Measuring VOCs in Refineries and Chemical Plants

University of Houston
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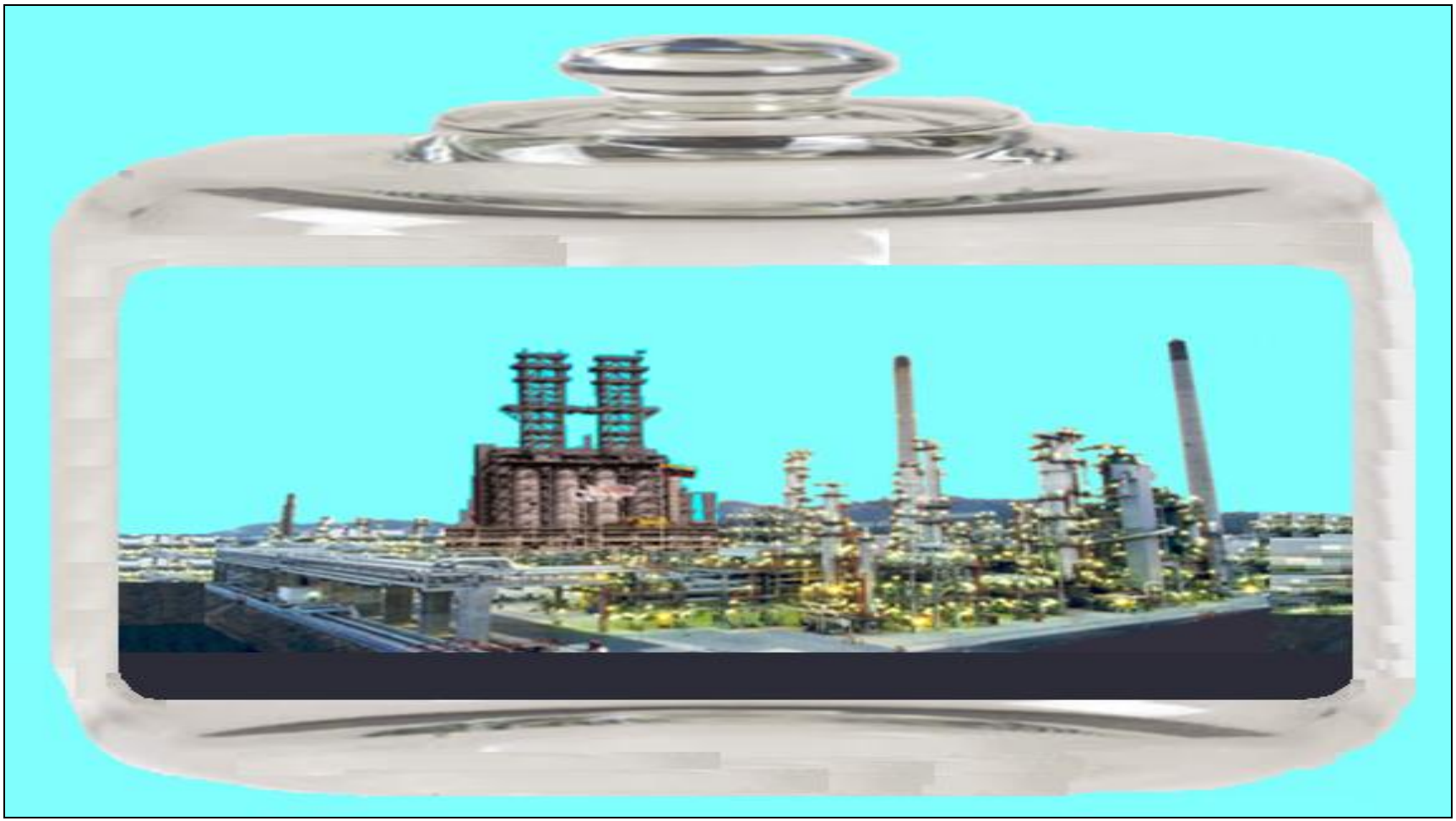
12 Topics

1. Measuring VOCs in Refineries
2. IR Camera
3. Texas Air Quality Study (TexAQS) in 2000
4. Differential Absorption LIDAR (DIAL)
5. Solar Occultation Flux
6. TexAQS II
7. Canadian Refinery DIAL Report – 2006
8. Measurement Options
9. Flares
10. Section 114 and Tonawanda Coke Company
11. Verification of DIAL and SOF
12. Best Available Control Technology and Measurements

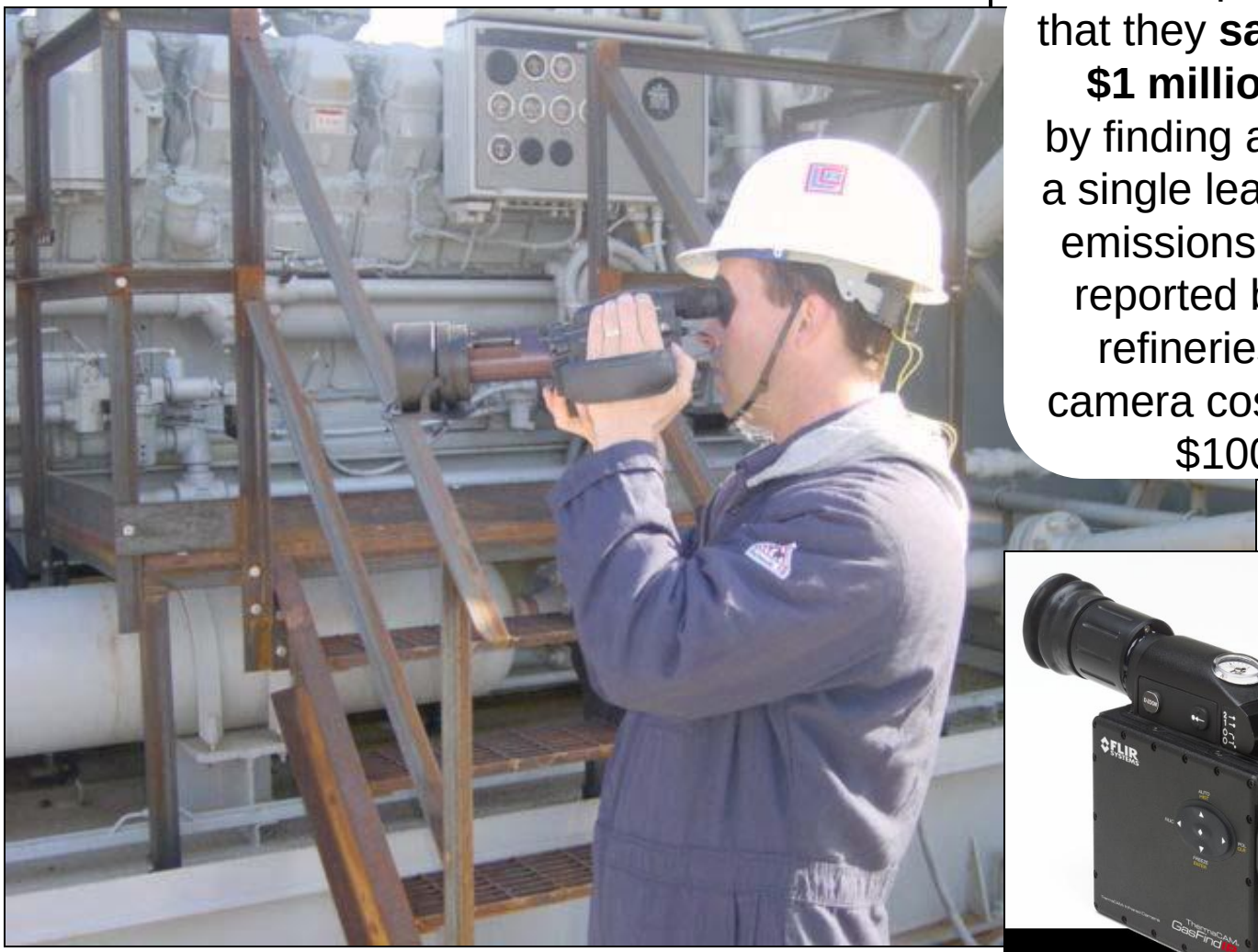
1. Measuring VOCs in Refineries



NOx, SOx, CO, etc. typically come out of stacks and can be measured there, in many cases with Continuous Emissions Monitoring Systems (CEMS). VOCs however can come from anywhere, hence quantifying them is very difficult. This presentation focuses on measuring VOCs.

2. The IR Camera

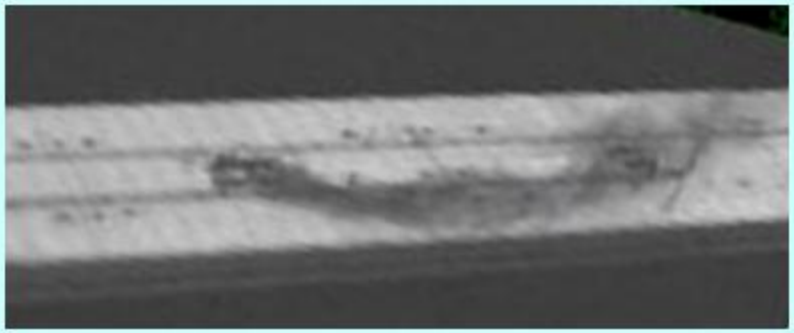
Some companies report that they **saved** over **$1 million/year** by finding and fixing a single leak! (more emissions than are reported by most refineries) The camera costs about $100K.



With the IR Camera VOCs appear as a dark cloud. It was developed around 2002-2003.

2. The IR Camera

Barge with naked eye

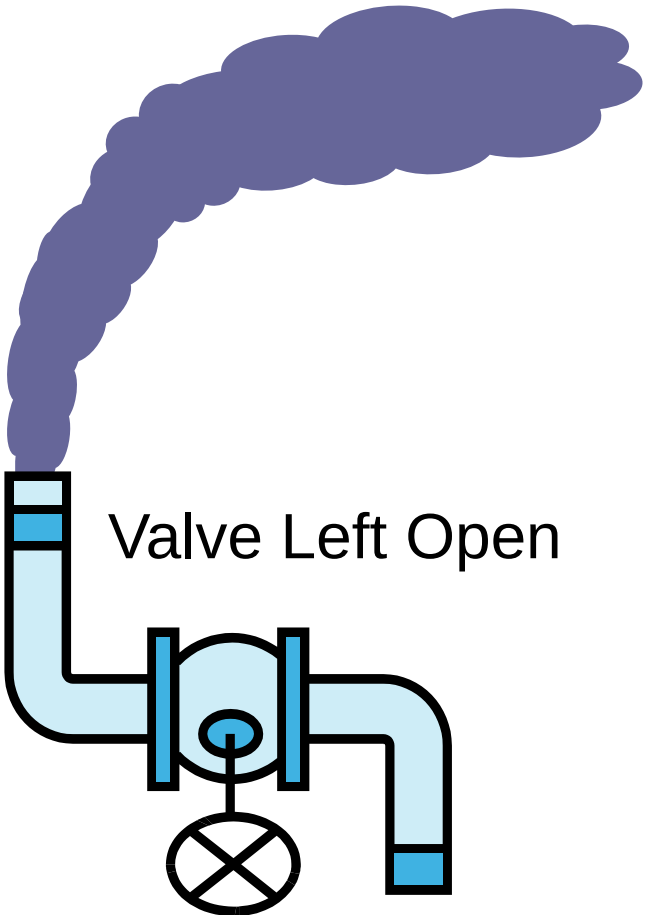


Barge with IR Camera

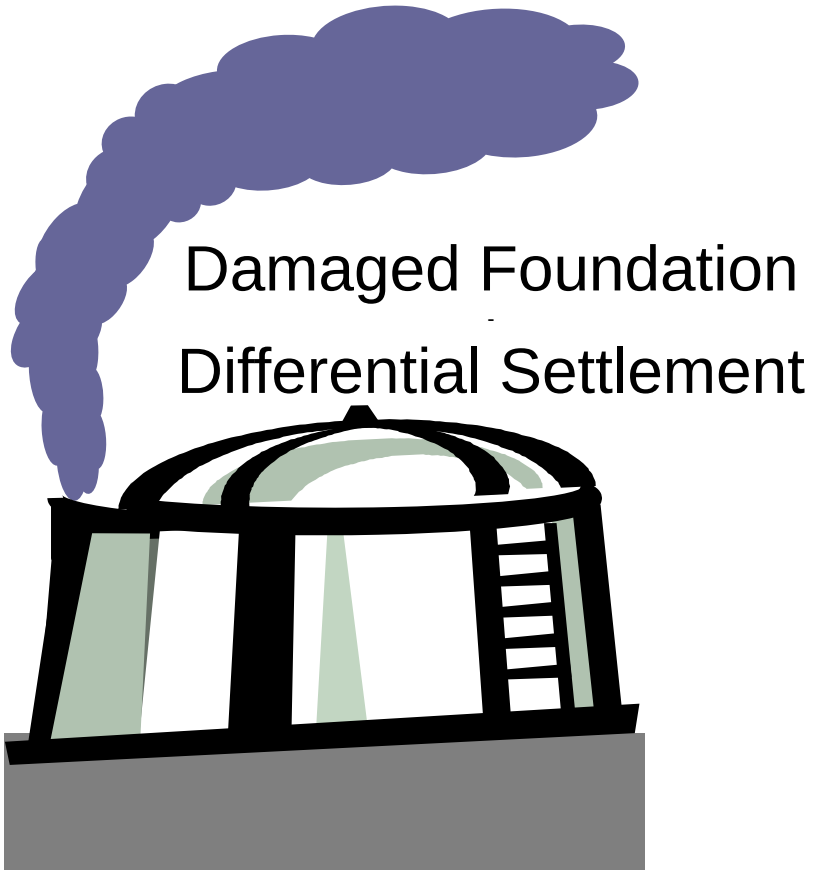
Different Barge with IR Camera

2. The IR Camera

IR Camera Finds $1 Million Leakers!!!



Cost to repair: $0



Cost to repair: $30 Million

2. The IR Camera

Some Limitations are…

In order to “see” a VOC plume sometimes you must try different times of the day, from different locations.

Operators may not know what compounds can or cannot be “seen” by IR cameras.

IR camera cannot “see” all VOC’s.

Operators who understand the concept don’t have a tool to determine which compounds are easier to be “seen” than others; work mainly based on experience.

This passive device is 2-3 times less sensitive than some others.

2. The IR Camera

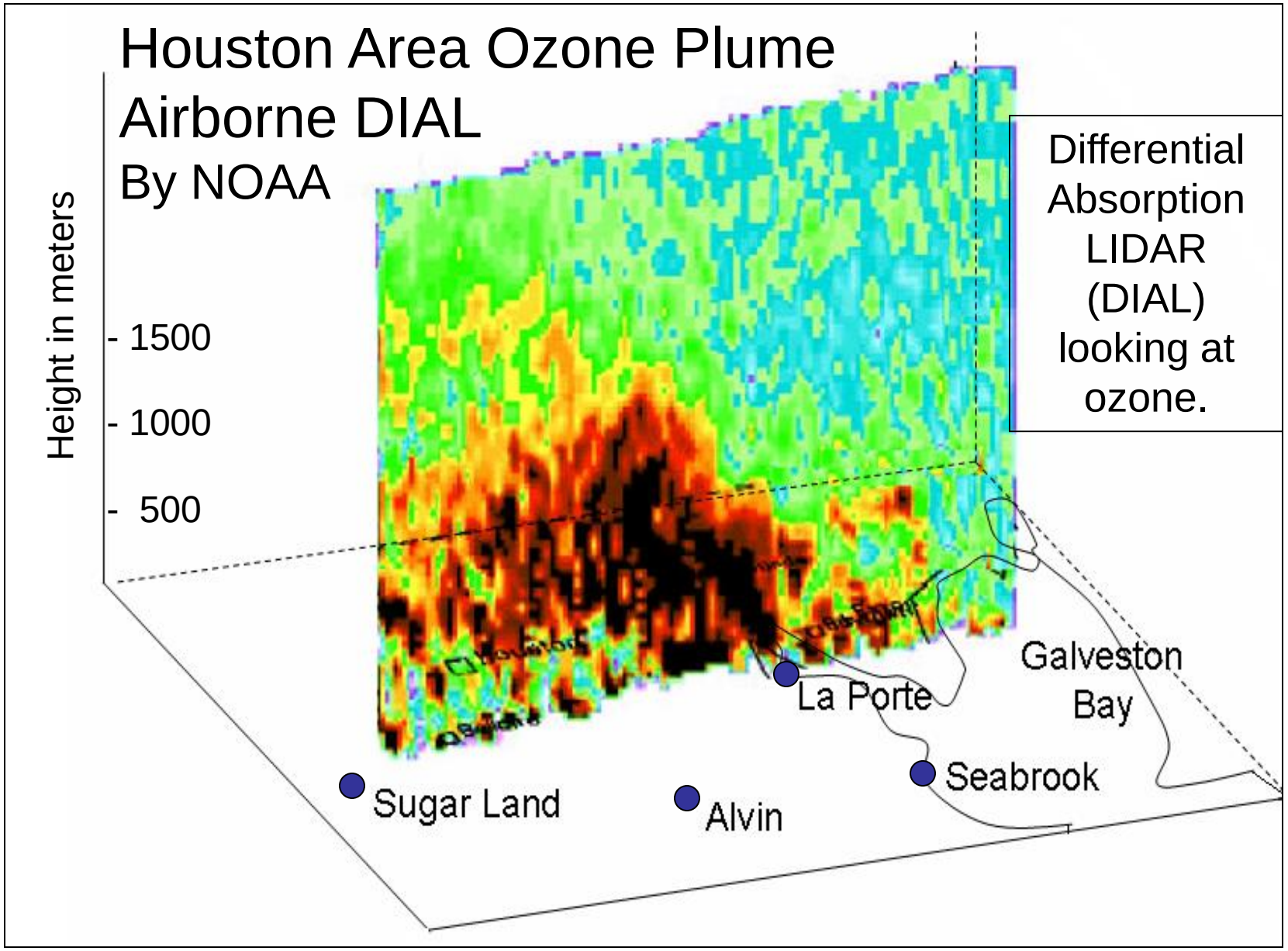
Legal Issues…

TCEQ does fly-overs, and based on pictures and video will require that companies take action.

The IR Camera does not quantify, so companies can claim that even though there are emissions, they may not be over the permitted levels.

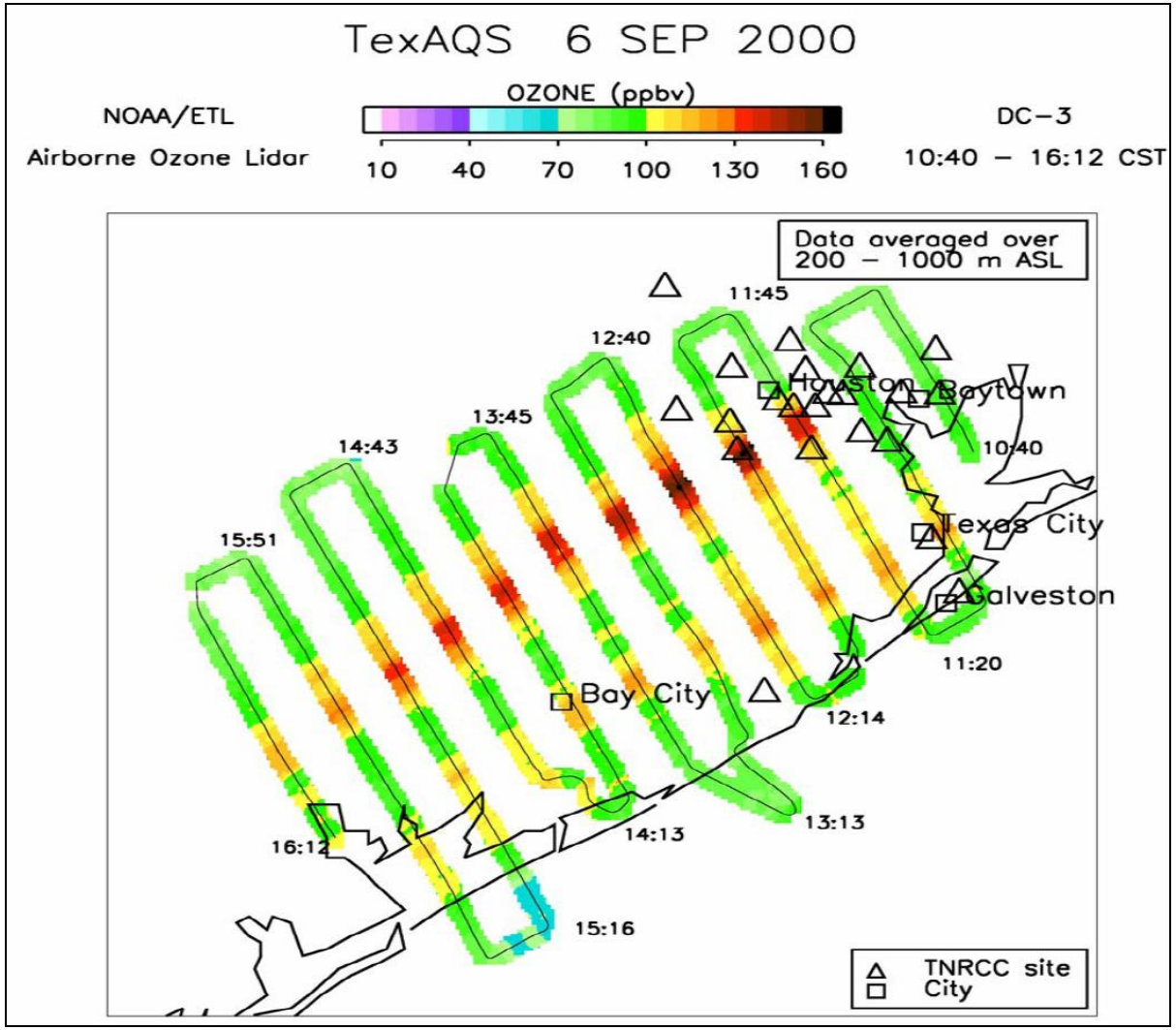
If you don’t measure, you don’t know, and there are no records…

3. Texas Air Quality Study (TexAQS 2000)



3. Texas Air Quality Study (TexAQS 2000)

Ozone on the Texas Coast



3. Texas Air Quality Study (TexAQS 2000)

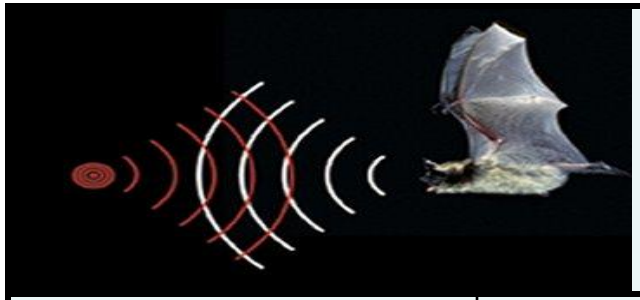
1. Almost without exception the ozone plume in Houston had its source in the Houston Ship Channel.

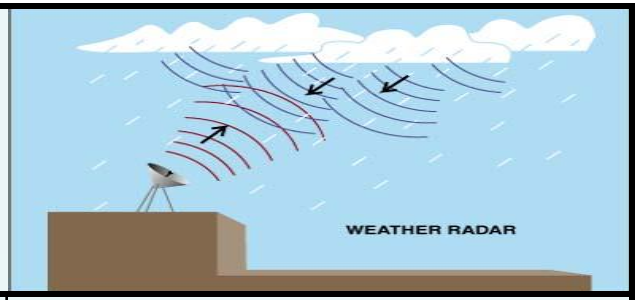
2. VOC emissions, especially ethene and propene, were found to be substantially higher than expected based on reported values.

3. Some said the error was a factor of 3-10 or 15, others said the error was a factor of 10-100.

4. Differential Absorption LIDAR (DIAL)

Detection By Reflection



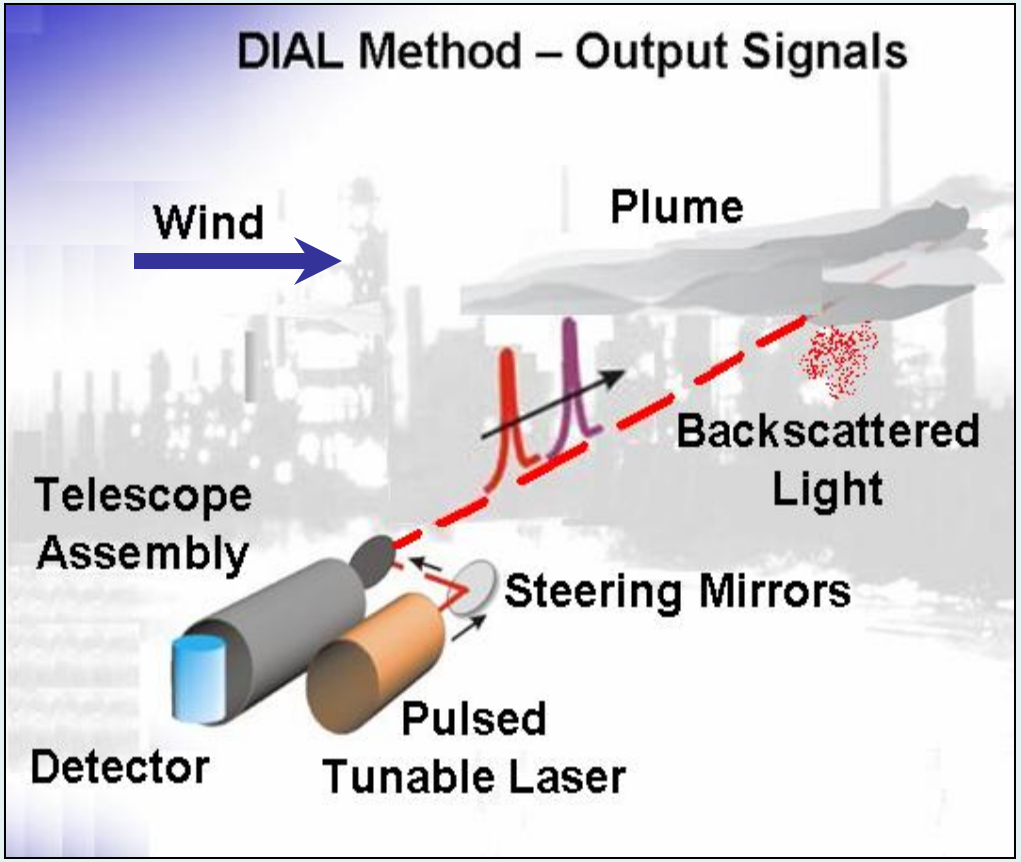


Method	Medium	Measures
SONAR Sound Navigation And Ranging	Sound Often Under Water	Location, Speed
RADAR Radio Detection And Ranging	Radio Waves High Energy EM	Location, Speed
LIDAR Light Detection And Ranging	Light Waves Single Wavelength	Wind Speed, Surveys
DIAL DIfferential Absorption LIDAR	Light Waves Dual Wavelength	Concentration, Composition, Location, Flux

4. Differential Absorption LIDAR

Lasers send dual-wavelength pulses towards a gaseous plume.

Back-scattered light returns to a detector assembly.



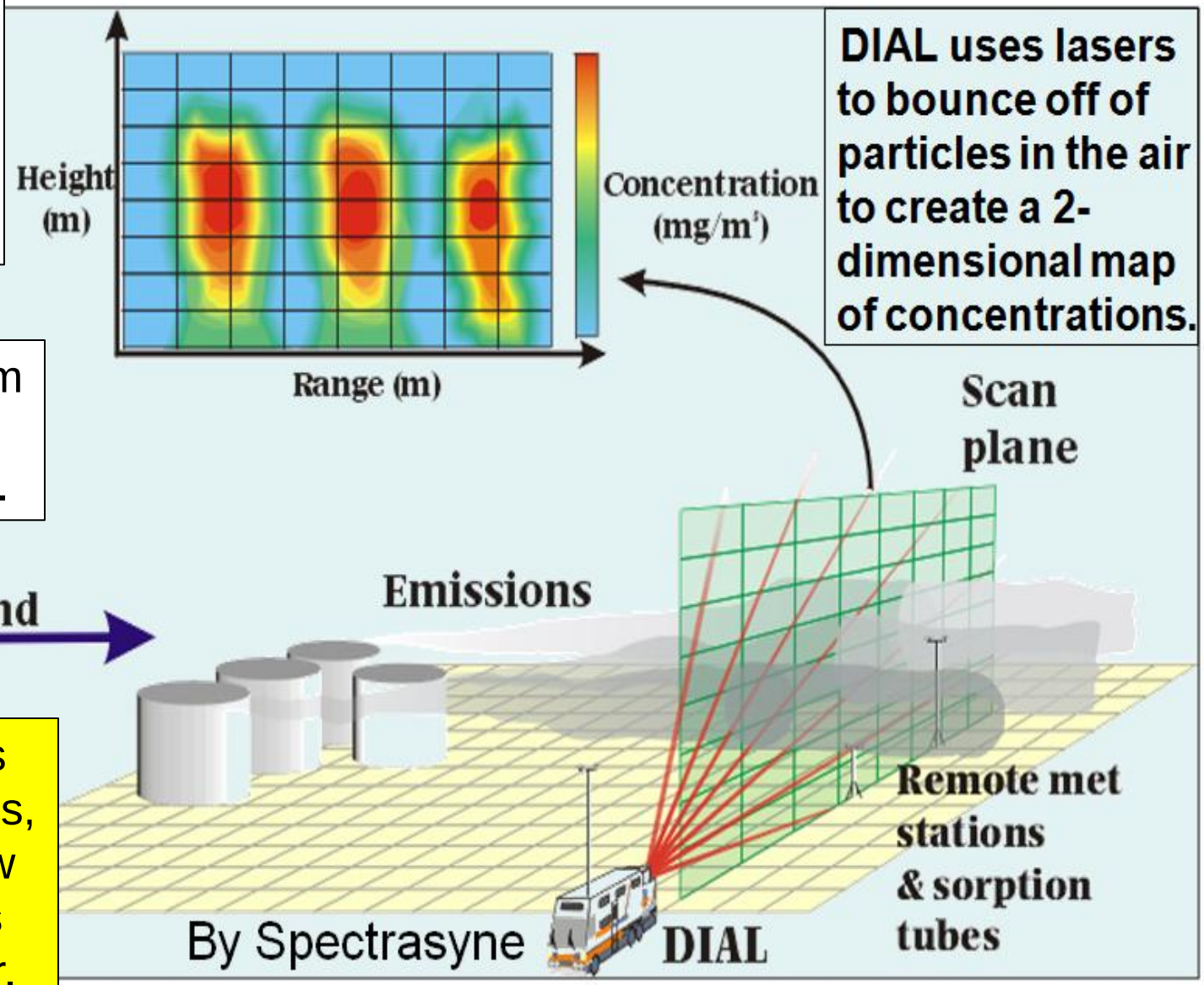
By Spectrasyne

4. Differential Absorption LIDAR
BP/Spectrasyne's System

By using the wind speed one can calculate the mass flux of VOCs in lbs/hour.

A new DIAL system would cost about $3 million to build.

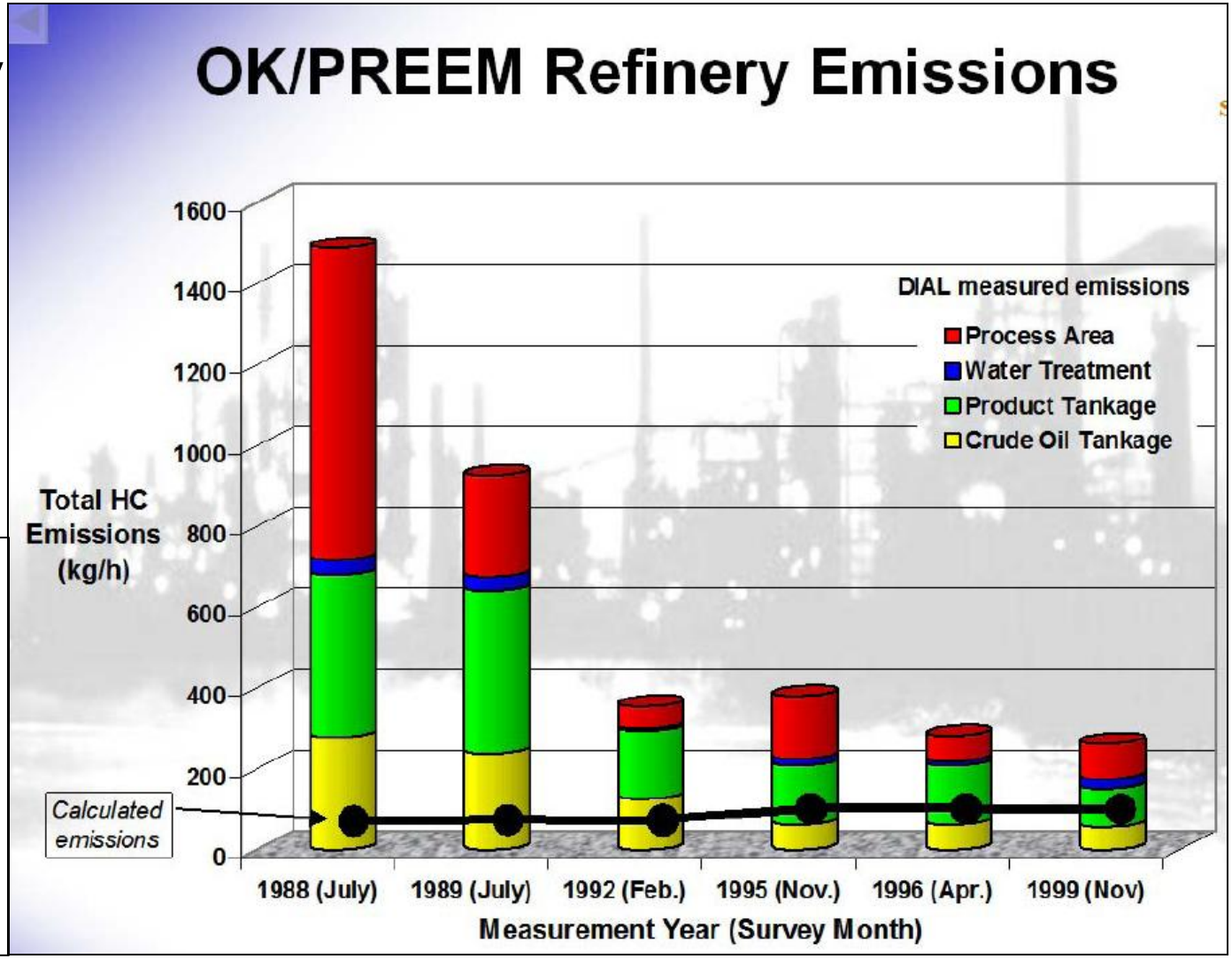
Other techniques give concentrations, but DIAL tells how much pollution is released per hour.



4. Differential Absorption LIDAR

BP found that emissions were underestimated by a factor of 20 in 1988.
They brought the technology to most European facilities in the next 5 years.
In 1992 they sold the technology to the BP employees who developed it.

The new company was called Spectrasyne.

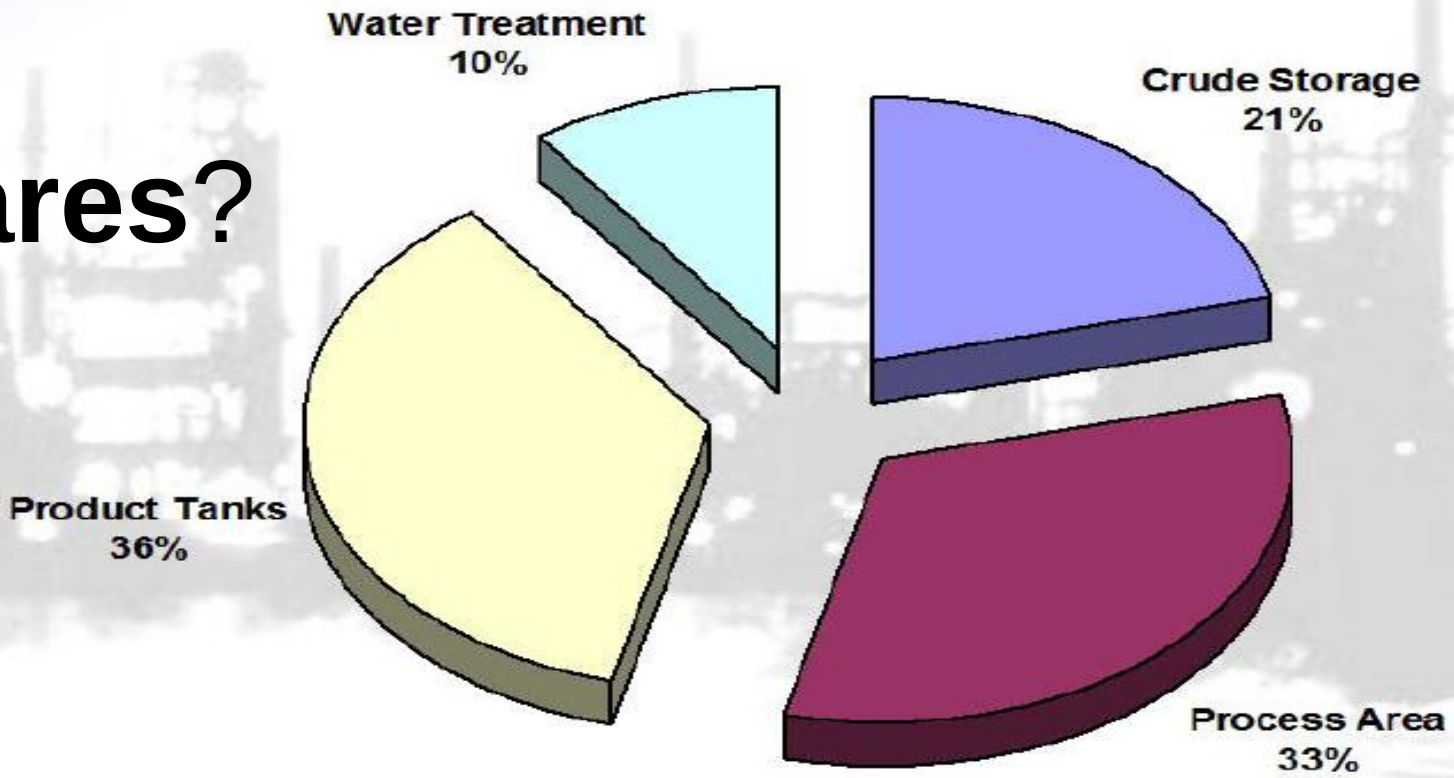


Note that the calculated emissions are constantly low and do not change much year to year.

4. Differential Absorption LIDAR

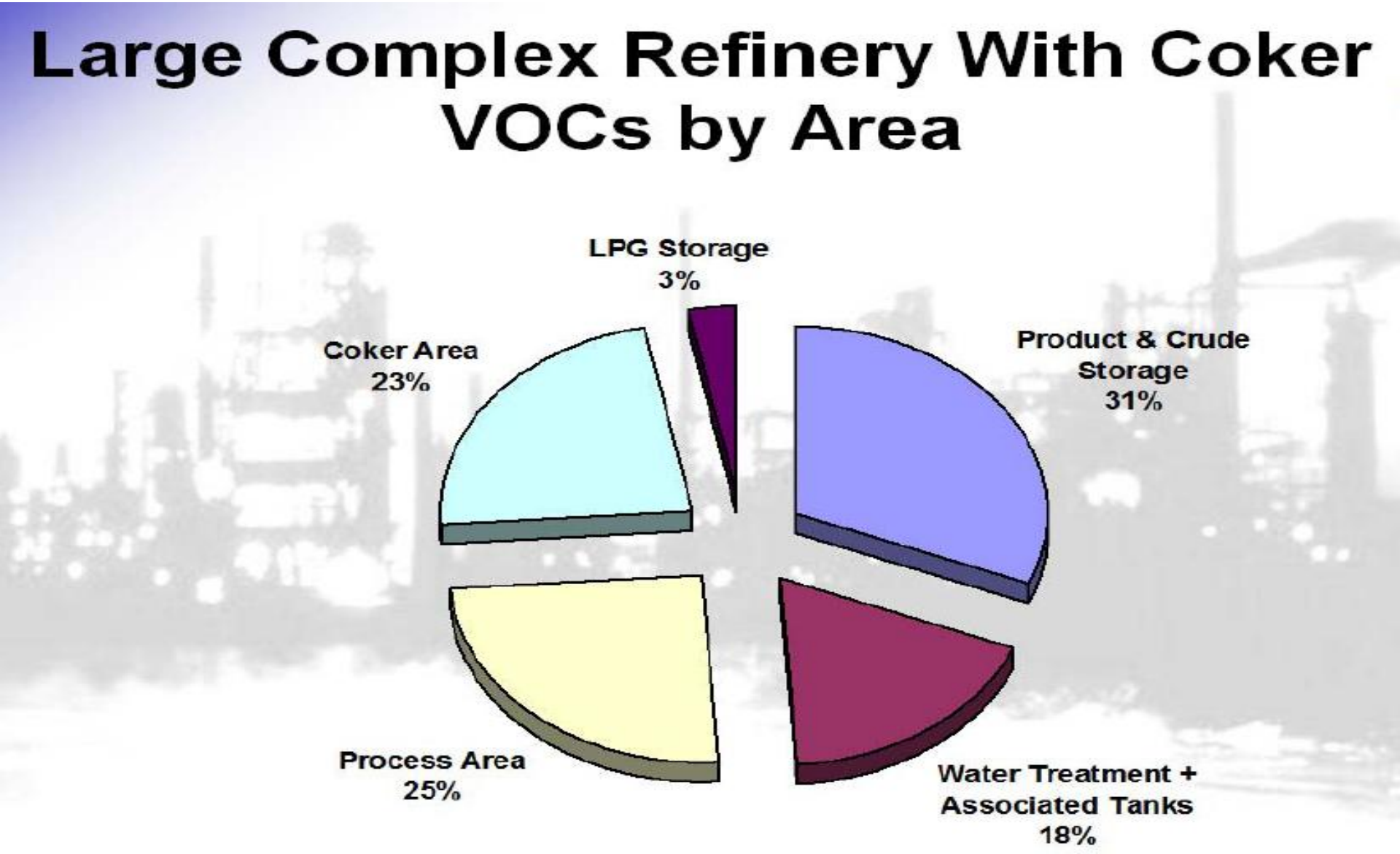
Simple Refinery Emissions by Area

Flares?



Spectrasyne performed numerous (~30) studies on refineries, and began to observe patterns on emission sources. In their experience flares were not a substantial source.

4. Differential Absorption LIDAR



By Spectrasyne

4. Differential Absorption LIDAR
Swedish Approach

In 1988 local Swedish Environmental Authorities saw that DIAL show refinery VOC emissions were 20 times higher than expected. In the next year, after making corrections, emissions were still 15 times higher than reported.

In 1992 the local environmental agency required all refineries to submit measured emissions. They did not have faith in the estimated emissions.

In 1995 they required all refineries to use DIAL.

In about 2002-2004 they required all refineries to measure using either DIAL or SOF. All have used SOF – because it is much cheaper.

4. Differential Absorption LIDAR
Shell's System

Shell in the UK had a DIAL system built in the mid-1990's.
Shell's system was set up with the intent to "sell" their DIAL expertise as solutions for emissions problems at other locations.
Shell developed a brochure on the web advertising their work, saying that, "If you are not measuring, you are just guessing."
The brochure listed several reasons why measuring was better than the standard estimating techniques.
In a 2000 paper/presentation Shell indicated that emissions from storage tanks were roughly 4 times higher than expected based on estimating techniques.
Shell was not able to find clients for their work, and shutdown their DIAL system around 2001 due to lack of funding.

4. Differential Absorption LIDAR
NPL's System

NPL assisted both BP and Shell in the development of their DIAL systems.
NPL built their own DIAL, but in about 2005 they purchased and refurbished the Shell DIAL and got rid of their own.
NPL has found substantial differences between reported and measured emissions.
NPL performed studies at BP Texas City, and Shell Deer Park.

4. Differential Absorption LIDAR Industry Perspectives

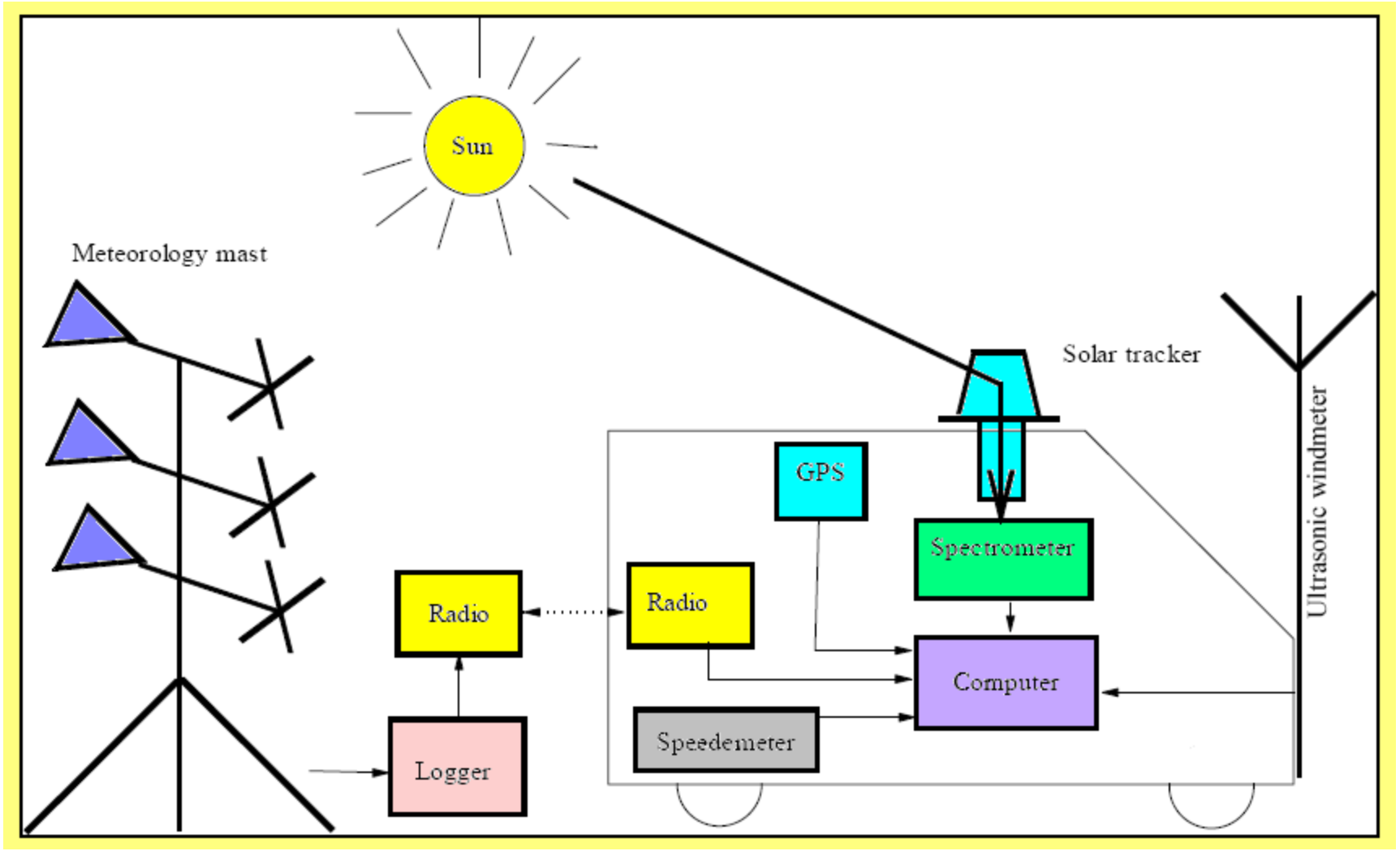
CONCAWE (Europe) published a number of reports about DIAL and one about DIAL and SOF.

In one case they concluded that their tank emission estimating techniques were accurate because the matched the DIAL results. (This presumes that they think DIAL is accurate).

CPPI issued a statement to refiners indicating that they could benefit from the results of the studies were done in Texas City and Deer Park before other DIAL studies are done in Canada.

API says that DIAL is good for finding leaks, but cannot extrapolate short term measurements into long term emission rates.

5. Solar Occultation Flux



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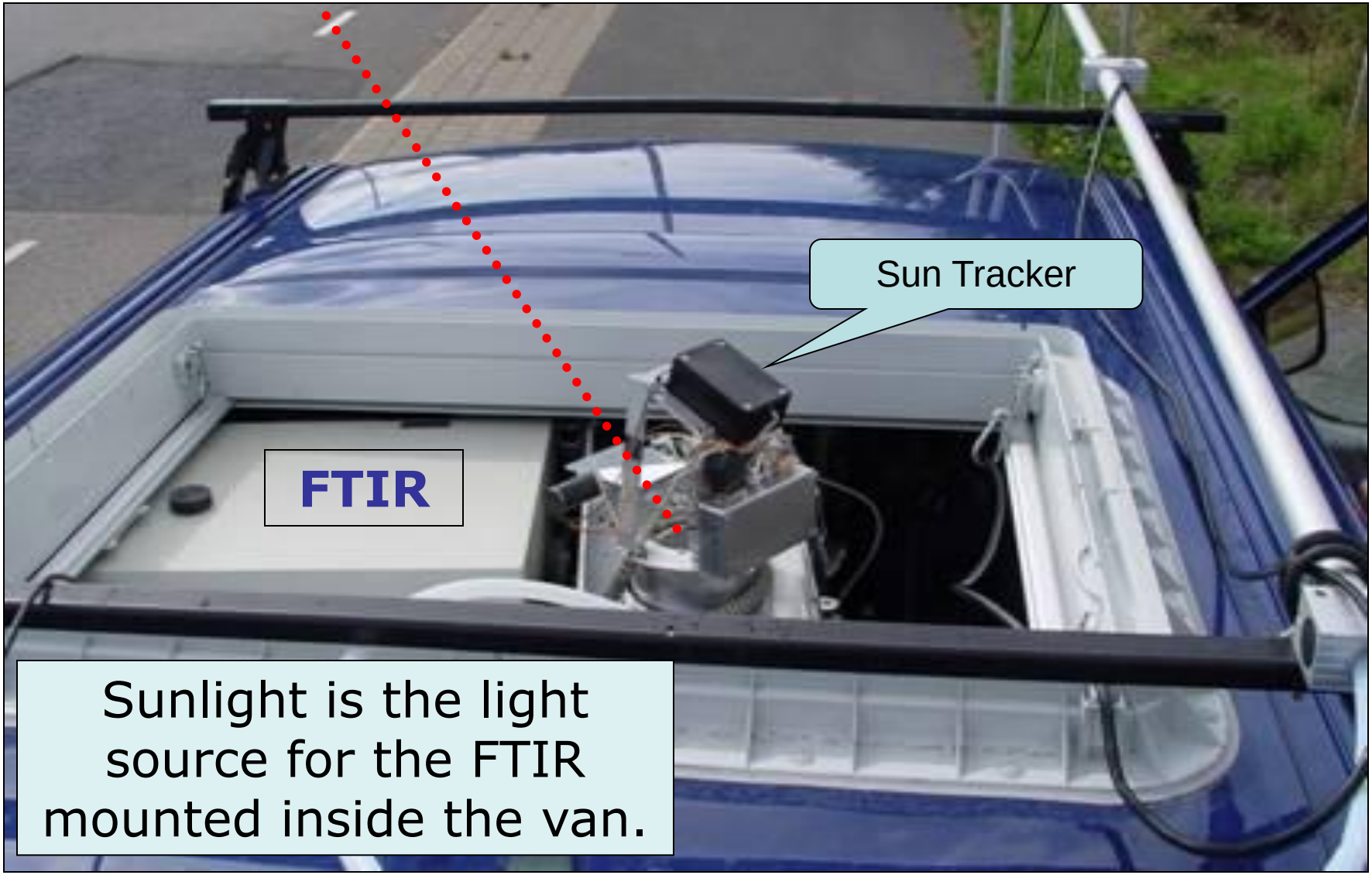
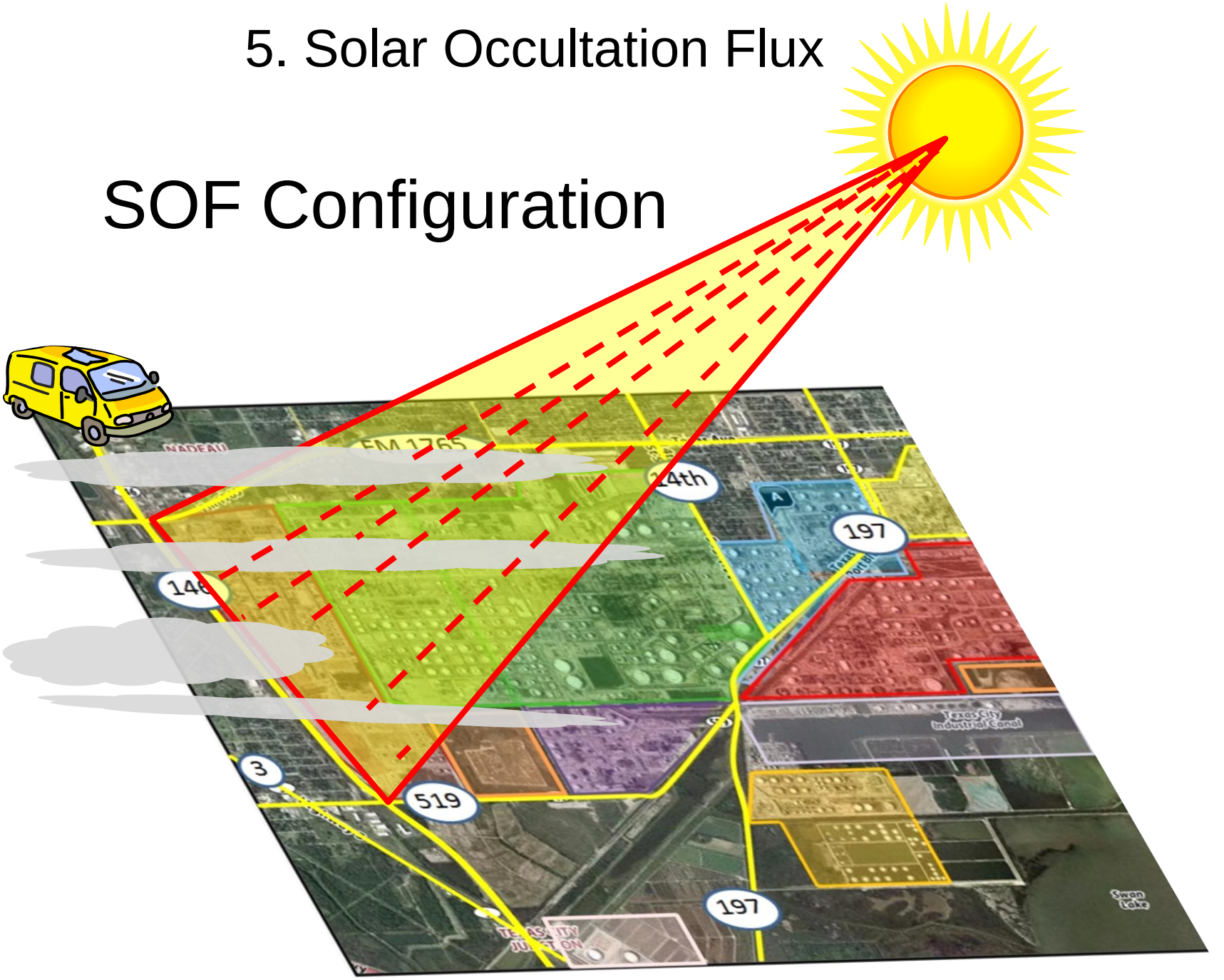
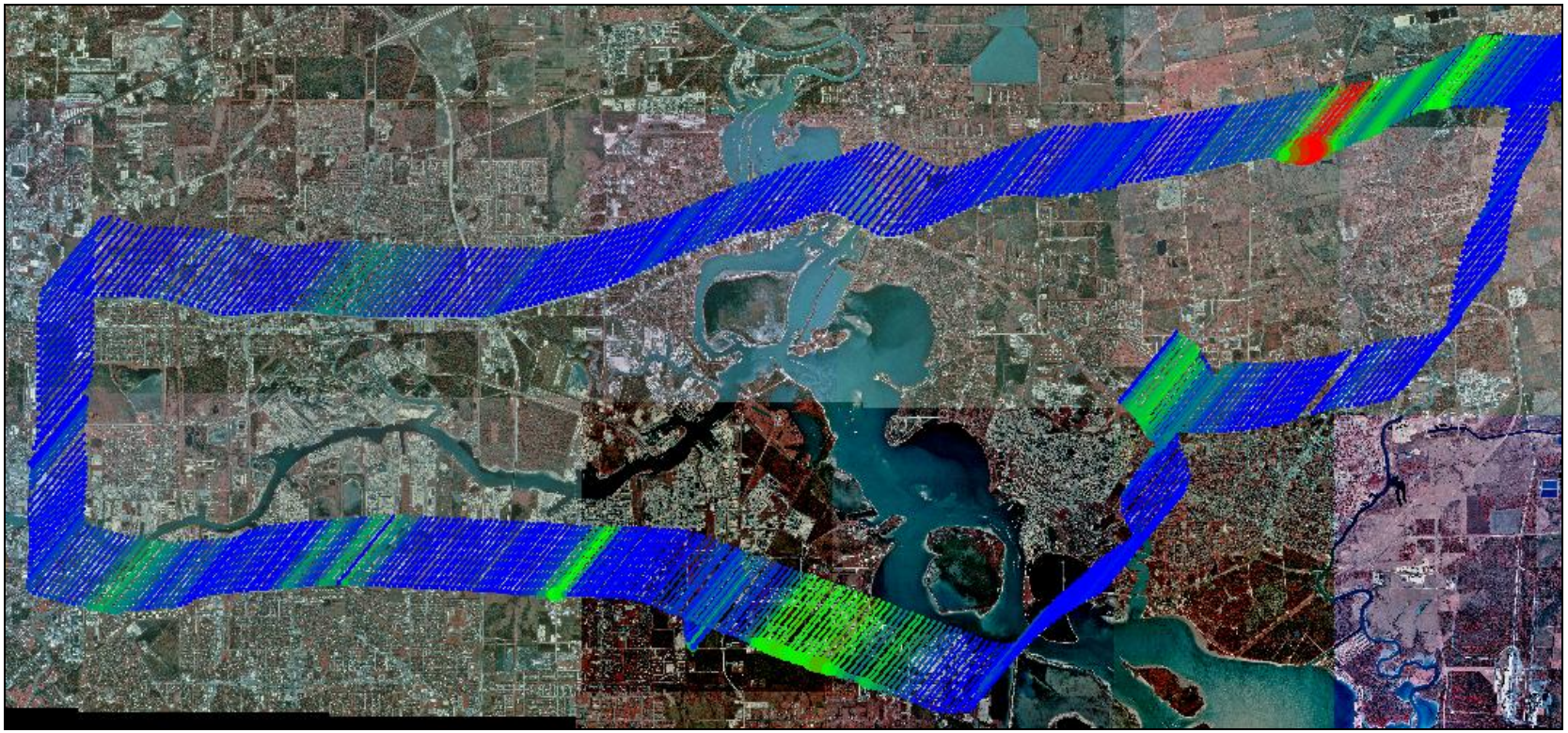


5. Solar Occultation Flux

SOF Configuration



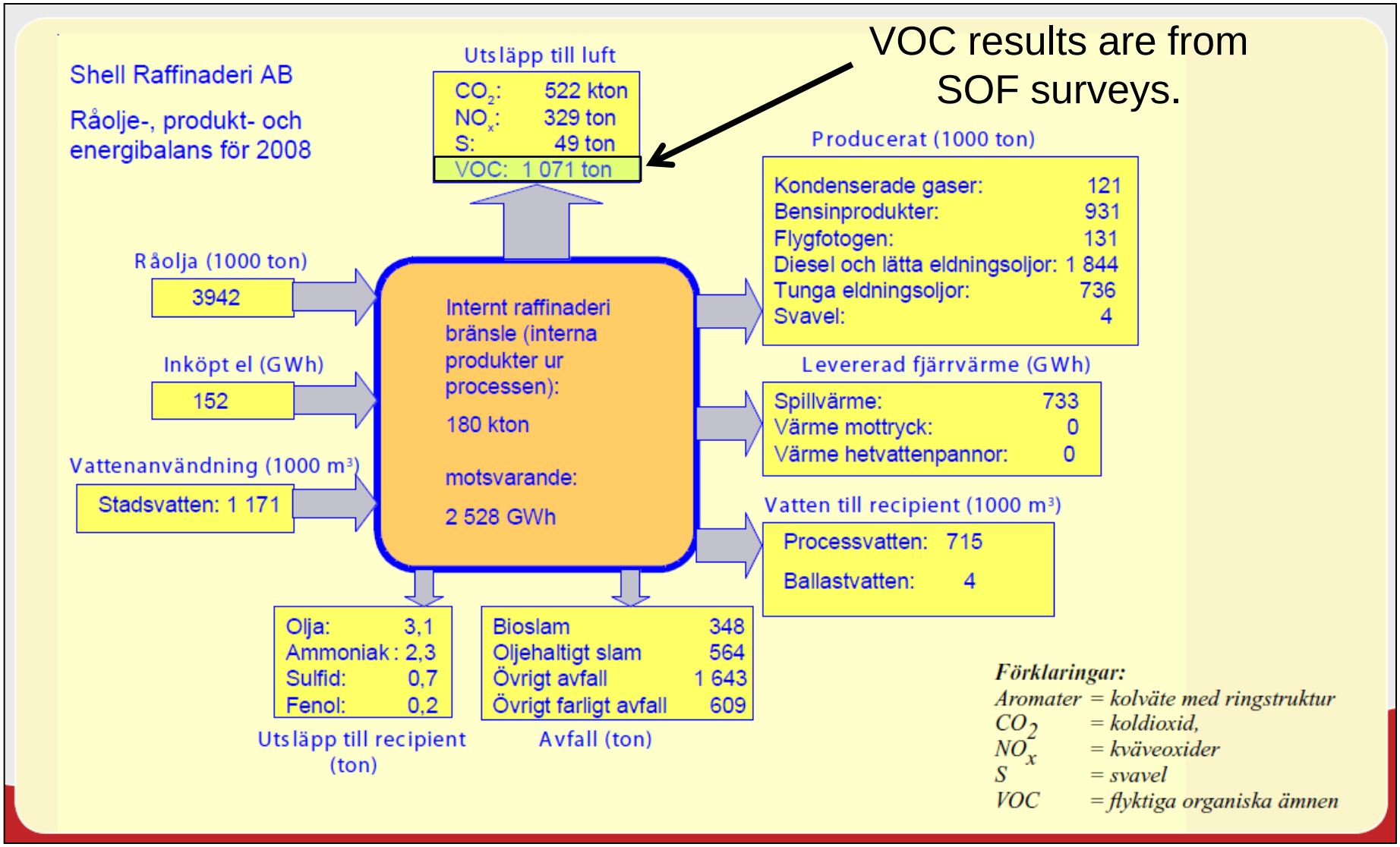
5. Solar Occultation Flux



SOF Measurements at the Houston Ship Channel

5. Solar Occultation Flux

This was taken from Shell Sweden's 2008 Annual Report to the Swedish Environmental Agency



http://www.shell.com/static//se-sv/downloads/about_shell/miljoredovisning_raff_2008.pdf

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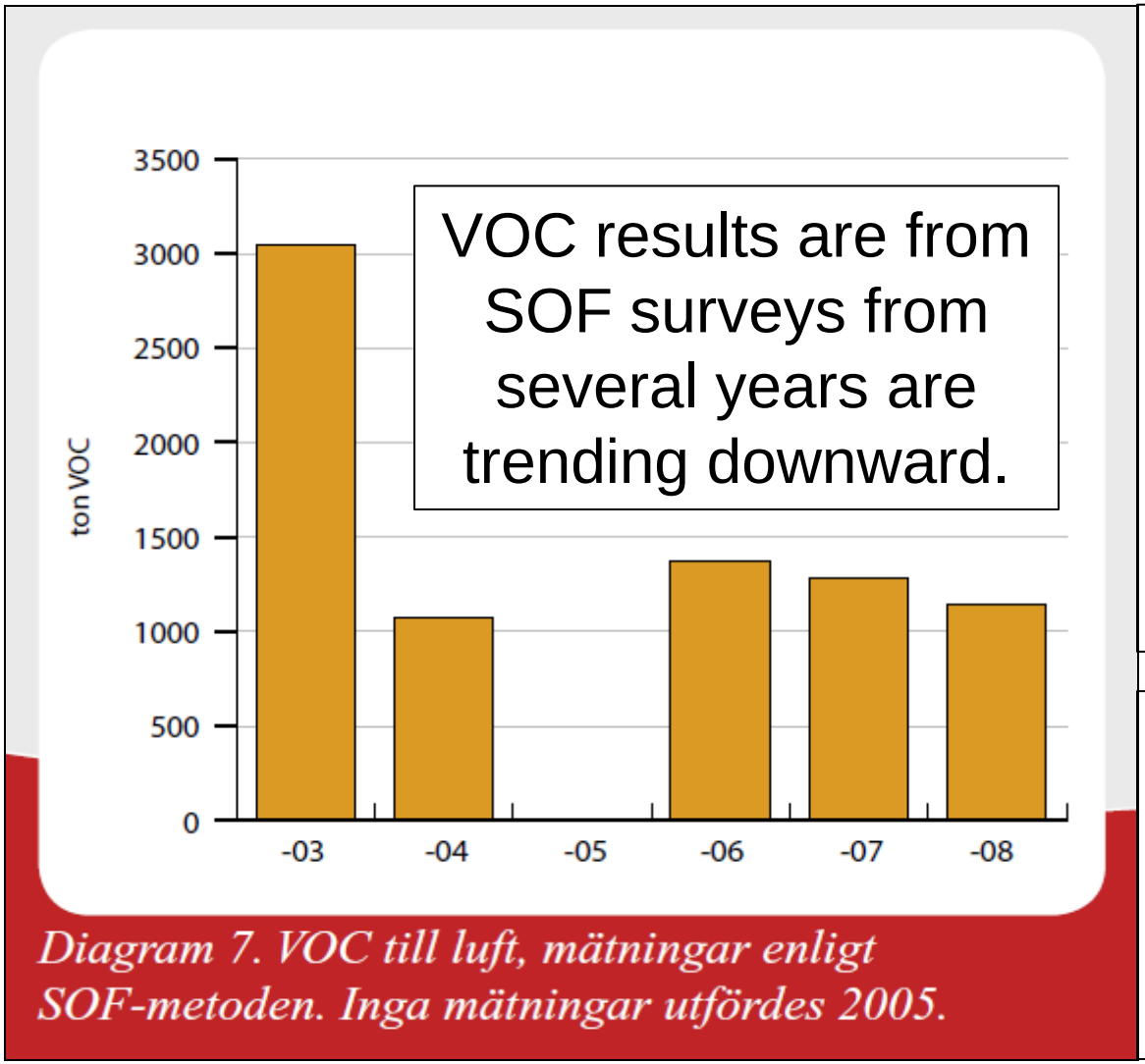


VOC emissions are low relative to emissions measured at other refineries, but the measured values are still 2-4 times higher than what is expected from AP-42 emission estimates.

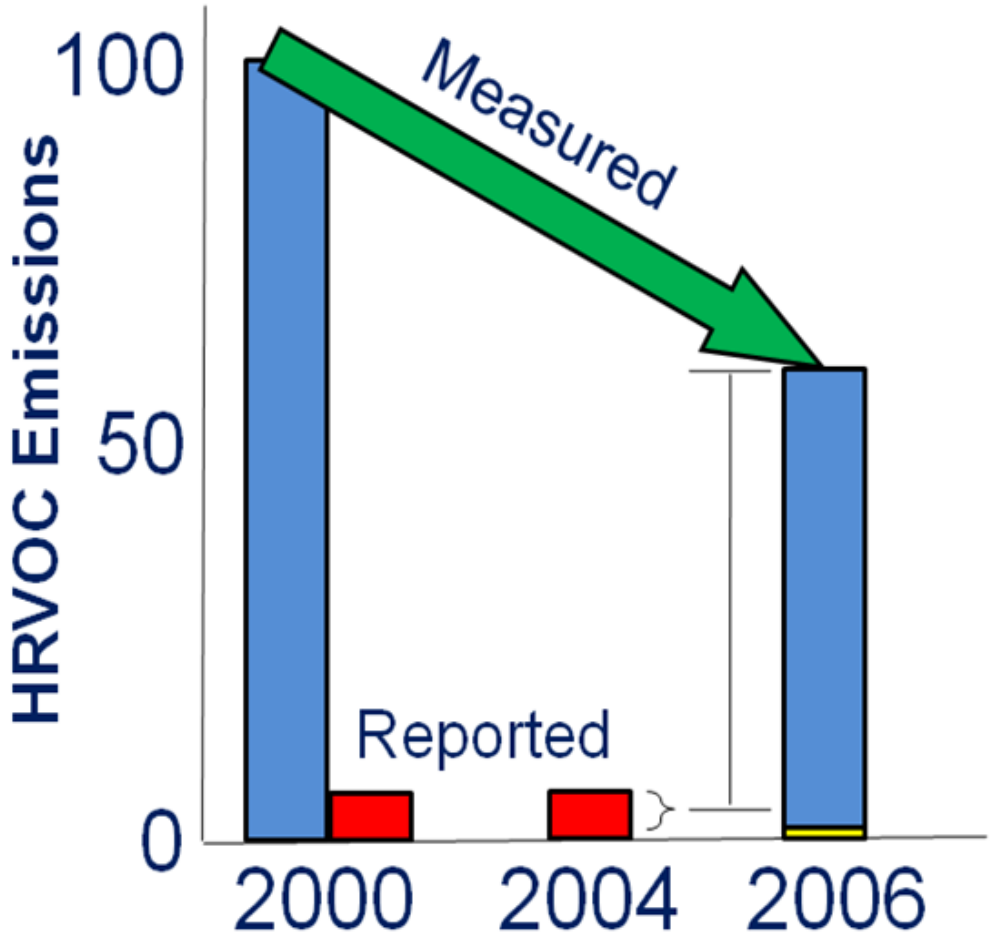
Remote sensing experts attribute the lower measured emissions to a decade of using DIAL prior to using SOF.

6. TexAQS II

TexAQS 2006 Rapid Science Synthesis

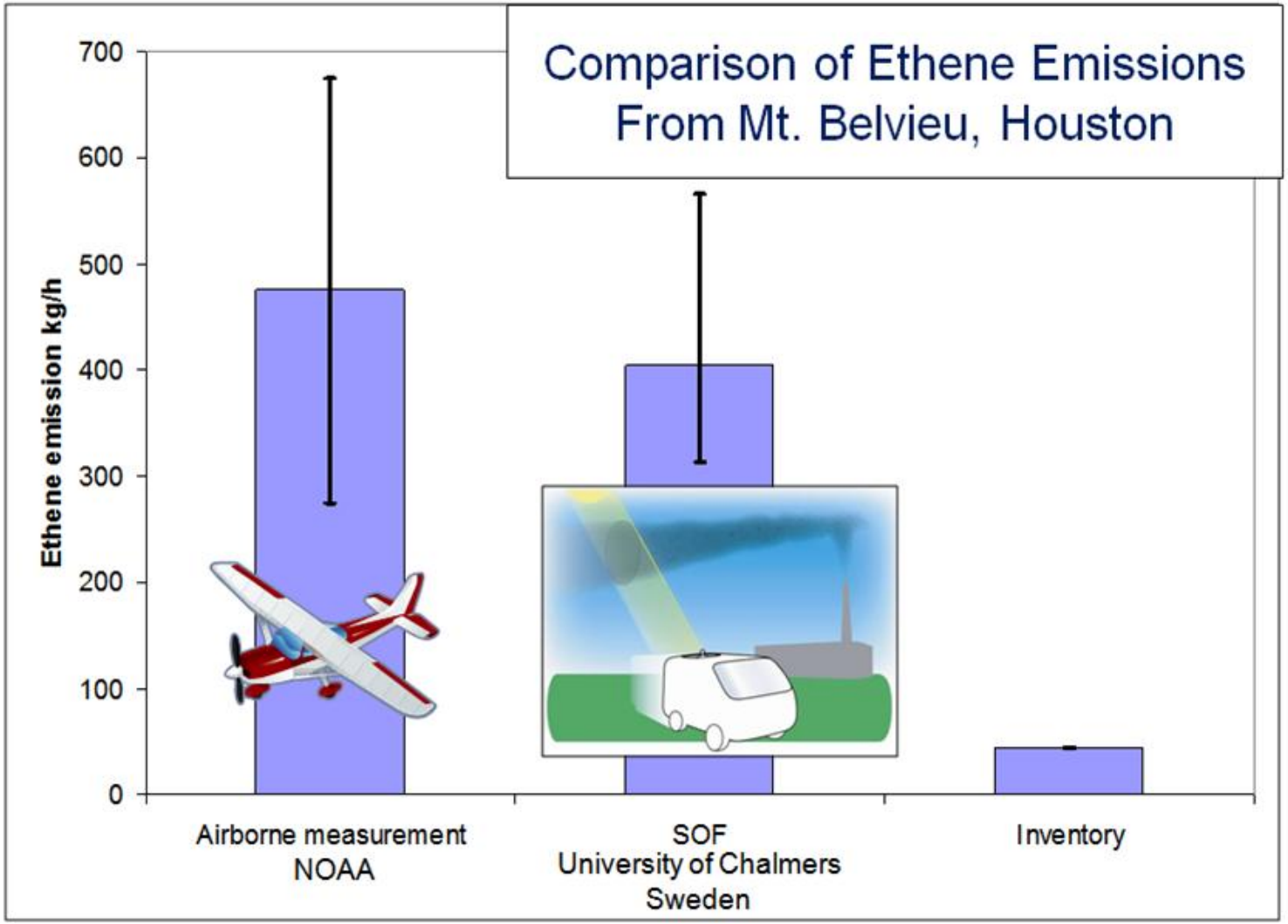
1. HRVOC (ethene) Emissions dropped 40% between 2000 and 2006.

2. In 2006 HRVOCs were still 10-50 times higher than reported in 2004.



6. TexAQS II

TexAQS 2006 – Aircraft & SOF



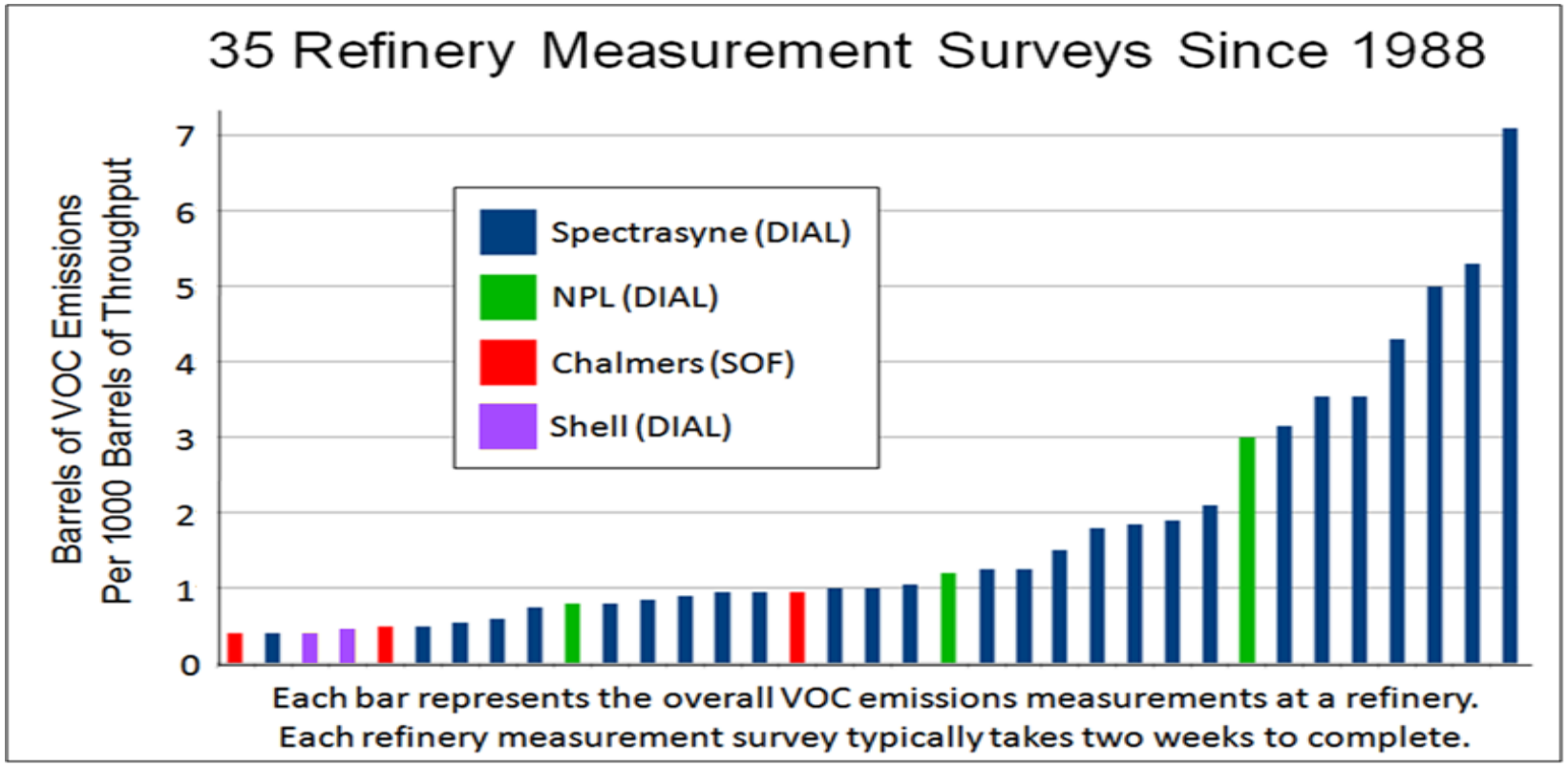
7. Canadian Refinery DIAL Report in 2006

1. A DIAL study at a refinery in Canada found that emissions were roughly 15 times higher than reported. Many of the high emissions were from the coker area and from a single tank.
2. For the U.S. the DIAL studies were no longer, “Those crazy Europeans…”
3. TCEQ plans DIAL study in Texas City
4. City of Houston plans DIAL study at Shell Deer Park
5. An unnamed company performed their own DIAL study.
6. EPA begins issuing section 114’s requiring DIAL studies at BP and at a Coke facility in New York.

7. Canadian Refinery DIAL Report in 2006

Industry comments…

1. "We never said that DIAL didn't provide accurate results…"
2. The readings that you obtain from a 2-3 week survey can't be translated into annual emissions. (i.e. "When you did that survey you caught us on a bad day/week.").



7. Canadian Refinery DIAL Report in 2006

Response…

1. When is a good day? 35 refinery studies at least 2 weeks long over 20 years all show substantially underestimated emissions.
2. Chemical engineers have underestimated VOCs for over 20 years. How will they do estimating GHGs?

“API is really pissed…”

8. Measurement Options

1. Swedish Based Approach – Roving SOF/DIAL

Advantages: Measures Flux, Measures at high altitudes (>1km), can provide better emissions estimates than AP-42, less total expense.

Disadvantages: Not continuous, main technologies are only in Europe and have not had extensive verification in the U.S., requires experts to interpret data, SOF requires direct sun.

2. TPC Houston Approach – Fence-line FTIR/VRPM/OTM-10

Advantages: Continuous measurement, rapid measurement response.

Disadvantages: Limited height measurement, limited ability to address transport, expensive (maintenance cost for open path FTIR is estimated at >$100K*/year), requires experts to interpret data, most need cryogen.

3. Auto-GC in Moveable Analyzer House (or Multiple Manifold) Approach

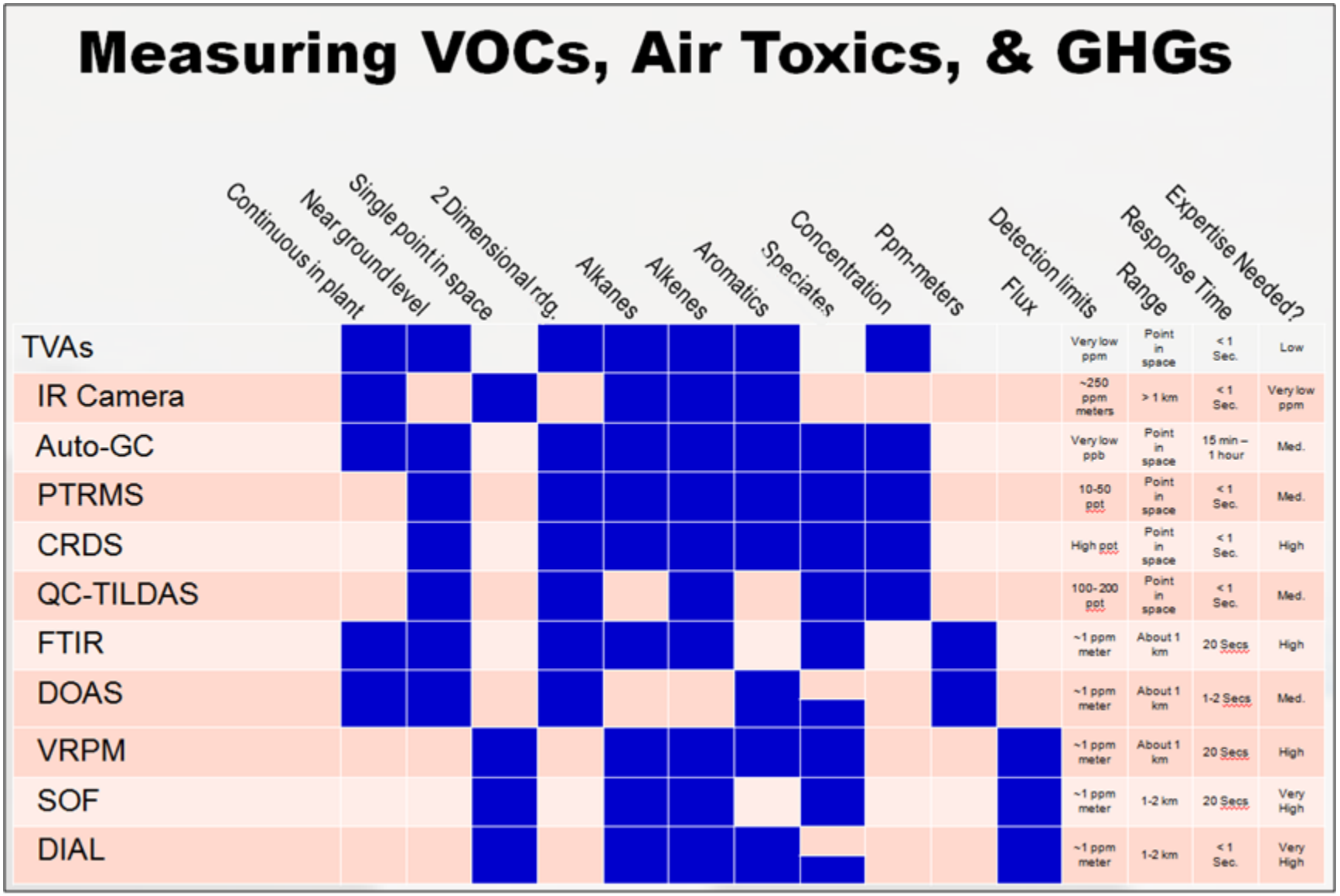
Advantages: Continuous measurement, separates compounds, can be moved to various portions of the plant as needed,

Disadvantages: Measures only one point in space, response is in minutes or hours, does not address transport. Expensive if required everywhere.

*Note: some estimates for open path FTIR annual maintenance are much higher.

8. Measurement Options

Several other technologies exist, with different advantages and disadvantages.



9. Flares

1. In the past few years California has passed regulation requiring flare minimization projects.
2. Texas (and elsewhere) has focused on improved flare performance. It has been determined that flaring destruction efficiency can be much lower than what is typically assumed (98%), but flare minimization projects are very expensive.
3. Continuous monitoring of flare emissions is not practical with current technology.
4. An option for evaluating flare performance is Passive IR. EPA has used this in legal actions to resolve issues with flares. Absolute numbers have errors, but it can identify when the best performance occurs.
5. DIAL can be used to do flare studies, and has been used in Europe for 20 different flare studies and in studies at refineries and chemical plants. Spectrasyne reports that flares are typically less than 5% of the total emissions.
6. According to Spectrasyne higher emitters at refineries are storage tanks, delayed cokers and wastewater facilities. They have done almost all of their 30 studies in Europe.
7. In the U.S. only one complete (or almost complete) study has been done at full feed rates – Shell Deer Park. In that study flares were a small contributor to overall emissions.

10. Section 114 and the Tonawanda Coke Company

1. EPA measured high benzene emissions near the Tonawanda Coke Company in New York.
2. EPA threatened to require Tonawanda to use DIAL per their CAA authority with a Section 114.
3. Tonawanda eventually agreed to perform the DIAL study without the legal action.
4. Tonawanda's estimates using API methods suggested emissions of 6 tons per year.
5. DIAL measurements showed that the actual benzene emissions were more than 10 times the estimated emissions.
6. DIAL results were used as the basis for Tonawanda to make changes.

11. Verification of DIAL and SOF

- We have not done full verification of either DIAL or SOF in the U.S.
- Verification should include double blind testing and releases of known amounts of gas or tracers with many researchers participating in the design, watching the experiment, reviewing the raw and final data. None of that is cheap.
- Some comparison studies have been made.
- Some researchers are concerned that the accuracy quoted by the vendors of 15-30% may be closer to +/- 50% or higher. (However modelers tend to be happy with +/-50% due to emission inventory problems).
- The main source of error is due to variability in winds. Some options exist to reduce the error caused by wind.
- Some modelers and the vendors themselves will say +/- 50% is much better than they are currently getting with the emissions inventory process.

12. Best Available Control Technology and Measurements

What is at Stake?

This issue is bigger than Houston, bigger than Texas…

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.