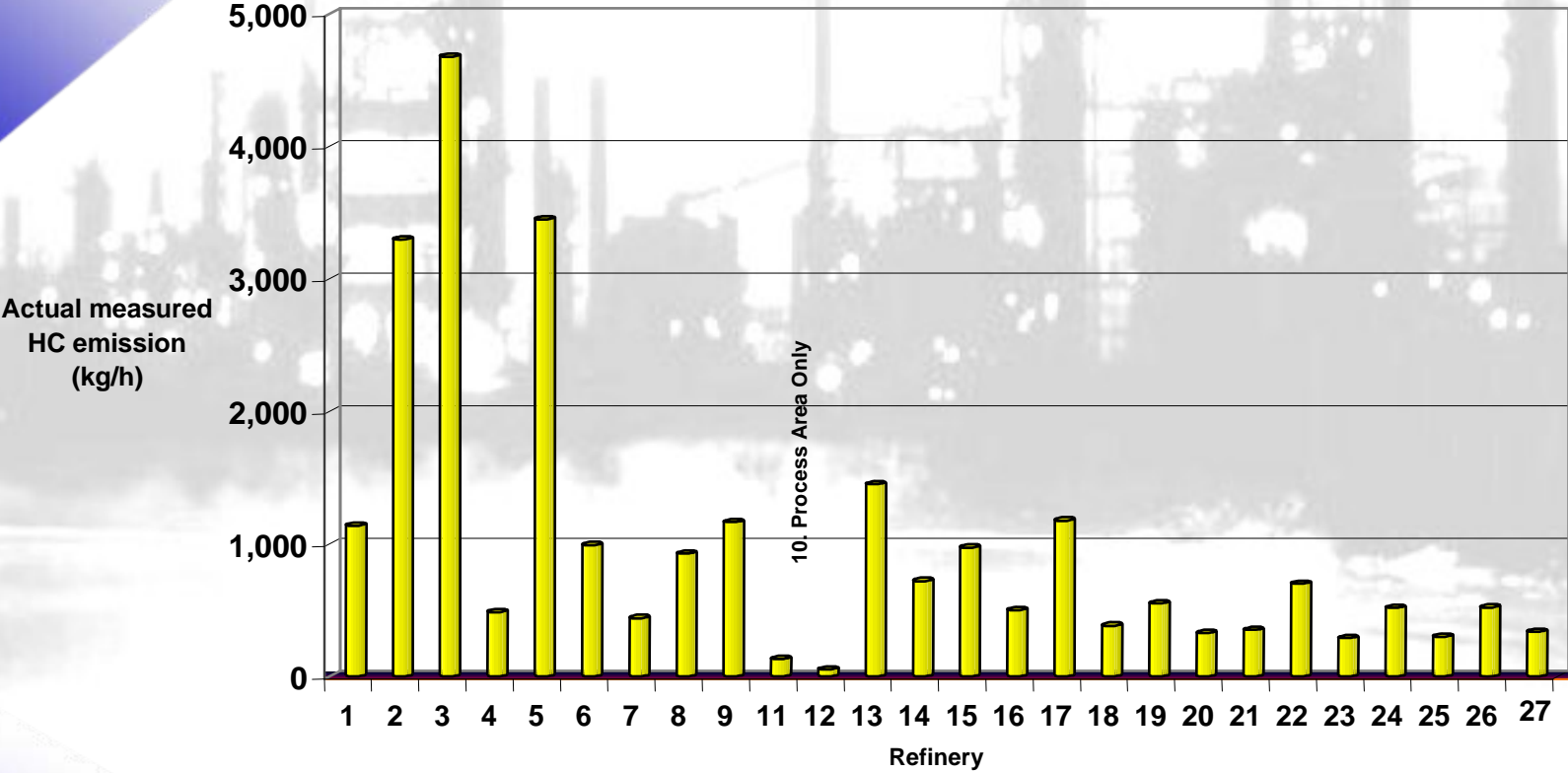
SO<sub>2</sub> (Incinerator Stack) 10%

# Spectrasyne DIAL Refinery VOC Emission Comparisons

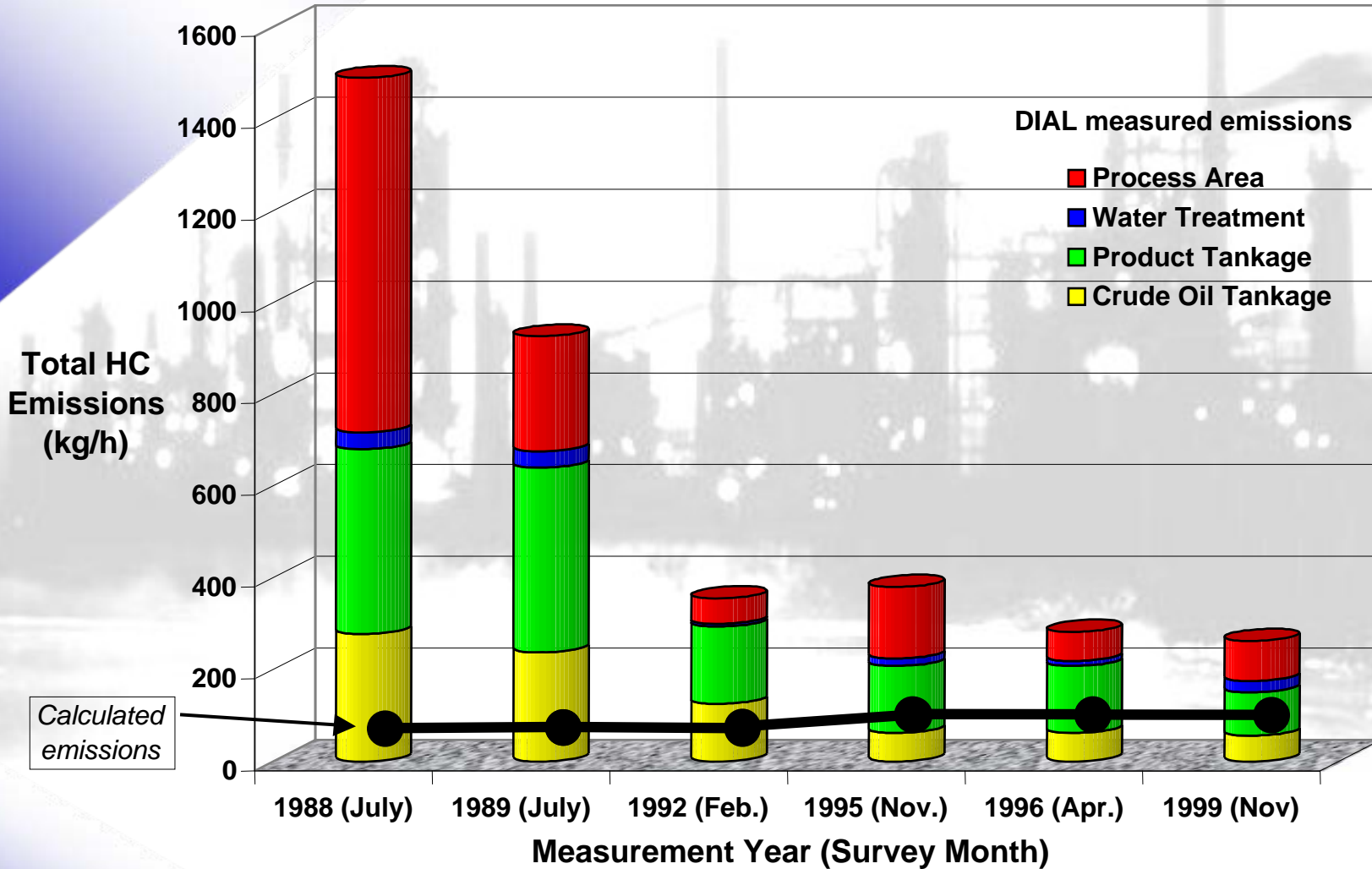




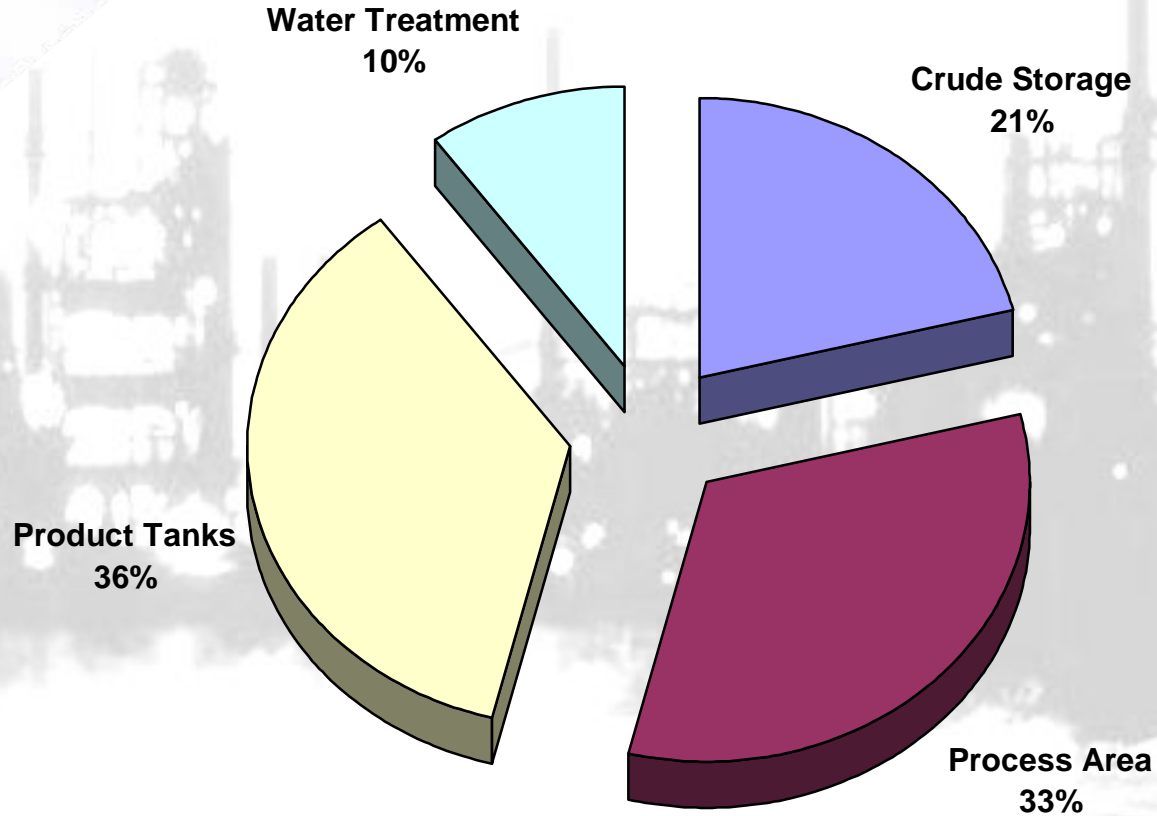
# Spectrasyne DIAL Refinery VOC Emission Comparisons



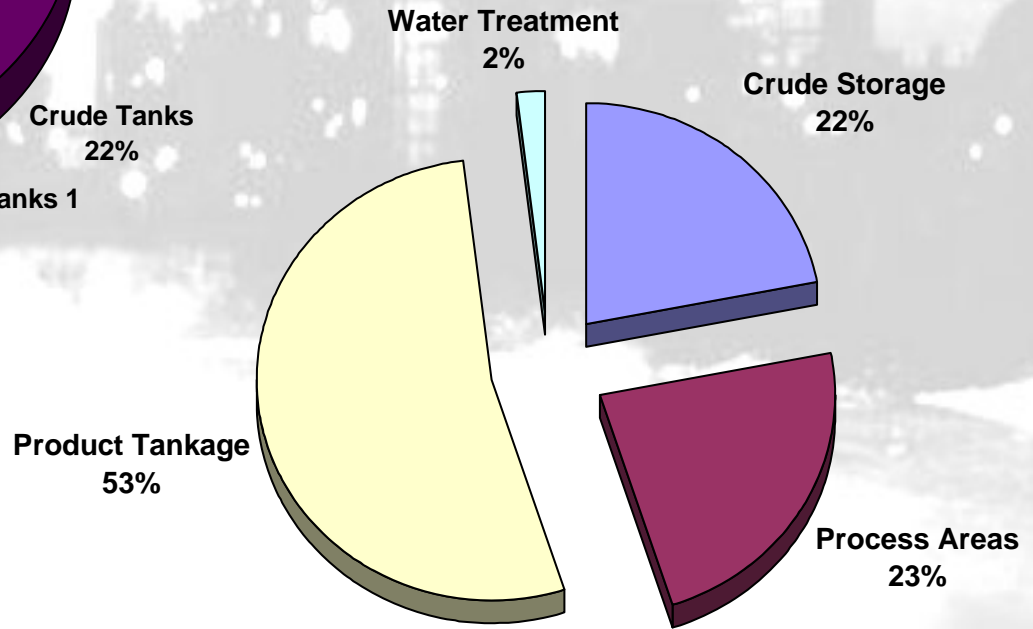
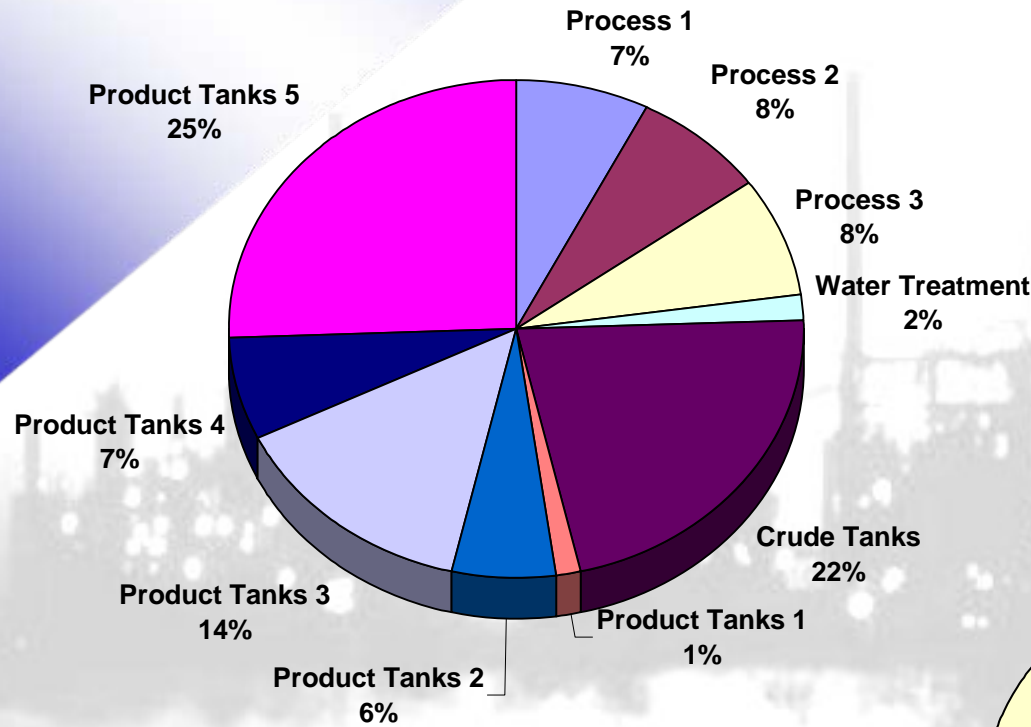
# BP/OK/PREEM Gothenburg Refinery Emissions



# Simple Refinery Emissions by Area



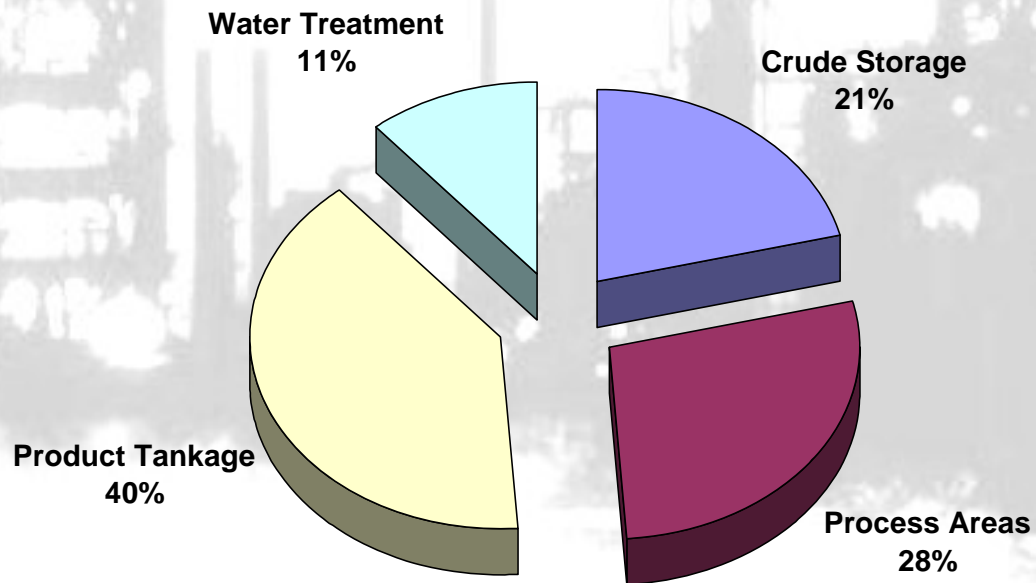
# Small Complex Refinery VOCs by Area



Flare % of Total Refinery Emissions

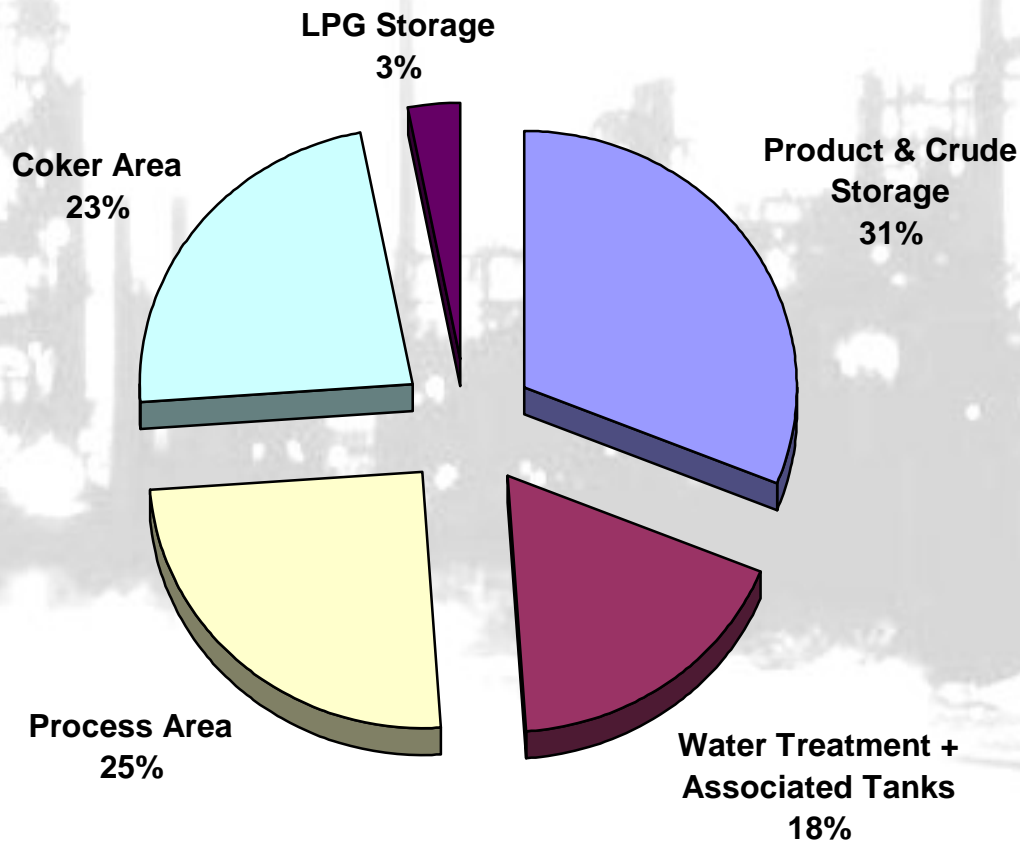
C2+ = 2.25%

# Complex Refinery VOCs by Area



# Large Complex Refinery With Coker

## C2+ VOCs by Area



### Flare % of Total Refinery Emissions

C2+ = 3.2%

CH4 = 4.8%

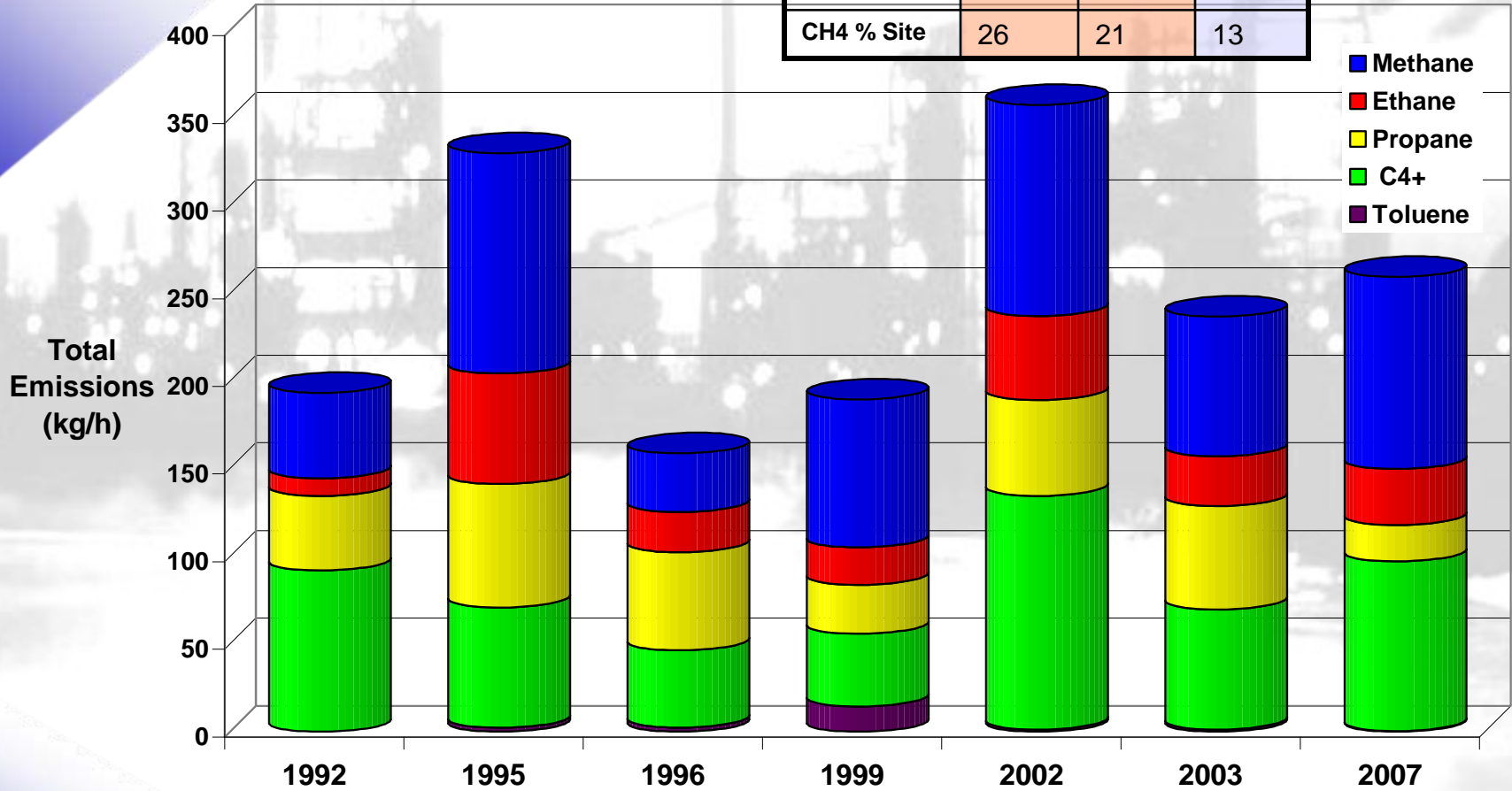
# Coker C2+ VOC Emission Comparisons

## Equivalent Hourly Mean kg/h over Cycle

	<b>Coker 1</b>	<b>Coker 2</b>	<b>Coker 3 (Case 1)</b>	<b>Coker 3 (Case 2)</b>
<b>Initial DIAL Measurements</b>	<b>305</b>	<b>N/A</b>	<b>652</b>	<b>269</b>
<b>DIAL Measurements with closed/flared blowdown and other improvements</b>	<b>72</b>	<b>96</b>	<b>36</b> <b>(Coke storage: 24 C2+/20 CH4)</b>	<b>(32 kg/h CH4)</b>

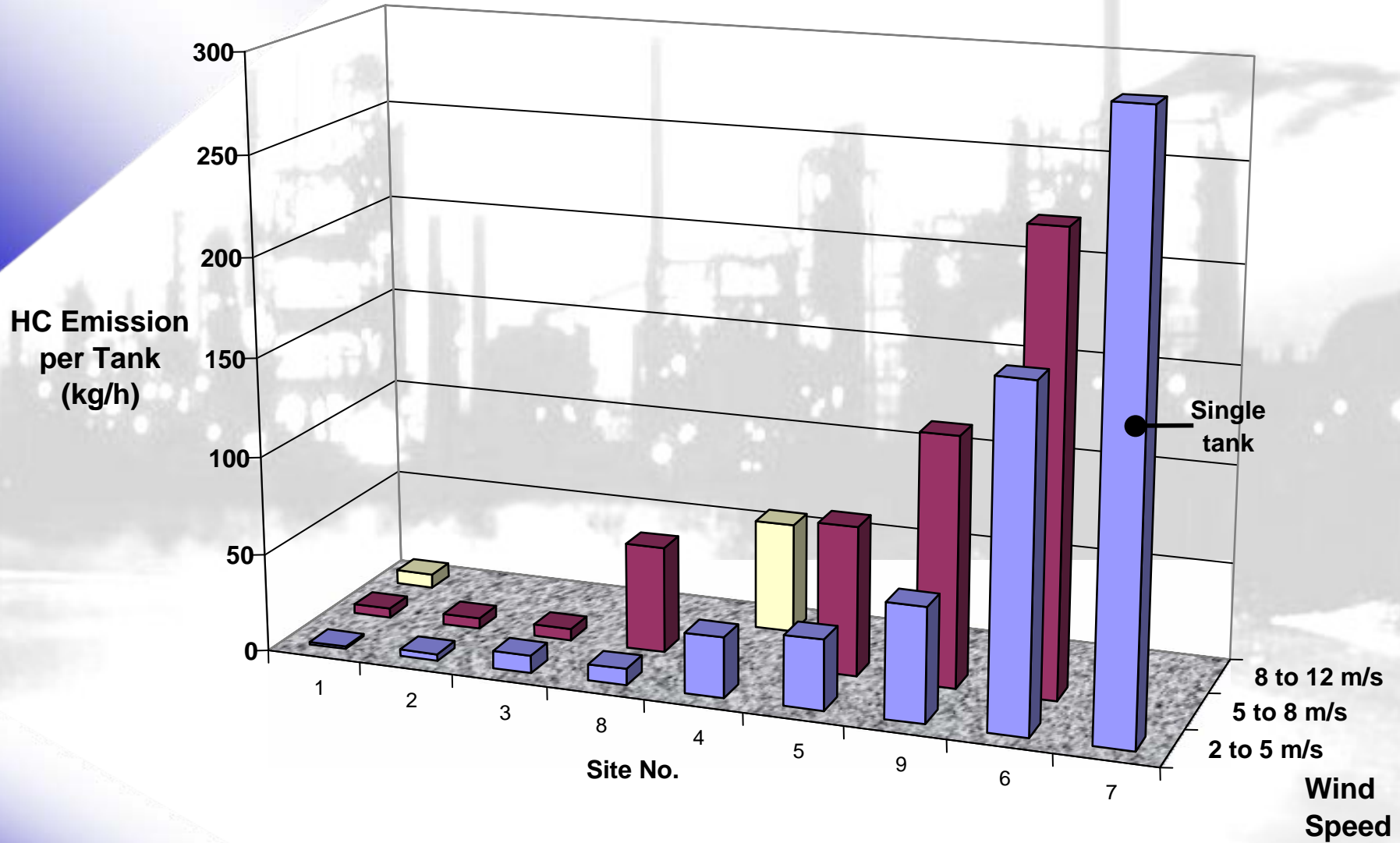
# North Sea Gas & Condensate Processing Plant

Flare Emission	Steam Raised flow	No Steam Raised flow	No Steam as found
<b>C2+ % Site</b>	6	8	3
<b>CH4 % Site</b>	26	21	13

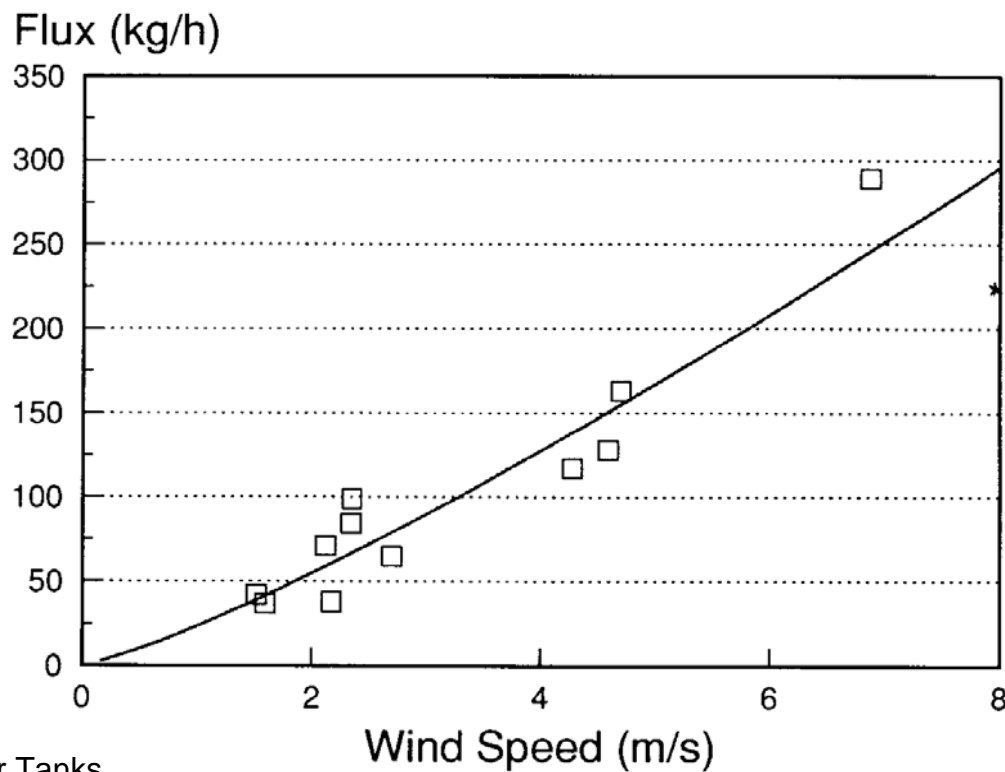




# Light Distillate Floating Roof Tank HC Emissions

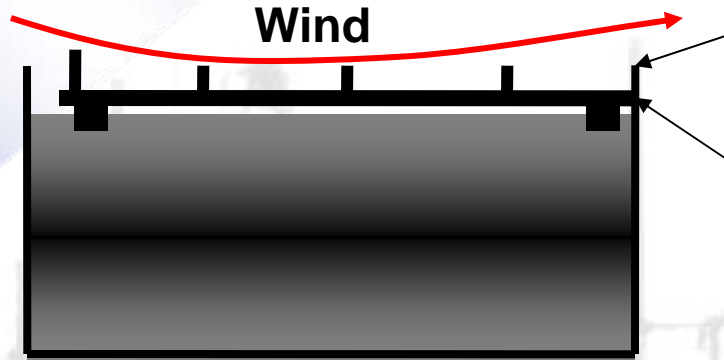


# Wind Speed – Emission Correlation Crude Oil Tanks



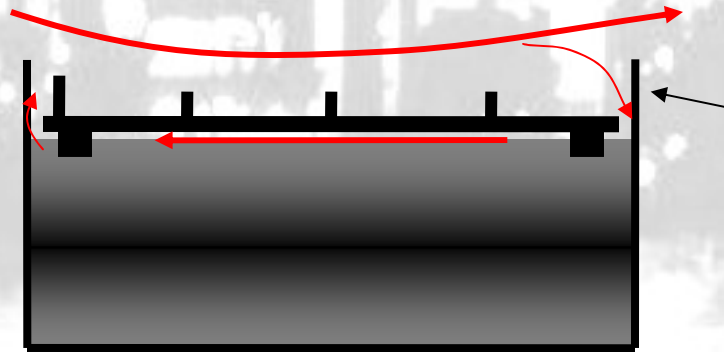
9 x 54m Diameter Tanks  
Floating Roof, some Secondary Seals

# Effect of Roof Level on Wind Penetration Into Rim Seals

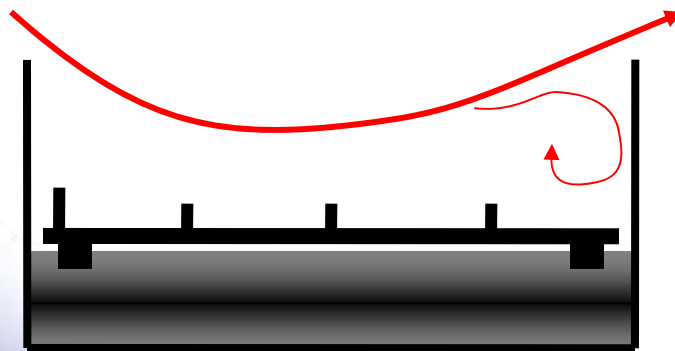


Small freeboard limits wind penetration into seal gap

Gap closes due to sail effect on roof fittings



Larger freeboard encourages wind penetration into seal gap



Very large freeboard shelters seals

# Factors Affecting Floating Roof Tank Emissions

## **. Size**

- Aspect Ratio
- Seal Condition
- Seal Type
- Roof Height
- Vapour Pressure
- Contents Temperature

## **. Wind Speed**

- Filling Rate
- Tank Movements
- Topography
- Solar Radiation
- Precipitation
- Ambient temperature

# Solution Gas Flare Site F Preliminary Data



## Site F Flare

	Mean Wind Speed & Dir'n	CH <sub>4</sub> (kg/h)	C <sub>2+</sub> (kg/h)	Ethylene (kg/h)	Benzene (kg/h)
Day 1	7.5 m/s SSE	10.7	5.3	1.6	0.01
Day 2	4.9 m/s NNE	35.4	21.9	3.7	0.01

# DIAL Measuring Airport Emissions



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# Thank You!



[www.spectrasyne.com](http://www.spectrasyne.com)

Texas Commission on  
Environmental Quality  
(TCEQ)  
Differential Absorbption Lidar  
(DIAL) Project  

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Summer 2007  
Texas City, Texas







# Project Objective

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- Compare DIAL measurements with emissions calculated using traditional emission factors and calculation techniques on sources that are difficult to measure (DTM)
- Measure emission sources located at a bulk storage facility and a refinery



# Site Cooperation

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- Cooperation from both sites during this project was considerable
  - Site staff worked late and weekends
  - Site access
  - Safety training
  - Process data



# Project Funding

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- Total project cost \$650,000
  - \$200,000 funded by new technology EPA grant
  - \$450,000 funded by TCEQ



# DTM Emission Sources

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- Storage tanks
  - Internal floating roof tanks
  - External floating roof tanks
    - Crude oil & refined gasoline
  - Fixed roof tanks
  - Heated tanks
- Delayed Coker
  - Volatile Organic Carbon (VOC) emissions
  - Benzene emissions
    - During decoking process



# DTM Emission Sources cont.

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- Flares
  - New process/emergency flare
  - Temporary flare
- Wastewater area
- Sulfur recovery unit (SRU)



# Project Status

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- Draft DIAL report has been released to the public
- TCEQ is currently reviewing plant process data to compare traditional calculations to DIAL measurements
- TCEQ is developing a contract to assist with the tank calculations
- TCEQ's final report - Fall 2008



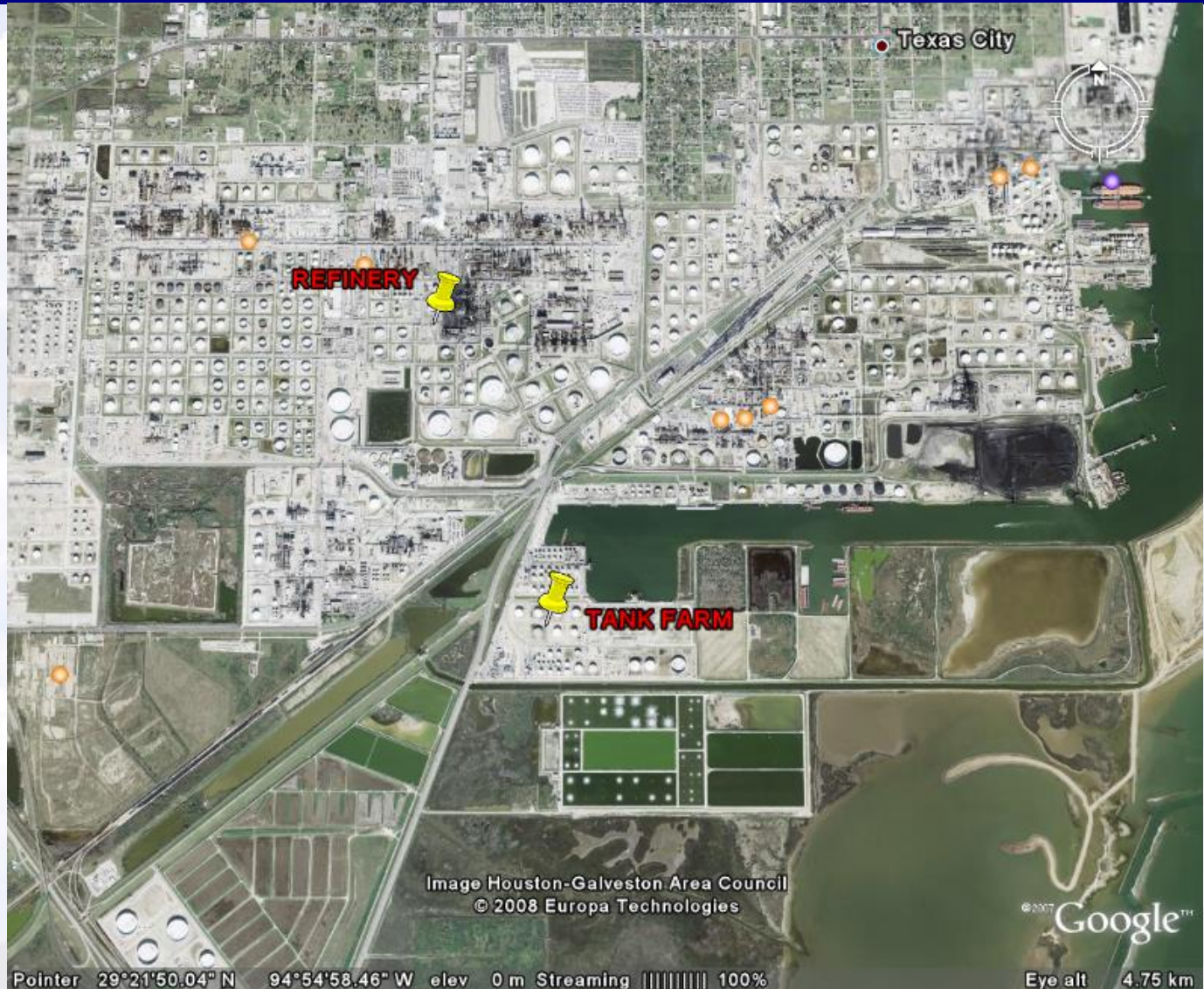
# Project Technology

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- DIAL- Service provided by National Physical Laboratory (NPL)
- Hawk Infrared Camera - Service provided by Leak Surveys Inc.
- UV-DOAS (Ultraviolet-Differential Optical Absorption Spectroscopy) - Provided by EPA
- Ambient Sampling - Performed by TCEQ staff and NPL



# Texas City Industrial Area







# Bulk Terminal

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- This site temporarily stores various liquids
  - The same tank may store multiple liquids during a calendar year
- Recently installed two new internal floating roof tanks
  - The floating roofs hang by cables from the top of the tank
  - The hanging roof has minimal holes in the roof and allows easier maintenance activity



# Bulk Terminal

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- Internal mixing in the a floating roof tank generated emission plumes identified by the infrared (IR) camera
  - This type of tank operation is not accounted for in EPA's TANKS program
- DIAL day time measurements July 16 -19
- DIAL night time measurements July 20



# Naphtha Tank 22

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- Wind conditions and DIAL location easily isolated Tank 22
- Negligible VOC vapor was seen by IR camera from top of tank under calm wind conditions
- Small amounts of VOC vapor was seen by IR camera under windy conditions
- Wind appeared to be blowing vapor between seals of tank



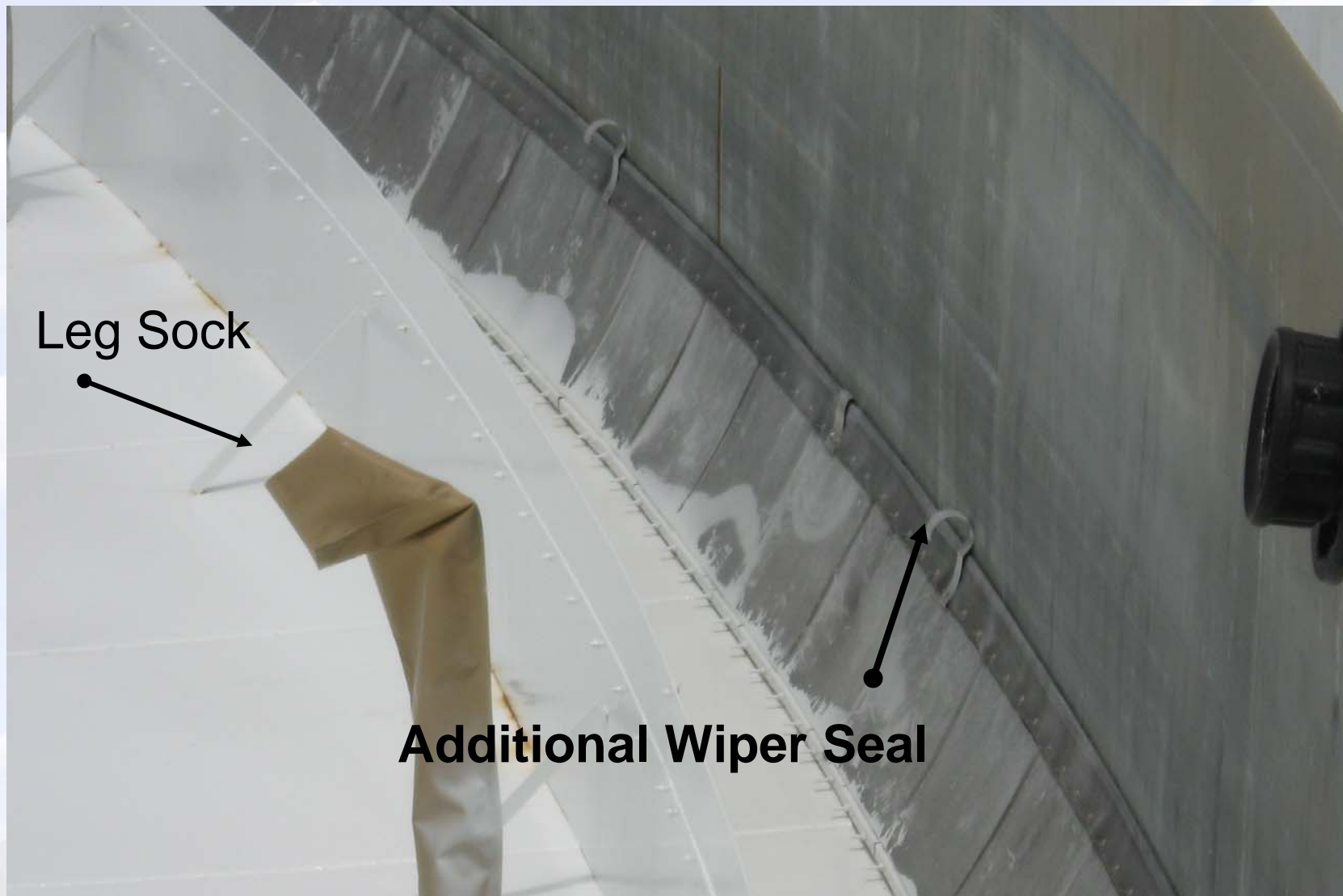
# Tank 22

---

- Well maintained
  - Recent turnaround and maintenance
- Had additional wiper seal
  - Not required by permit
- Roof leg supports has fabric “socks”
  - Not required by permit
- No obvious odor when camera team was on top of the tank
- Gauge pole openings were wrapped to avoid vapor loss



# Tank 22





# Tank 22





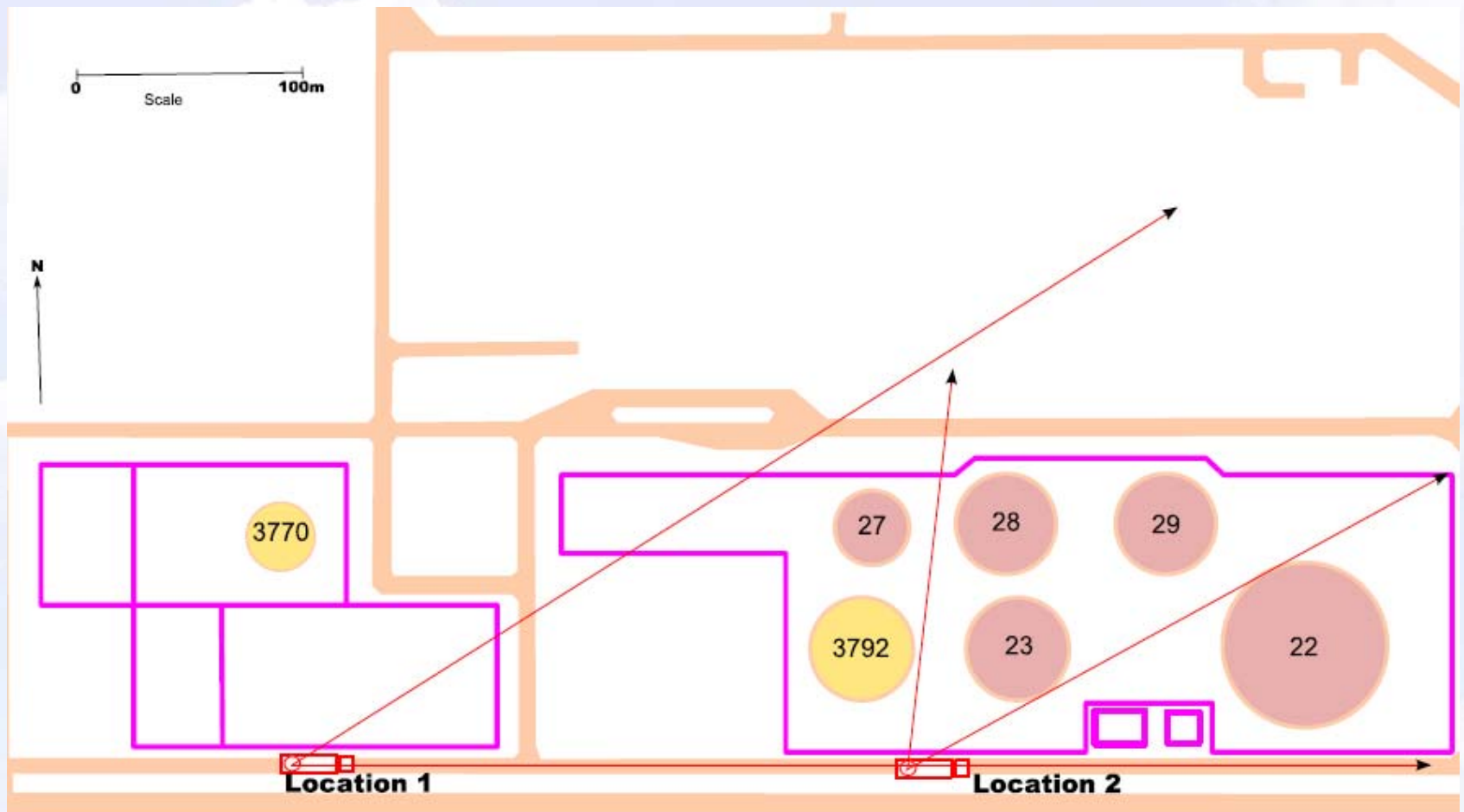
# Tank 22



**Wrapped Gauge Poles**



# Tank 22 DIAL Location







# Tank 22 Measurements

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- DIAL measurements 1 to 7 lbs/hr
- TANKS program emissions estimates using naphtha default parameters expected to be < 1lb/hr
- Tank appeared to be in excellent condition with additional controls not normally seen on other tanks



# Refinery

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- Refinery capacity was at 50% due to hurricane damage and turnaround projects
- Day time measurements July 25 – Aug 11
- Night time tank measurements August 5 - 8



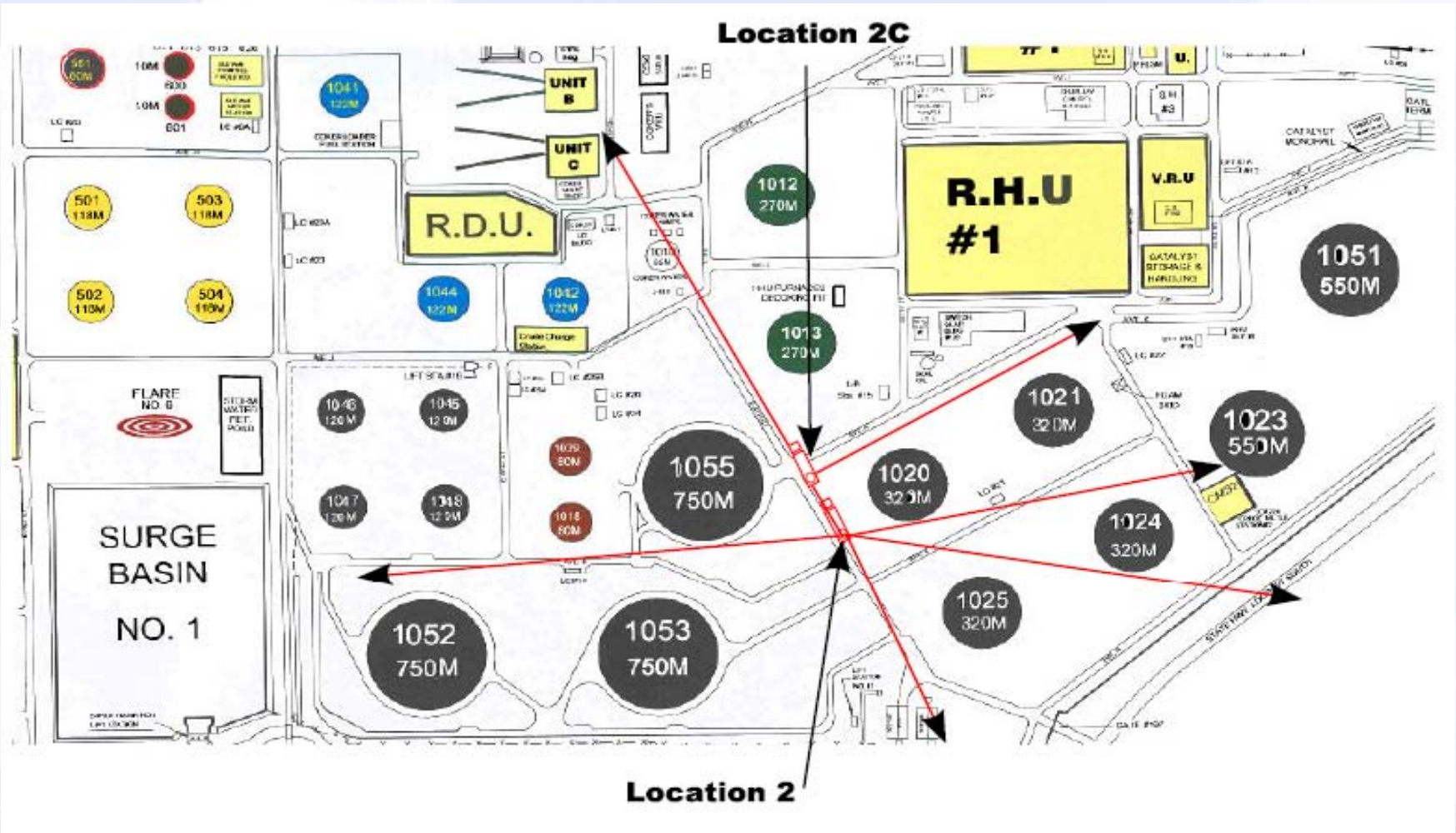
# Crude Storage Tanks

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- VOC odors were present when the IR camera team was on top of the crude tanks
- Significant amounts of hydrocarbon vapor was seen by IR camera from top of the crude tanks



# DIAL Location for Crude Tanks Measurements





# Crude Tank DIAL Measurements

Tank #	1020	1021	1024	1025	1052	1053	1055
Lbs/hr	<2	16	5	11	22 to 39	7	<5

TANKS program emissions estimates using crude oil default parameters expected to be < 1lb/hr



# Finished Gasoline Storage Tanks

---

- No VOC odors were present when the IR camera team was on top of the gasoline tanks
- Small amounts of VOC vapor was seen by IR camera from the top of the gasoline tanks
- DIAL measurements at the gasoline tank area were impacted by emissions from ground flare
- Ambient temperature was very hot during DIAL measurements





## Finished Gasoline Tanks 501 - 504

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- DIAL measurements of the group of tanks July 30
  - 2 to 18 lbs/hr
- TANKS program emissions estimates using gasoline default parameters expected to be 12 – 20 lbs/hr for the group of tanks





# Heated Oil Tanks

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- DIAL **night time** measurements on August 8
- Tank 60
  - Average DIAL emission rate 9 lbs/hr
- Tank 43
  - Average DIAL emission rate 6 lbs/hr
- TANKS program emissions estimates using fuel oil default parameters expected to be < 1lb/hr



# Coker Information

---

- Coker Design
  - 4 product cuts with overhead vapor sent to a **vapor recovery unit (VRU) or into the refinery fuel gas system**
- Coker furnace heats coker feed to 920° F
- The coker was on a 20 hour cycle
- The coker is a refinery process unit with expected fugitive VOC emissions
  - Leak detection and repair program (LDAR) tags were observed on the bottom of the furnace



DIAL position during a coker VOC measurement scan



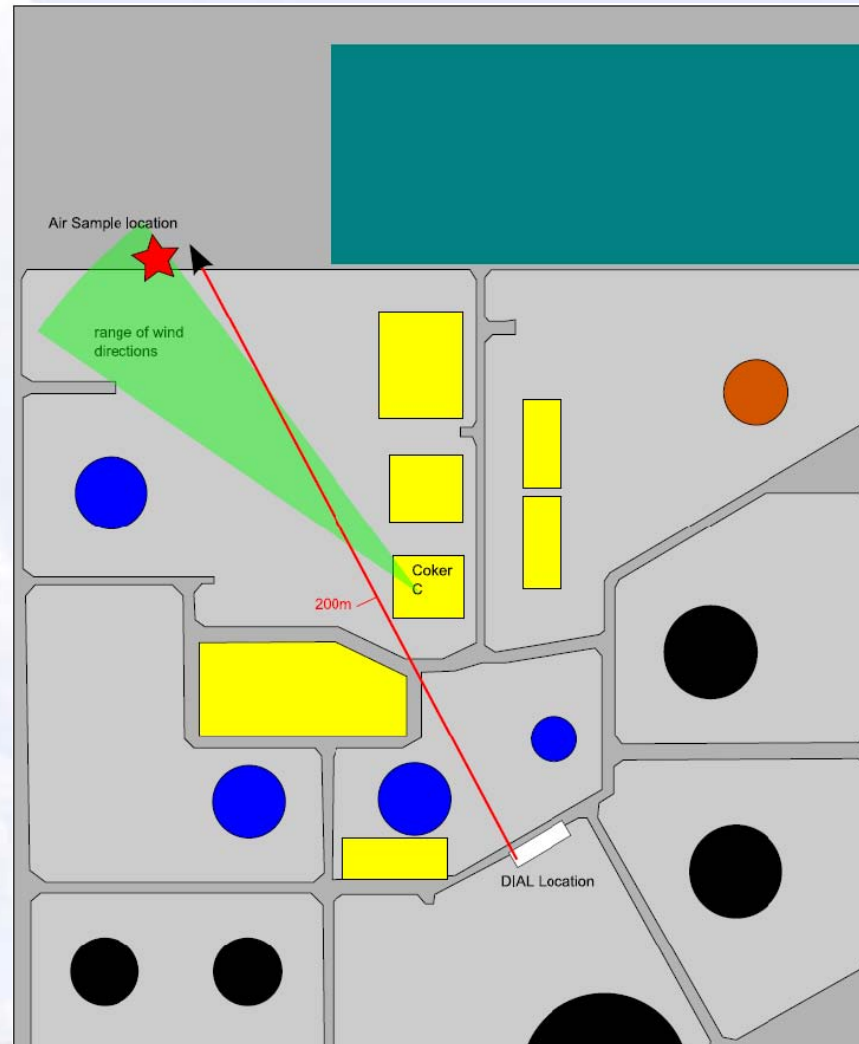
# Coker VOC Measurements

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- DIAL measurements were taken during all phases of the coker process
- DIAL day time coker VOC measurements
  - July 28, July 31, August 1 and August 3
    - 10 to 32 lbs/hr



# DIAL Location During Coker Benzene Measurement





# Coker Benzene Measurements

---

- DIAL benzene measurements
  - Measured during last six hours of the coking cycle including the decoking process
- DIAL measurements were at or below detection limits for benzene during most of the coking cycle
- Air samples were taken down wind of the coker during the decoking process
  - Tube measurements 1.33 ppb
  - Canister measurements <2.0 ppb



# Coker Benzene Measurements cont.

---

- The DIAL measured 1.5 to 2.1 lbs/hr of benzene emissions during the decoking process
- No background benzene emissions detected by the DIAL

A photograph showing an industrial flare stack on the left, emitting a bright orange and yellow flame. In the center is a tall, slender lattice tower with a platform at the top. To the right is another tall, solid cylindrical stack. The background is a clear, light blue sky. The text "Temporary Flare" is overlaid on the left side of the image.

Temporary Flare





# FLARES

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- DIAL measured emissions from two flares
- The temporary flare
  - The steam assisted temporary flare was burning a byproduct hydrogen/VOC stream normally sent to a unit that was in turnaround status
- The steam assisted ultra cracker (ULC) flare
  - Recently built emergency/process flare



# Temporary Flare

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- A large flame was visible in the day light during the measurement period
  - A high volume of 80% hydrogen waste gas was going to the flare
- Emissions measured down wind of the temporary flare on August 11
  - 1 to 15 lbs/hr when measured by DIAL
  - Preliminary efficiency of 99.7% DRE based on DIAL measurements and monitored flow to the flare



Temporary Flare

ULC Flare



# ULC Flare

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- No visible flame from the flare in day light
- A small flame was visible at night
- The BTU value and velocity were within the requirements of Code of Federal Regulations 60.18



# ULC Flare

---

- DIAL measured high VOC emissions from the ULC flare on August 11
- DIAL measured 88 to 326 lbs/hr
- Monitored flow to the flare ranged from 50 to 400 lb/hr
- Preliminary highest efficiency achieved was <85% DRE based on DIAL measurements and monitored flow to the flare



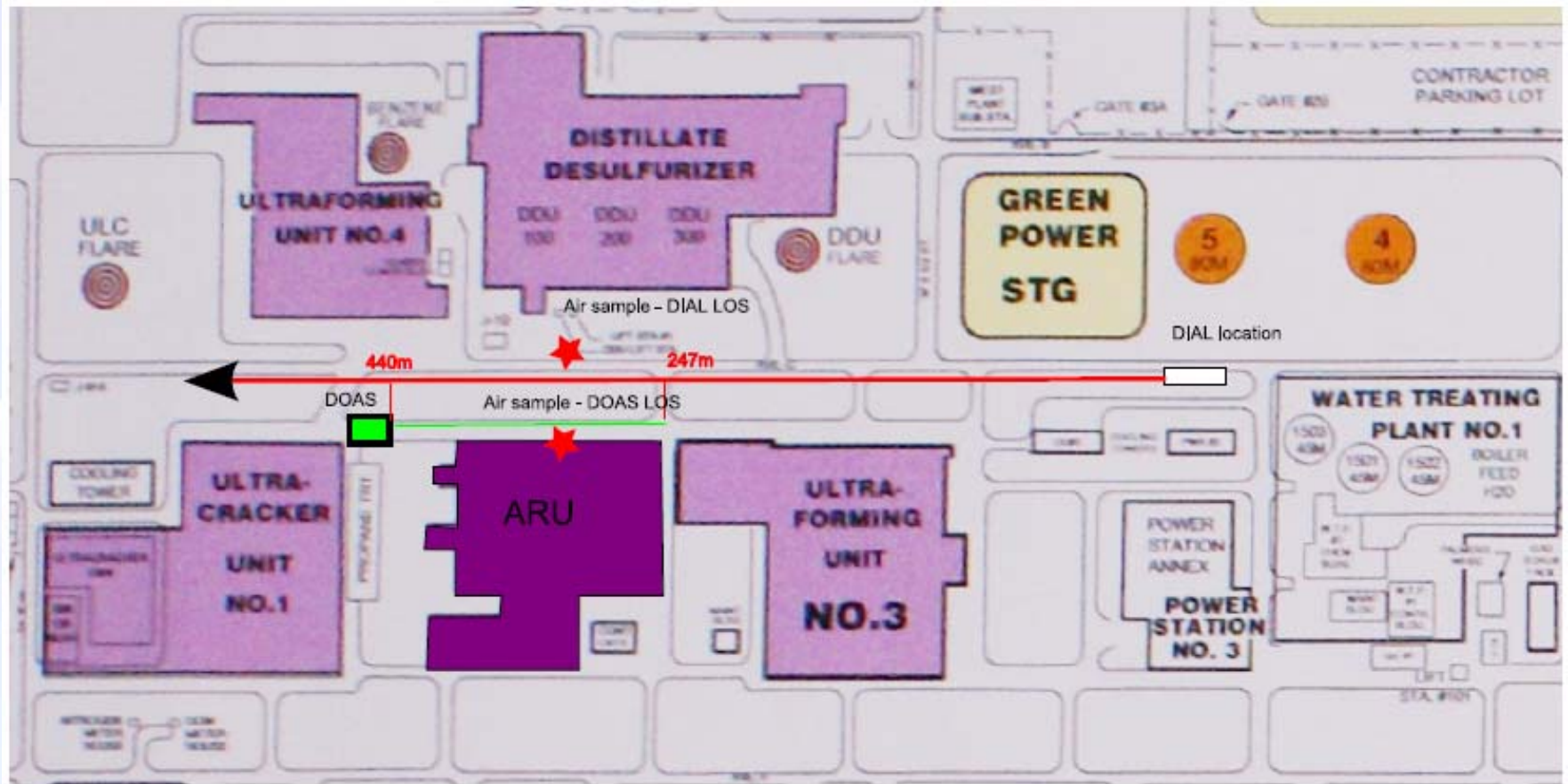
# ARU Benzene Measurements

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- Benzene measurements were taken by DIAL and an ultraviolet differential optical absorption spectroscopy (UV-DOAS) operated by EPA staff downwind of the aromatic recovery unit (ARU)
  - Benzene emissions were expected downwind of the ARU
  - Both tools measured concentration only



# ARU Benzene Measurement Location





# ARU Benzene Measurements cont.

---

- DIAL measurements
  - 1.6 ppb to 26.3 ppb
- UV-DOAS measurements
  - 5 ppb to 10 ppb
- Tube and canister samples
  - 1.44 ppb to 20.52 ppb





# Wastewater Treatment Area

---

- DIAL measurements on August 2
  - Limited DIAL scans of wastewater area
- Downwind of wastewater area secondary and tertiary effluent treatment facilities
  - Average DIAL emission rate 30 lbs/hr
- Downwind of oil/water separator
  - Average DIAL emission rate 7 lbs/hr
  - No hydrocarbon vapor seen by IR camera in separator area



# DIAL Technology Validation Techniques

---

DIAL measurements closely agreed with:

- Canister and tube samples
- UV-DOAS measurements
- Inline gas calibration cells provided by the refinery for propane, pentane, and benzene
  - Benzene
    - Actual 1000 ppm
    - DIAL prediction  $900 \pm 70$  ppm



# Preliminary Conclusions from the DIAL Study

---

- Low flow from routine processes sent to a large steam assisted emergency/process flare may not have an effective 98% DRE
- VOC and benzene emissions from the coker at this refinery were reasonably low
- DIAL measurements validated in field setting
- Night time tank measurements did not appear to be substantially different than day time measurements



# Preliminary Conclusions from the DIAL Study cont.

---

- DIAL gasoline tanks measurements were fairly close to calculated emissions using the TANKS program
- DIAL crude oil tanks measurements were 5 – 10 times greater than calculated emissions using TANKS program
  - Crude oil default parameter data in TANKS, including vapor pressure, needs to be investigated
  - Refined gasoline has pipeline specifications and **better known and expected vapor pressure values** for estimating tank emissions
- Chemical parameter default data for crude oil and mid-refined products in TANKS may need to be improved



# Areas for Further Investigation Identified by the DIAL Study

---

- Why are the crude and heated tanks measurements so high while the gasoline tanks measurements reasonably agree with AP-42 methodology?
- Vapor pressure of crude oil?
- Vapor pressure of heated heavy oil?
- How much do ineffective or poorly maintained tank seals and roofs contribute to increased emissions?



## Areas for Further Investigation Identified by the DIAL Study cont.

---

- A refinery can process a wide range of crude oil
  - Can high sulfur or “corrosive” crude oil impact floating roof seals and tank walls?
- Are entrained propane and butane slipping past floating roof seals?
  - Propane and butane are common refinery products from the atmospheric distillation process
  - West Texas crude can have >3% propane and butane content



# Contact Information

---

- Contact Russ Nettles at (512) 239-1493 or e-mail [rnettles@tceq.state.tx.us](mailto:rnettles@tceq.state.tx.us)

# Industrial emission measurements using the Solar Occultation Flux method

Johan Mellqvist,  
Chalmers University of Technology  
Göteborg, Sweden  
([johan.mellqvist@chalmers.se](mailto:johan.mellqvist@chalmers.se))

FluxSense AB, [www.fluxsense.se](http://www.fluxsense.se)



We believe that the standard approach to estimate VOC emissions (*API calculations for tanks and leak detection at process areas*) is associated with significant uncertainties and that **measurements are needed**, since:

- Leaks from cooling towers, flares, water treatment facilities, storage caverns, loading (trucks/ships), tank cleaning and repair etc, are not assessed in the standard approach.
- A significant fraction of the emissions comes from few malfunctioning equipment. This corresponds to a skew emission distribution in contrast to a gaussian one that is generally assumed in the standard approach.
- The last TEXAS air quality studies in 2000 and 2006 indicate discrepancies of a factor 5-50 between the standard approach and measurements around Houston

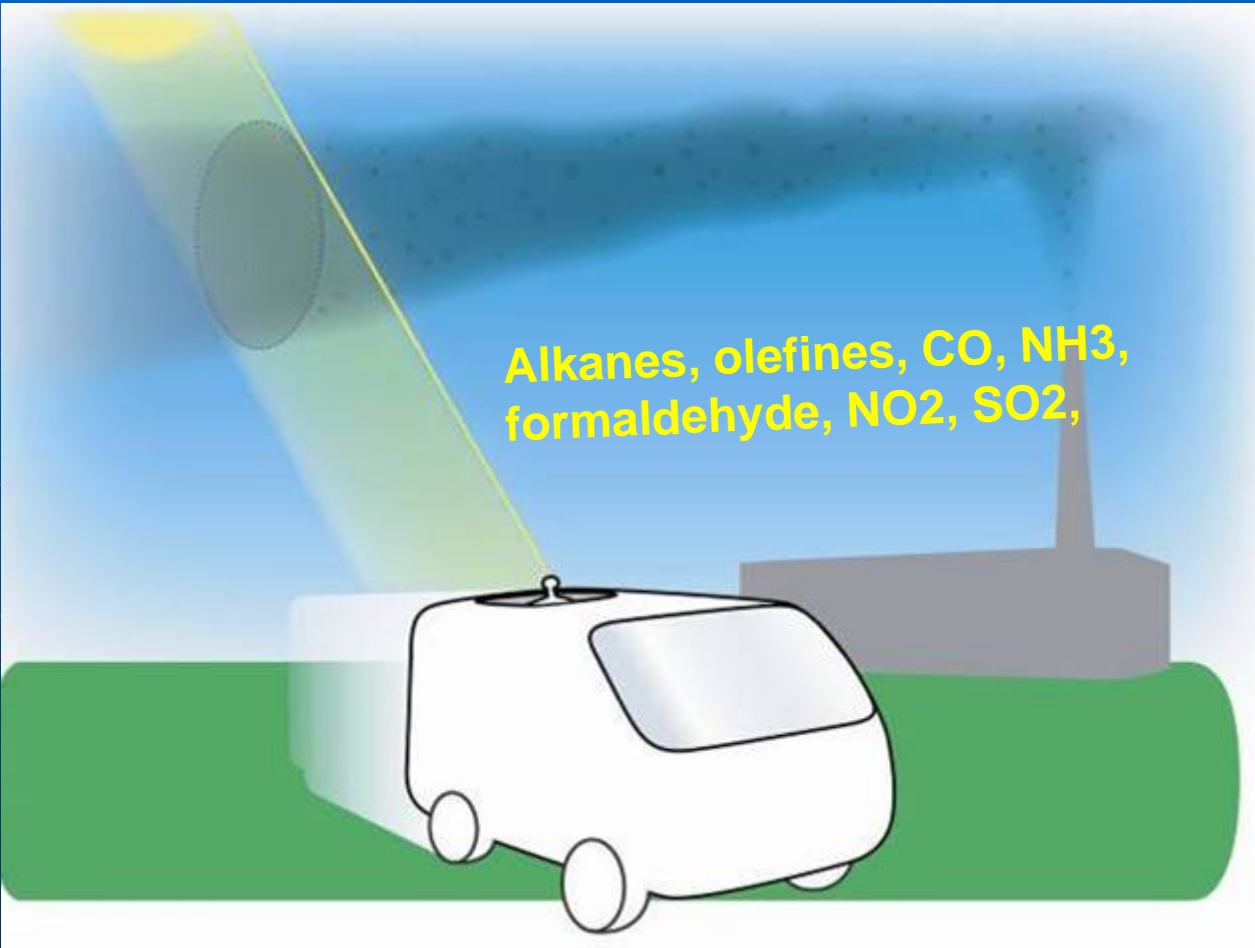
# Three techniques applied for studying fugitive VOC emissions

- SOF – (Mobil solar FTIR)
- TCT – (mobile extractive FTIR+tracer)
- IR camera

# Measurement activities using SOF and TCT for industrial monitoring

- KORUS- yearly monitoring of alkane emissions from Swedish refineries since 2001, -ongoing
  - Yearly monitoring of olefine emissions from two Swedish petrochemical industries (flares), since 2000 -ongoing
  - TexAQS 2006, HRVOCs, alkanes, NO2, SO2 -2006
  - Bitumen refineries Göteborg & Nynäshamn (emissions and validation) 2005/2006
- 
- Austria, Olefin plant (flares) 2008
  - France, Le Havre- refineries and petrochemistry 2008
  - Texas Houston, HRVOCs, formaldehyde 2009

# Method I: The Solar Occultation Flux method (SOF)



Alkanes, olefines, CO, NH<sub>3</sub>,  
formaldehyde, NO<sub>2</sub>, SO<sub>2</sub>,

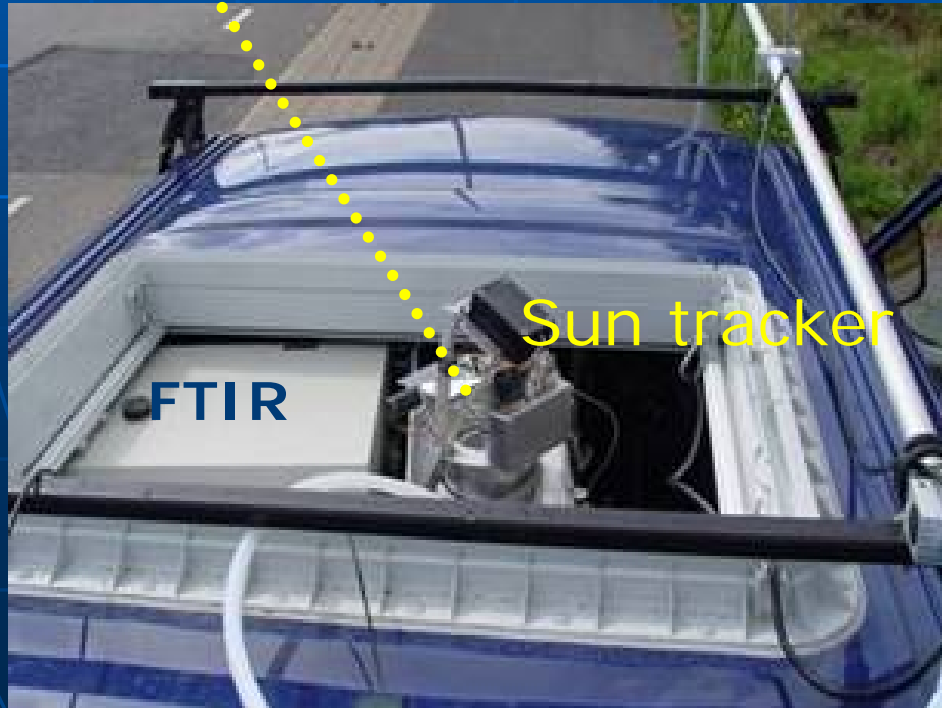
The number of molecules above the SOF vehicle are estimated for the key species, from spectroscopic analysis of the solar light.

The measurements are conducted while driving and hence is it possible to measure the total mass of molecules along the roads traveled.

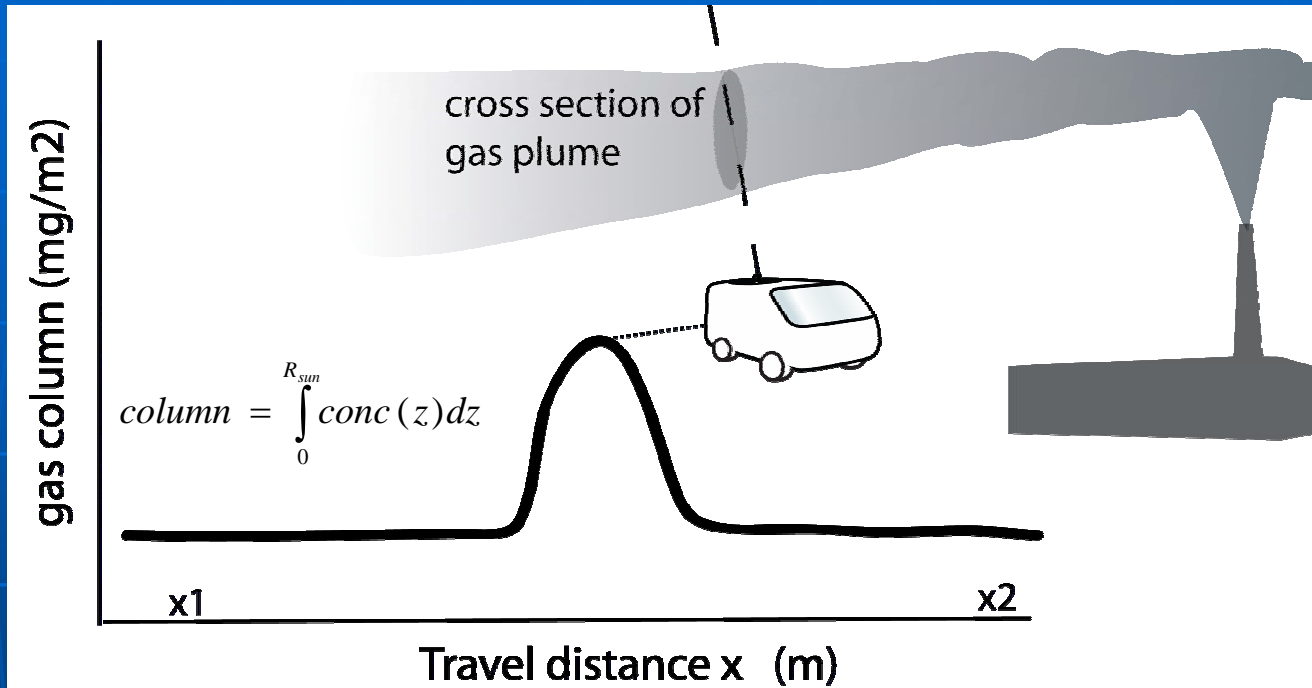
The total mass is multiplied by the wind which yields the flux in kg/s.

*The SOF-method provides an instant realtime overview of the leaks.*

*It is used to quantify VOC emissions from total facilities down to the level of a few tanks, but works only in the day in fair weather. The uncertainty is 20-50% depending on the object of study.*



# SOF Flux calculation, details



$$flux = F \cdot u'_{average} \int_{x1}^{x2} column(x) dx$$

Correction for solar angle and driving direction, relative to wind direction

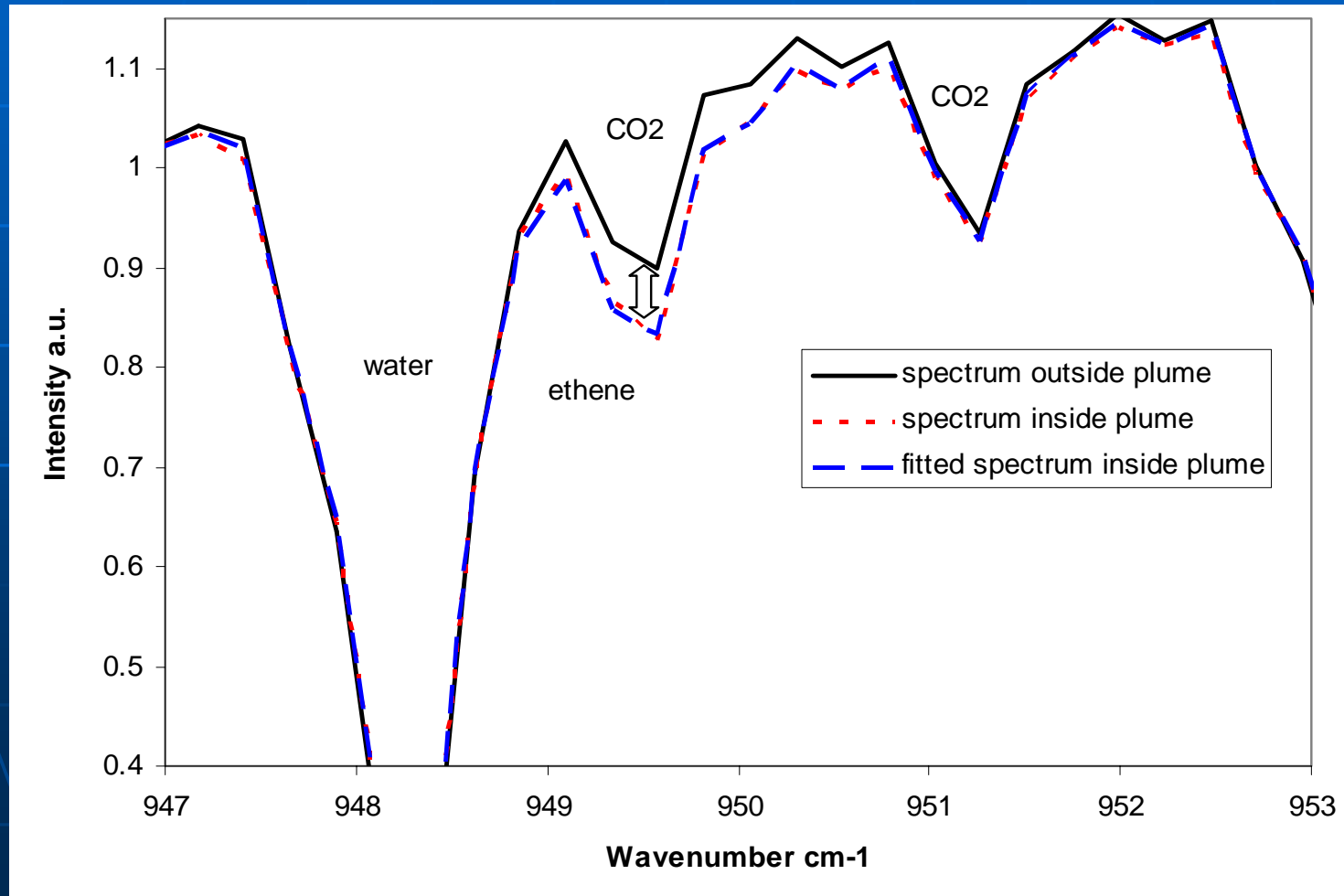
Wind

$$u'_{average} = \frac{\int_0^{H_{mix}} u' \cdot dz}{\int_0^{H_{mix}} dz}$$

$$F = \cos(SZA) \cdot \sin(u_{\alpha} - x_{\alpha})$$

Mellqvist April 1 2008

The spectroscopic analysis is conducted by multivariate analysis in which calibration spectra are fitted to the measured spectra. Here the spectroscopic retrieval of ethene is shown.



# Error budget

■ Retrieval method-interference:	10%
■ Line parameters	3%
■ Wind speed	27%
■ Wind direction	10%

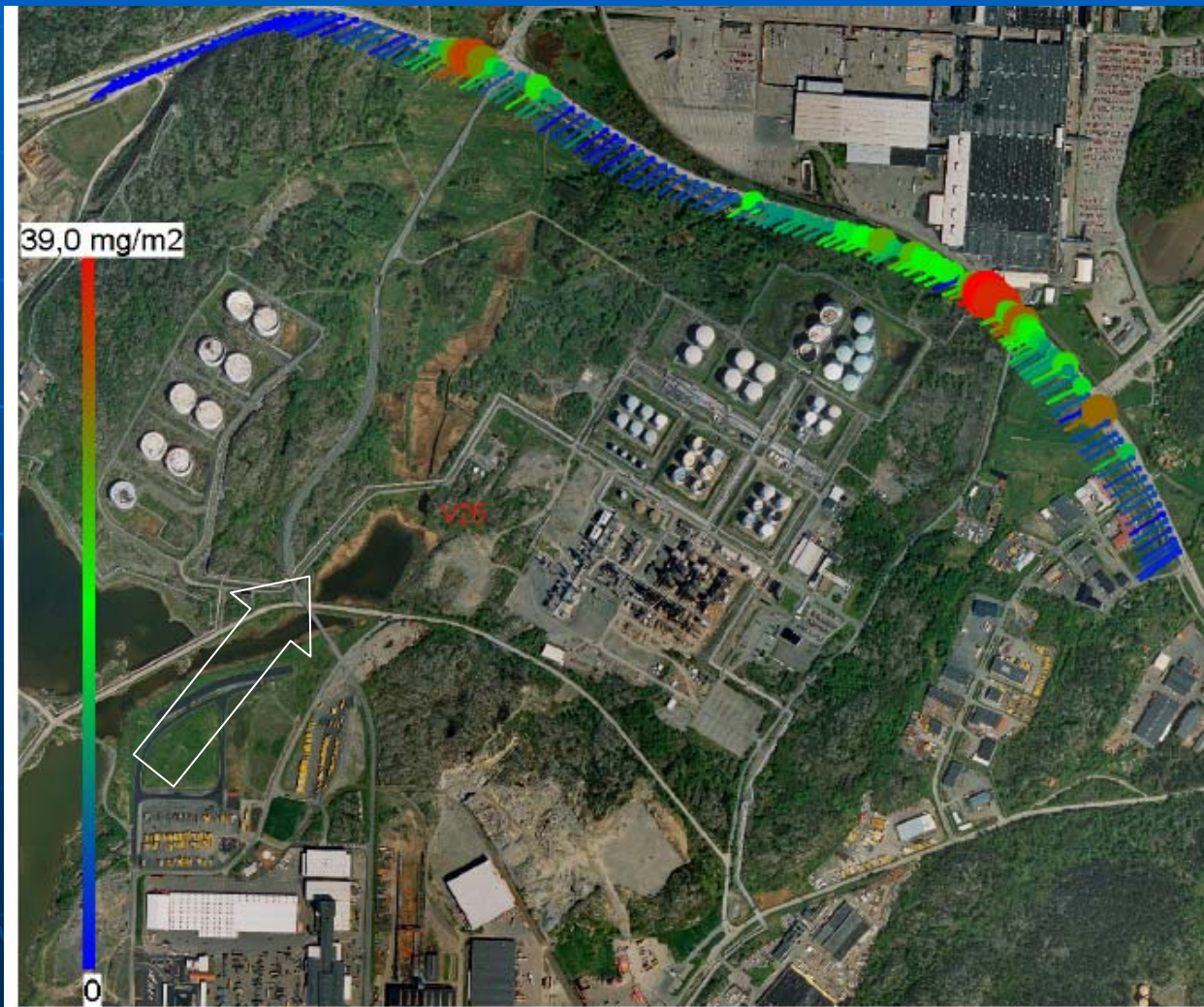
**Overall error = 30%**

**This budget was estimated for the far field measurements during the TexAQS 2006 study. It is however also consistent with validation experiments with controlled gas releases and technique comparisons, conducted elsewhere.**

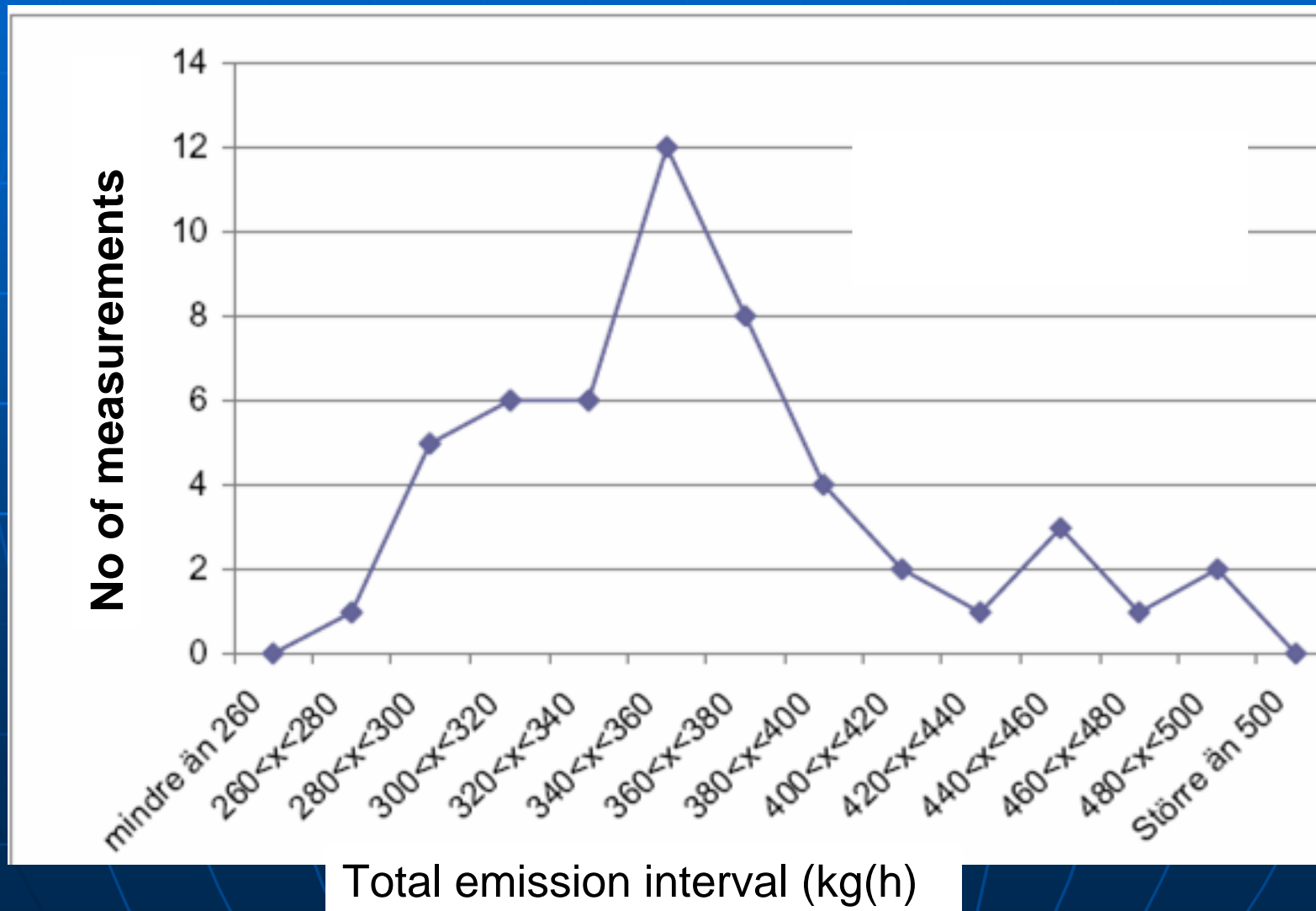


# Light oil refinery A. Total VOC emission measurement by SOF in the "far field"

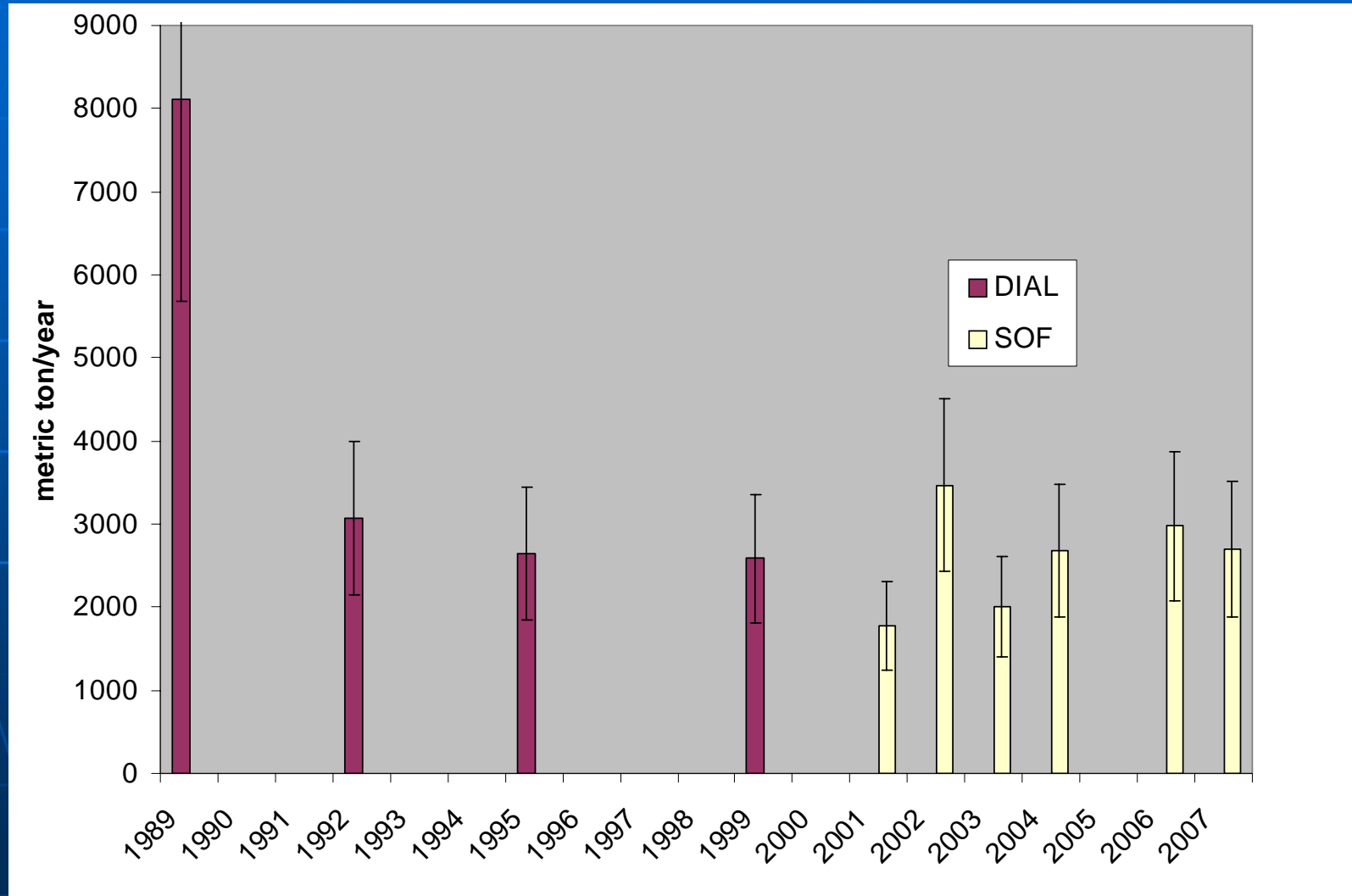
Blue color represents the lowest and red the highest alkane columns. The wind is indicated with the arrow.

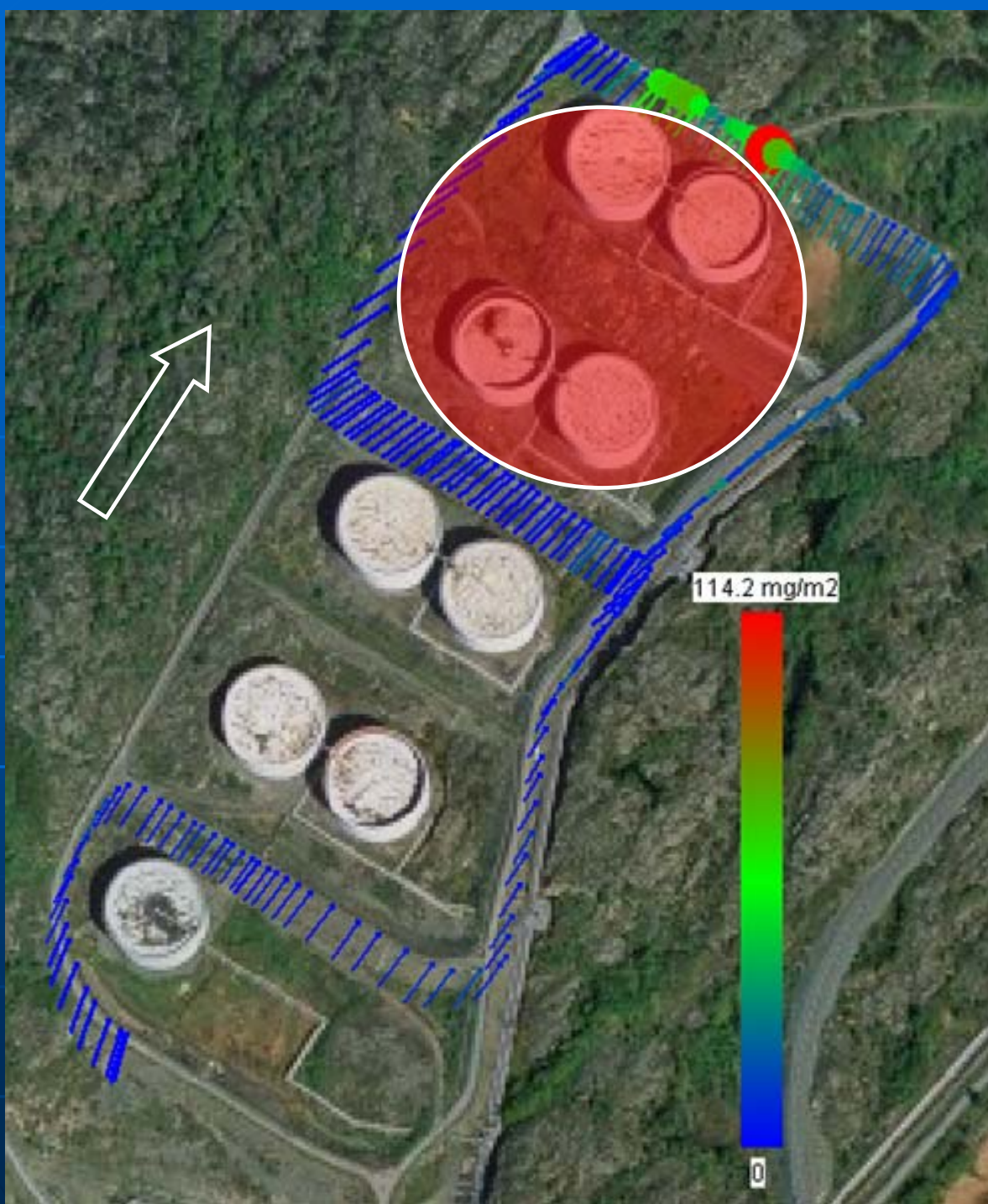


A histogram that shows the number of SOF measurements as a function of total emission interval at refinery A during 1 month in 2007



# VOC emissions measured by DIAL and SOF from refinery A with 5 Mton throughput (i.e. emissions corresponds to ~0.05% of throughput)





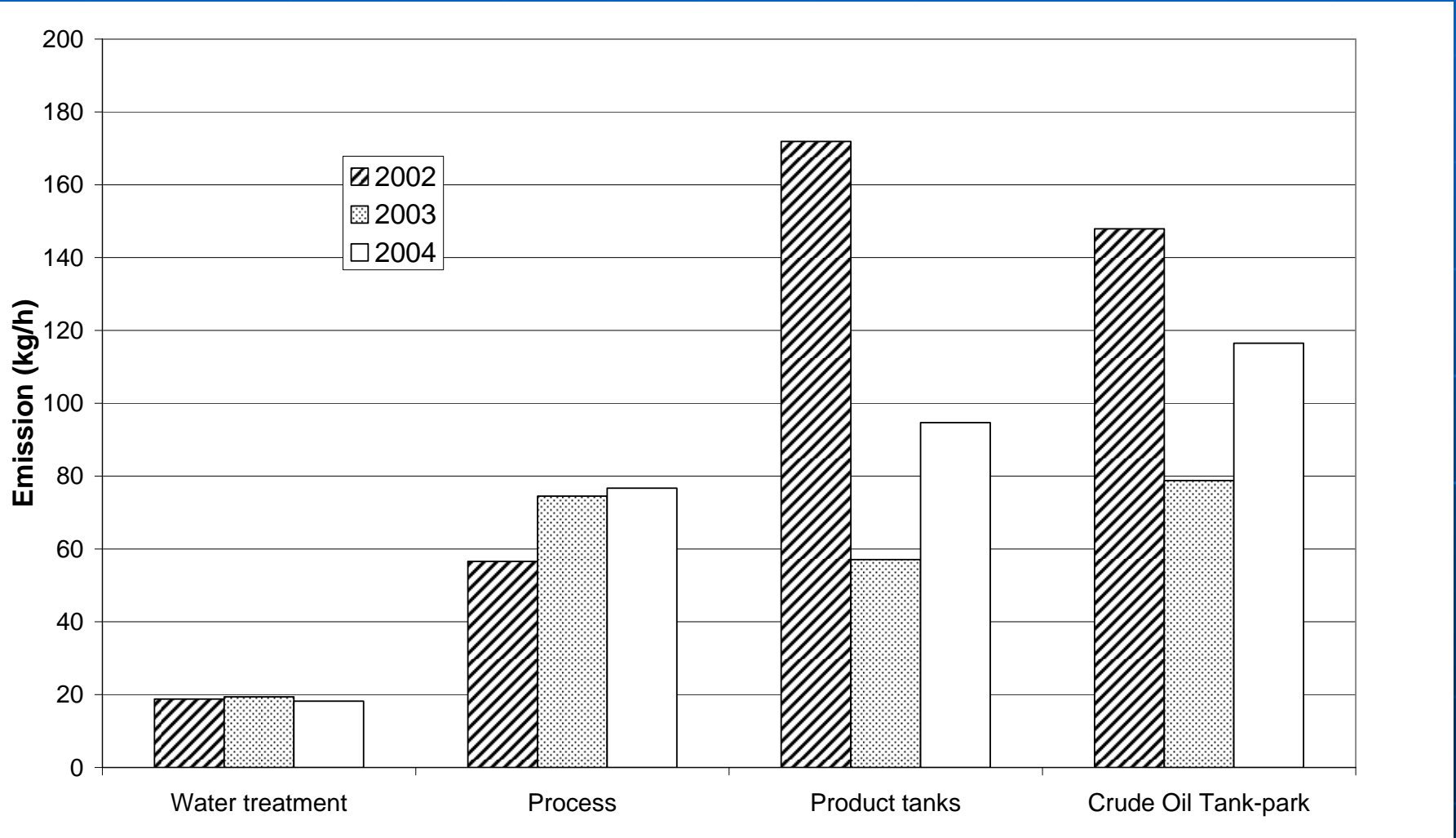
VOC emissions measured by SOF in the "near field" circling around leaking tanks. Blue color represents the lowest and red the highest columns. The wind is indicated with the arrow.

**Area emission =  
Outflow - Inflow**

# SOF procedure

- The measurements conducted in the "near field", close to tanks etc., are rescaled to sum up to "far field" measurements (0.5-2km), since the latter have a less disturbed wind field.

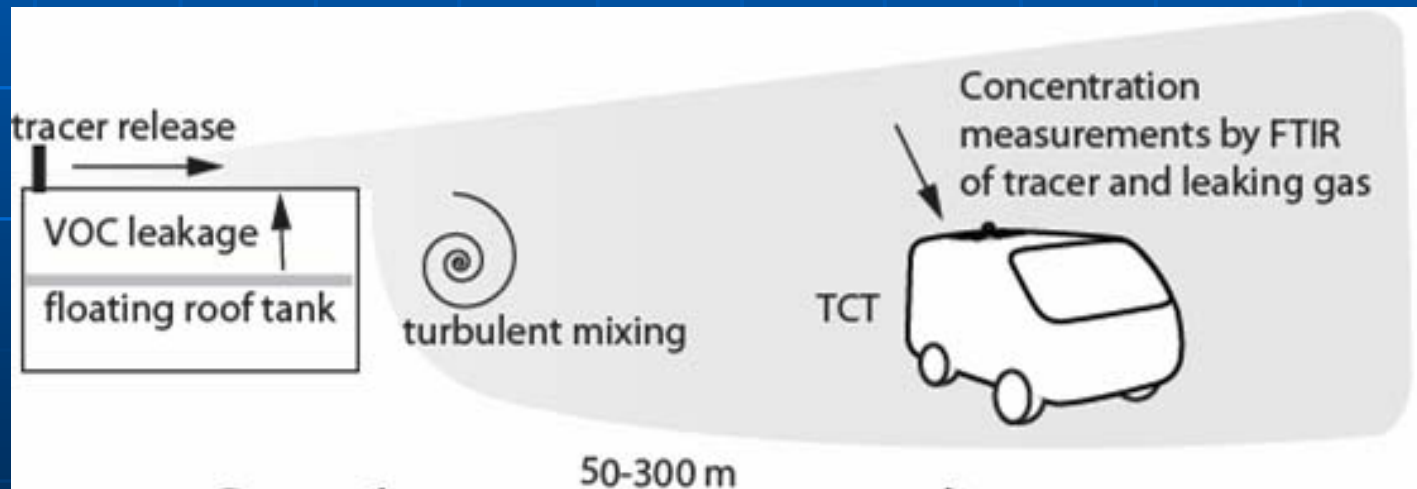
# Detailed VOC emissions obtained by SOF from refinery A (rescaled)



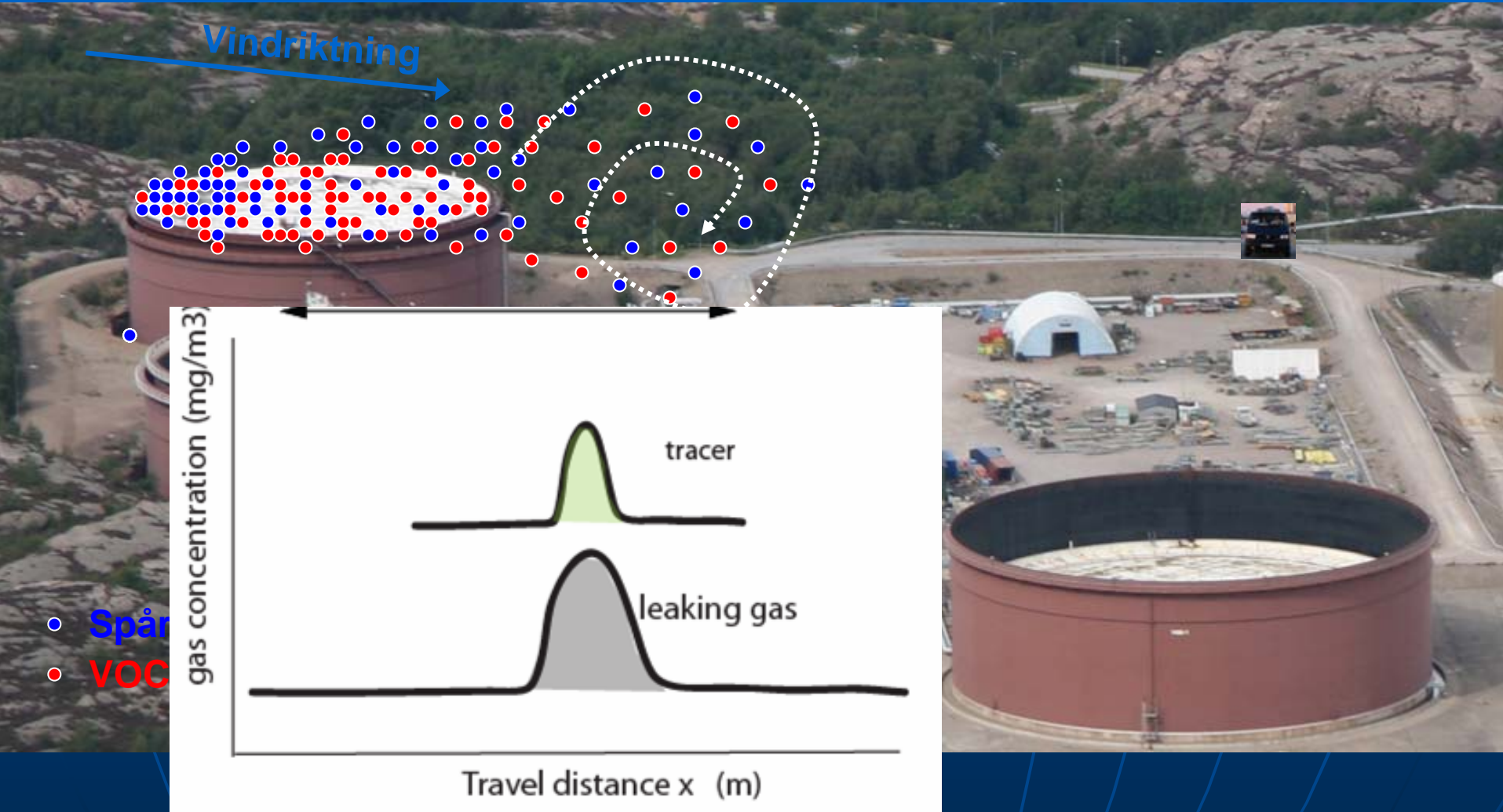
# Method II: The time correlation tracer (TCT) method

*Developed to be applied for measurements of:*

- Methane emissions from landfills
- VOC emissions from industry



# Tracer methodology – crude oil tank



The tracer provides the gas dispersion – the VOC/N<sub>2</sub>O concentration ratio, integrated across the plume is measured., yields the emission in kg/h



*The TCT method is used for more detailed studies of VOC emissions, such as emissions over tank filling cycles, ship loading, truck loading and repair. It works in the night. 15-40% uncertainty.*

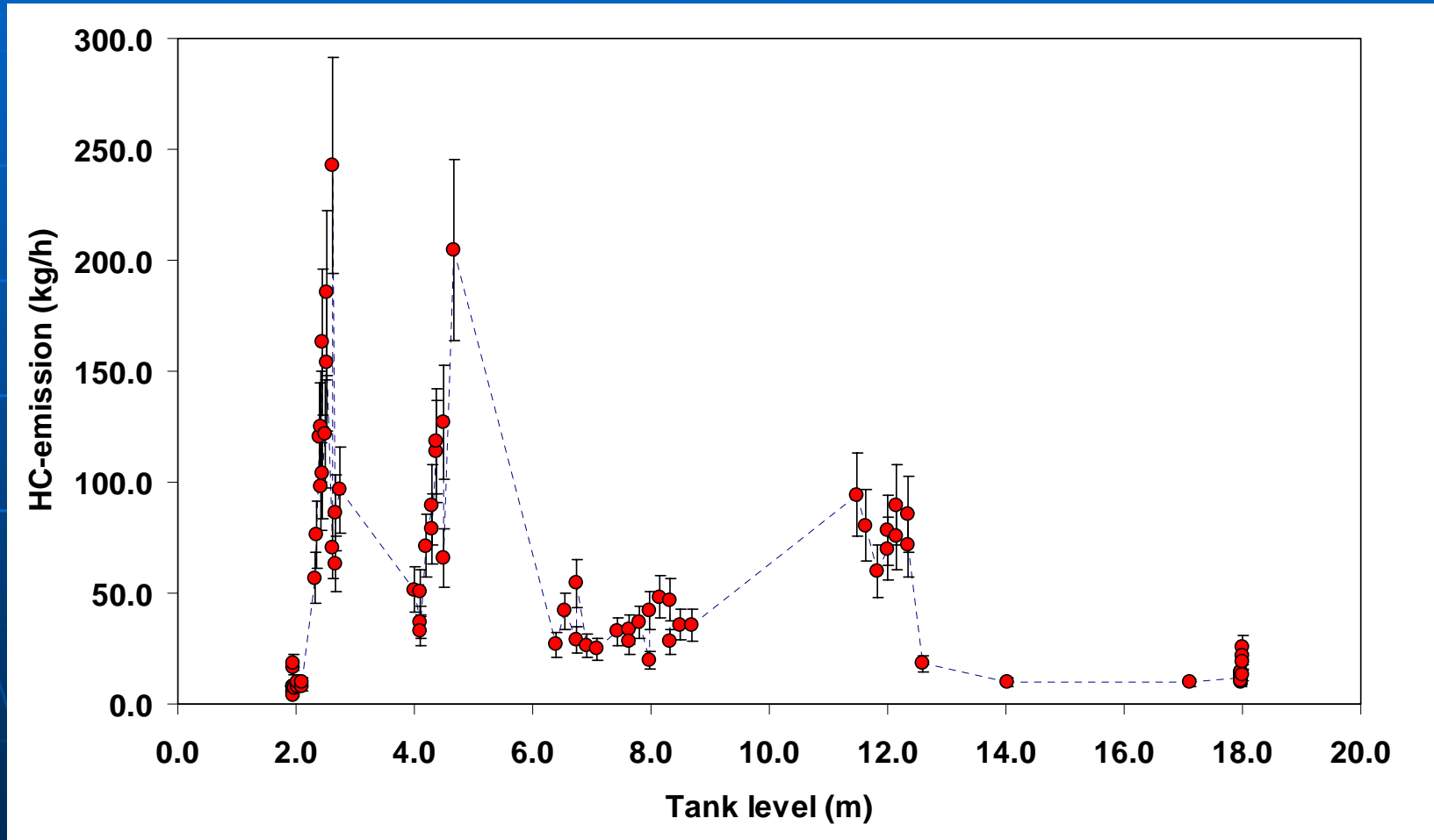


Mobile  
extractive  
FTIR

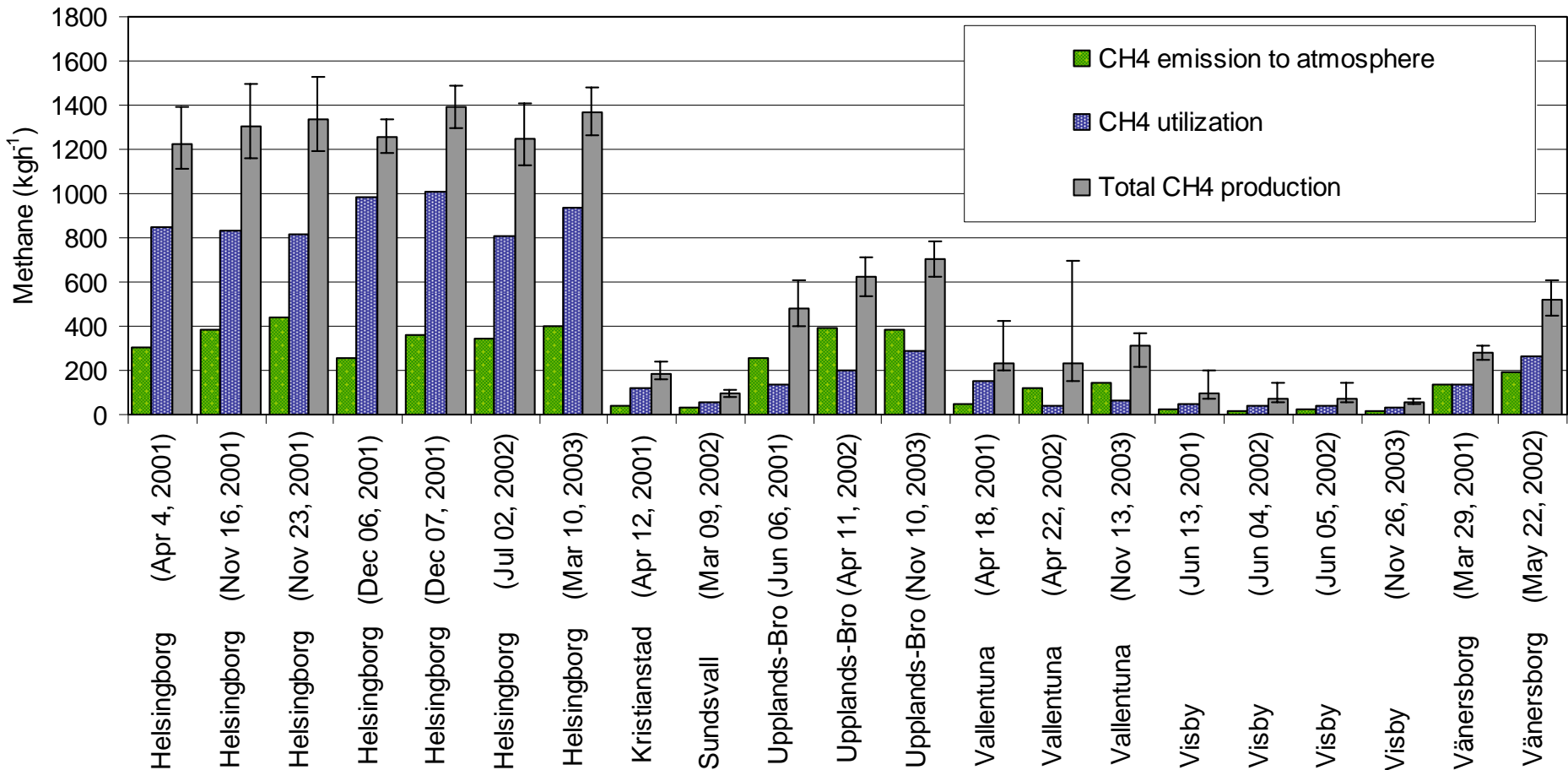


Controlled  
tracer  
releases

VOC emissions from a crude oil tank with an external floating roof with double seal measured by TCT over 24 hours for different filling levels. The tank has deformations at certain heights.



# CH<sub>4</sub> emission and production at 7 Swedish landfill sites



# Method III: Leak identification by an infrared camera



Results from a study where the emissions from tanks have been measured with TCT, calculated with the API model and leak search has been conducted with an infrared camera (FLIR).

<b>Service</b>	<b>Type</b>	<b>Emission TCT ton/year</b>	<b>Emission API ton/year</b>	<b># Leaks (FLIR)</b>
Crude oil slops	EFRT double seal	4	3	1
Crude oil	EFRT double seal	35	4	4
Crude oil	EFRT double seal	120	4	22
Reformate	IFRT double seal	<1	0.2	0
Heavy fuel oil	External roof	<1	1	0

We run a monitoring program, KORUS, at 3 Swedish refineries and at the oilharbor of Göteborg. The approach is to:

- Identify and quantify VOC leaks with SOF-TCT on a yearly basis
- Apply a midinfrared camera (FLIR GasFindIR) to find leaks at the tanks identified as large emitters by SOF-TCT
- Make an after control of leak repairs by re-measuring with SOF-TCT.

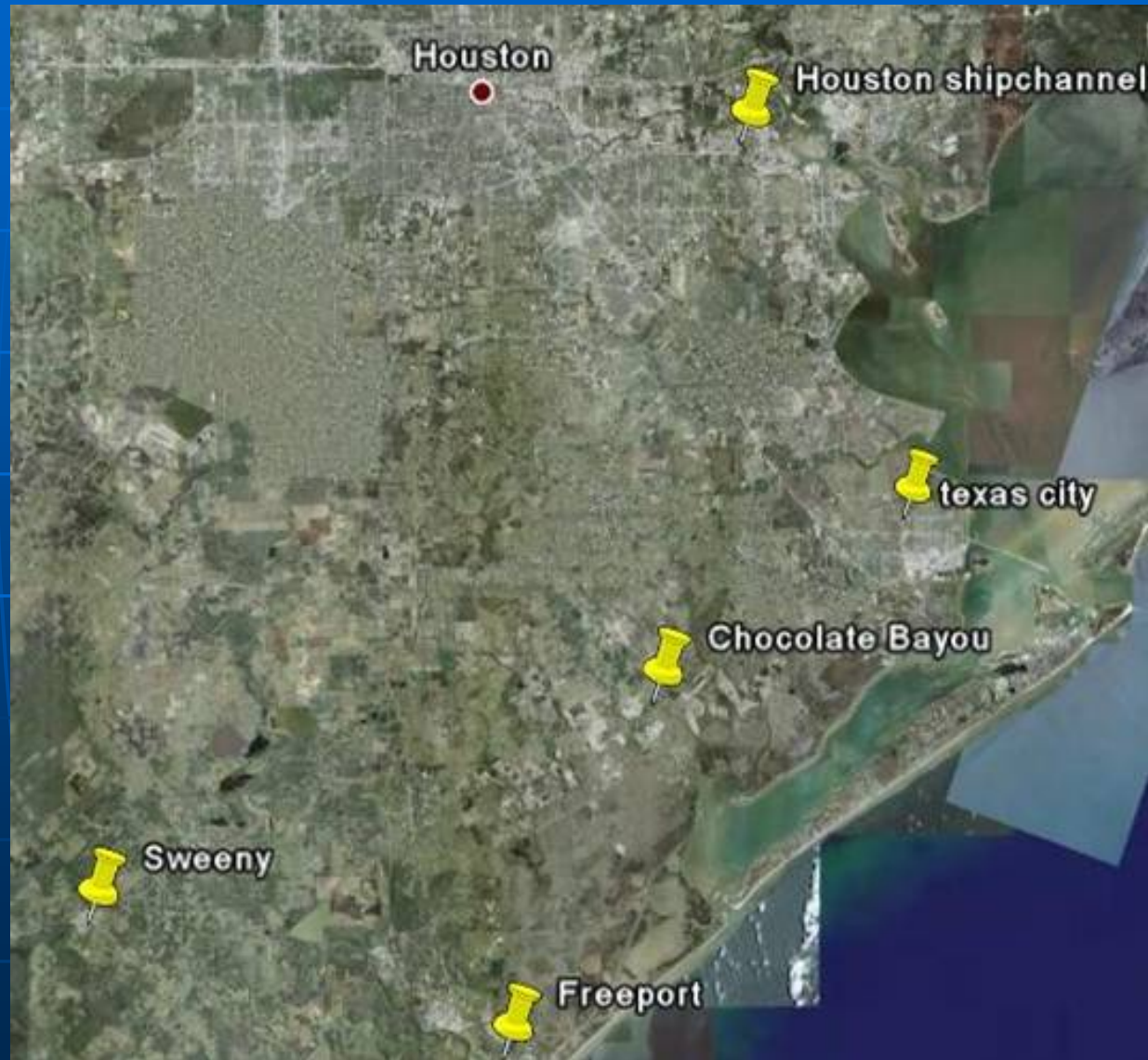
# TexAQs 2006

- During Texaqs 2000 airborne measurements of the ratio between VOC and NO<sub>x</sub> in the plumes indicated that the petrochemical industries emit 20-50 times more reactive VOCs than reported in inventories.
- We participated in the TexAQs 2006 campaign conducting direct emission measurements of VOC's, NO<sub>2</sub>, SO<sub>2</sub> and NH<sub>3</sub>, supported by the Houston advanced research center (HARC)\*

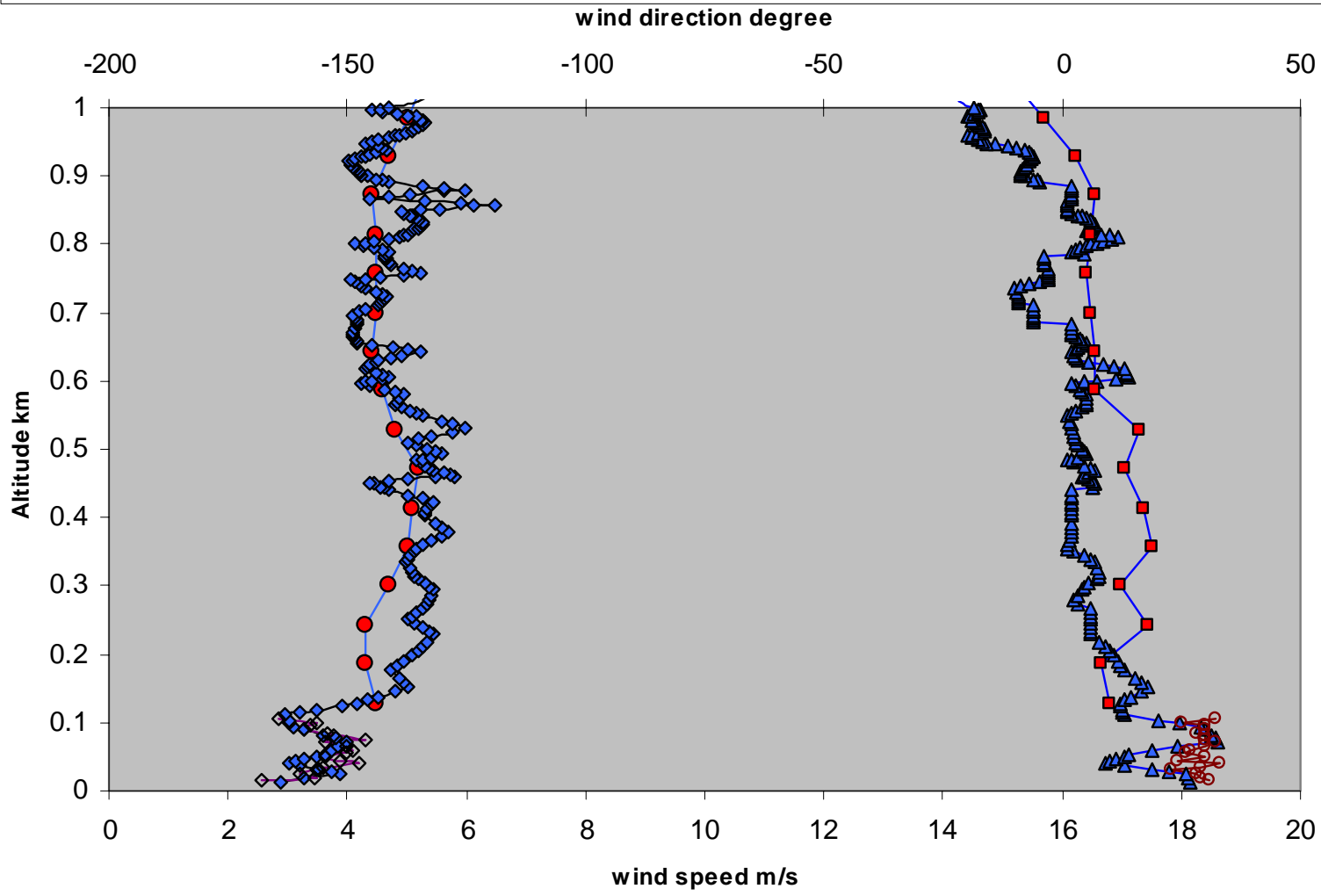
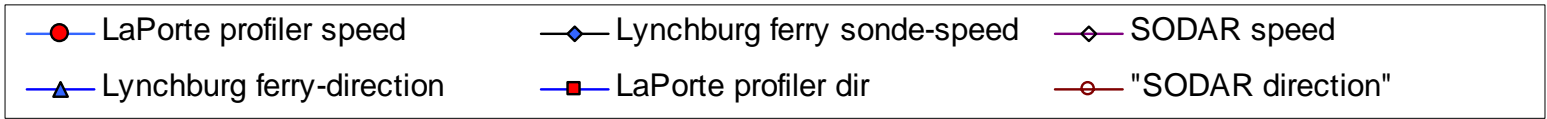
*\* Mellqvist, J, Samuelsson, J., Rivera, C. Lefer, B. and M. Patel, Measurements of industrial emissions of VOCs, NH<sub>3</sub>, NO<sub>2</sub> and SO<sub>2</sub> in Texas using the Solar Occultation Flux method and mobile DOAS, Project H-53, available at <http://www.tercairquality.org/AQR/Projects/H053.2005,2007>)*

# SOF during TexAQS 2006

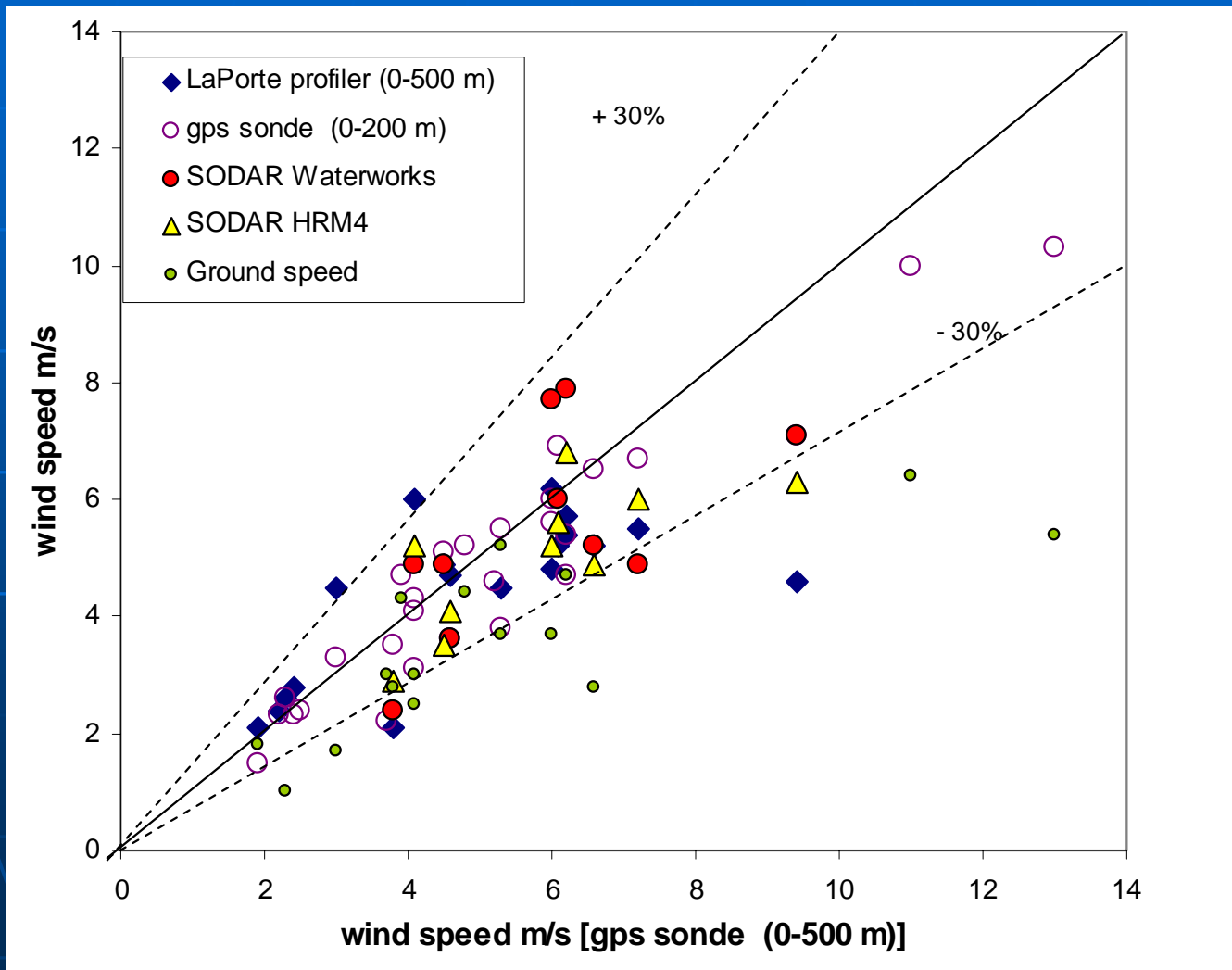
- 10 days of measurements in Sep 2006 were conducted in the vicinity of Houston
- Wind by GPS-soundings, SODAR, radar profilers
- Coordinated measurement with NOAA WP3 and Baylor Piper Aztec

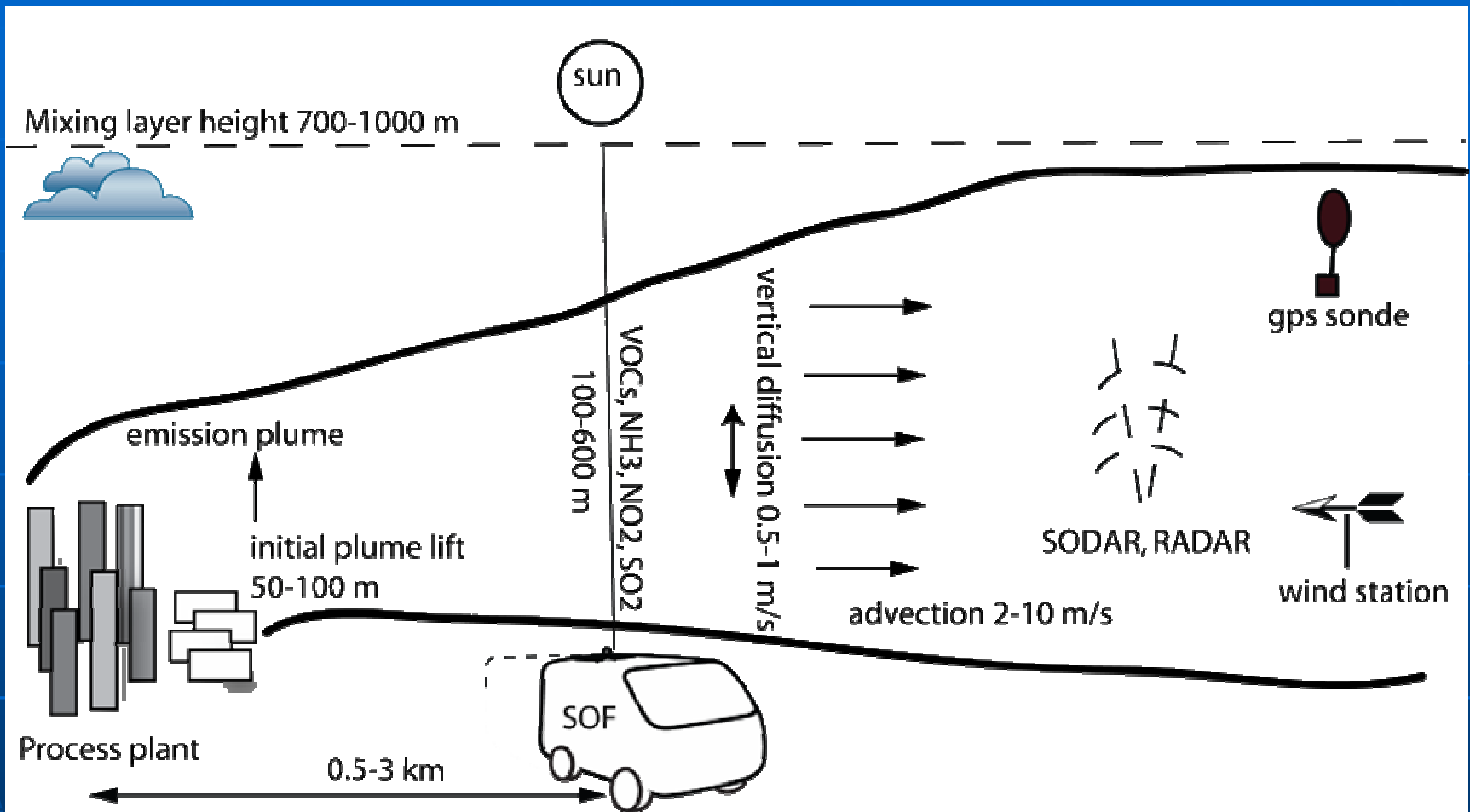






# Comparison of wind measurements in the HSC area relative to the average wind [0-500] m obtained with the GPS sondes

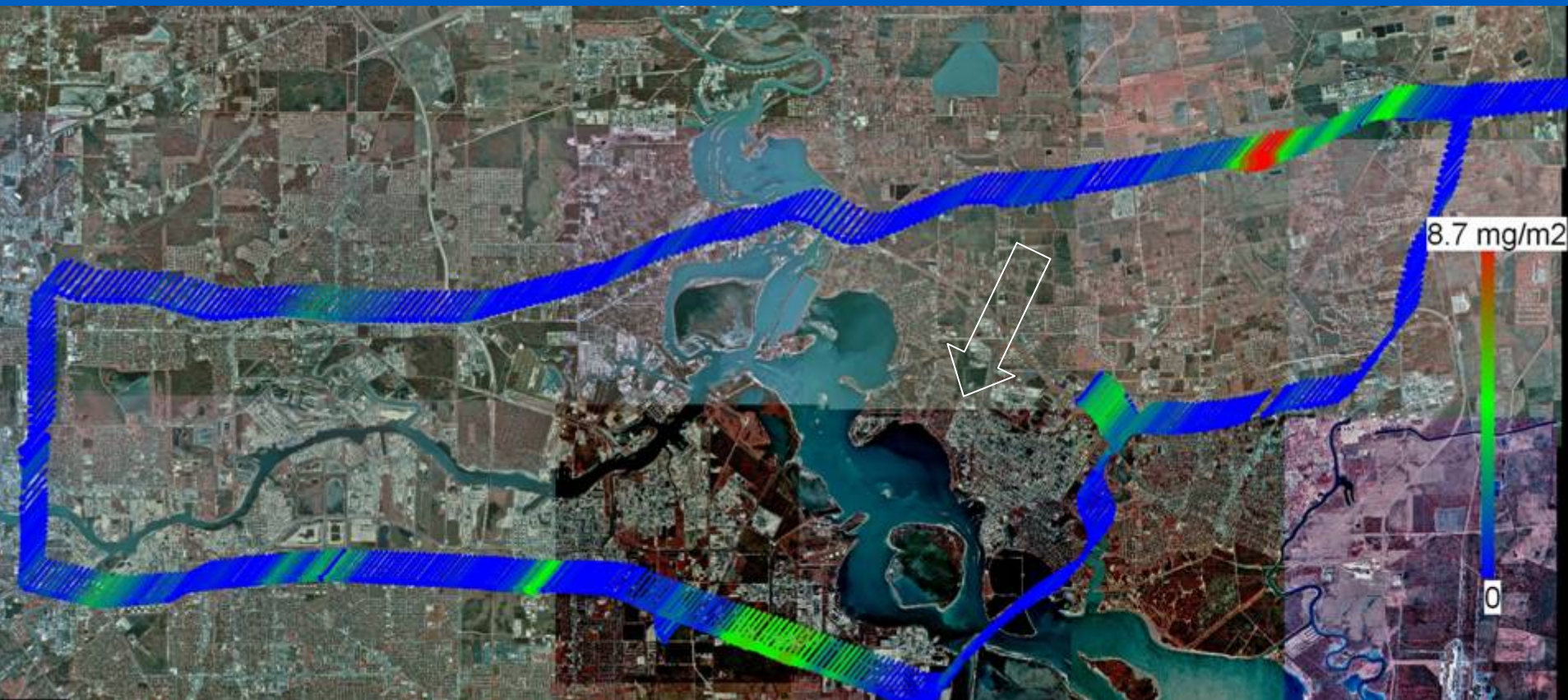




The measurements were typically conducted at 0.5 to 3 km distance from the sources 100-600 s. The assumption is then that the plume is distributed from the ground up to several hundred meters height and that the wind varies little with height. The average wind [0-200] m or [0-500] m was used , obtained from GPS sondes (4/day).

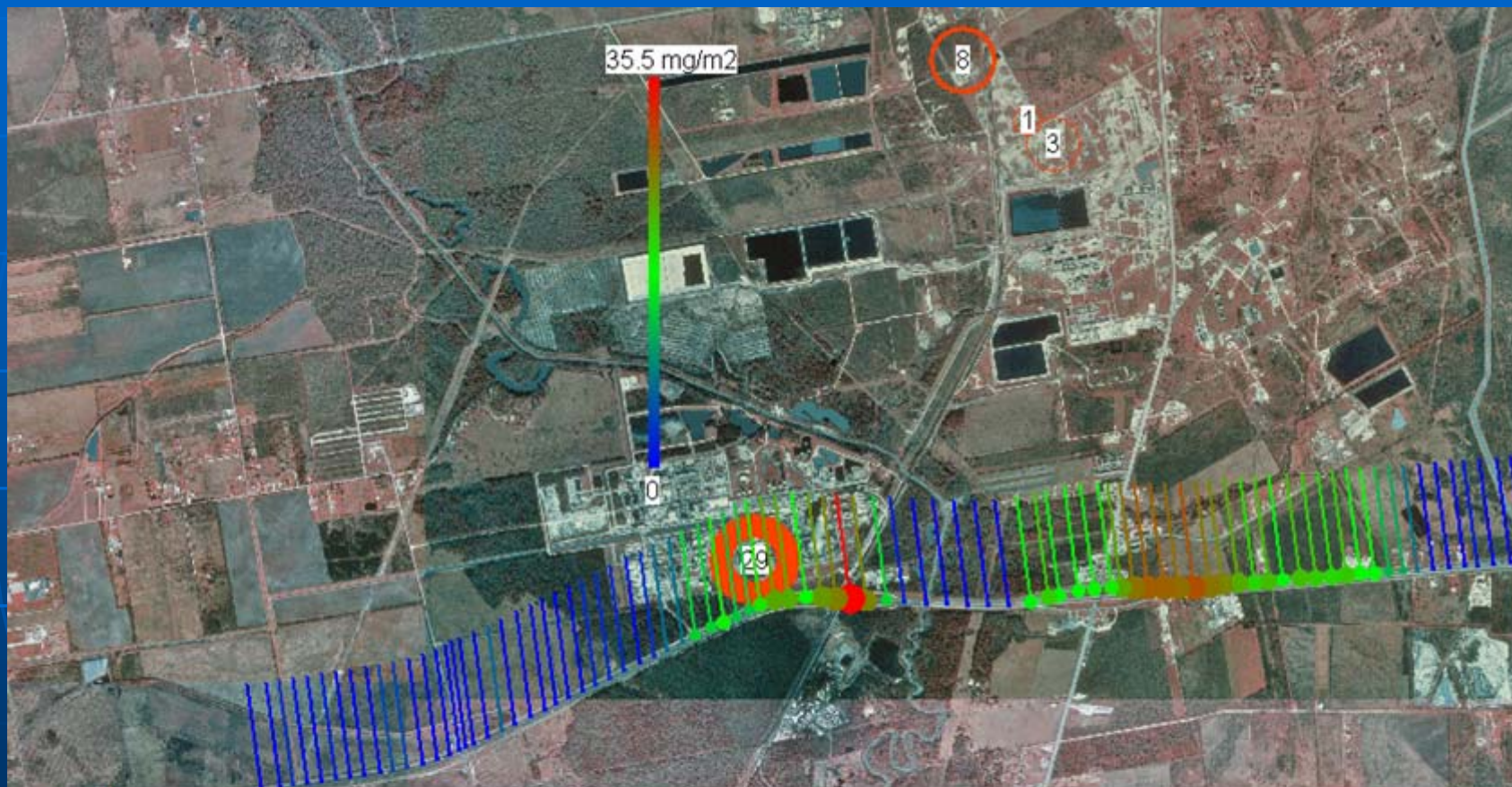
# "SOF box" measurement of ethene around the Houston ship channel on Sep 19

Here the colorcode correspond to the mass of ethylene measured in the solar light. The lines point towards the wind



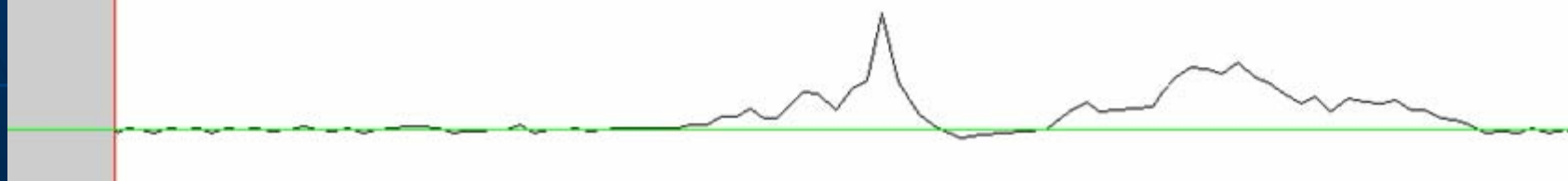
# Mt Belvieu Sep 25, ethene

(Here the colorcode correspond to the mass of ethylene measured in the solar light. The lines point towards the wind)

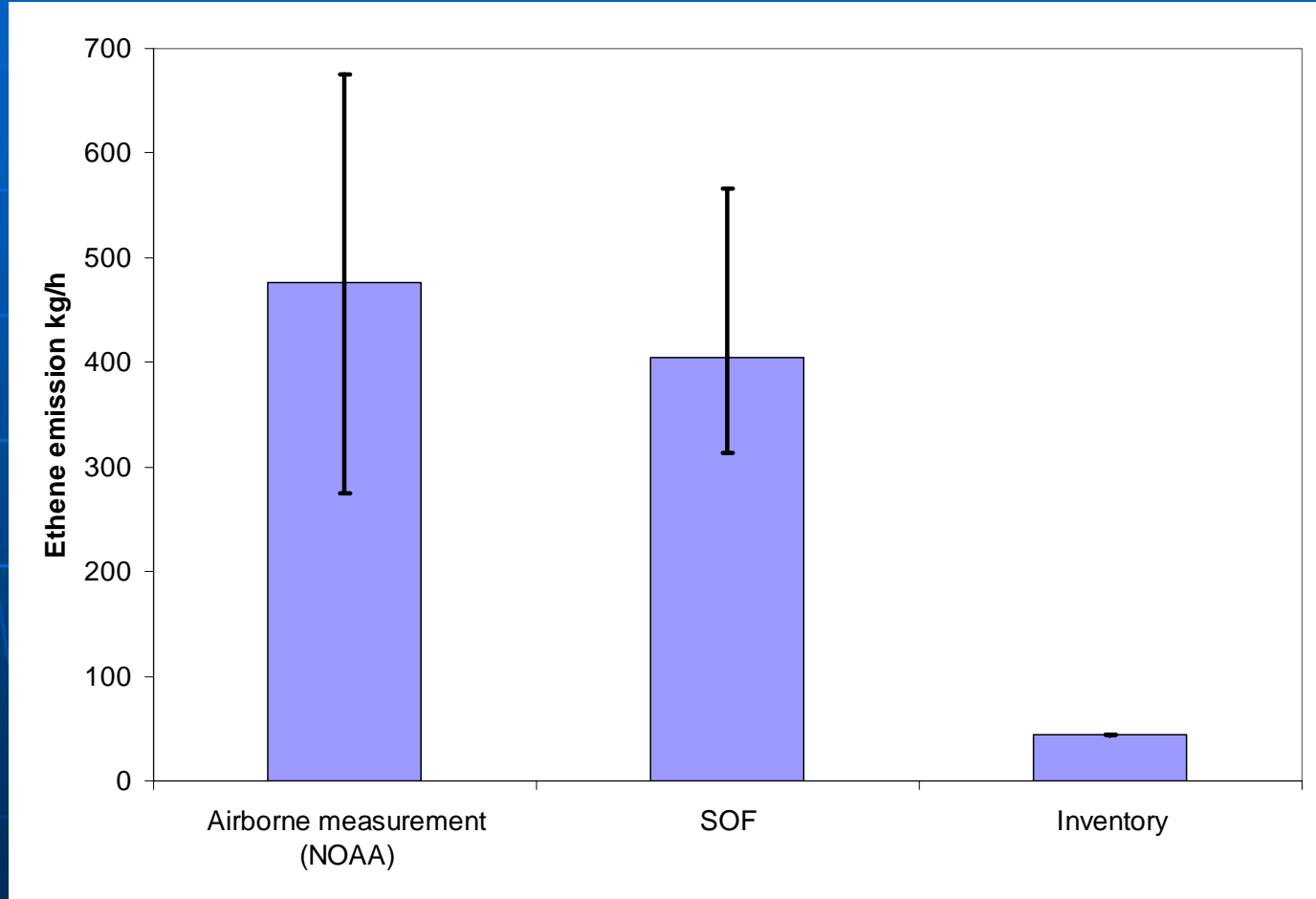


**Ethene, 566±35 kg/h**

- Total
- Meas with RMS error

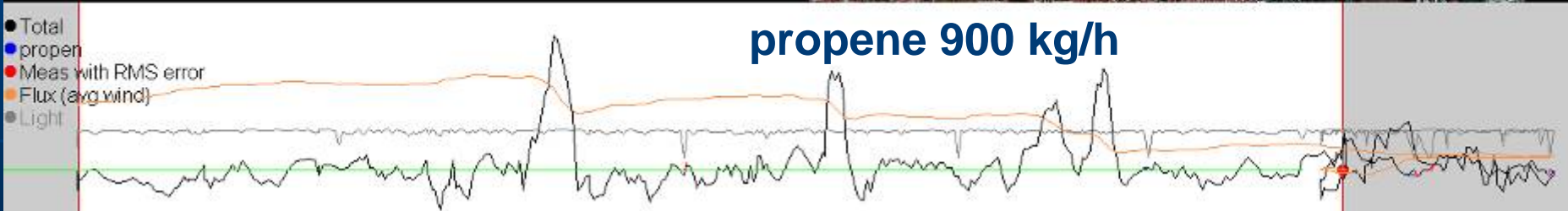
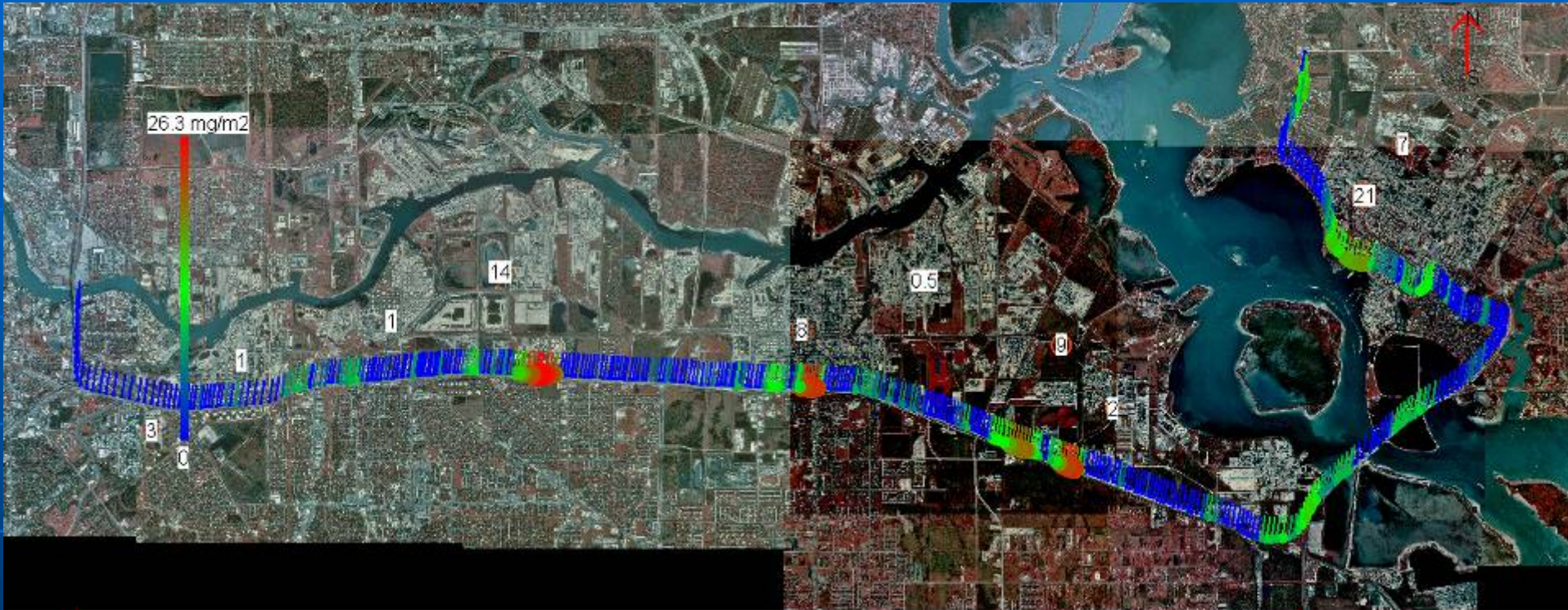


# Comparison of ethene emissions from Mt Belvieu, Houston, measured during Texas 2006 by SOF and airborne measurements by NOAA (Joost de Gouw)





# HSC Sep 25, propene,





# HSC Sep 06, Average emissions in kg/h

Species	SOF	Inventory	Factor
ethene	860±180	47	18
propene	1500±500*	60	25
alkanes	12400	1500	8
Tot VOC		3090	
NH3	190 ±20		
NO2	4500±1900	3089	1.5
SO2	5200 ±2400	2752	1.9

\* Uncertain due to large variability in the emissions Mellqvist April 1 2008

# VOC emissions compared to inventory

Species	Ethene kg/h		Propene kg/h		Alkanes kg/h		VOCs kg/h
	SOF.	Inv.	SOF	Inv.	SOF	Inv.	Inv.
HSC	860	47	1500	61	12400	1500	3090
Mt.Belview	404	44	400	9	860	260	265
Baytown	72	6	260	3	980	202	437
Texas City	83	8	-	-	2890	348	686
Channelview	64	11	-	-	-	42	170
Sweeny	163	4	126	4	3630	113	137
Freeport	250	21	-	-	-	44	148
Bayport	170*	4	-	-	-	94	151
Chocolate Bayou	136*	10	273	24	-	107	150

\* Few measurements

# Summary of results

- The hourly gas emission from the Houston Ship channel area corresponds to about 1 metric ton of ethylene, 1.5 tons of propylene, 12 tons of alkanes, 1/4 ton of NH<sub>3</sub> and about 5 tons of SO<sub>2</sub> and NO<sub>2</sub> each.
- For the VOCs this corresponds to 5-50 times greater emissions than reported in the 2004 TCEQ inventory. For NO<sub>2</sub> and SO<sub>2</sub> values, the discrepancy is less, factor 1.5 and 1.9, respectively. Similar discrepancies were observed for the other sites.
- The measured ethene emissions obtained with SOF agreed within a factor 2 with measurements conducted by the NOAA WP3 during TexAQS 2006 [Gouw 2007].
- The emissions for ethene and propene showed extreme short term variability, 100-2000 kg/h possibly due to flaring or other upset emissions
- The discrepancies between measurements and conventional estimates are consistent with differences observed elsewhere, e.g Sweden.

# EMISSION FACTOR UNCERTAINTY & the Role of Remote Sensing

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# Objective

1. To illustrate via an example using storage tanks that the variability in underlying parameters that define emissions impact the accuracy of any emission estimating protocol.
2. The degree to which estimation methods address this variability affects the accuracy of both measurement methods as well as emission factor methods.
3. While snap-shot methods may give a reasonably accurate instantaneous estimate, their inability to assess the underlying sources of instantaneous variability make them inappropriate to assess long term emissions.

# PREMISE

“Neglect of variability in the underlying parameters increases the potential uncertainty of an emissions estimate.”

If the variability in the underlying parameters is great, so will be the variation in actual emissions. The greater the variation in actual emissions, the greater the potential uncertainty in an emissions estimate that does not account for this variation.

# Uncertainty in Fixed-Value Emission Factors

- Fixed-value emission factors can have large uncertainties.
  - Actual values may range over a couple of orders of magnitude.
  - The fixed value represented by the emission factor lies at some random point in this range.
- A similar limitation holds true for estimating long-term average emissions from snap-shot-in-time measurements

# Uncertainty in Snap-Shot-in-Time Measurements

- As with a fixed-value emission factor, a snap-shot measurement represents only one point in the range of actual emissions.
- A snap-shot measurement cannot characterize either the average or the limits of the actual range. It is just a random point in the range.



# Limitations to Snap-Shot Measurements

- It is not technically defensible to extrapolate a snap-shot measurement beyond the time period within which the measurement was taken.
- It is misleading to characterize the short-term snap-shot measurement as a “measurement” of the long-term annual average emissions.
- There is no statistically defensible basis for correlating a single snap-shot measurement with annual average emissions.

# Storage Tank Emission Factors

- Developed from over 20 years of testing.
- Testing and emission factor development have been sponsored by API in cooperation with EPA.
  - Both parties receive and evaluate all data.
- These tests directly measure both:
  - Emission rates, and
  - Values of contributing parameters (*e.g.*, TVP, temp).
- BECAUSE – for data to have validity, the variations in parameters must be accounted for!

# Storage Tank Emission Factors

- Tank emissions are estimated differently than those from many other operations
- Not just a fixed-value emission factor
- Account for variations in underlying parameters for routine operations. For example:
  - When a tank is being filled, vapors are pushed out; when a tank is being emptied, no emissions occur
  - During daytime heating, vapors escape the tank; at night, fresh air is drawn into the tank, and no emissions occur

# Storage Tank Example of Parameter Variability

- Annual emissions basis:
  - Annual average temperature = 60°F
  - Stored liquid = gasoline
  - RVP = 9.3 psi (annual average)
    - 7 psi for April to August
    - 11 psi for Sept to March

# Storage Tank Example Annual versus Snap Shot

- Annual evaluation of vapor pressure function:
  - Annual average TVP = 4.8 psia
  - Annual average  $P^*$  = 0.099
- Snap shot on a warm afternoon in September:
  - Temperature = 80°F
  - RVP = 11 psi
  - TVP = 8.4 psia
  - $P^*$  = 0.208 (a factor of 2 difference in this one variable)

# Comparison of Existing Tank Emission Methods to DIAL Measurements

- DIAL study conducted by CONCAWE (Smithers, et al., “VOC Emissions from External Floating Roof Tanks: Comparison of Remote Measurements by Laser with Calculation Methods”, Report No. 95/52, Brussels, Jan 1995) concluded:
  - For storage tanks, the difference between DIAL measurements and API/EPA factor-calculated emissions was 10% over 90 hrs at 5 tanks
  - For barge loading, DIAL was within 10% of directly measured emissions; API/EPA factor-calculated emissions were within 3%

# Summary

- Current API/EPA emission estimating methods are accurate for estimating annual average emissions from routine operations of storage tanks.

# Underreported Emissions?

- Does the foregoing demonstrate that emissions are never underreported?
  - Not at all.
  - It simply demonstrates the statistical fact that extrapolating snap-shot measurements beyond the period of measurement is not valid.
- Under (or over) reporting of emissions is a separate issue which merits serious consideration.



# Role of Remote Sensing In Identifying Underreported Emissions

- Finding the sources.
  - Unaccounted for operations at known sources (*e.g.*, floating-roof landing losses).
  - Previously overlooked sources (*e.g.*, leaking heat exchangers).
  - Poorly maintained sources. (*e.g.*, failed rim seals on floating roofs).
- IR cameras hold significant promise!

# Smart LDAR

- That promise will be realized upon final rule promulgation by EPA, which will provide a method for using IR cameras to identify emissions



# Role of DIAL In

## Checking Current Emission Factors

- Measurement of downwind plume would:
  - Only check overall emissions, but
  - Not emissions from individual tank features.
- Thus useful for:
  - Field-proofing, but
  - Not for adjusting emission factors.
- This was done in the CONCAWE study.
  - In which DIAL measurements showed good agreement with API/EPA emission factors .

# Role of IR Cameras In Checking Current Emission Factors

- Current technology is effective in finding emission points and displaying their relative intensity.
  - Even if a plume is detected, it may be compliant.
  - Plumes direct attention to specific scenarios.
  - For example, flyovers may have led to investigation of floating-roof landings, if landings had not already been identified as a source.

# In Summary

- Emission rates from a given source or operation typically vary over a broad range.
- Fixed-value emission factors have inherent uncertainty, in that they represent only a single random point in that range.
- A similar limitation applies to the use of snapshot measurements to estimate long-term emissions!
- On the other hand, API/EPA storage tank emission factors *account for* variation in the parameters.

# Long-Term Application of OTM-10 Using DOAS in Industrial Settings

ORS Workshop Presentation  
April 1, 2008  
Eben Thoma



# Many Types of Area Sources



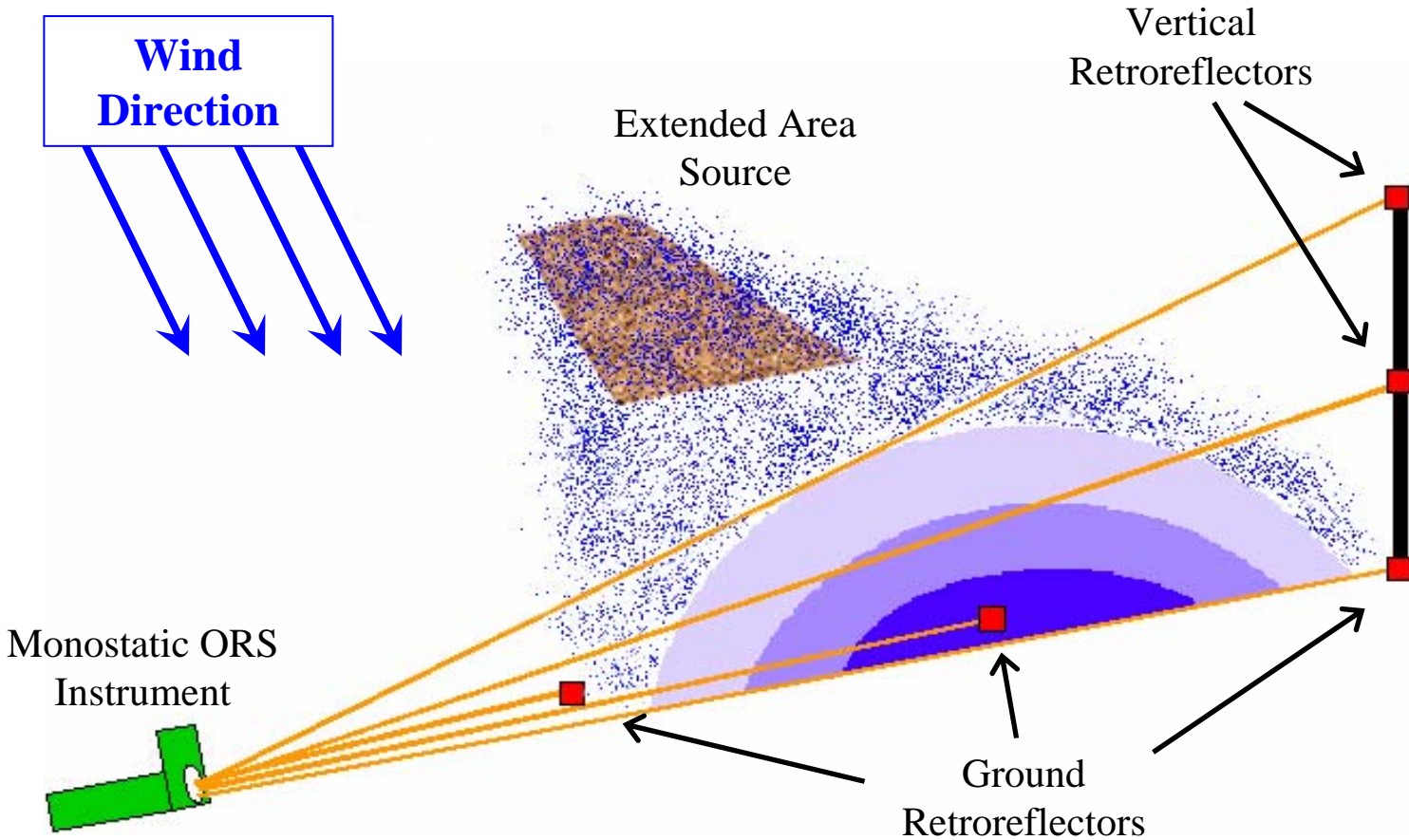
- Large Area
- Spatially Complex
- Temporally Variable



Different for Every Source

Episodic, Process Related,  
Diurnal, Seasonal, Atmospheric

# OTM-10 Area Source Measurement



Can be deployed for long duration monitoring



# Long Term Monitoring With OTM 10

- Advantages:

- Long term assessment of emissions variability
- 24/7 remote operation
- Low cost to operate (after install)

- Disadvantages:

- Fixed observation area (compared to DIAL)
- Data subject to wind direction

- Example Application:

- Measurement of Mercury from Chlor-alkali Facility using UV-DOAS  
E. Thoma, C. Secret, E. Hall, D. Jones, R. Shores, P. Groff (US EPA)  
R. Hashmonay, M. Modrak, M. Chase (ARCADIS), Phil Norwood (ECR)



# Mercury Cell Chlor-Alkali Facilities Background

- Produce H<sub>2</sub>, Cl<sub>2</sub>, KOH, and NaOH by electrolysis of brine solution
  - Liquid mercury (Hg<sup>0</sup>) used as cathode material for electrolytic cells
- Significant Hg<sup>0</sup> fugitive emissions can occur:
  - leaks in cell equipment and transfer piping
  - maintenance and repair of sealed equipment
  - Process upsets
- Most previous studies in Europe using DIAL (short term, 1-2 weeks)
- This an 8-week, 24/7 study (could have been much longer)

50m Water Tower



Lumex



OTM 10 Plane

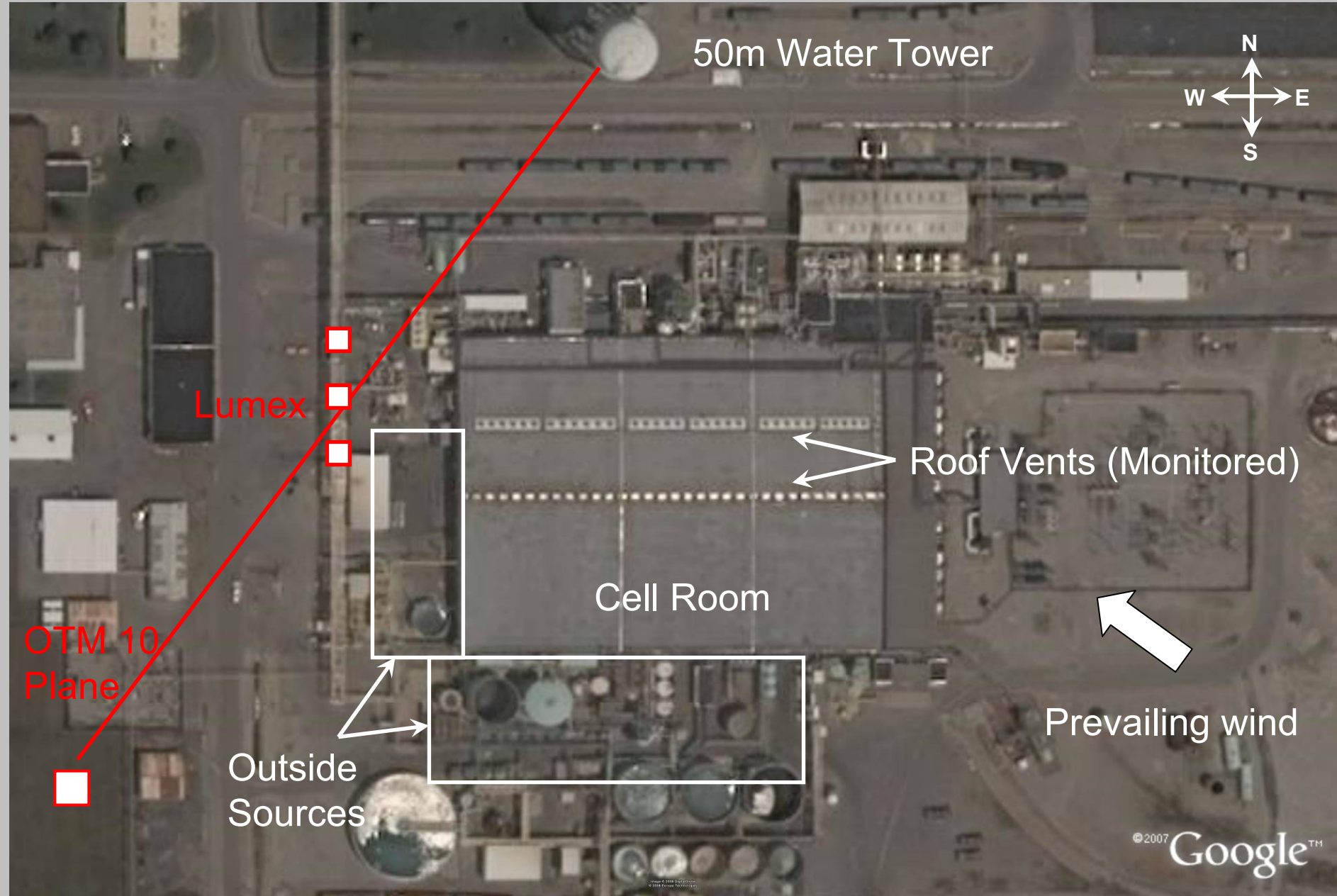


Roof Vents (Monitored)

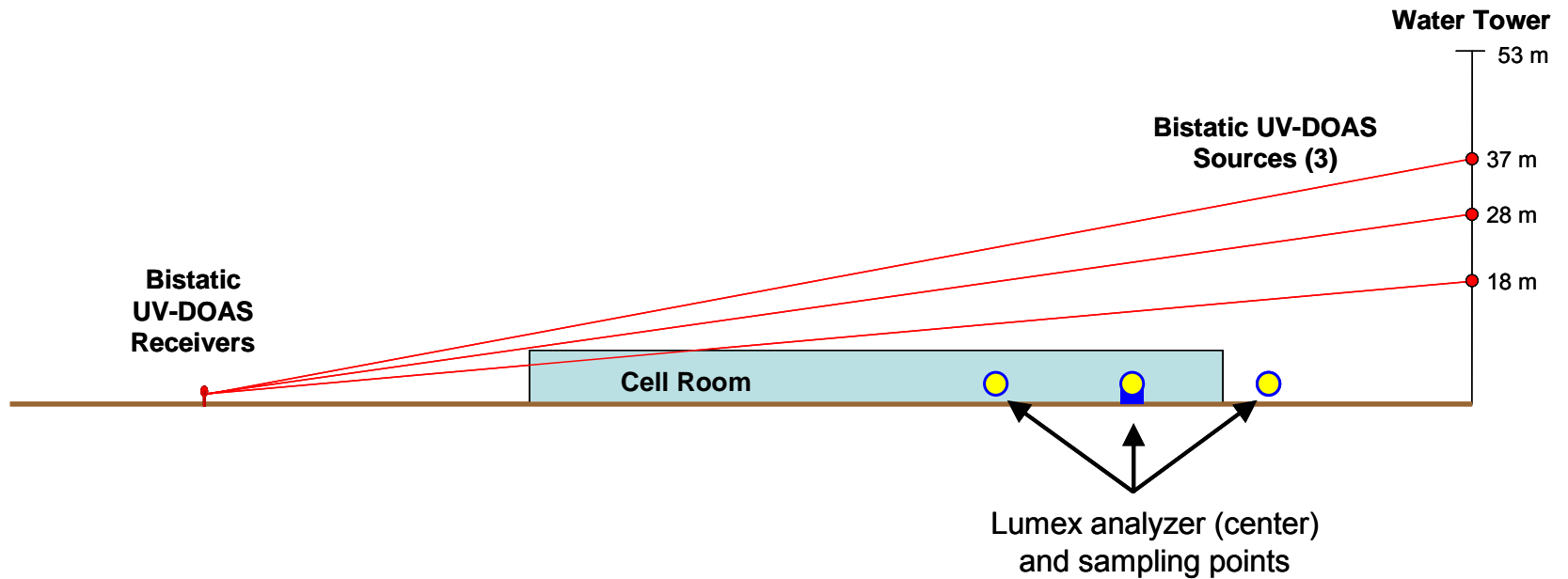
Cell Room

Prevailing wind

Outside Sources



# Side View of OTM 10 Configuration





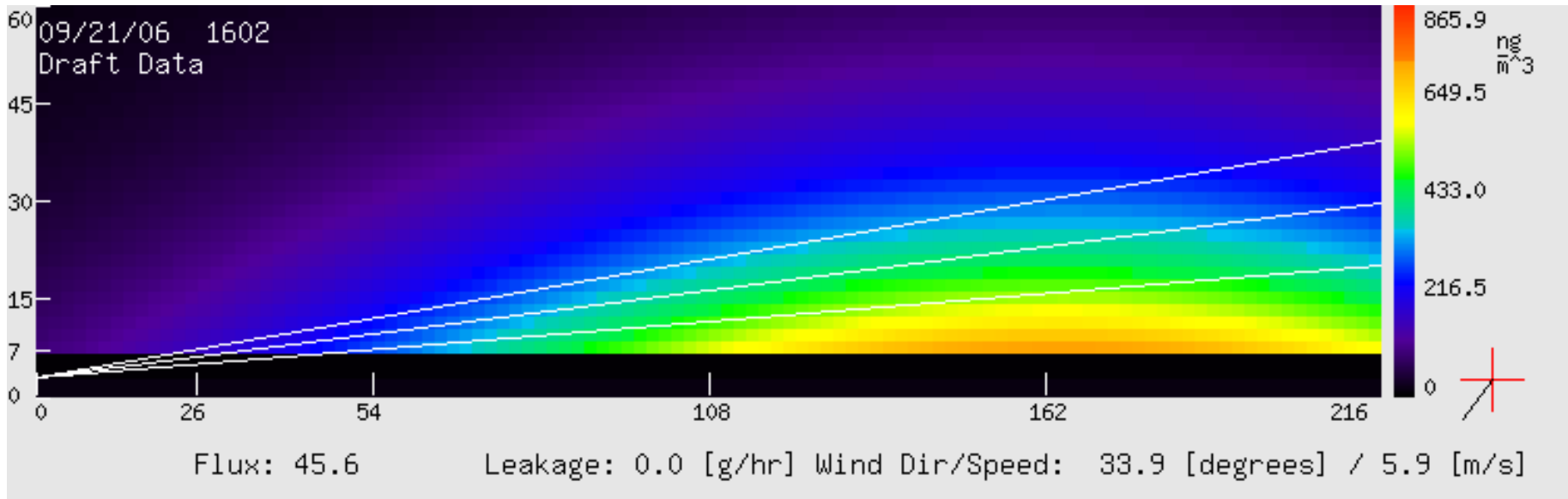
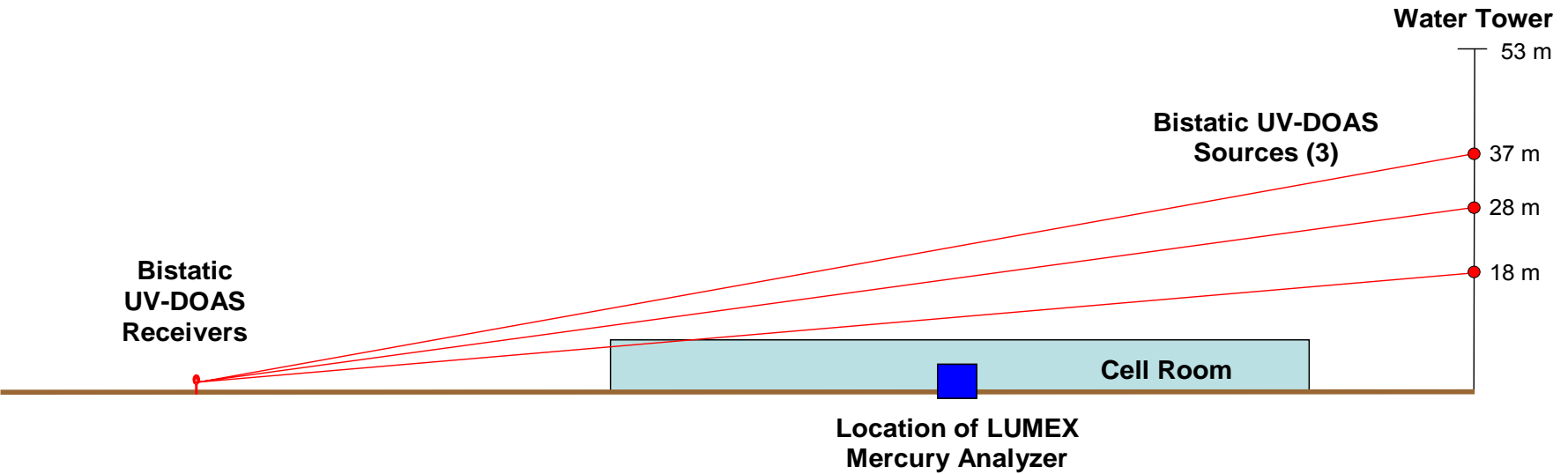






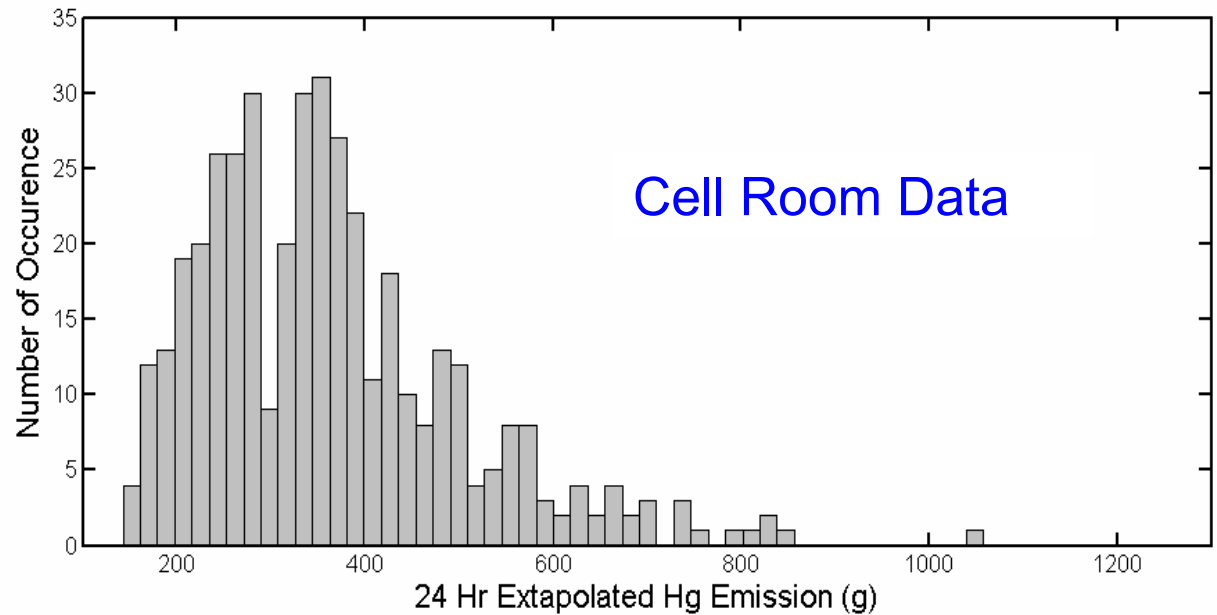
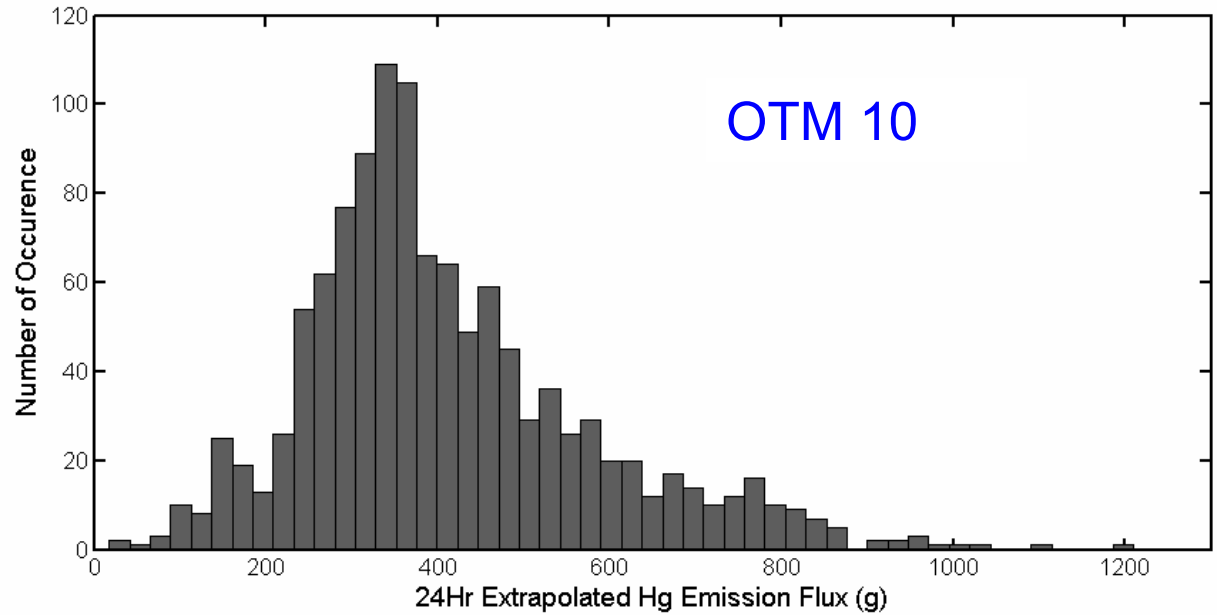


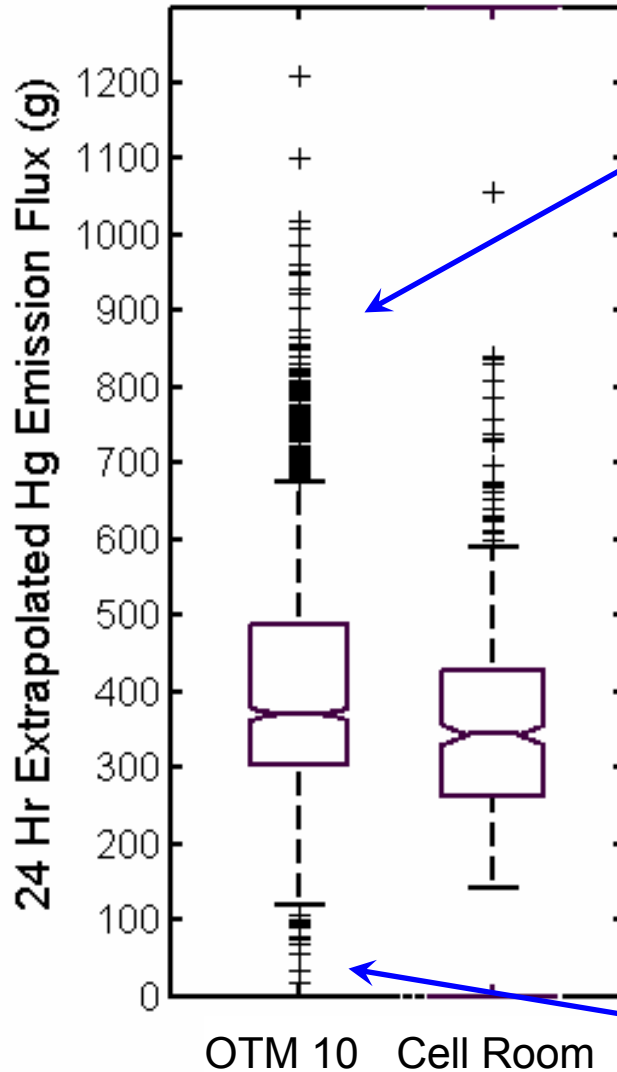
# OTM 10 Plume Reconstructions



Extrapolated from  
20 minute average

4 minute base  
period for OTM 10



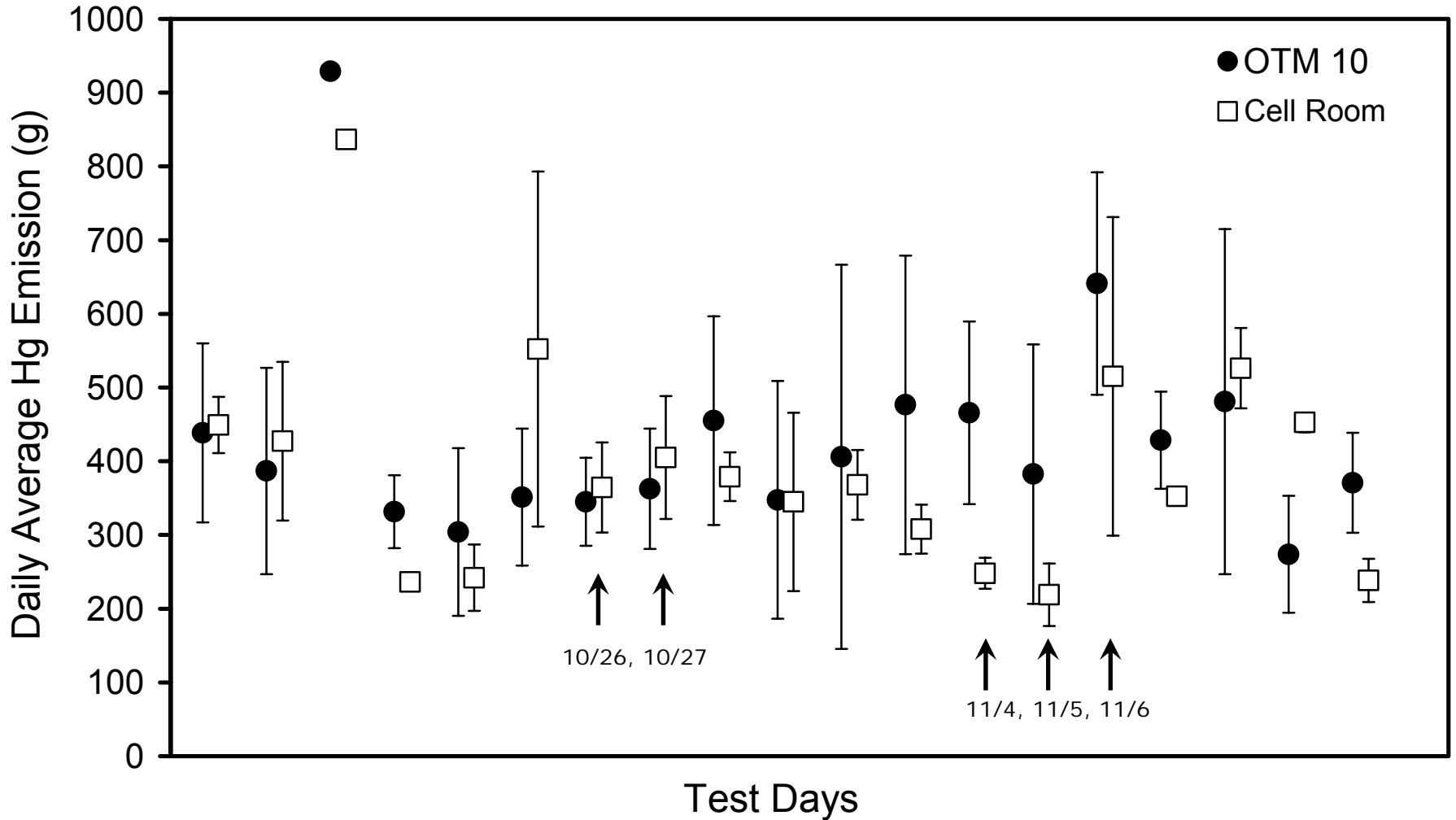


fugitive emissions outside cell room contributing

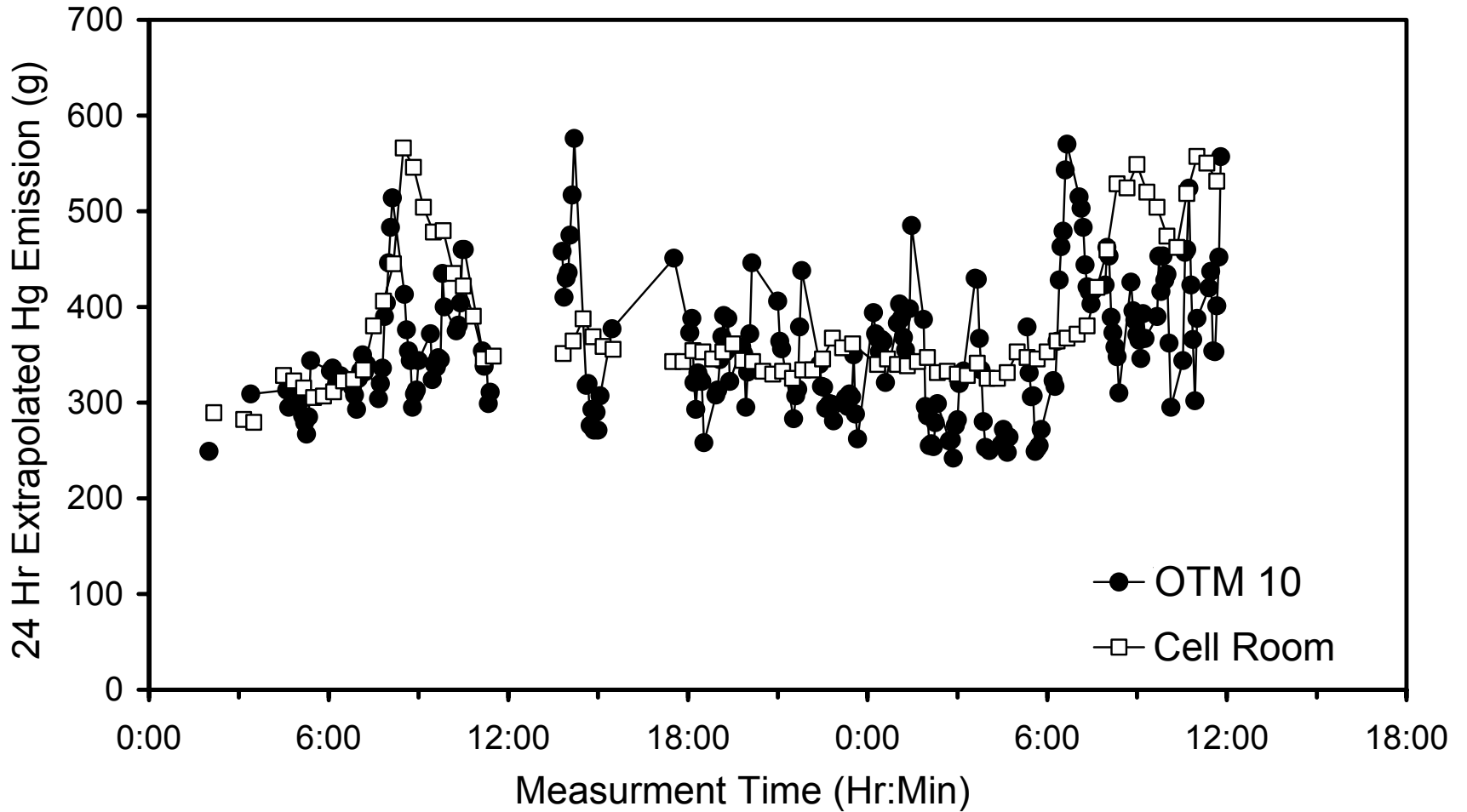
High values measured on 3 independent DOAS Beams

Low outliers indicate poor plume capture

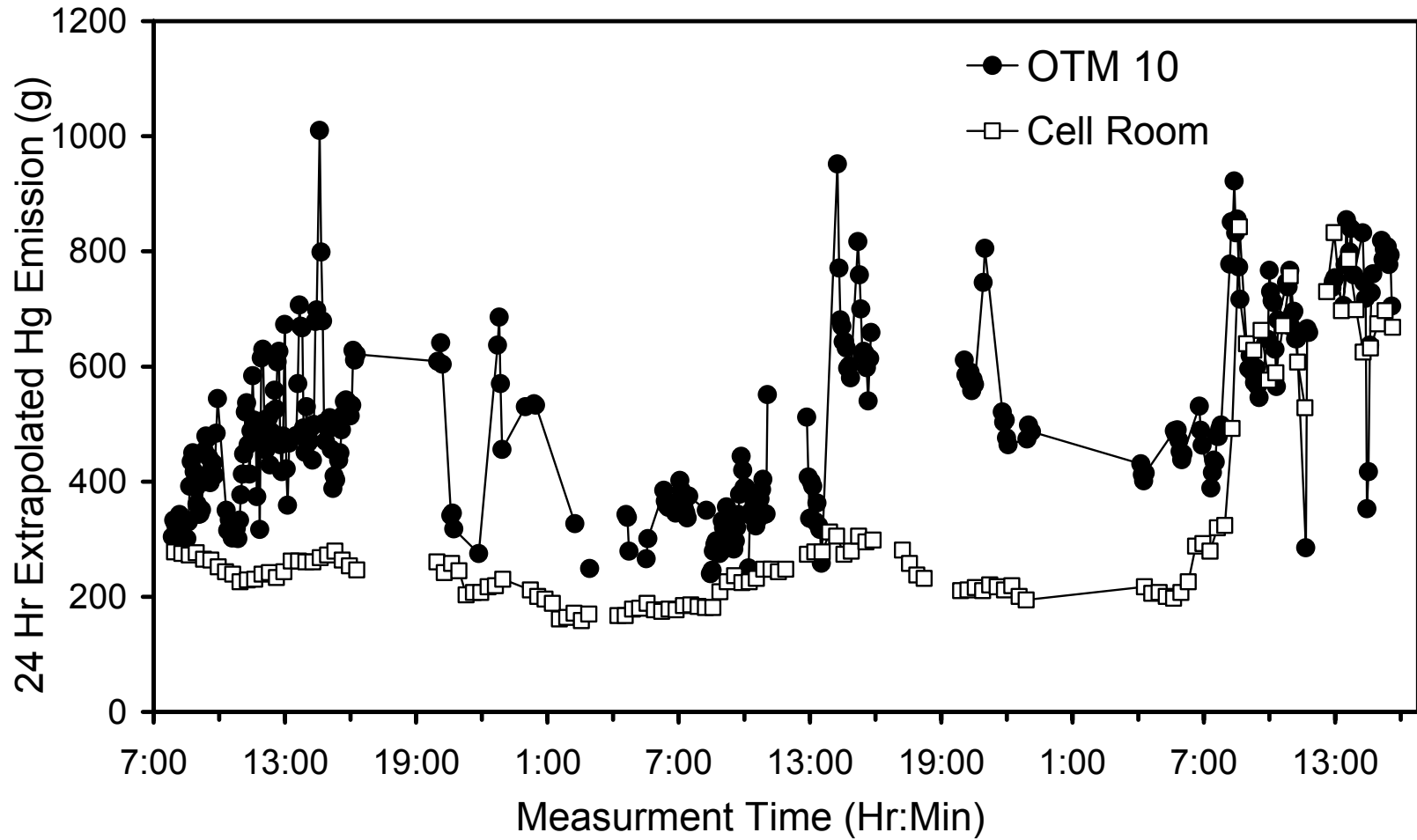
# Comparison of OTM 10 and Cell Room Data



# Comparison of OTM 10 and Cell Room Data



# Comparison of OTM 10 and Cell Room Data



# Summary

- Automated, Fixed-site OTM 10 deployments can assist in understanding the temporal variability of emissions
- Advantages:
  - Long term assessment of emissions variability
  - 24/7 remote operation
  - Low cost to operate (after install)
- Disadvantages:
  - Fixed observation area (compared to DIAL)
  - Data subject to wind direction

# Many forms Optical Remote Sensing

## Satellites / Airborne Platforms

- Very large spatial scale
- Modest detection/speciation capability
- Limited long-term monitoring

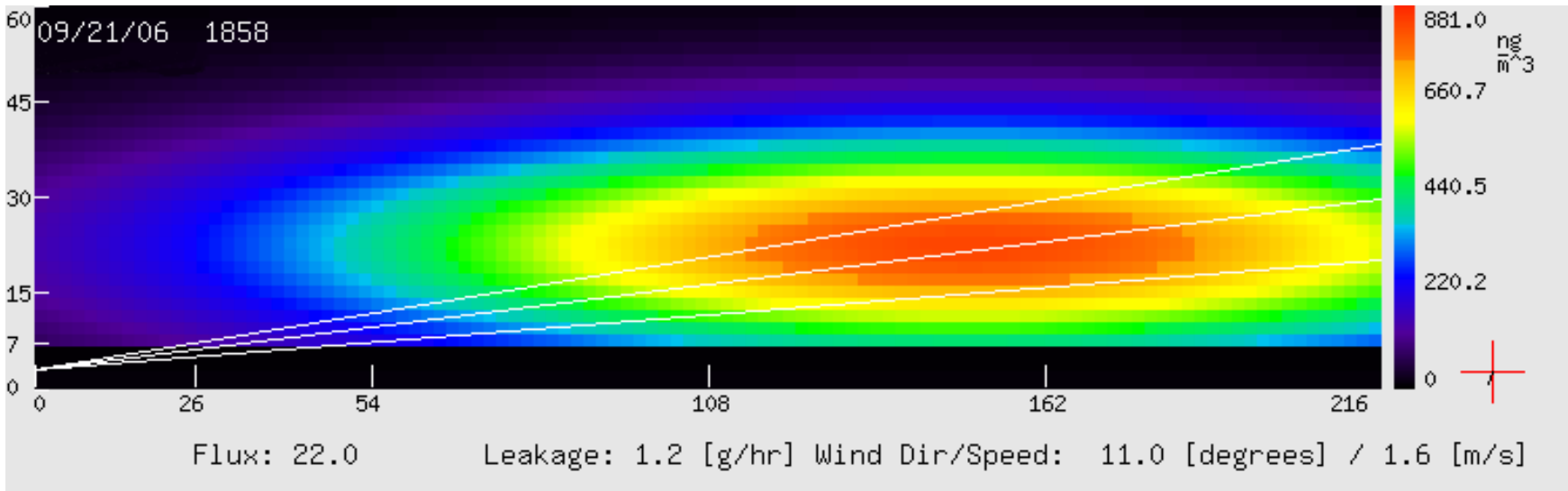
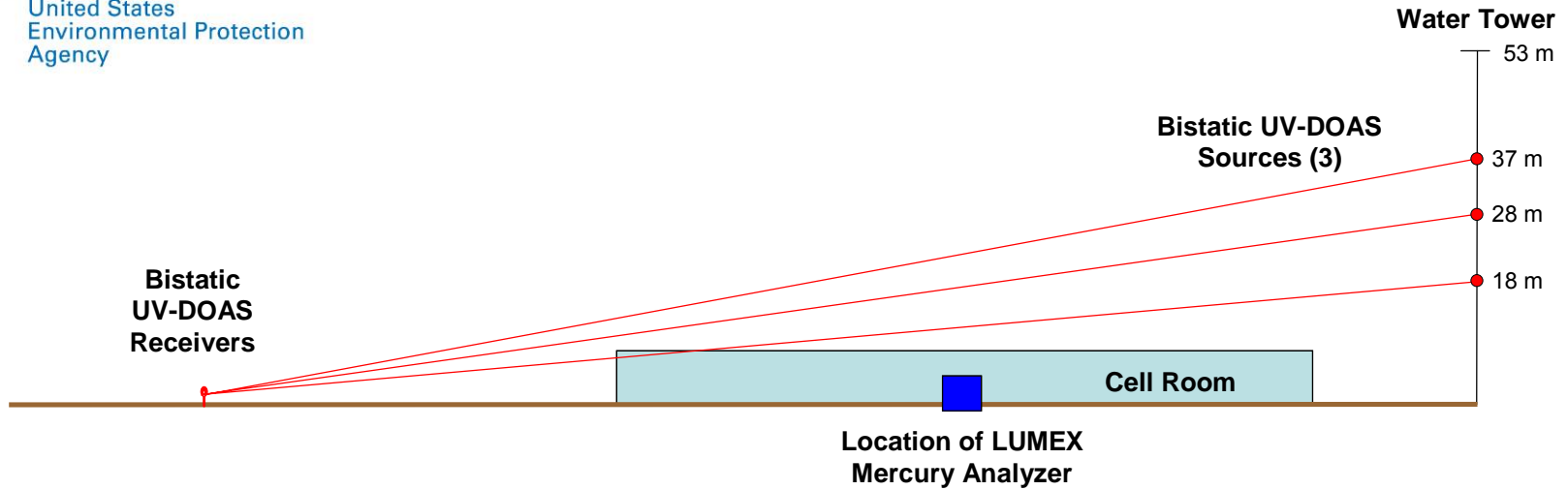
## DIAL and SOF

- Large scale
- Good detection/speciation capability
- Limited long-term monitoring

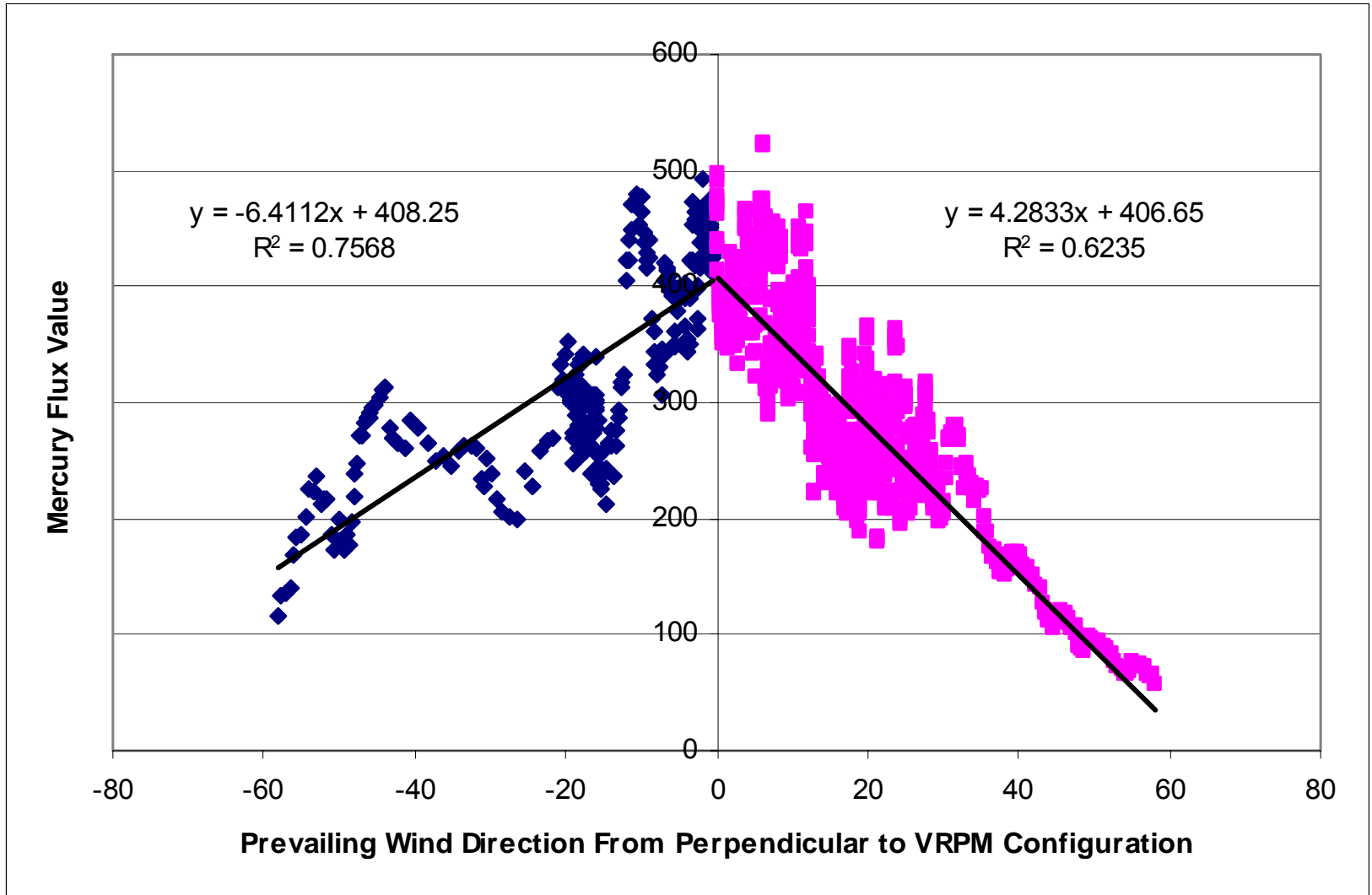
## Fixed-Deployment ORS

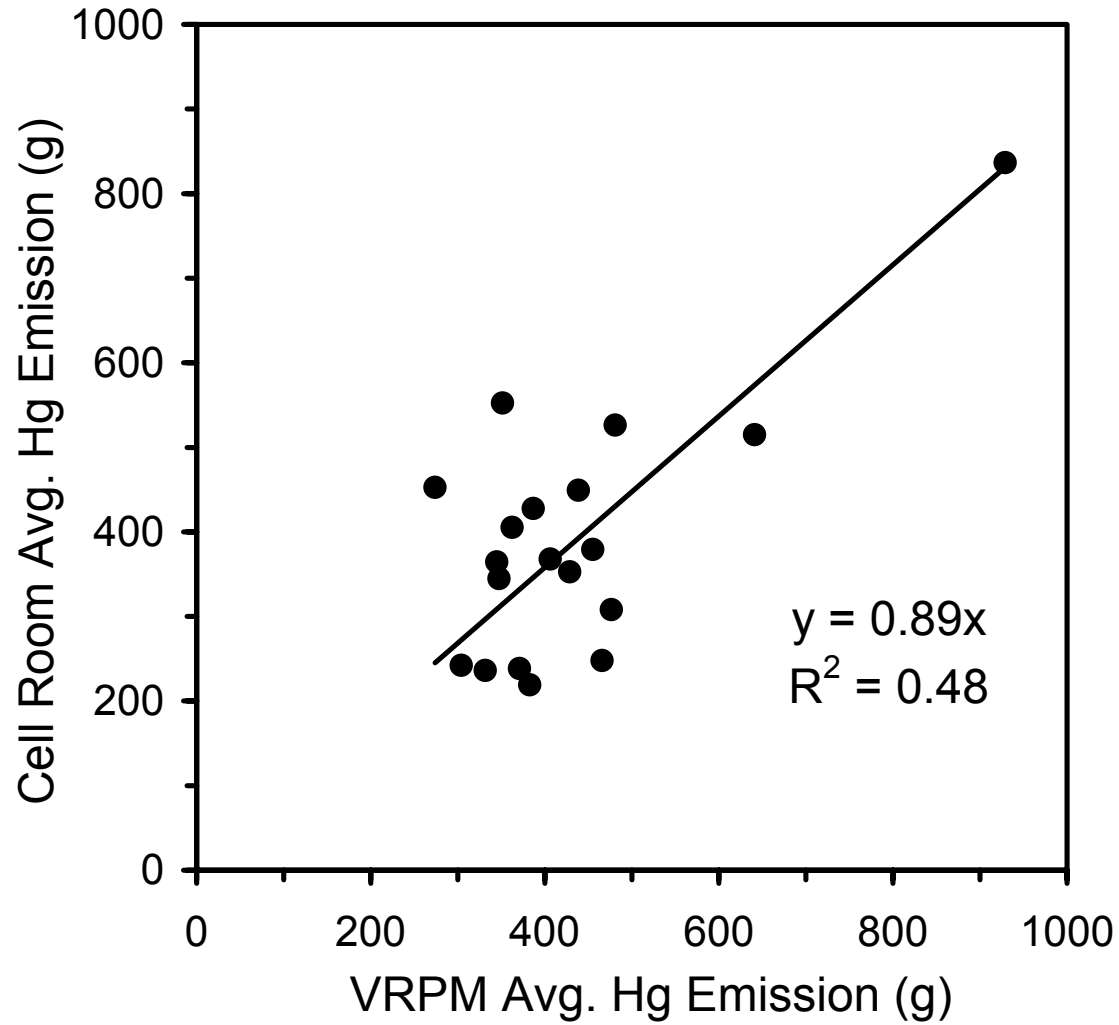
- Medium scale assessment
- Very good detection/speciation capability
- Long term monitoring capability



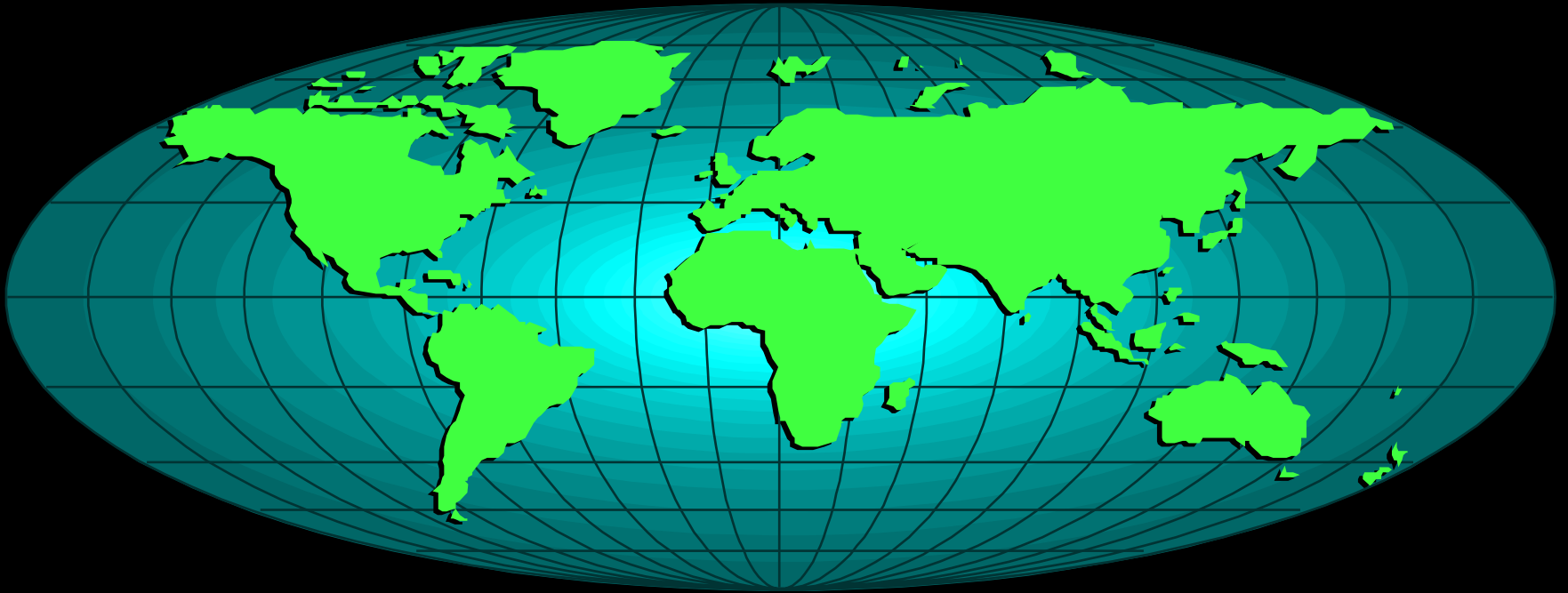


# Horizontal Plume Capture vs. wind dir.





# Continuous Fence-line Monitoring



2<sup>nd</sup> International Workshop  
On Remote Sensing of Emissions

# **FTIR Monitoring Modes**

# FTIR Monitoring Modes

---

- Active (Transmission) mode:

IR source in the FTIR, transmitted through a gas/liquid volume, and analyzed for identification and quantitation of species present

- Gas phase Monitoring

- \*Fence-line

- \* Stack

- \* Process streams

# Applications of Transmission Monitoring

---

- Liquid phase monitoring (Sparging):
  - \* Cooling towers
  - \* Condensate streams
  - \* Waste water streams

# FTIR Monitoring Modes

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- Passive (Radiance) mode:

FTIR is a passive receiver collecting radiation emitted by hot ( $>120$  C) gases, radiation received can be analyzed for identification and quantitation of species present

- combustion efficiency:

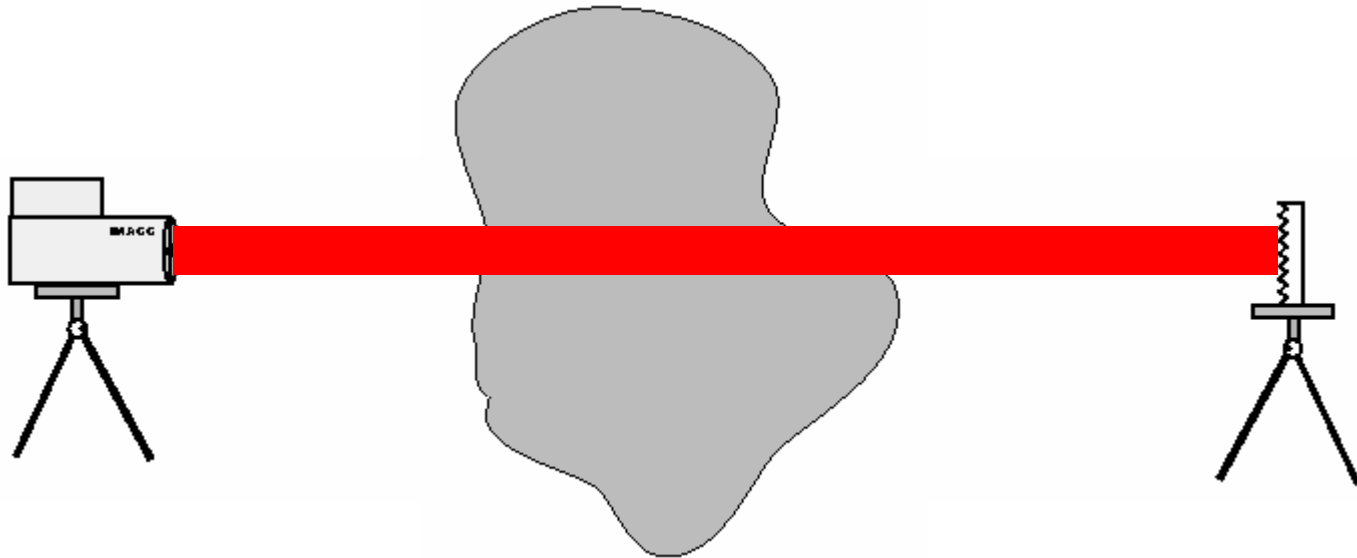
- \* Flares
- \* Burners
- \* Stacks



**Open-path  
Optical Detection  
(Transmission)**

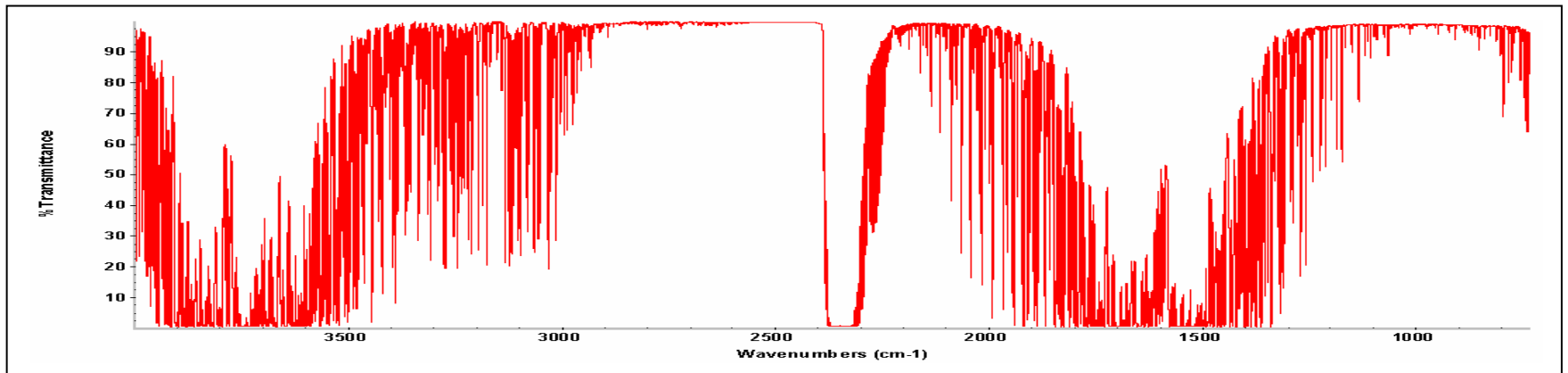
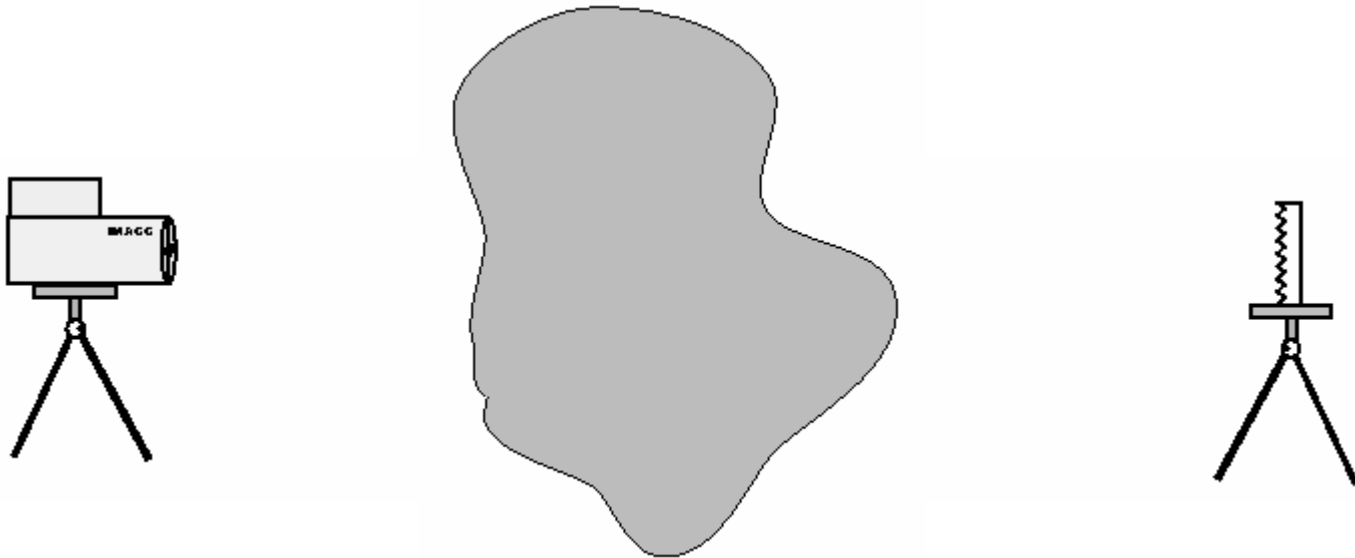
# Monostatic FTIR Transceiver

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# Monostatic FTIR Transceiver

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# **What Can An FTIR Monitor ?**

# Compounds Covered

---

- The FTIR can monitor most molecular species except for homonuclear diatomics ( $\text{Cl}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , etc.)
- The detection limit varies by compound but all can be detected to sub ppm-levels with small systems and to the low ppb-level with larger systems

# Detection Limits (ppb) for Select Compounds

Species	300 Meter Open Path	100 Meter Cell*	Species	300 Meter Open Path	100 Meter Cell*
acetaldehyde	20	30	cyclohexane	3	5
acetic acid	5	7 SL	1,2-dibromoethane	5	7
acetone	30	10	m-dichlorobenzene	3	5
acetonitrile	50	70	o-dichlorobenzene	3	5
acetylene	2	2	p-dichlorobenzene	2	3
acrolein	5	7	1,1-dichloroethane	10	10
acrylic acid	10	5 SL	1,2-dichloroethane	30	40
acrylonitrile	6	10	1,1-dichloroethylene	2	4
ammonia	2	3 SL	dimethylamine	20	30 SL
benzene	15	3**	dimethyl disulfide	10	15
1,3-butadiene	1	3	1,4 dimethyl piperazine	3	5
butane	HC		1,4 dioxane	2	3
butanol	15	20 SL	ethane	10	10
1-butene	10	15	ethanol	10	10 SL
cis-2-butene	25	30	ethyl acetate	4	4
trans-2-butene	10	15	ethylamine	20	10 SL
butyl acetate	5	7	ethylbenzene	20	30**
carbon disulfide	dry only	50	ethylene	1	3
carbon monoxide	1	4	ethylene oxide	10	15
carbon tetrachloride	2	2	ethyl mercaptan	50	70
carbonyl sulfide	2	3	formaldehyde	5	8
chlorobenzene	10	10	formic acid	2	3 SL
chloroethane	10	15	furan	3	5
chloroform	2	2	halocarb-11 (CCl3F)	1	1
m-cresol	20	15	halocarb-12 (CCl2F2)	1	1
o-cresol	4	8	halocarb-22 (CHClF2)	1	1
p-cresol	10	15	halocarb-113 (CFCl2CF2Cl)	2	2

# Detection Limits (ppb) for Select Compounds

Species	300 Meter Open Path	100 Meter Cell*	Species	300 Meter Open Path	100 Meter Cell*
hexafluoropropene	1	2	ozone	3	5
hydrocarbon continuum	10	15	pentane	HC	
hydrogen chloride	2	4	phosgene	1	2
hydrogen cyanide	5	4	phosphine	2	3
hydrogen sulfide	300	500	propane	10	10
isobutane	2	1	propand	20	30 SL
isobutanol	4	6 SL	propionaldehyde	10	15
isobutyl acetate	5	7	propylene	4	10
isobutylene	4	4	propylene dichloride	10	15
isoprene	4	5	propylene oxide	2	10
isopropanol	10	10 SL	pyridine	20	20
isopropyl ether	10	5	silane	1	1
methanol	4	6 SL	styrene	3	2
methylamine	20	20 SL	sulfur dioxide	30	30
methyl benzoate	20	30	sulfur hexafluoride	<1	0.1
methyl chloride	60	80	1,1,1,2-tetrachloroethane	4	6
methylene chloride	5	8	1,1,2,2-tetrachloroethane	20	16
methyl ether	10	15	tetrachloroethylene	2	2
methyl ethyl ketone	40	60 SL	toluene	25	10**
methyl isobutyl ketone	15	25 SL	1,1,1-trichloroethane	4	10
methyl mercaptan	40	60	1,1,2-trichloroethane	10	15
methyl methacrylate	5	5	trichloroethylene	2	3
2-methyl propene	2	4	trimethylamine	10	15 SL
morphaline	2	3	1,2,4-trimethylbenzene	5	7
nitric acid	1	2	vinyl chloride	4	5
nitric oxide	25	20	m-xylene	10	10**
nitrogen dioxide	50	50	o-xylene	20	5**
nitrous acid	5	7	p-xylene	20	10**

# **Open-Path Configuration Portable Monitoring**



# Portable FTIR Monitor – State of North Carolina



# Portable FTIR Monitor – State of North Carolina



**Open-Path Configuration  
Fixed Fence-line Monitoring**

# Imacc Monostatic FTIR Shelter

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# Imacc Monostatic FTIR on motorized Az/El Mount



# Imacc Monostatic FTIR System

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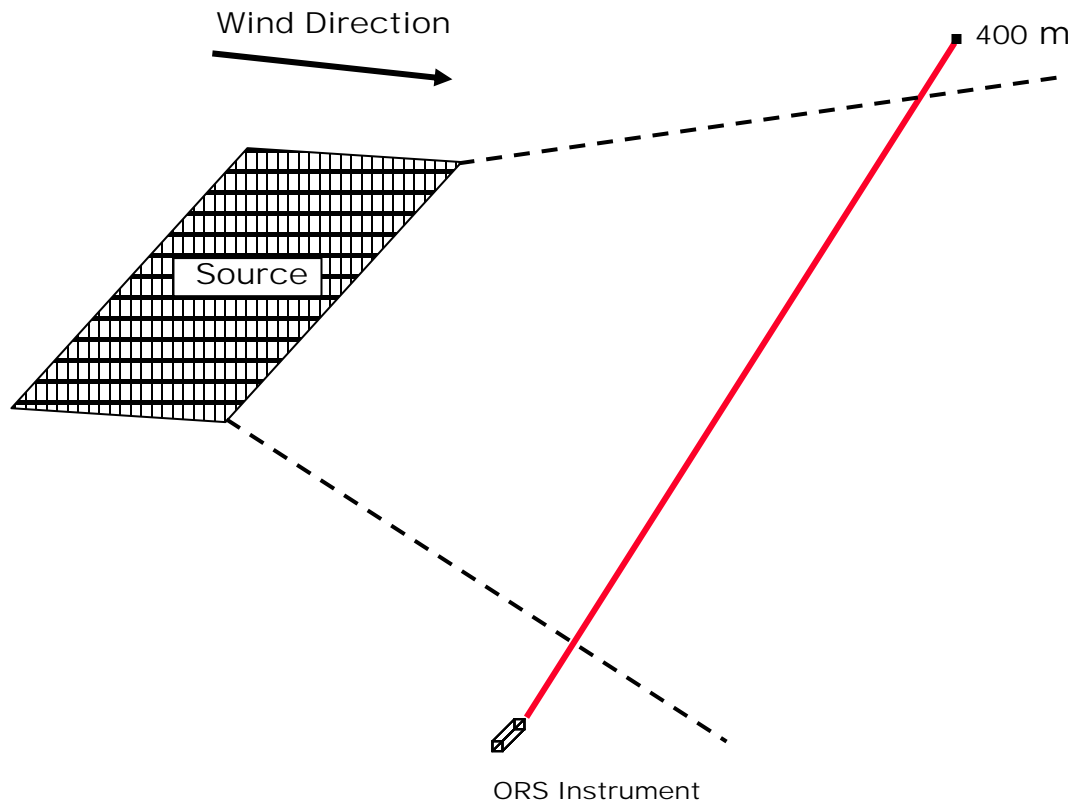


# Retro Array for Imacc Monostatic FTIR

---



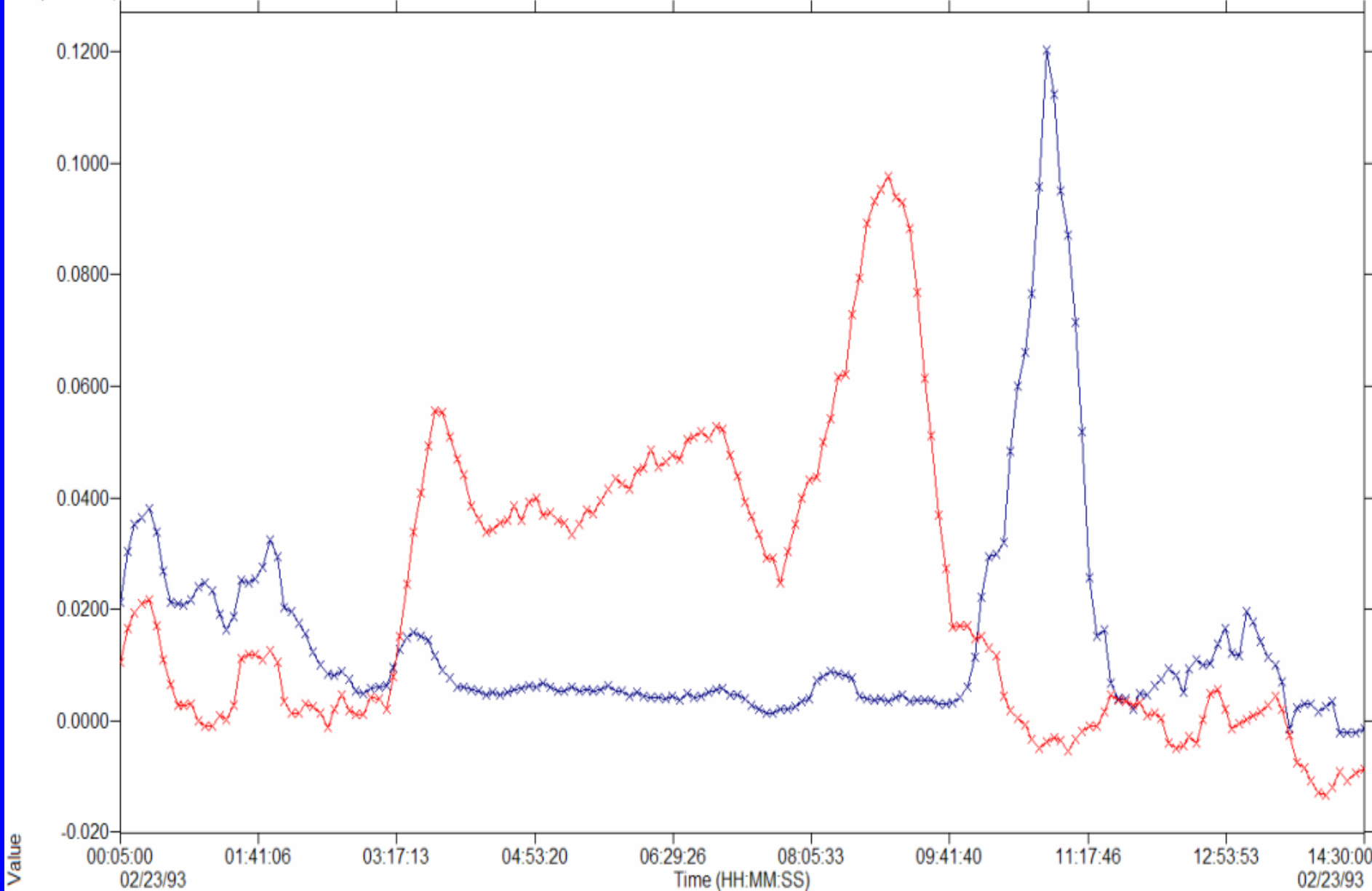
# Ground Level Plume Location



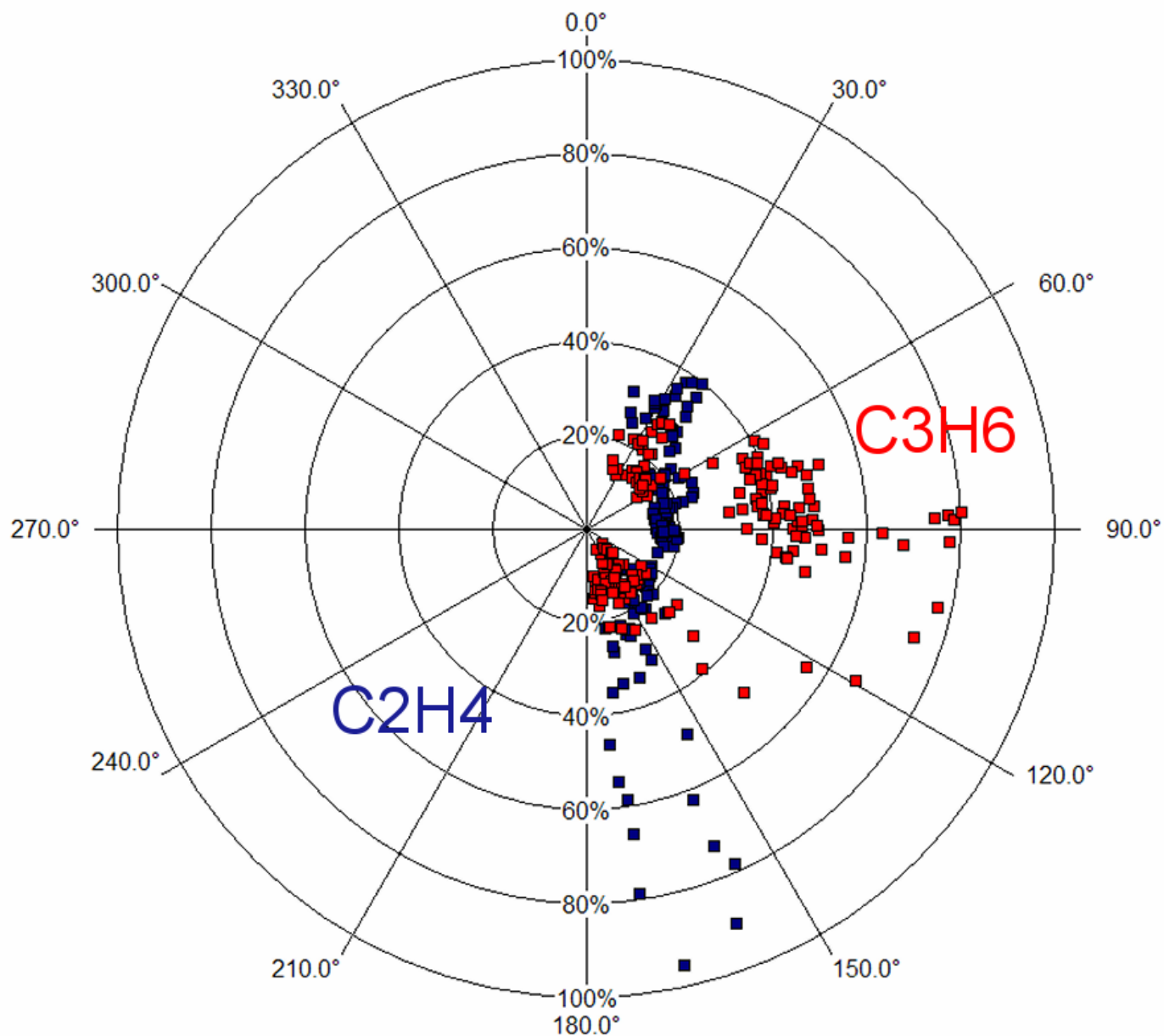


# Time Series Plot C2H4 & C3H6

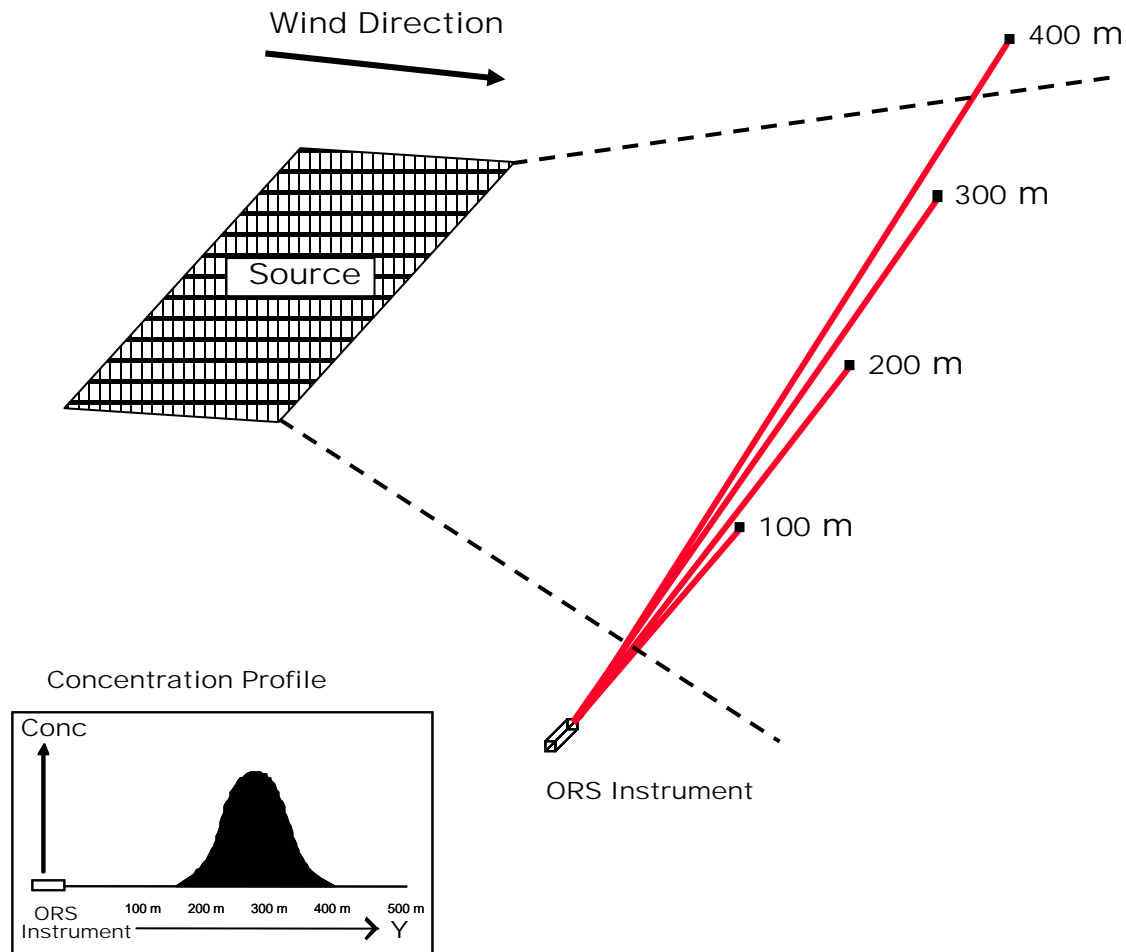
Group 1: C2H4, C3H6



# Wind Correlation Plot C2H4 & C3H6



# Ground Level Plume Location



# Retro Arrays for Monostatic FTIR



# Retro Arrays for Monostatic FTIR

---

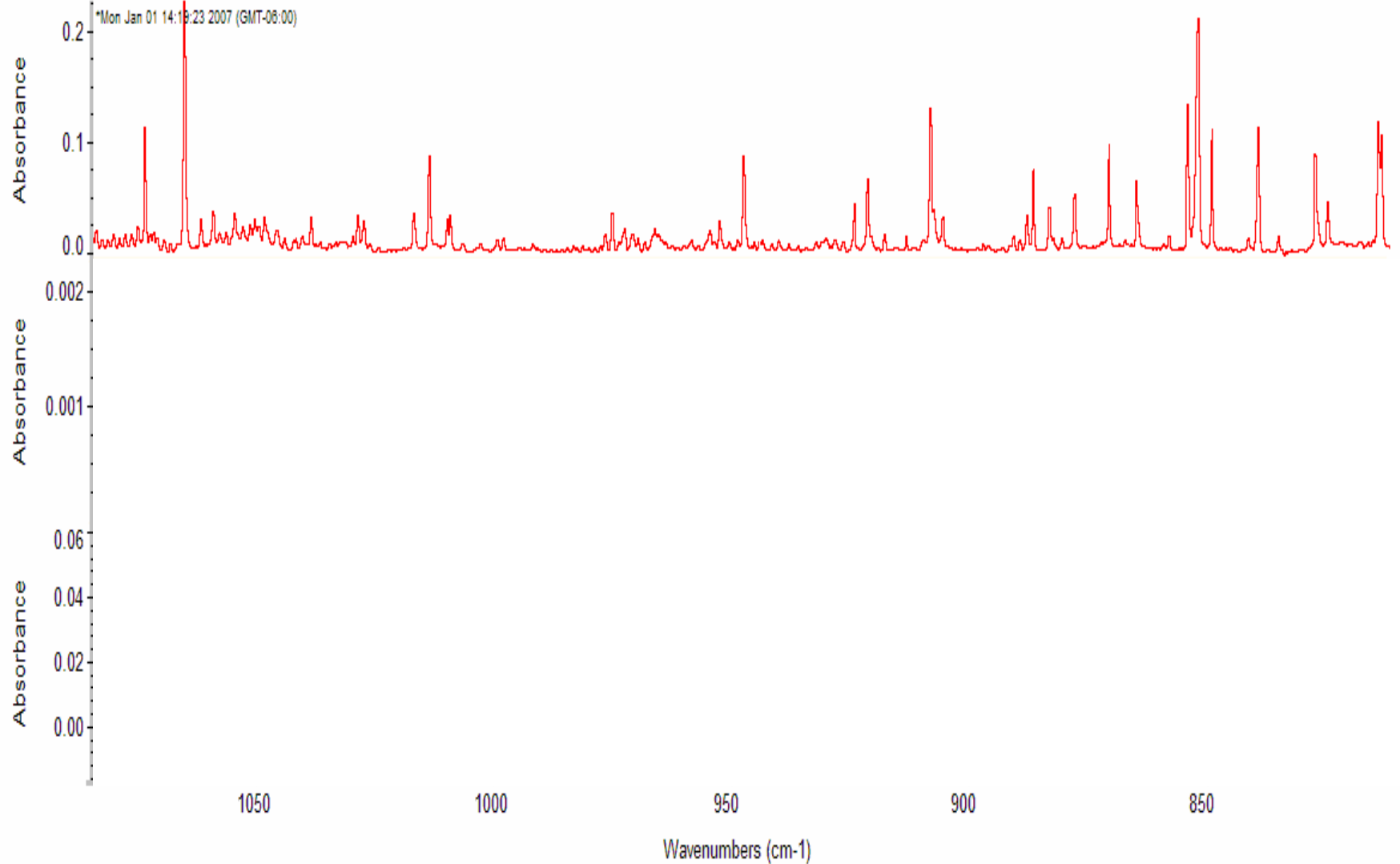


# Ground Level Plume Location

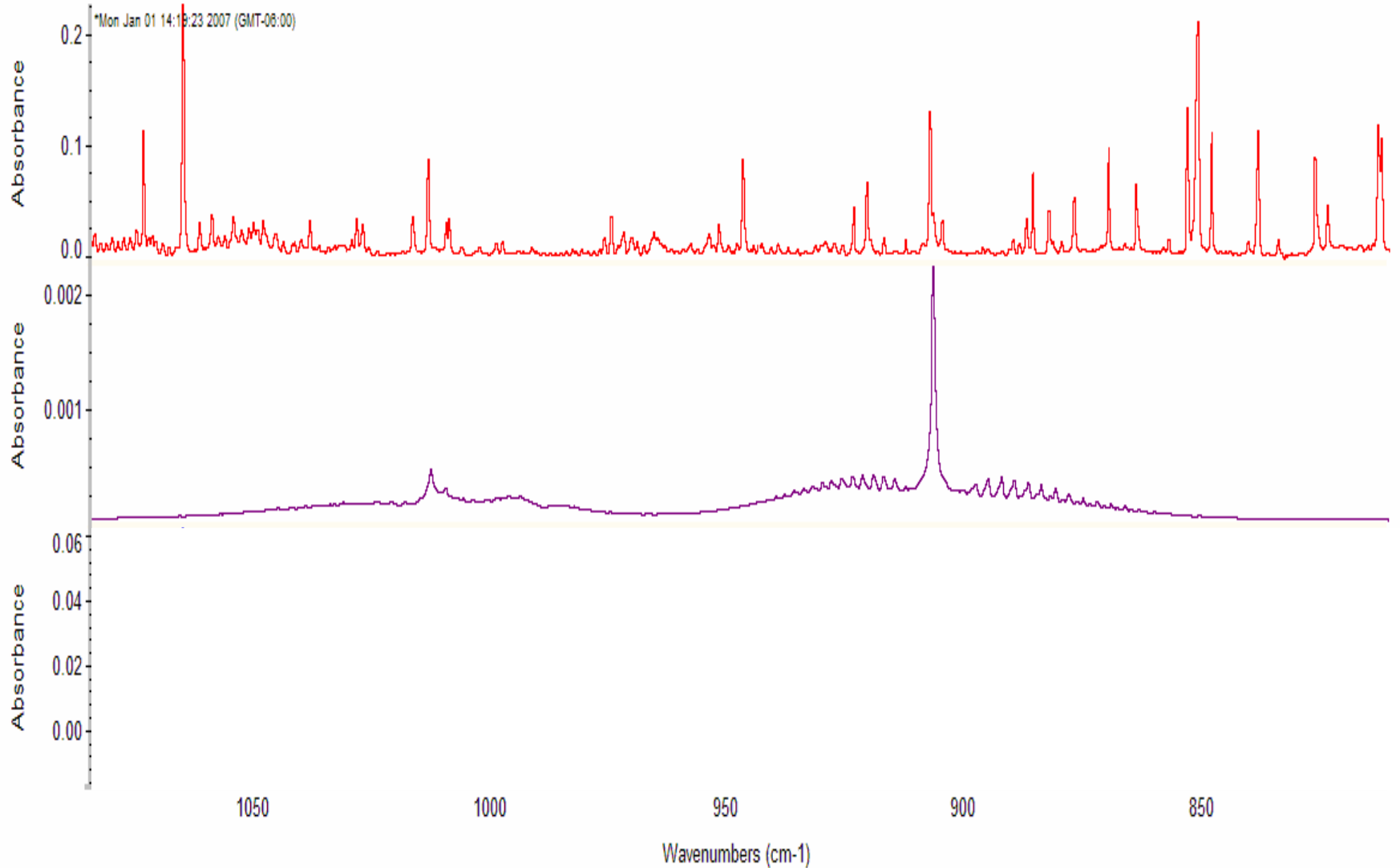
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# Typical 1,3 Butadiene Detection 400m Path

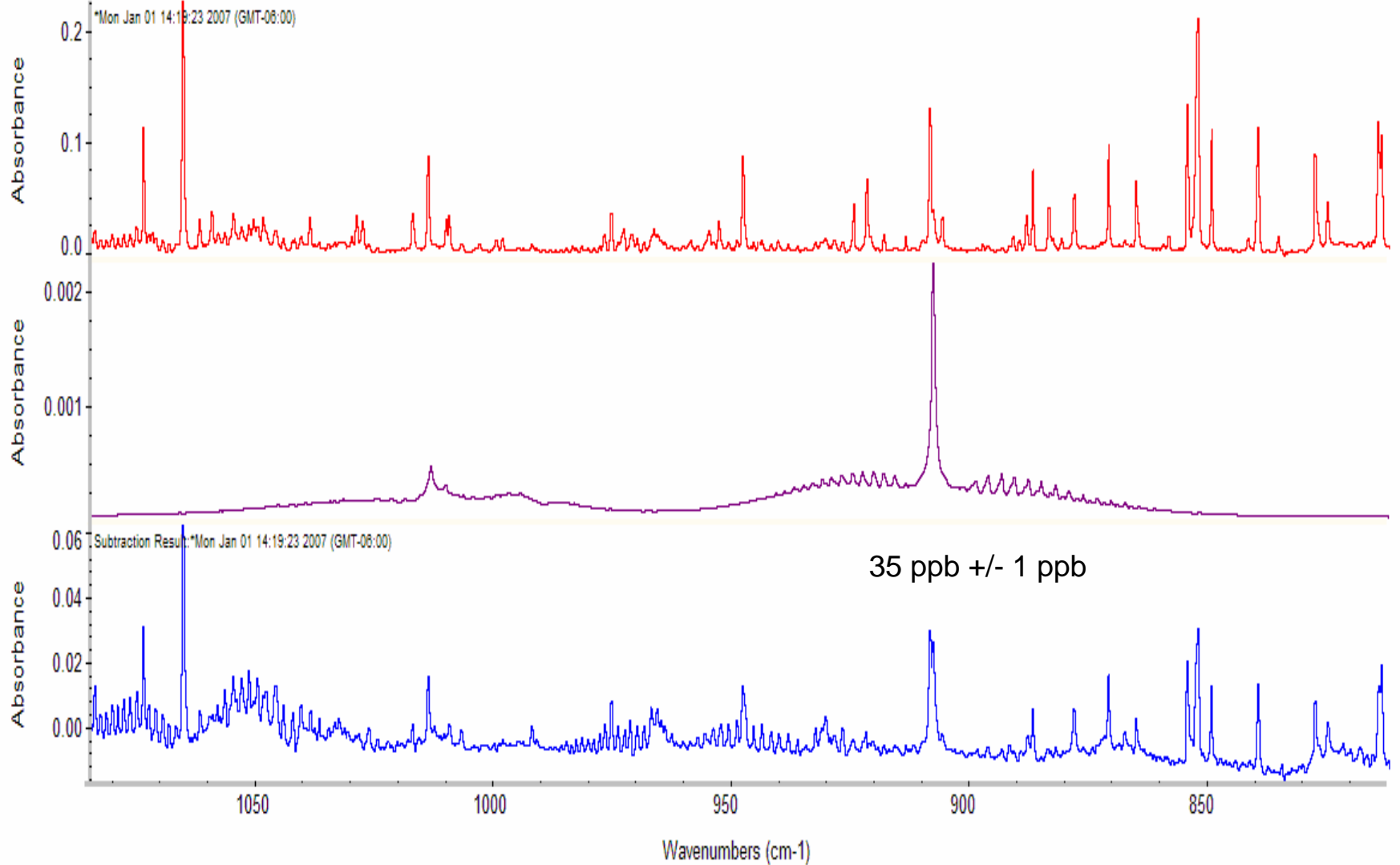


# Typical 1,3 Butadiene Detection 400m Path



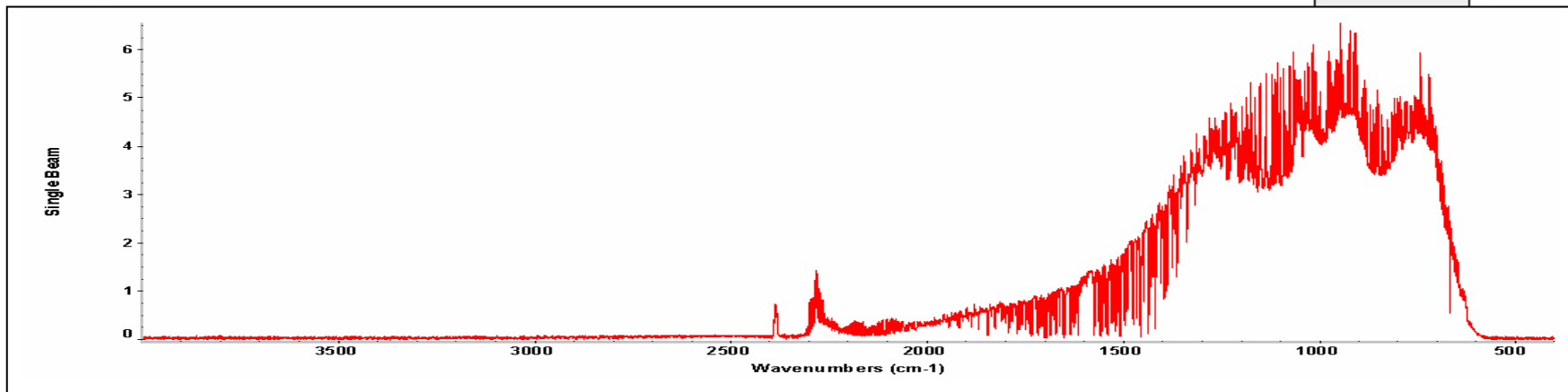
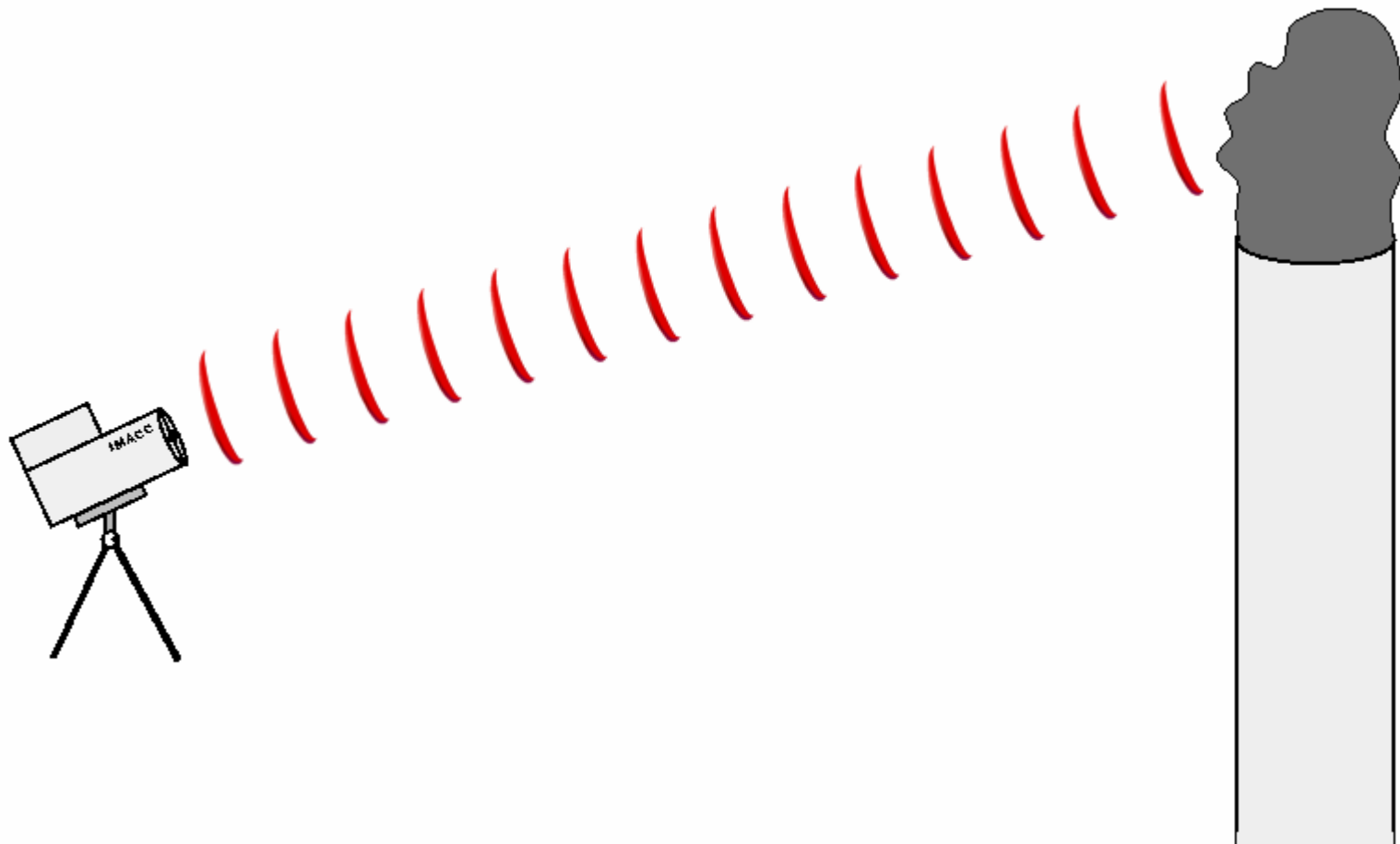


# Typical 1,3 Butadiene Detection 400m Path

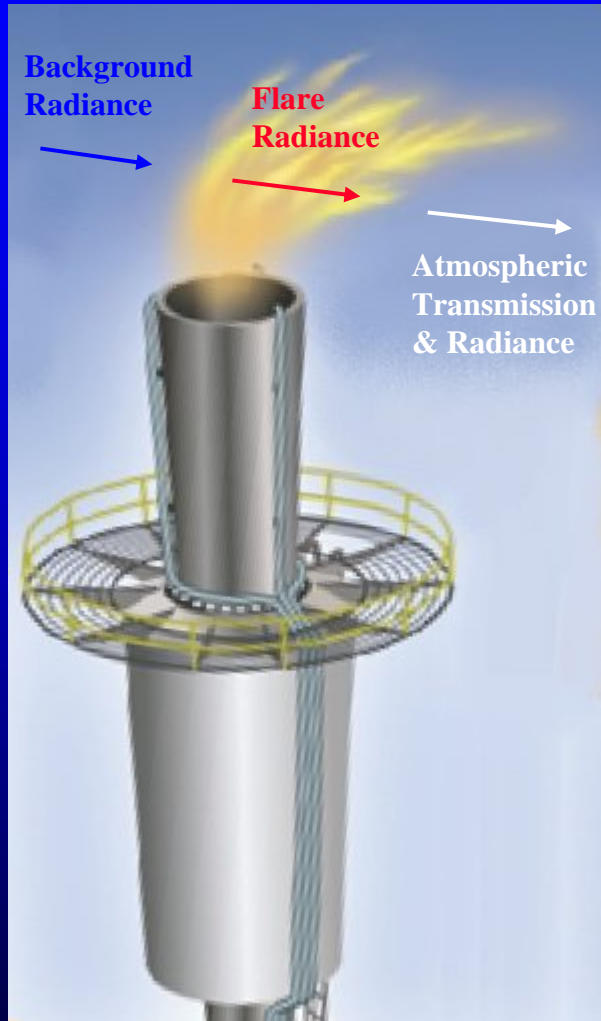


# Passive Radiance Mode Monitoring





# The Signal Observed



- The FTIR Signal arises from Four elements:
  - Background Radiance
  - Flare Radiance
  - Atmospheric path Radiance and Transmission
- The Total FTIR Signal is then:

$$R_b * \tau_{\text{plume}} \tau_{\text{atm}} + R_p * \tau_{\text{atm}} + R_{\text{atm}}$$

Generally Atmospheric Radiance  $R_{\text{atm}}$  is negligible if so:

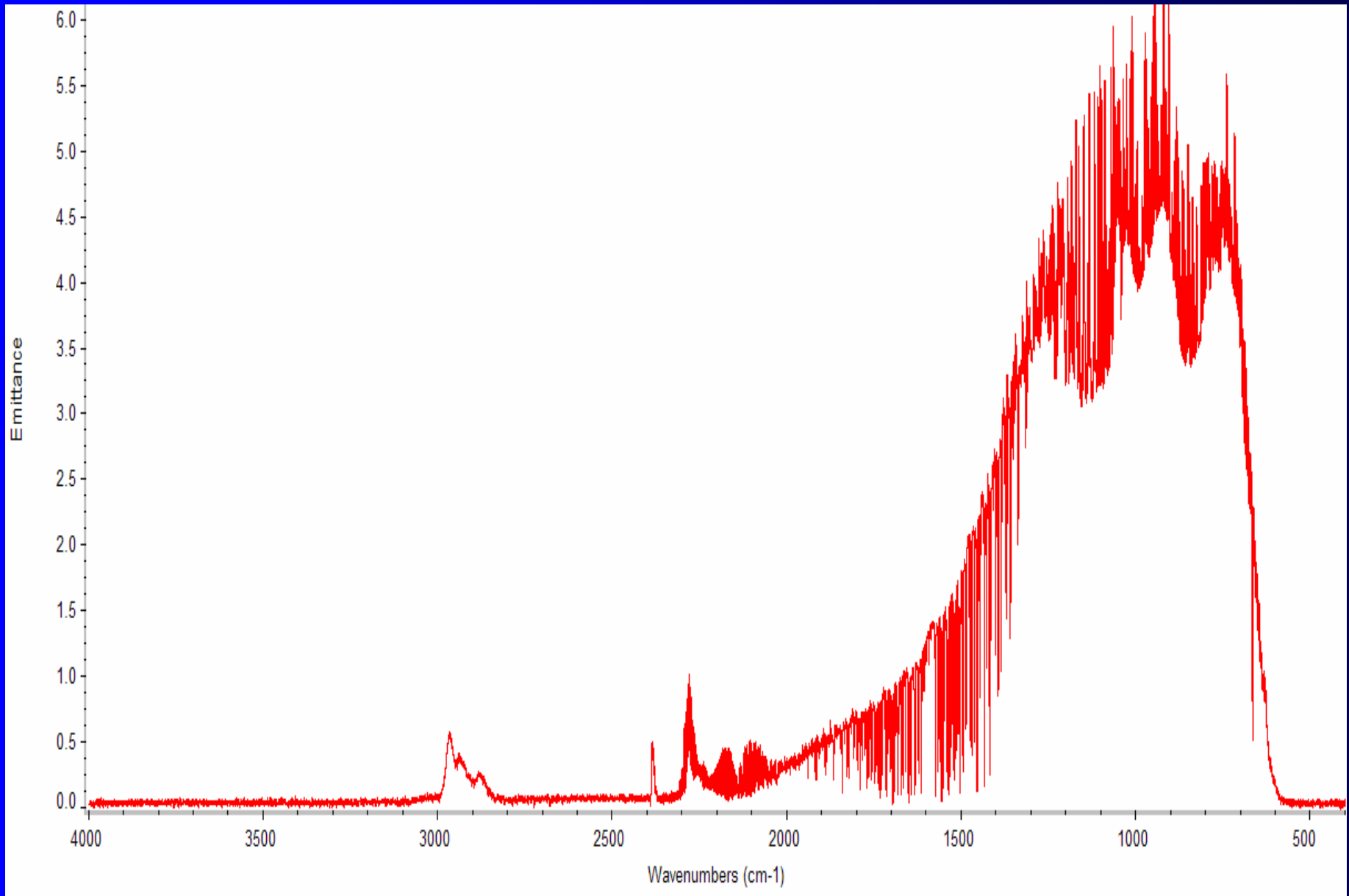
- The FTIR signal then reduces to:

$$R_{\text{obs}} = \{ (R_b - L_{\text{bb}}) * \tau_{\text{plume}} + L_{\text{bb}} \} * \tau_{\text{atm}}$$

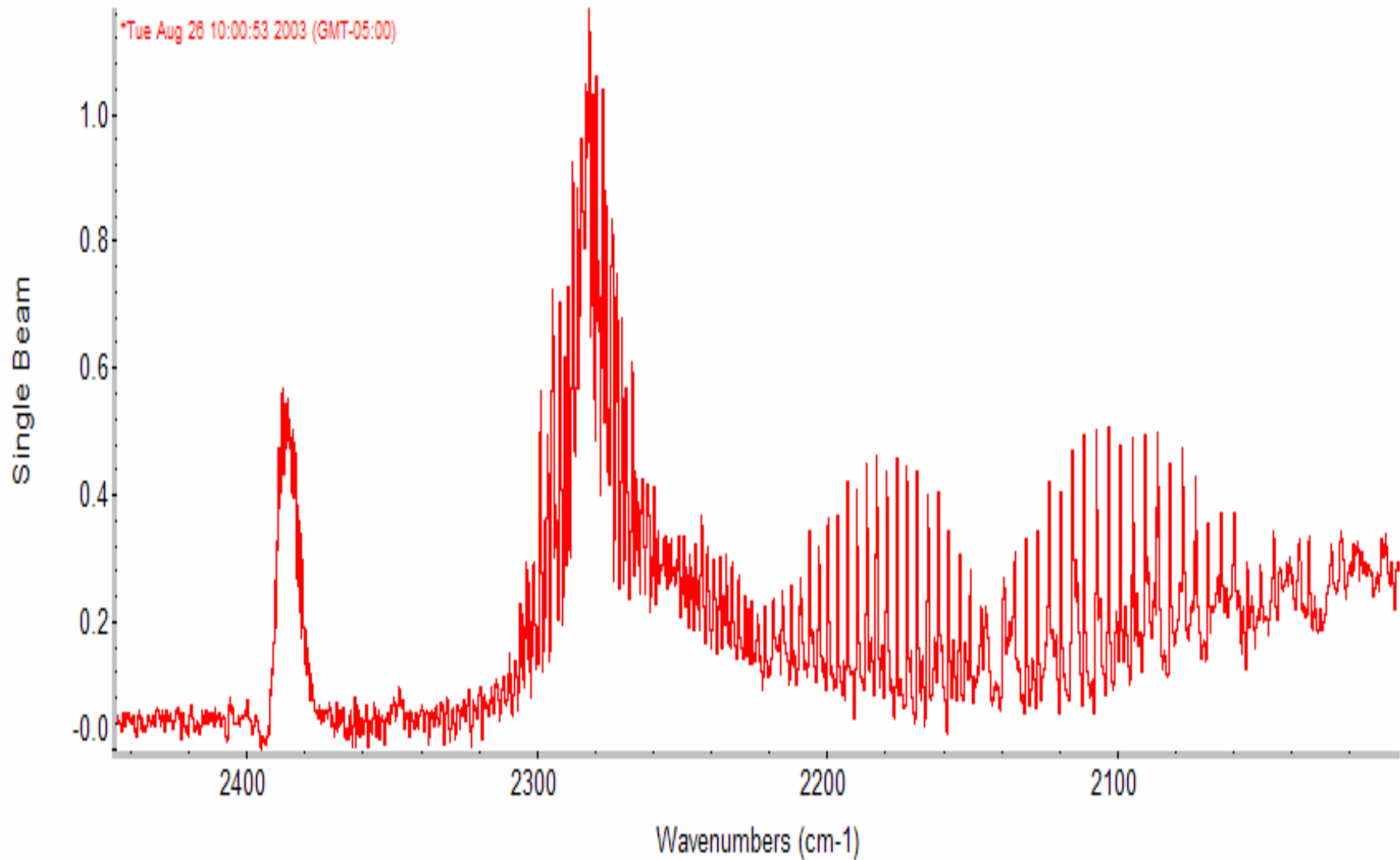
Where  $L_{\text{bb}}$  is the Black Body (Planck) function at the temperature of the plume

# Spectral Regions

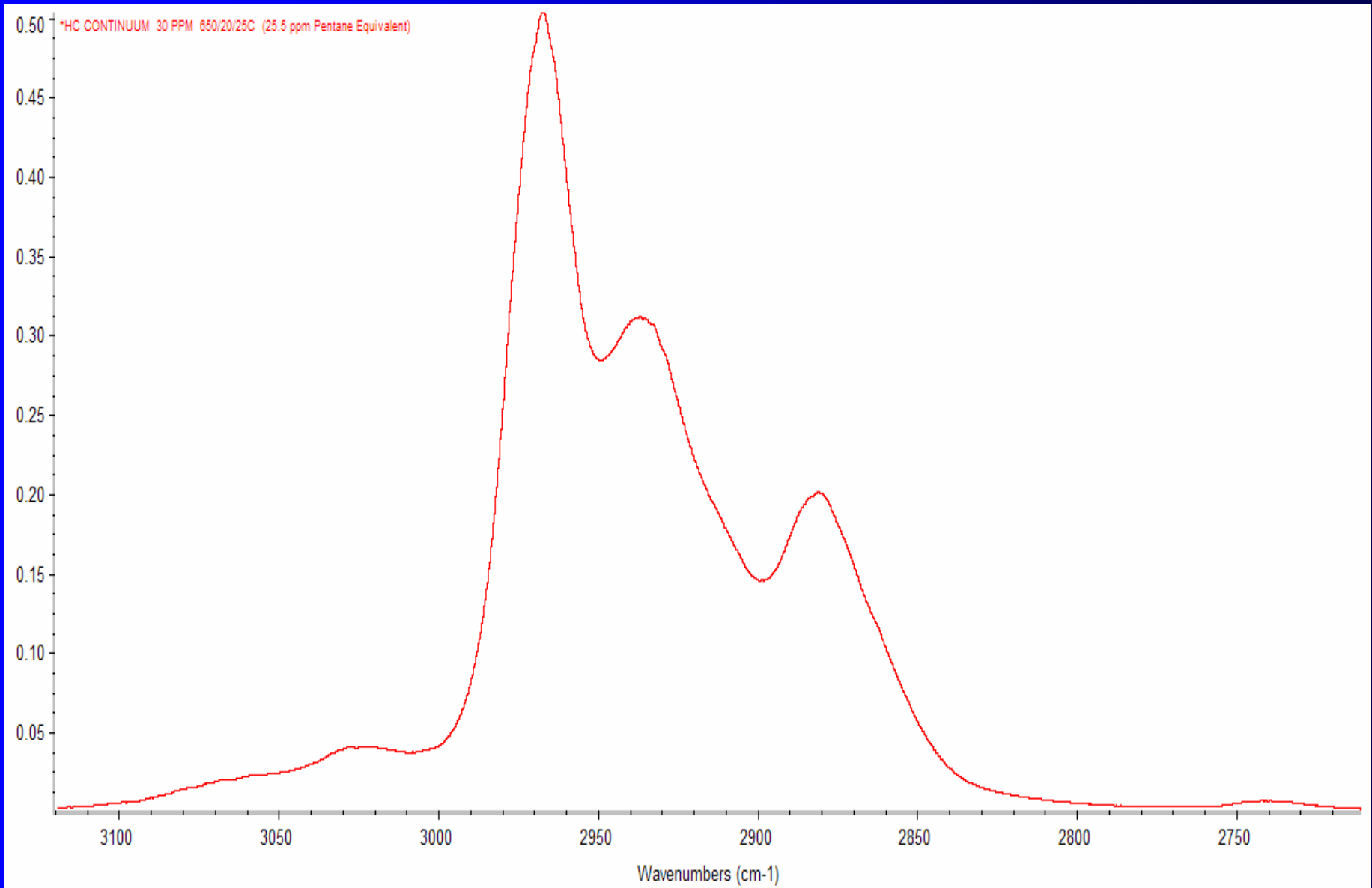
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# CO<sub>2</sub> and CO Emission Spectra



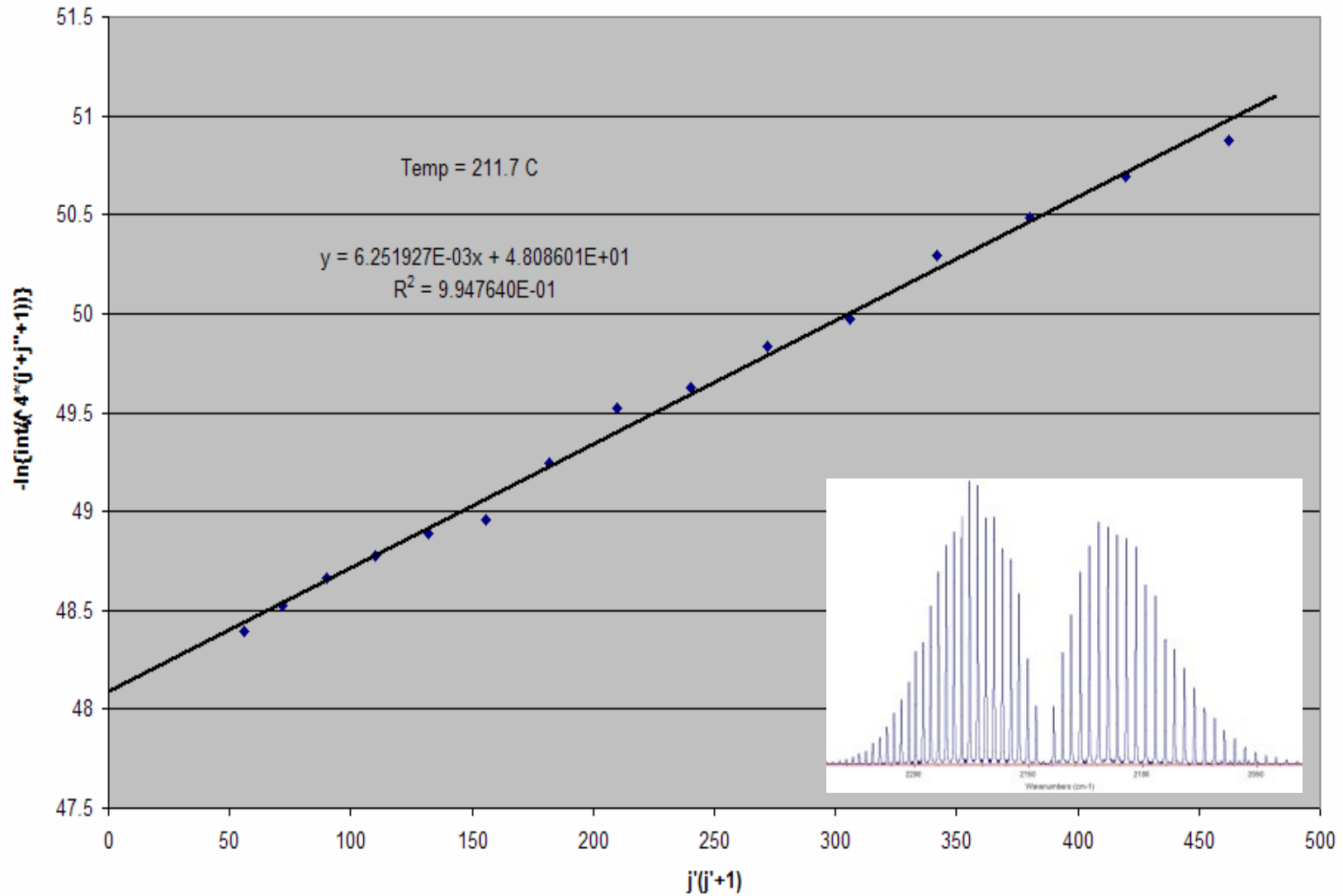
# “Total Hydrocarbon” Emission





# Temperature Determination

Temp Plot



# Flare Efficiency

---

- The efficiency of combustion is given by:

$$\frac{[CO_2]}{[CO] + [CO_2] + [THC] + Soot}$$

- CO, CO<sub>2</sub>, and CH<sub>4</sub> concentrations are easy to obtain.
- Total hydrocarbon can be assessed using the C-H stretch region, calibrating against a specific heavy organic or a mixture of organics.
- Speciation of non-methane organics is possible for lighter fractions (< C5) above a threshold concentration, all heavier compounds are part of the THC measurement

Examples of hardware

# Imacc Passive Radiometric-FTIR System

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# Passive FTIR At Plume Simulator

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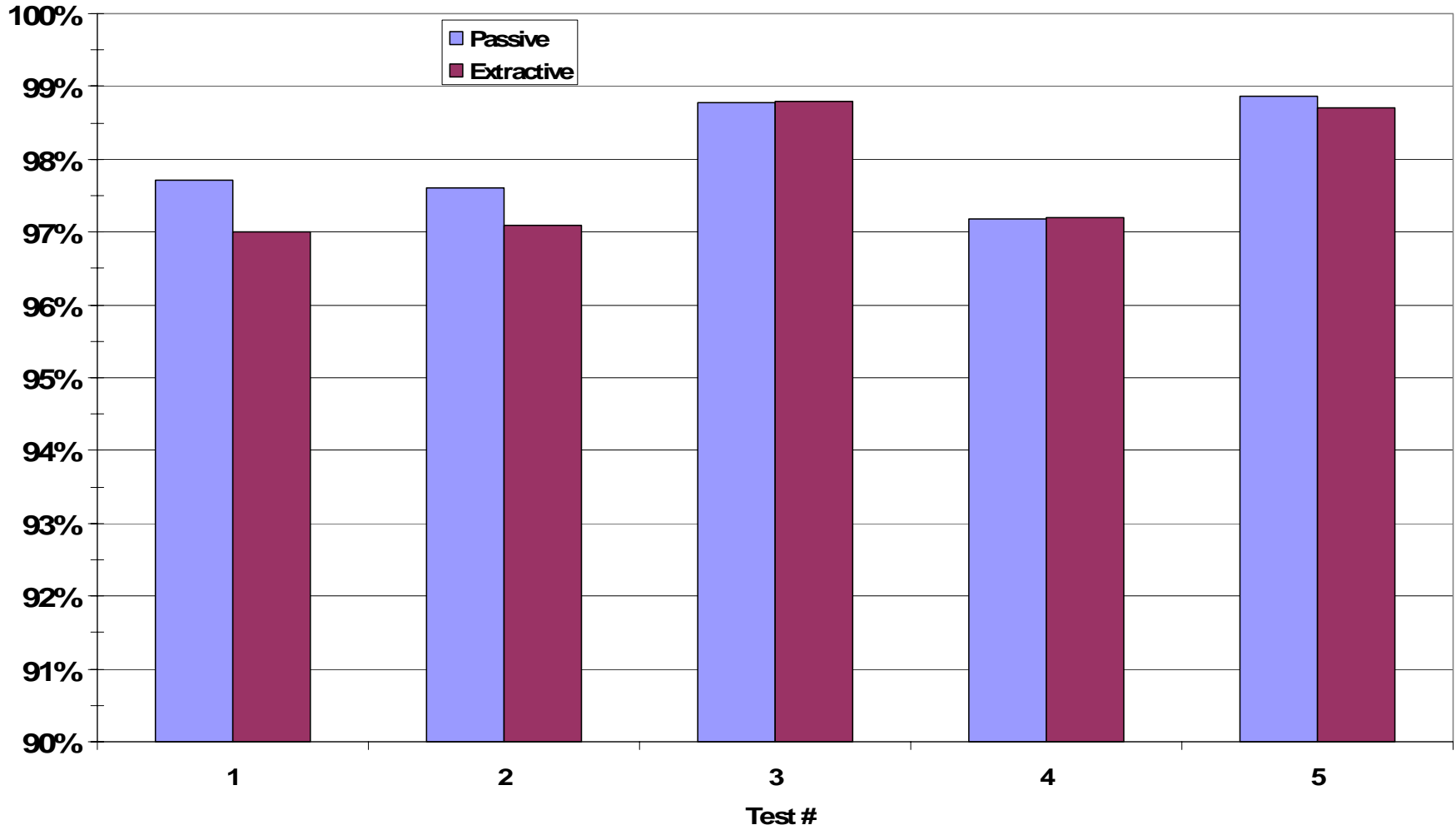
# Test Matrix for Plume Generator Tests

---

<b>Test #</b>	<b>Test Sequence Description</b>	<b>Target Temperature ( C )</b>	<b>Target Combustion Efficiency (%)</b>
1a, 1b	Low Efficiency / High Temp.	225	96.0
2a, 2b	Mid Efficiency / High Temp.	225	97.1
3a, 3b	High Efficiency / High Temp.	225	98.7
4a, 4b	Mid Efficiency / Low Temp.	150	97.1
5a, 5b	High Efficiency / Low Temp.	150	98.7

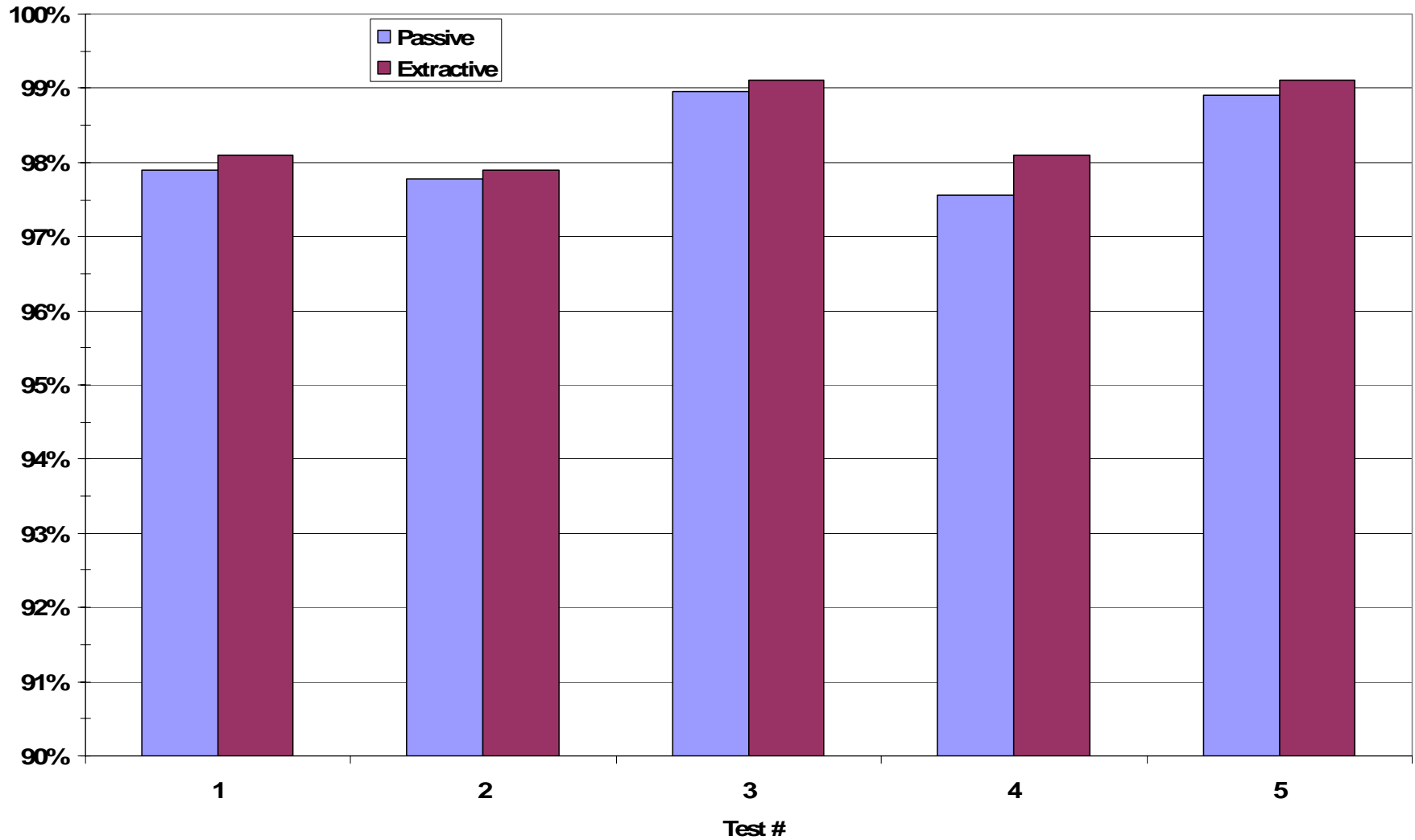
# Combustion Efficiency – All Gases

---



# Combustion Efficiency – NO Butane

---





# Passive FTIR At Flare Test

---



# Controlled Flare Test FTIR Data Summary

Data Averaging Period	Average Plume Temp. (°C)	Average Species Concentration (ppm-V)						Average Combustion Efficiency (%)
		CO	CO <sub>2</sub>	Butane	Ethylene	Propylene	Propane	
17:25:33 - 17:28:19	302	57	98,100	0.7	1.1	27	45	99.9 +/- 0.30
17:28:36 - 17:31:07	293	71	132,300	1.4	0.45	29	140	99.8 +/- 0.30
17:41:55 - 17:43:03	225	58	60,000	3.3	1.8	33	40	99.8 +/- 0.30
17:55:46 - 17:57:39	416	390	248,200	2.5	1.9	43	1255	99.5 +/- 0.30



*"That's all Folks!"*

# International Applications of OTM-10 in Chemical and Petroleum Industries

**Dr. Ram A. Hashmonay**  
**ARCADIS**  
**Research Triangle Park, NC**



Imagine the result

# USEPA OTM-10

<http://www.epa.gov/ttn/emc/tmethods.html>

FINAL ORS Protocol  
June 14, 2006

## Optical Remote Sensing for Emission Characterization from Non-point Sources

### 1.0 Scope and Application

1.1 *Introduction.* This protocol provides the user with methodologies for characterizing gaseous emissions from non-point pollutant sources. These methodologies use an open-path, Path-Integrated Optical Remote Sensing (PI-ORS) system in multiple beam configurations to directly identify "hot spots" and measure emission fluxes. Basic knowledge of a PI-ORS system and the ability to obtain quality path-integrated concentration (PIC) data is assumed. The user must be capable of using commercial software to utilize the procedures and algorithms explained in this protocol. The methodologies in this protocol have been well developed, evaluated, demonstrated, validated, and peer-reviewed.<sup>1-12</sup>

NOTE 1 — Any mention of a "PI-ORS system" in this protocol refers to the open-path PI-ORS instrument itself, as well as any associated components used, such as mirrors, scanners, and software.

This protocol does not discuss specific applications (e.g., hog farms, landfills), but provides general guidelines or procedures that can be applied. Detailed protocols for specific applications may be added at a future date.

1.1.1 *Scope.* This protocol currently describes three methodologies, each for a specific use. The Horizontal Radial Plume Mapping (HRPM) methodology was designed to map pollutant concentrations in a horizontal plane. The Vertical Radial Plume Mapping (VRPM) methodology was designed to measure mass flux of pollutants through a vertical plane, downwind from an emission source. The one-dimensional Radial Plume Mapping methodology (1D-RPM) was designed to profile pollutant concentrations along a line-of-sight (e.g., along an industrial site fence line). In future revisions to this protocol, additional PI-ORS emission monitoring methodologies (other than the methodologies described in this protocol) that address non-point sources can be added as validation data are generated.

1.1.2 *Choice of Instrumentation.* The choice of PI-ORS system to be used for the collection of measurement data (and subsequent calculation of PIC) is left to the discretion of the user, and should be dependent on the compounds of interest and the purpose of the study. The methodologies are independent of the particular PI-ORS system used to generate the PIC data. It is recommended for the HRPM, VRPM, and 1D-RPM methodologies that the typical expected concentration over the longer beams should be about 10 times the minimum detection limit of the instrument. When this is not the case, the user should replace nondetects with values of half the minimum detection limit (see Table A.3 in the Appendix A).

Address <http://www.epa.gov/ttn/emc/tmet> Go

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

## Technology Transfer Network Emission Measurement Center

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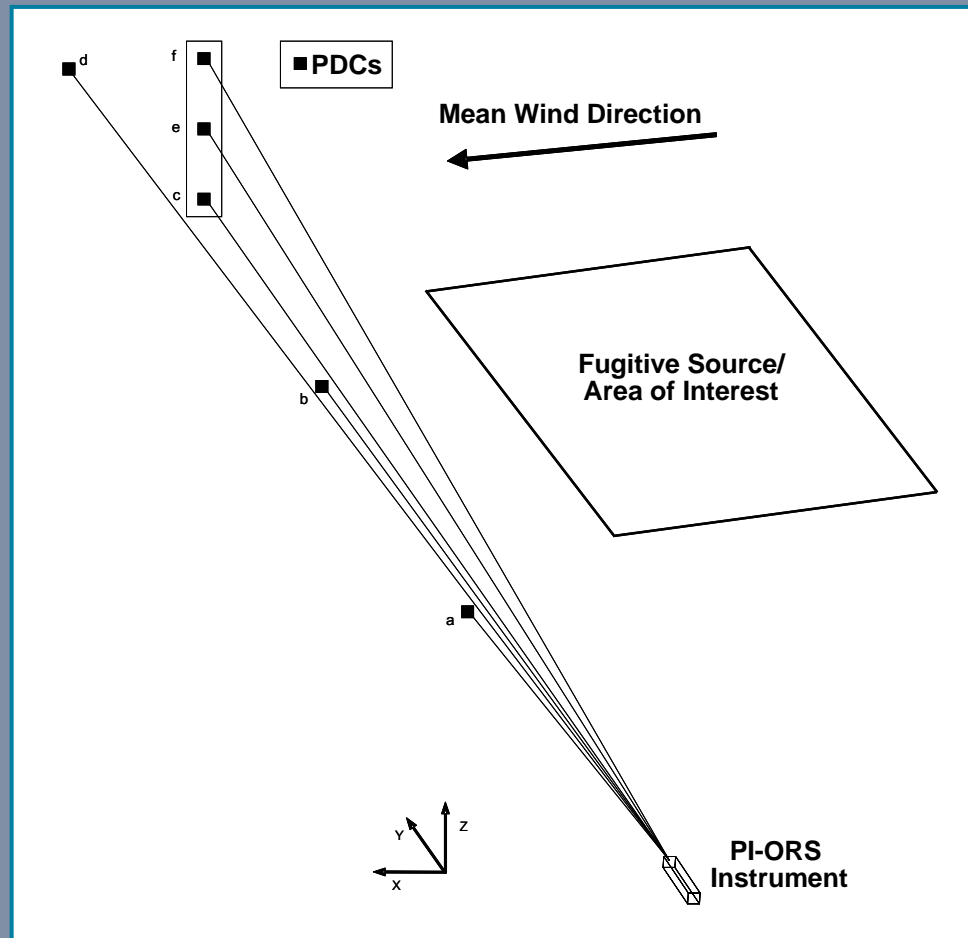
[EPA Home](#) > [Air & Radiation](#) > [TTNWeb - Technology Transfer Network](#) > [Emission Measurement Center](#)

### Test Methods

Test methods can be divided into several categories:

- [Category A: Methods Proposed or Promulgated in the FR](#)
- [Category B: Source Category Approved Alternative Methods](#)
- [Category C: Other Methods](#)
- [Category D: Historic Conditional Methods](#)

# VRPM to Measure Emissions Fluxes from Area or Fugitive Sources



# Current Applications

- U.S. EPA/Industry Landfill Studies
- U.S. EPA/Industry CAFO Studies
- U.S. EPA Superfund and Brownfield Sites
- FL DAQ and LDEQ: HF emissions from phosphate industries
- Petrochemical and Chemical Industry
- U.S. EPA Chlor-Alkali elemental mercury emissions
- U.S. EPA Gas Station Emissions
- USDA/AgriCanada
- World Bank GHG in Colombia

# Refinery in Israel





# Fenceline VRPM



# List of Compounds Detected

Acetylene

MTBE

Benzene

2-Methyl 1-Butene

n-Butane

Nitrous Oxide

Ethylene

n-Octane

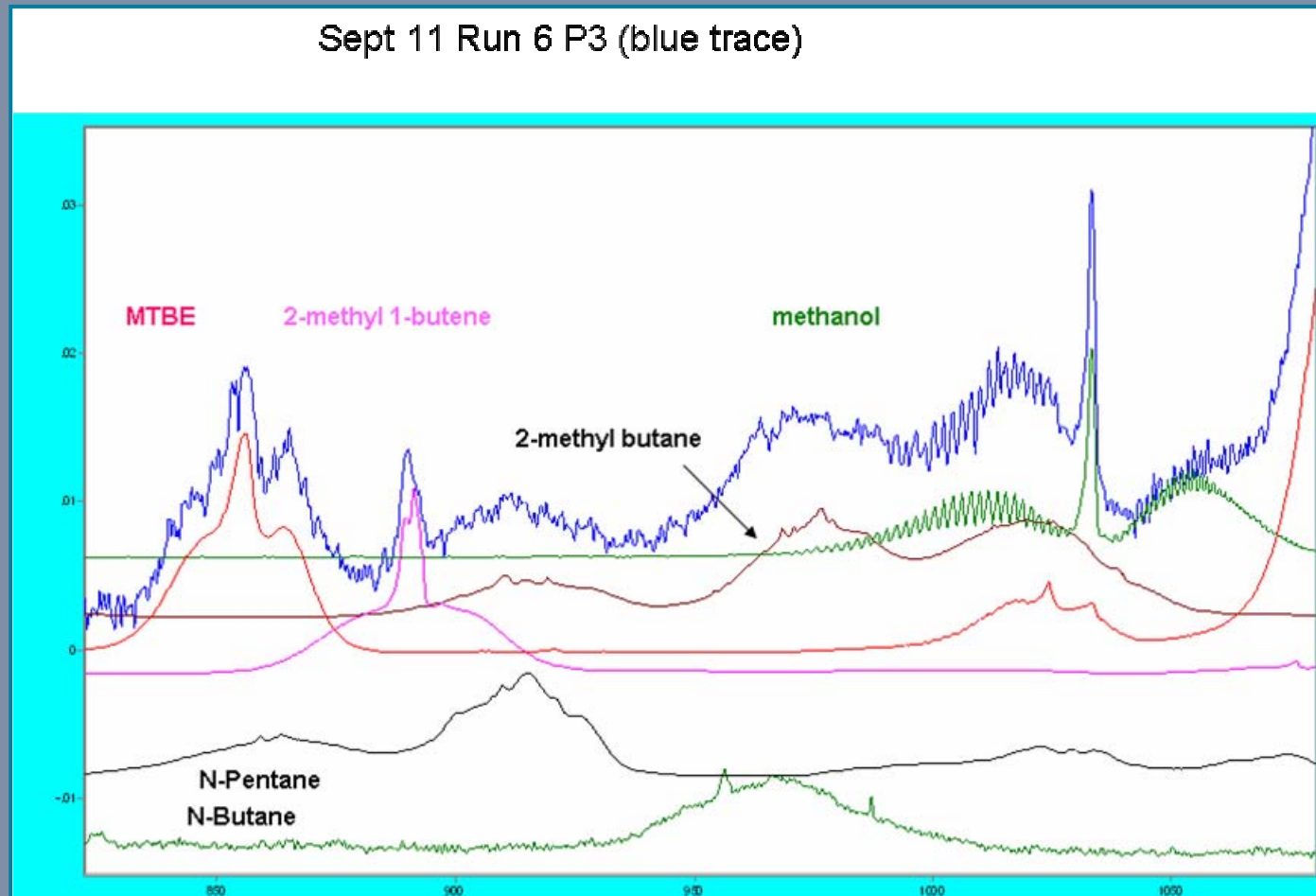
Methane

Toluene

Methanol

Propylene

# Fingerprint Spectrum in Refinery



# Spectral Validation of DIAL

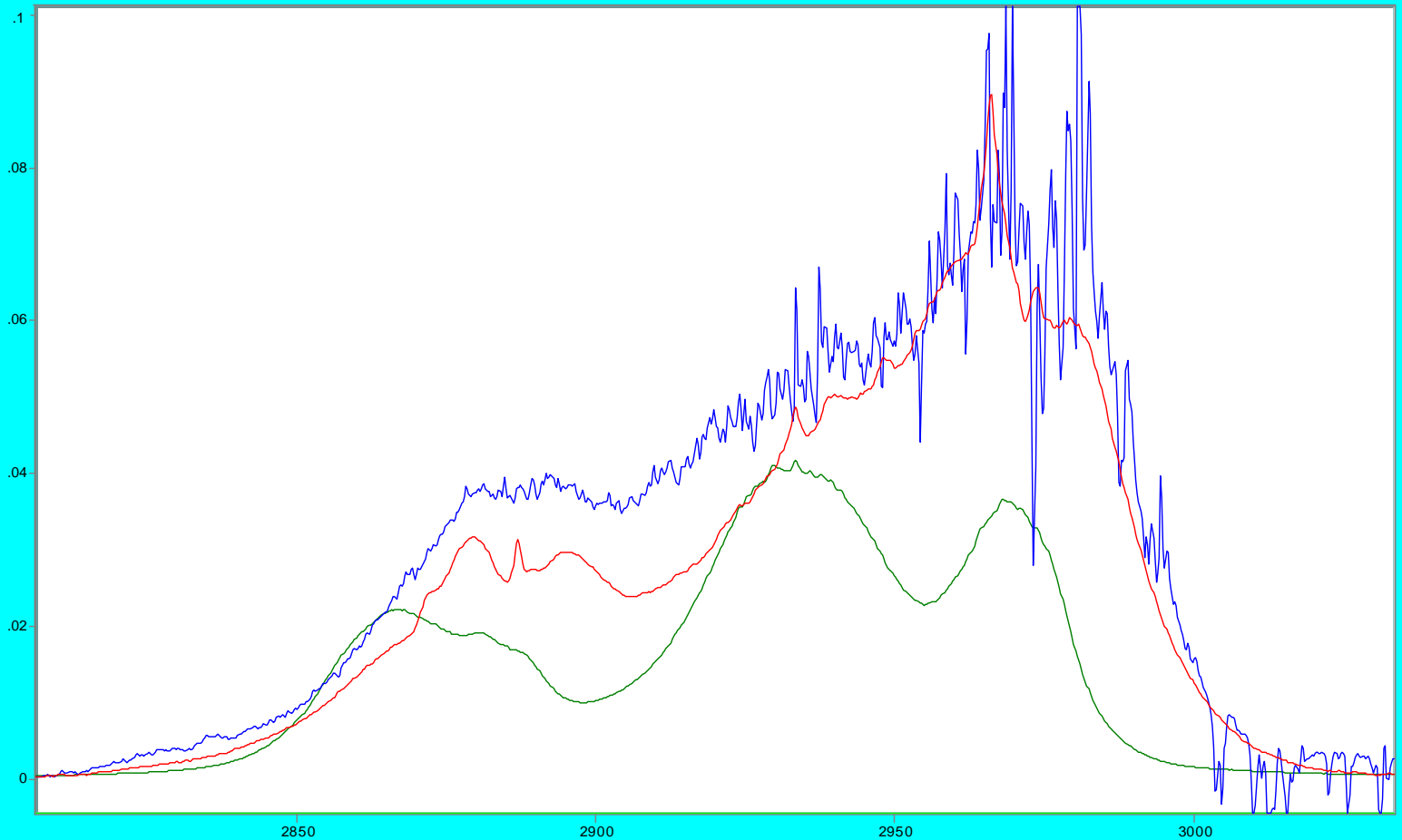
- Magnitude of the DIAL response (proportional to volumetric concentration) is being confirmed by OP-FTIR in the IR and UV-DOAS in the UV
- Real-time determination of the typical number of carbons (critical for accurate determination of mass concentration determination)
- See additional VOCs such as propylene, acetylene, ethylene, methanol, MTBE

# VOC Measurement in the North Direction

Blue: Run 5 M-3 F14

Red: n-Butane

Green: n-Octane

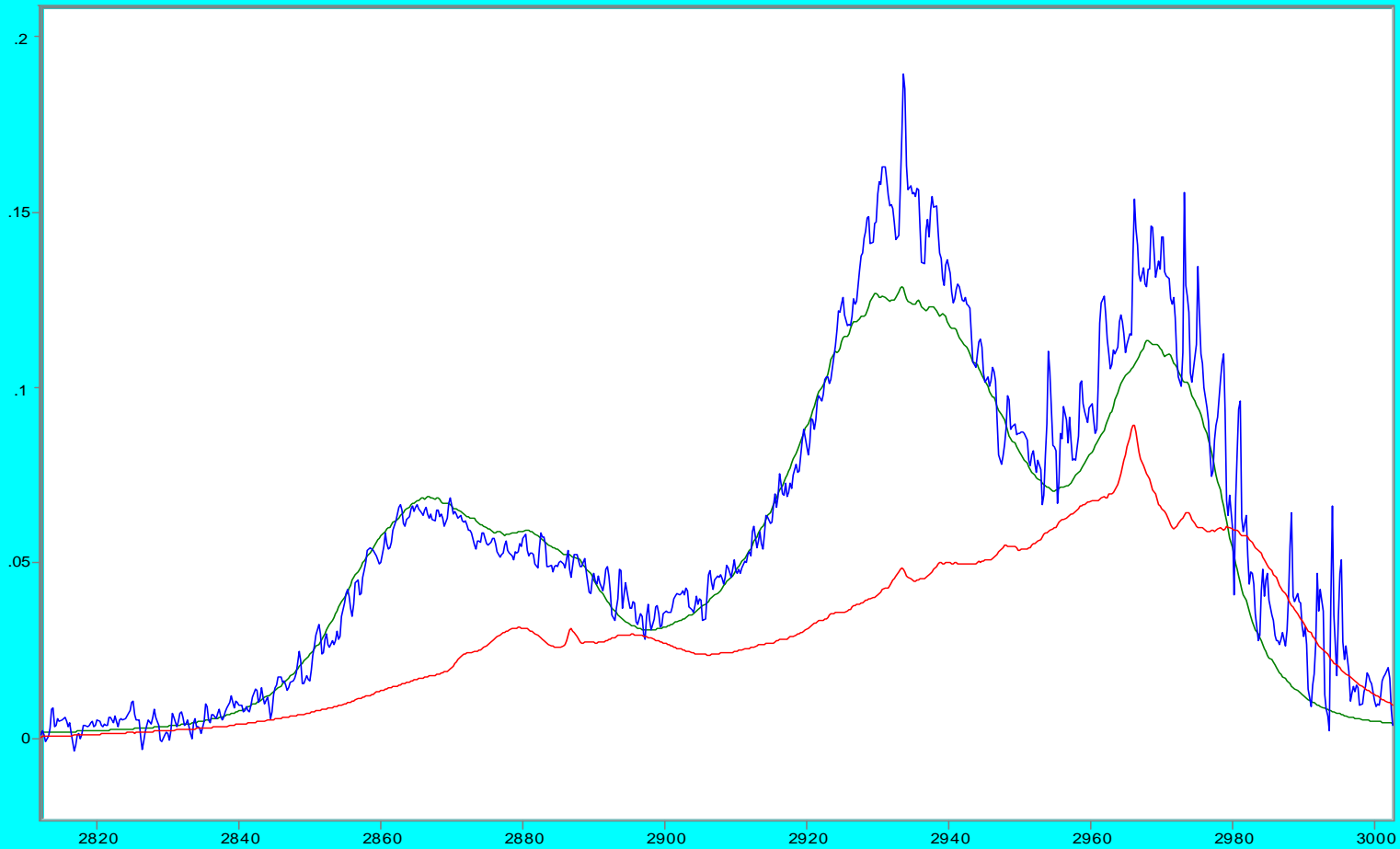


# VOC Measurement in the South Direction

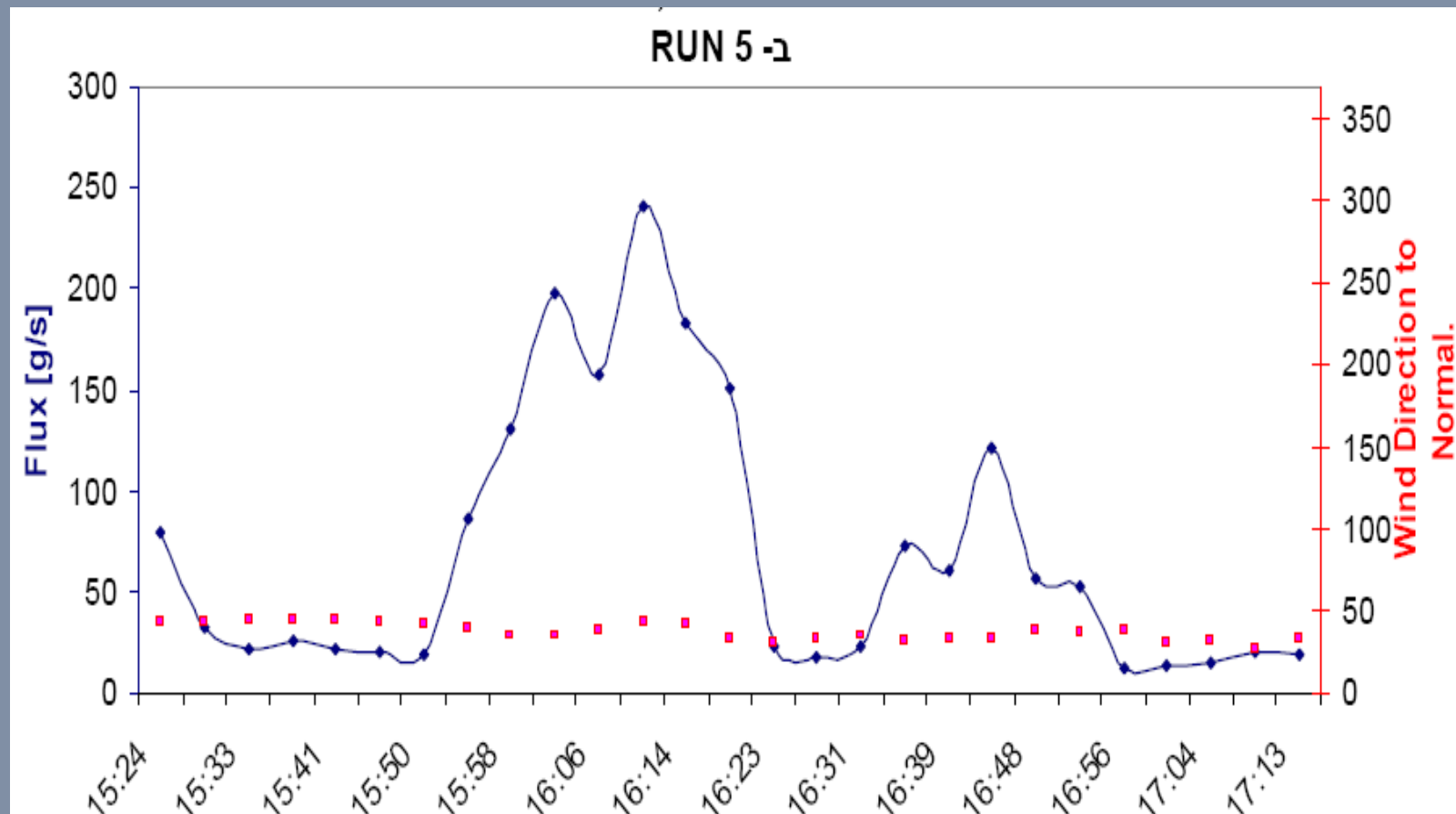
Blue: Run 5 M-1 F14

Red: n-Butane

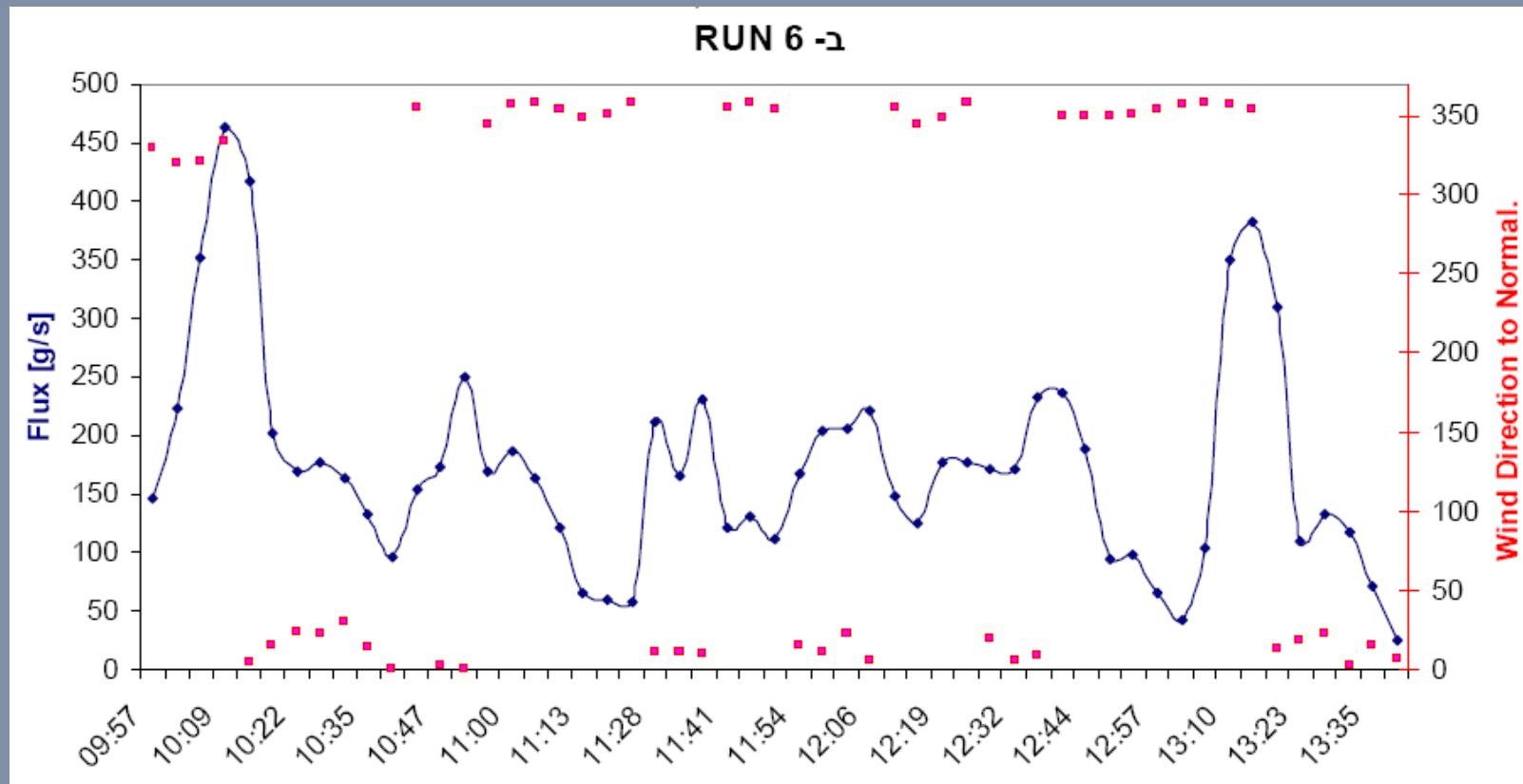
Green: n-Octane



# VRPM Time Series Run 5



# VRPM Time Series Run 6

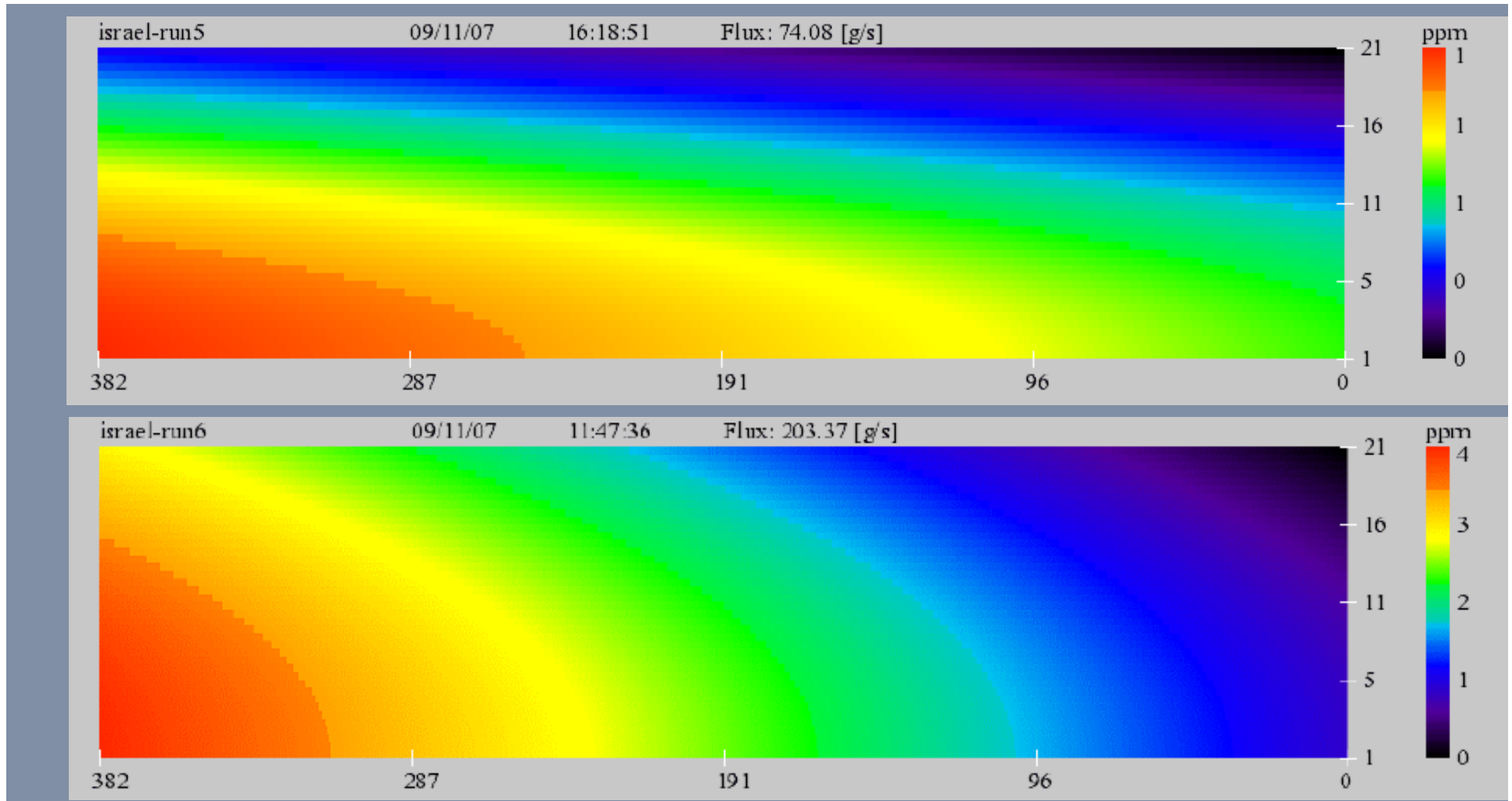




# Average Plume Map

74 g/s = 266 kg/hr

203 g/s = 731 kg/hr



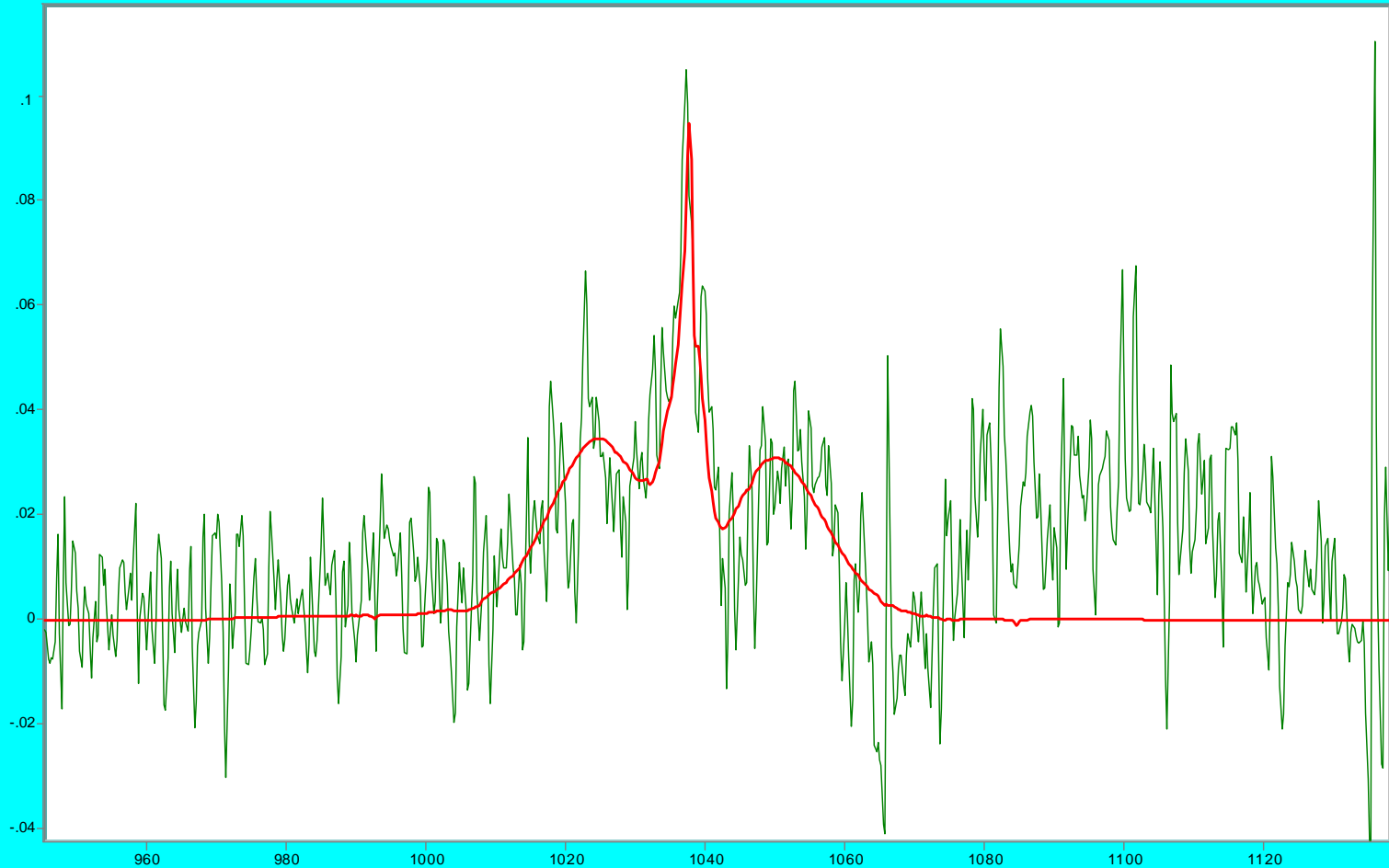
# Alberta Study

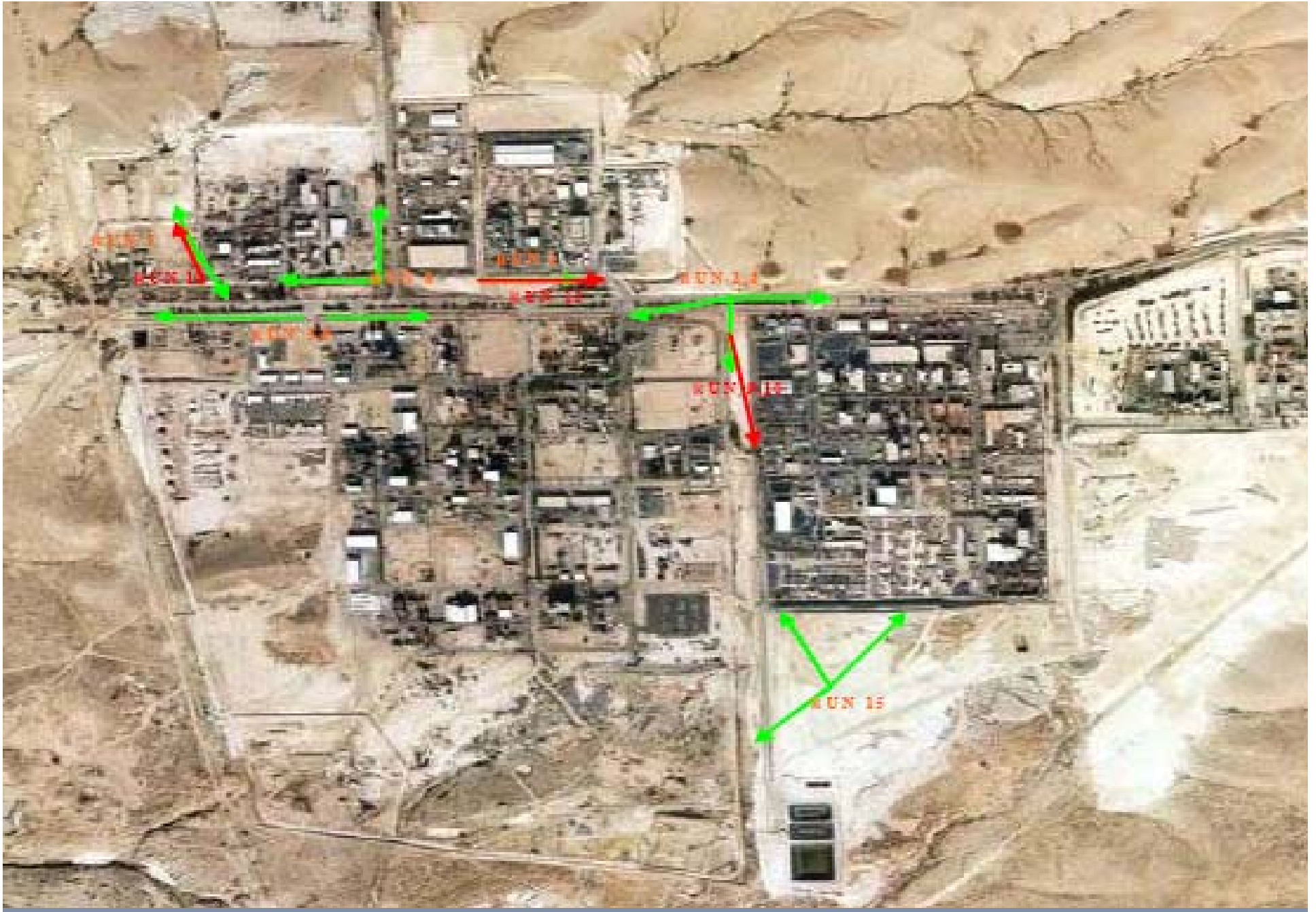
Area	C <sub>2+</sub> Hydrocarbon Emissions (kg/h)	% of Total Site Emissions
Coker and Vacuum Unit	211	17.1
New Process Area	68.3	5.5
Old Process Area North	105	8.5
Old Process Area South	56.8	4.6
Cooling Towers	164	13.3
Tanks- Crude Feed	141	11.4
Tanks- Intermediate Product	68.7	5.6
Tanks- Final Product	277	22.4
New Tank Farm	137	11.1
Bullets and Spheres	7.4	0.6
<b>Site Total</b>	<b>1237</b>	

Green:: Run 5 & Run 6

Red: Benzene Reference

**Benzene Conc. =  $112 \pm 12$  ppb**  
**Estimated Flux ~ 7 g/s ~ 30kg/hr**  
**Alberta Study ~ 3 kg/hr**



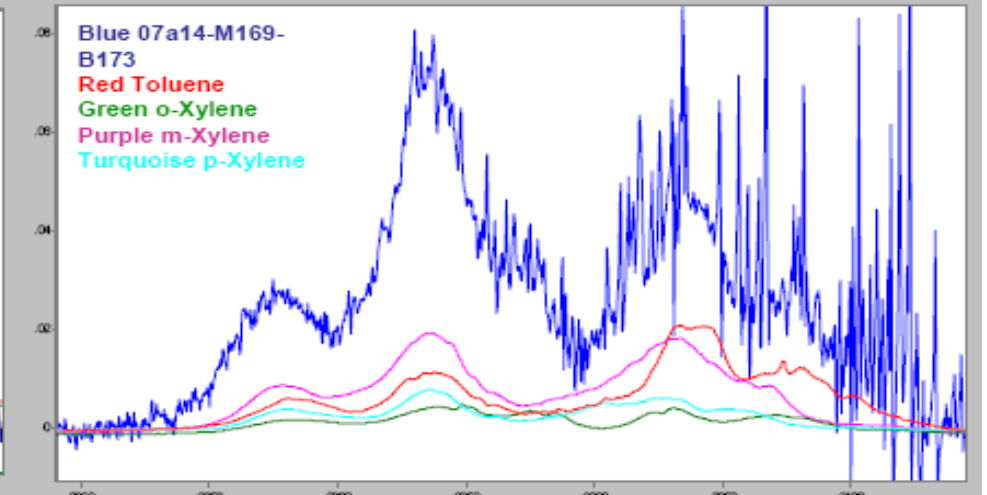
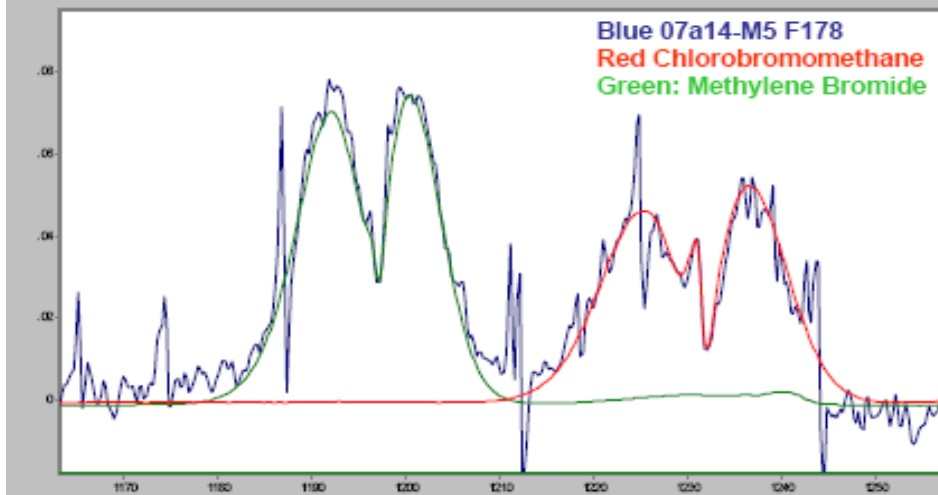
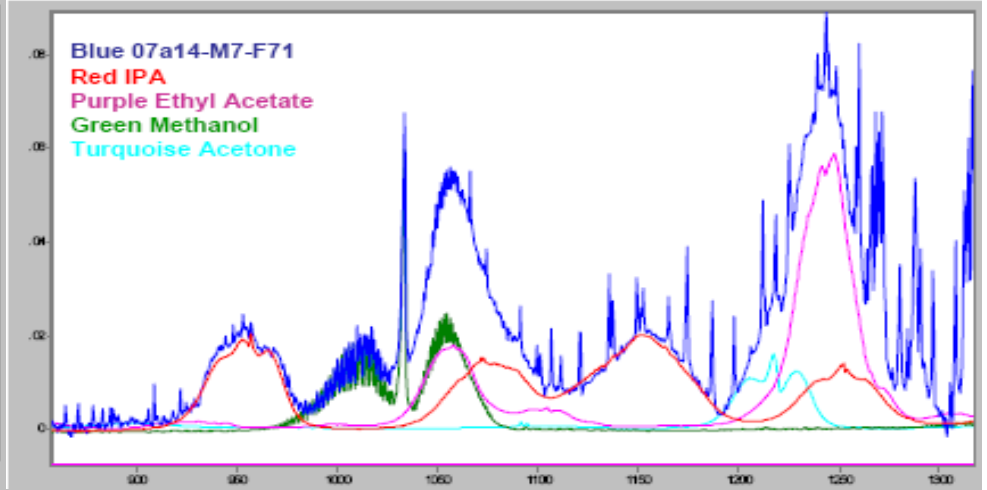
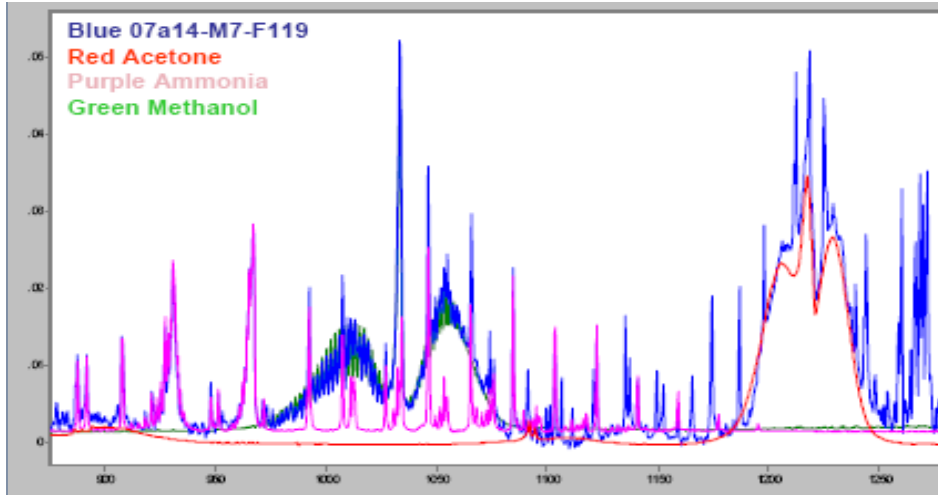


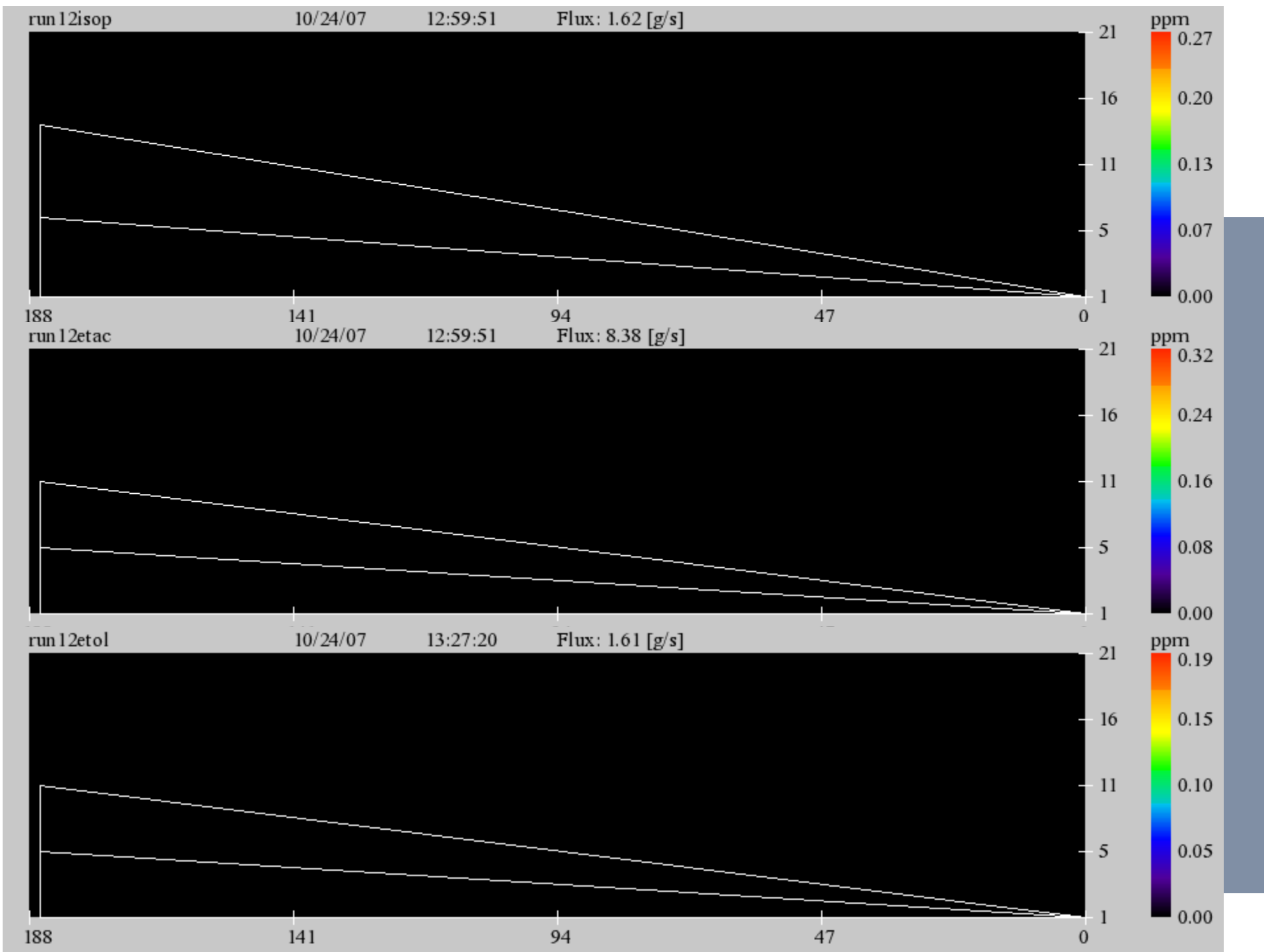


# List of Compounds Detected

Acetone	Dibromomethane	Methane
Ammonia	Dichloromethane	Methanol
Benzene	Dimethyl Amine	MIBK
Bromochloromethane	Dimethyl Carbonate	m-Xylene
Bromoform	Ethanol	Nitrous Oxide
Bromomethane	Ethyl acetate	o-Xylene
Carbon Tetrachloride	Formaldehyde	p-Xylene
Carbonyl Sulfide	Hydrogen Bromide	Toluene
Chlorobenzene	Hydrogen Chloride	Trichloroethene
Chlorodifluoromethane	iso-Propanol	

# Spectral Validation

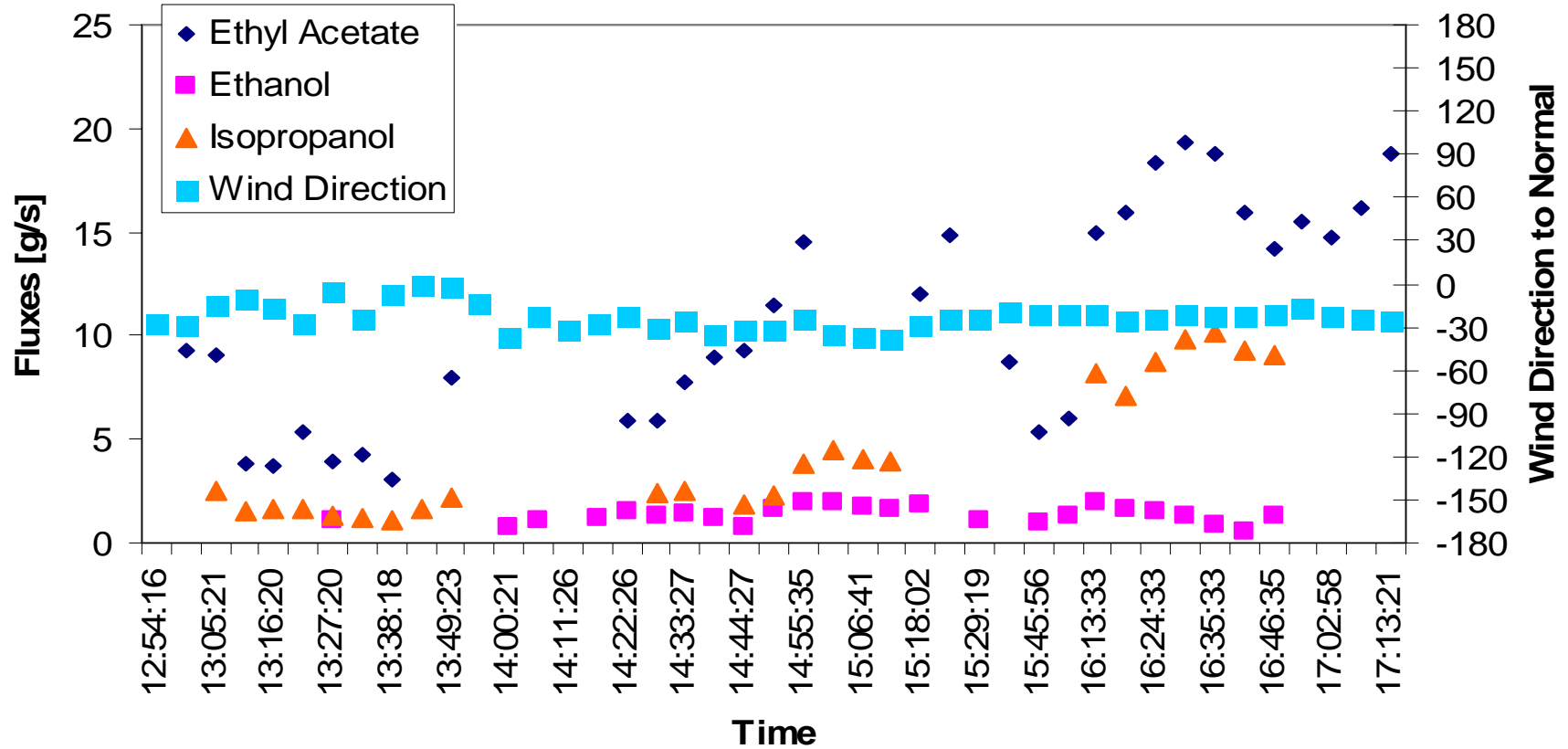




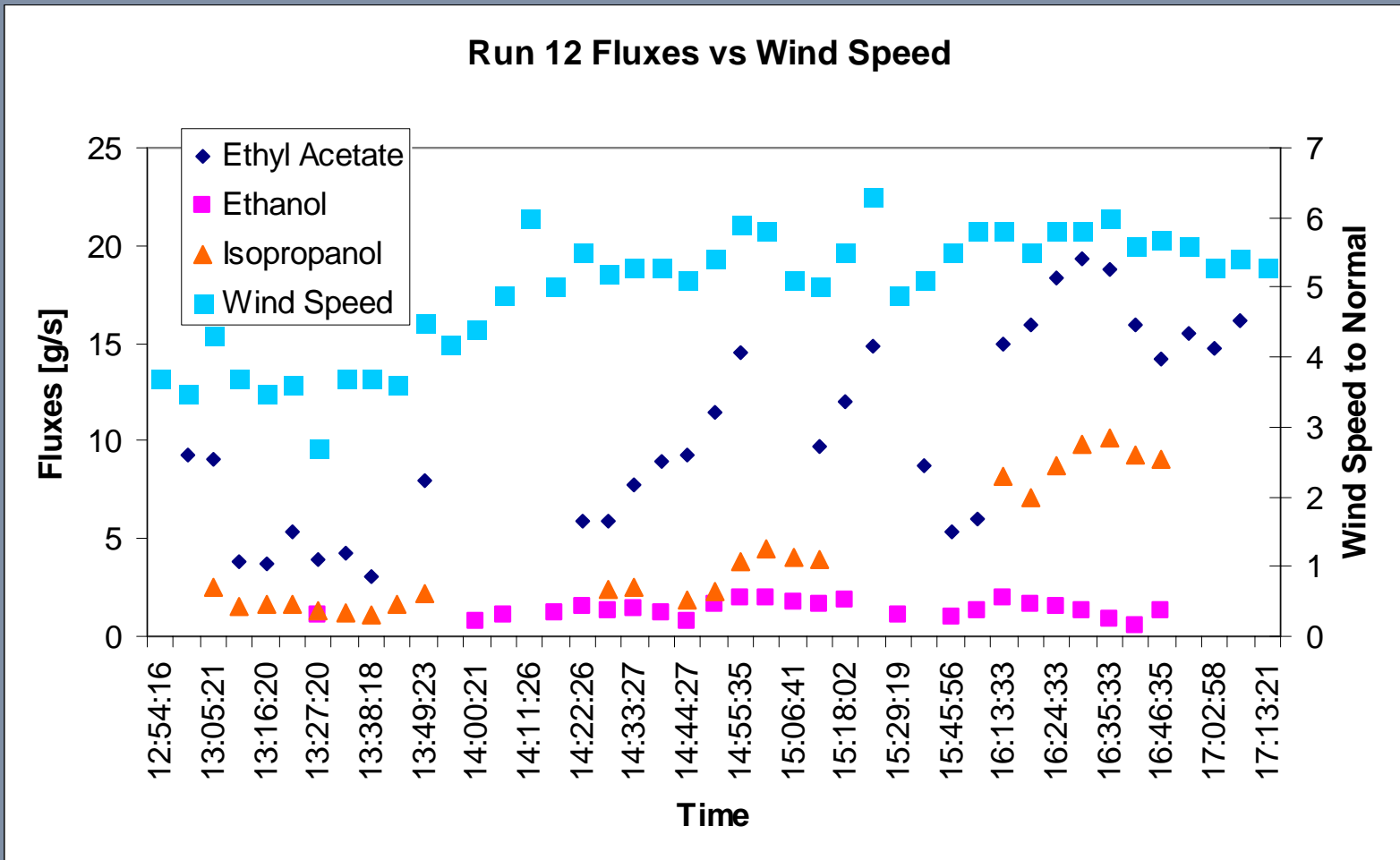


# VRPM Time Series Run 6

## Run 12 Fluxes vs Wind Direction



# VRPM Time Series with Windspeed

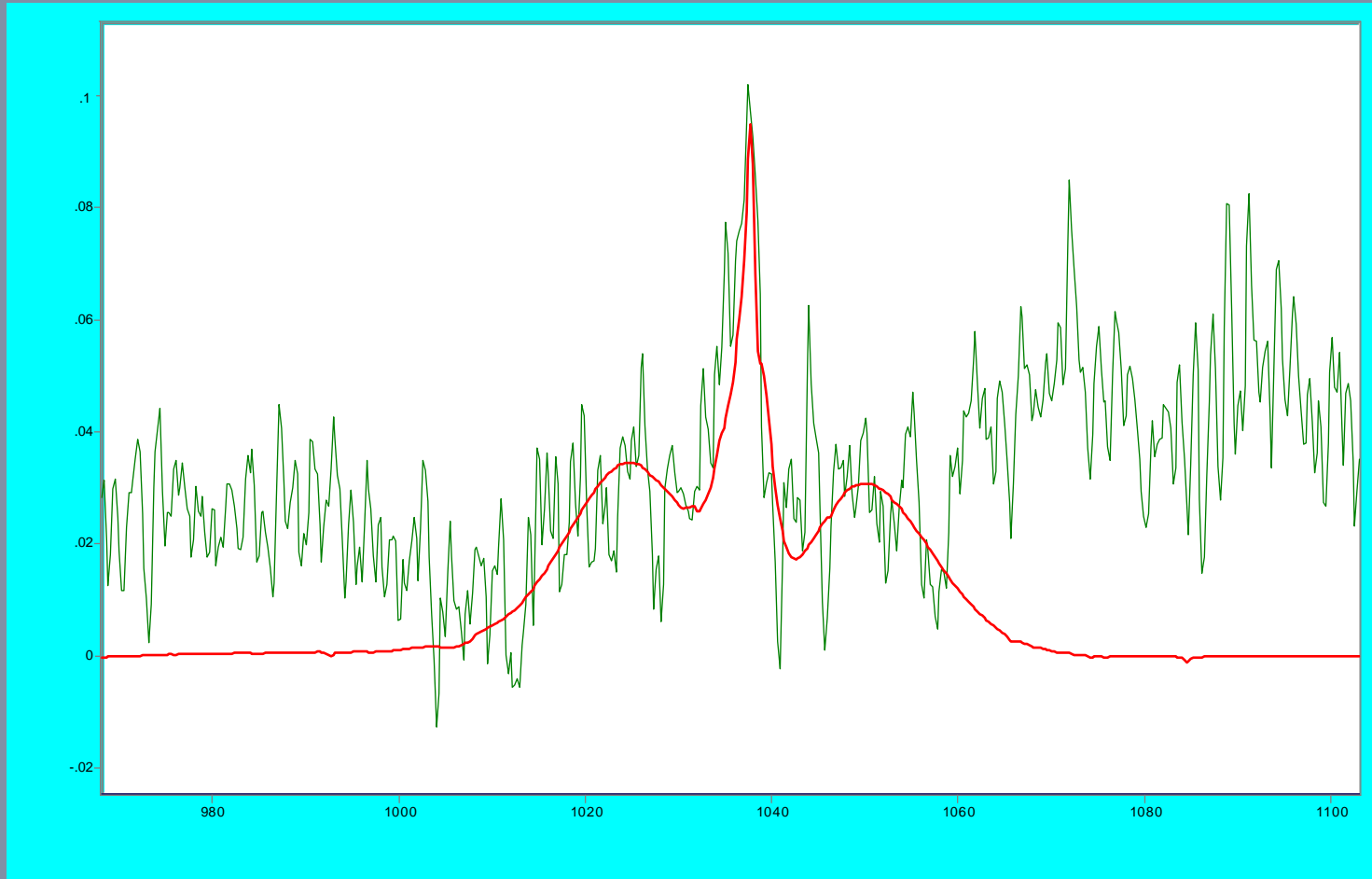


**Green: Ramat Run7**

**Red Trace: Benzene Reference**

**Benzene =  $121 \pm 23$  ppb**

**Path = 144m r.t.**



# Summary

- Smaller scale close to the ground emissions
- Some ORS provide good speciation and spectral evidence
- For each application different approach
- Industrial long term applications are in focus for the near future

Imagine the result



ITT

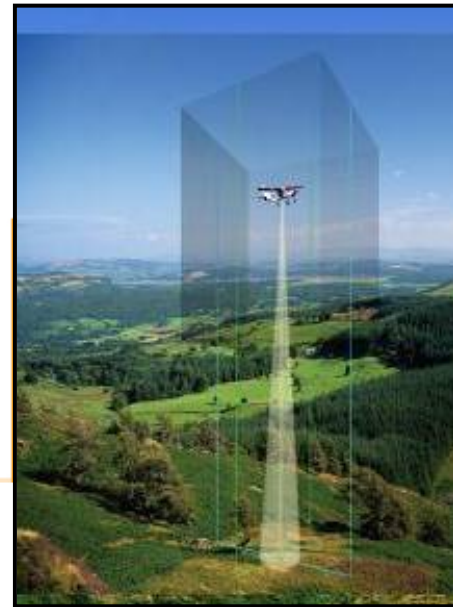
# Hazardous Liquid Airborne Lidar Observation Study (HALOS)

April, 2008

Steven Stearns

Daniel Brake

ITT Space Systems Division



*Engineered for life*

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# Airborne DIAL Leak Surveys And Environmental Monitoring

- Non-intrusive remote surveys.
- Differential Absorption LIDAR (DIAL) laser technology provides accurate leak detection and quantification.
- Captures survey-grade aerial mapping imagery of rights-of-way and surrounding areas.
- Captures color digital geospatial patrol video of rights-of-way and surrounding areas.
- Guaranteed survey coverage and results.



# ITT's Airborne Natural Gas Emission Lidar (ANGEL) Service



DIAL  
Sensor

Digital  
Video  
Camera

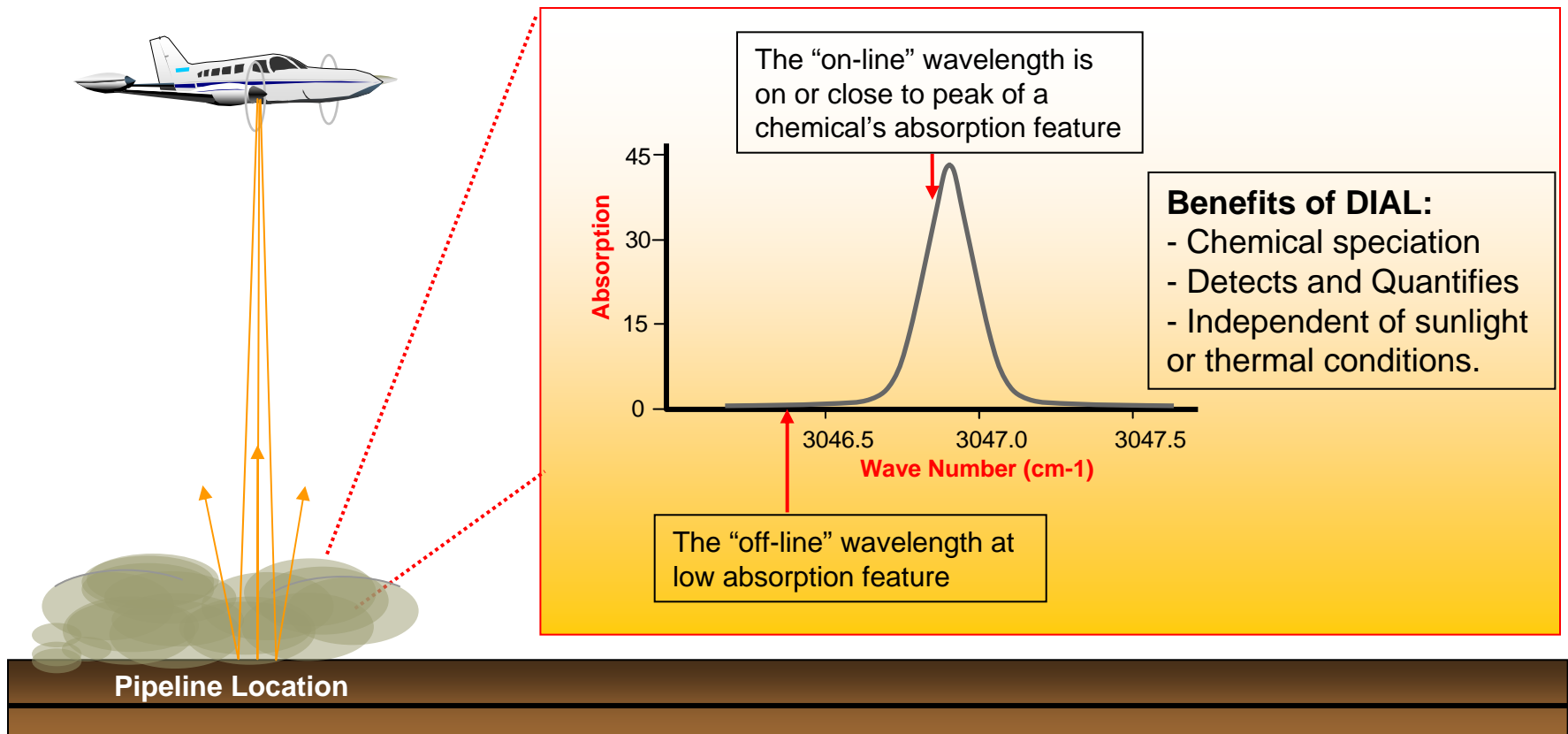


High  
Resolution  
Mapping  
Camera



# Gas Detection and Quantification Technology Behind the ANGEL Service

Differential Absorption Lidar (DIAL) is a pulsed laser technique that measures the difference in energy absorption between two specified wavelengths.



# Mapping Imagery

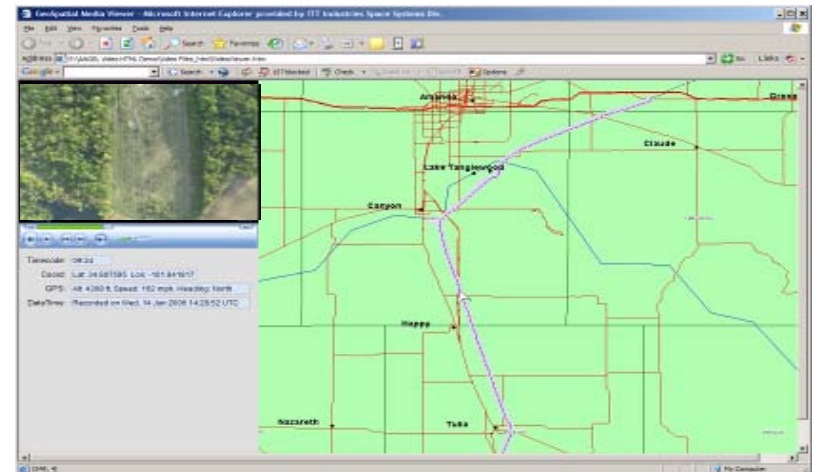
- Shows the exact location of the detected leak.
- Provides current, high-resolution imagery of your rights-of-way and surrounding areas.
- Seamlessly integrates with your enterprise geographical information system (GIS).
- Supports alignment sheets, HCA identification, threat identification, site permitting, engineering analysis, environmental studies, and emergency planning.



Mapping Imagery Provides One-Foot Ground Resolution

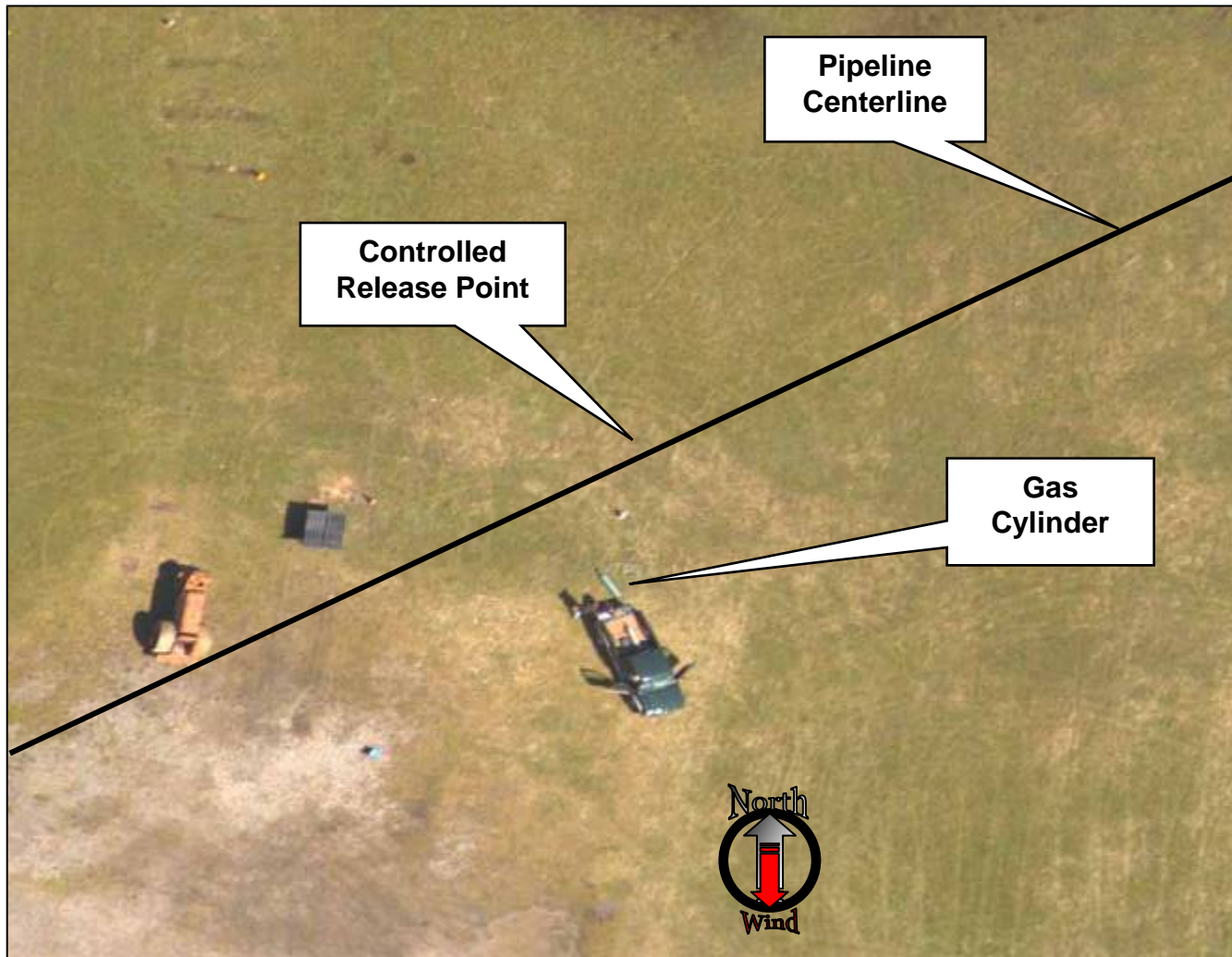
# Geospatial Patrol Video

- Allows you to easily patrol any pipeline segment from your desktop computer.
- Encodes video data with GPS information, so precise locations can be identified.
- Play, pause, fast forward, rewind, and even print video frames from digital files.
- Provides permanent record of aerial patrolling, easement conditions, encroachment monitoring, intrusion detection, and problem areas.

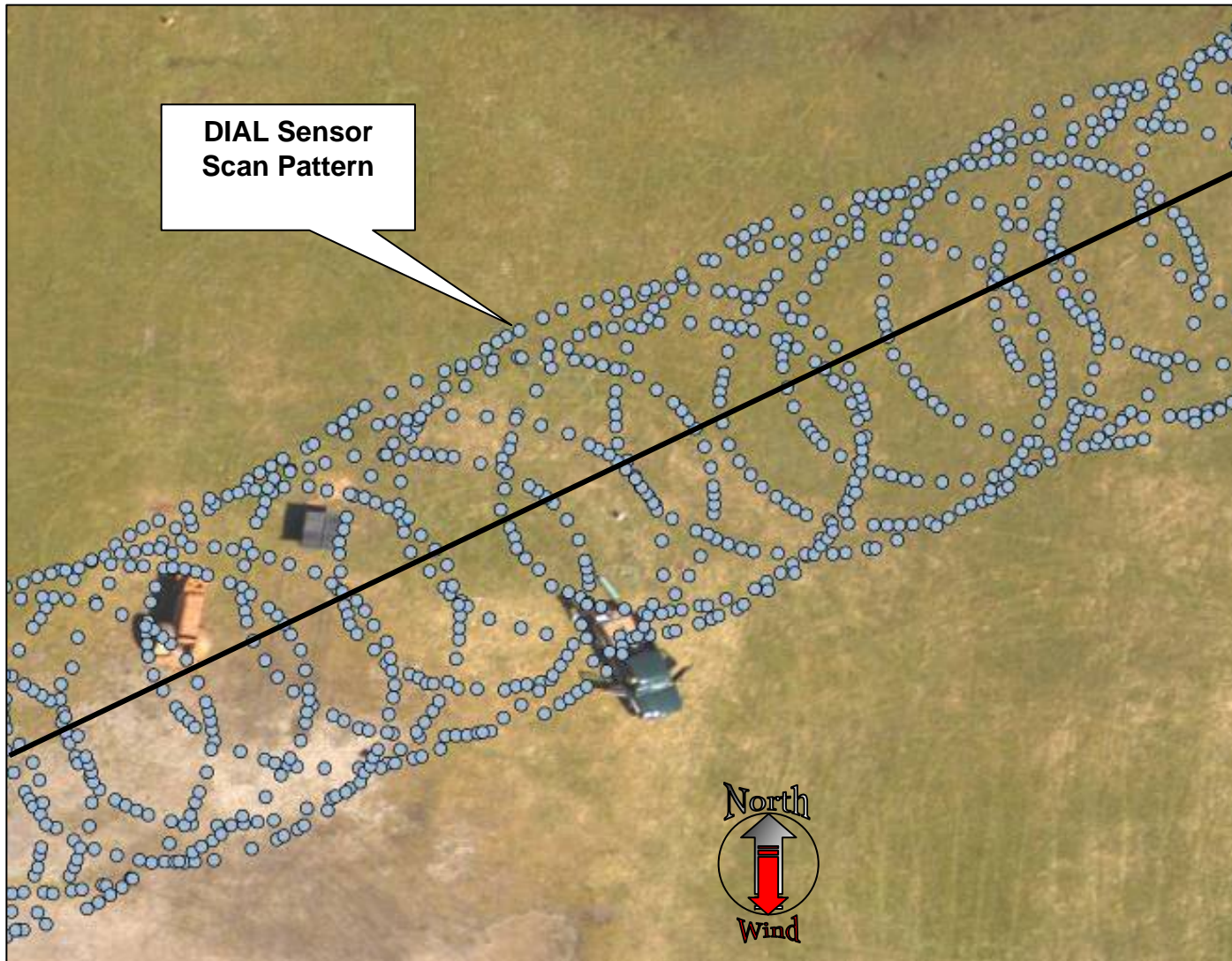


Integrated Digital Video with Electronic Maps

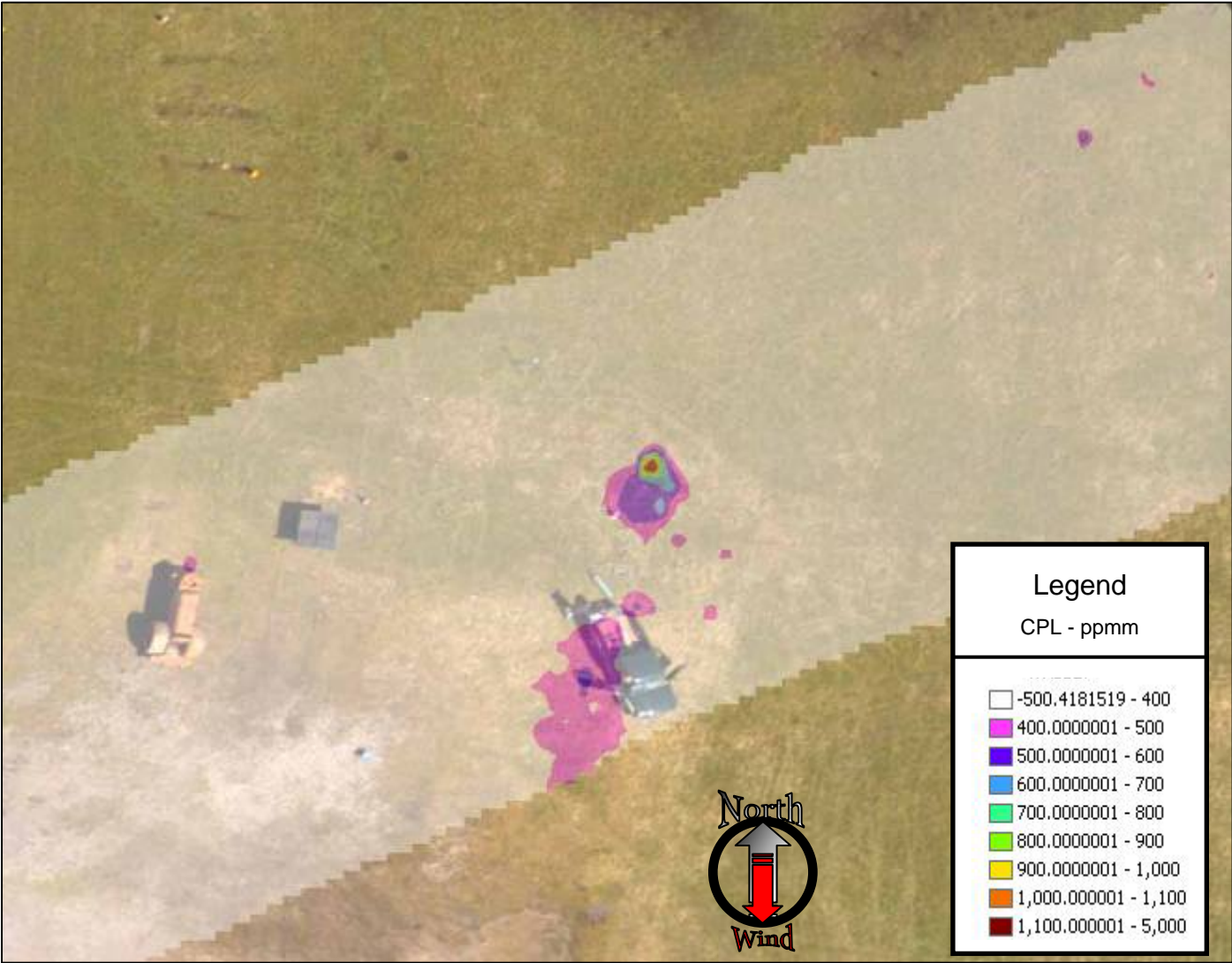
# Field Collection Site Geneseo, NY April 2007



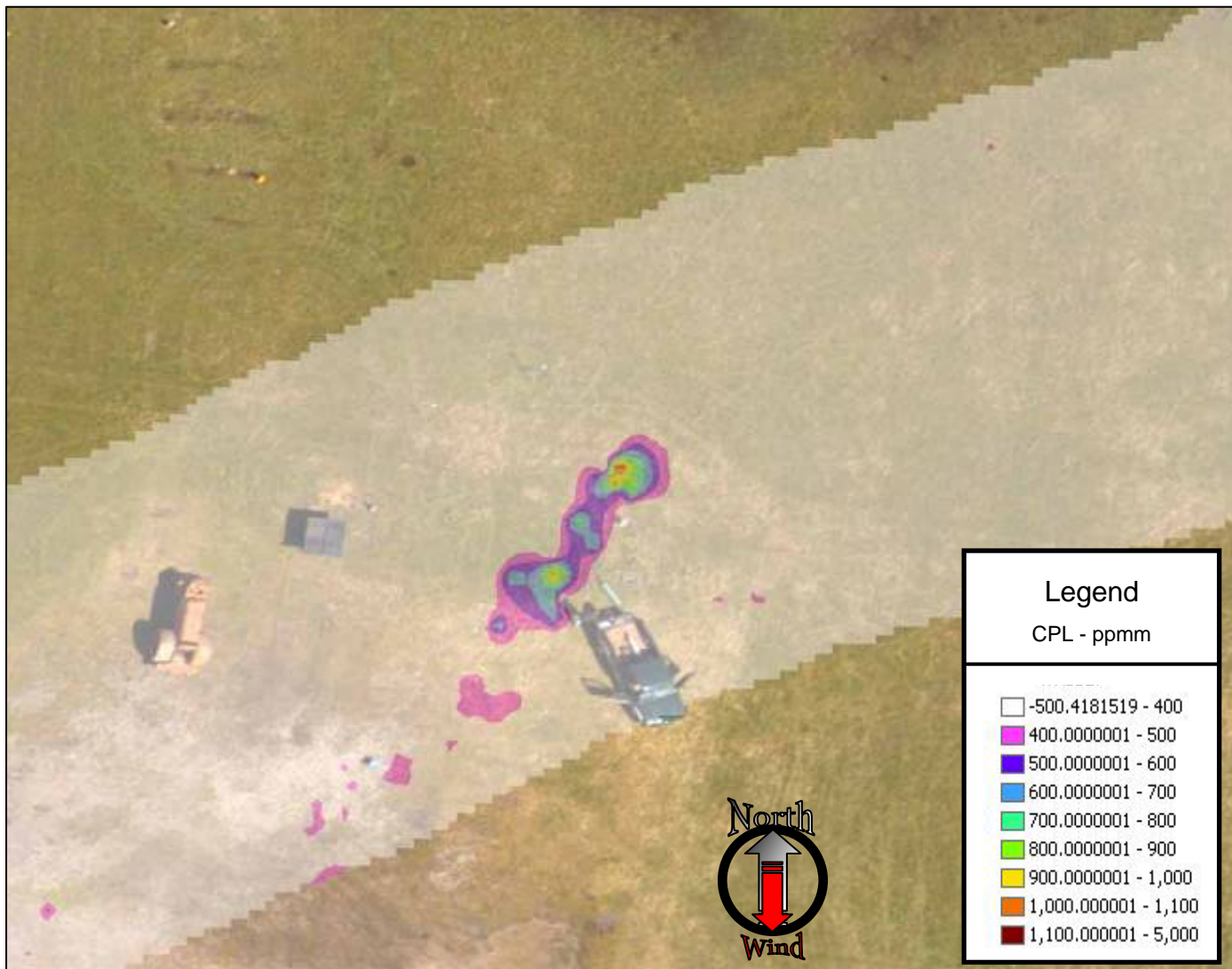
# Dial Scan Pattern Over Background



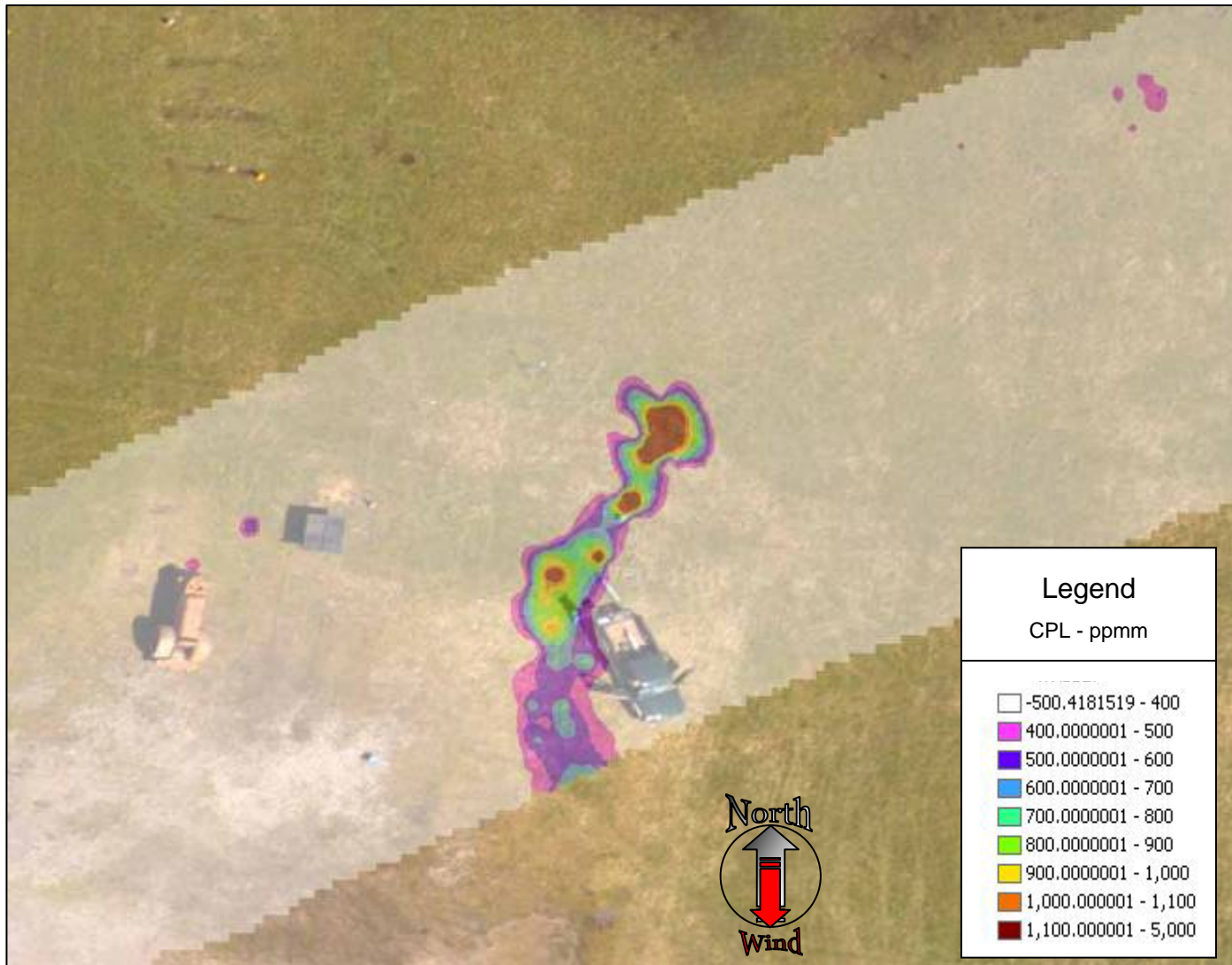
# Results – Methane Release Rate – 2.0 scfm



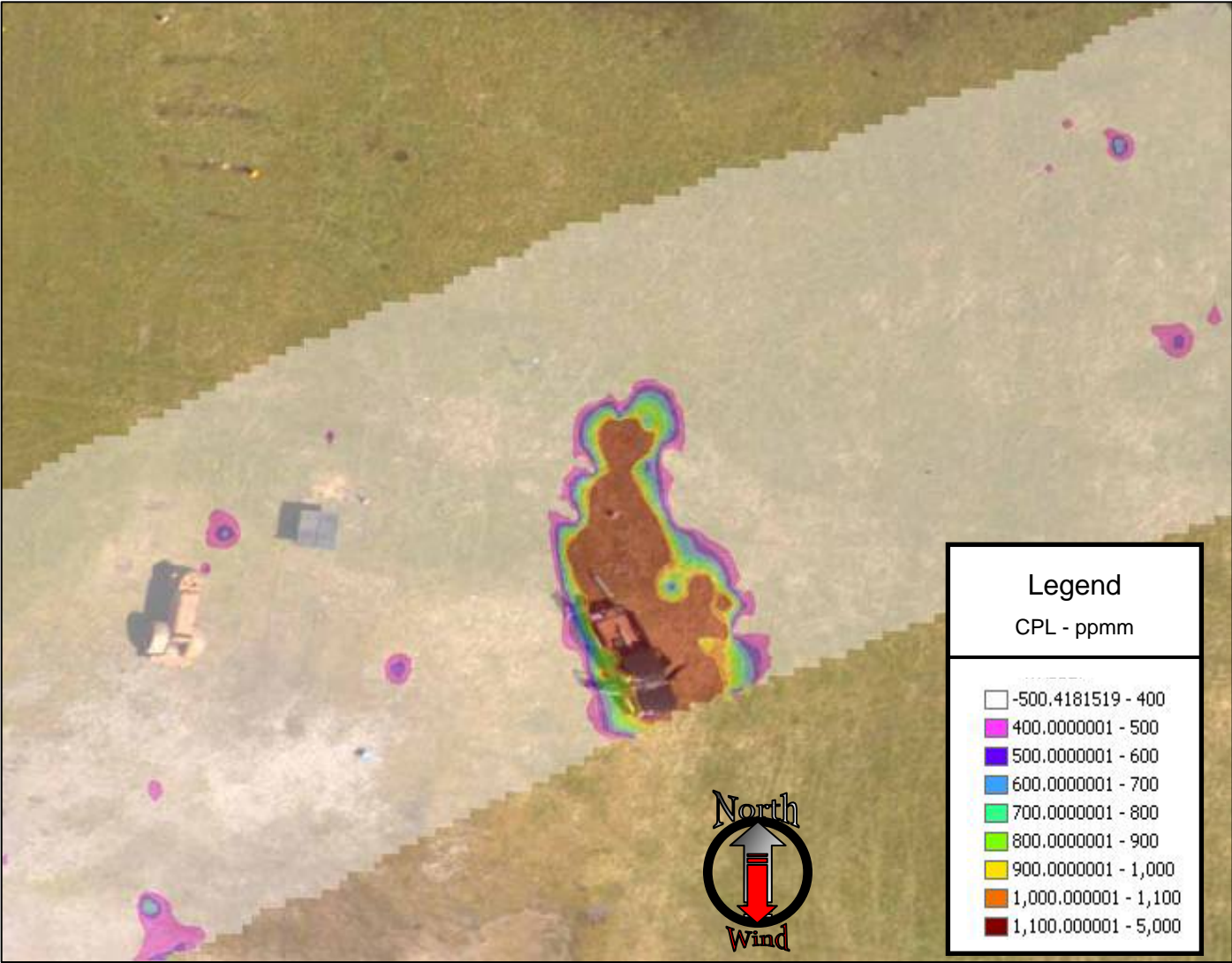
# Results – Methane Release Rate – 4.0 scfm



# Results – Methane Release Rate – 6.0 scfm

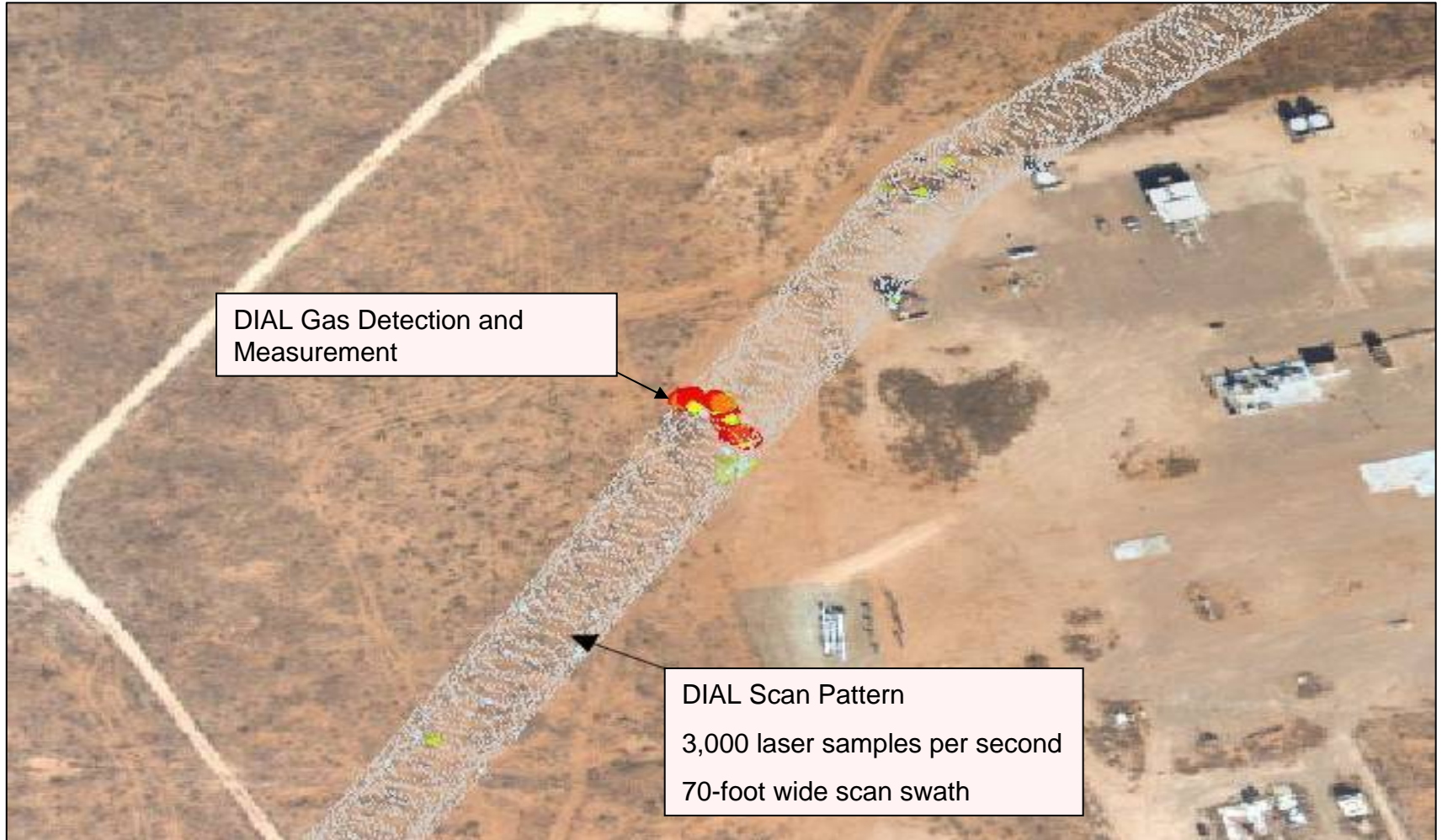


# Results – Methane Release Rate – 8.0 scfm





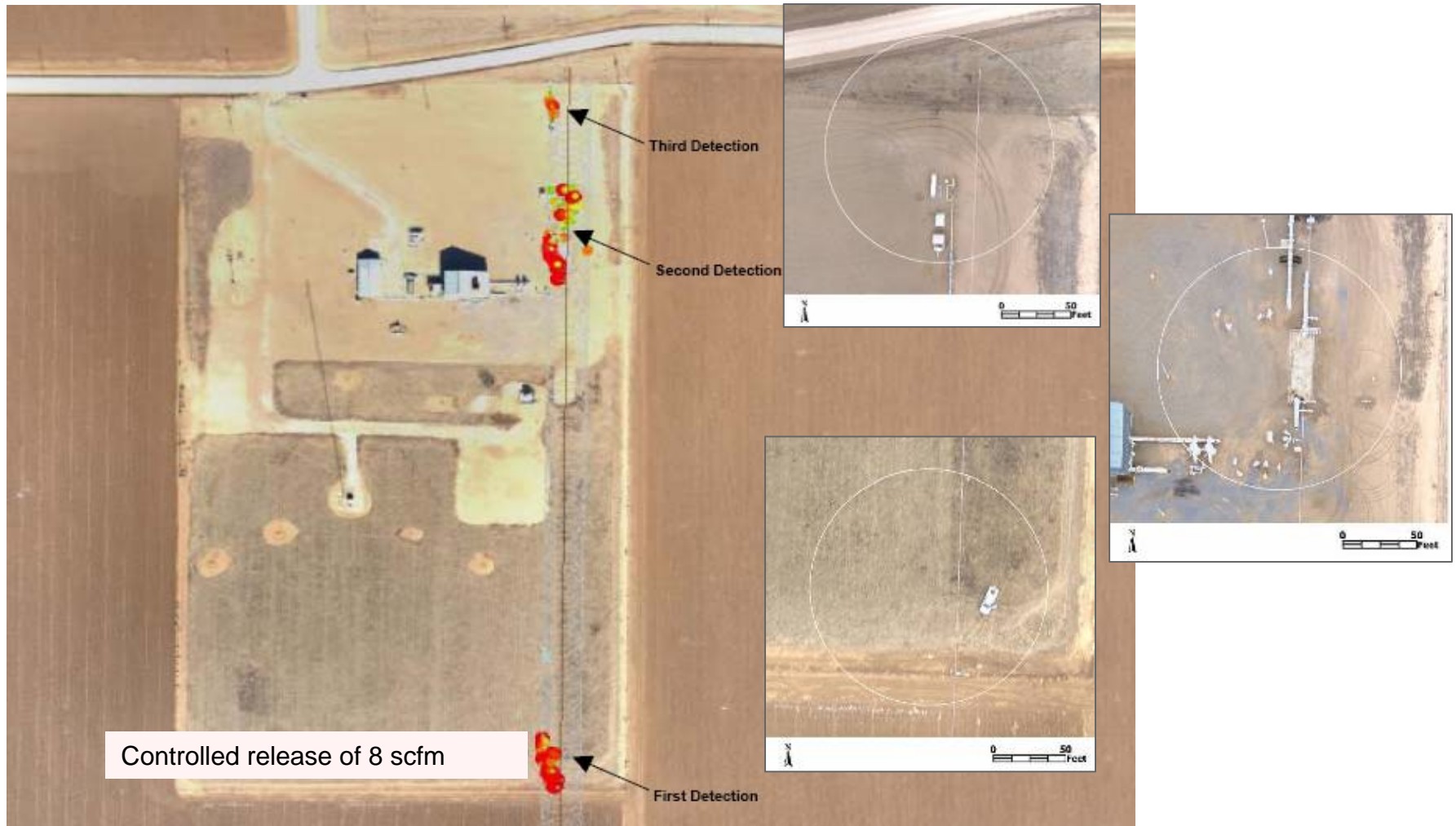
# Example: Natural Gas Transmission Pipeline Route – Texas



# Field Verification of Underground Pipeline Leak

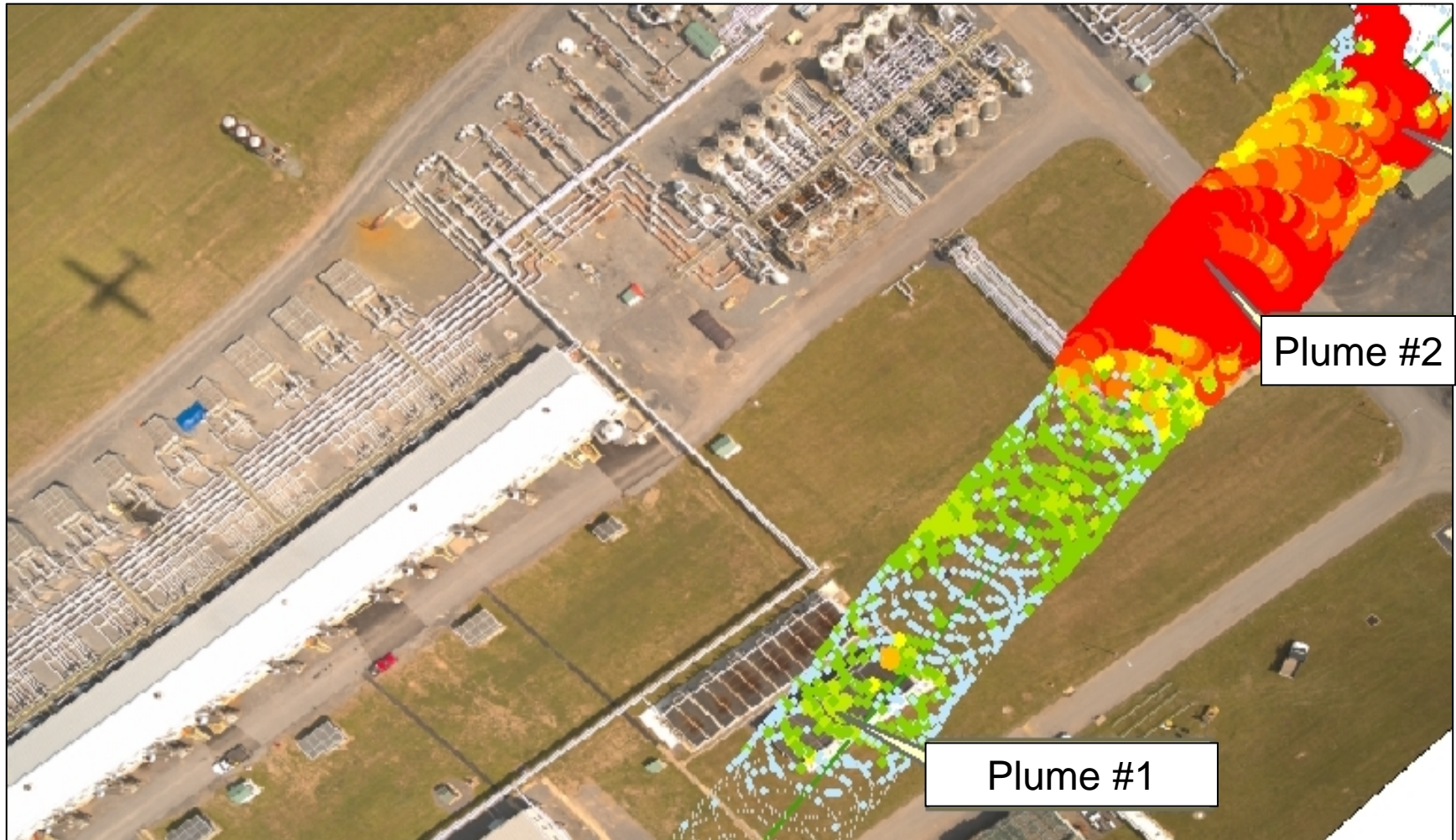


# Example: Compressor Station



Location D ANGEL Service Detection, 25 Jan 06 @ 10:16 AM

# Example: Processing Plant



# Example: Facility Leaks



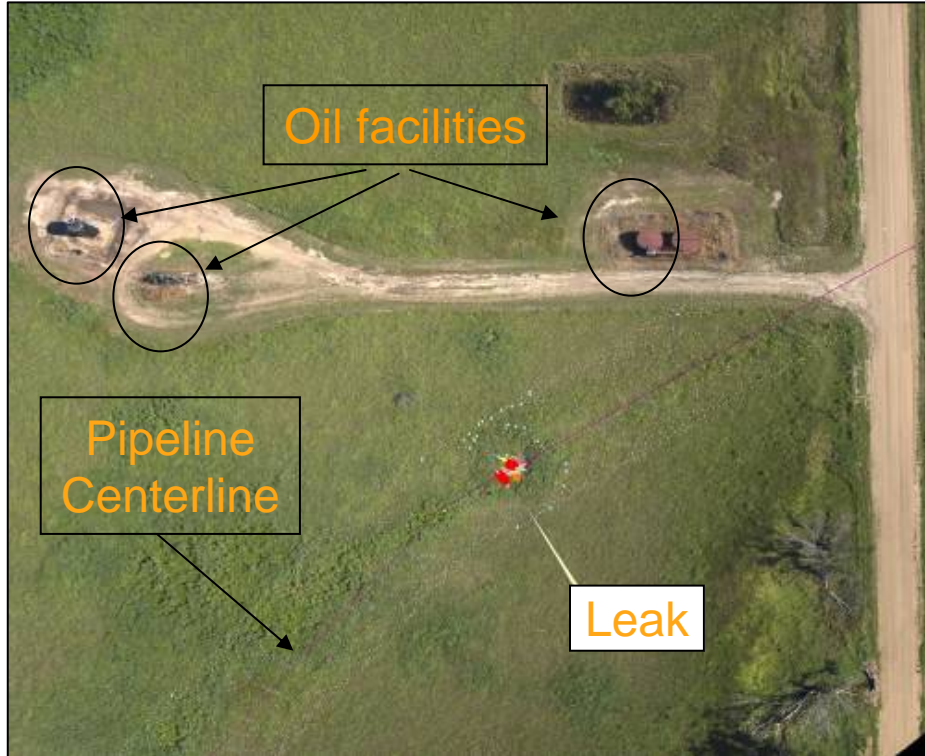
# Example: Underground Pipeline Leak – New York



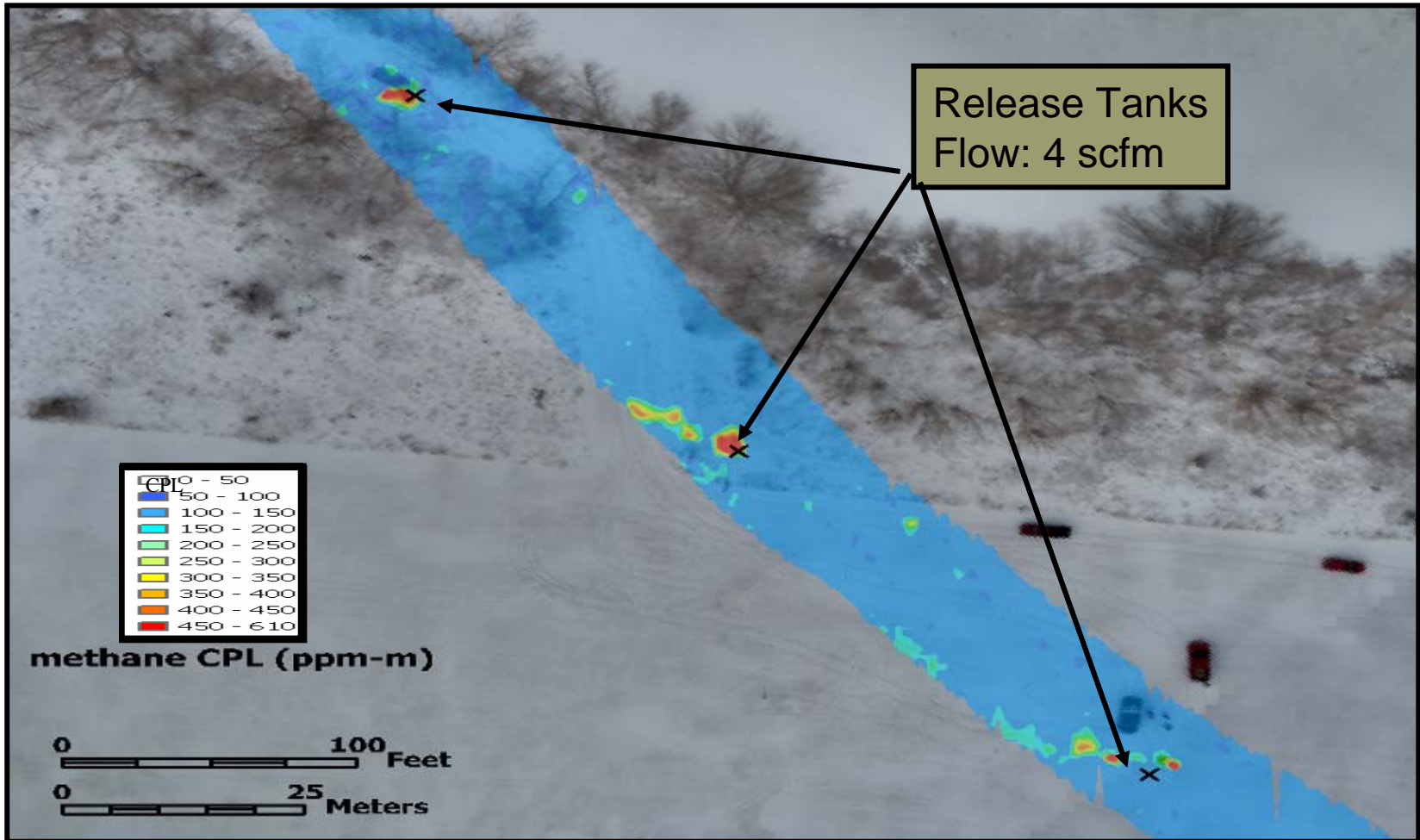
# Example: Underground Pipeline Leak - July 2007

Natural Gas Transmission  
Pipeline Operating at 700psi

Pipeline Crack



# Example: Snow Covered Right-Of-Way Controlled Release – New York





# The ANGEL Service is Fully Operational and Commercially Available

- Completed field validations with numerous pipeline owners/operators.
  - Over 8,000 miles of DIAL leak surveys and corridor/facility monitoring.
  - Atmos Energy, CenterPoint, Consumers Energy, El Paso, National Fuel, Northern Natural Gas, and ONEOK.
- Successfully completed cooperative development agreements with the US Department of Transportation and one other US Government agency.
  - RMOTC Test Range (Casper Wyoming) – September 2004.
  - HALOS (Hazardous Liquids Lidar Observation Study) – September 2006
  - Rapid Emergency Response (California w/ PG&E) – through January 2008

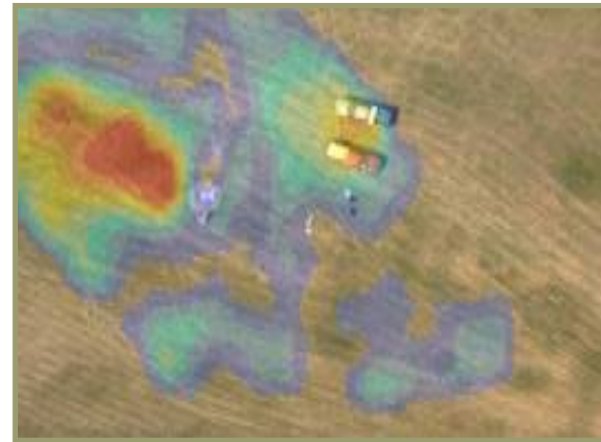


This research was funded in part under the Department of Transportation, Pipeline and Hazardous Materials Safety Administration. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Pipeline and Hazardous Materials Safety Administration, or the U.S. Government.

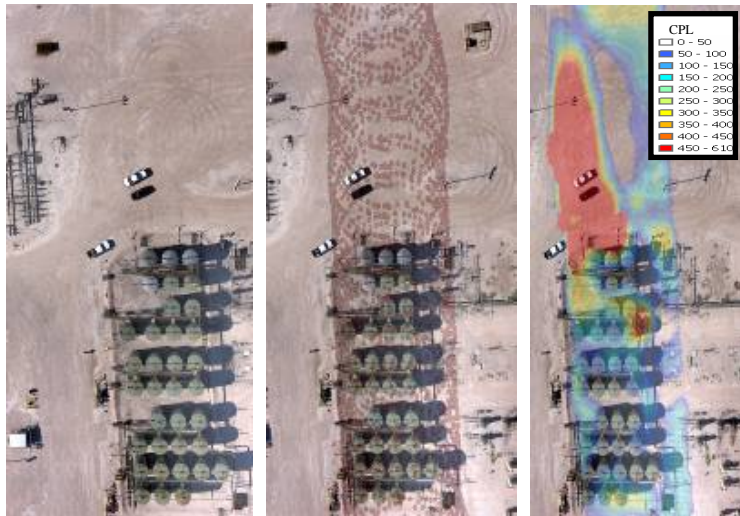
# Detection of Other Hydrocarbons



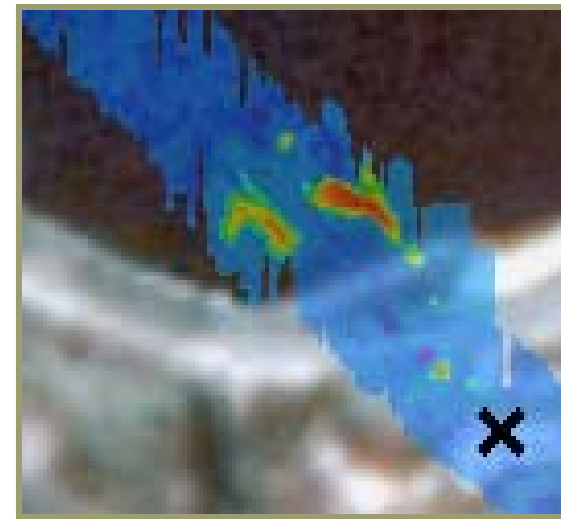
Natural Gas (methane)



LPG (propane)

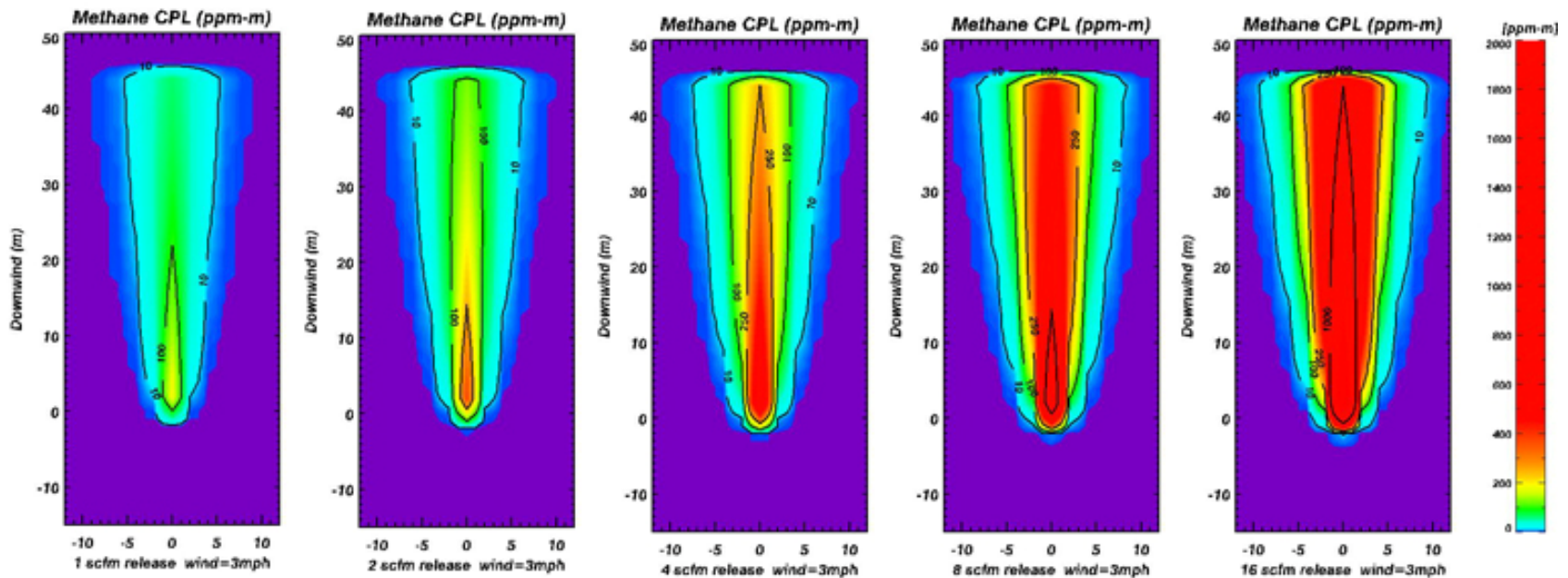


Natural Gas Condensates

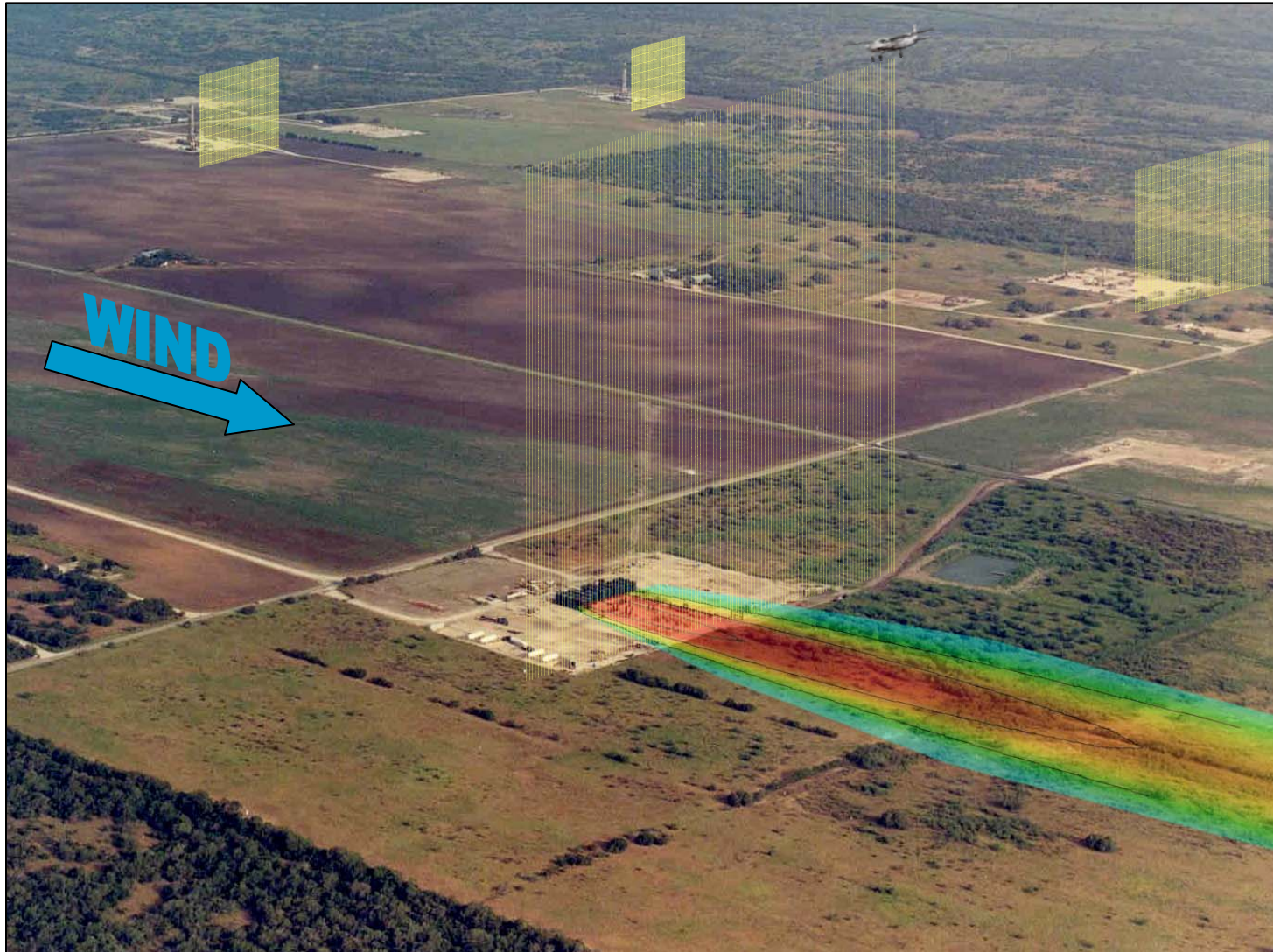


Gasoline Vapors

# Leak Rate Quantification Experiments



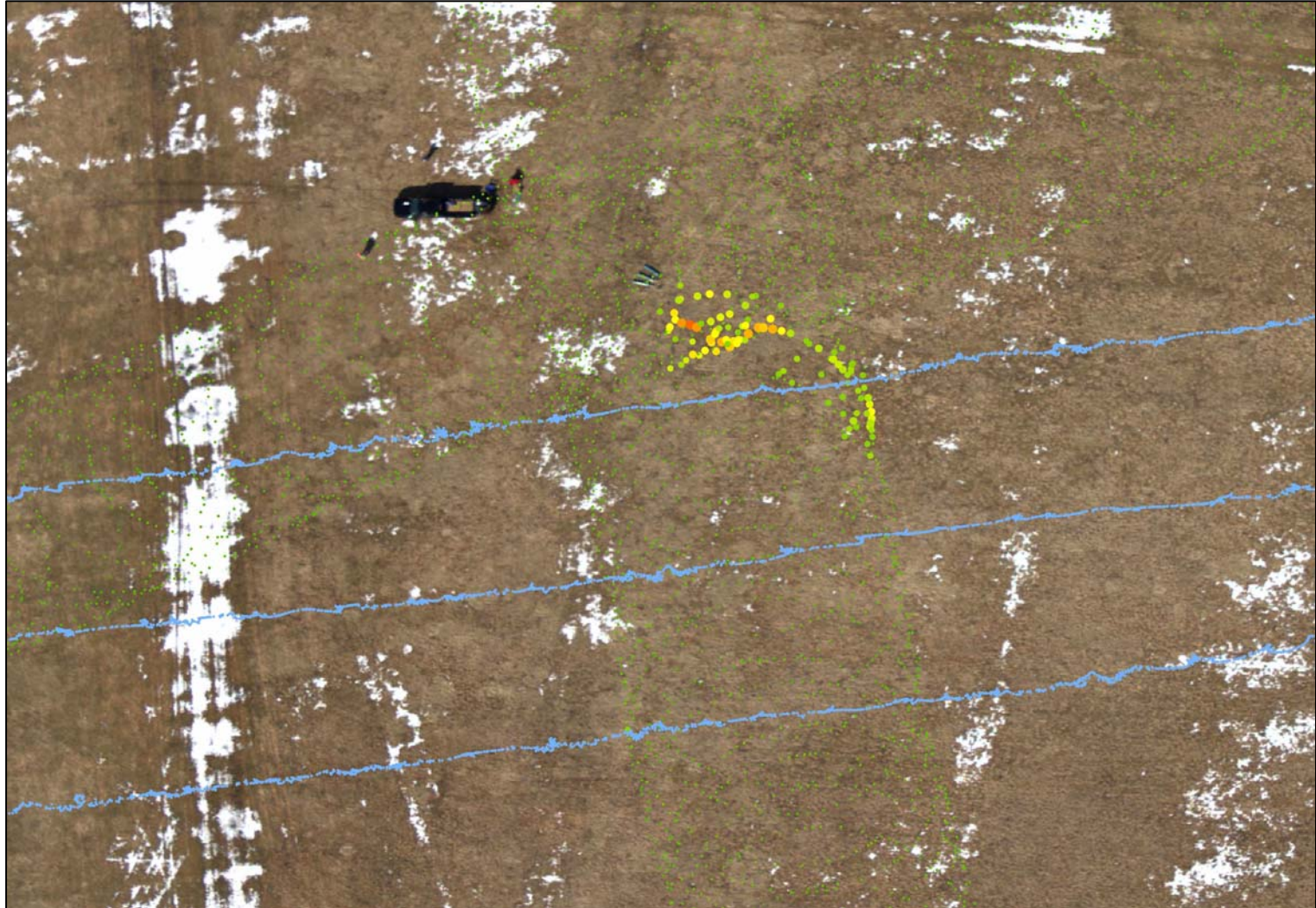
# Leak Rate Quantification



# Field Tests - Leak Rate Quantification



# Field Tests - Leak Rate Quantification



# Suggested Implementation: Combining Flux Measurements with Leak Detection

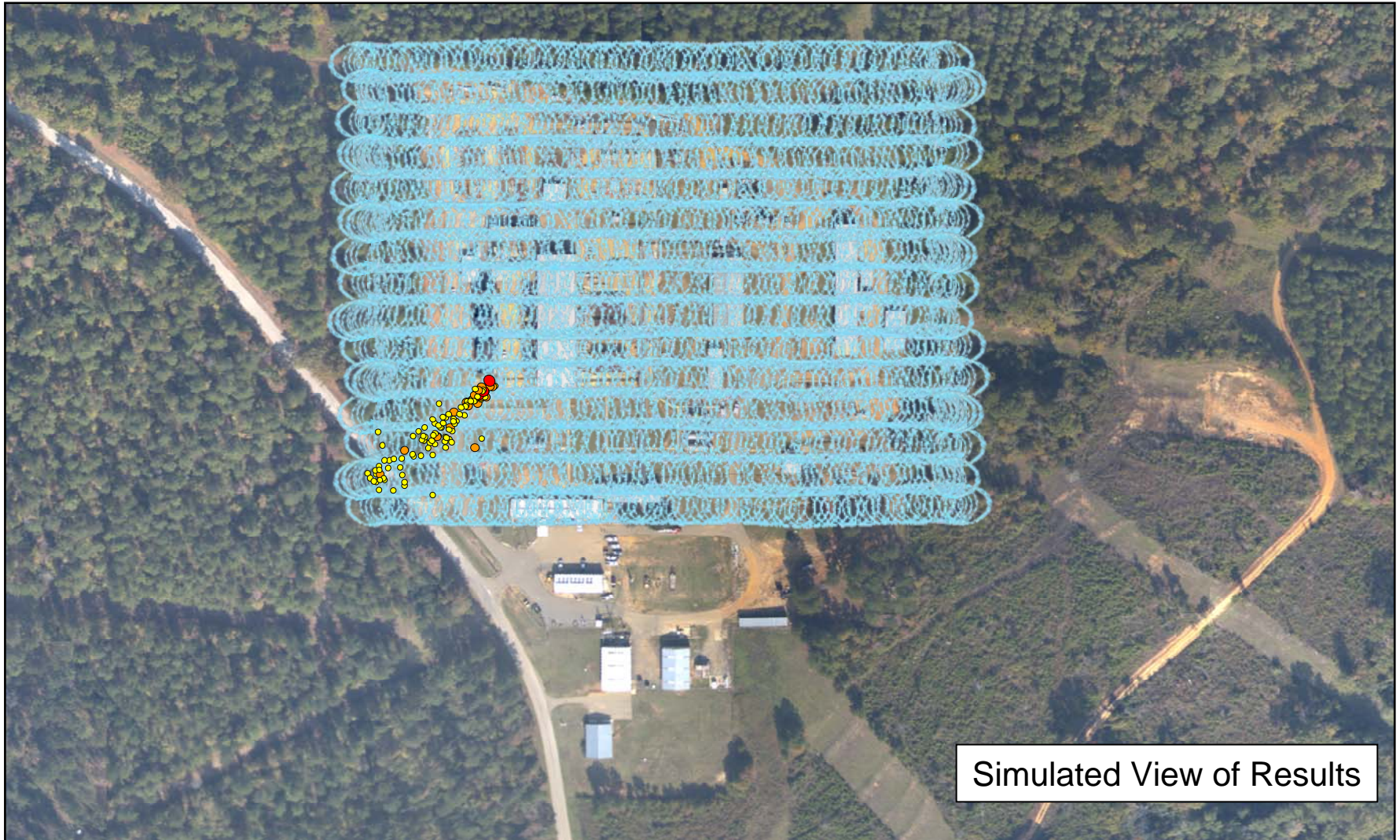
- Airborne DIAL Technology may be used to rapidly inspect multiple facilities/sites in a short time
- Single Flux Measurement pass at 120 mph takes 3 seconds for >500 foot long site
- When major emissions are detected, sites can be re-flown with conical scan approach to map the site and pinpoint the exact locations of the emission sources

# Measuring Methane Flux





# Broad Area Coverage - Facilities





**ITT**

# Hazardous Liquid Airborne Lidar Observation Study (HALOS)

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# **New Technologies to Meet Waste Program Needs**

Wednesday, April 2, 2008

Daniel Powell, U.S. EPA  
Office of Superfund Remediation and  
Technology Innovation  
(703) 603-7196  
[powell.dan@epa.gov](mailto:powell.dan@epa.gov)


# Technology Innovation and Field Services Division

- Advocate for technologies/provide services for:
  - Cleanup
  - Characterization (to date, soil, water)
  - Monitoring
  - Data management
- Focus across waste programs
- Most closely associated with Superfund
- Not a grant making organization
- Training, tech support, info delivery

# New Tools To Meet Program Needs, Mission

- Mission Needs:
  - Remediation performance (long-term, post construction)
  - Health and Safety, liability issues (fence-line monitoring)
  - Hot spot ID
  - Vapor intrusion
  - Reuse driver (fugitive emissions critical aspect; on or near landfills)
  - Waste methods guidance vs. regulatory requirements
  - Green Remediation

# Understanding the Market

- Superfund, waste programs not technology buyers
  - Selling a service, not a product
  - Role of clean-up contractors
  - Procurement issues
  - Budget issues
- 

# Understanding the Issues

- Who buys?
- “Approved” or “required” methods
- All decisions require same level of data
- Legal admissibility/defensibility
- The uncertainty issue
- Money for research and demonstration

# What We Hope to Achieve

- Project managers up to date on latest methods
  - Removal
  - Remedial
- Leveraging experience in air programs
- Improve information resources, training
- Increased understanding
  - Applications
  - Cost and performance
  - Limitations



# Where We Go From Here

- Building on existing tools
  - Vendor support pages
  - Internet seminars, technology brown bags
  - Case study, profile data bases
  - Cost and performance
  - Training infrastructure
  - Information delivery
- Continue learning process
- Demonstration projects?



# Quantum Cascade Lasers for Molecular Spectroscopy and Remote Sensing Applications

## Recent Advances and Future Directions

Gerard Wysocki

*Princeton University, Electrical Engineering Department, Princeton, NJ*

### OUTLINE

- Potential Applications in mid-IR
- Quantum Cascade Lasers (QCLs)
- External Cavity QCLs

PERFORMANCE CHARACTERISTICS AND EXAMPLE APPLICATIONS:

- CW, RT EC-QCL @  $\lambda = 5.3\mu\text{m}$
- High power, CW, RT EC-QCL @  $\lambda = 8.4\mu\text{m}$
- CW DFB-QCL based open path system test

- Summary and Future Directions

EPA ORS Workshop

April 1-3, 2008  
Research Triangle Park  
NC

Financial Support: DoE-STTR and NSF - MIRTHE



# Trace Gas Sensing Applications



**Environmental Monitoring**

**Urban and Industrial  
Emission Measurements**

**Fundamental Science**



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**Industrial Process Control**



**Law Enforcement and National Security**

**Applications in Medicine  
and Life Sciences**

# Laser Absorption Spectroscopy

---

- High sensitivity
- High selectivity
- Non-destructive
- Fast
- No sample preparation
- Remote sensing
- Field deployable

# Spectroscopic techniques for trace-gas detection

LASER SOURCE



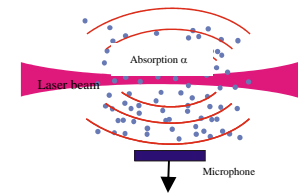
Multipass cell spectroscopy



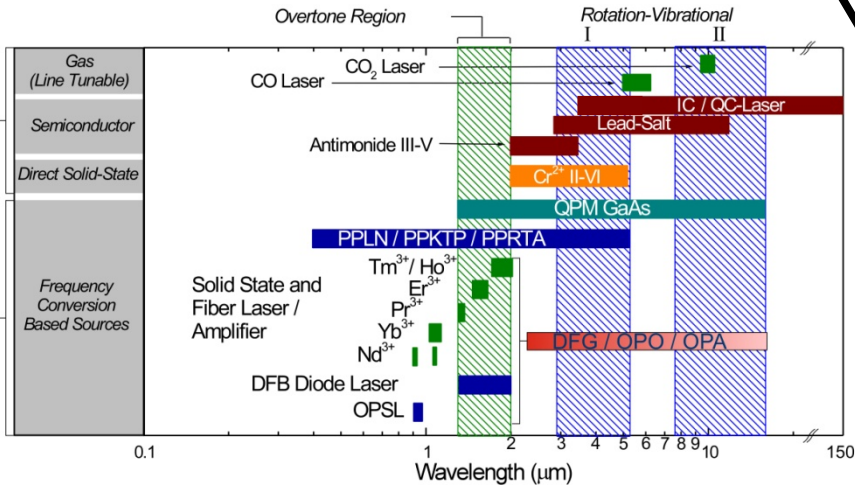
Cavity Ring Down Spectroscopy (CRDS)  
Cavity Enhanced Spectroscopy



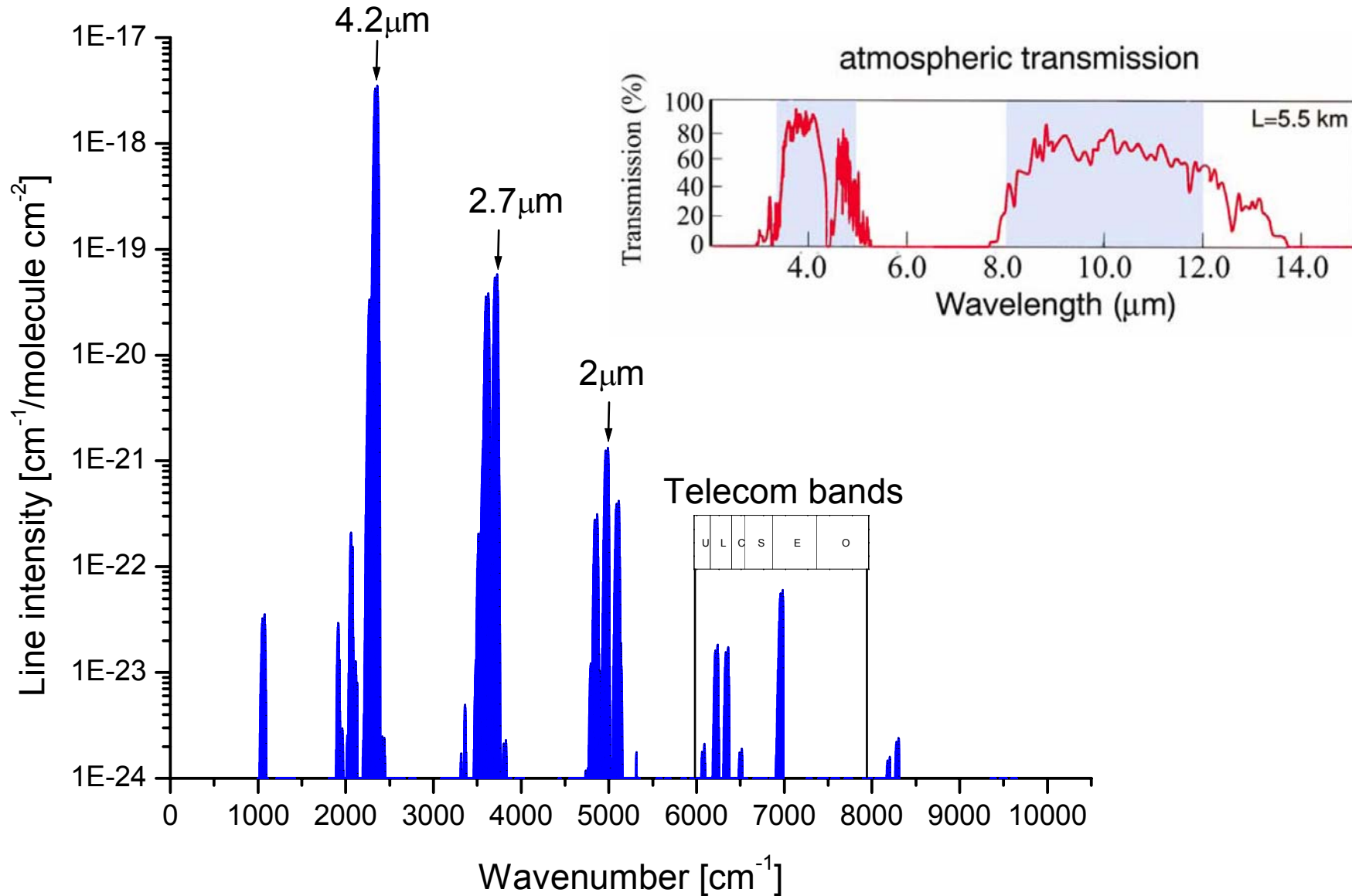
Photoacoustic Spectroscopy



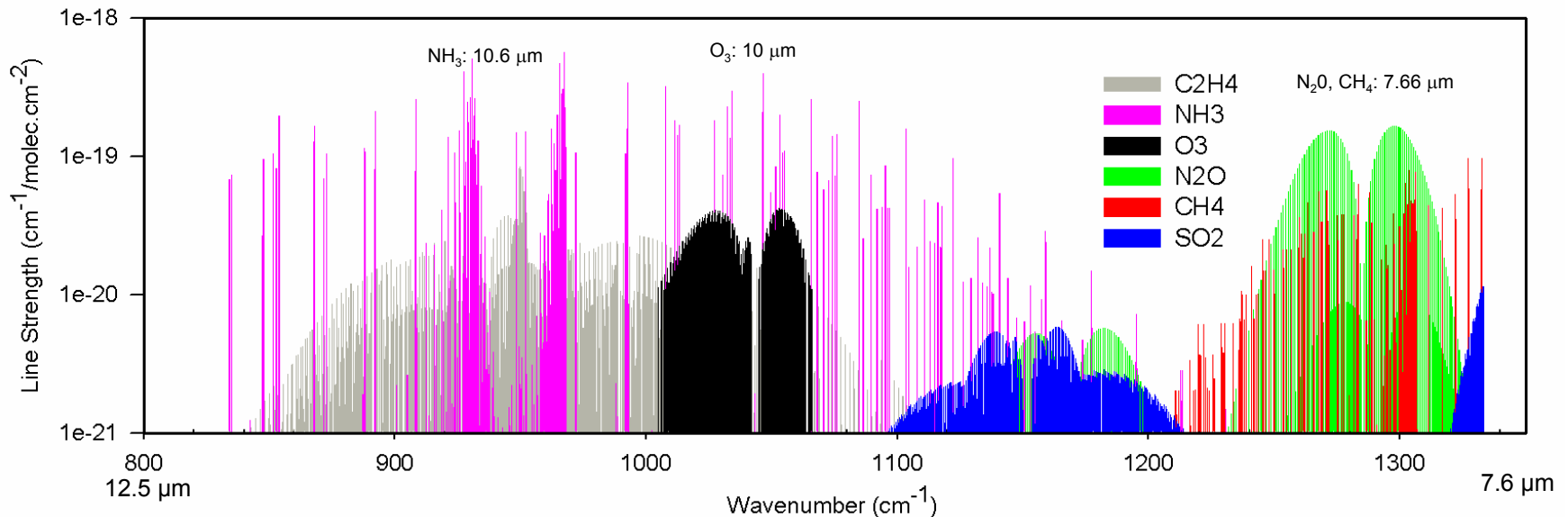
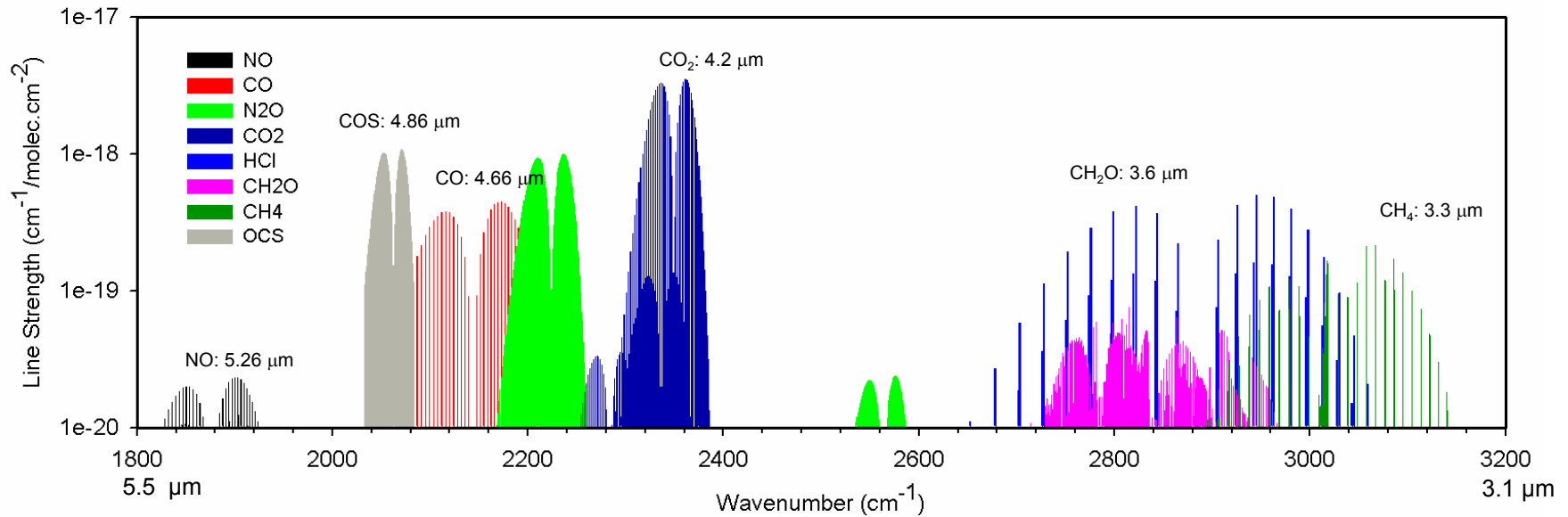
Remote sensing



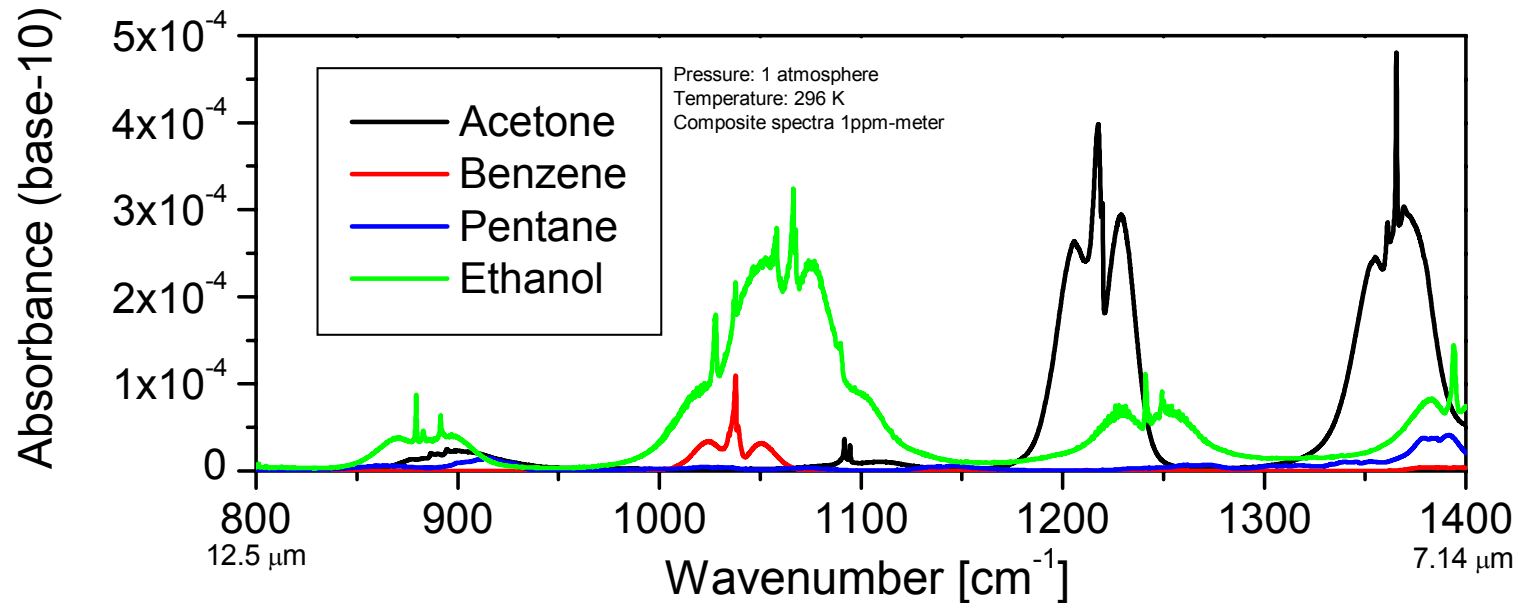
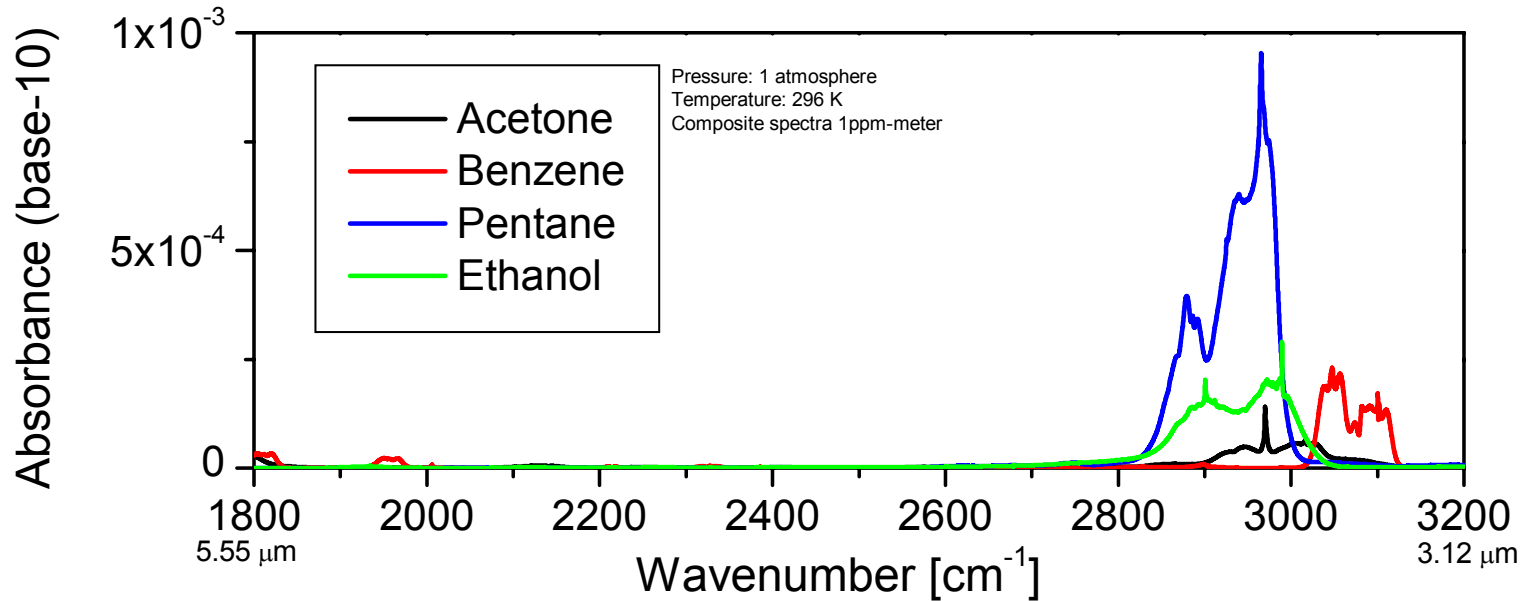
# CO<sub>2</sub> absorption spectrum



# Example Molecular Absorption Spectra within Mid-IR “Atmospheric Windows”



# Example Absorption Spectra of Broadband Absorbing Molecules





# Mid-IR Source Requirements for Laser Spectroscopy

<b><u>REQUIREMENTS</u></b>	<b><u>IR LASER SOURCE</u></b>
<b>Sensitivity (% to ppt)</b>	<b>Wavelength, Power</b>
<b>Selectivity (Spectral Resolution)</b>	<b>Single Mode Operation and Narrow Linewidth</b>
<b>Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers</b>	<b>Tunable Wavelength</b>
<b>Directionality or Cavity Mode Matching</b>	<b>Beam Quality</b>
<b>Rapid Data Acquisition</b>	<b>Fast Time Response</b>
<b>Room Temperature Operation</b>	<b>No Consumables</b>
<b>Field deployable</b>	<b>Compact &amp; Robust</b>

# Spectroscopic techniques for trace-gas detection

LASER SOURCE



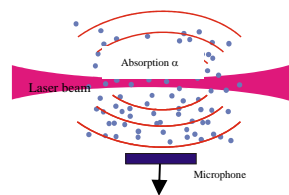
Multipass cell spectroscopy



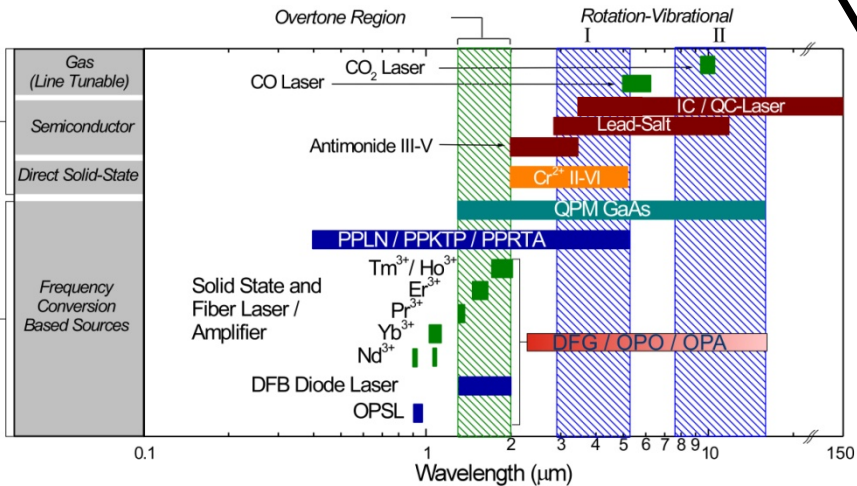
Cavity Ring Down Spectroscopy (CRDS)  
Cavity Enhanced Spectroscopy



Photoacoustic Spectroscopy

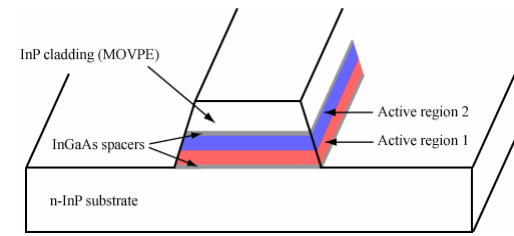
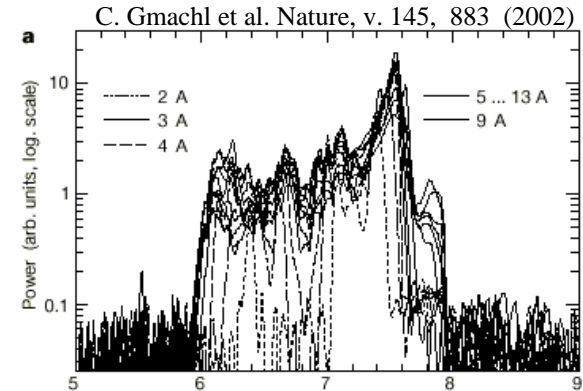
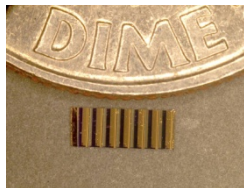


Remote sensing

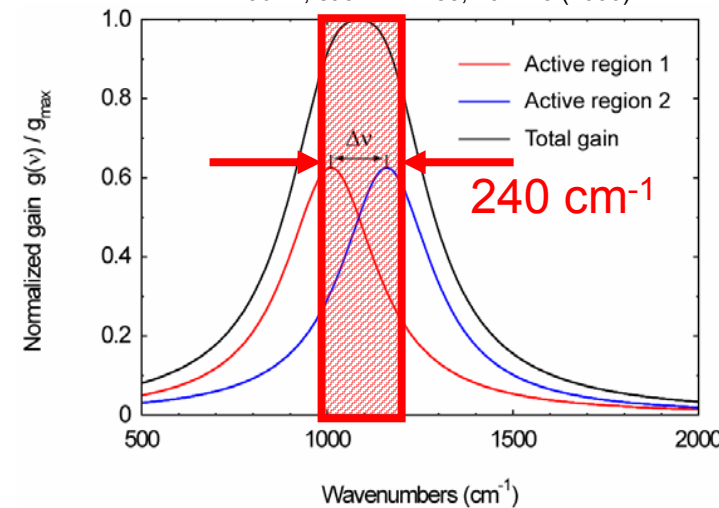


# Quantum Cascade Laser: Basic Facts

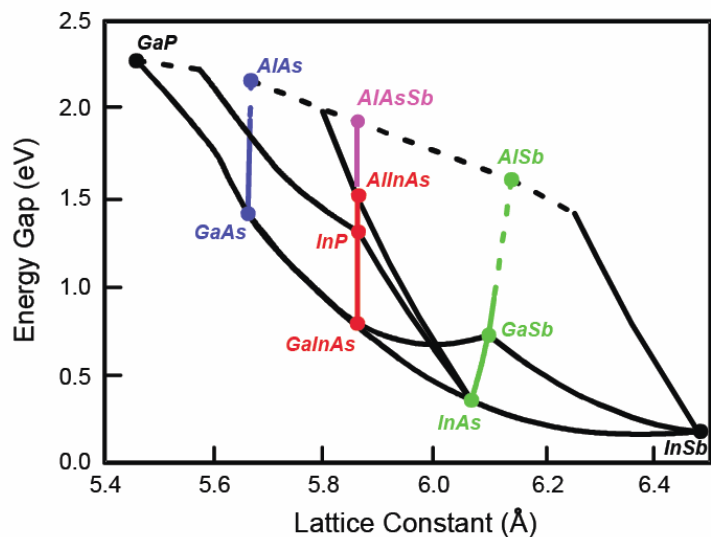
- Laser wavelengths cover the Mid-IR range ( $\sim 3 - 24\mu\text{m}$ , band structure engineering)
- High laser power ( $>500\text{mW}$  cw,  $>5\text{W}$  peak for pulsed)
- Tunable single frequency operation tuning: DFB (up to  $\sim 10\text{ cm}^{-1}$ ), EC ( $>200\text{ cm}^{-1}$ )
- High quantum efficiency (Cascading: 1 electron =  $N$  photons)
- High reliability, long lifetime
- Room temperature operation (CW: above RT)
- Compact



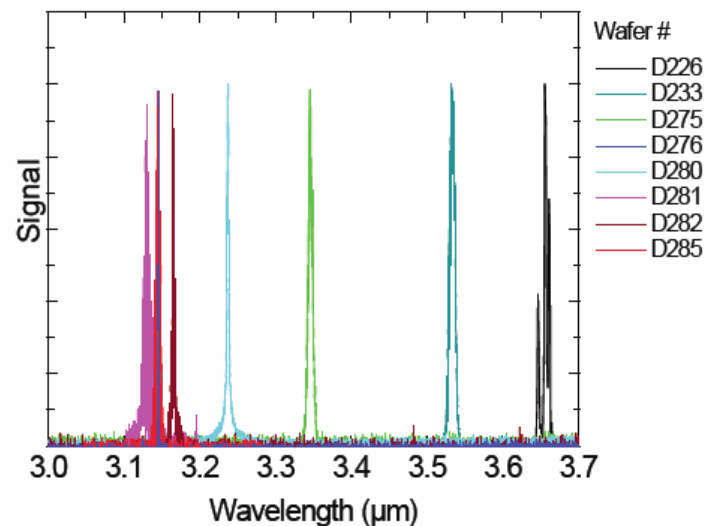
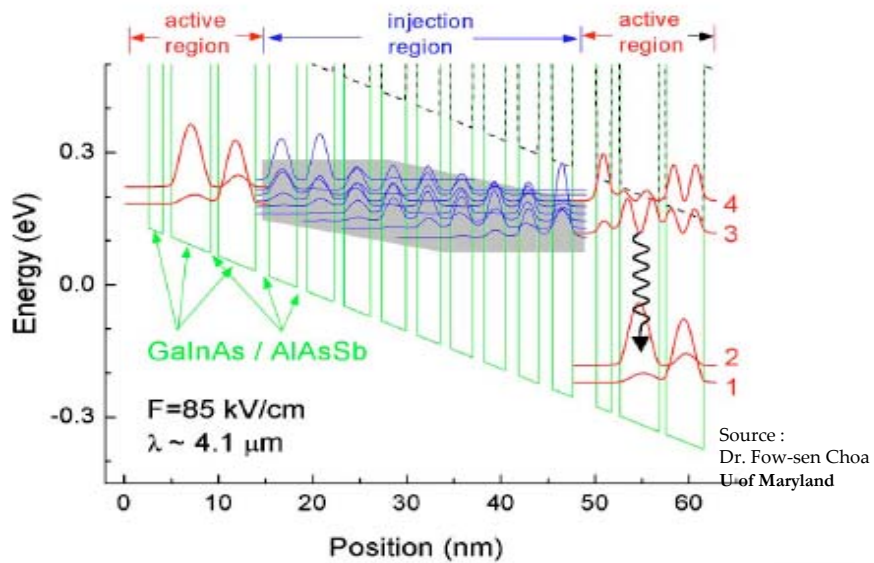
R. Maulini, et al. APL. 88, 201113 (2006)



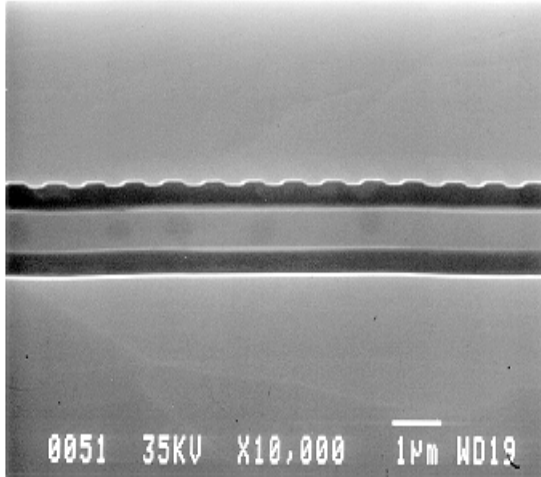
# Short Wavelength QCLs



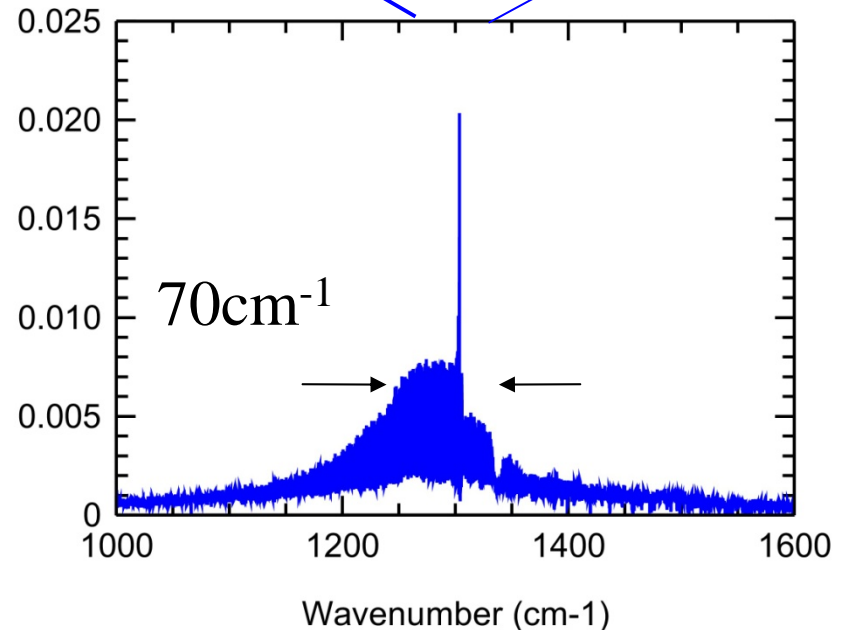
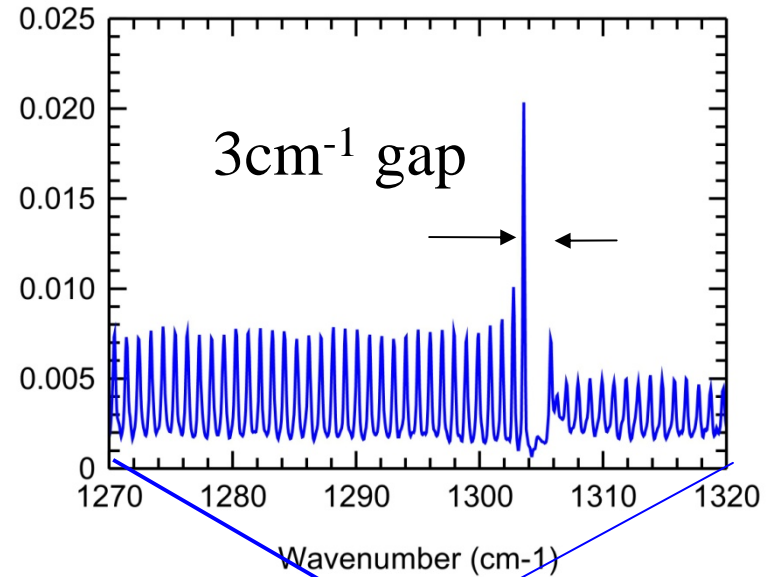
- Short wavelengths require larger energy offset
- An alternative material system
- InAs/AISb – the best material system for QCL in 3 $\mu$ m region (C-H stretch)
- Pulsed operation @RT was demonstrated



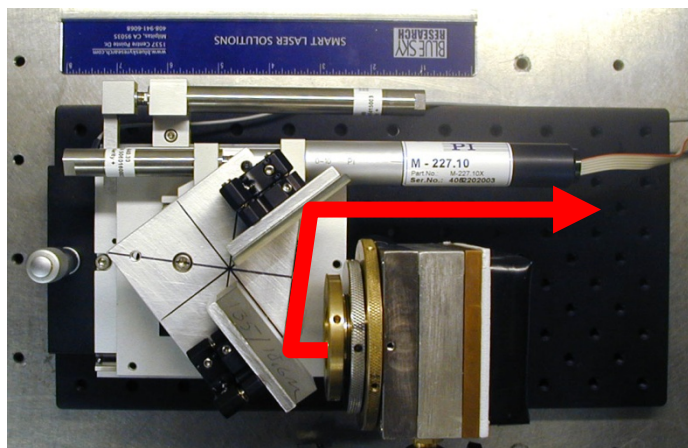
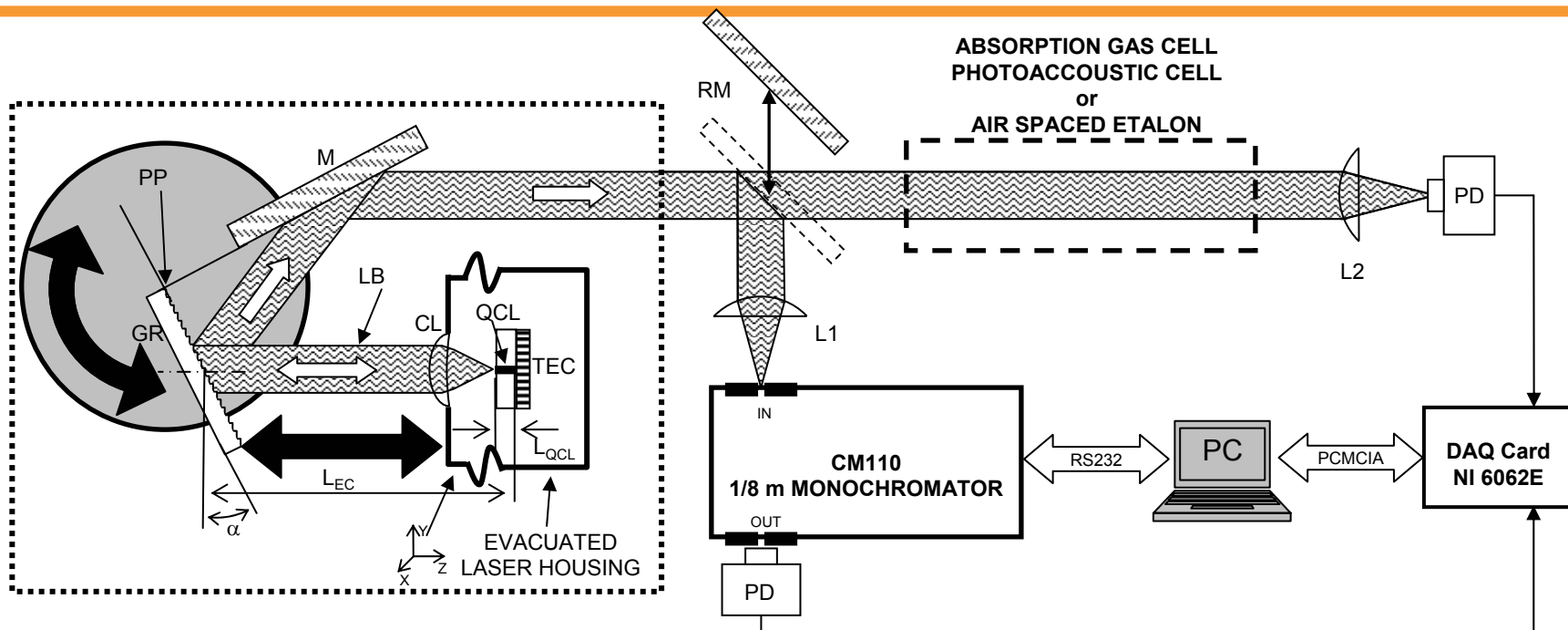
# Distributed Feedback - QCL



- Grating permanently etched into the waveguide
- Selects the proper mode (if we are lucky)
- Creates a local gap (stop band)
- The selected mode can occur on either side
- Total tuning range  $\sim 10\text{cm}^{-1}$  (thermal tuning)
- $2\text{-}3\text{ cm}^{-1}$  tuning with the injection current
- **Typical yield much lower than 10%**

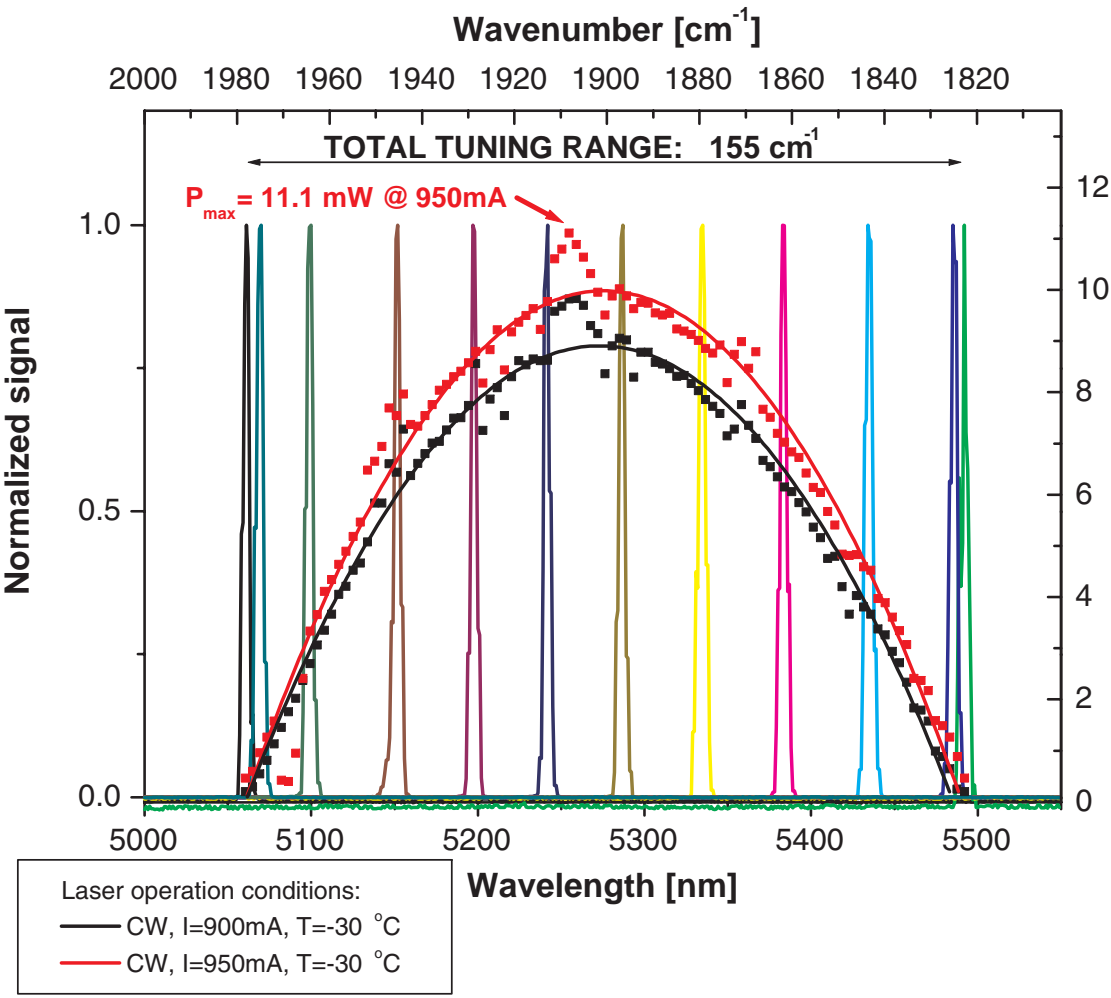


# Tunable external cavity QCL based spectrometer

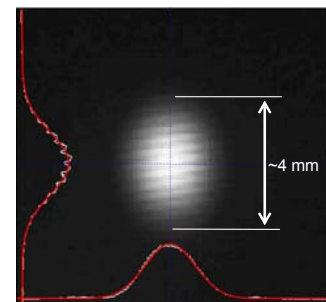
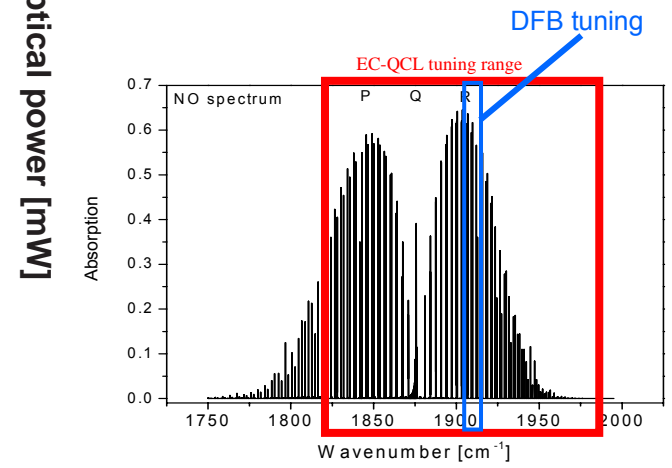


- High resolution mode-hop free wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + chilled water cooling)

# Wide Wavelength Tuning of a 5.3 $\mu\text{m}$ EC-QCL



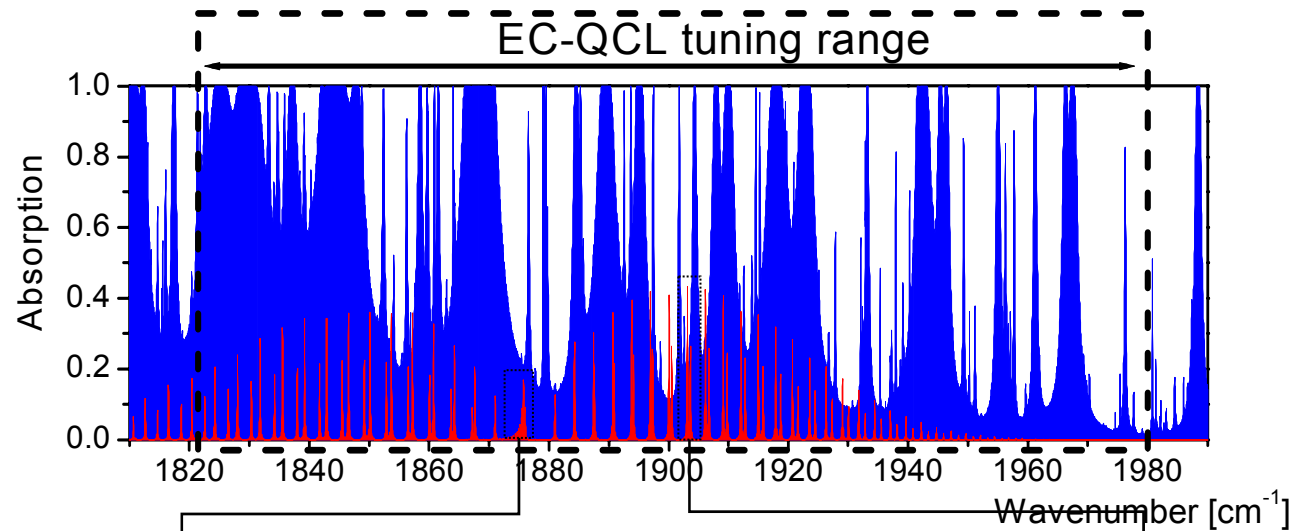
- Coarse wavelength tuning of **155  $\text{cm}^{-1}$**  is performed by varying diffraction grating angle
- Max. CW power  **$\sim 11\text{mW}$**



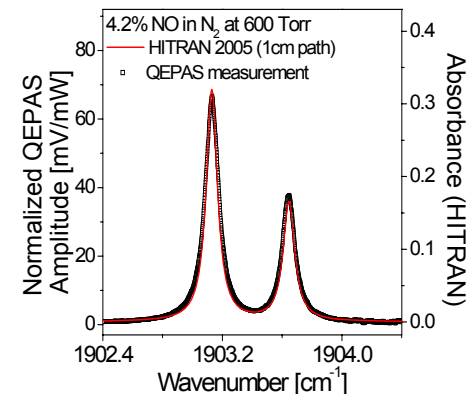
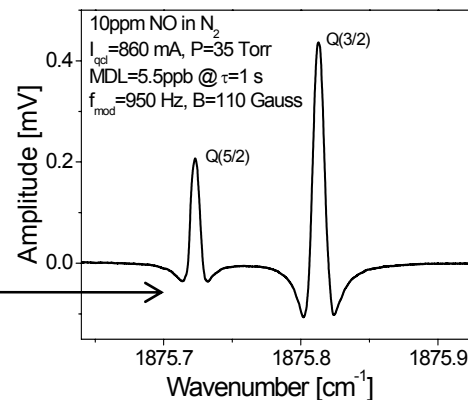
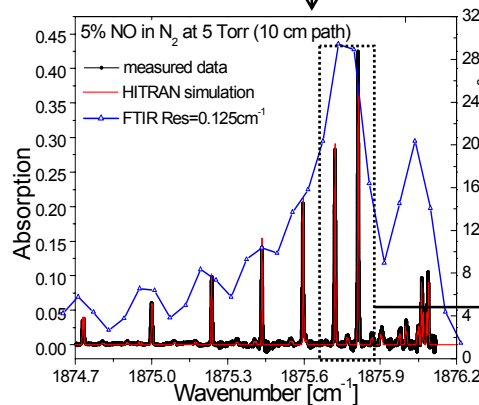
In collaboration with:



# High resolution spectroscopy with a 5.3 $\mu\text{m}$ EC-QCL



Access to NO Q(3/2) transition at 1875.8 cm<sup>-1</sup> for Faraday rotation spectroscopy

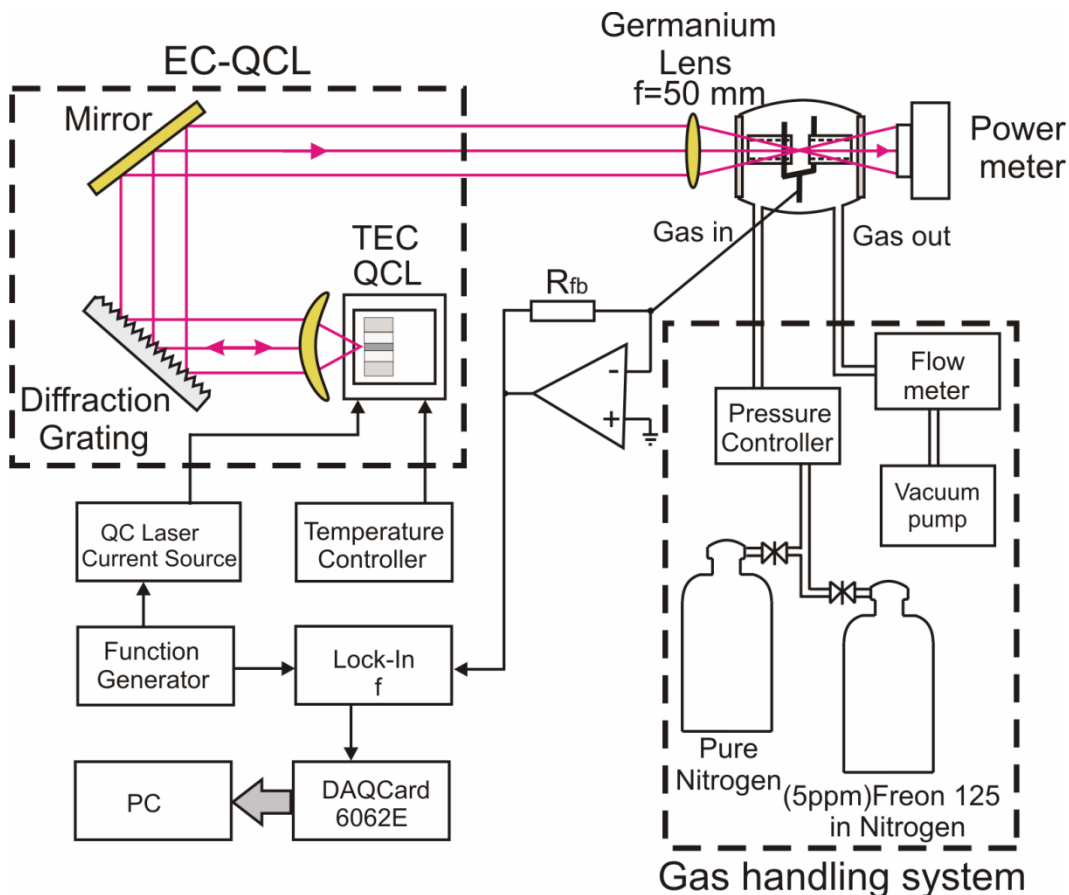


- Mode hop free scan of up to  $\sim 2.5 \text{ cm}^{-1}$  with a resolution  $< 0.001 \text{ cm}^{-1}$  (30MHz) can be performed anywhere within the tuning range

In collaboration with:



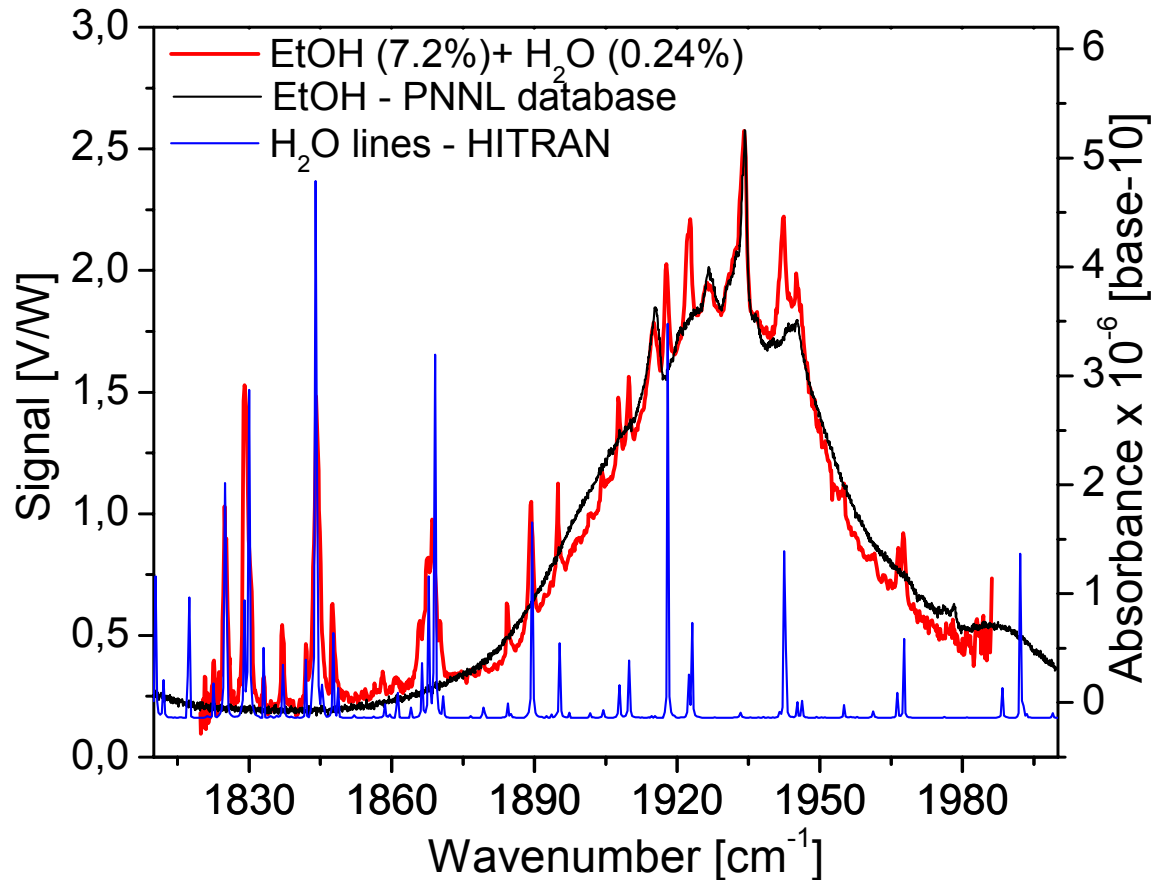
# QCL based Quartz-Enhanced Photoacoustic Gas Sensor



## QEPAS characteristics:

- High sensitivity (ppm to ppb)
- Excellent dynamic range
- Immune to environmental noise
- Ultra-small sample volume ( $< 1\text{ mm}^3$ )
- Sensitivity is limited by the fundamental thermal quartz tuning fork (QTF) noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

# QEPAS ethanol spectrum between 1825 & 1980 $\text{cm}^{-1}$



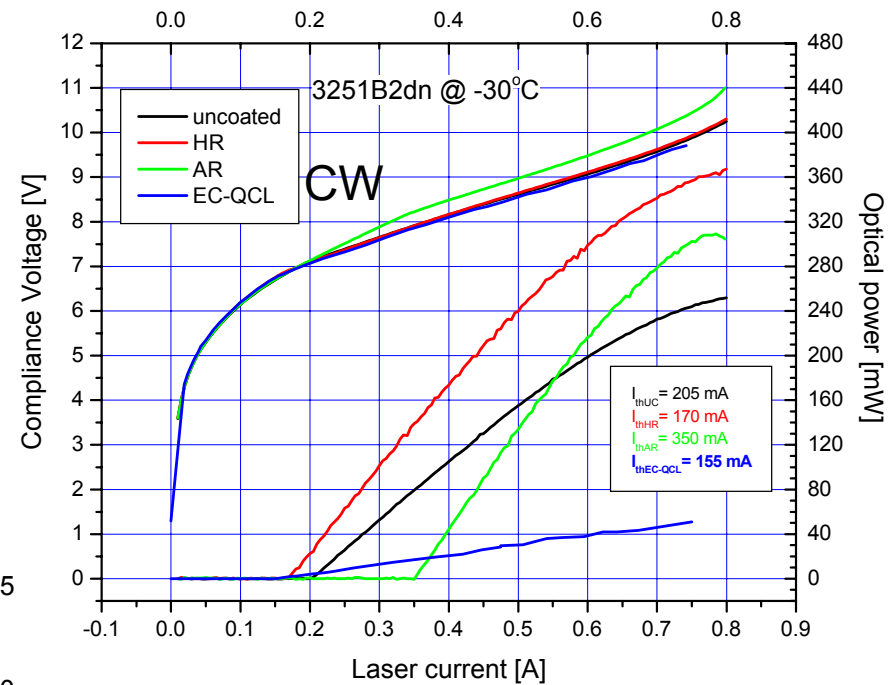
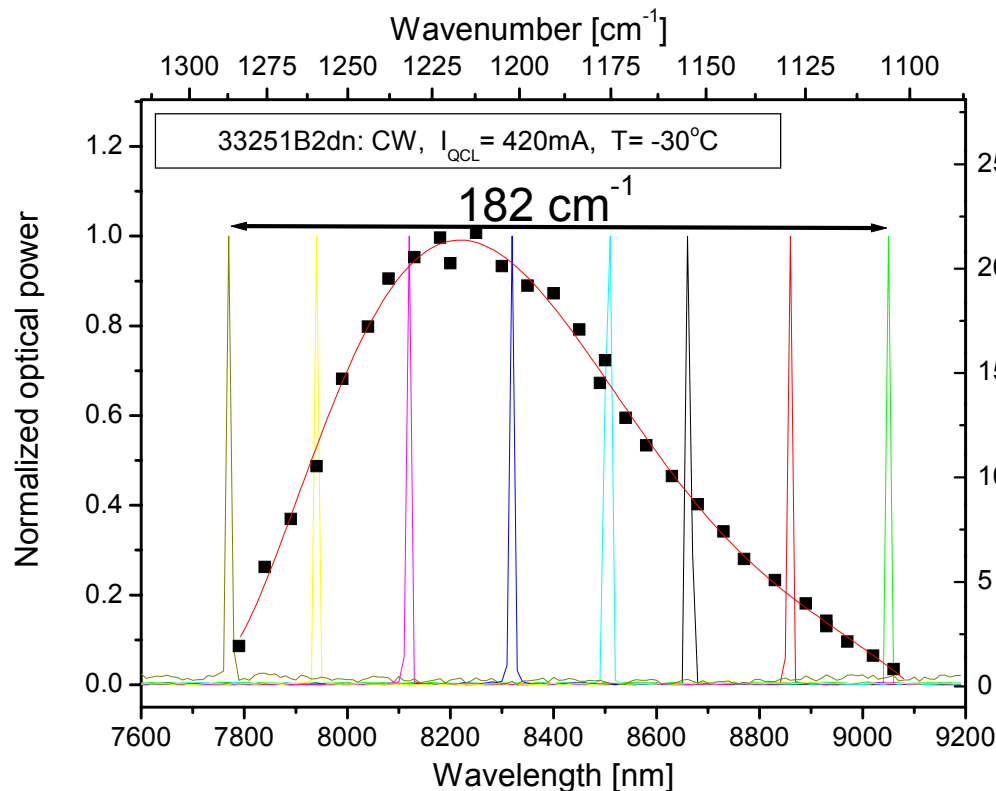
- Reference spectrum from the PNNL spectral database (black line).
- Sharp features on the ethanol spectrum correspond to the water absorption lines.
- Blue line depicts water absorption spectrum simulated using HITRAN database.
- Estimated resolution of a coarse wavelength scan  **$\sim 1.2 \text{cm}^{-1}$**

# EC-QCL emitting at $\lambda = 8.4 \mu\text{m}$

$P_{\text{EC-opt}}$  up to **50mW (cw)**

AR coating:

$$R_{\text{AR}} \approx 5 \times 10^{-4}$$



Tunability **182  $\text{cm}^{-1}$**

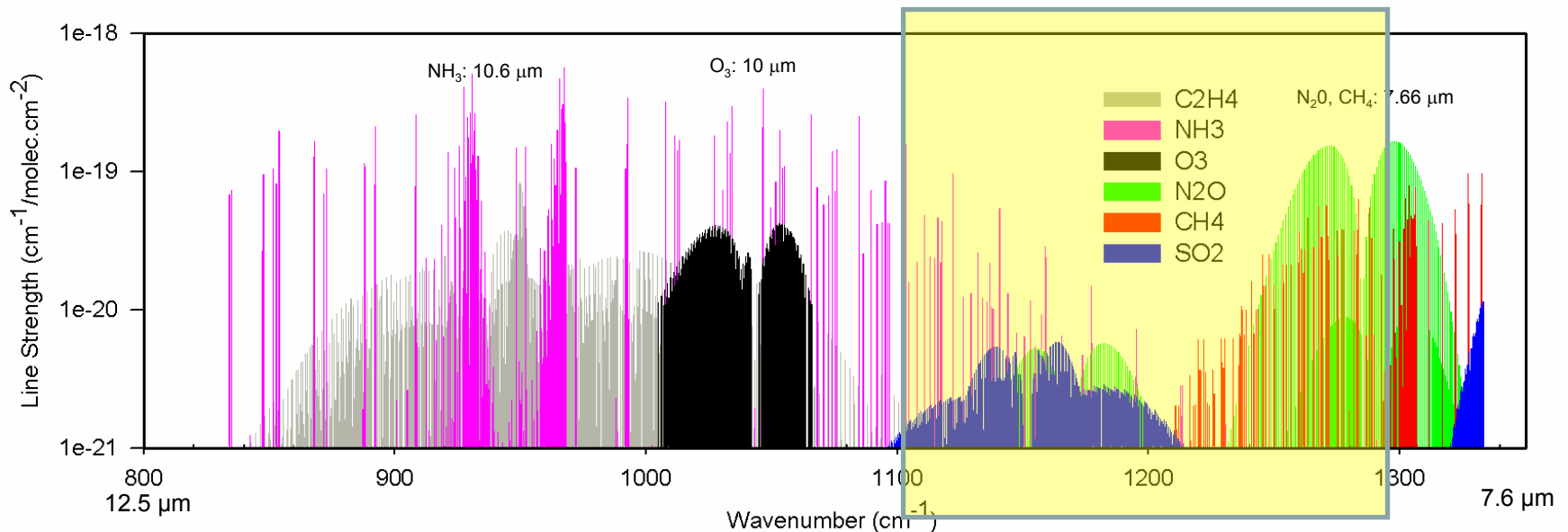
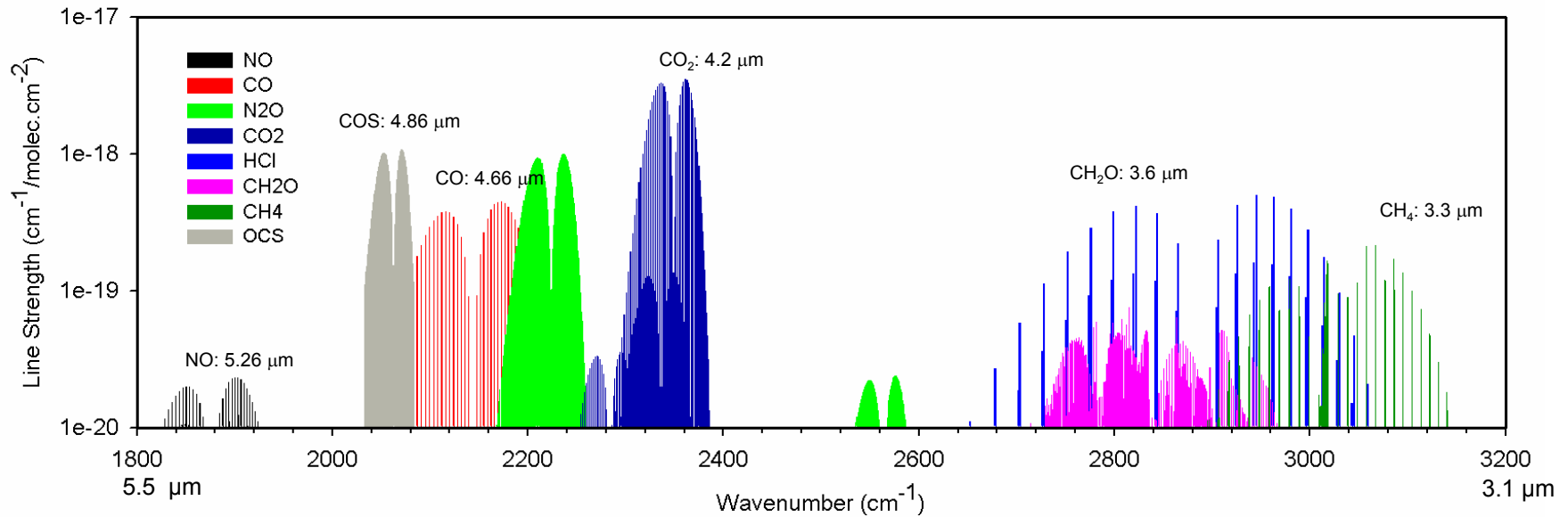
@8.4  $\mu\text{m}$  (7.77  $\mu\text{m}$  - 9.05  $\mu\text{m}$ )

**15.3 %** of the center wavelength

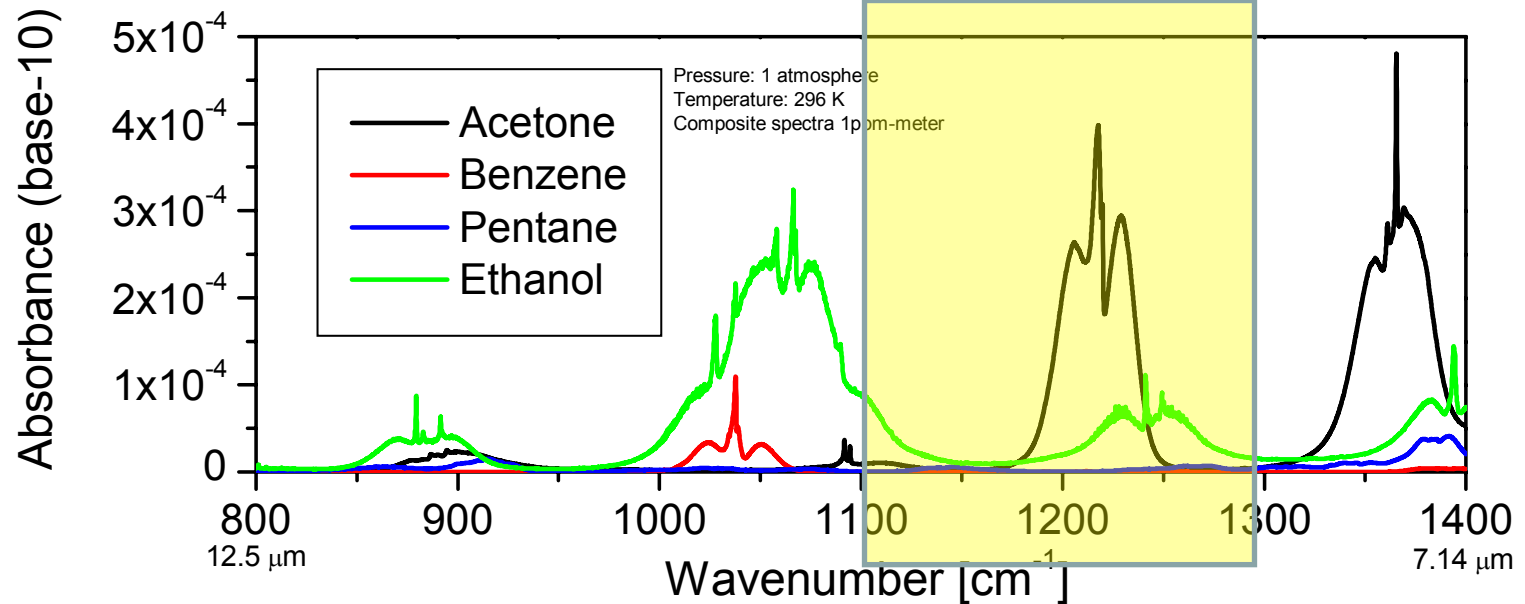
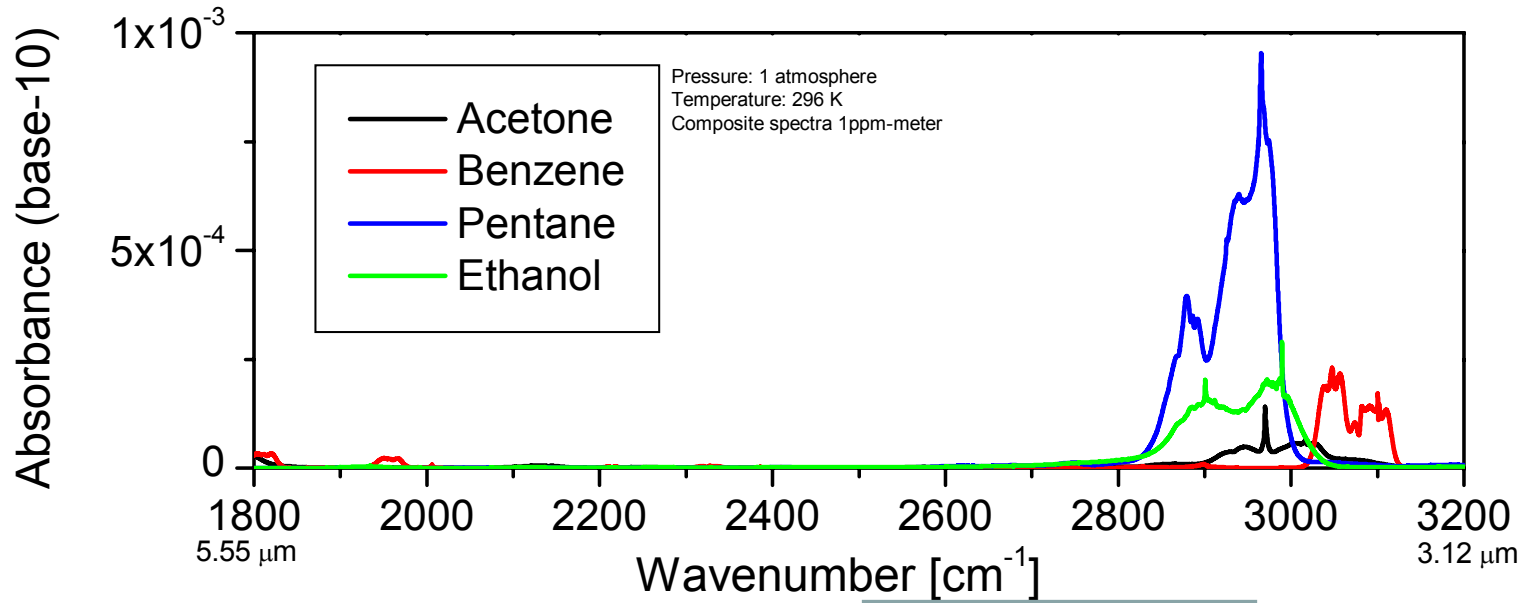
In collaboration with:



# Example Molecular Absorption Spectra within Mid-IR “Atmospheric Windows”

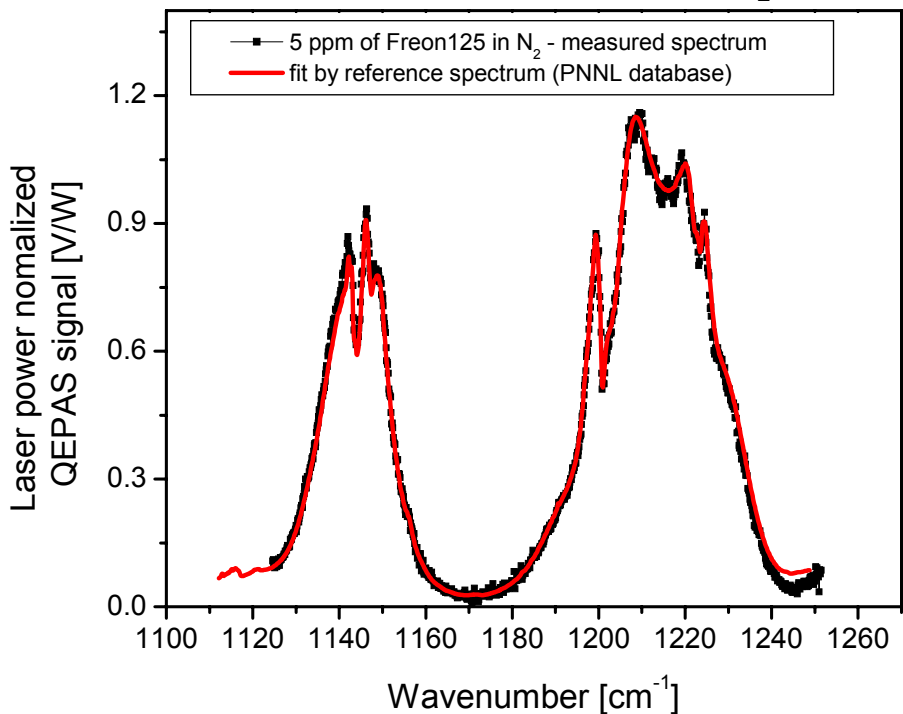


# Example Absorption Spectra of Broadband Absorbing Molecules



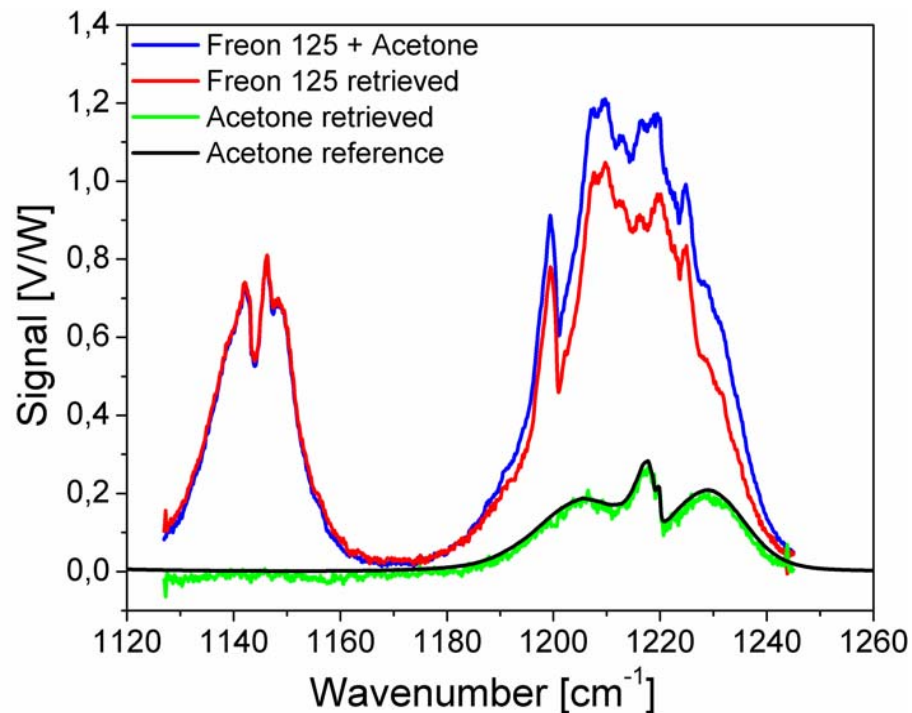
# Spectroscopy of Broadband Absorbers with Widely Tunable EC-QCL at $\lambda = 8.4 \mu\text{m}$

QEPAS concentration measurement of Freon 125 (5ppm mixture in  $\text{N}_2$ )



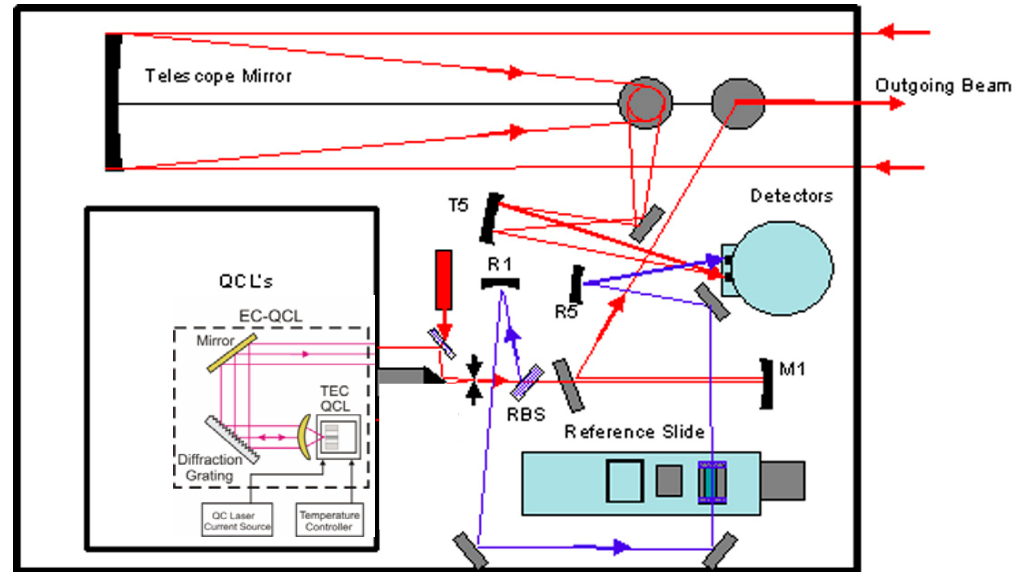
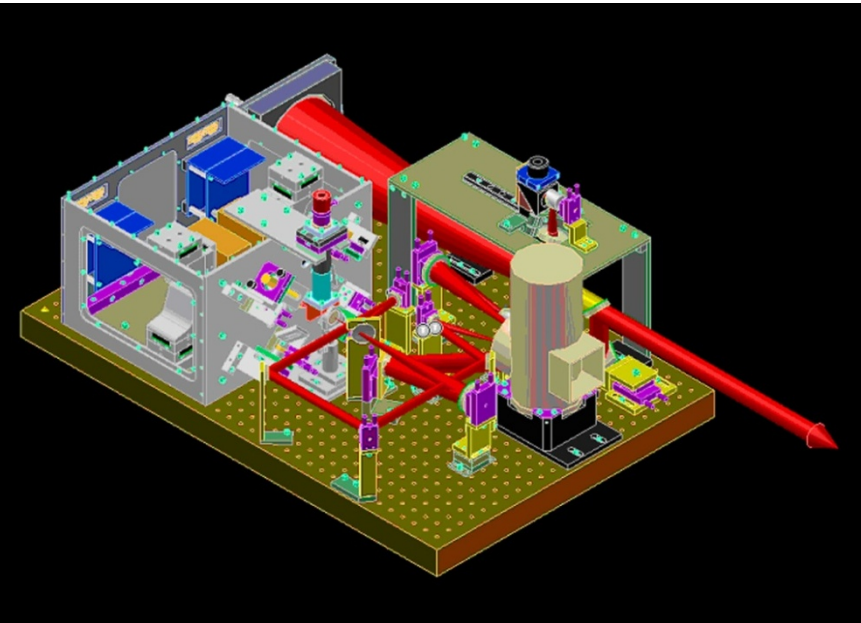
- Minimum detection limit ( $1\sigma$ ) of **~3 ppb** was obtained for Freon 125 with an average laser power of 6.6 mW

QEPAS concentration measurement of a Freon 125 and acetone mixture



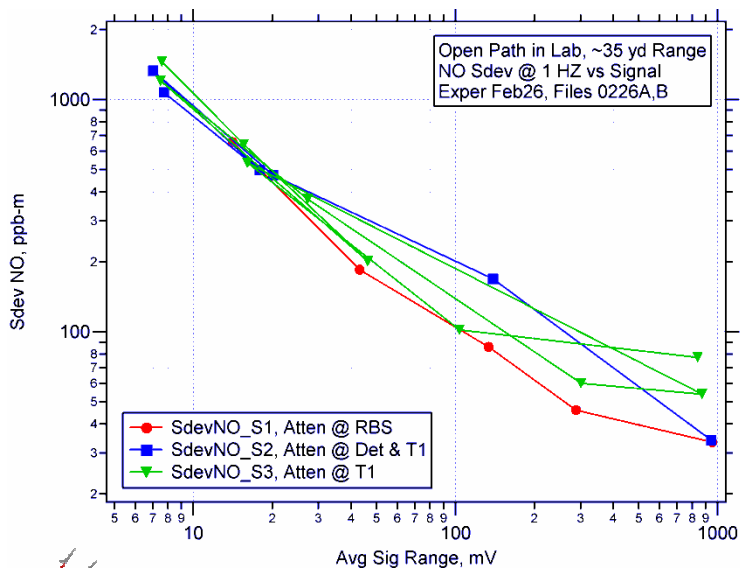
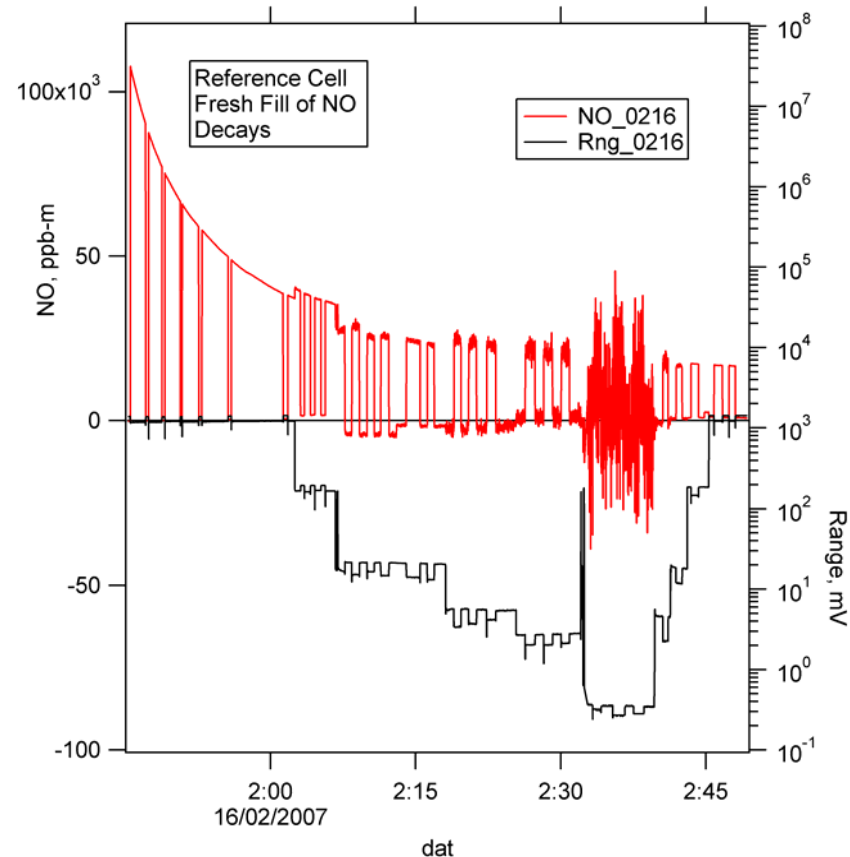
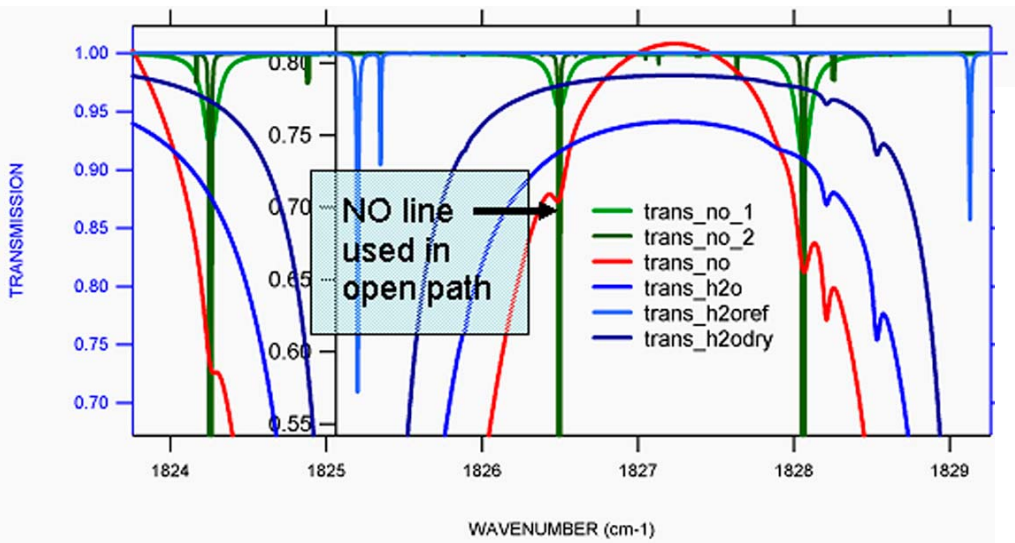
- Wide tunability enables excellent molecular selectivity for broad band absorbers

# Design of an EC-QCL Based Remote Sensing System



- An upgraded version of a four-laser pulsed QCL system
- The optical set-up, electronics and control software modified for CW-QCL operation
- First tests performed with a DFB CW-QCL operating at  $\sim 5.5\mu\text{m}$  (output power  $\sim 0.3\text{mW}$ )

# Laboratory System Performance Test



$$\text{for } D^* = 1.4 \times 10^{10} \rightarrow \text{NEP} = 1.6 \times 10^{-10}$$

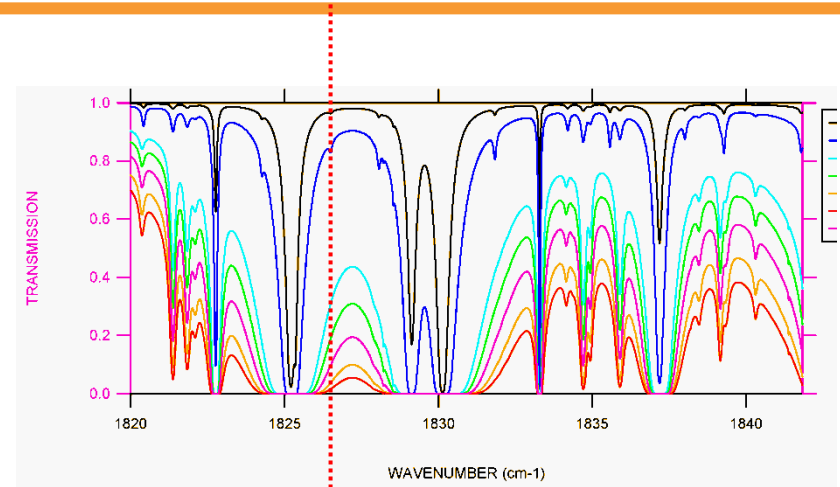
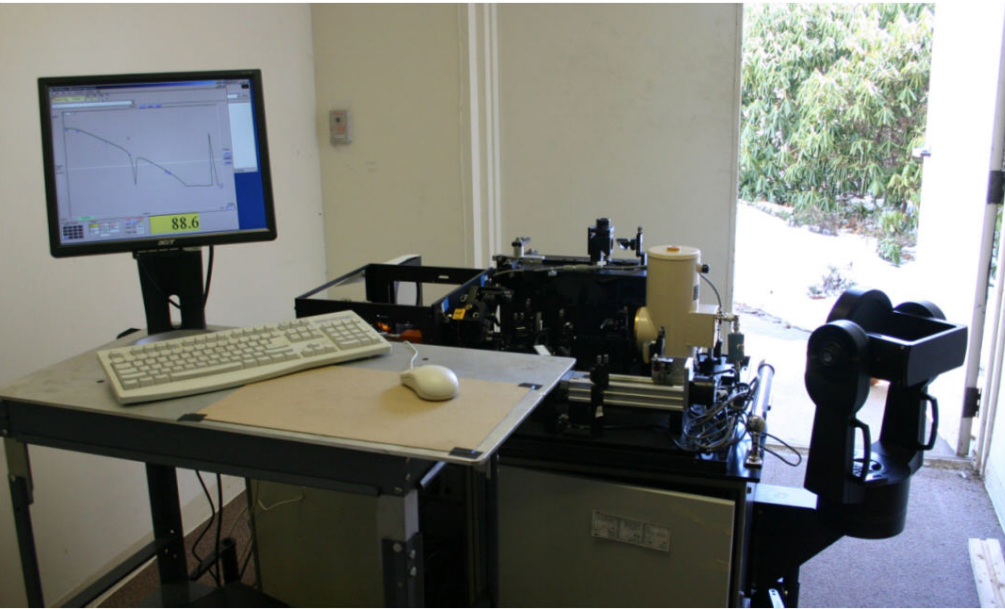
$$\alpha_o \approx 5 \times 10^{-7} \text{ (ppb-m)}^{-1}$$

$$\sigma(\text{NO}) = (\text{NEP} / P_{\text{received}}) / \alpha_o$$

$$\sigma(\text{NO}) \approx 10^{-4} / P_{\text{received}} \text{ [ppb-m]}$$

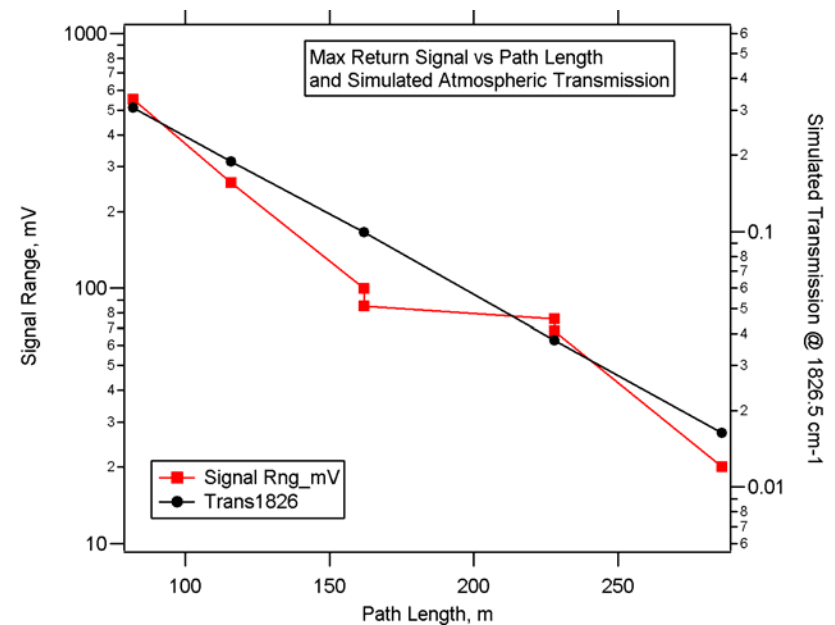


# Outdoor Open Path Measurements (Influence of Atmospheric Transmission)



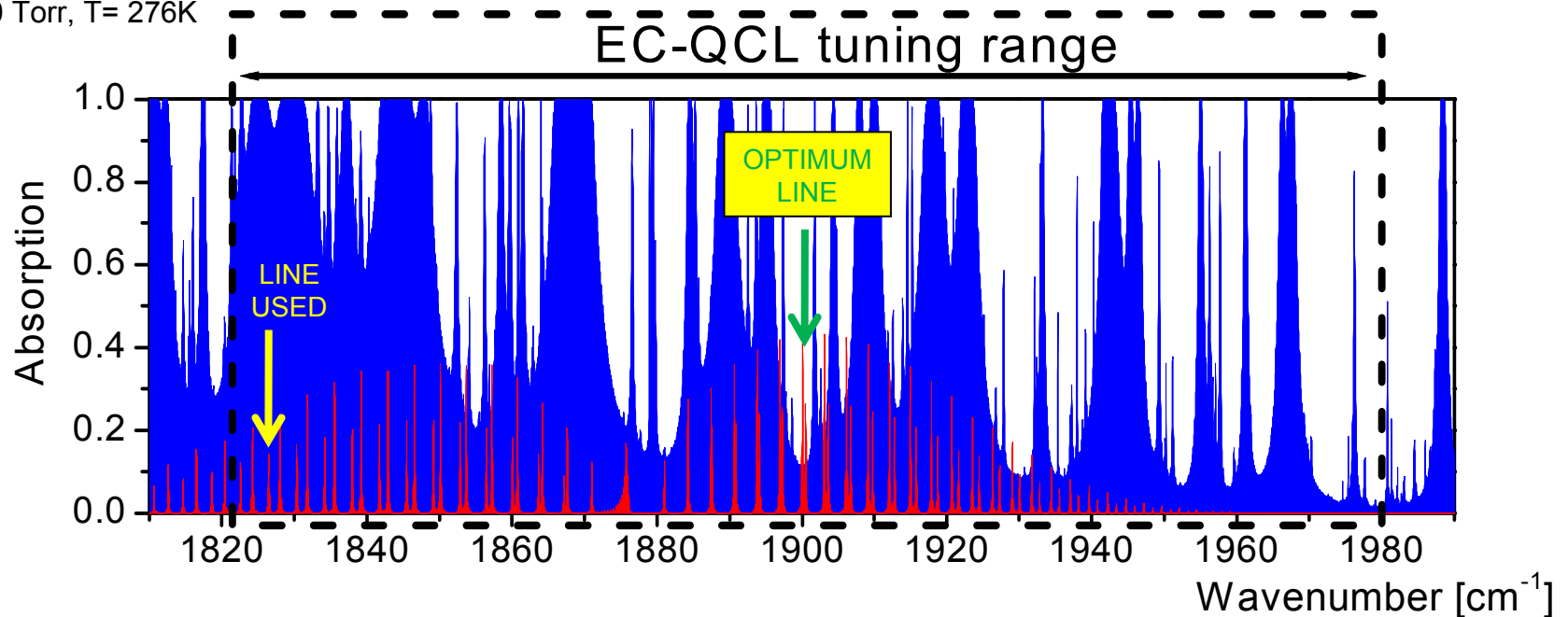
Open Path  
Measurements  
CW QCL  
1826  $\text{cm}^{-1}$

- Ranges  
(1/2  
total)
- #1, 41m
  - #2, 58m
  - #3, 81m
  - #4, 114m
  - #5, 143m



# High resolution spectroscopy with a 5.3 $\mu\text{m}$ EC-QCL

286m open path  
H<sub>2</sub>O mixing ratio: 0.006  
CO<sub>2</sub> mixing ratio: 380 ppm  
P=760 Torr, T= 276K



EC-QCL allows selection of an absorption line with:

- Higher Line Intensity
- Lower Spectral Interference
- Higher Atmospheric Transmission

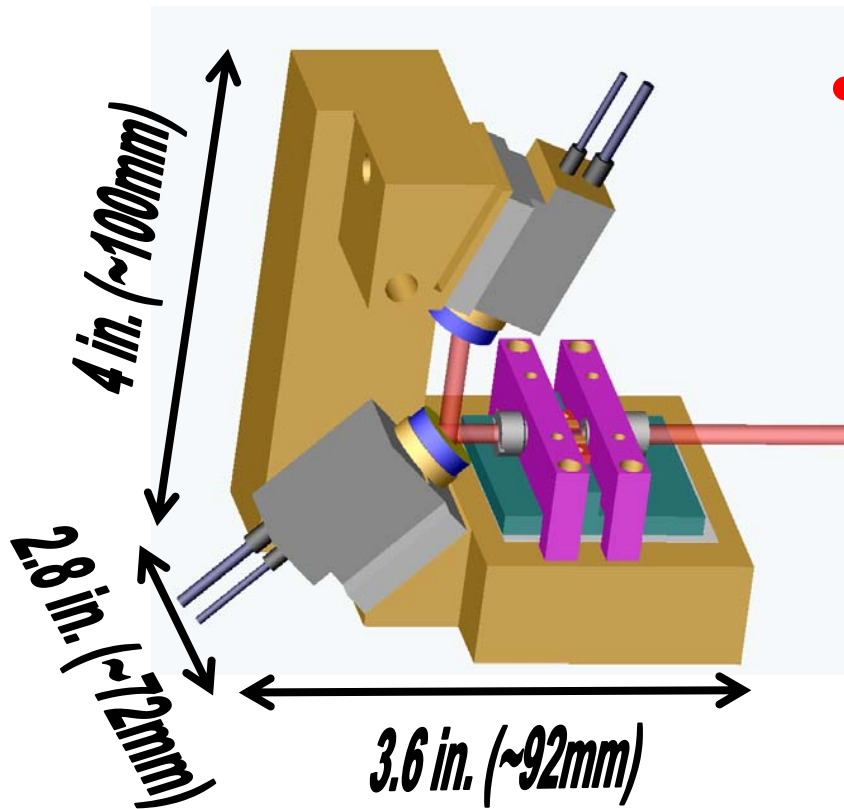
# EC-QCL for Laser Spectroscopy

<b><u>REQUIREMENTS</u></b>	<b><u>IR LASER SOURCE</u></b>
<b>Sensitivity (% to ppt)</b>	<b>Power</b>
<b>Selectivity</b>	<b>Single Mode Operation and Narrow Linewidth</b>
<b>Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers</b>	<b>Tunable Wavelength</b>
<b>Directionality or Cavity Mode Matching</b>	<b>Beam Quality</b>
<b>Rapid Data Acquisition</b>	<b>Fast Time Response</b>
<b>Room Temperature Operation</b>	<b>No Consumables</b>
<b>Field deployable</b>	<b>Compact &amp; Robust</b>

# Impact of EC-QCL on Remote Sensing

- **High beam quality**
  - Excellent directionality
  - High collection efficiency
- **High power (CW and pulsed)**
  - Inexpensive retro-reflectors
  - Diffuse scattering from arbitrary objects ( $\sim L^{-2}$ )
  - Long range operation  $\leftrightarrow$  High sensitivity
- **Broad tunability with high spectral resolution**
- **Pulsed operation (ns pulses)**
  - Atmospheric turbulence is frozen ( $\sim 0.1$  ms)
  - High peak powers (see above)
  - Intra-pulse spectral analysis can be used (100-1000ns, fast detector is required)
- **Direct modulation capability**
  - AM with injection current (WM, FM for QCLs)

# New design of fast broadly tunable EC-QCLs (2007/8)



- New optical configuration  
*Folded cavity (configuration #1)*
- Fast tuning capabilities:
  - Coarse Broadband Scanning  
( $\sim 55 \text{ cm}^{-1}$  @  $5 \mu\text{m}$ ) **up to 5 KHz**  
(compared to available technologies <10Hz)
  - High resolution mode-hop free tuning ( $\sim 3.2 \text{ cm}^{-1}$  @  $5 \mu\text{m}$ )  
**up to 5 KHz**  
(compared to available technologies 100-200 Hz)

# Summary & Future Directions

- **Widely tunable, continuous wave and thermoelectrically cooled EC-QCLs operating at 5.3 $\mu\text{m}$  and 8.4 $\mu\text{m}$**  were demonstrated
- **Mode-hop free wavelength tuning** enables high resolution (**<0.001 $\text{cm}^{-1}$** ) spectroscopic applications
- **PZT actuated mode tracking system** allows employing gain chips operating at both shorter and longer wavelengths in the same system
- Wavelength tunability up to **15%** of the center wavelength was demonstrated
- Output optical power up to **50 mW**
- The main limitation at the moment is the scanning speed (currently under investigation and will be significantly improved in our next generation EC-QCL designs  $\rightarrow$  kHz tuning rates)
- The novel broadly wavelength tunable quantum cascade lasers enable **new applications in laser based trace gas sensing**
  - Sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs
  - Multi-species detection

# Acknowledgements

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## **Rice University:**

- **Prof. Frank K. Tittel**
- **Prof. Robert F. Curl**
- **Rafal Lewicki – grad student**

## **Aerodyne Research Inc.:**

- **Dr. Barry McManus**
- **Dr. Mark Zahniser**
- **Dr. David Nelson**



# ORS Methods Development for Perimeter Air Monitoring During Manufactured Gas Plant Cleanups

USEPA Workshop on Remote Sensing of Emissions:  
New Technologies and Recent Work

OAQPS, OSWER, ORD  
April 2, 2008

Stephen F. Takach, Ph.D.  
Gas Technology Institute



# ORS Methods Development for Perimeter Air Monitoring During Manufactured Gas Plant Cleanups

## Presentation Contents

- **The Gas Technology Institute**
- **Industry Need**
- **GTI Methods Development Project**

# The Gas Technology Institute



- **The Gas Technology Institute is the leading research, development, and training organization serving the natural gas industry and energy markets**
- **GTI is dedicated to meeting the nation's energy and environmental challenges by developing technology-based solutions for consumers, industry, and government which are reliable, affordable, safe, and clean**
- **Accomplishments having major market impact for its 350+ member companies include:**
  - **creation of a guidebook for the remediation and management of former MGP sites**
  - **development of chemical-biological treatment methods for MGP-contaminated soil**

## Industry Need

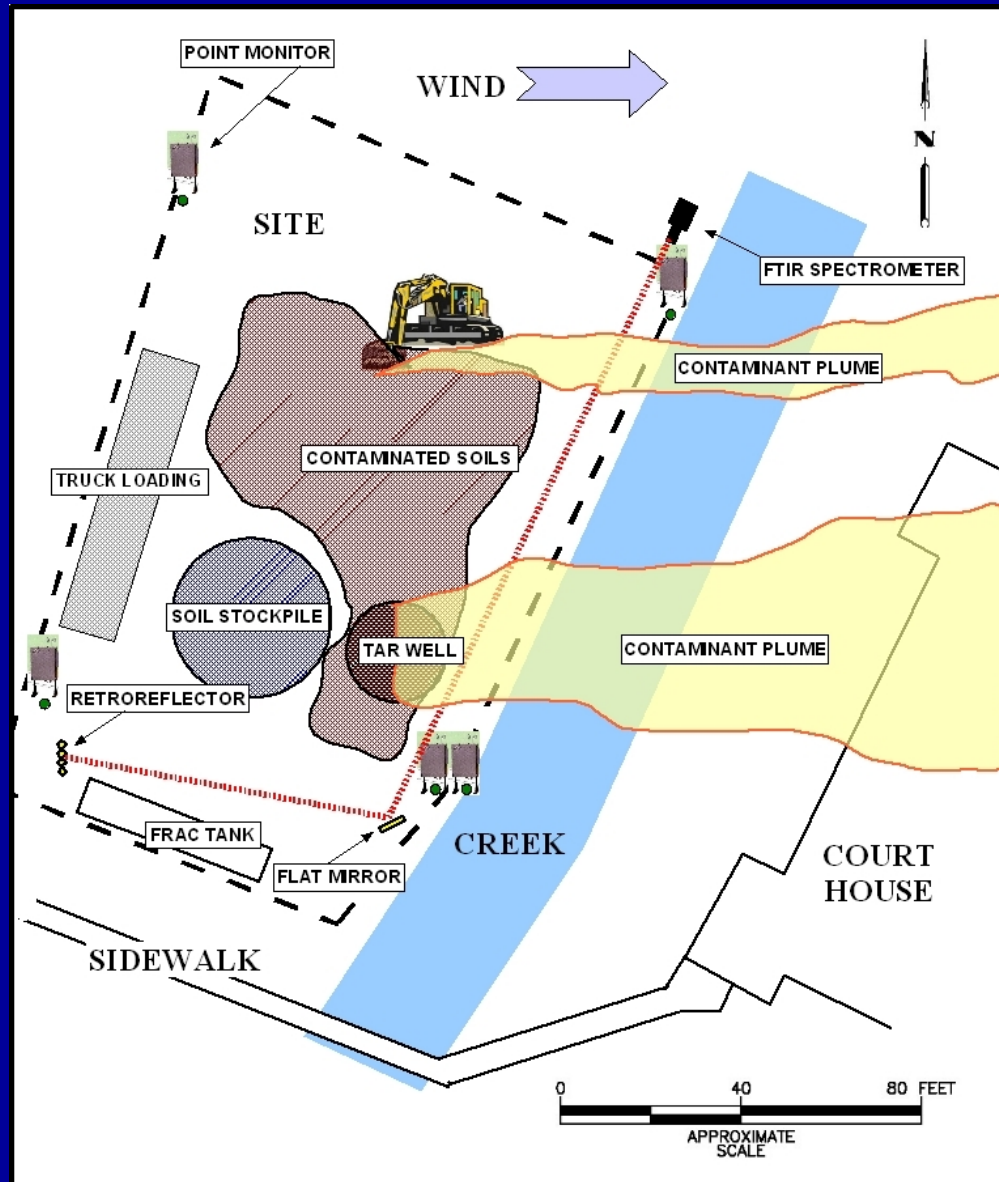


- From the mid-1880s until about 1950, manufactured gas plants generated combustible gas from coal and oil, and were widely used to meet heating, lighting, and cooking needs in cities and towns throughout the US
- Large volumes of coal tar created as a by-product of this process were often left behind in subsurface structures when these plants were dismantled, and are an ongoing source of contamination
- Utility companies are usually the responsible parties for site cleanup and redevelopment, having inherited most former MGP sites
- Although numerous VOCs and PAHs are emitted via the air pathway during MGP site cleanups, from a community exposure perspective, the controlling contaminants are typically benzene and naphthalene

## Issues and Concerns

- **Although the potential for long-term health impacts is generally considered small, local communities are not necessarily convinced, and there are several pending and historical lawsuits alleging unacceptable exposure**
- **Site owners are at legal risk:**
  - proximity of MGP sites to the community (as opposed to Superfund sites)
  - perception of risk due to odors (if it smells, it must be harmful)
  - a highly visible responding party (my gas company must have deep pockets)
- **Data quality issues are inherent with fixed-station (point-type) monitoring networks typically employed:**
  - naphthalene is difficult to monitor in real time
  - plumes often pass between monitoring stations undetected (spatial data representativeness)
  - the significance of long-term health impacts cannot be assessed until “after the fact”
- **An estimated 3,000 to 5,000 former MGP sites exist across the country alone**

# Spatial Data Representativeness Issue With Point Monitoring



# Open-Path FTIR Feasibility Demo at Northeast Utilities MGP Site, Easthampton, MA (Electric Power Research Institute, 2002)



## Atmos Energy's Shelby Street Former MGP Site Cleanup

- **Cleanup of the Shelby Street former MGP site in Bristol, Tennessee, was performed by Atmos Energy Corporation in November 2004**
- **Because the eastern site perimeter was within 30 meters of the Sullivan County Court House and the Bristol Police Department, it was incumbent upon Atmos to design a perimeter air monitoring program which protected both the local community and their own legal interests**
- **Atmos chose to employ open-path FTIR spectroscopy based on the EPRI results and a dissatisfaction with traditional, point monitoring during three prior MGP site cleanups**
- **Atmos's consultant, Minnich and Scotto, developed a data-management and reporting software program which successfully facilitated real-time, mitigative decision-making to ensure that pre-established, 24-hour-averaged, acceptable ambient air concentrations (AAACs) were never exceeded anywhere in the downwind community**
- **Ten-minute-averaged action levels (ALs) were assigned as conservative proxies for the 24-hour AAACs, and mitigative decision-making was based on the occurrence of AL exceedances at the nearest community receptor**

# GTI Methods Development Project

## Project Genesis and Objectives

- In 2005, GTI became very interested in Atmos Energy's success in applying their real-time ORS methodology during the Shelby Street former MGP site cleanup
- The Operations Technology Development (OTD) group, a consortium of GTI utility companies, is funding this 26-month program, "ORS Methods Development for Perimeter Air Monitoring During MGP Site Cleanups"
- The ultimate goal of this project is to perform the necessary R&D to make the ORS methodology for MGP site cleanups available to all GTI member companies
- **Project objectives:**
  - to compare ORS-based and traditional point-monitoring approaches
  - to enhance existing data-management and reporting software
  - to create a Methods Guidance document
- **ORS field work was performed during two active MGP site cleanups**
  - Pitney Court site, Chicago, IL (Peoples Energy)
  - Coney Island site, Brooklyn, NY (KeySpan)



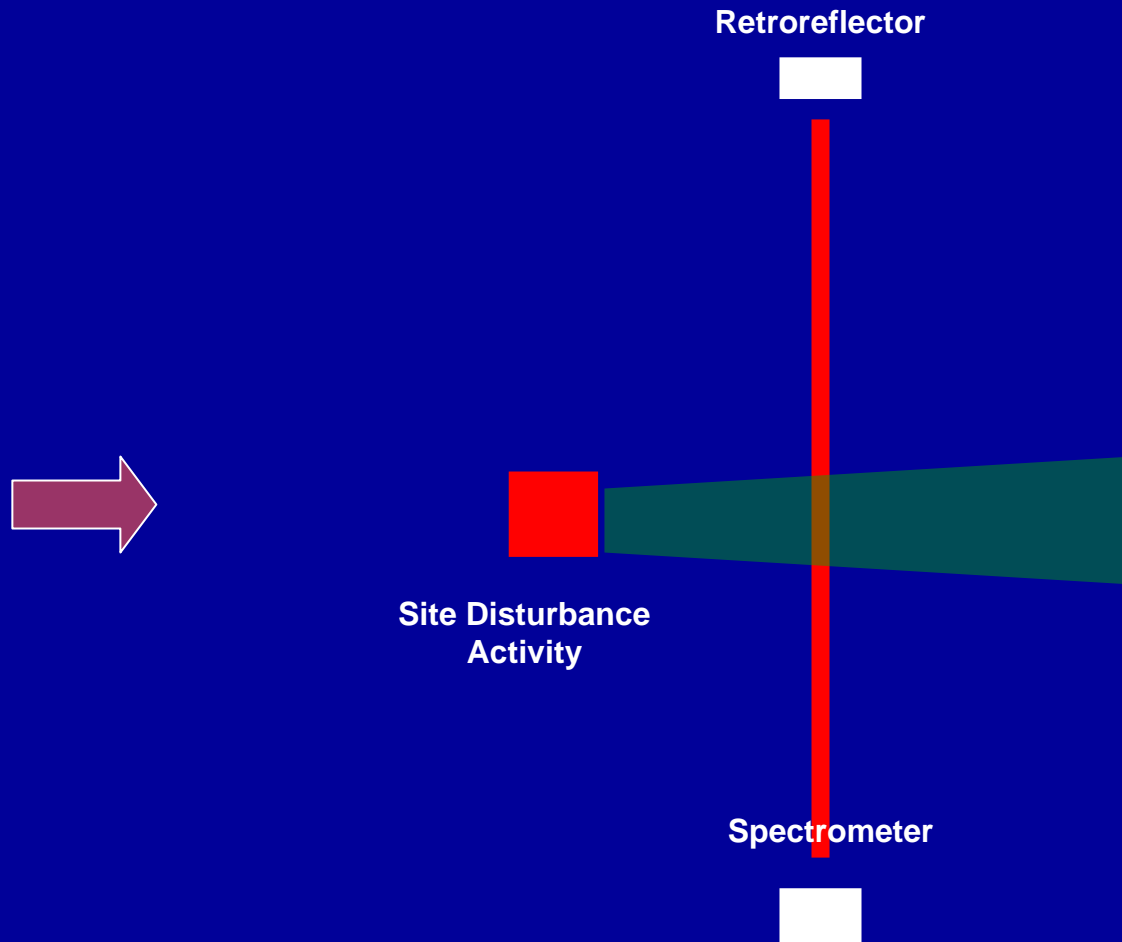
## Evaluation Committee

- **An Evaluation Committee was established at the project onset to maintain a focused direction and provide technical review of all deliverables**
- **The Evaluation Committee is comprised of representatives from diverse project stakeholders:**
  - **Alabama Gas Company (sponsor)**
  - **Atmos Energy Corporation (sponsor\*)**
  - **Baker & McKenzie, LLC**
  - **Gas Technology Institute**
  - **Illinois Environmental Protection Agency**
  - **KeySpan (a National Grid Company) (sponsor)**
  - **National Fuel Gas (sponsor)**
  - **New York State Department of Environmental Conservation**
  - **Northwest Natural (sponsor)**
  - **Peoples Energy Corporation**
  - **USEPA - National Environmental Response Team**
  - **USEPA - Office of Air Quality Planning and Standards**
  - **USEPA - Office of Research and Development**
  - **Wisconsin Bureau of Environmental and Occupational Health**

## Modified Cross-Sector-Averaging Technique

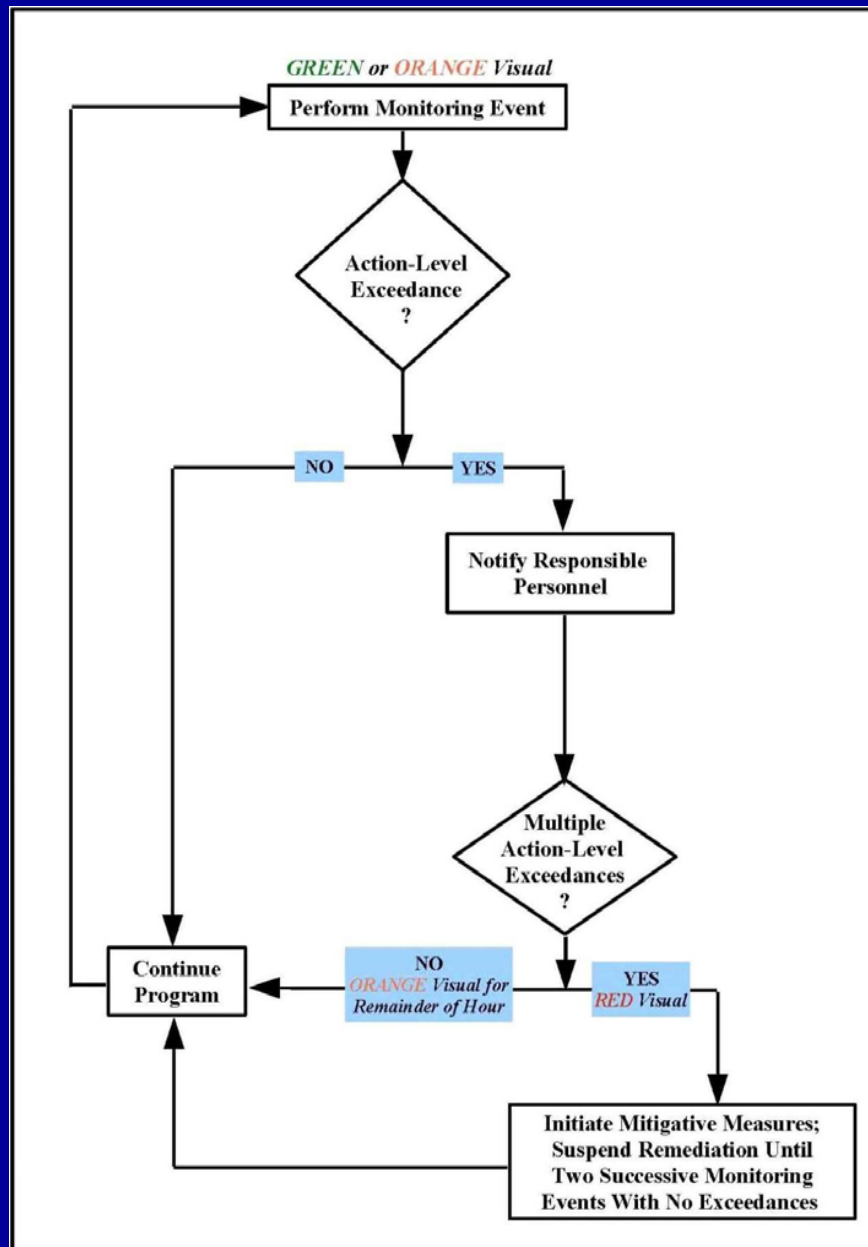
- In 1994, the USEPA (Region 7) developed the ***cross-sector-averaging technique***, an open-path FTIR air monitoring method for assessing downwind impacts from large industrial sources
- In 2003, Minnich and Scotto developed a technique refinement (applied at Atmos Energy's Shelby Street site) which provides absolute assurance, in real time, that emissions generated during the cleanup of former MGP sites do not pose adverse impacts to the local community
- The ***modified cross-sector-averaging (MCSA) technique*** employs the following three-step approach:
  1. Make a 10-minute-averaged FTIR measurement immediately downwind of the source
  2. Divide the path-integrated concentration by the plume width to yield a ***representative point concentration (RPC)*** across the plume as it crosses the FTIR beam
  3. Based on the onsite meteorology, apply a ***dilution factor*** to the RPC to assess compliance with a 10-minute-averaged AL at the nearest community receptor – a conservative proxy for the 24-hour-averaged AAAC

## Modified Cross-Sector-Averaging Technique (Cont'd)



dimensionally, ppm-m divided by m equals ppm

# MCSA Technique for Former MGP Sites: Decision Rule



## Consistency With USEPA's Triad Approach ([www.comptech.com](http://www.comptech.com))

- Triad manages hazardous waste site decision uncertainty through the employment of systematic planning, dynamic work strategies, and real-time measurement technologies
- Triad's primary intent is "to foster modernization of technical practices for characterizing and remediating chemically contaminated sites"
- The MCSA technique is fully consistent with Triad, and is used to eliminate mitigative decision-making uncertainty in the context of assessing community exposure during MGP site cleanups
- Conclusive evidence of acceptable community exposure is continually demonstrated, in real time, through:
  - full containment of the plume(s) at all times (systematic planning)
  - use of conservative, data-management and reporting software (dynamic work strategies)
  - use of open-path FTIR spectroscopy (real-time measurement technique)

## Pitney Court Site, Chicago, Illinois (Peoples Energy)



## Pitney Court Site, Chicago, Illinois (Peoples Energy) (Cont'd)



## Coney Island MGP Site, Brooklyn, New York (KeySpan)





## Coney Island MGP Site, Brooklyn, New York (KeySpan) (Cont'd)



## Coney Island MGP Site, Brooklyn, New York (KeySpan) (Cont'd)



# Data-Management and Reporting Software System

**FTIR Event 608 Made**

**FTIR Event Analysis**

Event Information: Event Date: 05/09/2007, End Time (local): 13:00, Measurement Configuration: 1, Monitoring Day: 2, Event #: 29

Project Information: Site Name: New York, Site Project ID: 2

Flame Calculation: Source Wt/ft (in): 1.0, Lateral Flame Spread (in): 4.8, Lateral Flame Meander (in): 9.2, Flame Wt/ft (in): 13.0

Applicable Dilution Factors: Site Perimeter: 0.1600, Community Exposure: 0.1000

Source Receptor Information: Source Type: ESCV 1, ESCV 2, Dimension (999 # no source exists): 1, 1, Source Wt/ft (in): 1, 1, Source Beam Dist. (measured feet): 20, 15, Distance from beam to nearest receptor: Perimeter Exposure (measured 5 m): 25, 30, Community Exposure (measured 5 m): 30, 40

Stability Class: B, C, D, E

Mean Wind Direction (degrees): 134, Acceptable Mean W/D Range: 3.9 to 11.5, Mean Wind Speed (m/s): ND, Sigma Theta (degrees): 13.5

Target Compound	FTIR (ppm-m)		Point Concentration (ug/m <sup>3</sup> )				
	Conc.	MDL	Flame Meas.	Site Perimeter Meas.	Community Meas.	Community AL	
ethyl benzene	ND	4.95	1953	(274)	2400	(179)	2400
propylene	ND	3.7	1226	(208)	2000	(133)	2000
styrene	ND	3.85	1272	(211)	2000	(137)	2000
chlorobenzene	ND	0.2	75	(12)	1050	(8)	150
carbon disulfide	ND	2.5	229	(220)	2000	(85)	2000
styrene	ND	0.95	284	(47)	2000	(131)	2000
ammonia	ND	0.13	19	(2)	3000	(1)	3000
toluene	ND	2.9	800	(133)	2000	(162)	2000
styrene	ND	0.95	311	(52)	21000	(34)	17110
benzene	ND	2.6	638	(106)	3710	(89)	1240
naphthalene	3.3626	1.04	1597	265	820	173	280

Legend: (N): MDL (default in parenthesis), (M): # N, AL 1, (L): AL, (G): # L, N, AL, (R): # L, AL, (S): # L

Records: 40 of 95

PICMET-2 Event Screen



Portable Meteorological Station



PICMET-2 Computer



Open-Path FTIR (right) and UV (left) Spectrometers

# Data-Management and Reporting Software Screen (Coney Island Site)

**Automated Mode - Coney Island (GTI-02)**

Event Analysis	Set-up	Event Reports																																																																																																						
<b>Event Information</b> * Event Date: 05/08/2007 * End Time (local): 1050 Measurement Configuration #: 1 Monitoring Day: 2    Event #: 16 <b>Onsite Activity</b> <input checked="" type="checkbox"/> Removal of Contaminated Soil <input type="checkbox"/> In-Situ Treatment <input checked="" type="checkbox"/> Maint. of Stockpiled Materials <input type="checkbox"/> No Activity																																																																																																								
<b>Project Information</b> Site Name: Coney Island    Site/Project ID: GTI-02																																																																																																								
<b>Plume Calculation</b> Source Width (m): 1.0 Lateral Plume Spread (m): 4.8 Lateral Plume Meander (m): 6.2 Plume Width (m): 12.0																																																																																																								
<b>Applicable Dilution Factor</b> Fenceline Exposure: 0.1660 Offsite Exposure: 0.1080																																																																																																								
<b>Source-Receptor Information</b> <table border="1"> <thead> <tr> <th></th> <th>Source 1</th> <th>Source 2</th> </tr> </thead> <tbody> <tr> <td>Source Type</td> <td>EXCV</td> <td>STK PILE</td> </tr> <tr> <td colspan="3">Dimension (999 if no source exists)</td> </tr> <tr> <td>Source Width (m)</td> <td>1</td> <td>1</td> </tr> <tr> <td>Source-Beam Dist. (nearest 1m)</td> <td>20</td> <td>15</td> </tr> <tr> <td colspan="3">Distance from beam to nearest receptor</td> </tr> <tr> <td>Fenceline (nearest 5 m)</td> <td>25</td> <td>30</td> </tr> <tr> <td>Offsite (nearest 5 m)</td> <td>35</td> <td>40</td> </tr> </tbody> </table>				Source 1	Source 2	Source Type	EXCV	STK PILE	Dimension (999 if no source exists)			Source Width (m)	1	1	Source-Beam Dist. (nearest 1m)	20	15	Distance from beam to nearest receptor			Fenceline (nearest 5 m)	25	30	Offsite (nearest 5 m)	35	40																																																																														
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<b>Measurement</b> <table border="1"> <thead> <tr> <th rowspan="2">Target Compound</th> <th colspan="2">ORS (ppm-m)</th> <th colspan="4">Point Concentration (ug/m3)</th> </tr> <tr> <th>Conc.</th> <th>MDL</th> <th>Plume Meas.</th> <th>Site Perimeter Meas.</th> <th>AL</th> <th>Community Meas.</th> <th>AL</th> </tr> </thead> <tbody> <tr> <td>ethyl benzene</td> <td>ND</td> <td>4.95</td> <td>1790</td> <td>(297)</td> <td>24000</td> <td>(193)</td> <td>2400</td> </tr> <tr> <td>p-xylene</td> <td>ND</td> <td>3.70</td> <td>1338</td> <td>(222)</td> <td>22000</td> <td>(145)</td> <td>22000</td> </tr> <tr> <td>m-xylene</td> <td>ND</td> <td>3.81</td> <td>1378</td> <td>(229)</td> <td>22000</td> <td>(149)</td> <td>22000</td> </tr> <tr> <td>chloroform</td> <td>ND</td> <td>0.20</td> <td>81</td> <td>(14)</td> <td>1050</td> <td>(9)</td> <td>150</td> </tr> <tr> <td>carbon disulfide</td> <td>ND</td> <td>2.50</td> <td>640</td> <td>(100)</td> <td>37200</td> <td>(70)</td> <td>6200</td> </tr> <tr> <td>o-xylene</td> <td>ND</td> <td>0.85</td> <td>307</td> <td>(51)</td> <td>22000</td> <td>(33)</td> <td>22000</td> </tr> <tr> <td>ammonia</td> <td>ND</td> <td>0.19</td> <td>11</td> <td>(2)</td> <td>3200</td> <td>(1)</td> <td>3200</td> </tr> <tr> <td>toluene</td> <td>ND</td> <td>2.76</td> <td>867</td> <td>(144)</td> <td>3700</td> <td>(94)</td> <td>3700</td> </tr> <tr> <td>styrene</td> <td>ND</td> <td>0.95</td> <td>337</td> <td>(56)</td> <td>21000</td> <td>(36)</td> <td>17110</td> </tr> <tr> <td>benzene</td> <td>ND</td> <td>2.60</td> <td>691</td> <td>(115)</td> <td>3710</td> <td>(75)</td> <td>1240</td> </tr> <tr> <td>naphthalene</td> <td>6.2511</td> <td>1.04</td> <td>2730</td> <td>453</td> <td>830</td> <td>295</td> <td>280</td> </tr> </tbody> </table> <p>Notes: [ MDL default in parenthesis]    <b>Brown</b> if ½ AL ≤ [ ] &lt; AL  <b>Green</b> if [ ] &lt; ½ AL    <b>Red</b> if AL ≤ [ ]</p>			Target Compound	ORS (ppm-m)		Point Concentration (ug/m3)				Conc.	MDL	Plume Meas.	Site Perimeter Meas.	AL	Community Meas.	AL	ethyl benzene	ND	4.95	1790	(297)	24000	(193)	2400	p-xylene	ND	3.70	1338	(222)	22000	(145)	22000	m-xylene	ND	3.81	1378	(229)	22000	(149)	22000	chloroform	ND	0.20	81	(14)	1050	(9)	150	carbon disulfide	ND	2.50	640	(100)	37200	(70)	6200	o-xylene	ND	0.85	307	(51)	22000	(33)	22000	ammonia	ND	0.19	11	(2)	3200	(1)	3200	toluene	ND	2.76	867	(144)	3700	(94)	3700	styrene	ND	0.95	337	(56)	21000	(36)	17110	benzene	ND	2.60	691	(115)	3710	(75)	1240	naphthalene	6.2511	1.04	2730	453	830	295	280
Target Compound	ORS (ppm-m)			Point Concentration (ug/m3)																																																																																																				
	Conc.	MDL	Plume Meas.	Site Perimeter Meas.	AL	Community Meas.	AL																																																																																																	
ethyl benzene	ND	4.95	1790	(297)	24000	(193)	2400																																																																																																	
p-xylene	ND	3.70	1338	(222)	22000	(145)	22000																																																																																																	
m-xylene	ND	3.81	1378	(229)	22000	(149)	22000																																																																																																	
chloroform	ND	0.20	81	(14)	1050	(9)	150																																																																																																	
carbon disulfide	ND	2.50	640	(100)	37200	(70)	6200																																																																																																	
o-xylene	ND	0.85	307	(51)	22000	(33)	22000																																																																																																	
ammonia	ND	0.19	11	(2)	3200	(1)	3200																																																																																																	
toluene	ND	2.76	867	(144)	3700	(94)	3700																																																																																																	
styrene	ND	0.95	337	(56)	21000	(36)	17110																																																																																																	
benzene	ND	2.60	691	(115)	3710	(75)	1240																																																																																																	
naphthalene	6.2511	1.04	2730	453	830	295	280																																																																																																	
<p style="text-align: right;">Start    Stop    Exit</p>																																																																																																								

# Methods Guidance Document: Contents

## **Preface**

## **Forward**

### **1 Introduction**

- 1.1 Context
- 1.2 Content
- 1.3 Terminology

### **2 Background**

- 2.1 Environmental and Public Health Concerns
- 2.2 The Data Quality Objective Process
- 2.3 Traditional Monitoring Methods

### **3 Method Description**

### **4 Measurement Needs**

- 4.1 Path-Integrated Concentration Data
- 4.2 Meteorological Data
- 4.3 Spatial

### **5 Special Considerations**

- 5.1 Reporting and Data-Management Software
- 5.2 Facilitation of Mitigative Decision-Making
- 5.3 Logistics

### **6 References**

## **Attachments**

**A Cost Comparison: MCSA Technique vs. Traditional PAM Approach**

**B MCSA Methods Testing**

## ORS-Based Perimeter Air Monitoring: Identified Benefits

- **Cost**
  - The MCSA technique is substantially less expensive than fixed-station, point-monitoring systems typically employed during MGP site cleanups
- **Community Acceptance / Litigation Avoidance**
  - The high-tech nature of open-path FTIR spectroscopy allays public fear and invariably leads to the community's endorsement of the selected cleanup remedy
  - Public confidence reduces the occurrence of psychosomatic symptoms which can lead to well-intentioned, but unnecessary, lawsuits
  - The permanent, electronic retention of the records evidencing insignificant community exposure, together with the raw FTIR measurement spectra themselves, provide a compelling defense against legal claims – thereby reducing the risks of frivolous lawsuits

## GTI's Vision



- **This innovative technology improves the management of MGP site cleanups by revolutionizing how perimeter air monitoring is performed**
- **Legal and political roadblocks to the effective and expeditious cleanup of MGP sites are eliminated**
- **Each MGP site cleanup is performed within a “partnership triangle” comprised of the site owner, responsible regulators, and the local Community**



# Landfill Applications of Optical Remote Sensing Technology

Presentation for 2nd International Workshop  
on Remote Sensing of Emissions at EPA-RTP

*Susan Thorneloe* [Thorneloe.Susan@epa.gov](mailto:Thorneloe.Susan@epa.gov)

*Eben Thoma, PhD* [Thoma.Eben@epa.gov](mailto:Thoma.Eben@epa.gov)

*Research Triangle Park, North Carolina*



**Office of Research and Development**  
National Risk Management Research Laboratory  
Air Pollution Prevention and Control Division

April 2, 2008



# Presentation Outline

- Landfill gas health and environmental concerns
- ORS RPM Field Test Programs
  - Completed research and available reports
  - Work in progress
- Conclusions





# Landfill Gas (LFG) Health & Environmental Concerns

- Landfills are the largest source of methane in the U.S.
  - Emissions result from decomposition of biodegradable waste in municipal landfills; construction & demolition debris landfills; industrial landfills; and brownfield sites
- LFG contains 40-60% methane, 60-40% CO<sub>2</sub>, and trace constituents of volatile organic compounds (VOC), hazardous air pollutants (HAPs), and persistent bioaccumulative toxics
- Landfills identified in EPA's Urban Air Toxic Strategy for residual risk evaluation
  - More than 30 HAPs detected in LFG
  - Updated LFG concentration data suggest H<sub>2</sub>S concentration may be increasing (EPA, 2007 - <http://www.epa.gov/ORD/NRMRL/pubs/600r07043/600r07043.pdf> )
- Concern for explosive potential of the gas and odor nuisance

# Trends Impacting Emissions

- Adoption of wet/bioreactor operations where
  - Porous materials are used as alternative covers to promote infiltration (resulting in larger loss of fugitive emissions)
  - Time lag occurs between liquid additions and LFG capture/control
- More widespread use of landfills for recreational use or development
  - Desire is to put controls in and walk away. However, effective LFG control requires maintenance of cap and well field over time.
  - ORS can be used to identify appropriate sites and assess existing LFG control.
- Increasing interest in improved GHG inventories; quantifying uncontrolled emissions from landfills is considered key to implementing successful mitigation strategies.



# ORS Technology Using Radial Plume Mapping (RPM)

- The RPM method using ORS instrumentation is considered preferred approach for characterizing fugitive emissions from large area sources such as landfills. However, landfills pose unique challenges as compared to other area emission sources.
- Research was sponsored by the U.S. EPA's Office of Superfund Remediation and Technology Innovation, Technology Integration and Information Branch under its Monitoring and Measurement for the 21st Century (21M2) initiative.
- For further information on ORS technology—

<http://www.clu-in.org/programs/21m2/openpath/>

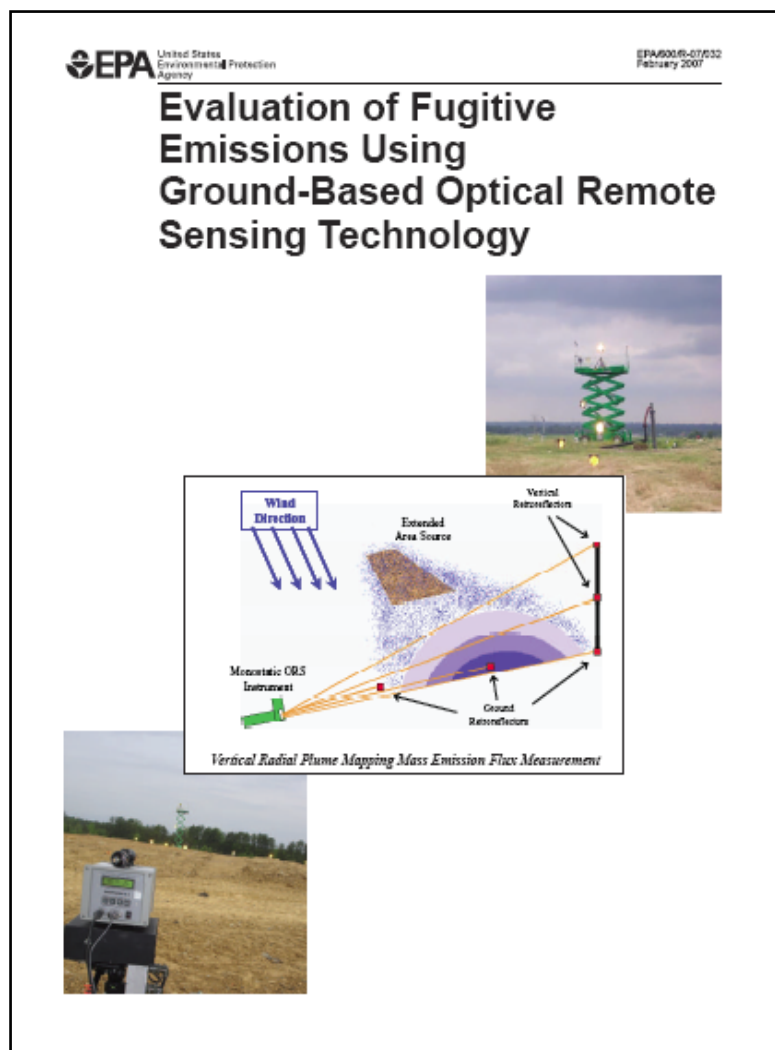
- For further information on EPA protocol for conducting ORS measurements— <http://www.epa.gov/ttn/emc/tmethods.html>

# Scanning Boreal Tunable Diode Laser System & Open-path Fourier Transform Infrared (OP- FTIR) Spectrometer



# Final Report from EPA Field Tests Using ORS Technology

- Available at:  
<http://www.epa.gov/ORD/NRMRL/pubs/600r07043/600r07043.pdf> )
  - Provides overview of ORS technology and application to landfills
  - Includes summary of previous field tests at brownfield and superfund sites
  - Includes results from plume capture study conducted in 2006



# Orange County Demonstration in 2005



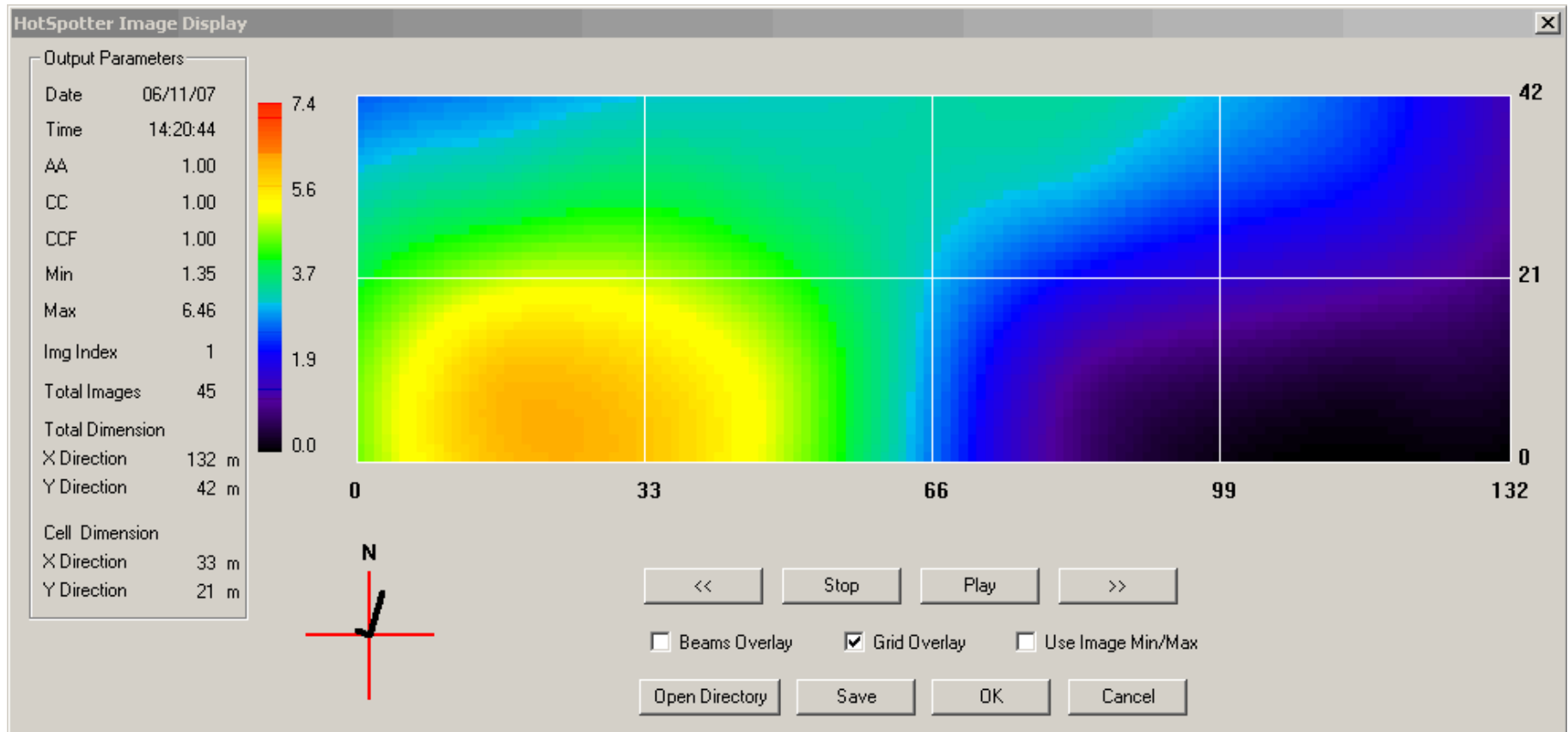


# Radial Plume Mapping Software

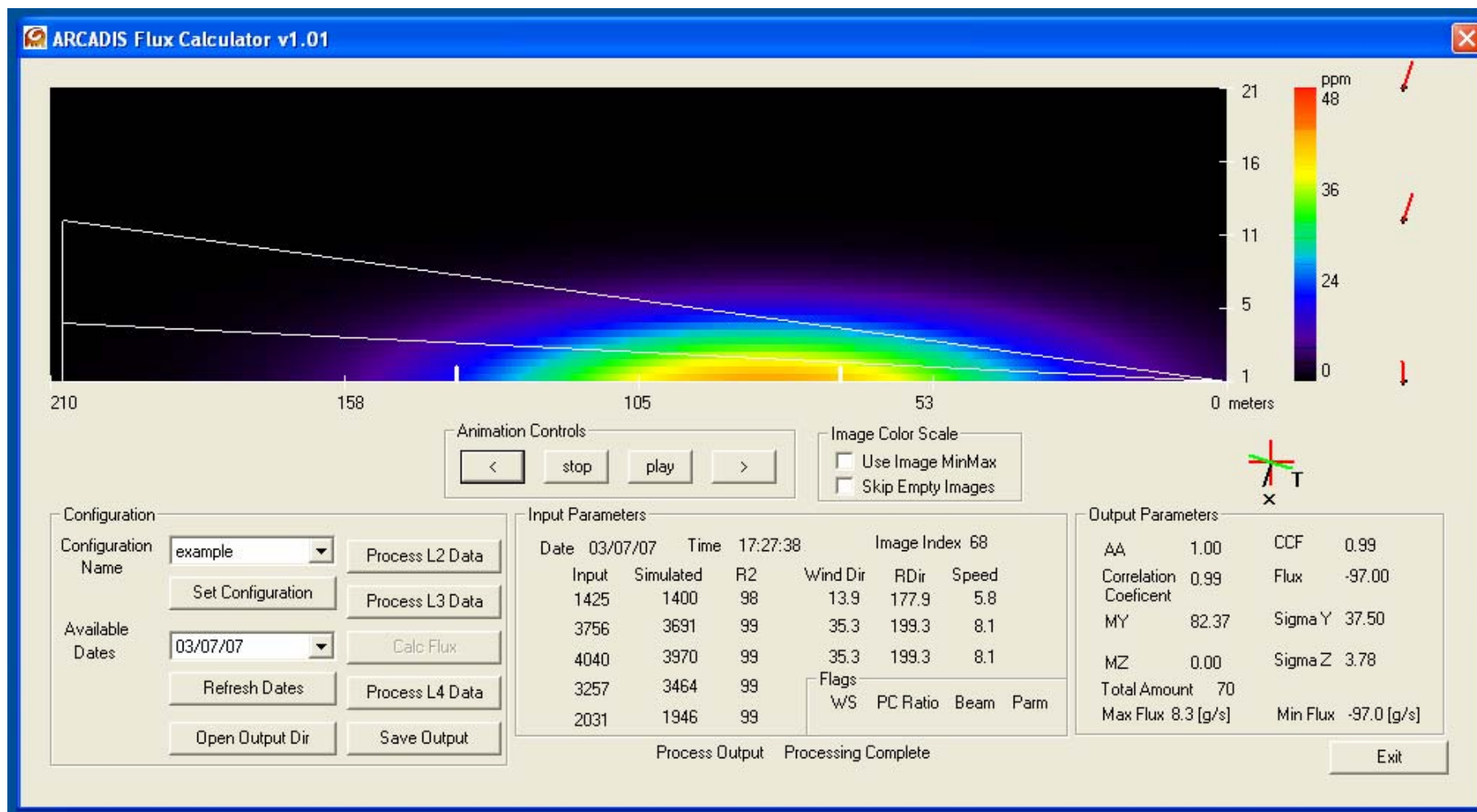
- ARCADIS RPM software was used during the demonstration
- The software displays the measured concentrations, and horizontal and vertical plume maps in near real-time



# Horizontal RPM Output from Software



# Vertical RPM Output from Software





# EPA Landfill Gas Publications Providing ORS-RPM Data

*Measurements of Fugitive Emissions at Region I Landfill (EPA-600/R-04-001, Jan 2004)*

<http://www.epa.gov/appcdwww/apb/EPA-600-R-04-001.pdf>

*Evaluation of Former Landfill Site in Fort Collins, Colorado Using Ground-Based ORS Technology (EPA-600/R-05/-42, April 2005)*

<http://www.epa.gov/ORD/NRMRL/pubs/600r05042/600r05042.pdf>

*Evaluation of Former Landfill Site in Colorado Springs, Colorado Using Ground-Based Optical Remote Sensing Technology (EPA-600/R-05/-41, April 2005)*

<http://www.epa.gov/ORD/NRMRL/pubs/600r05041/600r05041.pdf>

*Evaluation of Fugitive Emissions Using Ground-Based Optical Remote Sensing Technology (EPA/600/R-07/032, Feb 2007) —*

<http://www.epa.gov/ORD/NRMRL/pubs/600r07032/600r07032.pdf>



## Other ORS Landfill Gas Publications

*Measurement of Fugitive Emissions at a Bioreactor Landfill (EPA 600/R-05-Aug 2005)*

<http://www.epa.gov/ORD/NRMRL/pubs/600r05096/600r05096.pdf>.

*Measurement of Fugitive Emissions at a Landfill Practicing Leachate Recirculation and Air Injection (EPA/600-R-05/088, June 2005)*

<http://www.epa.gov/ORD/NRMRL/pubs/600r05088/600r05088.pdf>

*Guidance for Evaluating Landfill Gas Emissions from Closed or Abandoned Facilities (EPA-600/R-05/123a). Available at:*

<http://www.epa.gov/ORD/NRMRL/pubs/600r05123/600r05123.pdf>.

*Case Study Demonstrating the U.S. EPA Guidance for Evaluating Landfill Gas Emissions from the Somersworth Sanitary Landfill; Somersworth, NH (EPA/600/R-05/142)*

<http://www.epa.gov/ORD/NRMRL/pubs/600r05142/600r05142.pdf>

## EPA Report in Review

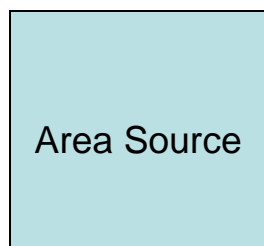
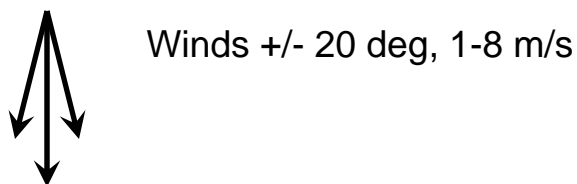
- Quantifying Uncontrolled Air Emissions from Two Florida Landfills Using ORS RPM
  - Report submitted into peer/QA review as of March 08
  - Both sites are using leachate recirculation to accelerate waste decomposition
  - Obtained samples of header pipe gas to determine landfill gas composition including trace constituents
  - Anticipate report to be released by Fall 2008



# Challenges for EPA OTM 10 Landfill Applications

- Landfills are large and complex areas sources
  - Additional landfill guidance for OTM 10 is considered need to ensure capture of total emissions across entire landfill footprint
- Cooperative Research and Development Agreement (CRADA) with Waste Management is helping to gather information to advance OTM 10 applications to landfills. Research includes
  - Conducting field studies at 12 U.S. landfills using ORS RPM
  - Use of tracer release studies and different test configurations to evaluate capture of total emissions including side slopes and difficult topographies
- Draft EPA report to be completed by Fall 2008

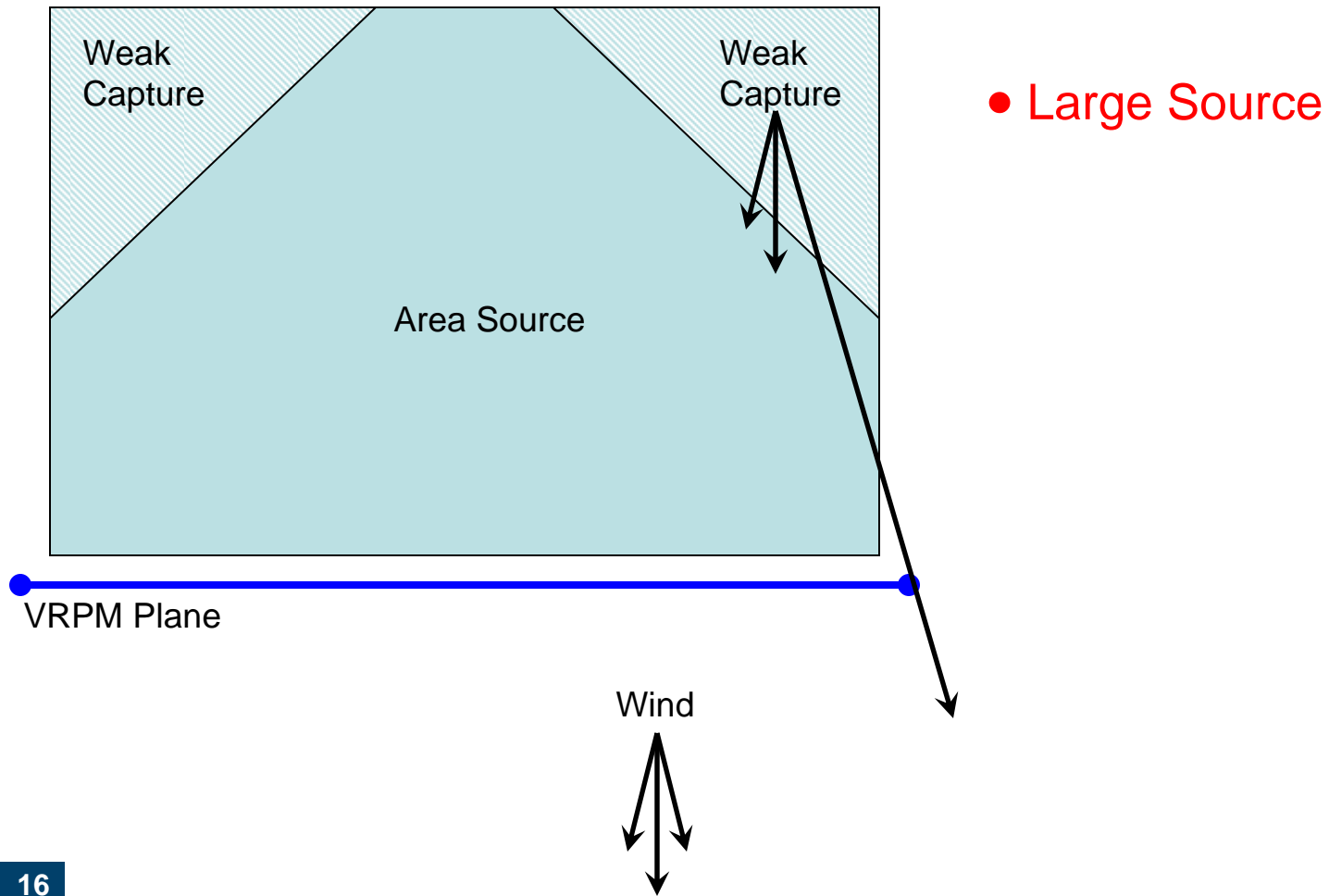
# Standard OTM 10 Application (Non Landfill)



- Small Source
- No Nearby Sources
- Flat Topography
  - good wind sweep
  - no nearby structures
- Temporal Stability

OTM 10 verification studies based on this scenario

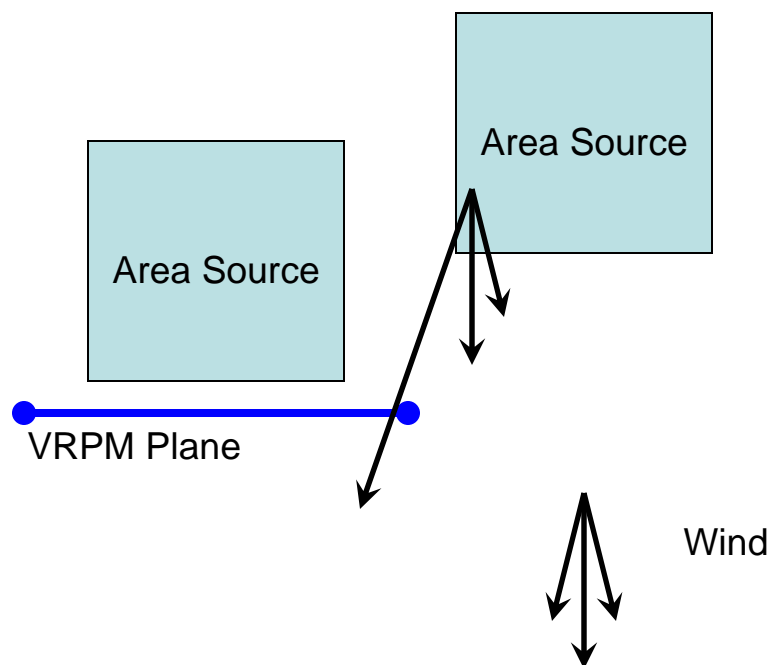
# Landfill Challenge: Large Source





# Landfill Challenge: Nearby sources

- Large Source
- Frequent Nearby Sources



# Landfill Challenge: Complex Topography

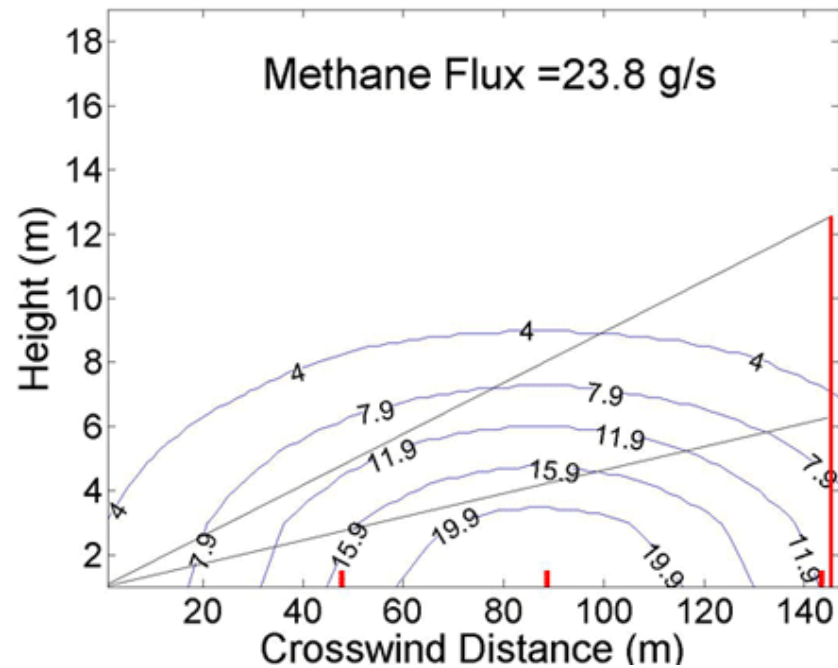
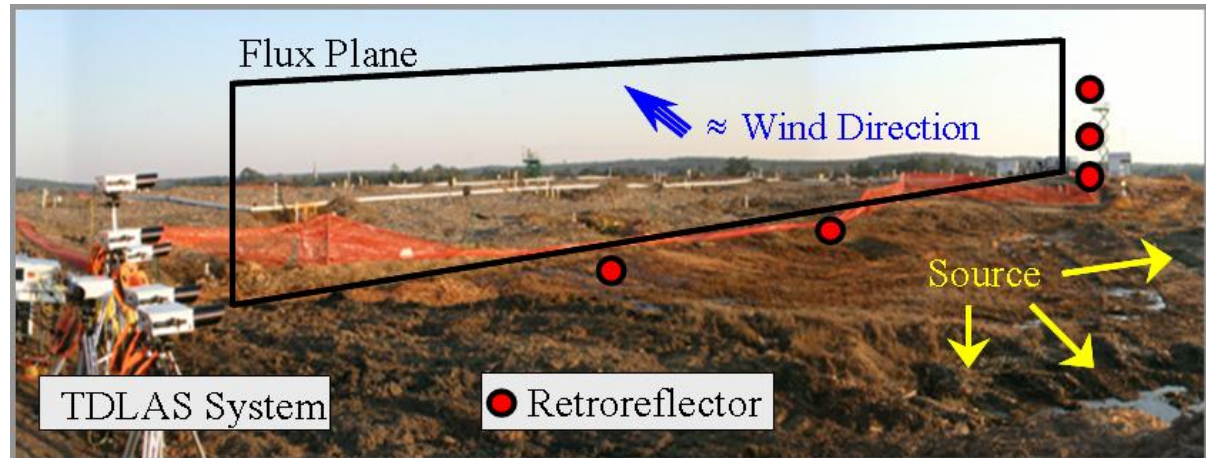
12 m Scissor Jack



- Large Source
- Frequent Nearby Sources
- Complex Topography

# Landfill Challenge: Temporal Capture

10 second VRPM  
measurement  
Bioreactor Cell



# Challenges For OTM 10 for Landfill Applications

## Standard Application

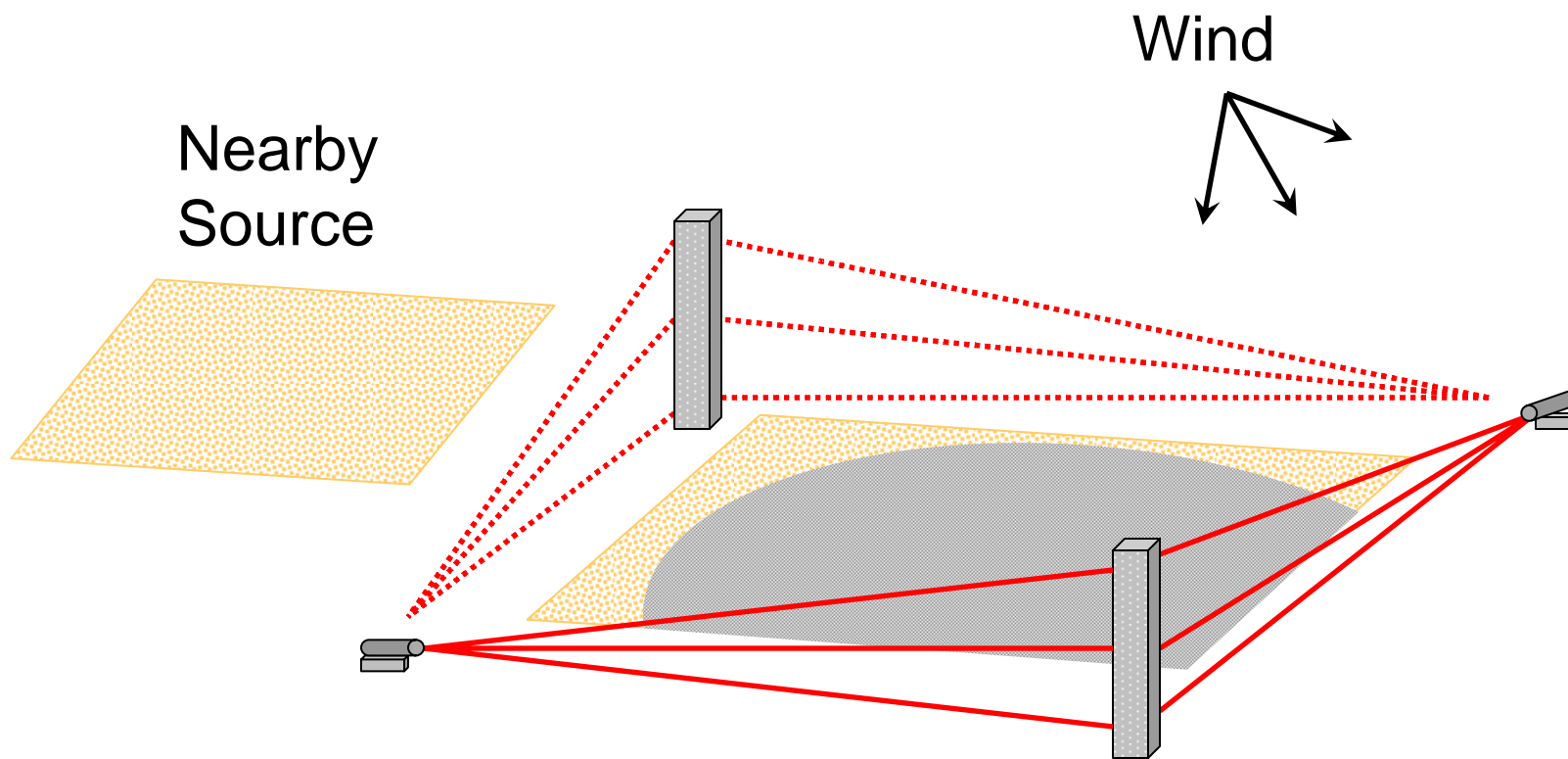
- Small Source
- No Nearby Sources
- Flat Topography
- Temporal Stability

## Landfill Application

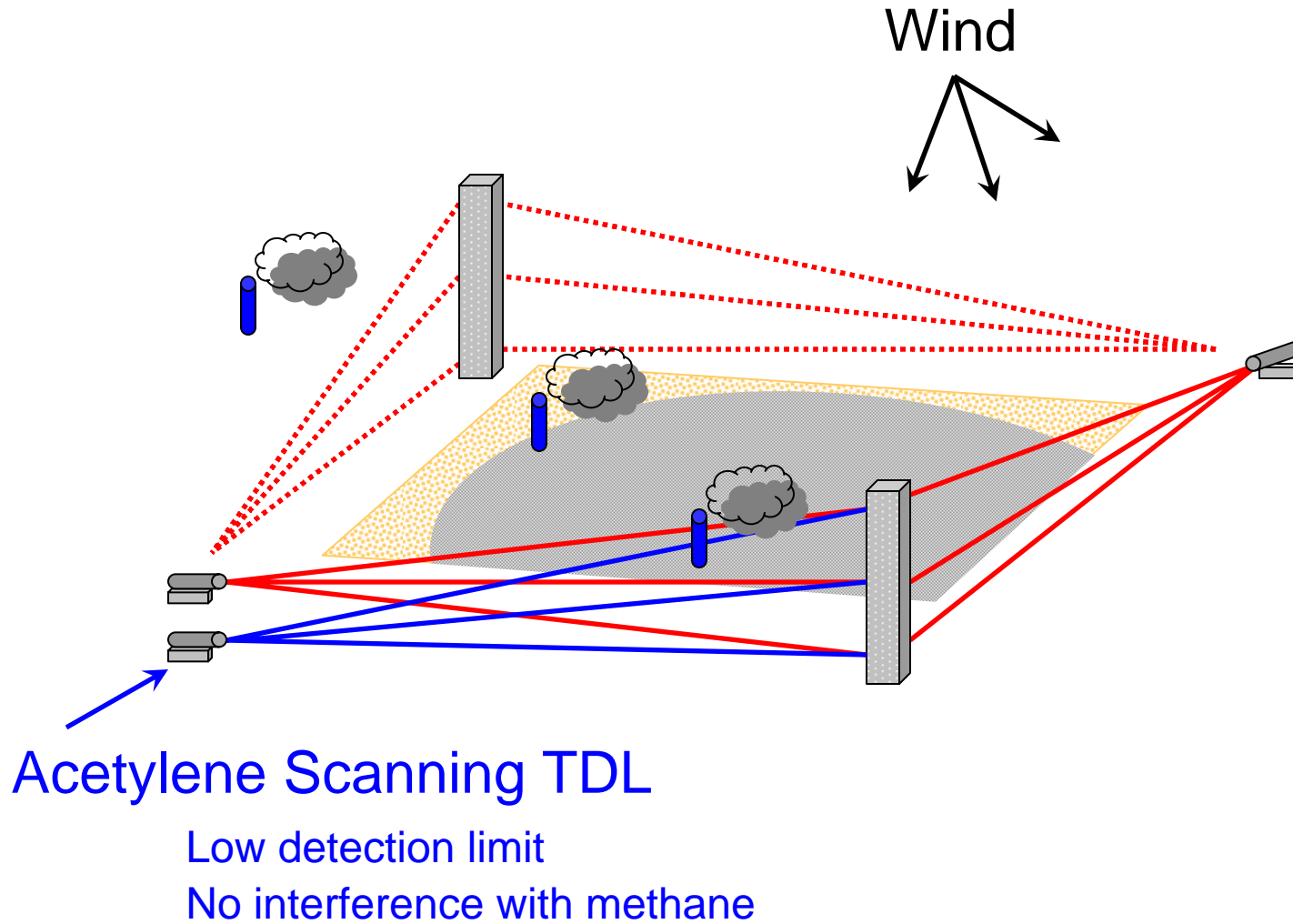
- Large Source
- Frequent Nearby Sources
- Complex Topography
- Temporal Variability?

Use Novel OTM 10 configurations and Tracer release studies to improve understanding

# Four Corners Technique



# Tracer Release Studies



## Project Status

Date	Location	Date	Location
<b>1/14/08-1/18/08</b>	<b>Lancaster, CA *</b>	7/7/08-7/11/08	Spruce Ridge, MN
<b>1/28/08-2/1/08</b>	<b>Kirby, CA *</b>	7/21/08-7/25/08	Outer Loop, KY
<b>2/11/08-2/15/08</b>	<b>Tricities, CA*</b>	7/28/08-8/1/08	Outer Loop, KY
<b>2/25/08-2/29/08</b>	<b>Atascacita, TX *</b>	8/18/08-8/22/08	Mountain View, CA
<b>3/10/08-3/14/08</b>	<b>Outer Loop, KY *</b>	9/15/08-9/19/08	Maplewood, VA
3/31/08-4/4/08	Maplewood, VA	10/6/08-10/10/08	Outer Loop, KY
4/21/08-4/25/08	Atlantic, VA	10/20/08-10/24/08	Metro, WI
5/12/08-5/16/08	Metro, WI	11/3/08-11/7/08	Mountain View, PA
6/9/08-6/13/08	Kirby, CA	11/17/08-11/21/08	Atascacita, TX
6/23/08-6/27/08	Tricities, CA	12/1/08-12/5/08	Clearview, MS

- **Field Studies Completed**
- **Draft Report – Fall 2008**

# Conclusions & Next Steps

- ORS RPM is being used to quantify uncontrolled emissions from landfills
- Although preferable to flux boxes, challenges exist for landfill applications.
- Ongoing research will help develop data and information to provide additional guidance for OTM 10 landfill applications.
- Series of reports are available through this research and are available on line. As new reports and guidance are completed, they will be available online.





# Emissions From Animal Feeding Operations

Richard Shores, Eben Thoma  
Emission Characterization and Prevention Branch

April 2, 2008



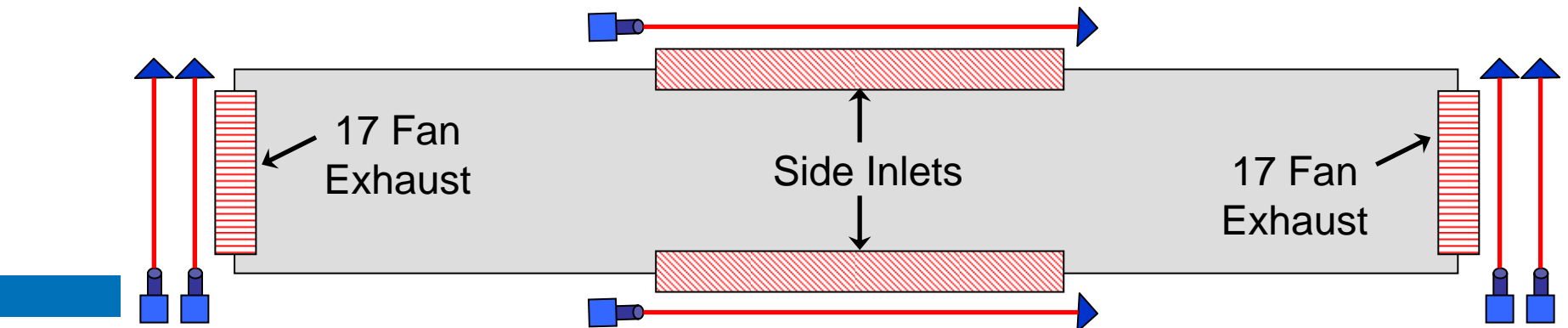
## Emission Characterization

- Fugitive Sources and Open Path Measurements (1995)
- Hog and Chicken Farming Operations (1996)
- Ventilation Design- Power and Natural (1997)
- Vertical Radial Plume Method (2002)
- On-Site waste water Treatment system (2003-2008)
- OAQPS Method Designation: OTM 10 (2006)
- Consent Agreement with Industry (2007)

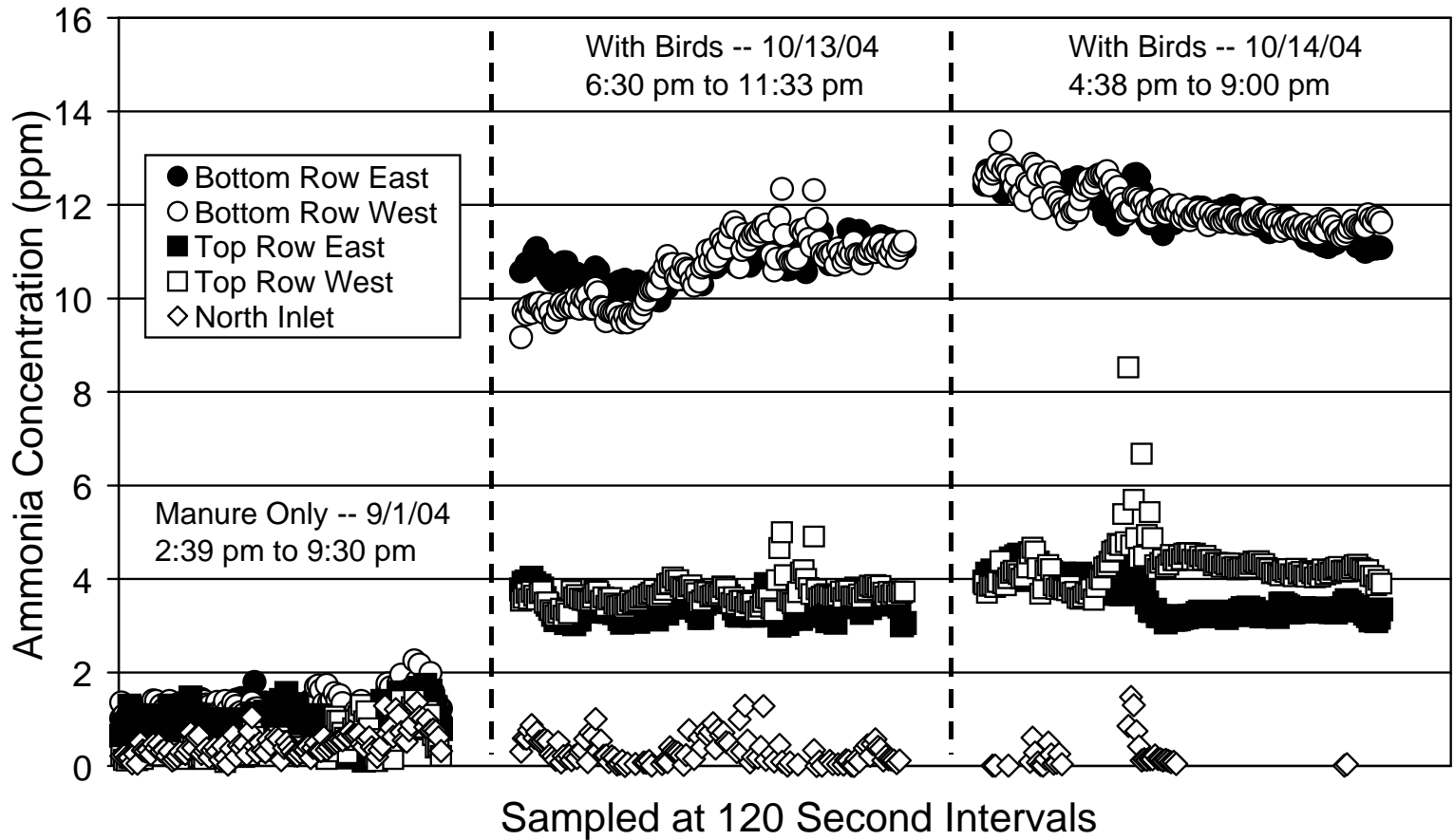
# Poultry House Emissions Using Unisearch TDL



- 100,000 Layer Hens
- 600 ft Long x 50 ft Wide
- High-Rise Tunnel Ventilated
- Birds on Top Level
- Manure on Bottom Level



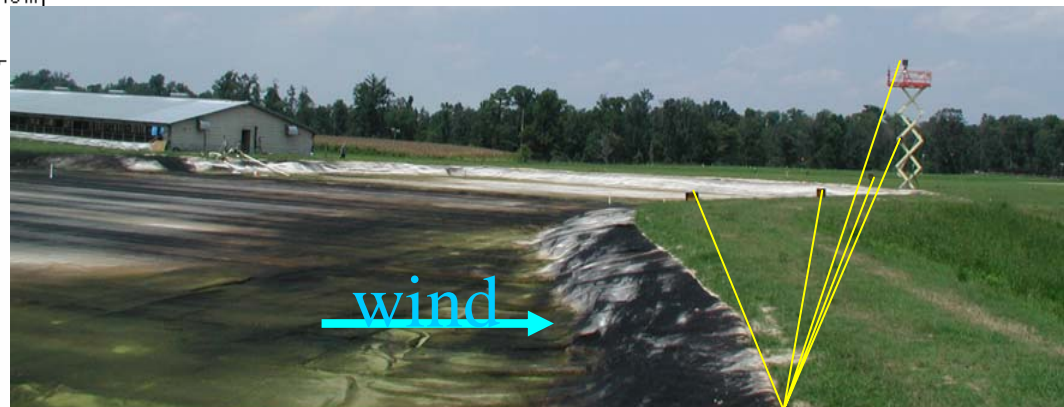
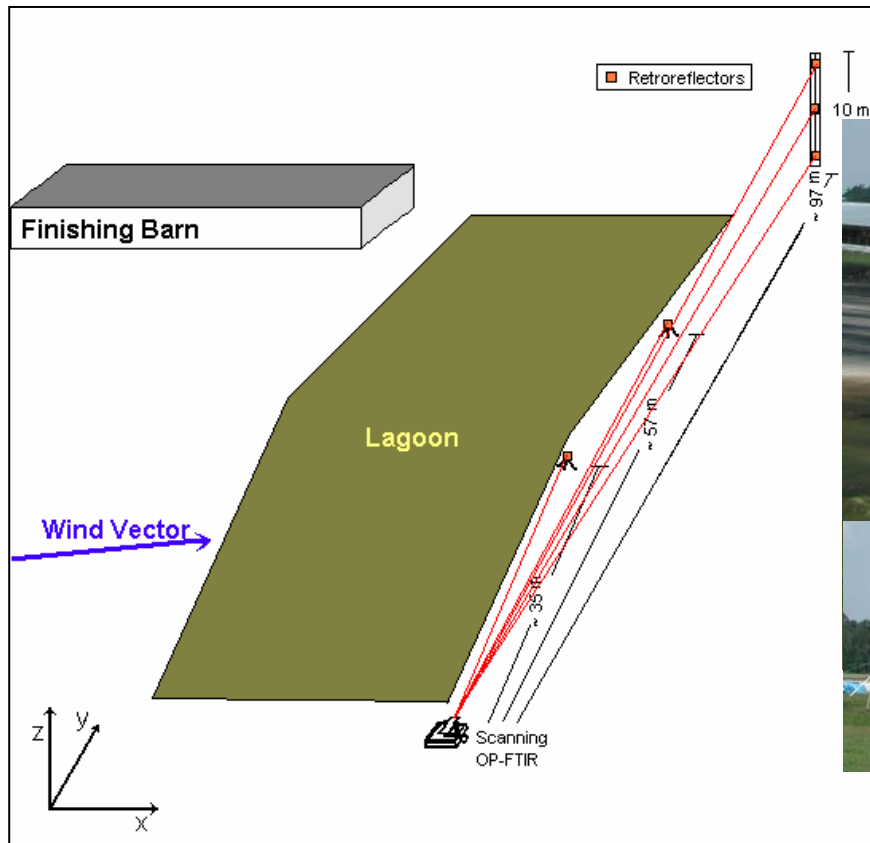
# Poultry House Ammonia Measurements



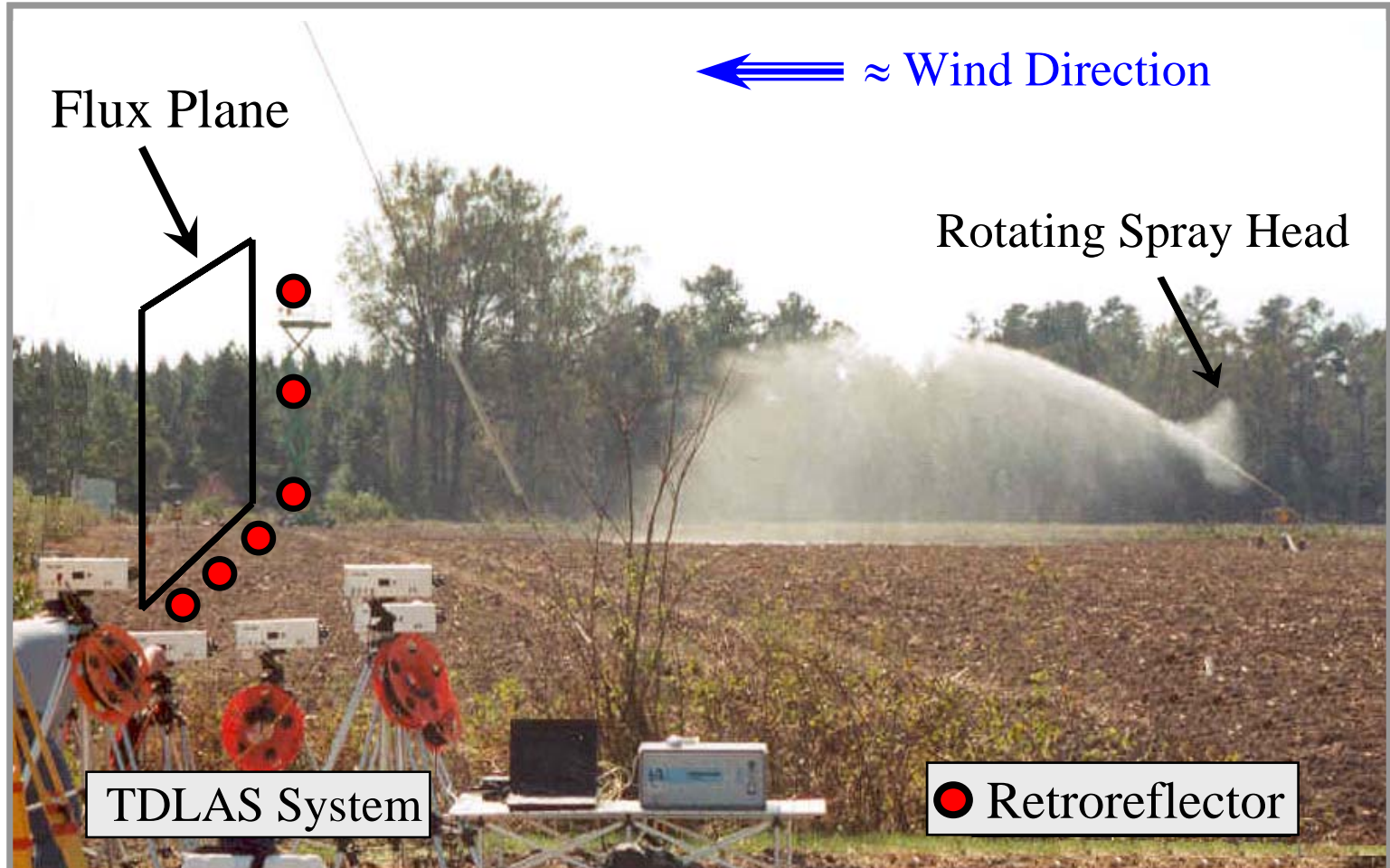
# Naturally Ventilated Swine Barn Using Unisearch TDL



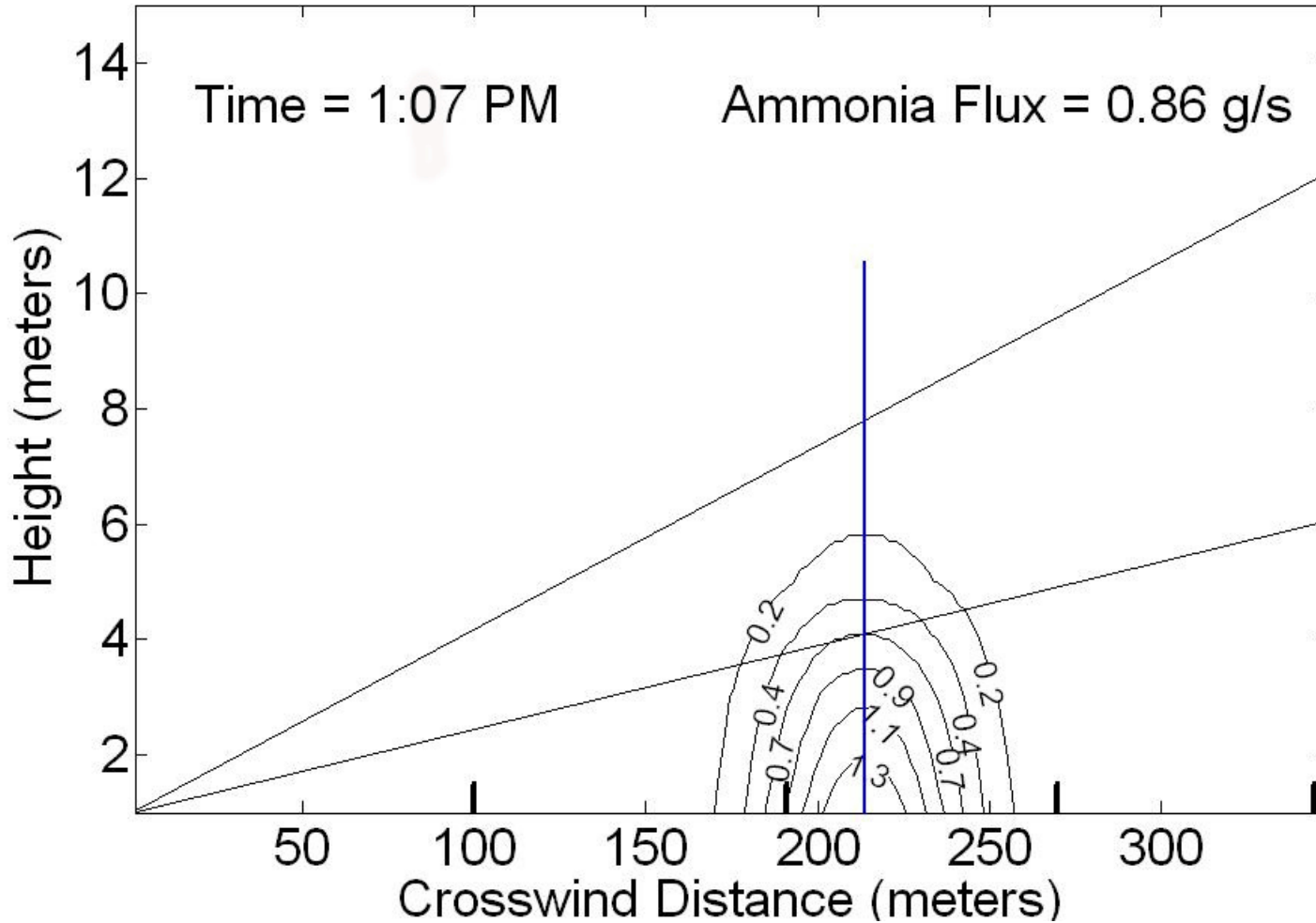
# Technology Evaluation Using FTIR and Vertical Radial Plume Method



# Flux Measurement During a Spray Event Using Unisearch TDL and VRPM

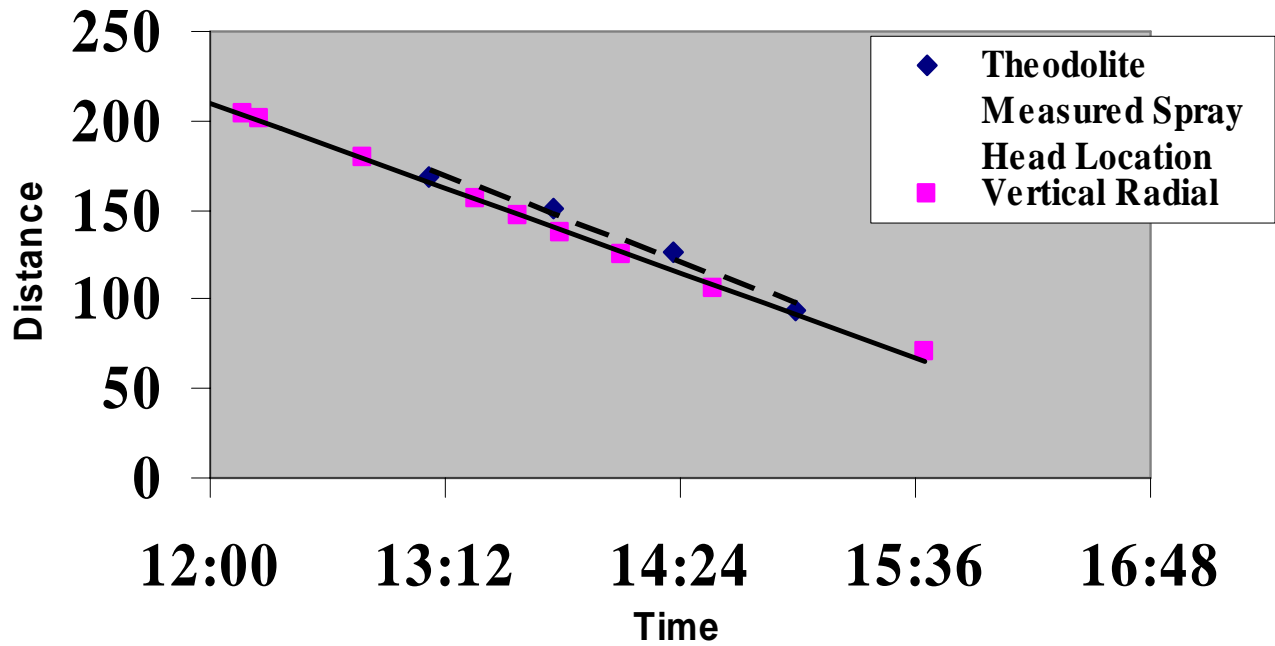


# VRPM Results for Lagoon Spraying Operation

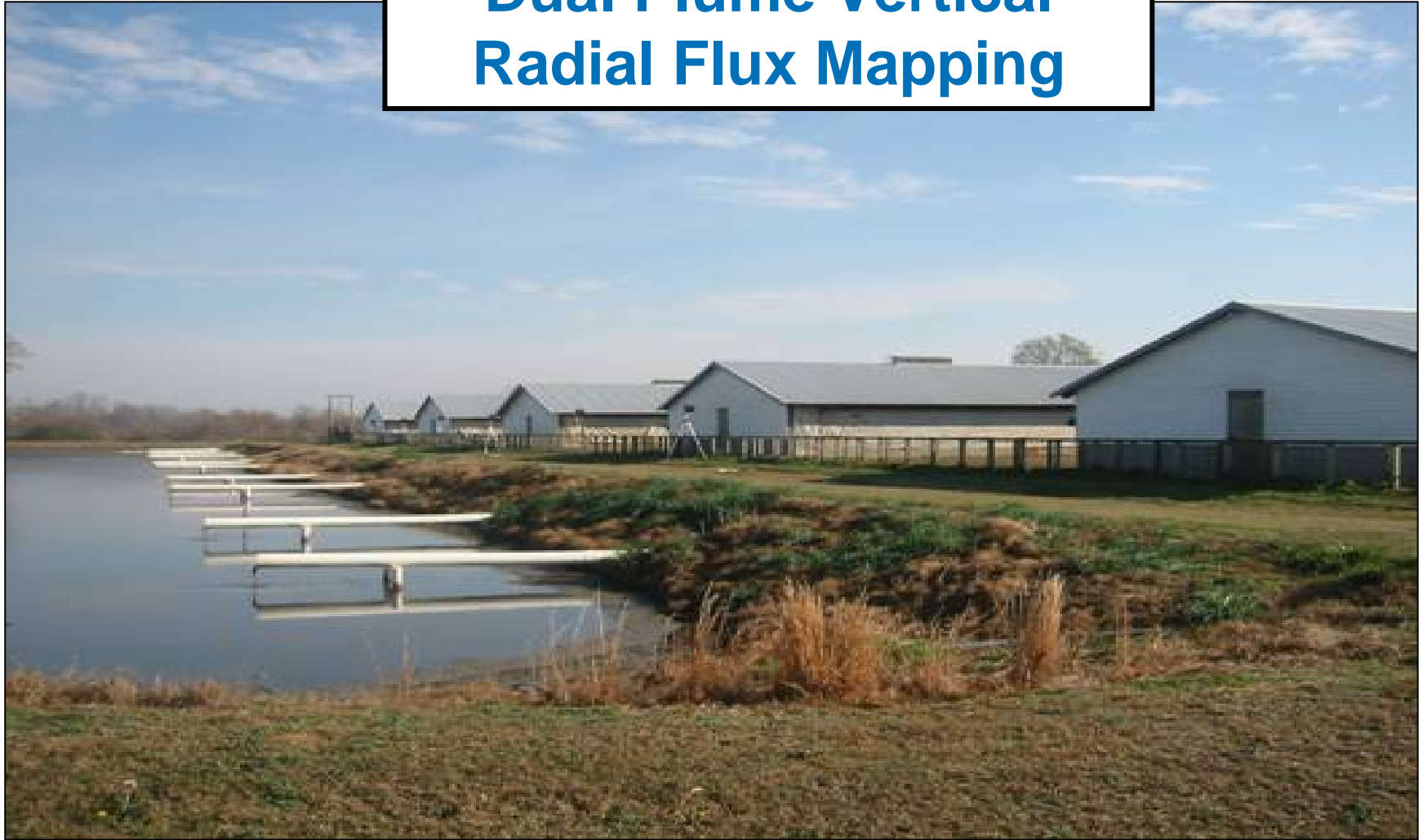




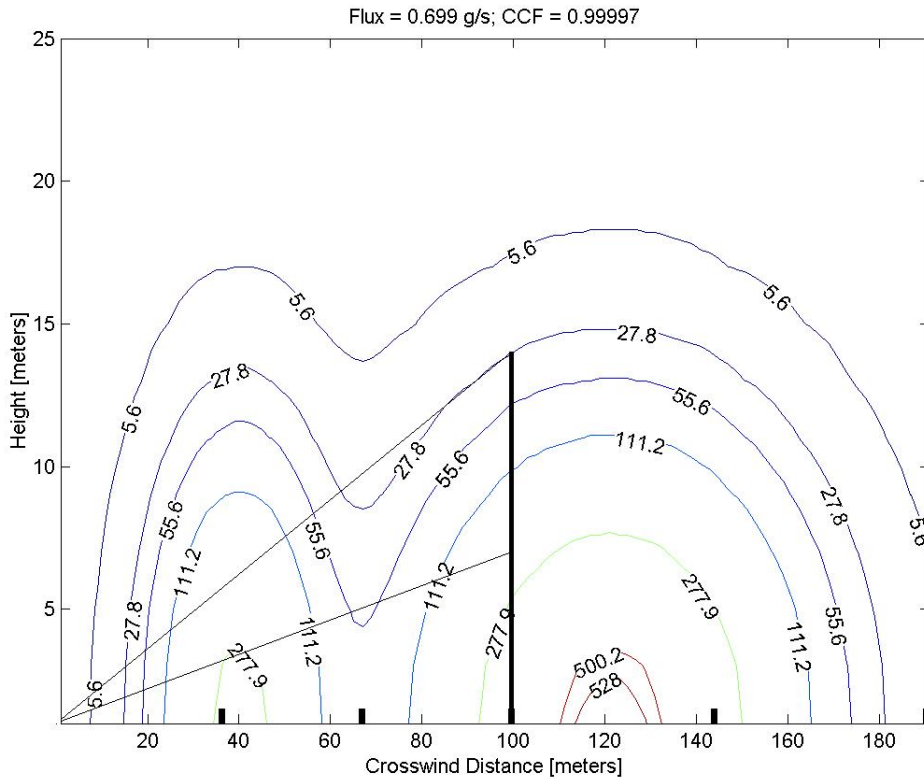
## Source Location



# Large Fugitive Sources Dual Plume Vertical Radial Flux Mapping



## Dual Plume Flux Mapping with OP-FTIR / VRPM Downwind of Barns and Lagoon

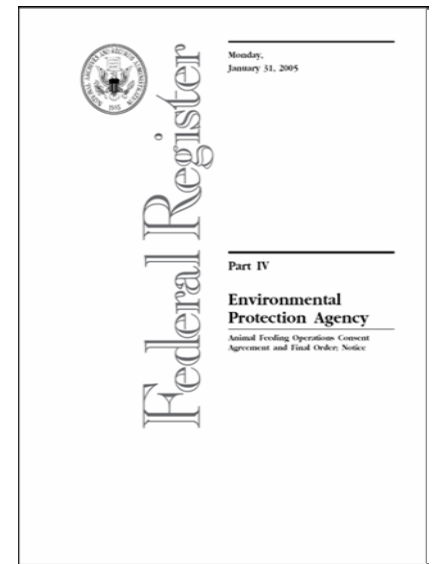


- Can resolve multiple plumes
- Here 5 naturally ventilated barns to left and lagoon to right
- Real time software displays total flux as collected
- Annual Emissions = 24 tons



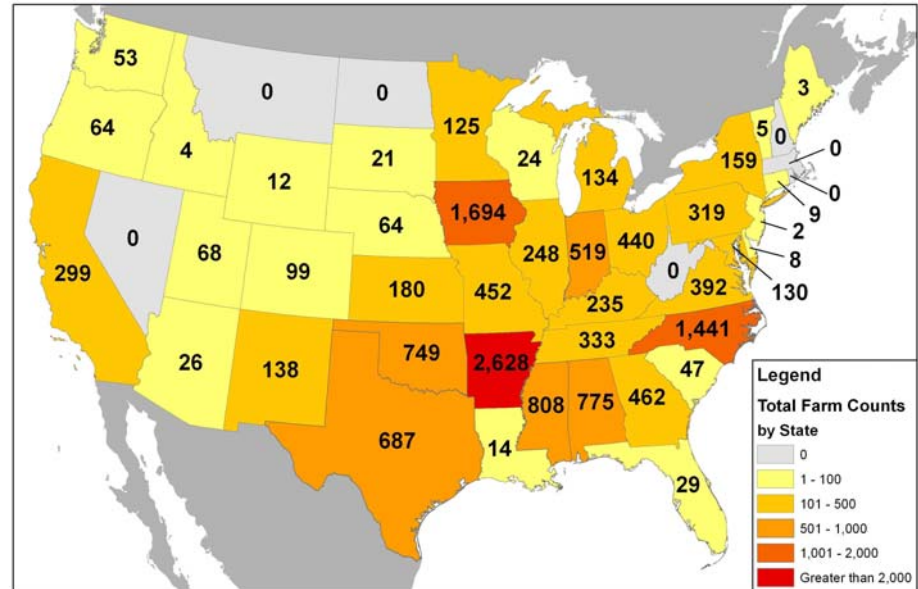
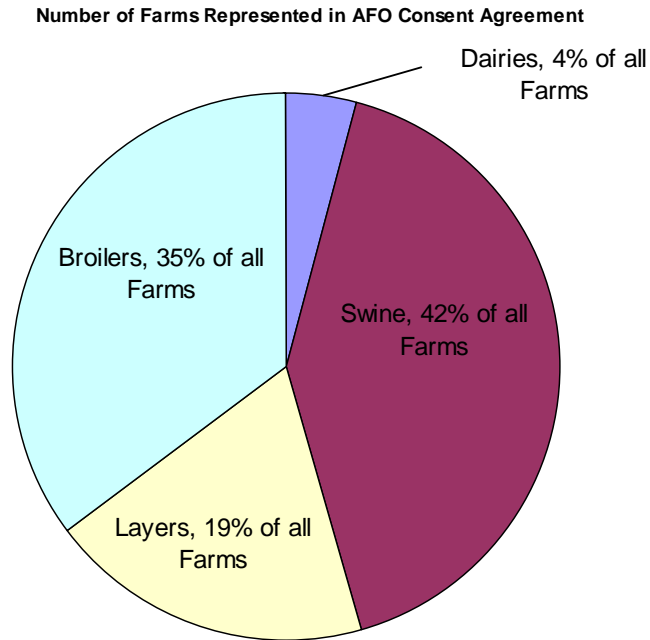
# Consent Agreement

- Voluntary consent agreement open to contract growers and integrators. Industry agrees to pay to conduct emissions testing.
  - Swine
  - Poultry
    - Layers
    - Broilers
    - Turkey
  - Dairy
- Federal Register Notices:
  - Signed on Jan. 21, 2005
  - Published on Jan. 31, 2005 (70 FR 4958)
  - “Initial” public comment period closed on March 2, 2005
  - Re-opening comment period from April 1 through May 2, 2005
  - Extending signup period to July 1, 2005
- Information available at:
  - [www.epa.gov/fedrgstr](http://www.epa.gov/fedrgstr)
  - [www.epa.gov/airlinks/airlinks3.html](http://www.epa.gov/airlinks/airlinks3.html)
  - [www.epa.gov/compliance/resources/agreements/caa/cafo-agr-0501.html](http://www.epa.gov/compliance/resources/agreements/caa/cafo-agr-0501.html)
  - <http://cobweb.ecn.purdue.edu/~odor/NAEMS/index.htm>

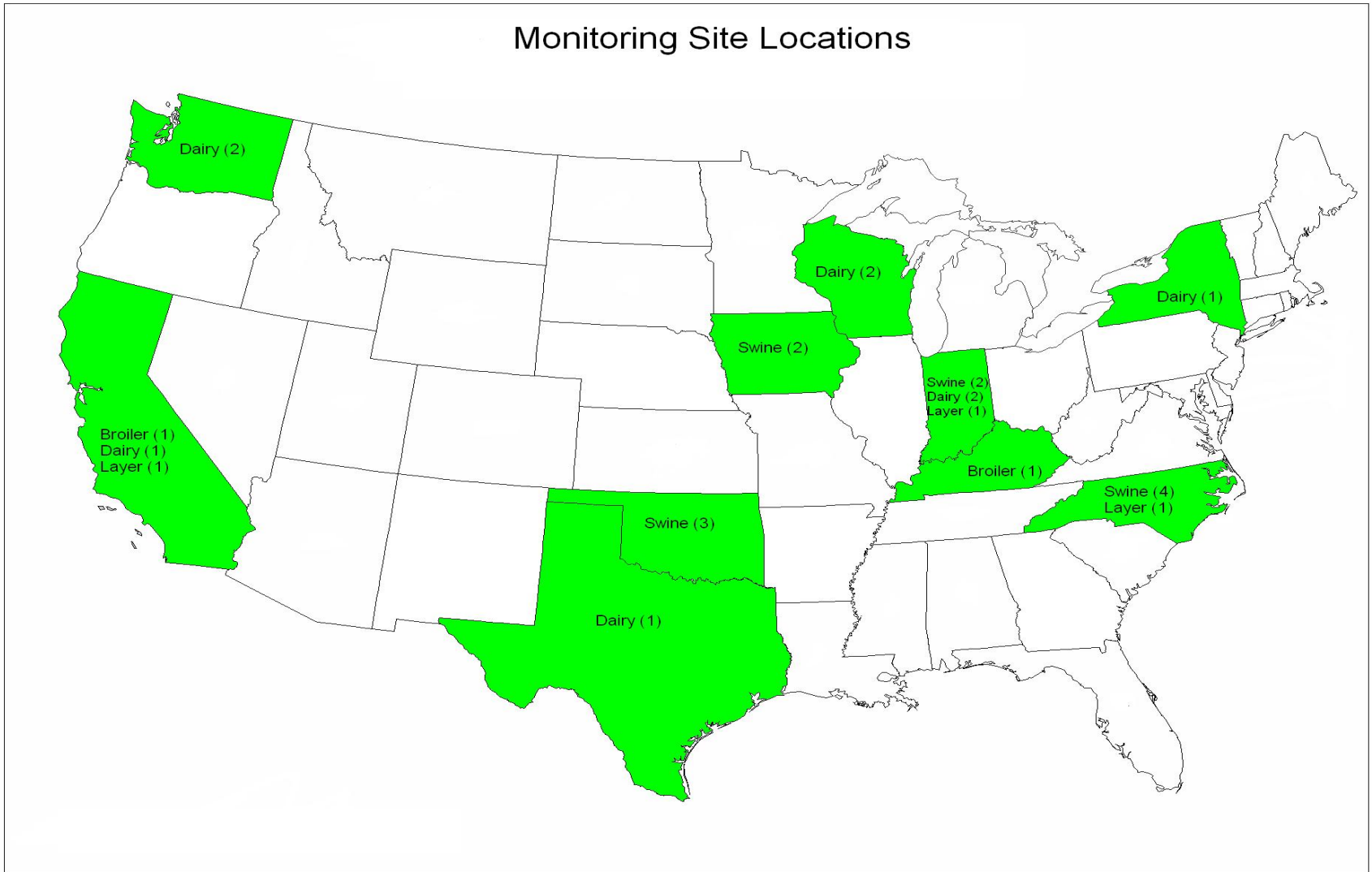


# Monitoring Study - Signups

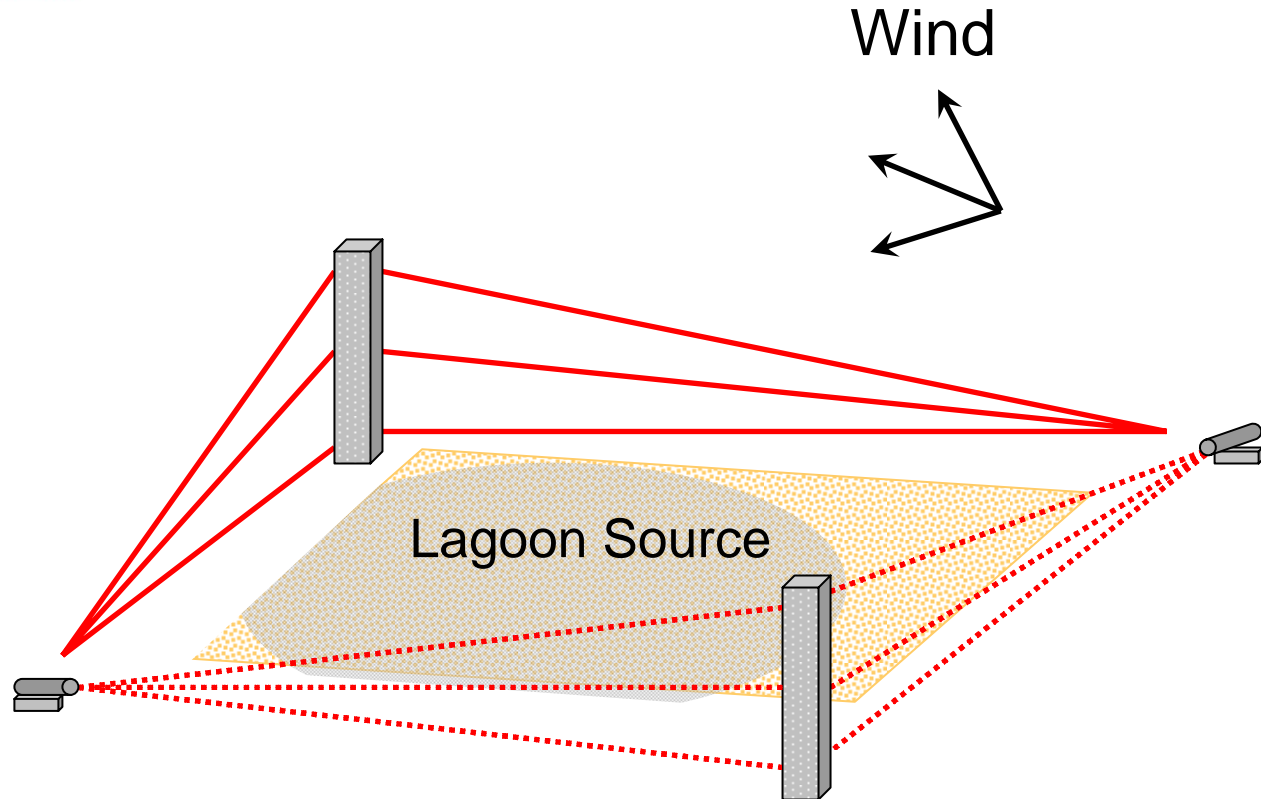
- EPA received approximately 2,700 agreements representing over 13,000 farms.



## Monitoring Site Locations



# Four Corners Technique



4-Corners Technique is more forgiving to wind direction changes- Using Boreal Gas Scanner

## Conclusions

- Measurement techniques developed in APPCD incorporated into NAEMS
- Consent agreement measurements begin in 2007
- Construct, demonstrate and evaluate an on-site waste water treatment system



# Panel 1

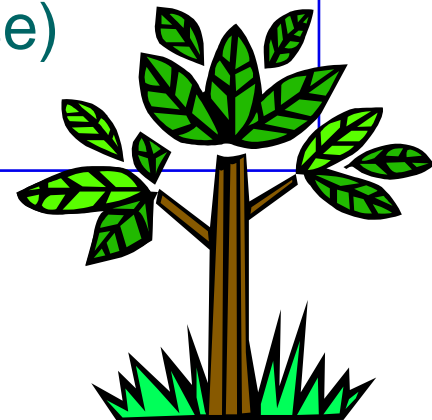
The European experience in the  
US/Canadian context:

**Ideas on a protocol on  
measurement strategies**

Lennart Frisch

Agenda Enviro AB

[lennart.frisch@agendaenviro.com](mailto:lennart.frisch@agendaenviro.com) (or .se)



# Personal background

**M.Sc. Chemistry and Physics**

**Process Engineer and head of process data systems at an Oil refinery**

**Environmental head officer Provincial Government/County Administration**

**National advisor to the Swedish EPA on major process industry environmental issues**

**Member of Swedish EPA national board on industrial compliance control**

**Member of the Swedish EPA Scientific Committee on Air quality**

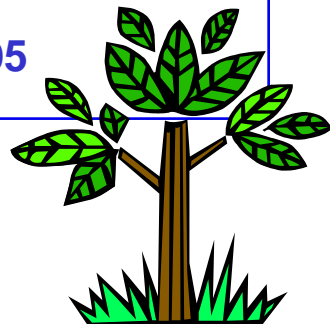
**Responsible for the design, building up and running of the first Swedish regional emissions data base on all emissions to air**

**Swedish representative to the EU commission network on implementation and enforcement of environmental law (IMPEL)**

**Swedish representative to the EU commission on Environmental Management and Audit Systems (EMAS/ISO 14 001)**

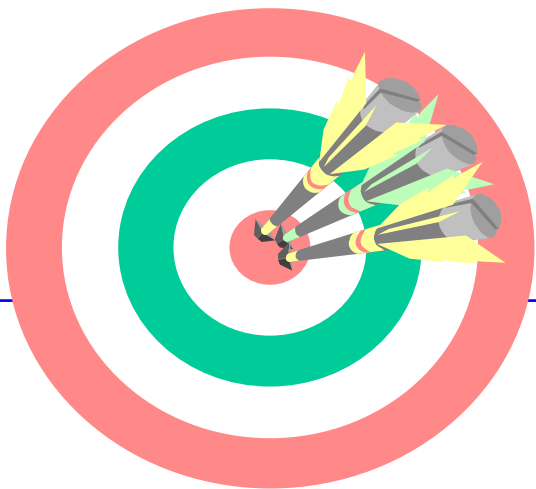
**Certified environmental lead auditor according to ISO 19 011 (14 001, 9001) since 1997**

**Board member of the Swedish Clean Air Association since 1995**



# Objective

**Continuously reduced emissions**  
**leading to**  
**emissions at constantly low levels**



# General

Identify sites of **need** to measure

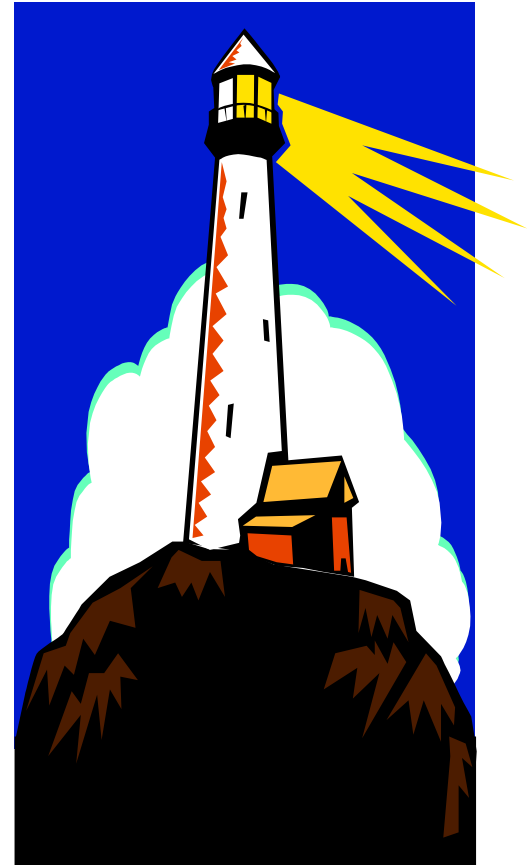
Identify **what** to measure

- Substances
- Functional parts of sites
- Certain operations
- Annualized data

Carry out a **number of** (strategic) measurement campaigns

Define on **beforehand**

- Objectives,
- Reporting need,
- Report distribution,
- Cost-carriers etc.



# At site

Identify on beforehand measurement **devices** needed and **positions** for each functional part

Continuous **dialogue** with staff at site on

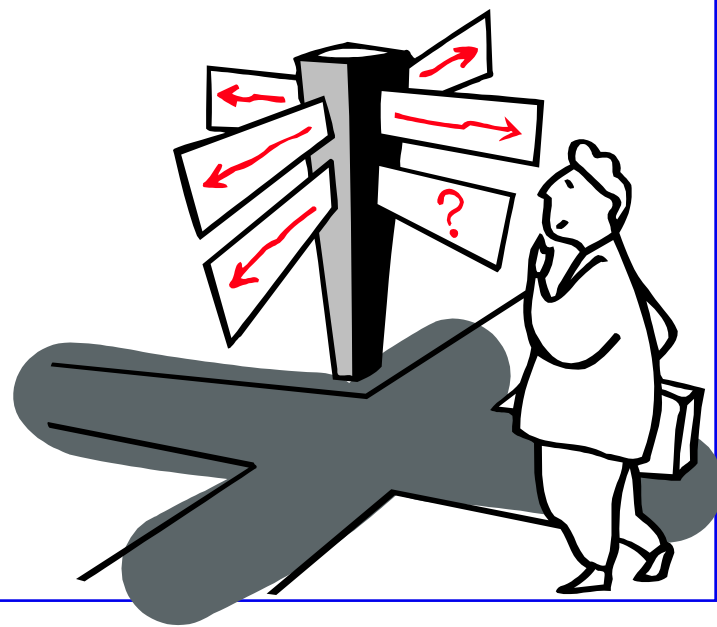
- dissemination and documentation of production data
- throughput or equivalent per functional part
- storage movements
- hick-ups etc.

**Multiple scans to**

- cover differing operations
- annualize data

**Preliminary reporting at site on**

- fluxes
- VOC-distribution



# Measurement reporting

## Final reporting (**contractual** agreement)

- time (2 months)
- content
- depth
- summaries

## Initial Authority data **assessment**

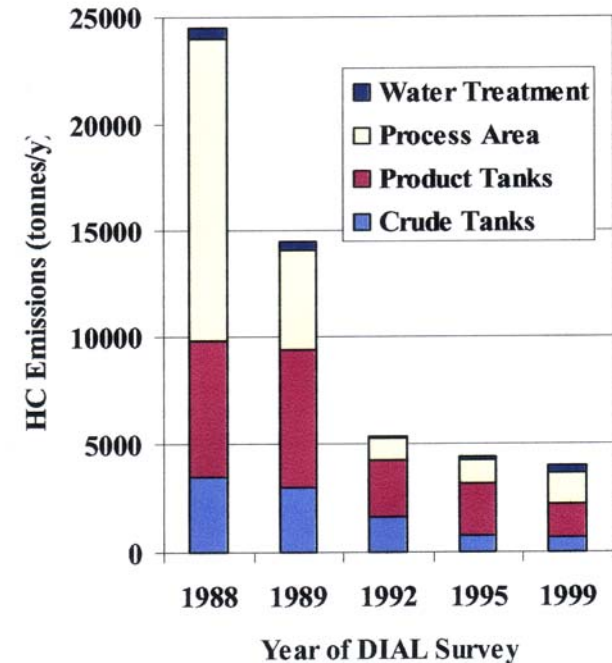
## Site **dialogue**

## Decisions on

- practical report distribution
- practical external dialogue

## Decisions (**authority prescriptions**) on

- need for repeated measurements
- LDAR-checks design and frequency



# Follow-up

Use achieved results to answer

Initial **flux** measurements at **each site** (economic pay-off)

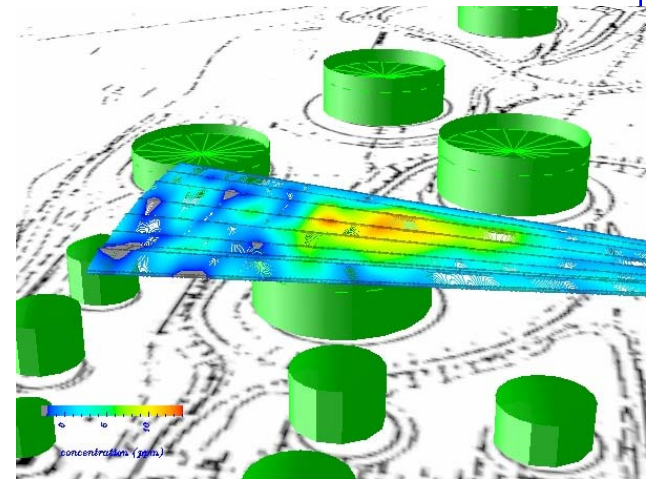
Possibilities to **generalize** data for **functional parts** related to

- operations/service
- maintenance level
- equipment age and use

Design modern **LDAR** programmes

- use of mobile cameras or equivalent
- high frequency
- documentation

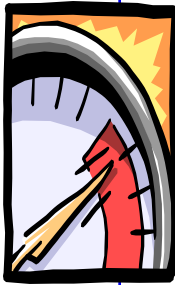
→ Decide on the use of flux measurements on a **national scale**





# Identifying reliable equipment

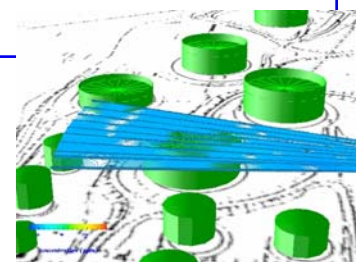
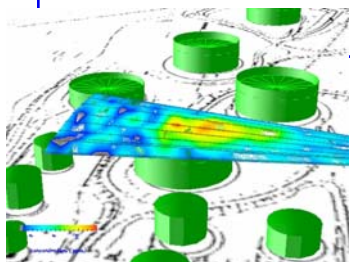
## Parameters to consider:



- Team with profound industry experience
- **Earlier records**
- Ability to cover all relevant VOC:s (alkanes, alkenes, alkynes, aromatics esp. benzene, cyclopentanes, C<sub>2</sub>-C<sub>15</sub>, halogenated, methane)
- **Detection limits of relevant VOC species**
- Repeatability (relevant scan frequency)
- **Mobility (covering relevant functional sites)**
- Dependence on ambient factors (wind speed, wind direction, sun, rain etc.)
- **Reporting facilities and response on level, content and delivery in time**

## Testing method:

Measurement on known (varying) release of “difficult” but relevant VOC(:s) **and/or** parallel measurements with different measurement equipments





# Report (pdf)

commissioned by the  
**Swedish County Administration of  
Västra Götaland, Göteborg  
(Länsstyrelsen) and the Swedish EPA**

**Report #2003:56**

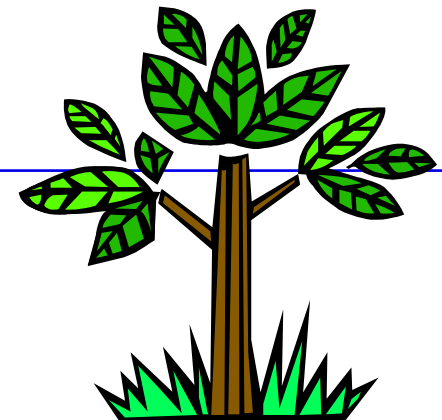
[http://www.o.lst.se/o/Publikationer/Rapporter/2003/2003\\_56.htm](http://www.o.lst.se/o/Publikationer/Rapporter/2003/2003_56.htm)

# LENNART FRISCH

## Agenda Enviro AB

[lennart@agendaenviro.com](mailto:lennart@agendaenviro.com) (or .se)

[www.agendaenviro.com](http://www.agendaenviro.com) (or .se)



# Synergism

# Synergism In Optical Monitoring Technologies

- We think of one technology versus another in considering a monitoring program
- We need to think not of a technology but of a total capability offered by combined technologies
- Combining technologies can provide more than individual technologies can provide on their own

# Synergism In Optical Monitoring Technologies

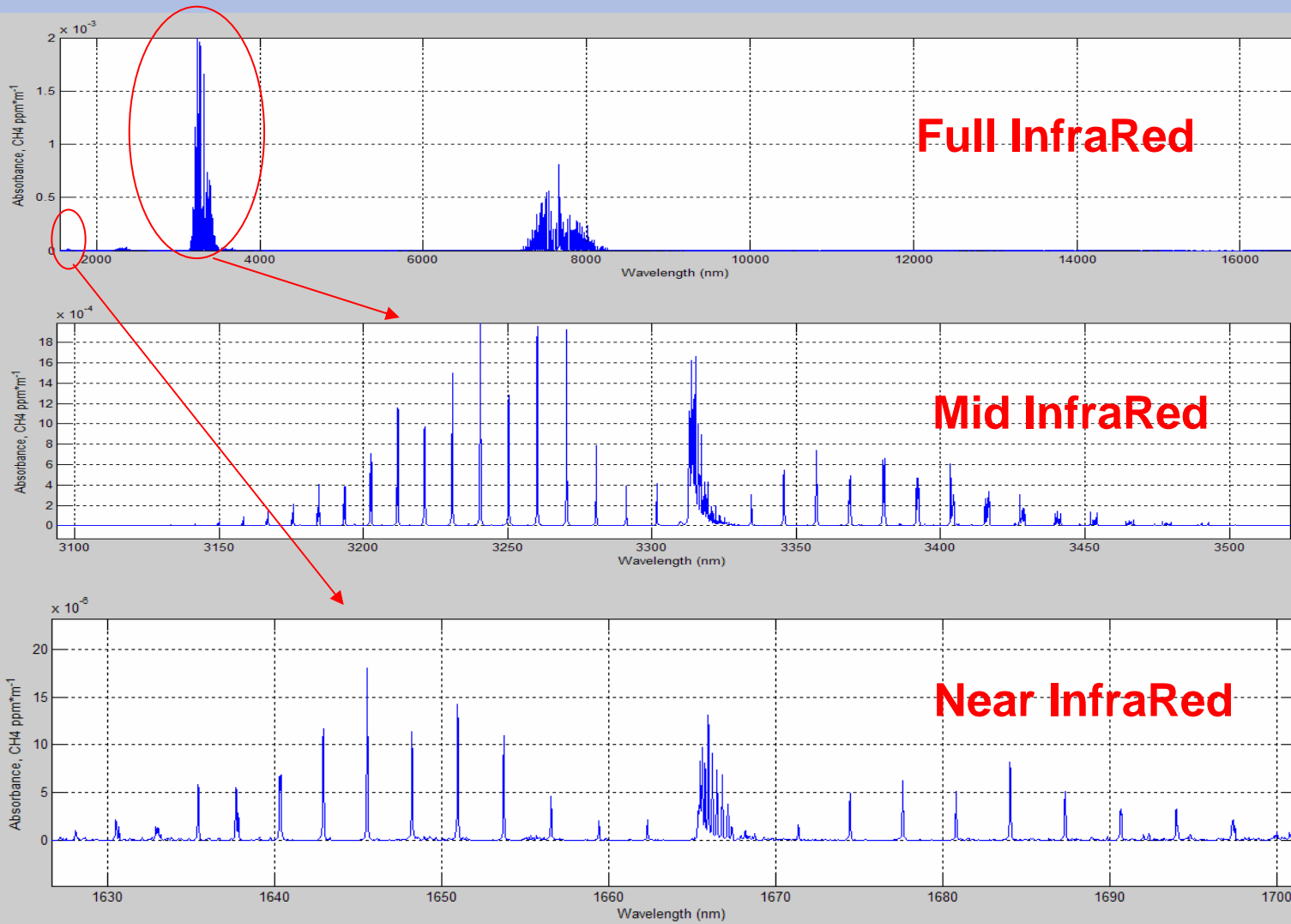
- Current optical monitoring technologies offer powerful capabilities
- However, each has its own strengths and weaknesses
- Combining technologies offers the best opportunity to meet all the needs of current monitoring requirements
- For example:
  - Lidar with its capability of mapping plumes combined with near ground-level FTIR/DOAS measurements can provide plume distribution and plume composition
  - Solar occultation can locate “hot” spots in facilities this in conjunction with 2D RPM in those “hot” spots can locate major emitters in large industrial complexes

# Synergism In Optical Monitoring Technologies

Many other examples are possible but the bottom line is:

**Synergism**

# Example: CH<sub>4</sub> absorption in NIR



## Available Gases

HF

HCl

HCN

CH<sub>4</sub>

NH<sub>3</sub>

CO

CO<sub>2</sub>

C<sub>2</sub>H<sub>2</sub>

H<sub>2</sub>S

H<sub>2</sub>O

NIR – weak absorptions → only small molecules can be measured

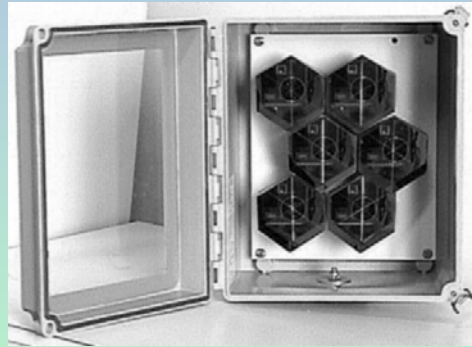


# TDL Products for Gas Monitoring



## GasFinder2 (GF)

Portable single-channel, open path/ambient gas detector



## GasFinderMC (MC)

Fibre-coupled, multiple-channel (up to 8) gas monitor for open path, stack, or process monitoring — shown with long open path head.



## GasFinderFC (FC)

Portable single-channel, fibre-coupled stack gas detector



## Short Open Path Head



## Vehicle mounted Probe



## Transceiver Unit of Cross Duct Probe

# Energy & Environmental Applications

- Leak Detection surveys with Scanning GasFinder2 system
  - Quantify CH<sub>4</sub> fluxes from gas plants, landfills and other area sources
  - CH<sub>4</sub> and NH<sub>3</sub> emissions from intensive animal feeding operations
  - CO<sub>2</sub> sequestration studies with ARC and British Geological Survey
- Fixed Leak Detection installations with GasFinderMC
  - HF leak detection in Refinery Alkylation Units
  - H<sub>2</sub>S leak detection in sour gas production and processing
  - CH<sub>4</sub> leak detection in Natural Gas processing
- Mobile Leak Detection with GasFinderAB
  - Airborne and ground-based
  - CH<sub>4</sub> leak detection in Natural Gas pipelines and distribution
  - CH<sub>4</sub> & CO<sub>2</sub> emissions from landfills and other area sources
- Other Environmental monitoring
  - Ambient, stack and process HF monitoring in Primary Aluminium
  - CO<sub>2</sub> emissions monitoring from coal-fired power plants

# Leak Detection in a Process Unit

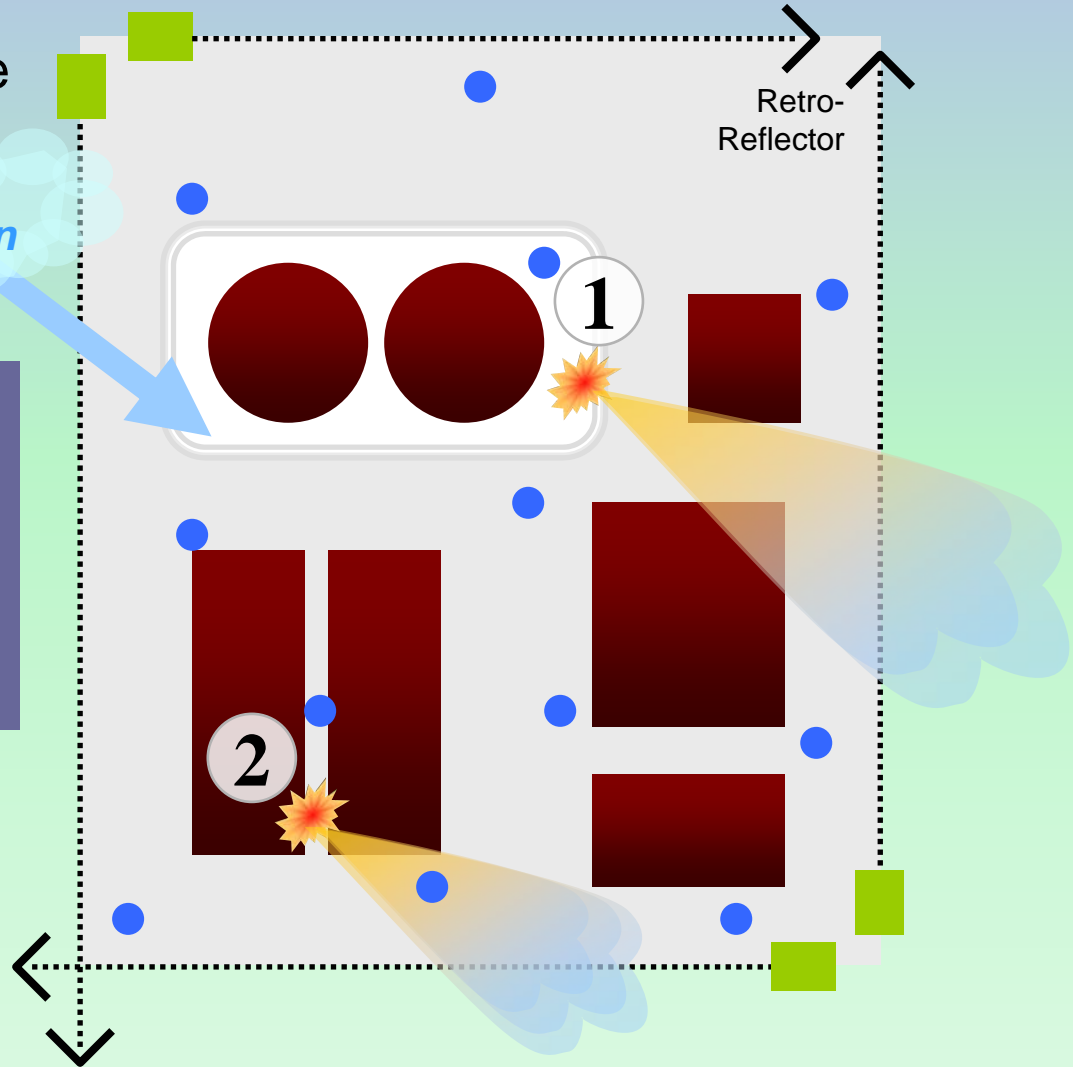
**GasFinderMC** paths provide complete perimeter coverage

*Wind Direction*

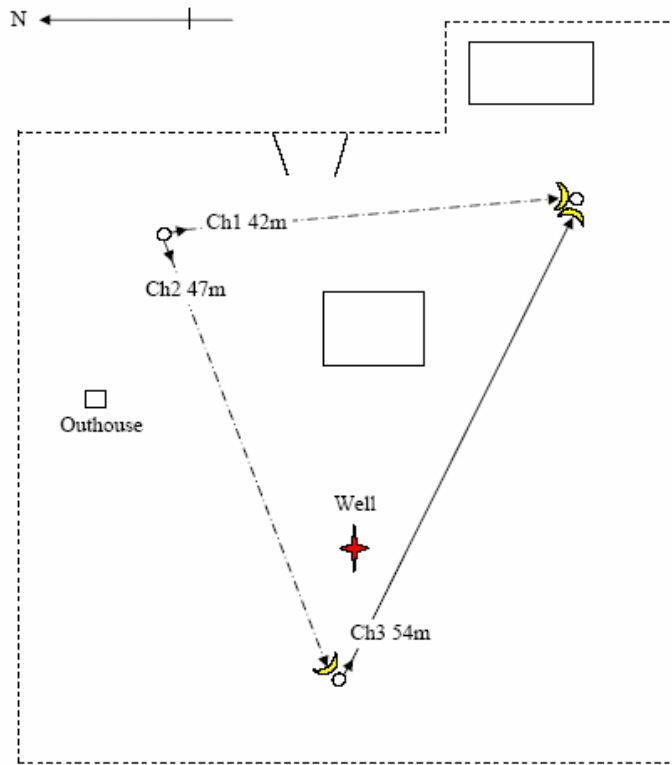
*Note that **leak 1** creates a cloud that is not detected by any point sensors*

***Leak 2** is detected by 1 or 2 point sensors*

- Point sensor
- ☀ Source of leak
- **GasFinder** heads



# Typical Sour Gas Well Installation

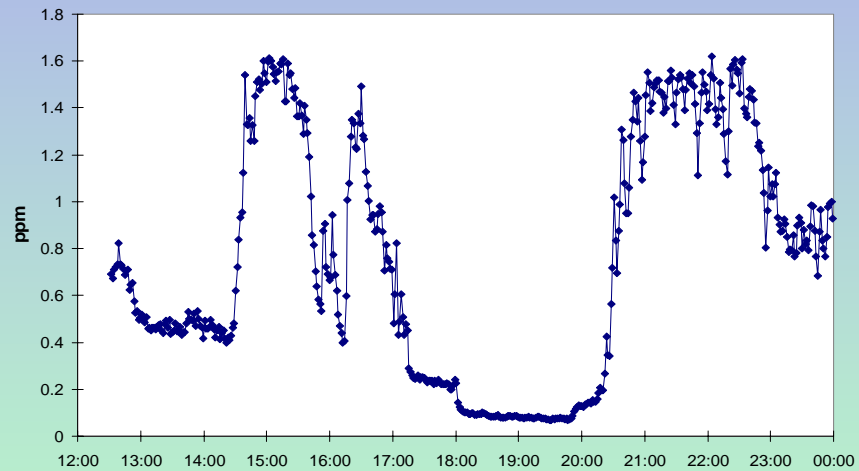




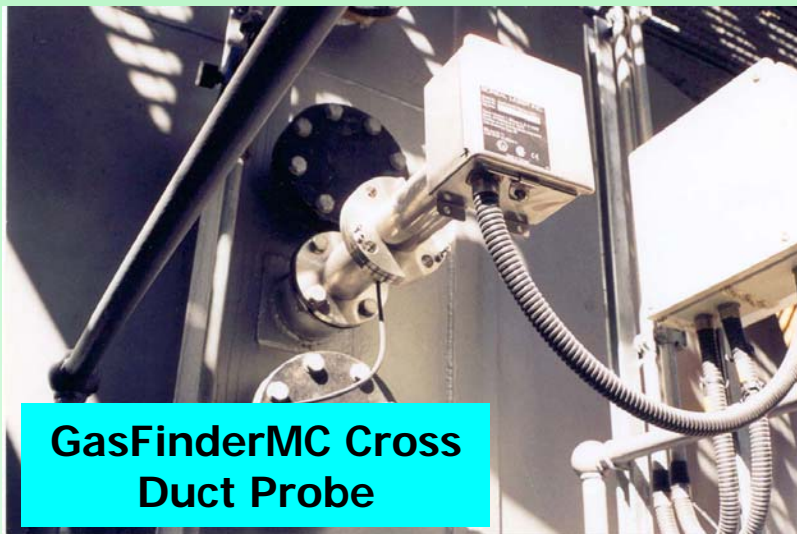
# HF monitoring in Aluminum Smelters



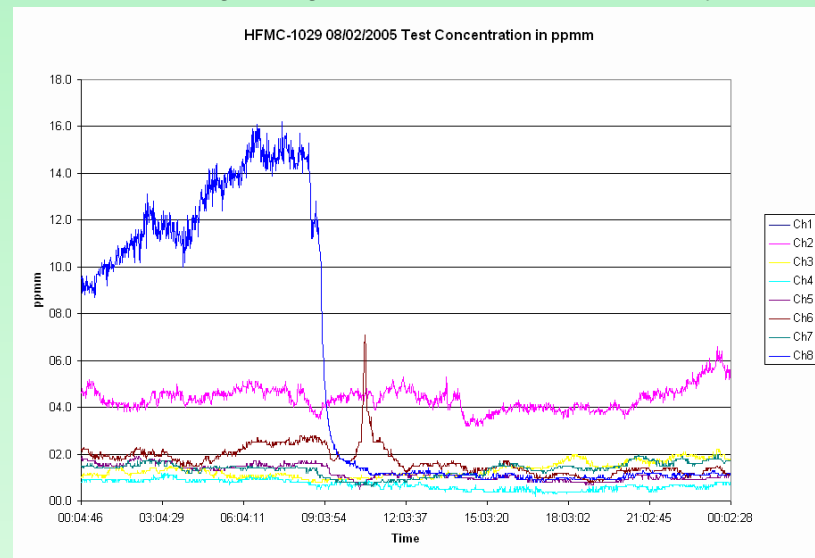
**GasFinderMC Open Path Transmitter**



HF gas in the roof of an aluminum smelter. From 14:20 to 16:35 anodes were being changed; a break at 16:00 can easily be seen.



**GasFinderMC Cross Duct Probe**



Data from installation of 8 duct probes as in previous slide on a multiple filter scrubber in aluminum smelter

# Point Source EI's:

## The Good, the Bad and the Ugly

1. 35 Refinery Studies since 1987:  
VOC's Ugly
2. TexAQS 2000 Field Study:  
NOx Good, VOC's Ugly
3. IR Cameras (HAWK, FLIR):  
Unexpected VOC's Bad, Maybe Ugly?
4. TexAQS 2006 Aircraft and SOF:  
NOx Even Better, VOC's better, but still Ugly



# What is at Stake?

---

1. Point Source EI's as a basis for Policy
2. BACT/MACT Credibility
3. Permits & Control Strategies for...
  - a. Ozone
  - b. Air Toxics
  - c. Greenhouse Gases
4. Cap and Trade Programs

I.E., billions of dollars all over the world.



# Ground Level Point Monitors (GLPMs)

GLPMs are good because they:

1. Measure the concentrations of what people breathe.
2. Track trends over time.

However they are also “bad” because:

1. They don't tell you...
  - a. When a plume passes over head.
  - b. Where you are in a plume.
  - c. How big the plume is.
  - d. Where the plume came from.
2. GHGs have different challenges from ozone and air toxics that GLPMs don't address.

# Future State EIs Will Use 2DRSCMs\*

\*2 Dimensional Remote Sensing Concentration Maps

- Quantify & Isolate VOCs and check on deteriorating maintenance over time (LDAR is not enough).
- Chemical Engineers – Apply Process Knowledge and Good Engineering Judgment.
- Identify Typical, Extreme Upset and Ideal Process and Meteorological Conditions and Do the Math.
- Chemists – Use Best Analytical Techniques and Accepted Protocols. Share raw data.
- Operators (and others) – Develop an Environmental Culture = Personal Safety.
- Understand the Economics – If the Greenest Refineries Become Less Competitive, No One Wins.

# Panel 2

# Lessons Learned from Previous Studies and How to Learn from Them Through Standard Test Practices



Jan Montclief  
Spectrasyne, Ltd

# Components of a DIAL Survey

## 1. DIAL

**Hardware**

**Latest optical & computer equipment**

**Software**

**New acquisition & processing suites**

## 2. Team

**Experience - 145 surveys**

**Skill, dedication & knowledge**

## 3. Protocols

**Operating procedures**

**Science Base**

# Spectrasyne DIAL Survey Protocols



## OPERATING PROCEDURES

1. Pre Survey Site Assessment- Logistics/Safety etc
2. Detailed Proposal-Species/Time allocations etc
3. On-Site – Plant and Tankage
  - Throughout Day – Weather Forecast/ Actual Wind Data -- Appropriate DIAL & Met mast/Sorption Tube Positions.
  - Move as and when necessary
  - Upwinds - appropriate positioning or frequent moving
  - Appropriate Site Data/Liason
4. On-site – Flares – Different Protocols
5. On-site – Process Cycle Studies – Different protocols/very close plant personnel liason
6. Reporting- continuing site liason

# DIAL Survey Protocols

## SCIENCE BASE

## DAILY ROUTINE

- |                              |                                    |
|------------------------------|------------------------------------|
| 1. Energy optimisation UV/IR | 1. DIAL location (Orientation etc) |
| 2. UV/IR Alignment check     | 2. Met Mast deployment             |
| 3. Wavelengths set-up        | 3. Acquisition System Checks       |
| 4. IR Detector set-up        | 4. Scan plane definition           |

- Scoping Scans
- Sorpton tube/cannister positioning
- MEASUREMENTS
- On-line calibrations
- IR Species changes as required
- “On-line” Data Processing to Mass Emissions and Concentration Profiles checking for anomalies
- Continuous Site Liason
- Reporting Outlines
- Strict Adhesion to Safety Rules

# DIAL Science Base Protocols

## Other System Checks

- Dye energy/shape/linewidth change when required
- NdYAG energy optimisation
- Calibration gas cell checks/refilling
- UV Species changing - detection optics/dye/dye laser optics



# The Rose Project

## ROSE - Remote Optical Sensing Evaluation

ROSE, a 3 year research and technological development project funded by the European Commission under the Competitive and Sustainable Growth Programme (Project no: G6RD-CT2000-00434).

### AIMS AND OBJECTIVES

This project will determine QA/QC parameters defining the performance of Remote Optical Measurement Techniques in support of future EC standardisation. Calibration tools and testing methodologies will be designed and validated using a variety of commercial remote optical instruments.

### CONSORTIUM

The ROSE project team includes representatives from 6 countries:

- Draeger Sicherheitstechnik GmbH (Germany)
- NCSR "Demokritos" (Greece)
- Norsk Elektro Optikk A/S (Norway)
- Sira Ltd (UK)
- **Spectrasyne Ltd (UK)**
- Spectronix Ltd (Israel)
- ttz Bremerhaven (Germany)
- University "Politehnica" of Timisoara (Romania)
- University of Reading (UK)
- University of Surrey (UK)

# Optical remote sensing – standardisation and operating protocols

**Rod Robinson**

Environmental Measurements Group

Quality of Life Division

National Physical Laboratory

UK

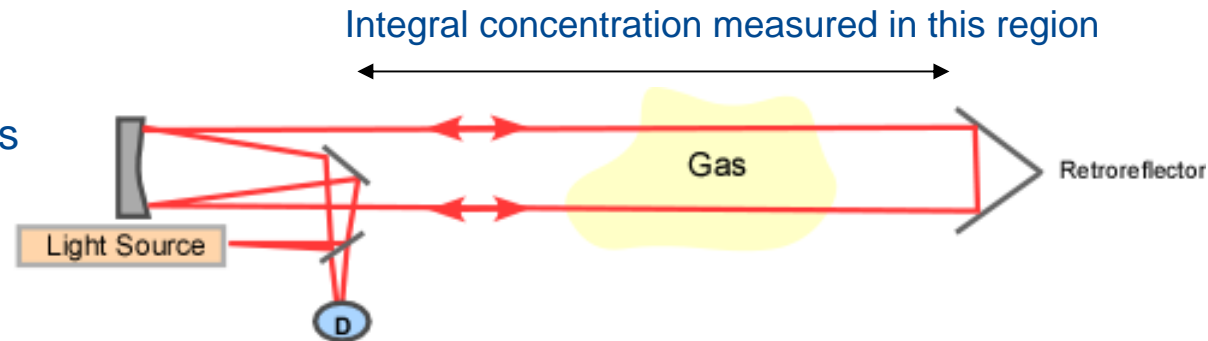
[rod.robinson@npl.co.uk](mailto:rod.robinson@npl.co.uk)



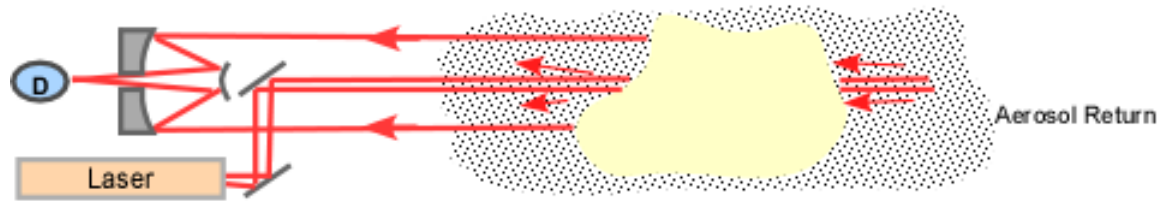
# Optical Open path configurations

- Active or passive
- Single or double ended
- Range resolving or path-integral
- Single optical path or imaging

Active systems

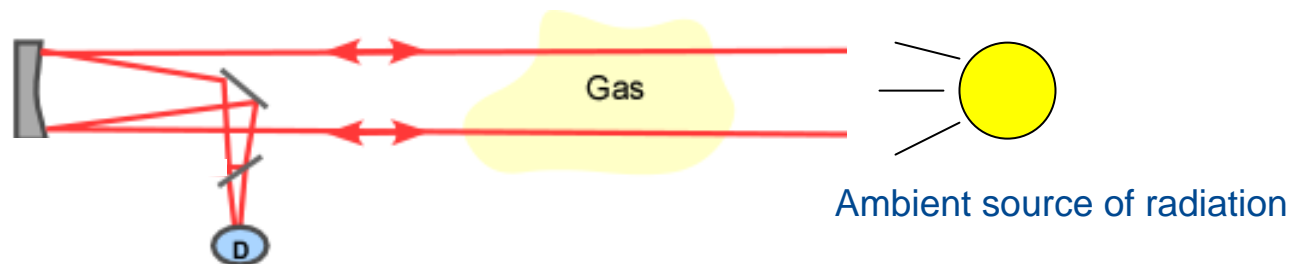


Integrated-Path Measurement



Range-Resolved Measurement

Passive systems



# NPL DIAL Performance

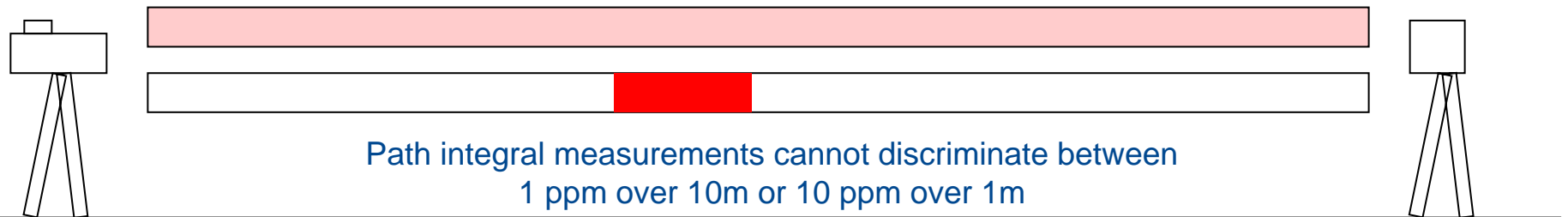
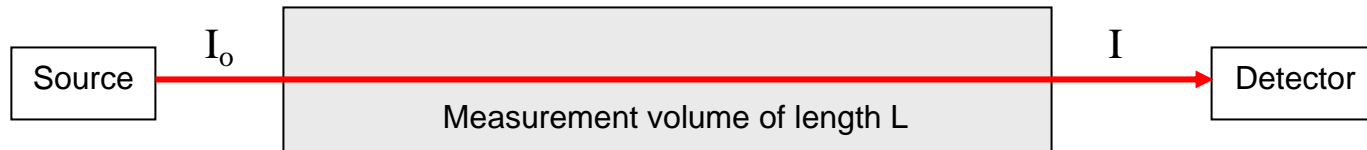
Infrared DIAL System			UV/Visible DIAL System		
Species	Sensitivity	Max. Range	Species	Sensitivity	Max. Range
CH <sub>4</sub>	50 ppb	1 km	NO	5 ppb	500 m
C <sub>2</sub> H <sub>2</sub>	40 ppb	800 m	NO <sub>2</sub>	10 ppb	500 m
C <sub>2</sub> H <sub>4</sub>	10 ppb	800 m	SO <sub>2</sub>	10 ppb	3 km
C <sub>2</sub> H <sub>6</sub>	20 ppb	800 m	O <sub>3</sub>	5 ppb	2 km
higher alkanes	40 ppb	800 m	Hg	0.5 ppb	3 km
HCl	20 ppb	1 km	Benzene	10 ppb	800 m
N <sub>2</sub> O	100 ppb	800 m	Toluene	10 ppb	800 m
CH <sub>3</sub> OH	200 ppb	500 m	Xylene	20 ppb	500 m

NB. The sensitivities apply at a range of 200 m  
for a 50 metre plume

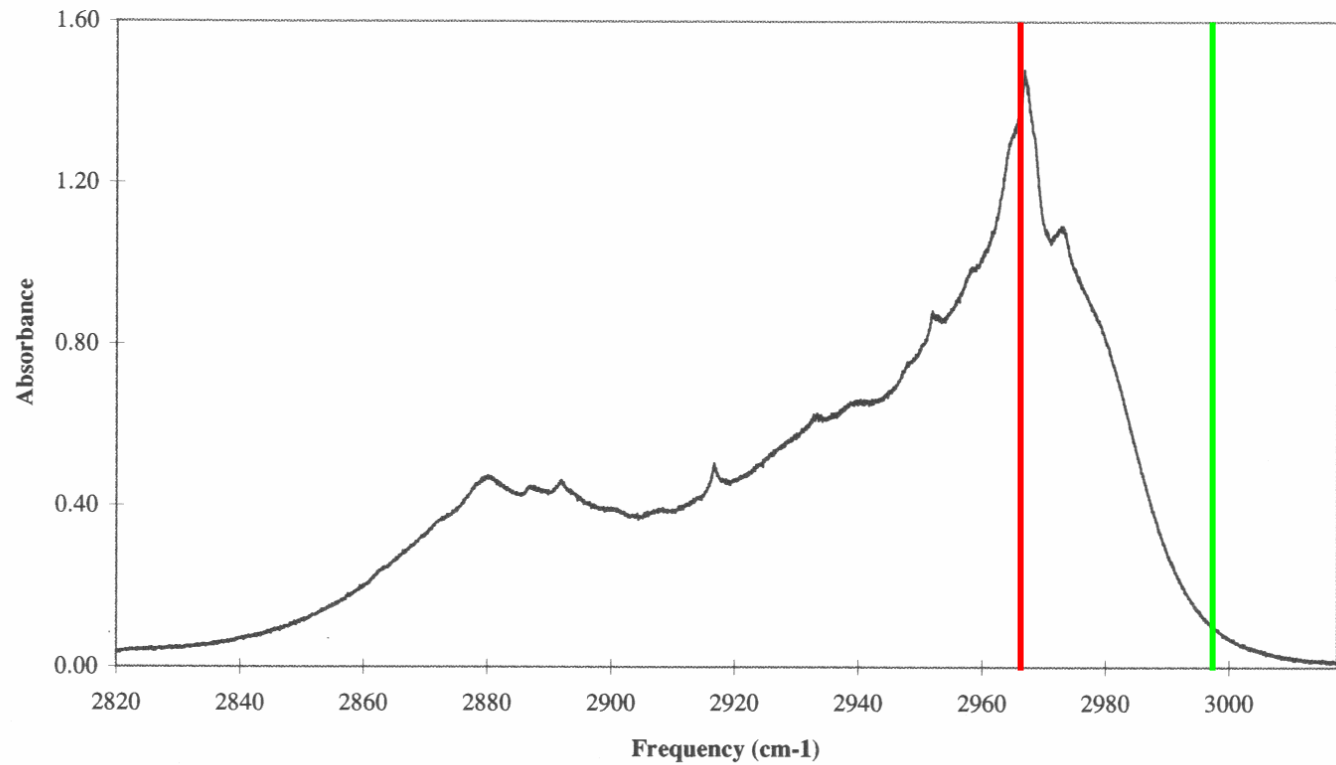
**Any statement of ORS detection in ppb/ppm, should specify over what  
path-integral**

**(NB table in OTM 10 does not specify the path length)**

## Direct Absorption Spectroscopy

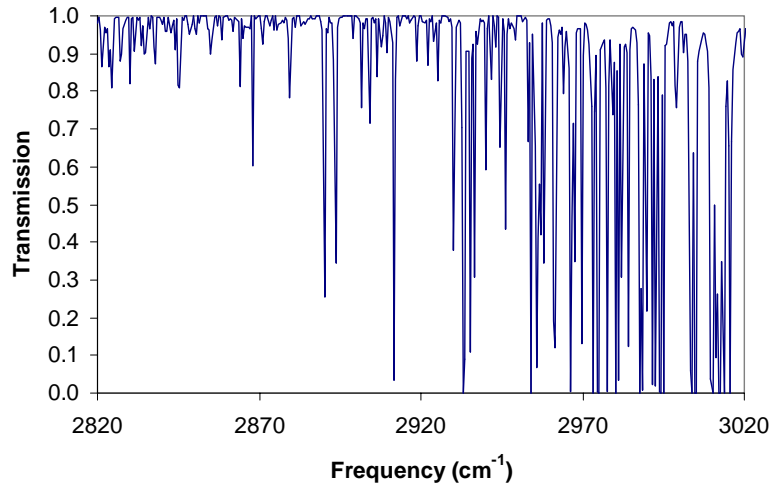


**Gasoline**  
**Absorption Spectrum of Unleaded Petrol**

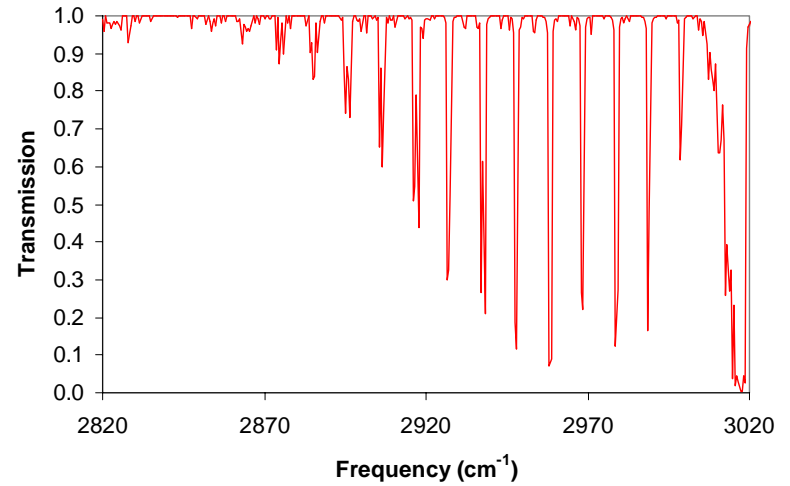


# Atmospheric absorption

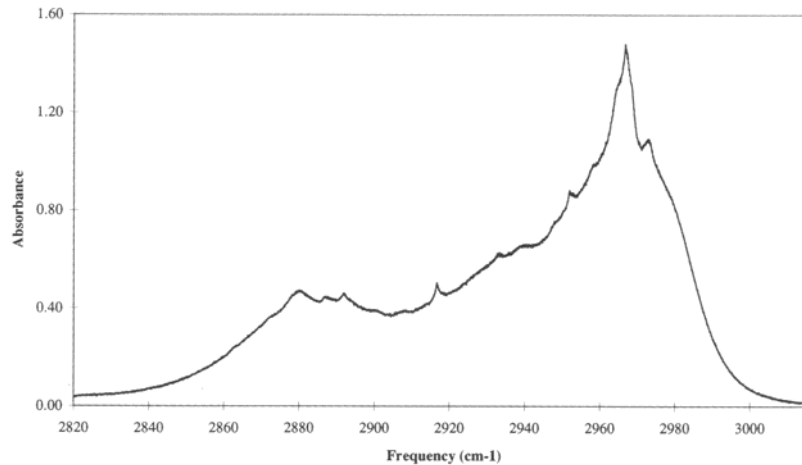
Atmospheric Water Vapour Transmission (500 metres)



Atmospheric Methane Transmission (500 metres)

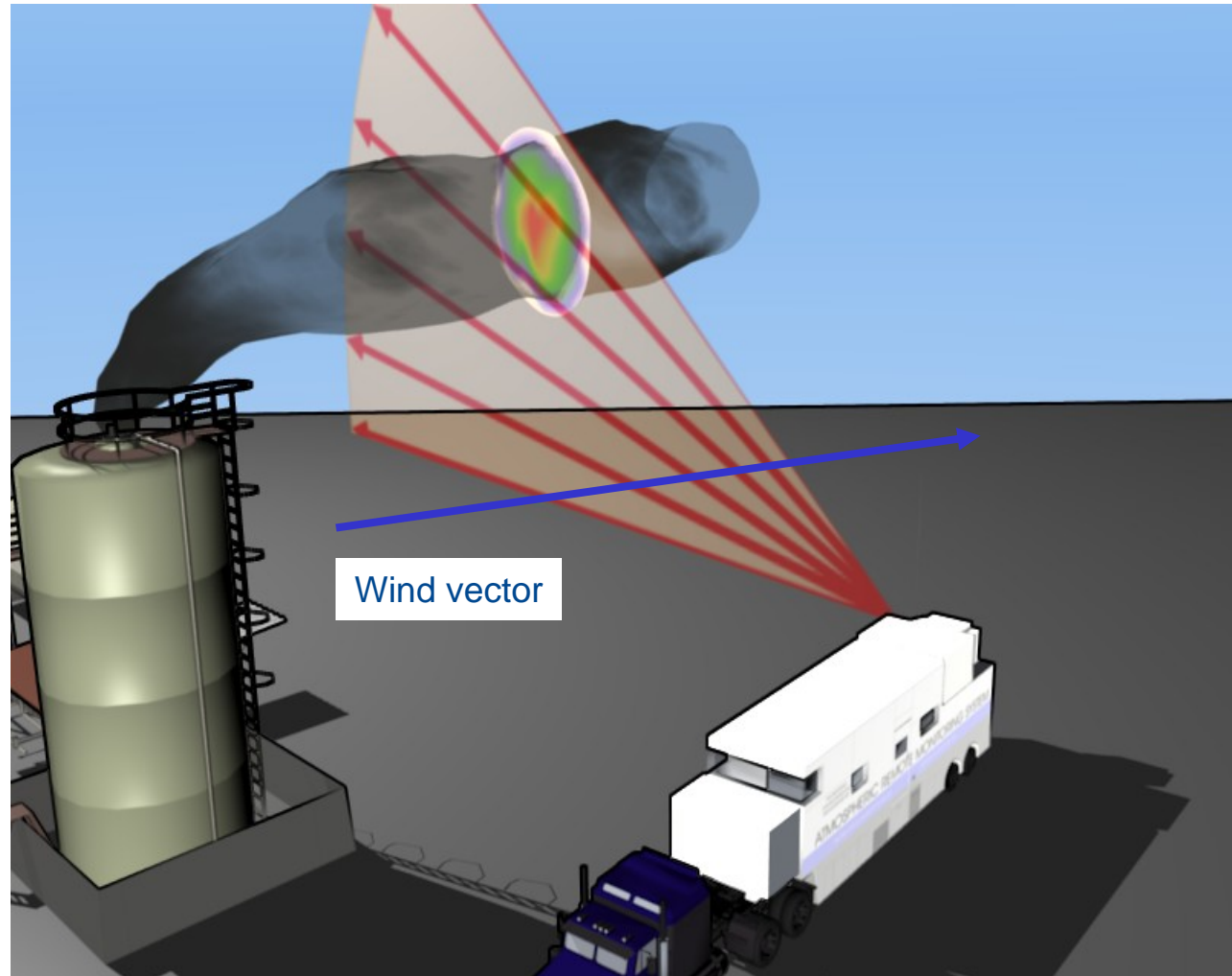


Absorption Spectrum of Unleaded Petrol



# DIAL measurement configuration for flux measurement

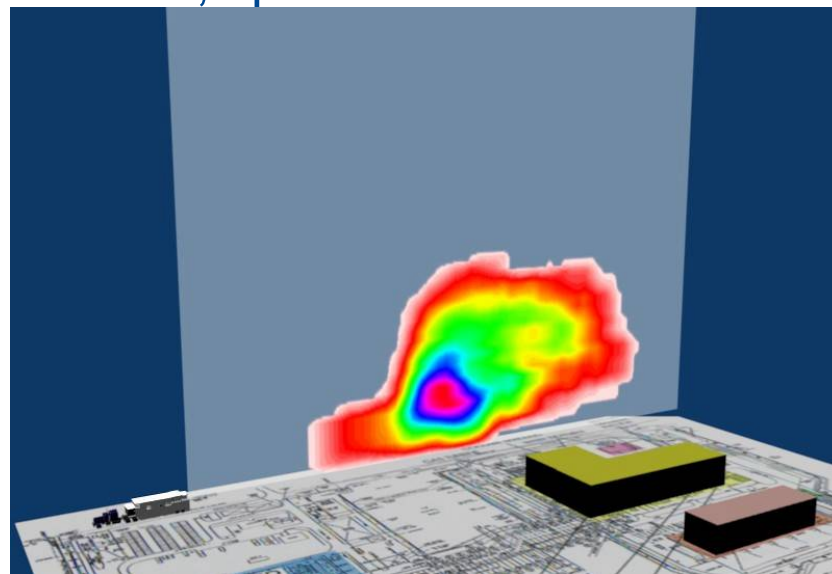
- Vertical scans enable plume mapping and flux calculation
- Combine integrated concentration with simple wind field to give flux
- Can measure away from source – less complex wind





# Some of the steps that should be addressed

- System operation
  - Control of system parameters – source power, wavelength etc
  - Calibration, traceable spectroscopy
- Path integral concentration measurement
  - DIAL is path integral – it just has a **lot** of paths
- Measurement configuration
  - Scan configuration, wind measurement, speciation
- Concentration integral
  - Time variation
  - Spatial coverage
- Wind field
- Flux calculation
  - Species covered
  - Field conditions



- European standards, CEN WG 18 Open path methods
  - Targeted at ambient monitoring
  - Standards for OP-FTIR and DOAS
  - NPL may initiate DIAL standard
- VDI standard 4210:Blatt 1
  - Remote sensing - Atmospheric measurements with LIDAR - Measuring gaseous air pollution with DAS LIDAR
  - <http://www.krdl.din.de/cmd?artid=17250263&contextid=krdl&bcrumblevel=1&subcommitteeid=54776217&level=tpl-art-detailansicht&committeeid=54739087&languageid=de>
- OTM 10
  - Long path-integral, tomography

# Examples of field validation measurements

- Repeated DIAL measurements downwind of a source of a known **flux** of methane agreed to within +/- 10% of emitted value (10 kg/hour)
- Comparison with a line of pumped absorption tube samplers inside chemical plant agreed with DIAL measurements of :
  - aliphatic hydrocarbons to within +/- 12%
  - toluene to within +/- 15%.
- VOC emission measurements from a petro-chemical storage facility made by DIAL and standard point sampling methods agreed to within +/- 8%.
- Recent validation work as part of US studies this summer –
  - Comparison with CEM monitored source (SO<sub>2</sub>)
  - Comparison against DOAS open path system (Benzene)
  - Comparison with point samples

# Windowless Cell for 'Free-space' Calibration



- 10 m long x 1 m diameter
- External calibration of open-path instruments
- No reflections from windows
- On-line monitoring of internal conditions
- Dynamic operation
- Also provides range-resolution data for lidar-type instruments

# Contents of a protocol

- Scope
- Measurement aim/objective
- Site specific protocol
  - Inc H&S
- Calibration
- System QA/QC
- Meteorology and speciation measurement
- Data quality checks
- Processing algorithm
- Data audit trail



# Important Open-path QC concepts

- Development of Data Quality Indicators (DQIs):
  - Simple tests that verify operational condition
- In-Field Calibration Checks:
  - Open-path optical cells (function cells)
- In-Field Instrument Comparisons:
  - Co-aligned optical paths during source measurement

# Open-path In-Field DQIs

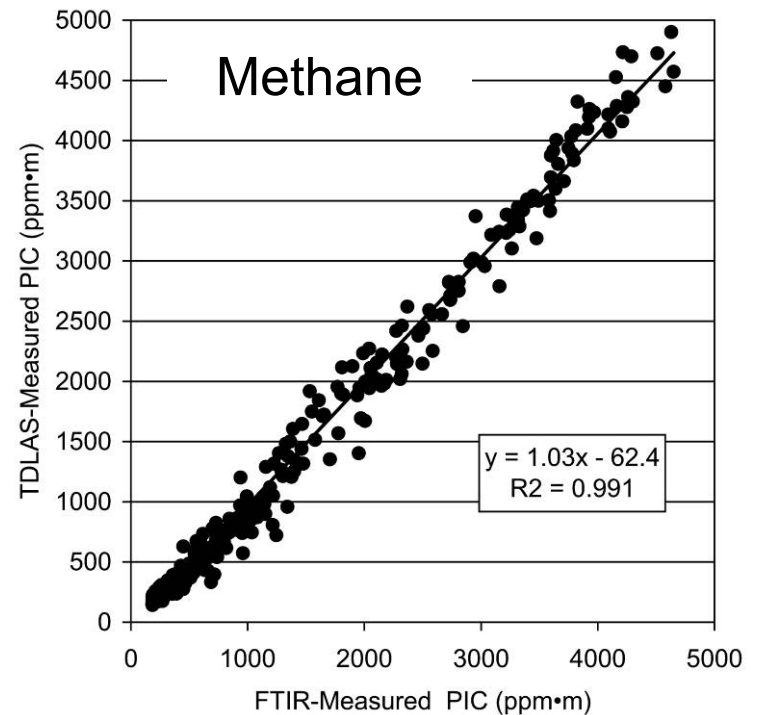
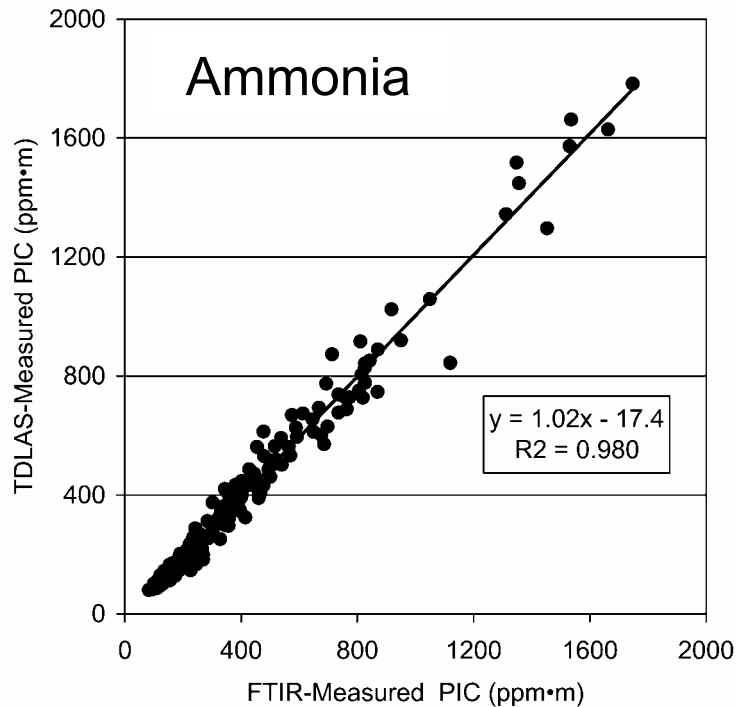
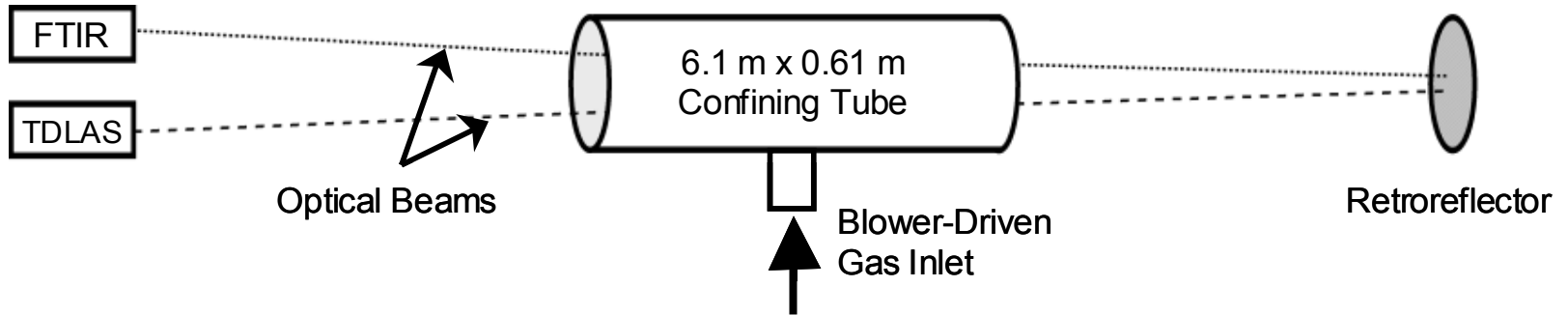
- FTIR:
  - Signal return
  - Single beam ratio
  - S/N ratio
  - N<sub>2</sub>O
- UV DOAS and TDL:
  - Signal return
  - Fit deviation
  - Function Test
- DIAL:
  - Reference frequency, S/N, Signal return (others?)

# Calibration Checks (Cells with windows)

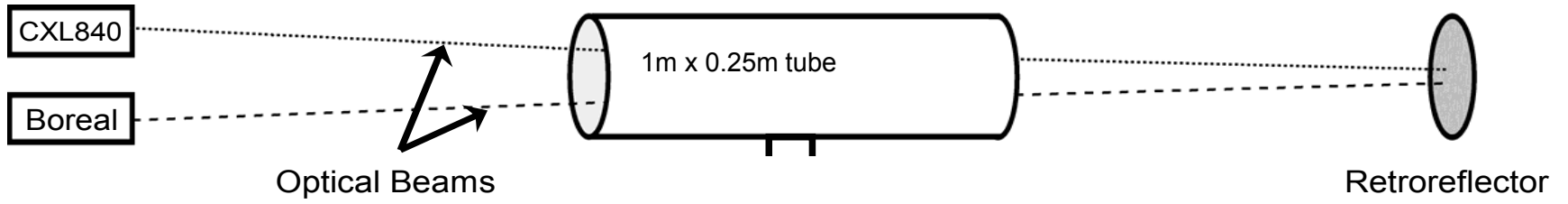




# Instrument Comparisons (Large windowless tube)

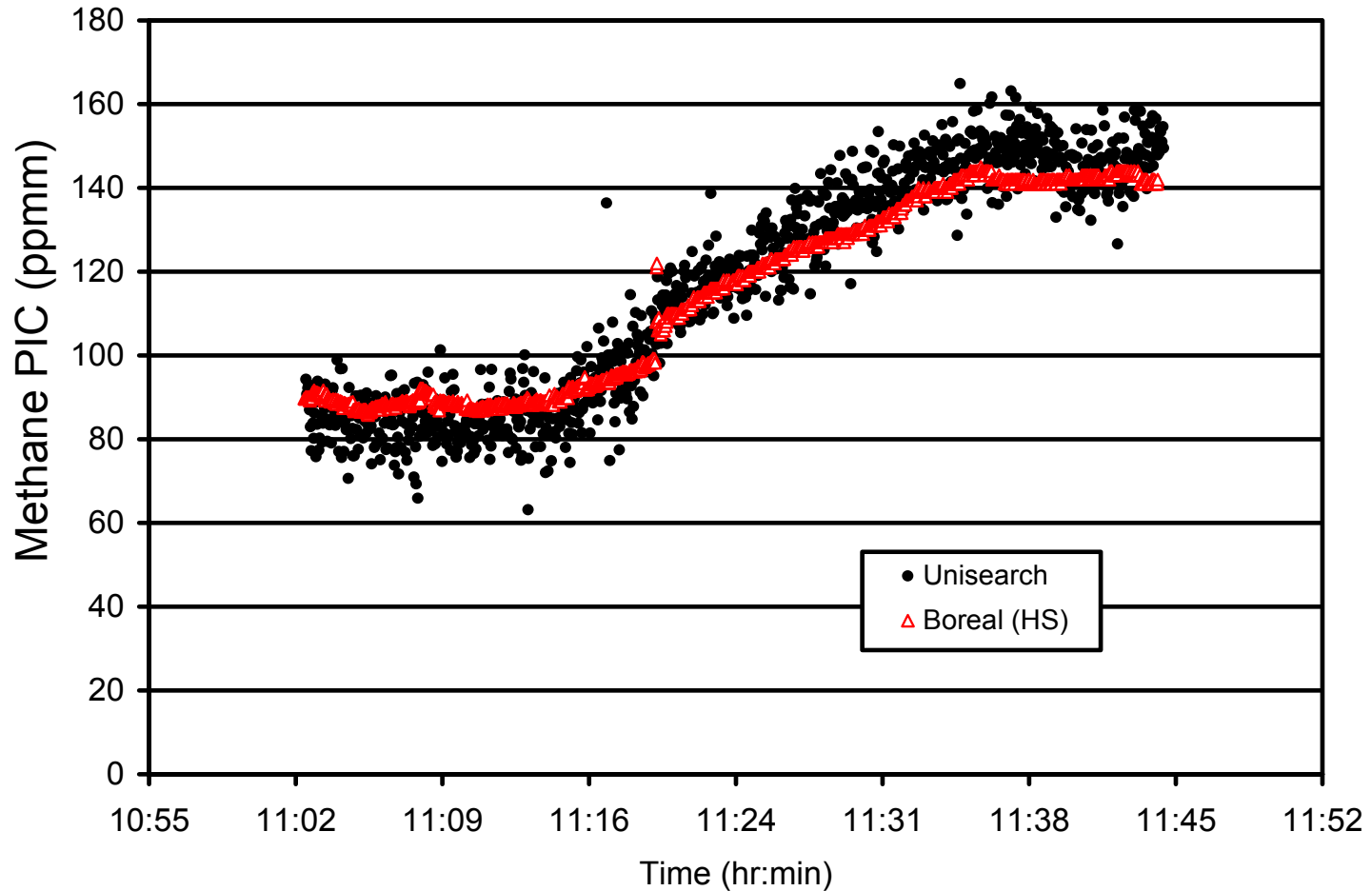


# Performance Comparison (Closed Cell)

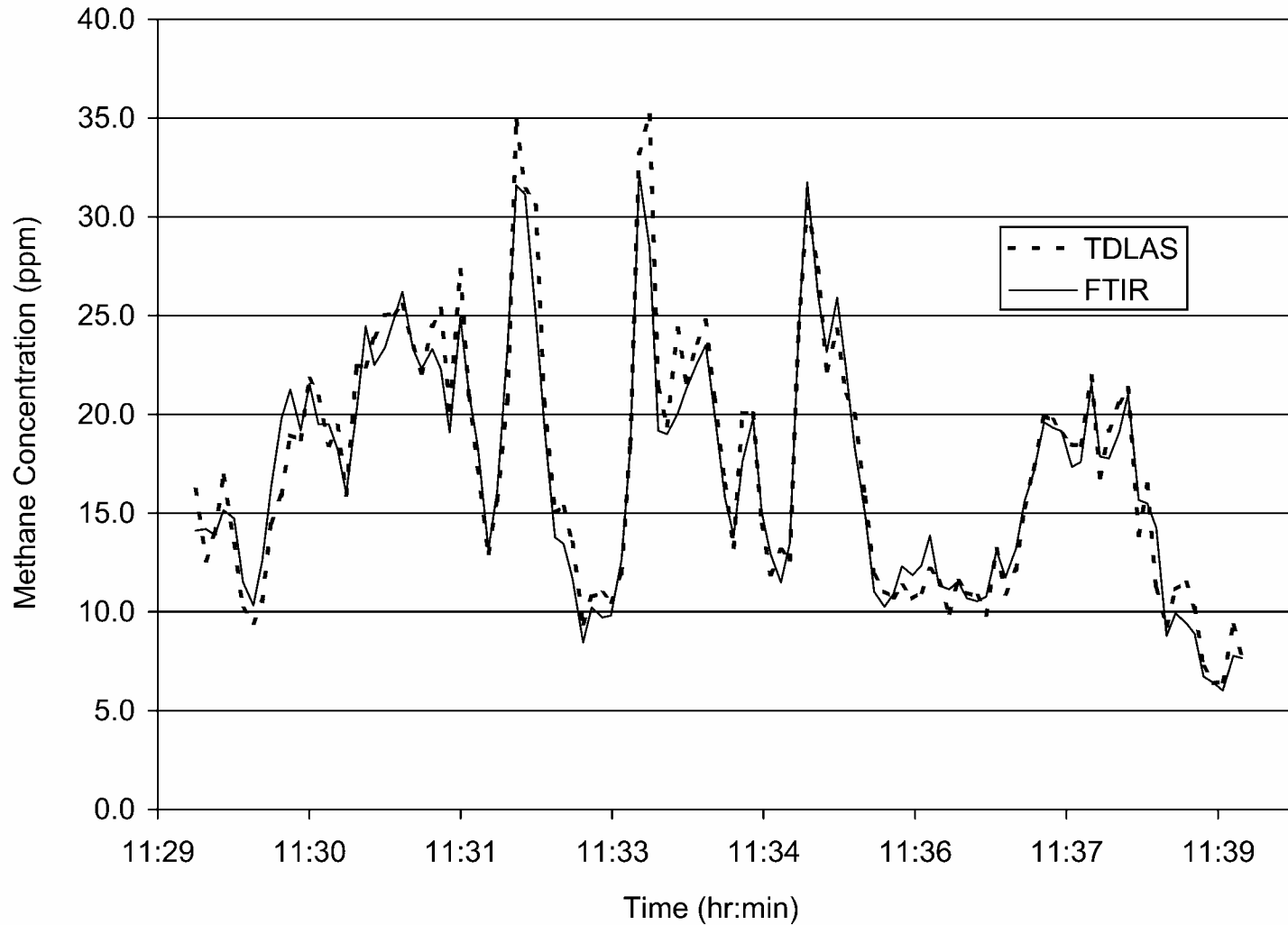


# Comparison of Two TDL Systems

Comparison of Boreal (HS) and Unisearch TDLs 041505



# In-Field Instrument Comparison (Co-aligned at landfill)



# Panel 3



Environment  
Canada

Environnement  
Canada

Canada

# Advances In The Application Of Optical Remote Sensing (DIAL) Technology in North America

Second International Workshop on VOC Fugitive Losses

Roy McArthur, Pollution Data Division  
Environment Canada  
April 1 - 4, 2008



# Presentation Outline

---

- Shift to Direct Measurement of emissions
- North American experience
- Current and Upcoming Projects
- Quality assurance Plan



# Shift to Direct Measurement of Emissions

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- US EPA Office of the Inspector General Report: “found emission factors for petroleum refineries, wood products and ethanol production emissions were significantly in error and endorsed EPA policy shift toward direct monitoring and measurement of emissions. March 22, 2006  
<http://www.epa.gov/oig/reports/2006/20060322-2006-P-00017.pdf>
- US EPA released our First Fugitive VOC Workshop report: Most significantly a large body of observations in Sweden, UK and Canada have found that measured VOC emissions at refineries were 10-20 times higher than emissions estimated from standard emission factors. October 25-27, 2006  
[http://www.emsus.com/downloads/voc\\_fugitive\\_losses.pdf](http://www.emsus.com/downloads/voc_fugitive_losses.pdf)



# Shift to Direct Measurement of Emissions

---

- On Sept 4, 2007 EPA proposed new residual risk rules for refineries to provide additional health protection by adding new requirements to the existing rule for certain storage vessels and wastewater treatment units. New work practice standards for the detection and repair of leaks from refinery cooling towers.
- The Clearstone Engineering report commissioned by Environment Canada on the European and North American experience with DIAL: “The DIAL technology is unique in its ability to rapidly develop near real-time two- and three-dimensional mapping of the atmospheric emissions plume from point, line and complex area or volume sources.”

# Canadian Experience

---

- Successive DIAL applications at a refinery in Sweden realized total hydrocarbon reductions of over 84%.
- EC has funded and co-funded DIAL demonstration projects at industrial facilities from 2003 through 2005 performed in collaboration with the:
  - Canadian Association of Petroleum Producers (CAPP), and
  - Ontario and Alberta Ministries of the Environment.

# Canadian Experience

---

- EC's demonstration studies highlighted the unique ability of DIAL in the quantification and source apportionment of VOCs and other emissions across complex processing facilities.
- Plant-wide fugitive emissions have been found to be many times higher than reported emissions for a number of gas plants and a refinery studied in Canada
  - These findings were similar to those obtained from measurements performed in over 130 studies undertaken in Europe since 1990



# Canadian Experience

---

- CAPP members recognized the importance of the technology for recovering valuable losses from leaking equipment and have conducted a number of private DIAL studies in the oil patch.
- Published reports on the use of DIAL technology from the Edmonton refinery study and other DIAL measurements are available from the Alberta Research Council ([www.arc.ab.ca/Index.aspx/ARC/8300](http://www.arc.ab.ca/Index.aspx/ARC/8300)) and the Spectrasyne ([www.spectrasyne.ltd.uk/html/home.html](http://www.spectrasyne.ltd.uk/html/home.html)) web sites.
- Subsequent to the DIAL study of the Edmonton refinery, the US EPA began co-funding DIAL demonstration projects. EPA to fund \$40 Million in direct measurement programs over the next fiscal year.

# Current & Upcoming Projects

---

The Fugitive Losses Workshop led to a number of DIAL initiatives, including:

## **1. The Texas Commission on Environmental Quality (Russ Nettles)**

- Conducted DIAL study of a Refinery in Texas City plus representative petroleum facilities the Ship Channel;
- The 28 days DIAL testing concluded in August of 2007 and draft report presented for comment;
- Co-funded by US EPA.

## **2. A Private Refinery Study was completed in Texas.**

# Current & Upcoming Projects (Cont'd)

---

## 3. City of Houston Air Quality Office

- Planned DIAL study of air toxics (i.e. Butadiene, benzene, PAHs) from petrochemical and refining operations.
- Expected launch in 2008?
- Study to be co-funded by the U.S. EPA and the City of Houston.

## 4. Canadian Studies

- Expected DIAL study at a steel mill (with focus on quantification of VOC, PAH, Hg releases from coking operations) as well as a possible study at a petroleum refinery operation;
- Expected launch in fiscal 2008/09;
- Study may be co-funded by Environment Canada, and the provinces of Ontario and Alberta.

# Quality Assurance

- Quality assurance for ORS was established as an important development opportunity at our first workshop.
- It is important for regulators and facility operators: level playing field with good information available for project planning and air quality management.
- Since most of the release comes from only a few big sources, LDAR costs would diminish.
- QAP would assure consistent comparable results and lead to continuous improvement, reduce uncertainty.
- Cross comparison of different ORS results would improve the results, reliability (i.e., DIAL, SOF, etc).

# Quality Assurance

---

- Species by species comparisons/validation is desirable (i.e., an SO<sub>2</sub> release is not relevant in establishing certainty in the measure of HRVOCs).
- The skills and experience of EPA authorities would be of great value in the development of a QAP.
- The experience of professional practitioners will be invaluable in the development of an effective QAP
- QAP development will insure the growth of quality emission measurement, an essential component of air quality management



# Collaboration

---

- Web meetings
- Educational Web Seminars
- Online Tools



**Project Description:** A space to learn about web conference tools, team-based website packages, instant messaging, and other tools available to EPA employees

### Project Members

[Show Info](#)

**Project Owner**

- Jean Balent

**Members**

- Annabel Waggoner
- Art Donner
- Barry Nussbaum
- Bernice Betts
- Brenda Gaillard
- Bruce Means
- Carlyn Perry
- Carolyn Offutt

[Send an email to all project members](#)

To chat with other members, [install Oracle Messenger](#).

### Project Calendar

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Mar 2008						
Sun	Mon	Tue	Wed	Thu	Fri	Sat
						1
2	3	4	5	6	7	8
9	10	11	12	13	14	15
16	17	18	19	20	21	22
23	24	25	26	27	28	29

### Message Board

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[Web conferencing needs?](#) - Preview  
0 responses - Last post by Jean Balent

[User Capacity Web Conference Test](#) - Preview  
1 response - Last post by Jean Balent

[Issues with Sametime](#) - Preview  
3 responses - Last post by Jean Balent

[Post New Topic](#)  
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Folder	Name	Info	Size	Date Posted
EPA Distance Collaboration				
AIM				
EPA Portal				
EPA Science Connector				
EPA Teleconferencing Serv				
GoToMeeting				
Oracle Collaboration Works				
Oracle Messenger				
Oracle Web Conferencing				
Outreach Strategy				
QuickPlace				
Sametime				
Sametime Connect				
WebEx				
	<a href="#">Distance Collaboration Tool Seminar F...</a>		93 KB	02/25/2008
	<a href="#">Getting Access to the EPA Portal</a>		97 KB	02/13/2008
	<a href="#">IM and Video options</a>		84 KB	03/09/2008
	<a href="#">Internet Seminar Possibilities</a>		86 KB	11/30/2007
	<a href="#">OSWER Collaboration Tool Experiences</a>		6271 KB	02/14/2008
	<a href="#">Online Workspace Possibilities</a>		82 KB	11/30/2007
	<a href="#">Summary of Some Collaboration Tools</a>		26 KB	03/11/2008
	<a href="#">Web Conference Needs Survey</a>			03/11/2008

# Understanding the Market

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- Selling the service
- EPA may not be a customer; but EPA and other Regulatory Agencies DO influence!
- <http://www.cluin.org/vendor/>



# EPA Collaboration Tool

The screenshot shows a web browser window displaying the EPA Innovative Technologies website. A red oval highlights the top navigation bar and search area. The browser's address bar shows the URL <http://www.epa.gov/tto/>. The website header includes the EPA logo and the text "U.S. ENVIRONMENTAL PROTECTION AGENCY". The main heading is "Innovative Technologies". Below this, there is a search bar with the text "Search: All EPA This Area" and a "Go" button. The main content area features a "Welcome to the Technology Innovation Program" banner and a paragraph describing the program's purpose. A sidebar on the left lists various navigation options, and a "TIP's News Corner" box on the right displays recent news items. The footer contains the text "Site maintained by: Technology Innovation Program, Office of Superfund Remediation and Technology Innovation, Office of Solid Waste and Emergency Response" and links to "EPA Home", "Privacy and Security Notice", and "Contact Us". The system tray at the bottom shows the date and time as "Friday, March 28th, 2008" and "9:12 PM".

ORACLE  
Conference ID: 221515  
Share Nothing  
Michael Adam  
Network Connection  
Michael Adam: No desktop areas shared  
Poll Preferences Conference Details Help  
Click to Share  
US EPA http://www.epa.gov/tto/

U.S. ENVIRONMENTAL PROTECTION AGENCY  
**Innovative Technologies**  
Recent Additions | Contact Us  
Search:  All EPA  This Area  Go  
You are here: [EPA Home](#) » [OSWER](#) » [Superfund](#) » Innovative Technologies

**Welcome to the Technology Innovation Program**

The Technology Innovation Program's Web Site provides information about characterization and treatment technologies for the hazardous waste remediation community. It offers technology selection tools and describes programs, organizations, publications for federal and state personnel, consulting engineers, technology developers and vendors, remediation contractors, researchers, community groups, and individual citizens. Our goal is to create an information support net for all technology decision makers who address contamination of soil or groundwater.

**TIP's News Corner**  
What's new from TIP  
» TIP Spotlight  
» New Publications  
» Courses & Conferences  
» FEDBizOps  
» TechDirect  
» New Videos  
Live Web Events  
[EXIT Disclaimer](#)  
» Apr 3: Decontamina...  
» Apr 10: Monitoring ...  
» Apr 10: Characteriz...  
» Apr 17: Risk Assess...  
» Apr 22: Earth Day G...  
» Apr 24: Protocol fo...  
Browse or Search All 177 Archived Live Web Events

Site maintained by: Technology Innovation Program, Office of Superfund Remediation and Technology Innovation, Office of Solid Waste and Emergency Response

[EPA Home](#) | [Privacy and Security Notice](#) | [Contact Us](#)

Last updated on Friday, March 28th, 2008.

start  
Collaboration.ppt  
OAQPS Works...  
EPA BTSC PA 5...  
2 Windows E...  
Environmental ...  
Innovative Tec...  
Document1 - M...  
Google  
Trusted sites  
100%  
9:12 PM



**EPA** United States Environmental Protection Agency **Technology Innovation Program**

Comments | Site Map | EPA Home | Home

Print Version | We Need Your Feedback | **CLU-IN Search**

# CLU-IN Studio

- Internet Seminars**
  - > Upcoming Live Seminars
  - > Archived Internet Seminars
- Videos**
- Conference Webcasts**
  - > Upcoming Conference Webcasts
  - > Archived Conference Webcasts

<http://www.cluin.org/studio/default.cfm>

**<http://www.cluin.org/studio/>**

# http://www.cluin.org/studio/seminar.cfm

- What's Hot? What's New?
- Remediation
- Characterization and Monitoring
- Training
- Initiatives and Partnerships
- Publications and Studio**
- Databases
- Software and Tools
- TechDirect and Newsletters
- Vendor and Developer Support
- About CLU-IN

**EPA** United States Environmental Protection Agency

**Technology Innovation Program**

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## Publications and Studio

**i** For more information on Internet Seminars, please contact:

Jean Balent  
 Technology Integration and Information Branch  
 (703) 603-9924  
[balent.jean@epa.gov](mailto:balent.jean@epa.gov)

### Internet Seminars



CLU-IN's ongoing series of Internet Seminars are free, web-based slide presentations with a companion audio portion. We provide two options for accessing the audio portion of the seminar: by phone line or streaming audio simulcast. More information and registration for all Internet Seminars is available by selecting the individual seminar below. Not able to make one of our live offerings? You may also view archived seminars below. [\[En español\]](#)

**PODCAST**  
 Subscribe to our Internet Seminar archive podcast feed [\[Podcast Help\]](#)

- **Upcoming Live Seminars (Information, Dates, & Registration)**
- **Archived Internet Seminars (Slides & Audio from Past Offerings)**

**> Upcoming Live Seminars**

Some comments we've received about Internet Seminars. . .

*"Great job overall. great job on snuffing out the background noise! The instructors did a wonderful job and I appreciate the opportunity to take this web streamed training session."*  
 — U.S. NRC Government Employee

[View All Comments](#)

**Cancel Registration** [For Apr 3: Decontamination and Decommissioning of Radionuclide Sites](#)

**April 2008** May 2008

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
		1	2	3 ITRC Decontamination...	4	5
6	7	8	9	10	11	12

<http://www.cluin.org/vendor>

**CLU-IN**

What's Hot? What's New?

Remediation

Characterization and Monitoring

Training

Initiatives and Partnerships

Publications and Studio

Databases

Software and Tools

TechDirect and Newsletters

Vendor and Developer Support

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**Vendor and Developer Support**

**i** For more information on Vendor/Commercialization Support, please contact:

Carlos Pachon  
 Technology Integration and Information Branch  
 (703) 603-9904  
[pachon.carlos@epa.gov](mailto:pachon.carlos@epa.gov)

The vendor support area provides technology developers and vendors with tools to help advance technologies through all stages of product development from bench scale to full commercialization. The materials cover a broad range of topics that include business planning, marketing, financing, and technical issues and sources.



The topics are organized into six sections arranged, approximately, in the order in which they are encountered in developing and commercializing a technology. Each section addresses a particular group of activities that lead to the advancement of a technology from the germination of an idea to research, development, testing, and finally to commercial application. The sections are listed below.

Publications | FedBizOpps (Mar 24-28) | Comments | **Vendor E-briefings for EPA**

Includes Air monitoring for remediation and waste sites

This website contains references to a number of sources outside EPA. While we consider the contents of these publications to be of general merit, its listing in an Environmental Protection Agency website is for information purposes and does not constitute an endorsement of the views and opinions of the authors or the products or services of the companies with which they are affiliated.

States Environmental Protection Agency Technology Innovation Program

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## Vendor and Developer Support

### For E-briefings for EPA

### E-briefings for EPA

The Technology Innovation Program is providing a web-seminar forum for vendors (products and services) to educate an internal government audience about technologies and innovative strategies for using technologies. The seminar will include environmental program employees from EPA, other Federal and State governments. If you wish to present your product or service, please contact Michael Adam ([adam.michael@epa.gov](mailto:adam.michael@epa.gov)), and provide your contact information, and subject of the proposed educational presentation.

Conclusion include:

Commercial entity must have a technology relevant to cleaning up hazardous-contaminated lands as judged by the professional judgment of EPA waste managers (see "[professional judgment](#)" below).

Commercial entity:

- must have Federal/State representative projects, OR
- must have Federal or State formal technology evaluation, OR
- must be able to document use through a treatability study (demonstration of methods applicability, etc) the use of a technology at a Fed/State led project will be required to sign a waiver for participation ([11KB/1p/PDF](#)) stating
  - i. that they will not be compensated for participation in this event, and,
  - ii. participation does not constitute endorsement by EPA of any specific company, its employees, its services or its specific technologies or brand names, and,
  - iii. agree that they will not use this briefing forum as a promotional endorsement in marketing and advertising efforts, and,
  - iv. that they grant EPA and the briefing participants permission to copy, distribute, make derivatives, or display publicly the materials provided during the presentation, and the presentation recording for Federal purposes.

must be designed to provide training, research results, and information

## Professional Judgment

The Technology Innovation Program will use professional judgment to determine topic selection and inclusion in that topic based on:

- X Topic/technology needs as expressed by present audiences, Agency offices, etc
- X Relevancy to hazardous-waste issues, including (not limited to):

XXXX  
XXXX

**c. Air monitoring technologies to monitor and remediation of contaminated land and sites.**

--The more evidence you can show the better. Use evaluations, use at sites (case studies, Reports, etc.

--No guarantees about audience  
-- Educational

-- Our best interest to try and get the



# What we want to learn (Educate Us!)

---

- Project managers → up to date on latest methods, strategies, and technologies
  - Removal
  - Remedial
- Leveraging experience in air programs
- Improve information resources, training
- Increased understanding
  - Applications
  - Cost and performance
  - Limitations



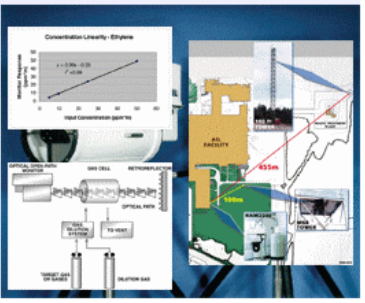
- Home
- 21M<sup>2</sup> Home
- Background
- Needs
- SBIR
- Project Status
- Literature Search
- Technology Focus Areas
- Contacts

EPA United States Environmental Protection Agency

Technology Innovation Program

# Measurement and Monitoring Technologies for the 21st Century (21M<sup>2</sup>)

## OPEN PATH TECHNOLOGIES: MEASUREMENT AT A DISTANCE



Open path technologies measure the concentrations of chemicals or particulates across an open path of air. They do this by emitting a concentrated beam of electromagnetic energy into the air and measuring its interactions with the air's components. Some instruments (e.g., ultra-violet differential optical absorption UV-DOAS spectra) are capable of measuring only a few compounds simultaneously, while the Fourier transform-infrared FTIR spectra and others can measure a large number of compounds simultaneously. The most practical use of open path instruments provides average chemical concentrations over a set distance. This feature has an advantage over point-source measurements that may miss high-concentration plumes running between sampling devices or are too difficult to use in inaccessible areas. Conversely, open path instruments generally are not deployed to detect hot spots within a single line of measurement. An exception to this rule is the infrared video camera, which provides a real time visualization of fugitive gas plumes but cannot speciate or quantitate the gasses in the plume.

Differential absorption light detection and ranging (DIAL-LIDAR) instruments project a laser wavelength that is strongly absorbed by the target compound and a second nearby wavelength that is not absorbed by the target compound. The difference in intensity of the two return signals can be used to calculate the concentration of the target compound. These instruments are generally used to identify and quantitate one chemical at a time. However, they are capable of measuring the concentration of the target compound at any specified distance from the instrument; hence, they can be used to plot concentration contours that are used to identify high and low areas within the plume.

Although Raman open path instruments are capable of quantitating and speciating a large number of organic and inorganic compounds, they have relatively high detection limits. They are applied mostly to identifying unknown substances in emergency response situations and drug enforcement activities. The following table contains a summary of open path instrumentation characteristics and general uses. A thorough discussion of each instrument can be found at:

- > UV-DOAS
- > OP-FTIR
- > LIDAR
- > Raman Spectroscopy
- > Tunable Diode Lasers (TDLs)

- Summary Table
- Updated for 2007
- Technical Bulletin?

# Comments?

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**Michael Adam**  
**703.603.9915**  
**adam.michael@epa.gov**

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**U.S. EPA OSWER Technology Innovation Program**  
***<http://www.epa.gov/tio> & <http://www.cluin.org>***

# **Small Group Discussions**

**Group 1**  
**Blueprint for Future ORS**  
**Field Studies**



# Recommendations/Approach

- Workgroup will continue
- Solicit professional associations for representatives to participate with the workgroup
- Three products were identified to be developed by the Workgroup

# Matrix comparing ORS Technologies

- Work in progress, matrix structure to be developed by Workgroup and sent to provider experts
- Identify different means of doing ORS Studies
- Agree on what those techniques are, what they can produce, maturity, cost (?)
- A number of information sources were identified
- Eben Thoma will take the lead

# WebSite

- A location for the Matrix
- Community can use as reference, to identify ORS techniques, providers
- Location for reports, references
- List of issues that should be addressed



# QA Process

- Rod and Jan will expand their list of protocols and disseminate to group
- Walter will assemble existing approved QA plans
- Group will identify QA guidance to be recommended
- Issues to be addressed include meterology, facility characteristics, validation/verification.  
representativeness
- Dennis Mikel will take the lead

# Remote Sensing of Emissions and Emission Inventories

2<sup>nd</sup> EPA Workshop on Remote  
Sensing of Emissions

Workgroups 3 and 4

April 3, 2008

# Issues

1. Obstacles to using remote sensing to estimate emissions
2. Opportunities to use remote sensing to estimate emissions

# Obstacles to Using RS to Estimating Emissions

- Lack of accepted protocols for most RS
- High costs for using RS (real and perceived)
- If unreported emissions are detected using RS, operator may have regulatory problems due to credible evidence/data liability
- Currently, it's difficult to extrapolate short term measurements to long term emissions

# Opportunities for Using RS to Estimate Emissions

- Find upsets so they can be fixed
- Provide additional data to inform the determination of emission factors and address the variability in emission factors

# Using RS to Find and Fix

- If RS enables a facility to find and fix leaks and other upsets, actual emissions may come closer to estimated emissions
- So, without any change to regulations or emission factors, emission estimates are more accurate
- Everybody's happy

# Using RS to Inform Emission Factors

- Emission factors will continue to be needed (for example, to estimate emissions for hypothetical scenarios)
- Traditionally, EPA (thru AP-42) has not addressed long-term vs short term emission rates
- There appears to be a need for shorter term emission rates
- RS can provide data to address emission rates, typically short term

# Using RS for Fenceline Measurements

- Fenceline measurements suitable for use for long term monitoring
- Use RS to inform temporal variations
- Ground-truth large scale inventories
- Replace or complement emissions monitoring



# Conclusions and Recommendations

- We need to think in a broader way that would promote and/or allow RS
  - An RS comparison matrix for regulated community is needed, addressing cost and applications
- RS data can be used to adjust emission estimates and reduce emissions
- RS can also be used to measure ambient concentrations at the fenceline
- We need promulgated RS methods that can be used in permitting and other regulatory uses