Solar Occultation Flux (SOF) measurements around the Sweeny power plant and in the Houston Ship Channel area -H53

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- Development of methods for measuring gas emissions: ship, agriculture, petrochemistry, refinery, landfills, megacities.
- Atmospheric research: Stratospheric ozone, climate gases, vehicle emissions
- Volcanoes

The optical remote sensing group

Radio and Space

Chalmers University of Technology

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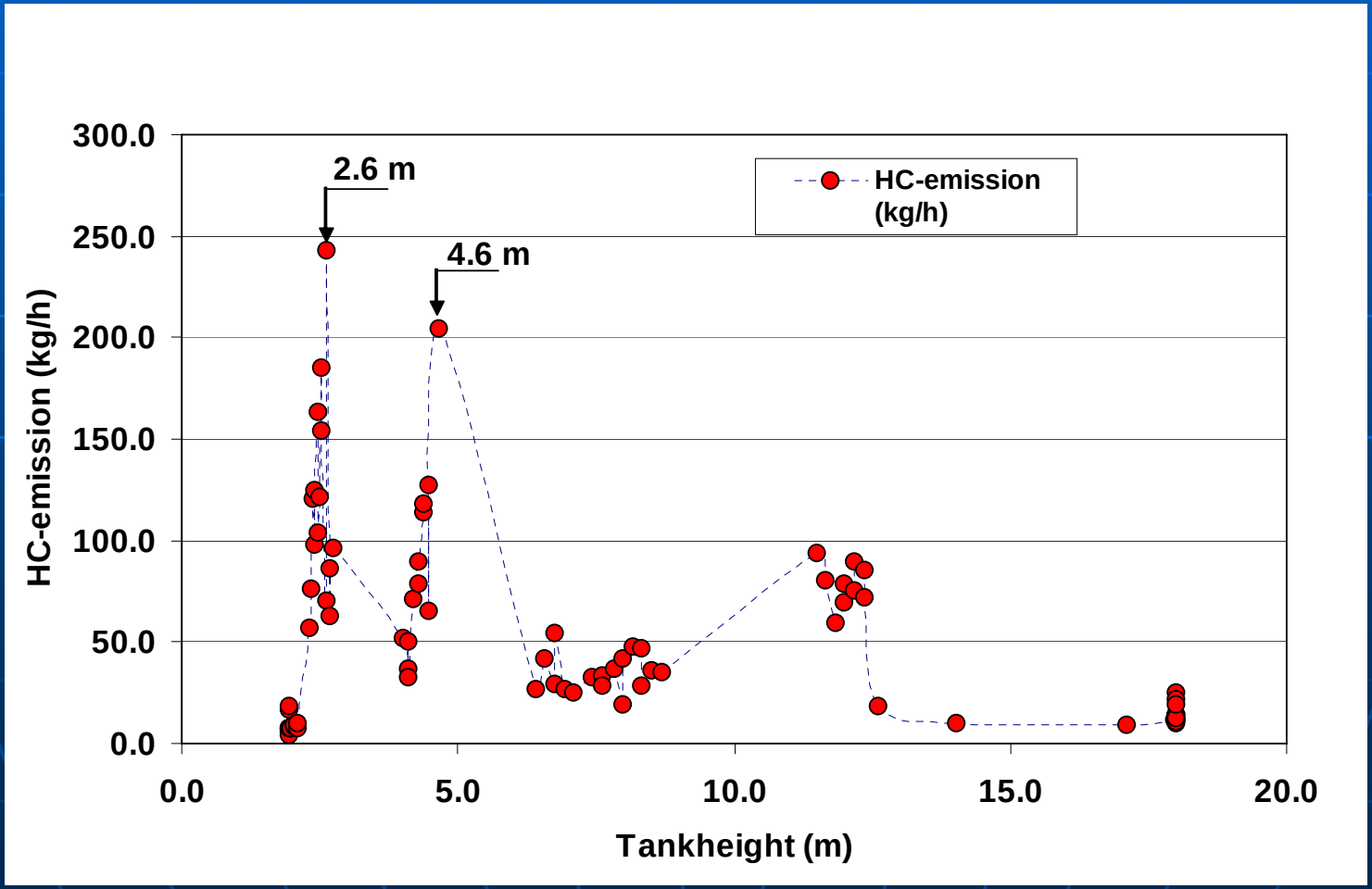
Aim

- Estimate total emissions (tons/day) of VOCs (+NO2, SO2), primarily alkanes and olefines, being emitted from Sweeny chemical facility and the Houston Ship Channel, using the Solar Occultation Flux method (SOF)

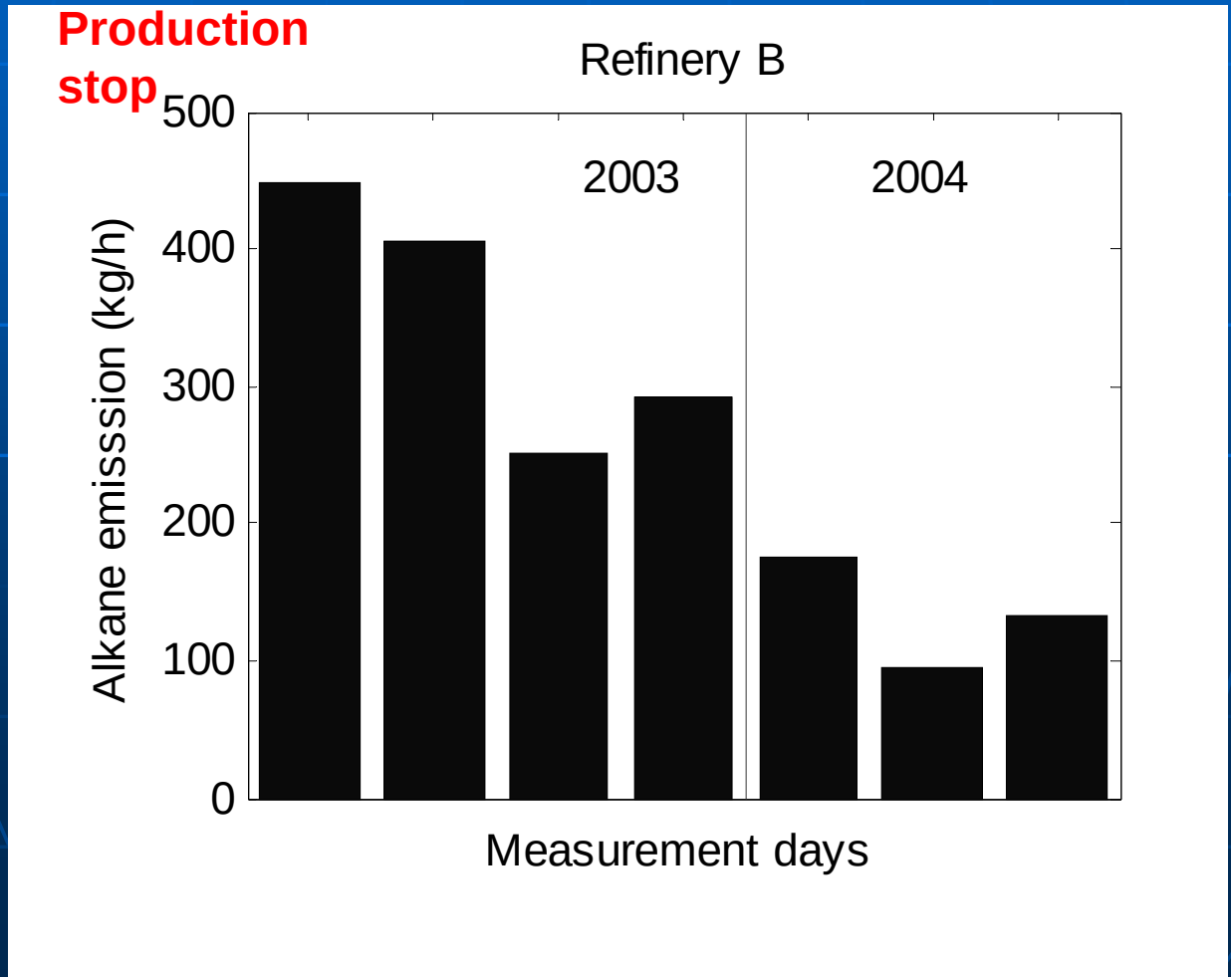
Why measure instead of the standard approach with EPA- 21 and tanks model?

- Leaks from cooling towers, flares, water treatment facilities, storage caverns, loading (trucks/ships), tank cleaning an repair etc, are not assessed in the standard approach
- Typical results on Swedish refineries shows that fugitive emissions from the process stands ONLY for 20-50% of the hydrocarbon emissions and the rest is crude oil tanks 20-30%, product tanks 20-40% and water treatment 5-10%
- The last TEXAQ-I campaign indicates dicrepancies of a factor 5 between the standard approach and measurements in the Houston shipchannel
- A significant fraction of the emission comes from few malfunctioning equipment:
  - DIAL measurements in early 1990's in Sweden showed discrepancies up to a factor of 20 compared to estimates.
  - The flares in a petrochemical plant may emit as much as the whole polyethylene plant (SOF 2000)
  - Tank emissions are highly variable

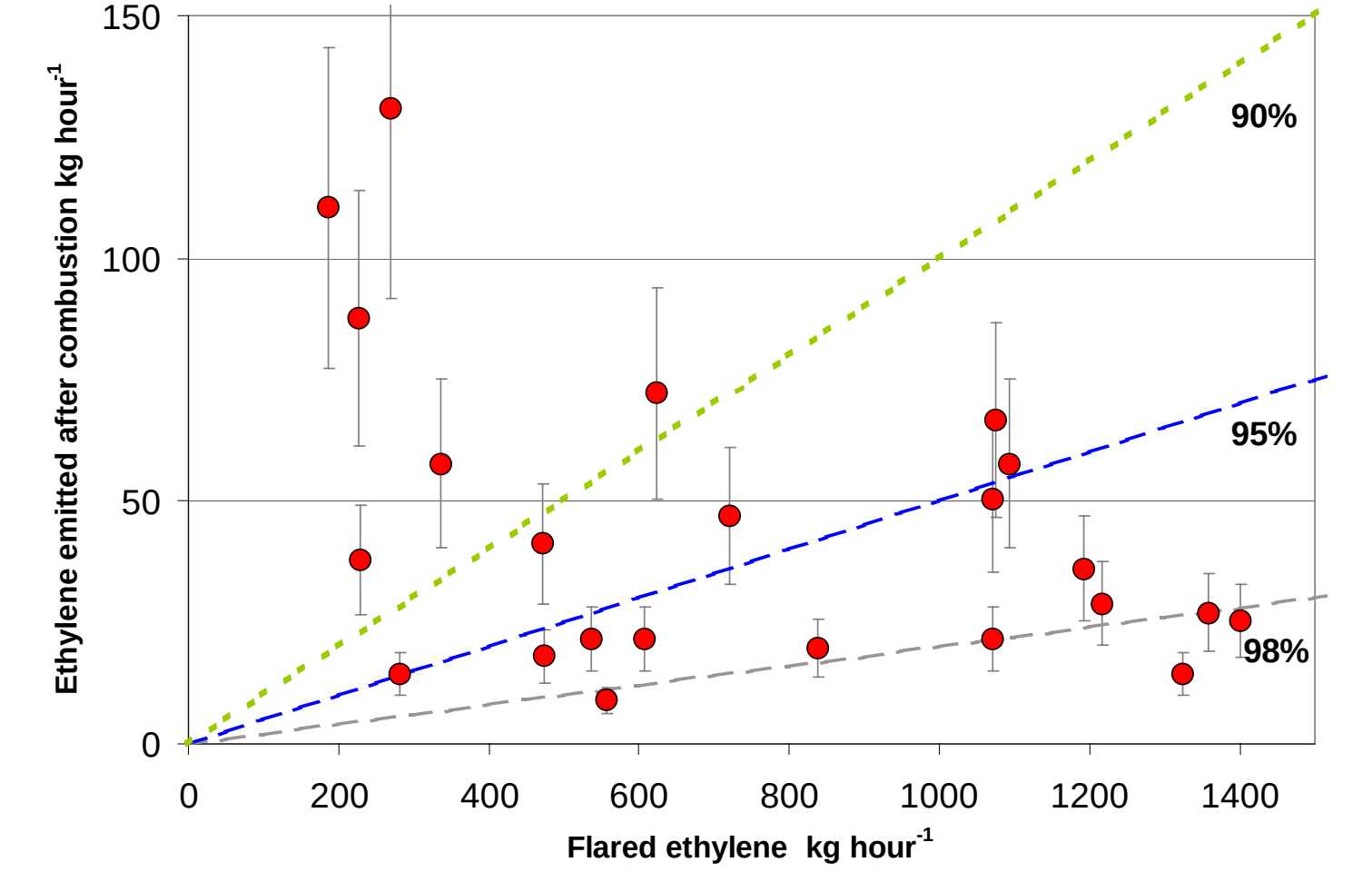
Alkane emission from a crude oil tank with a double sealed floating roof, measured by FTIR+tracer



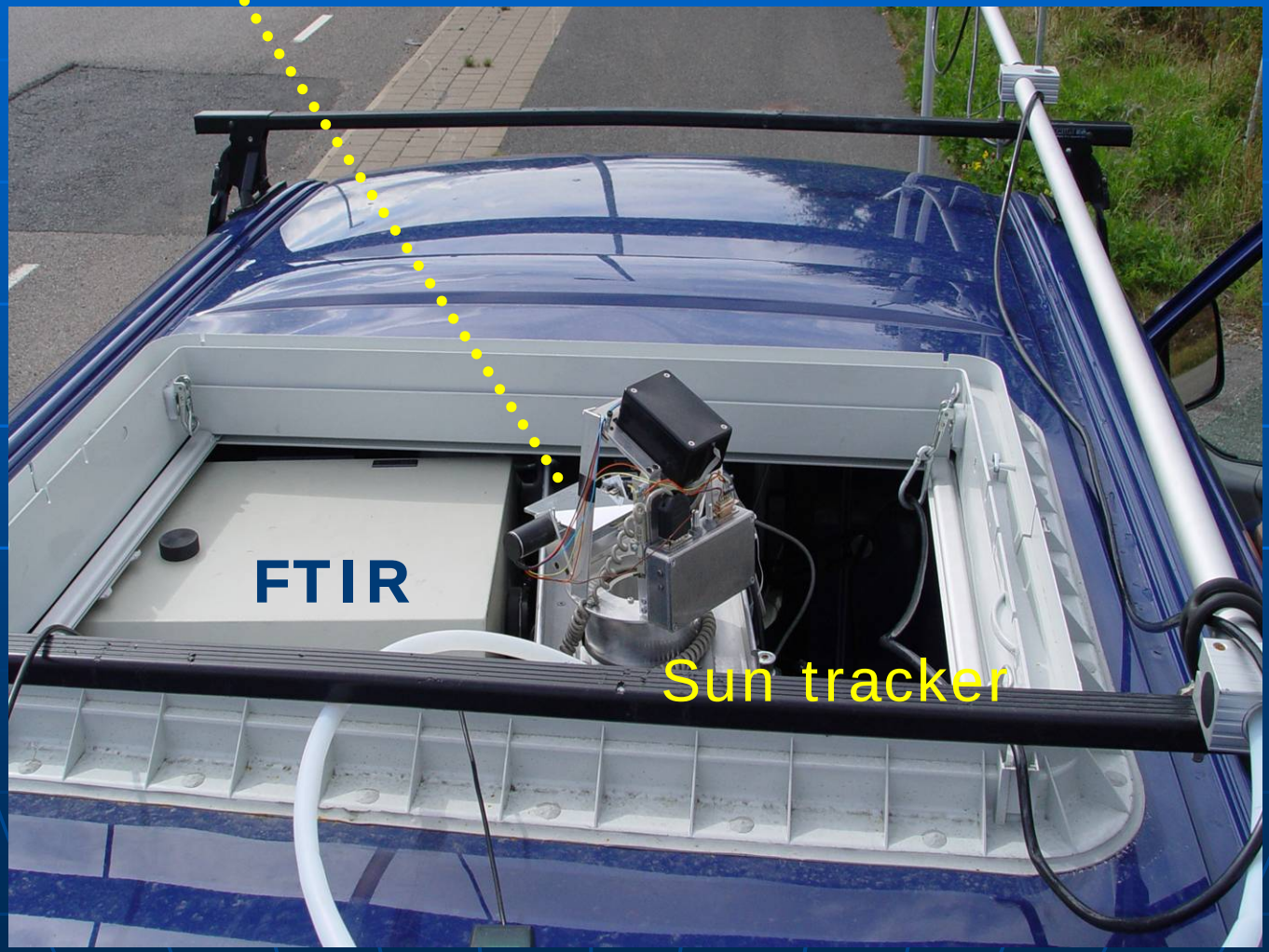
Measurements of total VOC emissions from a refinery after a major maintenance stop (SOF method)



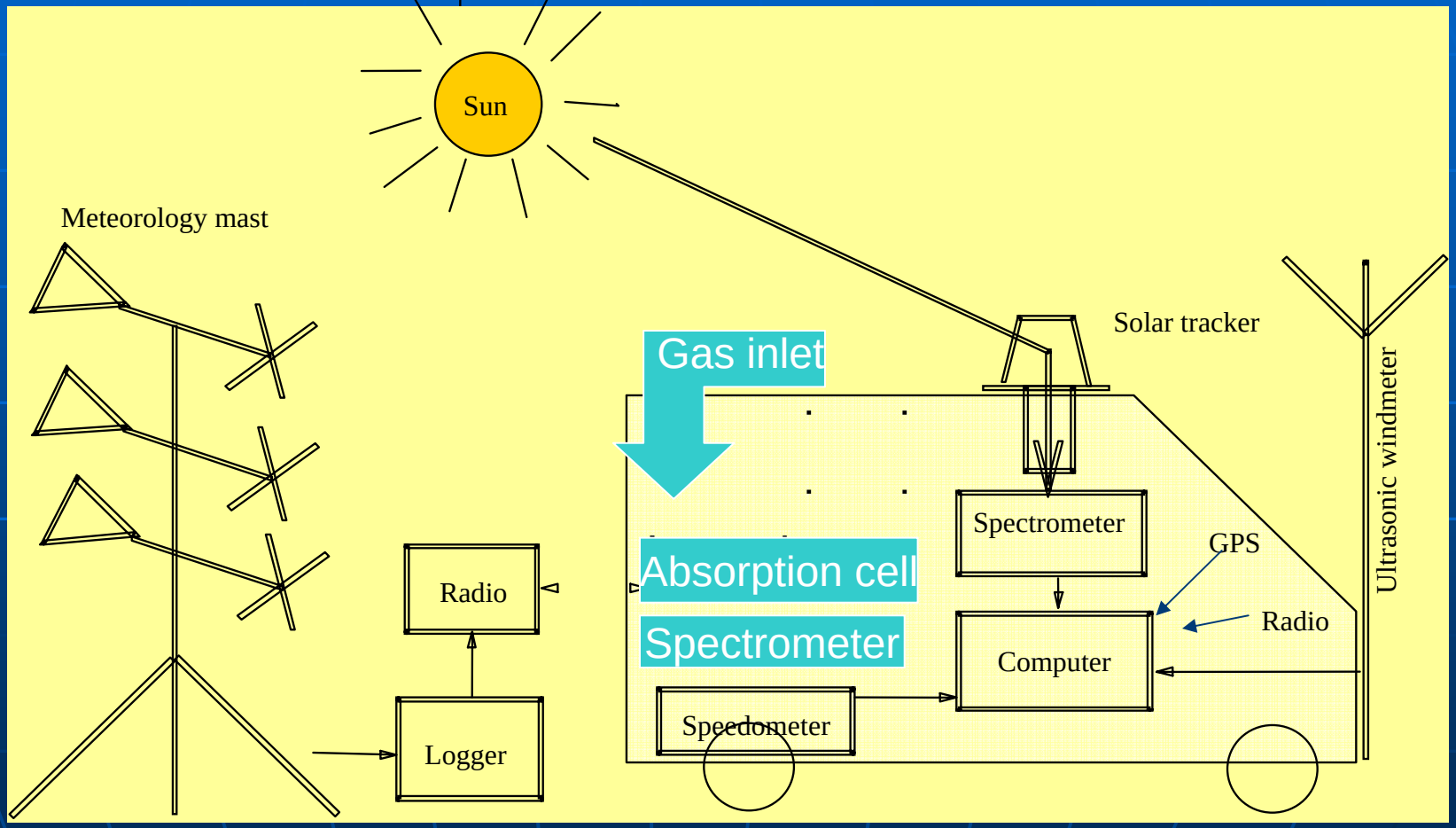
Ethylene emission versus flared amount



The Solar Occultation Flux method (SOF)



During SOF measurements a **line integrating** (solar) FTIR spectrometer is used together with a **point measuring** one

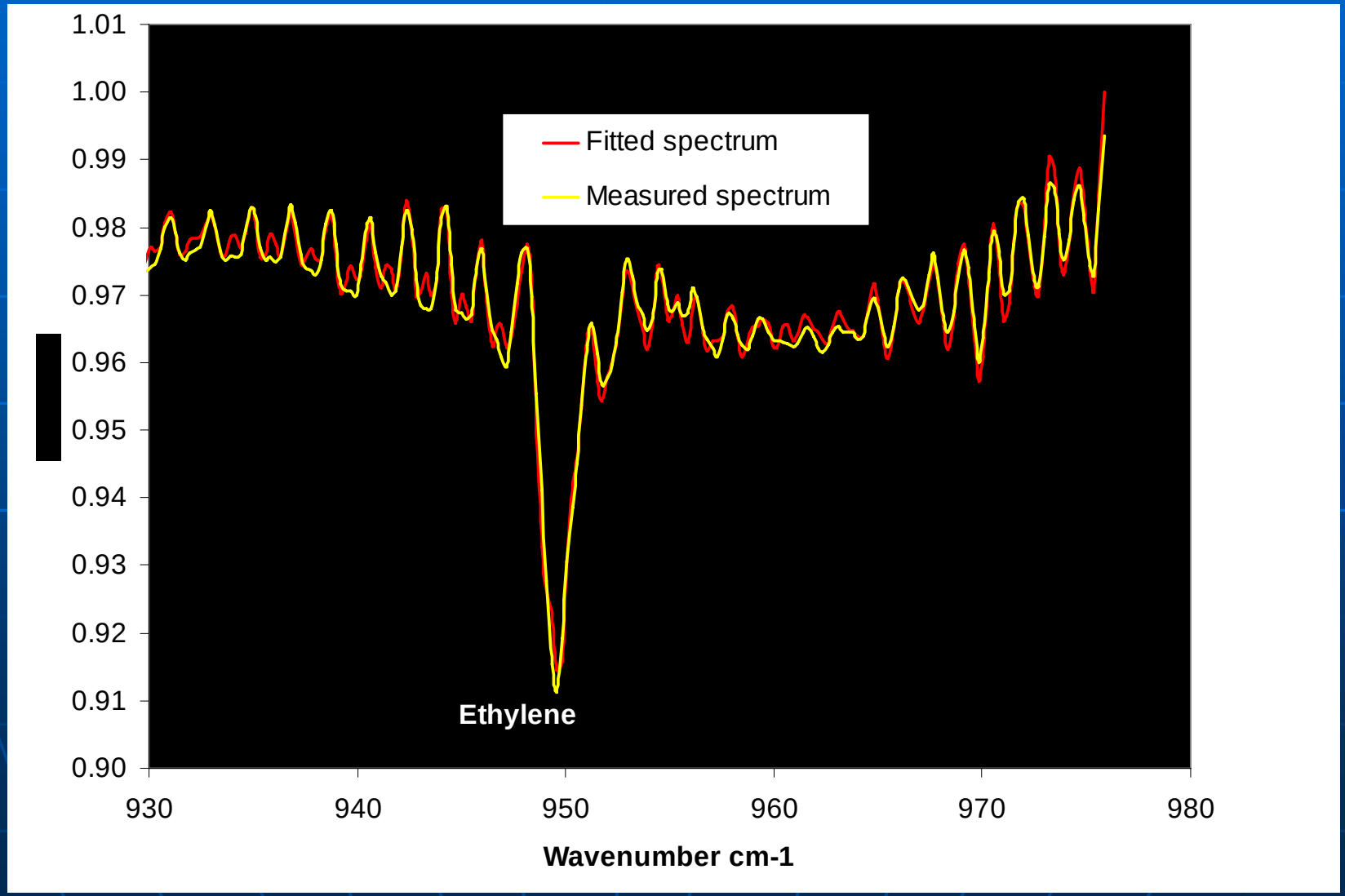


Spectral retrieval of the gas column in the solar light

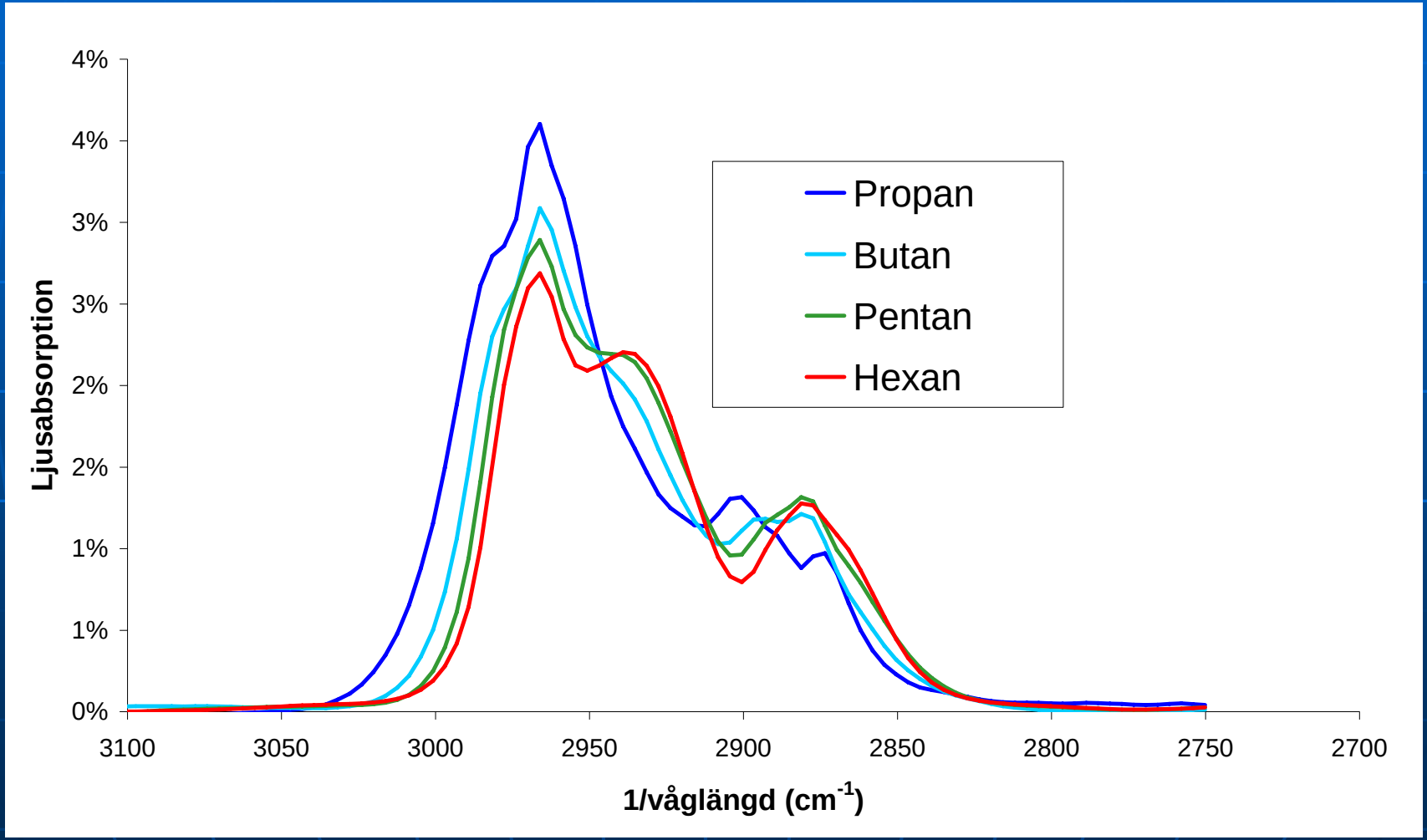
Calibration spectra are calculated from published data: HITRAN 2000, NIST, PNL, and the Hanst library.

- The retrieval is conducted by spectral fitting (least square) of the calibration spectra to the measured ones, using published codes
  - SFIT2 (Rinsland-Connor, NASA),
  - NLM, MALT (Griffith, Uni Wollongong)
  - QESOF (Kihlman, Chalmers)

Finger print of ethene in the plume of a polyethylene plant in infrared solar light. (Also a fitted laboratory spectrum is shown)



Alkane spectra



Alkanes more tricky to measure than alkenes !

- Alkanes from refineries are measured in the 3 µm region
- The measurement correspond to the amount of C-H bindings
- In this region the specificity is low but it is possible to obtain the average weight of the molecules
- Comparison with GC shows that the alkanes from crude oil can be measure with very good accuracy (0.2%±5%)

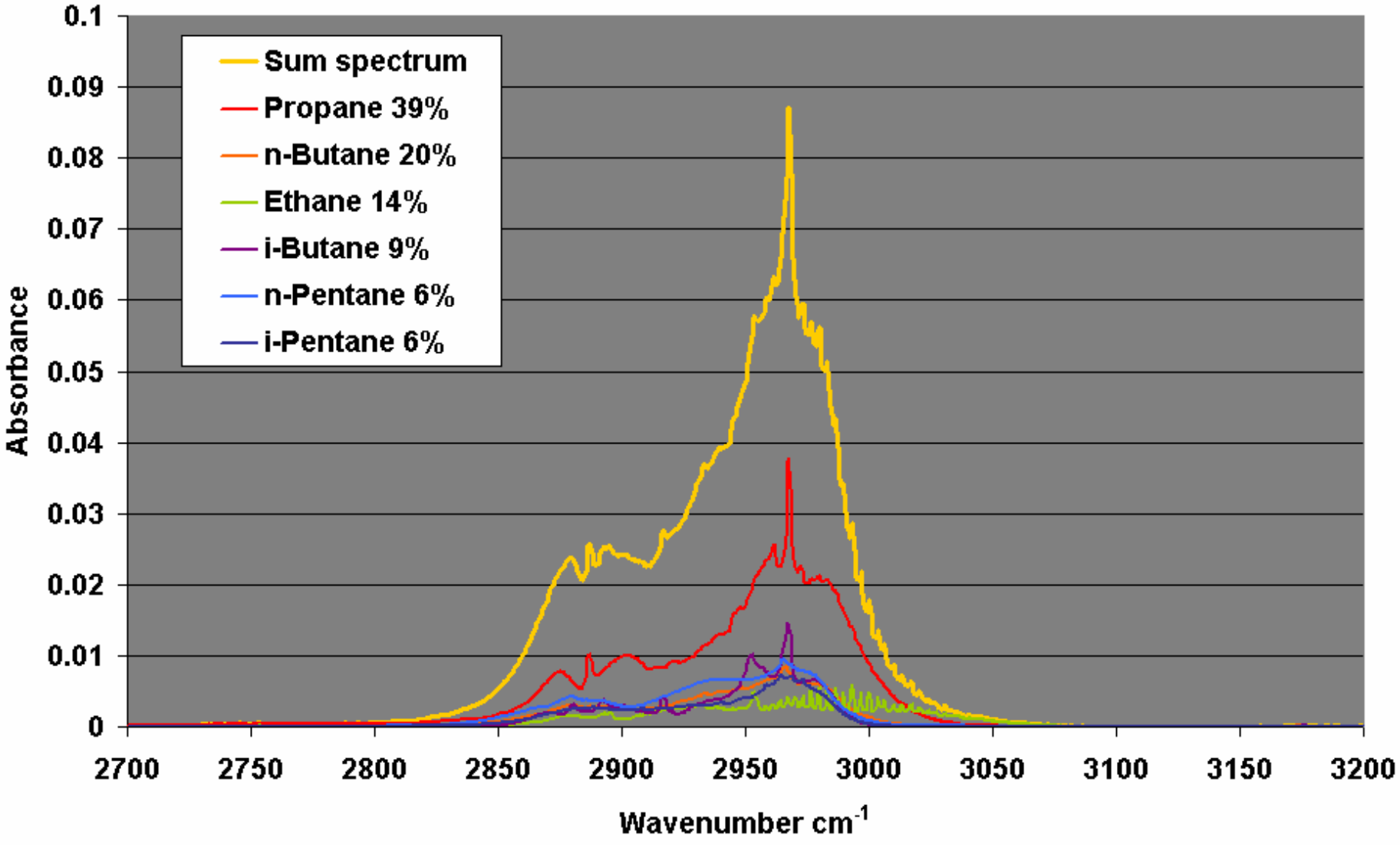
What VOCs are emitted from crude oil?

Compound	Mixing ratio by molecules (%)	Mass ratio (%)	Cross sensitivity as mass of Butane
Propane	38.78	32.50	0.98
n-Butane	20.28	22.41	1.00
Ethane	14.48	8.28	0.26
Iso-Butane	8.69	9.59	1.60
n-Pentane	6.20	8.49	1.01
Iso-Pentane	5.66	7.76	1.29
Decane	1.44	3.88	0.74
Hexane	1.12	1.82	0.94
n-Heptane	0.27	0.51	0.76
Octane	0.05	0.11	0.55
Nonane	0.01	0.03	0.42
Toluene	*0.21*	*0.37*	*0.04*
Benzene	*0.09*	*0.13*	*0.00*
Ethylbenzene	*0.06*	*0.12*	*0.27*
1,2,4-TMB	*0.11*	*0.24*	*0.00*
1,3,5-TMB	*0.01*	*0.02*	*0.00*
m+p-xylene	*0.07*	*0.14*	*0.03*
o-xylene	*0.03*	*0.05*	*0.10*
Etene	0.10	0.05	0.02

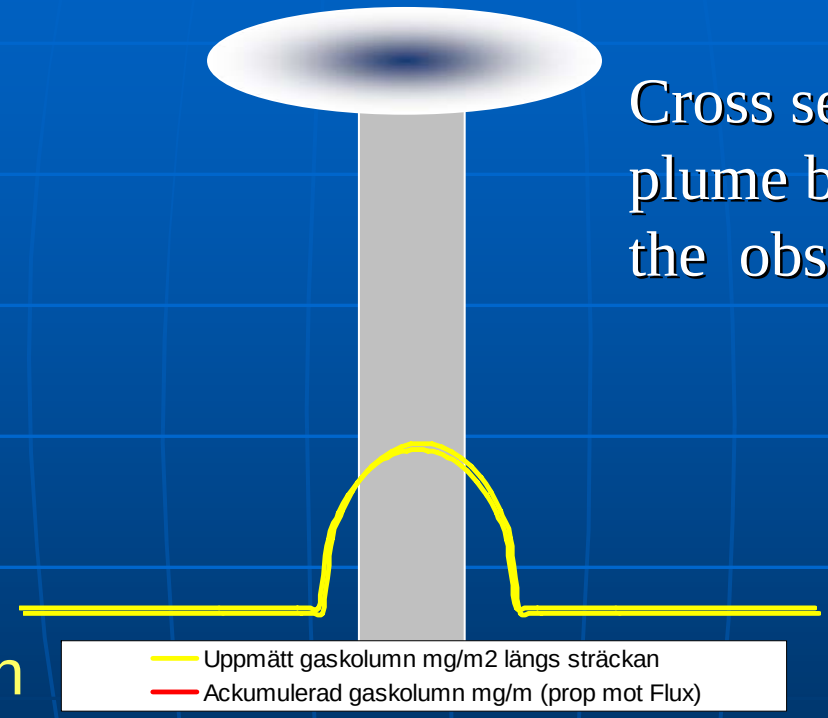
98.5 % of the mass correspond to alkanes,

1% Aromatics and 0.5% alkenes

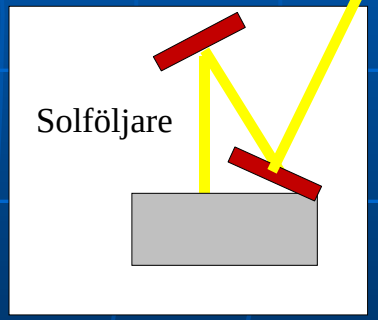
Synthetic IR spektrum: sum of the spectra of the components in in a crude oil tank plume,



SOF (Solar Occultation Flux) method

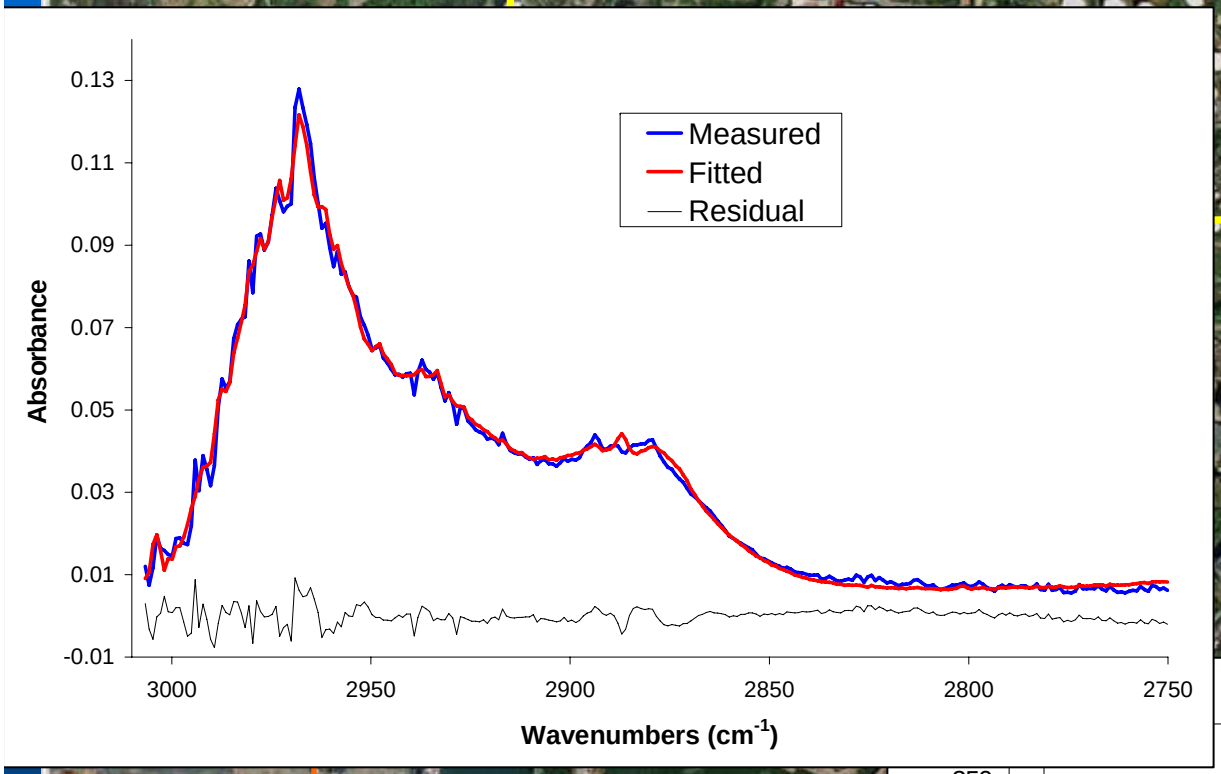


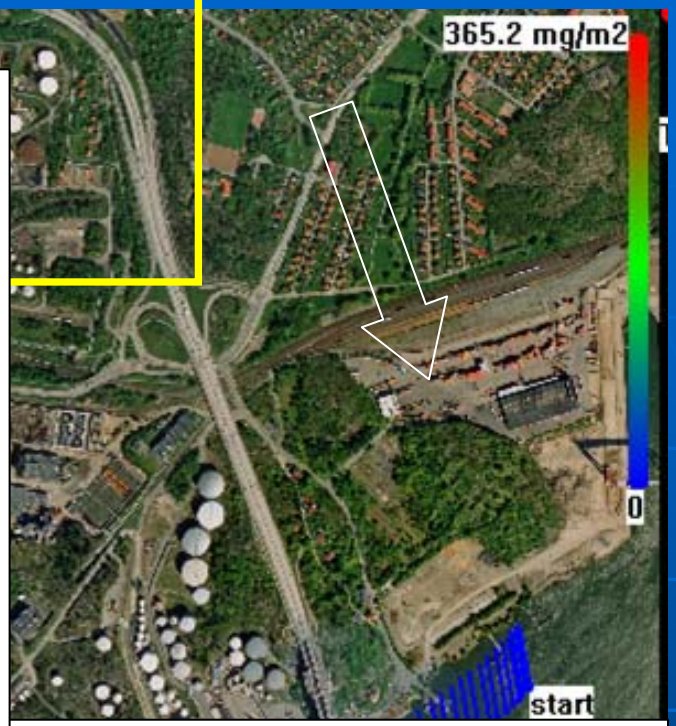
Cross section of a flue gas plume blowing towards the observer



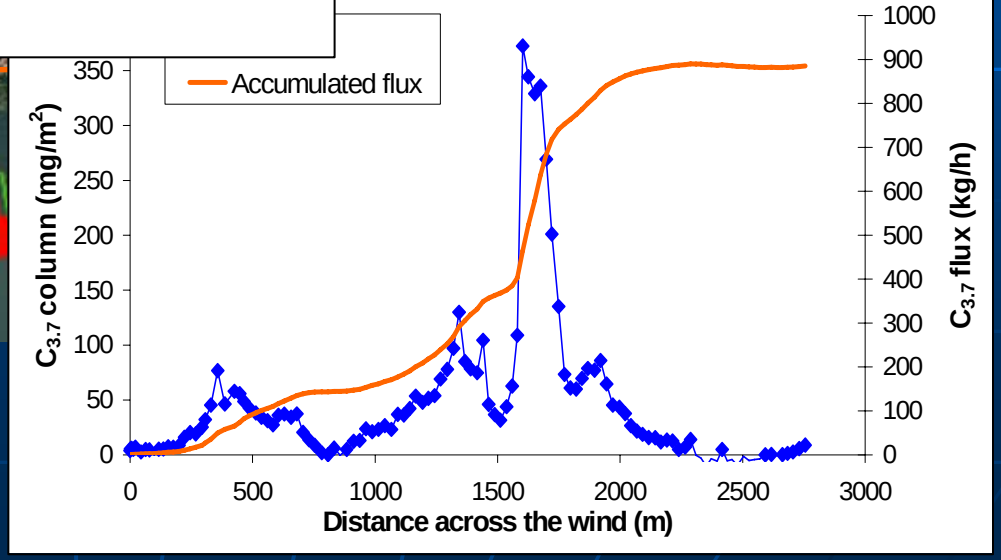
Gas column

Flux=Accumulated gas column * windspeed

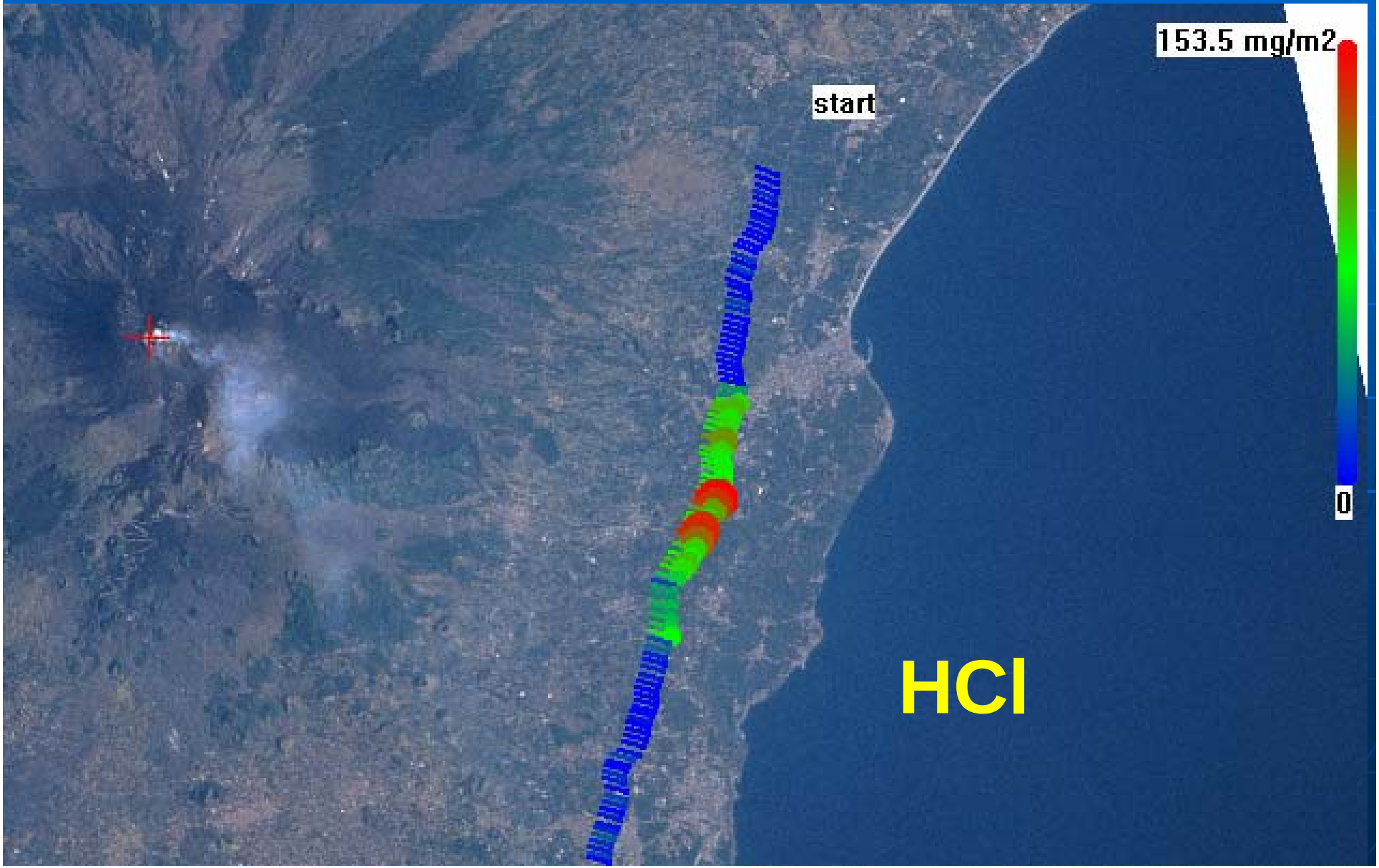




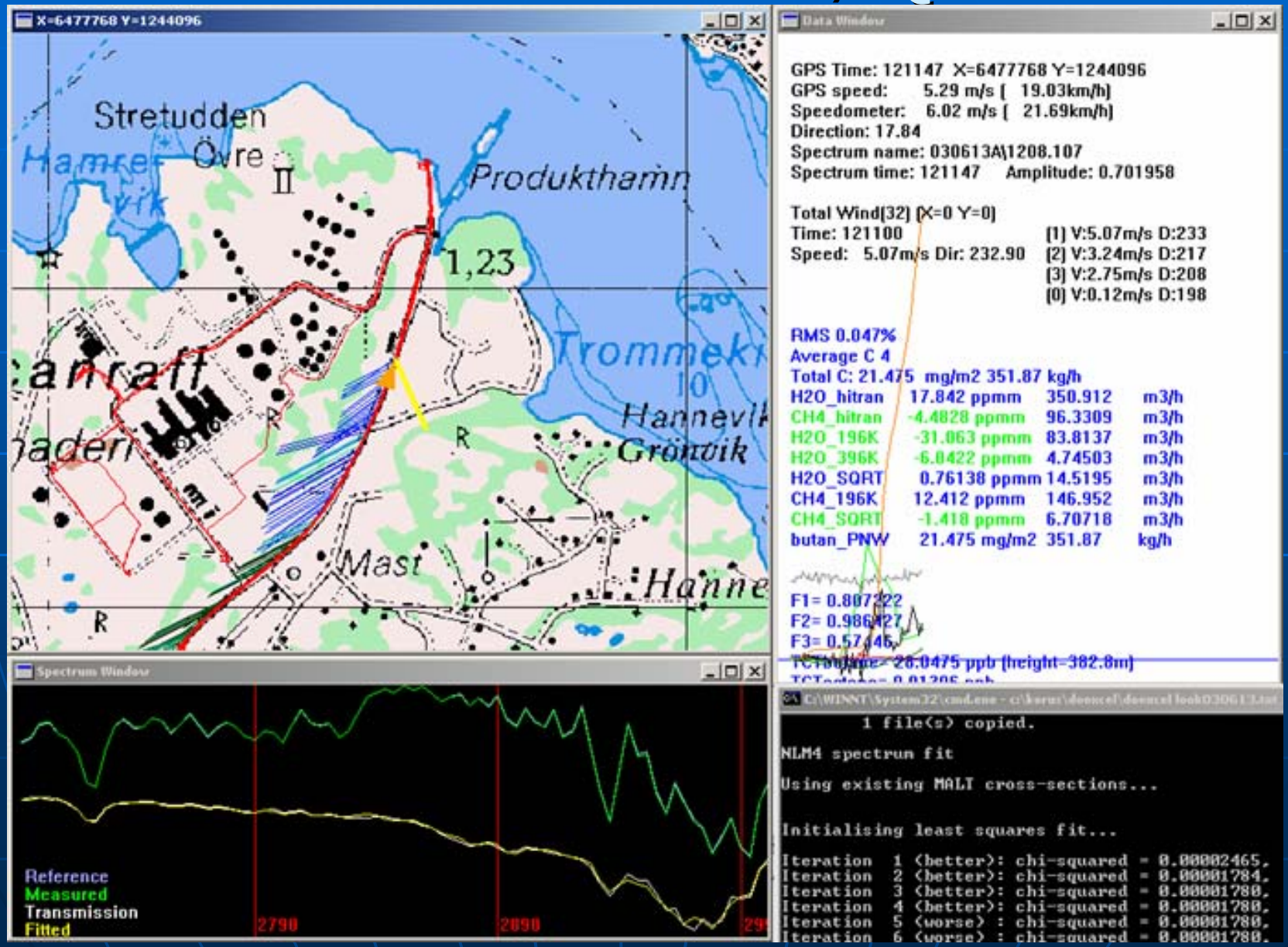
SOF-measurement from a ship in the Göteborg harbor



Volcanic emissions of HCl, Mt Etna Sicily



Automatic retrieval, QESOF



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SOF

- The SOF method was developed in 1997 (patented)
- Measurable species includes VOCs (alkenes, alkanes) ammonia, formaldehyde, CO, HCl, HF, NO_2 and SO_2
- Typical accuracy 20-30%, dominated by uncertainty in the wind field
- Experience:
  - SOF is used since 3 years in an on-going Swedish program (KORUS) for monitoring of the VOC leakages from the Swedish refineries and petrochemical plants.
  - The technique has been applied for volcanic measurement of SO2, HCl, and HF in an EU project with several campaigns at Mt Etna and Popcatepetl
  - Participation in campaigns in Mexico city 2003 and 2006, using the SOF metod (CO, NH3, HNO3, ethylene). Two similar campaigns around Milano (CO, formaldehyde). A new one in March 2006.

Main Activity during TEXAQII 2006

- Quantitative measurement of VOC fluxes around the Sweeny facility (generic olefine plant) that can be used to compare against reported VOC emissions (alkanes, olefines and NO2). If possible site access. (Sep 11-24)

Sweeny


Sweeny
Image © 2006 TerraMetrics
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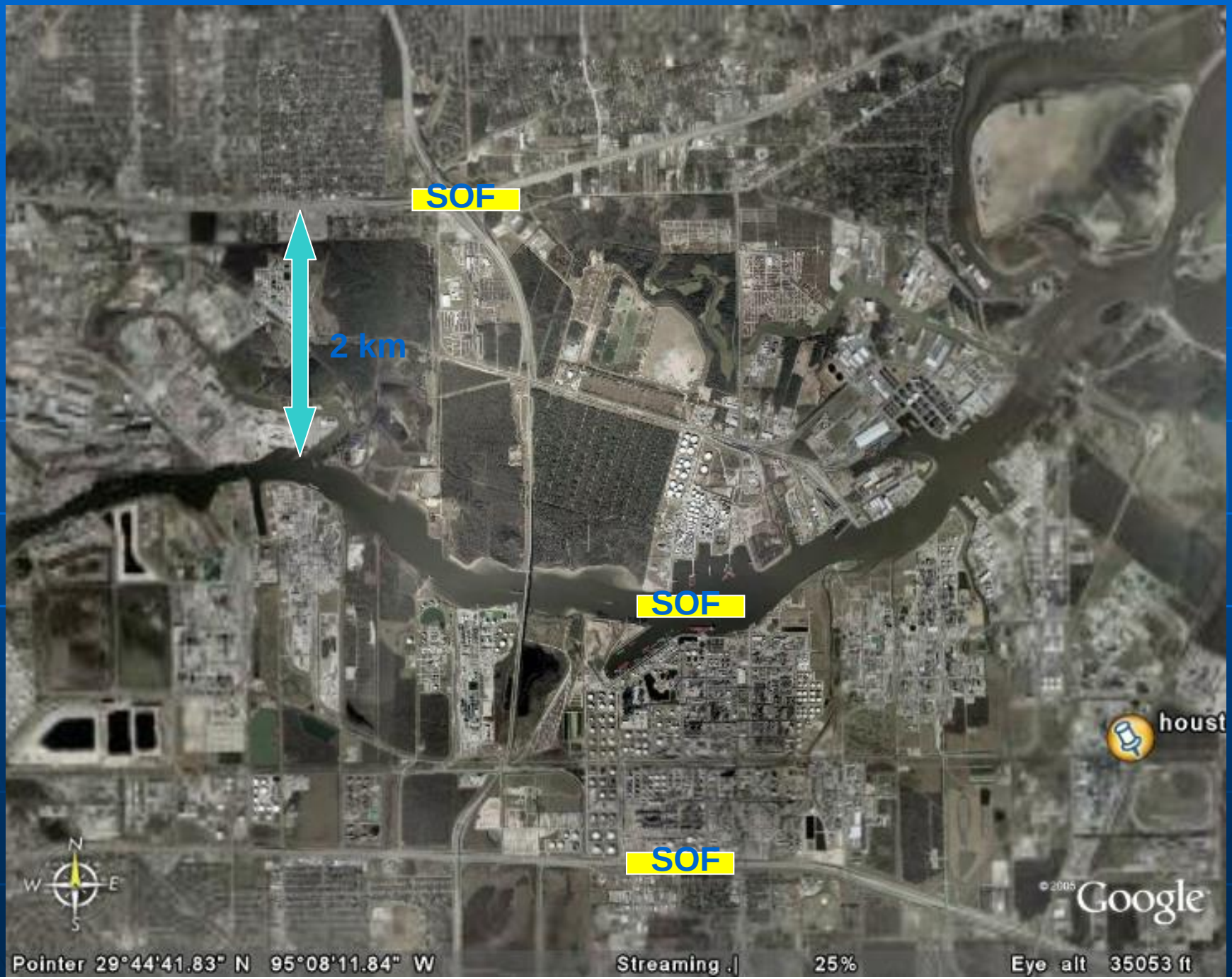
Image © 2006 DigitalGlobe
© 2005 Google
Pointer 29°04'22.72" N 95°44'50.65" W
Streaming 100%
Eye alt 3580 ft

Main Activity II

- Measurements at various distances from the HSC for total flux estimation, plume evolution and comparison with airborne measurements (alkanes, olefines, formaldehyde, CO, NO2, SO2) and studies of downwind plume evolution (Aug 21-Sep 3)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2 km
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© 2005 Google
Pointer 29°44'41.83" N 95°08'11.84" W
Streaming .|
25%
Eye alt 35053 ft

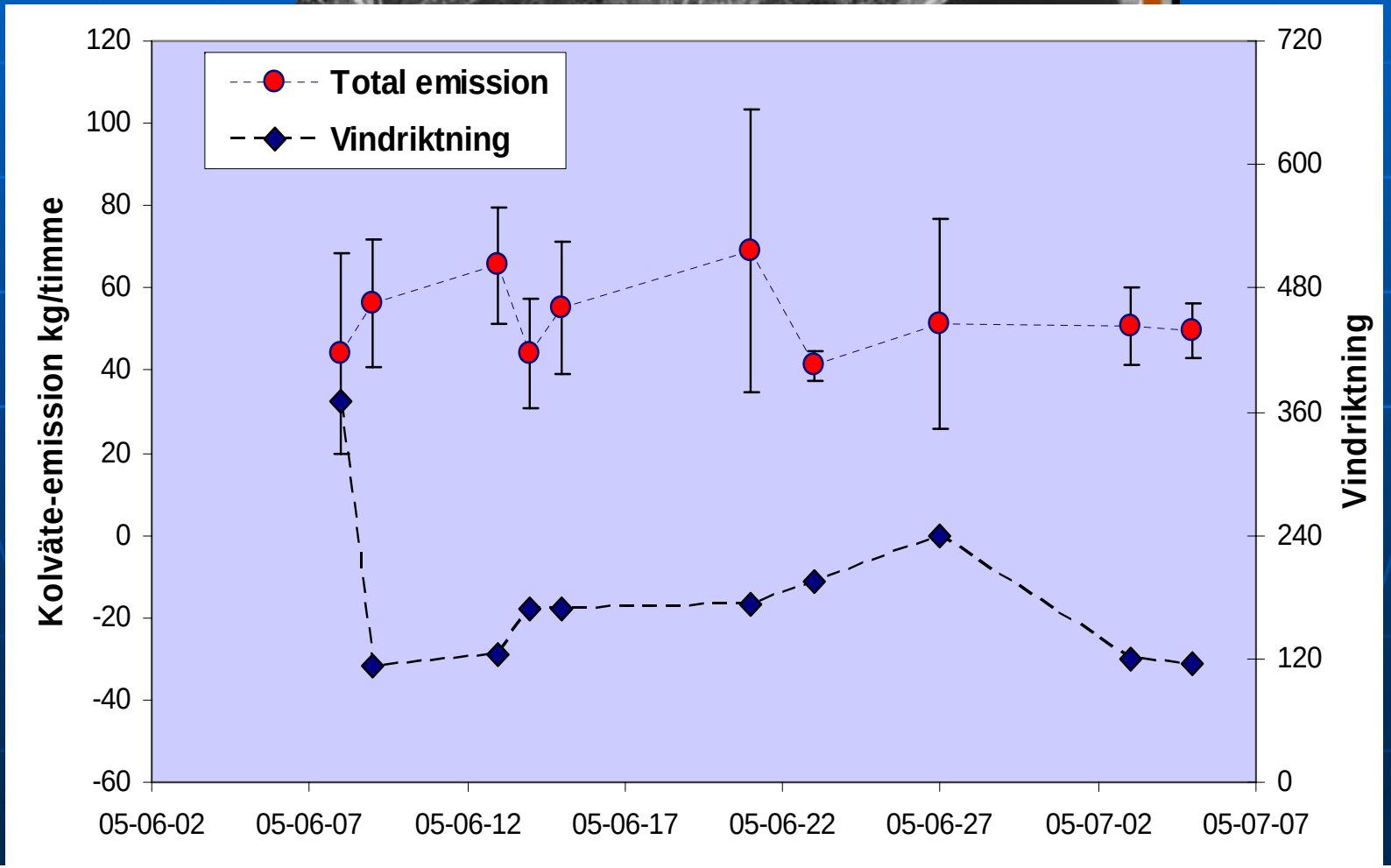
Other possible activities

- Other possible activities: -
  - An isolated refinery (Baytown+other)
  - Other isolated petrochemical plants (Freeport, Choc. Bayou)
  - Waste water plant emissions Texas City,
  - Loading dock operations,
  - Other high emission locations as determined by the most recent LSI HAWK camera analysis

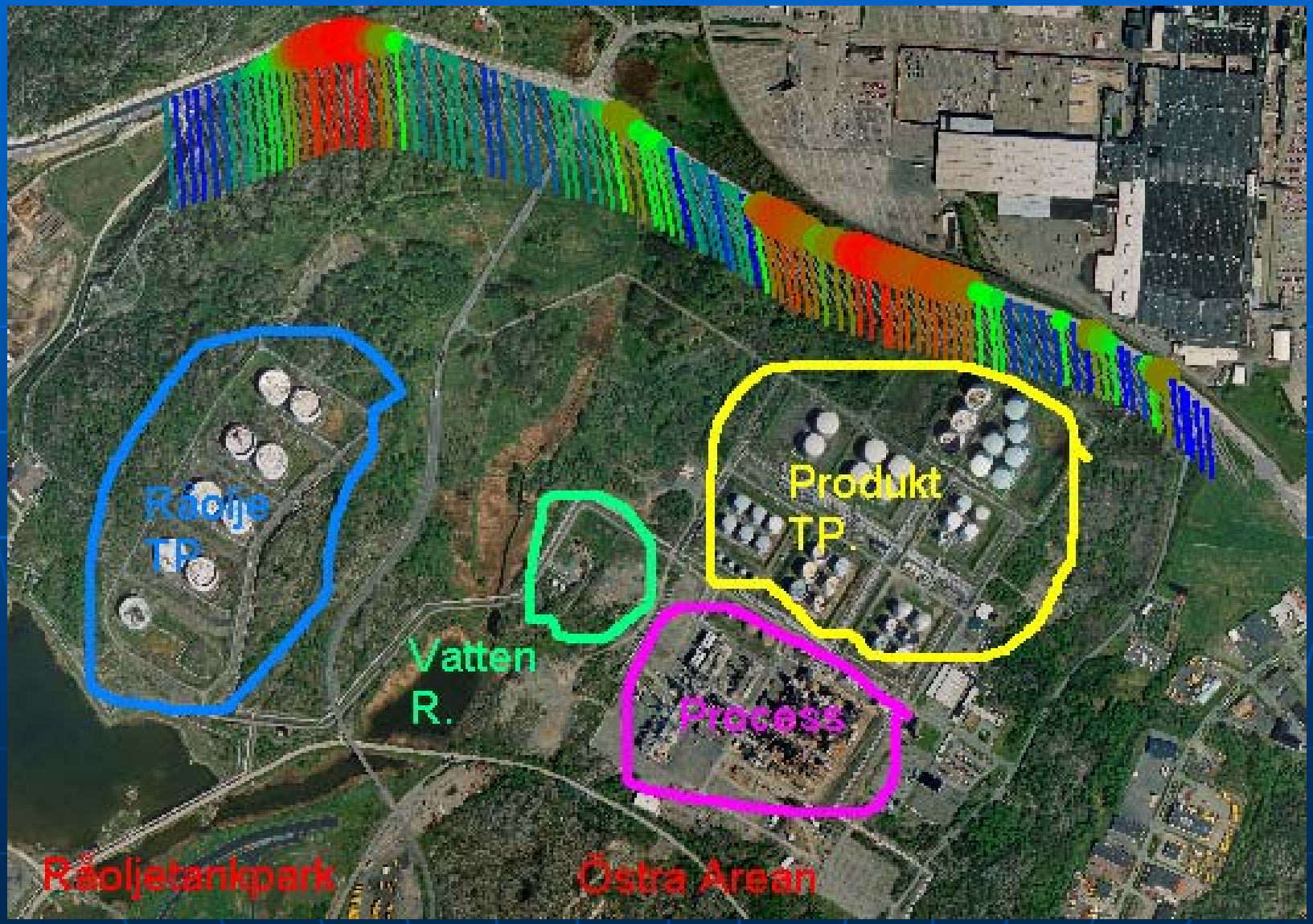
Examples

Total VOC emissions from a Bitumen refinery

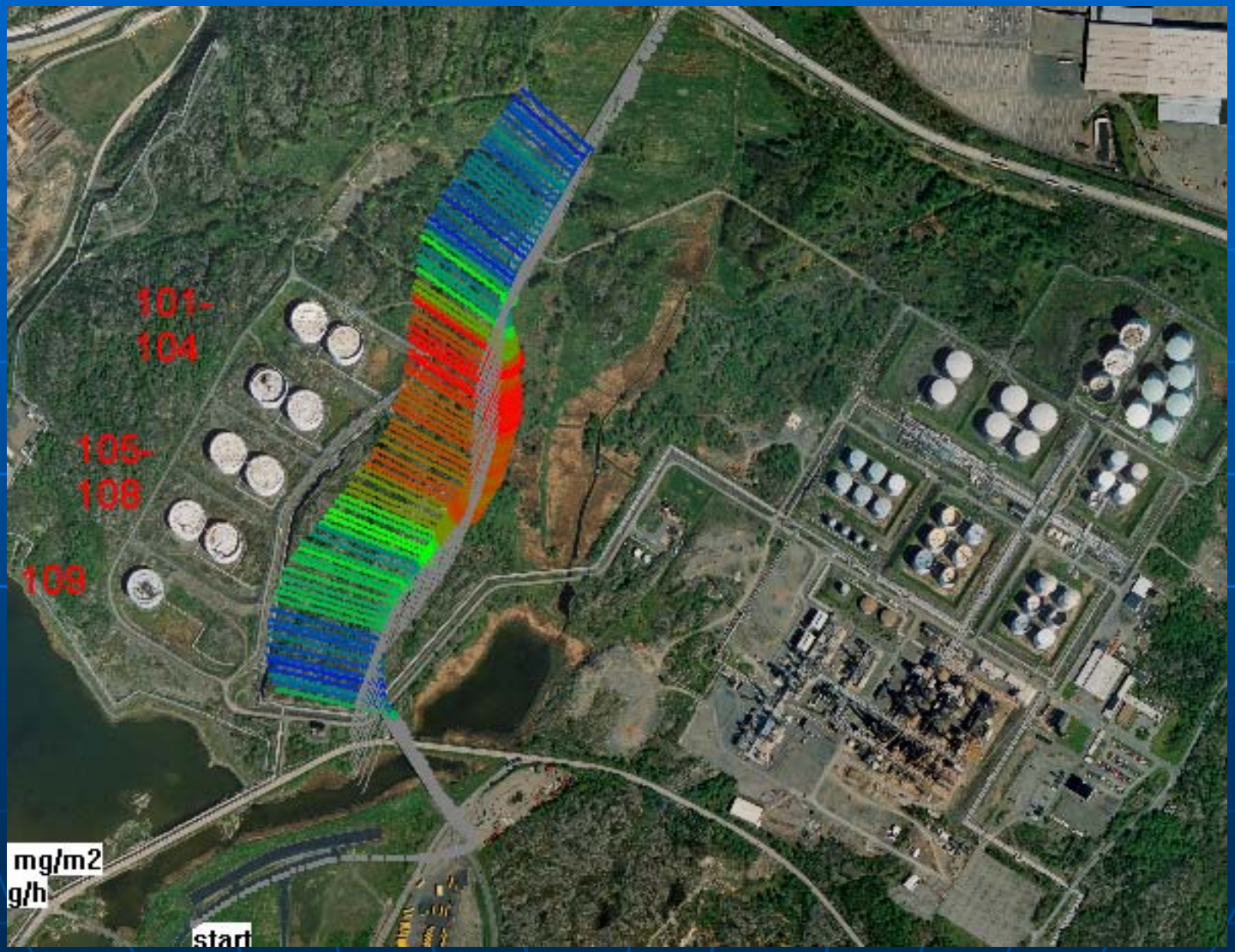
(54 individual measurements) 50 kg/h ±14%



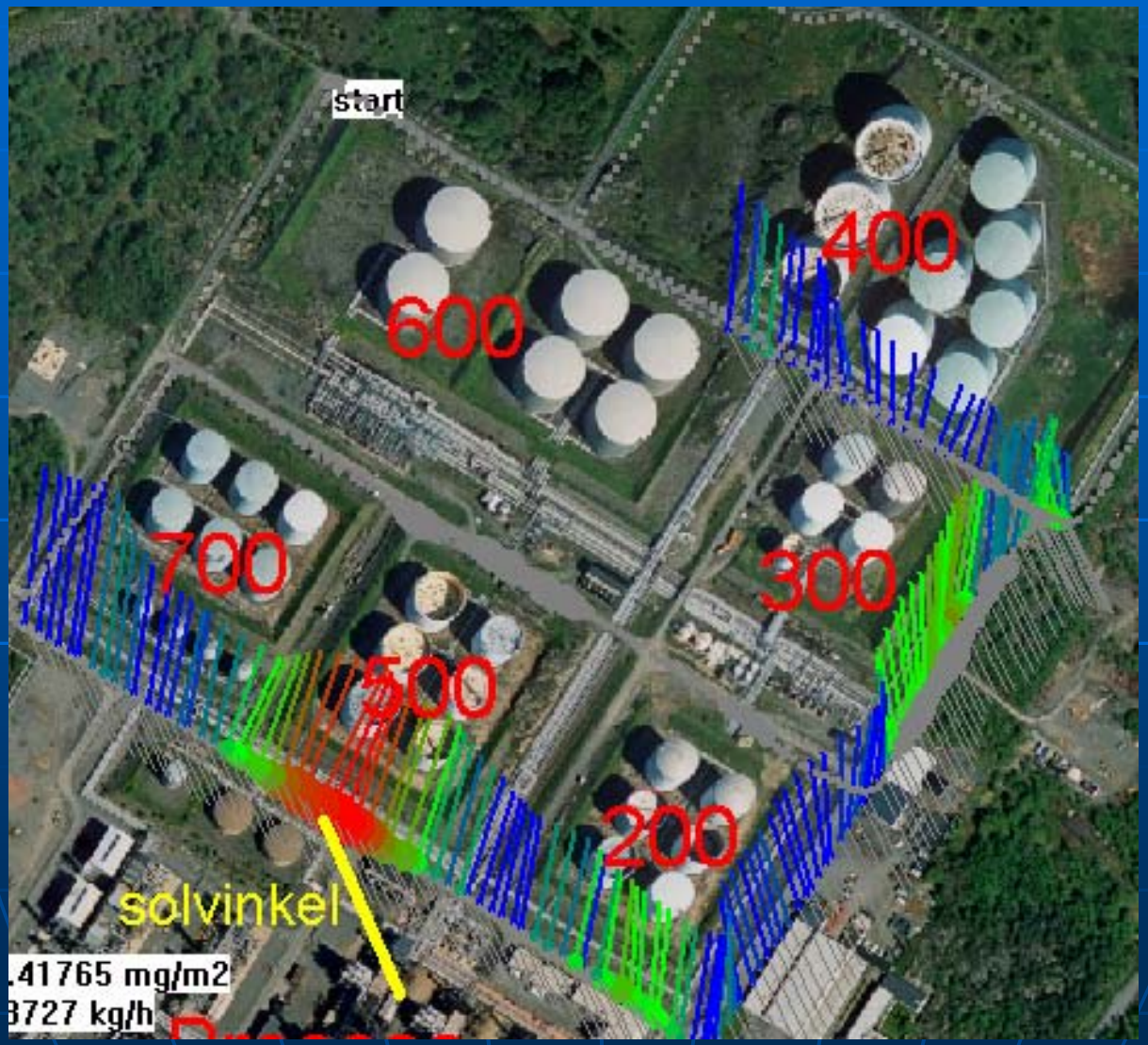
Refinery measurement



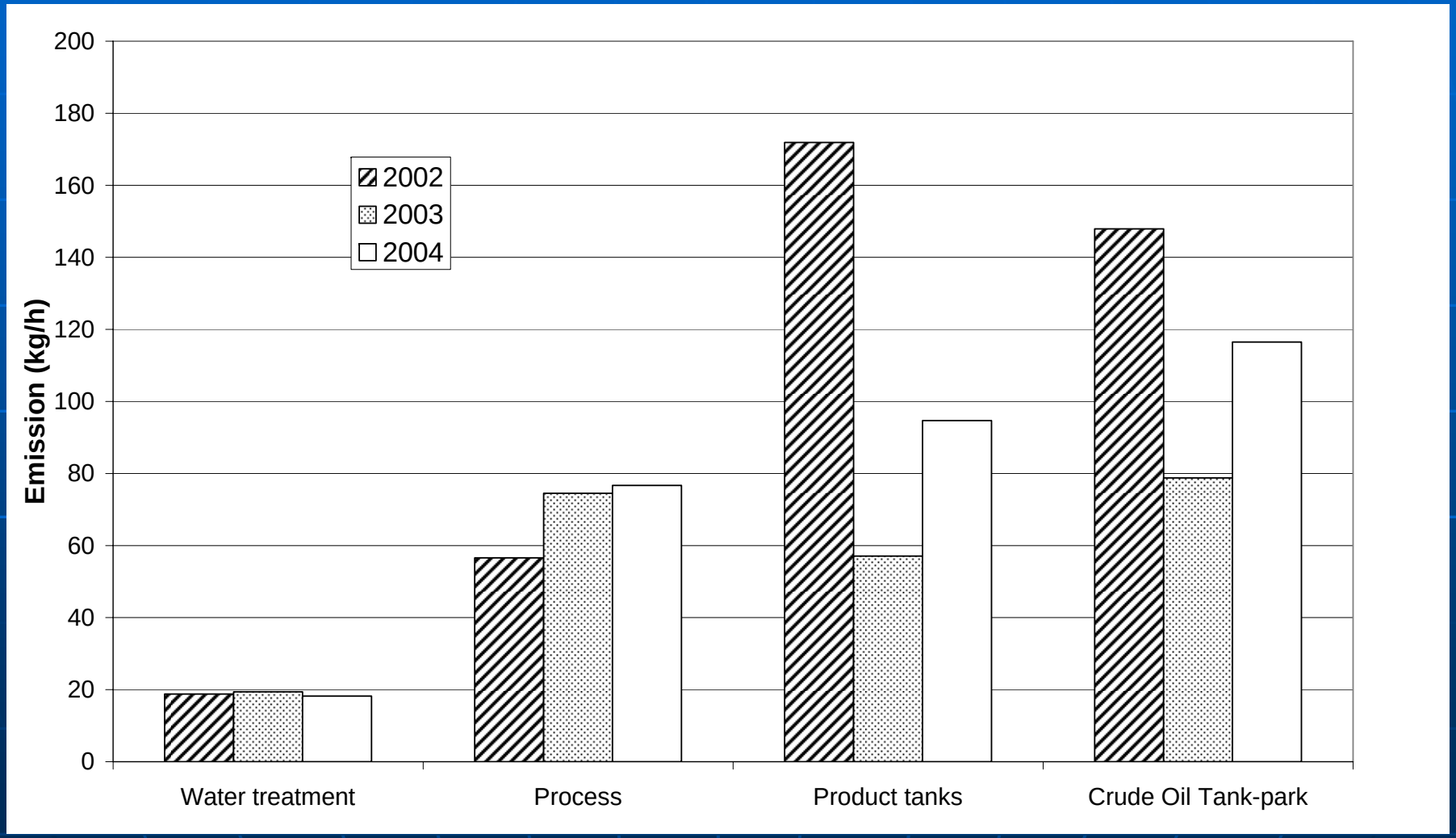
Crude oil tanks



Leakage search /screening



Area emissions (rescaled)



Total VOC emissions from 4 industrial sites

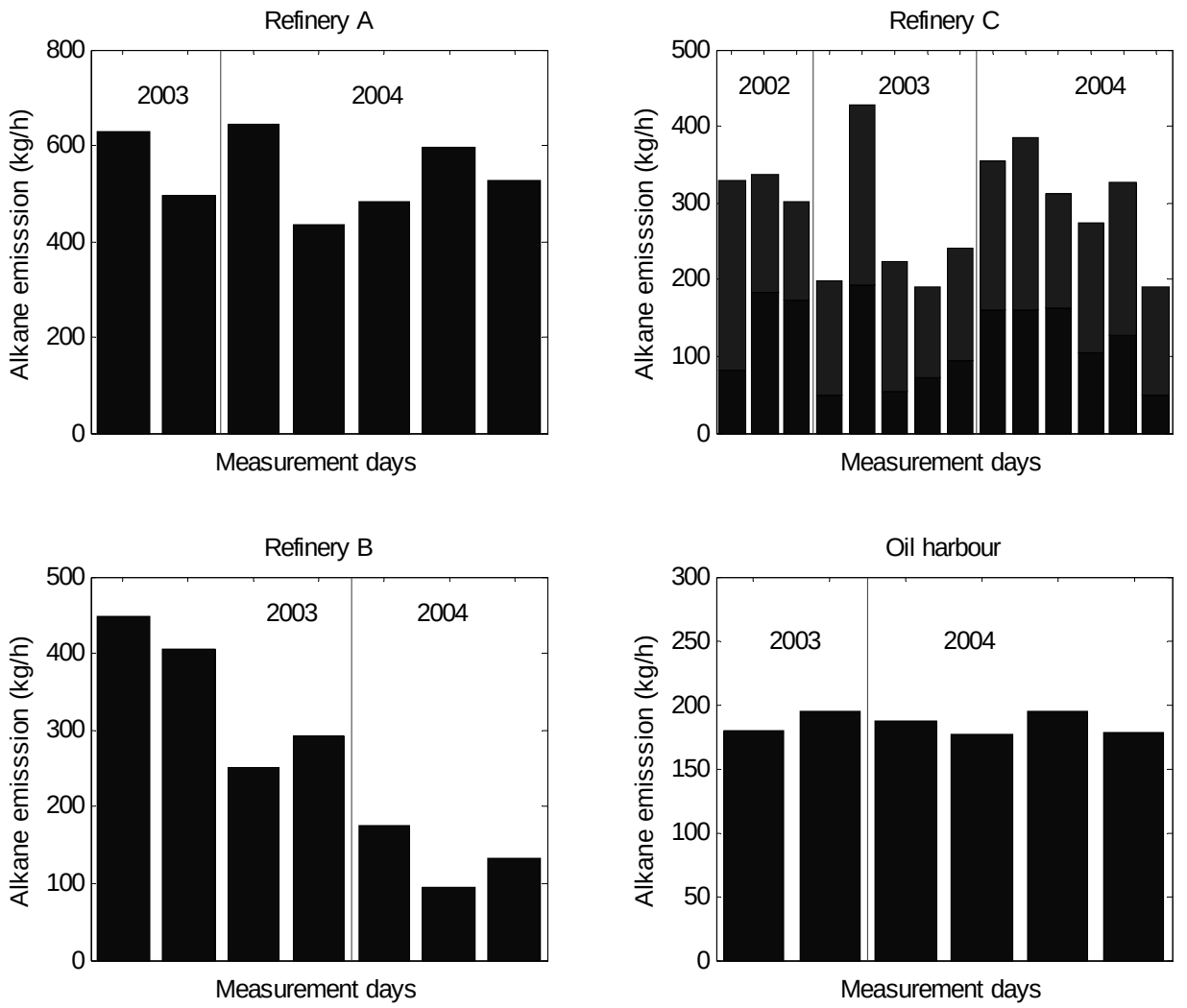


Figure 5. The figure shows the measured daily averaged total emission on each industry.

Three Swedish refineries measured twice over 3 years (KORUS)

- Alkane emissions (C4) typically 0.06 % of production
- Aromatic species 0.005% of production
- Intermittent emissions correspond to 5-10% of yearly emission
- Typically contributions to emission
  - Process area 30%
  - Crude oil 30%
  - Product Storage 30%
  - Water treatment 10%

Error budget and validation experiments

Error budget

- Retrieval method: 5-10%
- Lineparameters 5-10%
- Optical artifacts/interference 10-15%
- Wind field 15-25%
- Sum = 20-35%

Vind variation relative to 25 m (TAPM 3D-model)

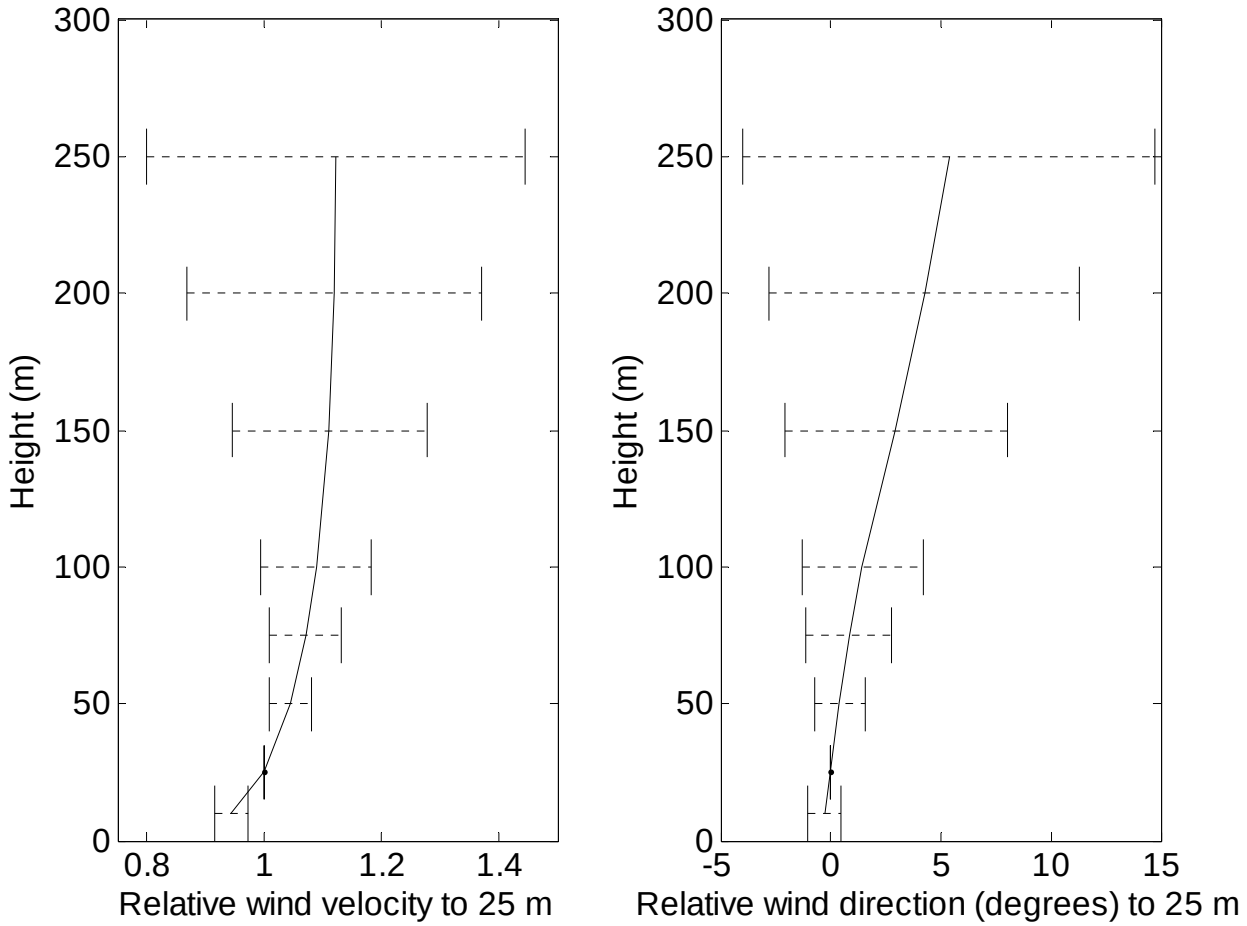
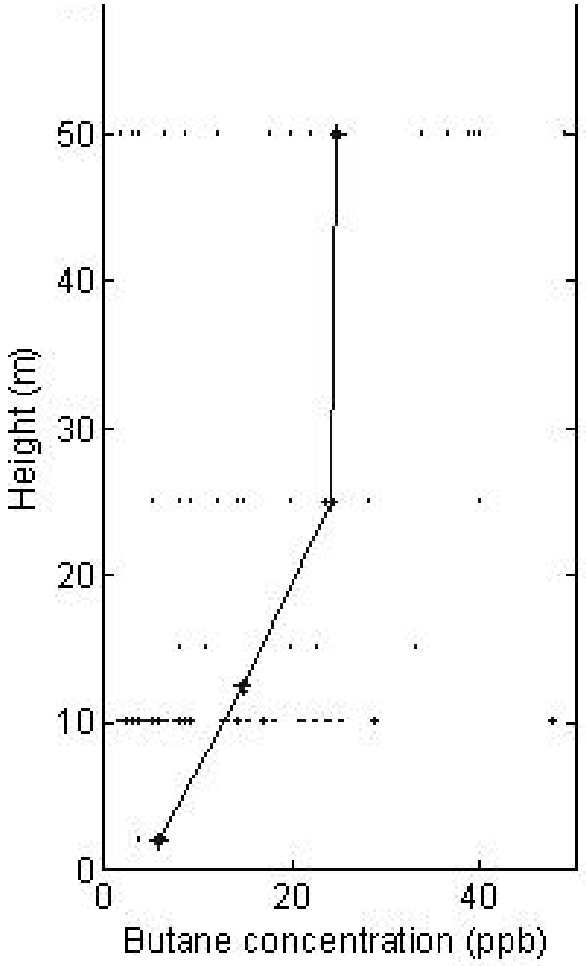


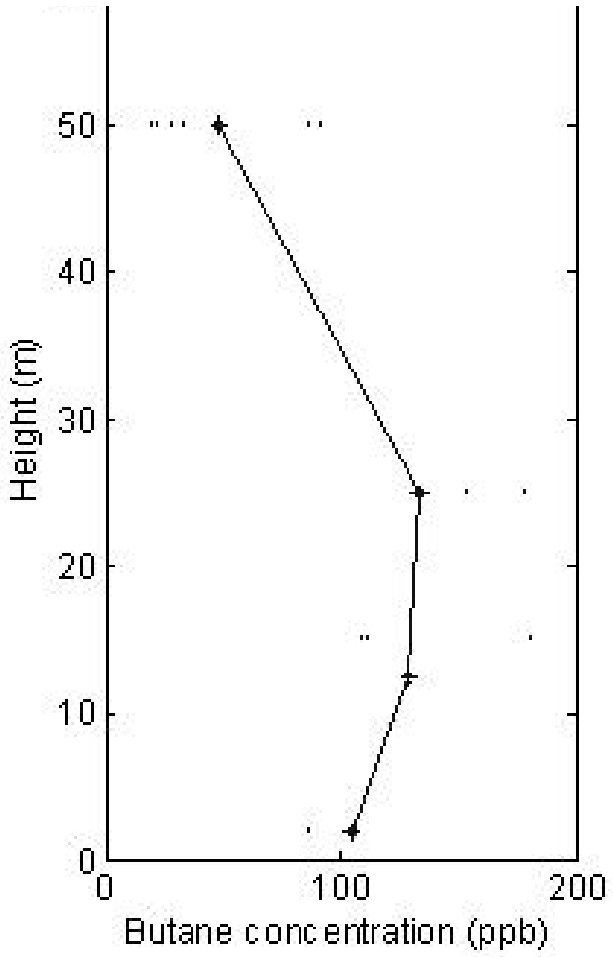
Figure 1. The figure shows the wind velocity and wind direction profile retrieved by simulation and averaged over daytime all sunny days with a wind-speed of 3-6 m/s at ground. The error bars indicate standard deviation between daily averages.

Measured height concentration profile of VOC downwind a refinery

Process plume



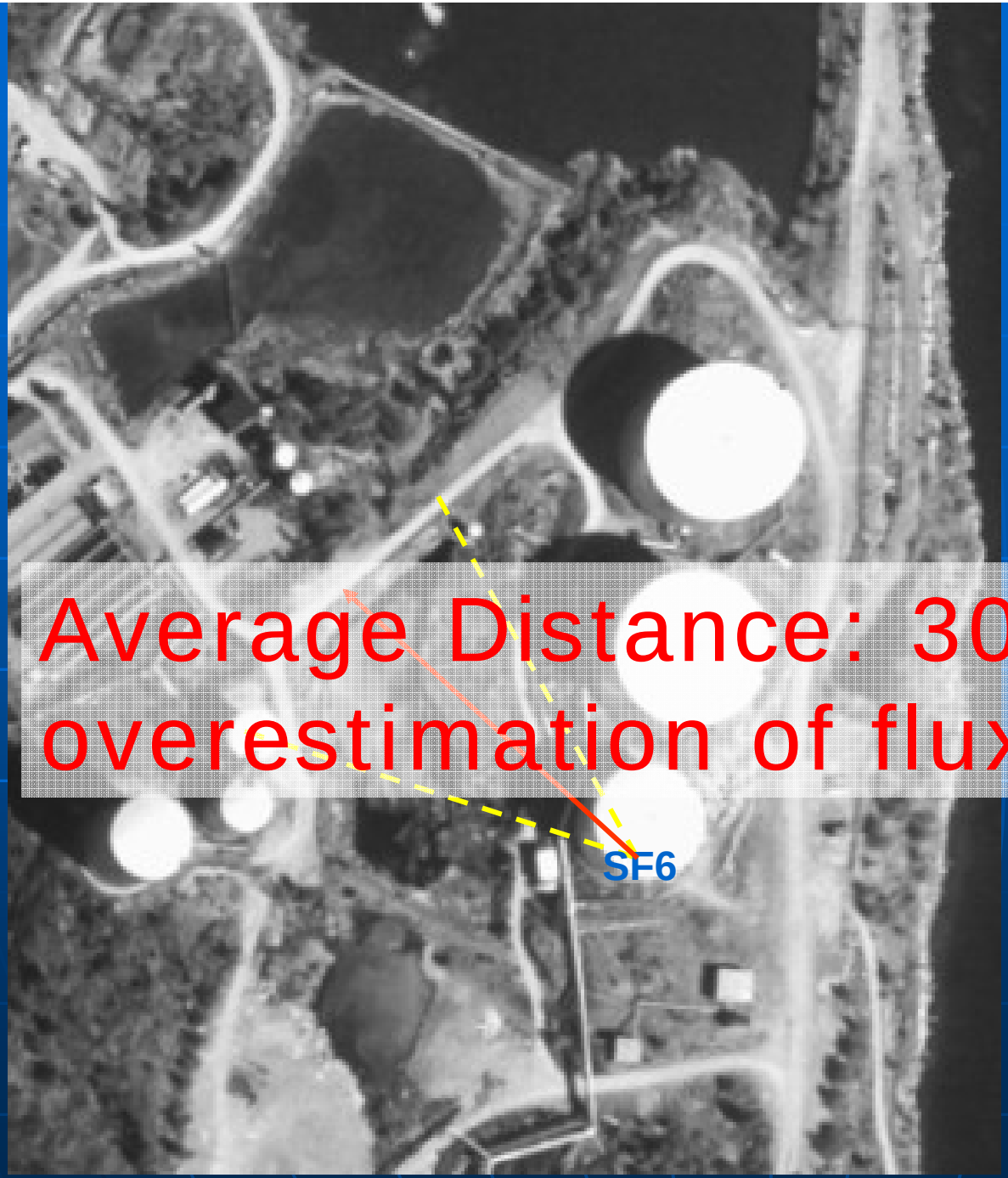
Tank park plume



Validation by conducting controlled tracer releases (SF6) from a 17 m high mast.

Table 1. Summary for each day in year 2002, for which tracer release experiments measurements were conducted at the Åby field.

Day	**Emitted SF_6 (kg/h)**	**Calculated average (kg/h)**	**Number of accepted traverses**	**Average wind speed (m/s)**	**Average wind direction**	**Error**
May-22	1.9	2.3±1.3	4	4.9-8.6	152°-169°	21%
May-23	2.0	2.2±0.6	15	3.9-5.6	120°-142°	10%
June-03	2.0	1.6±0.9	16	2.7-5.3	235°-273°	-20%
June-04	1.9	2.0±1.4	9	5.9-7.8	152°-191°	5%

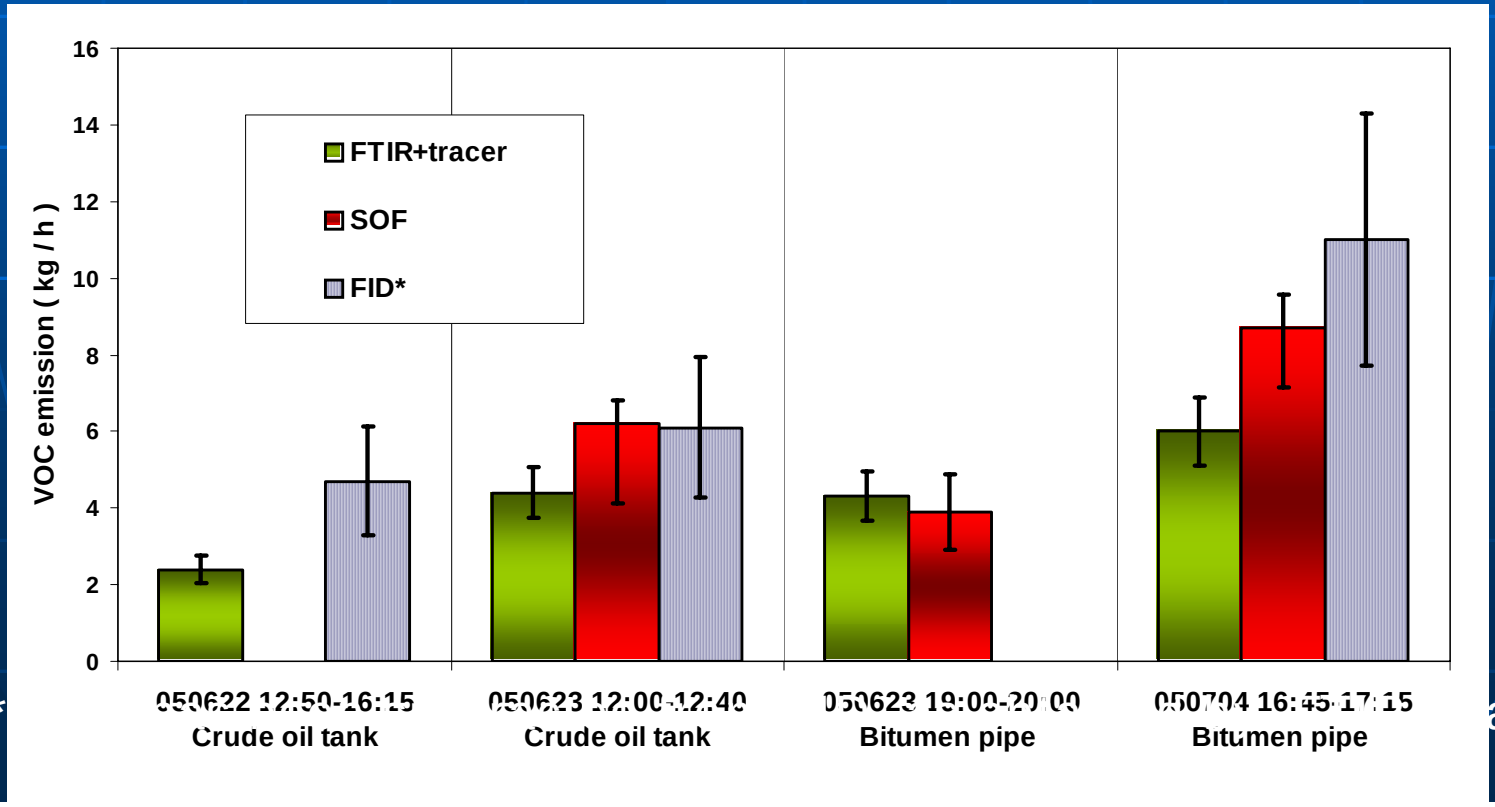


Validation by conducting controlled tracer releases (SF6) from a crude oil tank.

Average Distance: 30% overestimation of flux

Validation of 3 different techniques by conducting VOC emission measurements from a single crude oil tank with a single vent with forced ventilation

1. Extractive FTIR+tracer, 2. SOF 3. FID+forced ventilation



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Comparison between SOF and DIAL, process area measurements Göteborg

	SOF kg/h	DIAL kg/h
2003	75±20%	
2004	76±20%	

- For oil refinerys and oil depots the SOF and DIAL techniques seem comparable (within 30%)
- But considerable discrepancies for emissions from heavier oil (bitumen)