

Quantifying fugitive emission of VOCs using the Solar Occultation Flux technique (SOF)

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ORS group Chalmers



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

Radio and Space

Chalmers University of Technology

CHALMERS



- **Fugitive emission monitoring**
- **Leakage search**
- **Volcanic monitoring instruments**

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Experience

- Applied research of using long path DOAS and FTIR since end of 1980's.
- Involved in the Network for the Detection of Stratospheric Change since 1994, conducting high resolution FTIR measurements of the sun
- Mobile solar FTIR measurements (SOF) for investigating ethylene emissions from 3 petrochemical plants in Sweden. Fugitive emissions and flare efficiency.
- Mobile solar FTIR measurements (SOF) for investigating alkane emissions from refineries and storage facilities (3 plants Sweden, 1 in Italy and 1 in Mexico City)
- Column studies of CO, HCHO, NH₃ in mega cities, Mexico city-2003 and Milano (Po valley) 2002/2003
- Volcanic monitoring (Mt Etna 2000, 2004, Mt Serrat, Poas,..)

References*

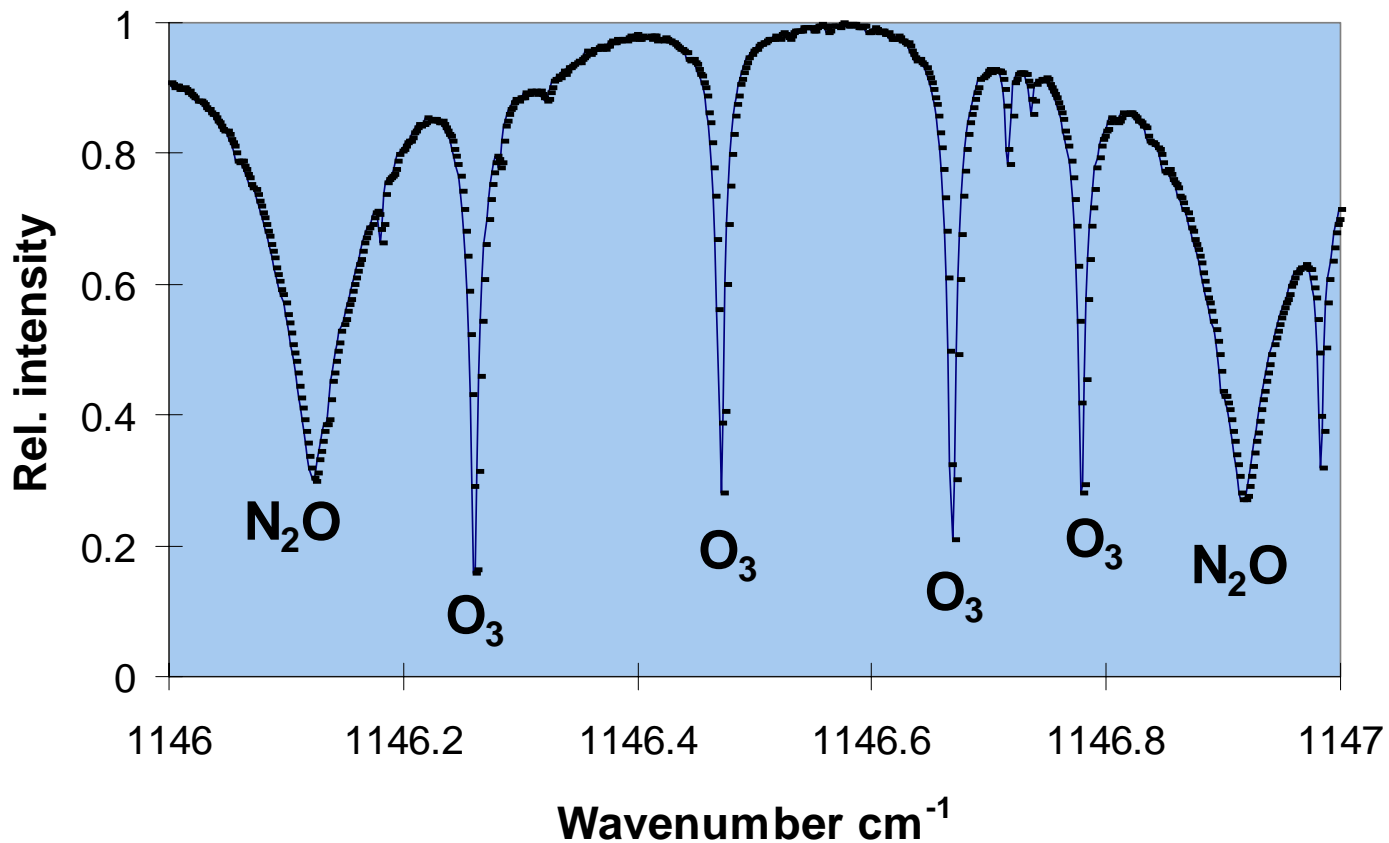
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- Galle B., Oppenheimer C., Geyer A., McGonigle A. and Edmonds M. "A miniaturised ultraviolet spectrometer for remote sensing of SO₂ fluxes: a new tool for volcano surveillance". *Journal of Volcanology*, 119, 241-254, 2002.
- Galle B, et al., " Measurement of ammonia emission from spreading of manure using gradient FTIR techniques", *Atmospheric Environment*, 34, 4907-4915, 2000
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- Mellqvist, J., Galle, B. and Burton, M., *Cross section measurements of the emission plume of Mt Etna using the Solar Occultation Flux method*, Peter Francis memorial workshop, London, October 24-26, 2001
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* *The SOF method has not yet been properly published, but during this year two papers will be submitted. One regarding SOF measurements on volcanoes and one on refinery measurements.*

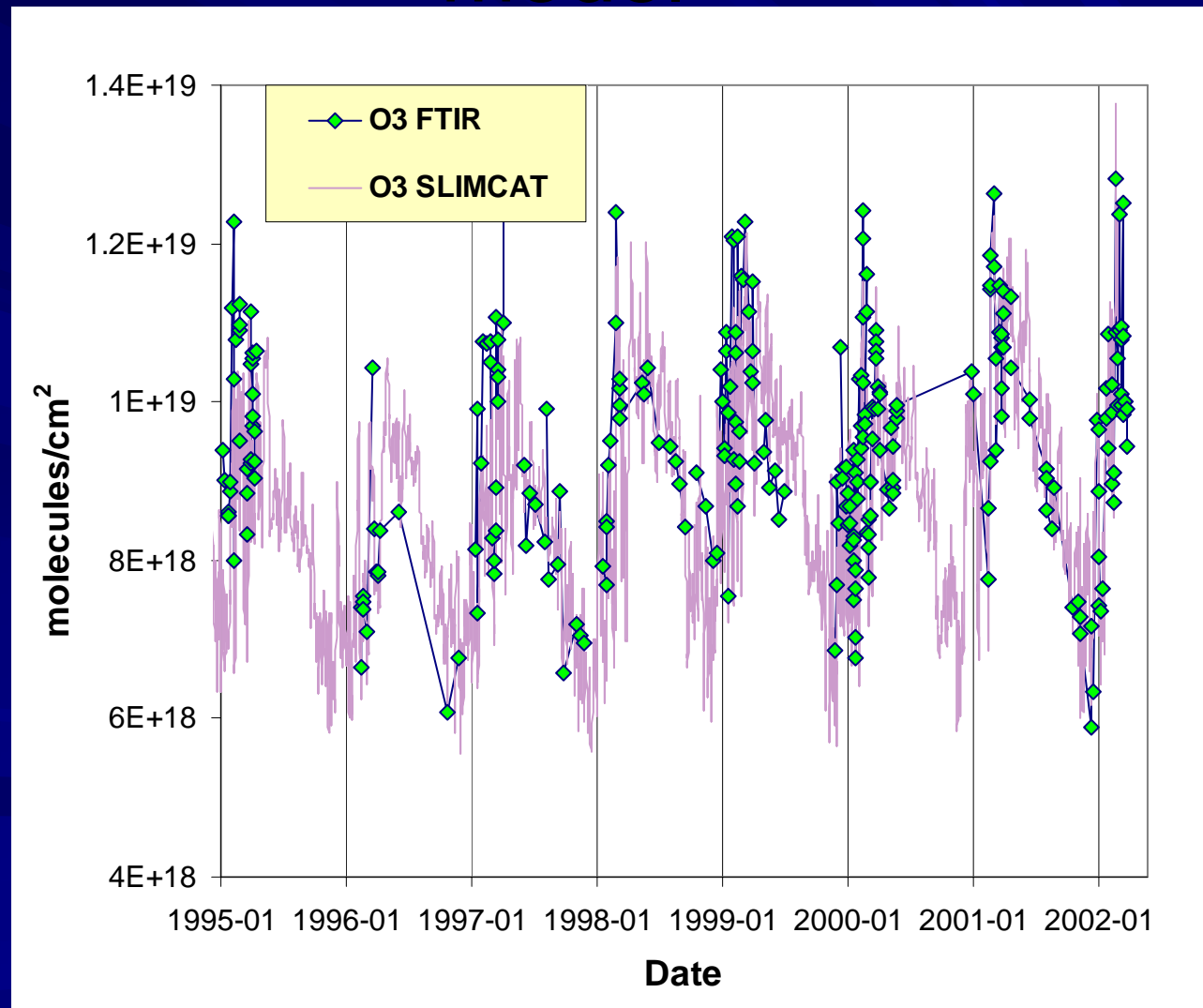
Stratospheric measurements within the Network for the Detection of Stratospheric Change (NDSC), conducted at Harestua, Norway since 1994



FTIR spectrum of the sun around 9 μm



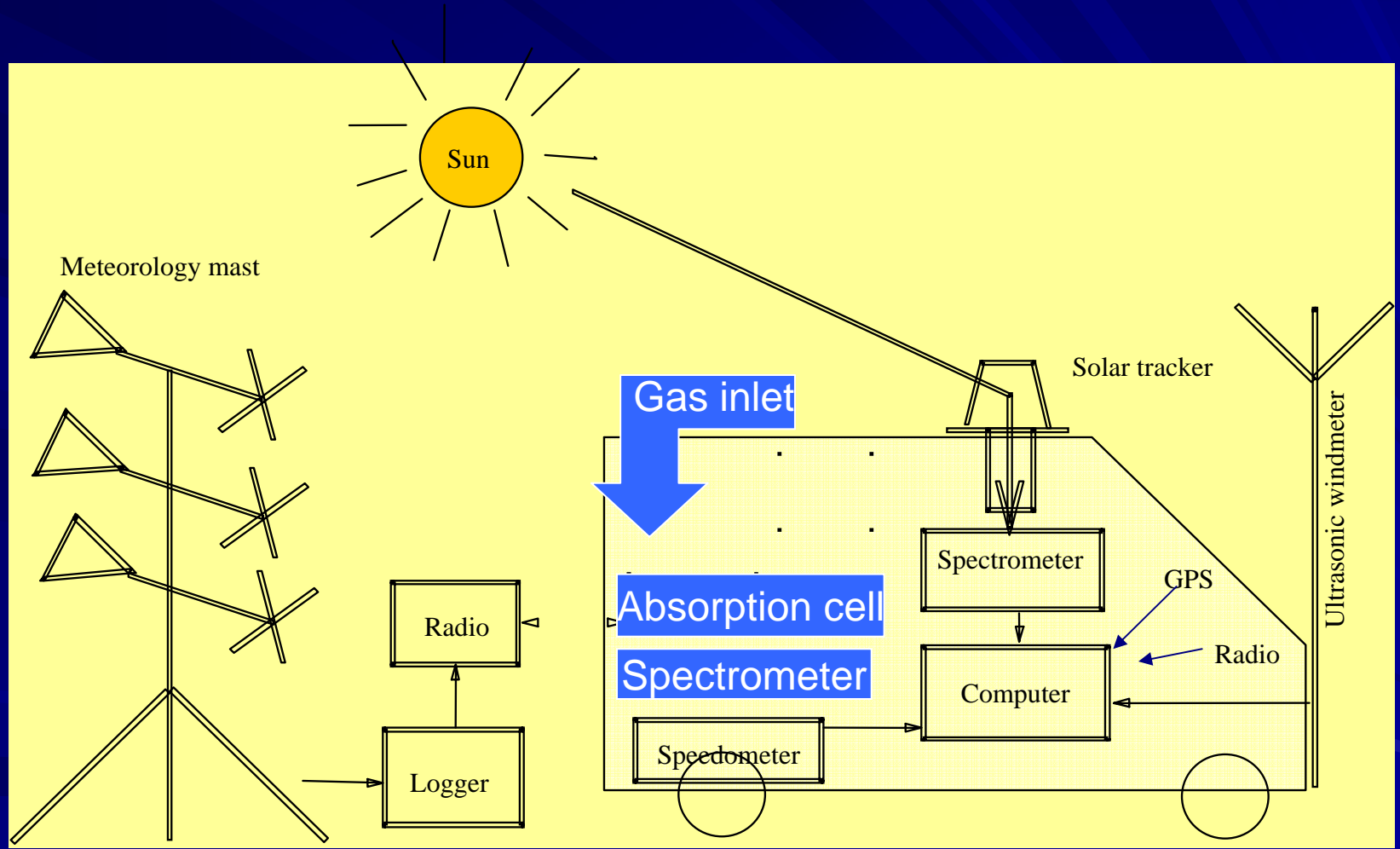
Ozone column Harestua and comparison to the Slimcat 3D model



The Solar Occultation Flux method (SOF)



Setup



Today we have 2 SOF instruments.
The smaller system will be modified and optimized
for ethylene/propylene measurements



SOF

- The SOF method was developed in 1997 (patented)
- Applications already demonstrated include agriculture, megacities, petrochemical industries, refineries, ships and volcanoes.
- A point source of 0.5 kg/h can be measured 50 m downwind with a precision of 3% and accuracy of 30%.
- More cost effective and faster than the DIAL method
- Measurable species includes VOCs (alkenes, alkanes) ammonia, formaldehyde, CO, HCl, HF, NO₂ and SO₂

SOF Retrieval

- Cross sections from HITRAN 2000, NIST, PNL, and the Hanst library are used.
- The retrieval is conducted by fitting calibration spectra to the measured ones, using several published codes
 - SFIT2 (Rinsland, NASA),
 - NLM, MALT (Griffith, Uni Wollongong)
 - CLS (homemade)

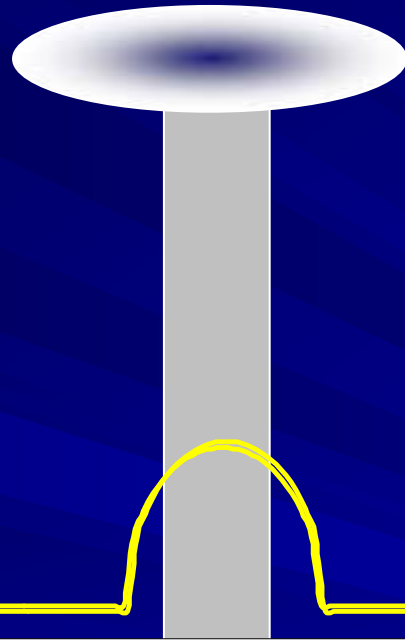
Activities of the Chalmers group in using the SOF method for urban pollution studies

- Recent participation in the Mexico city campaign, coordinated by Luisa and Mario Molina, MIT, conducting both column studies and emission studies using the SOF method (CO, NH₃, HNO₃, ethylene)
- Two similar campaigns have been conducted in 2002 and 2003 in the Po valley around Milano (CO, formaldehyde).
- Running of a program (KORUS) for monitoring the VOC leakages from the Swedish refineries and petrochemical plants. (Several studies have been done on plants which emitting ethylene).

Why measure

- Typical results on Swedish refineries are 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 standard approach with EPA-21 and tank model, means that measurements reflecting the real (unperfect) situation will only be done in the process areas. Malfunctioning storage tanks are for instance not considered. Our experience is that these often correpond to a high fraction of the leakages.
- DIAL measurements during the early 1990's in Sweden have shown discrepancies up to a factor of 20 compared to estimates.
- The last TEXAQ campaign indicates dicrepancies of a factor 5 between the standard approach and measurements
- Leaks from cooling towers, flares, water treatment facilities, storage caverns, loading (trucks/ships), tank cleaning an repair etc, can not be asessed using calculation methods nor EPA 21.

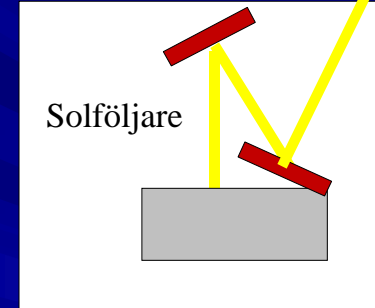
SOF (Solar Occultation Flux) method



Cross section of a flue gas plume blowing towards the observer

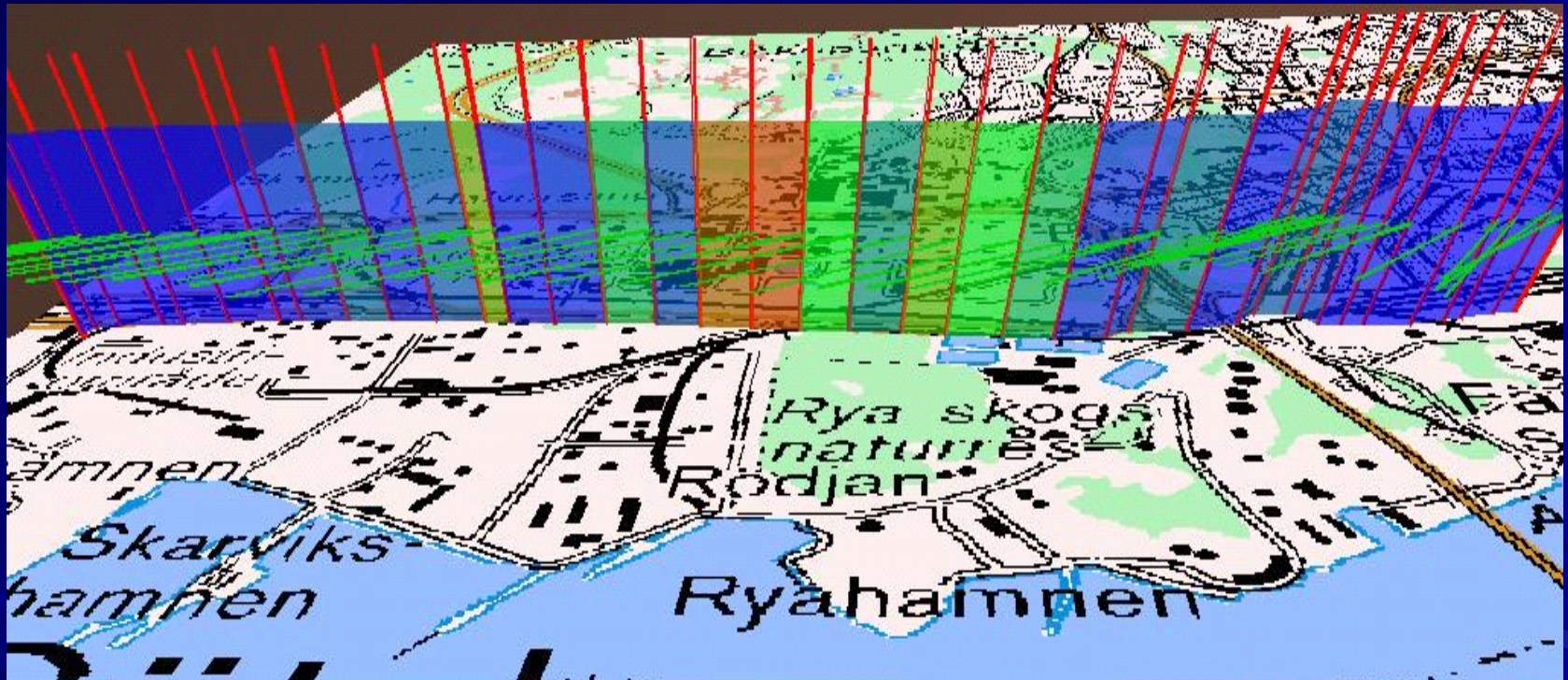
Gas column

- Uppmätt gaskolumn mg/m² längs sträckan
- Ackumulerad gaskolumn mg/m (prop mot Flux)



$$\text{Flux} = \text{Accumulated gas column} * \text{windspeed}$$

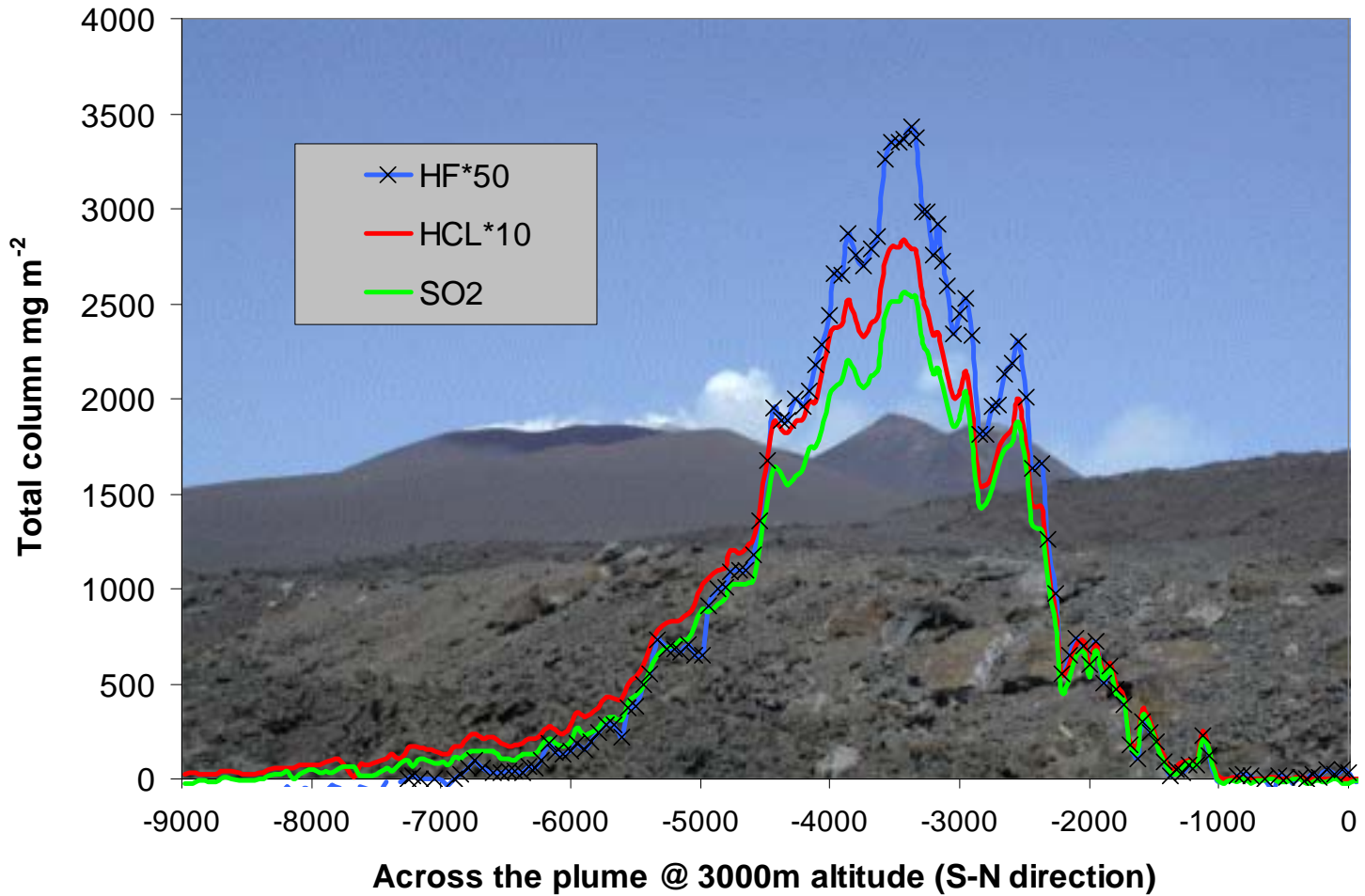
A 3D plot, of SOF measurements in the oilharbor of Göteborg. Red corresponds to more hydrocarbon.



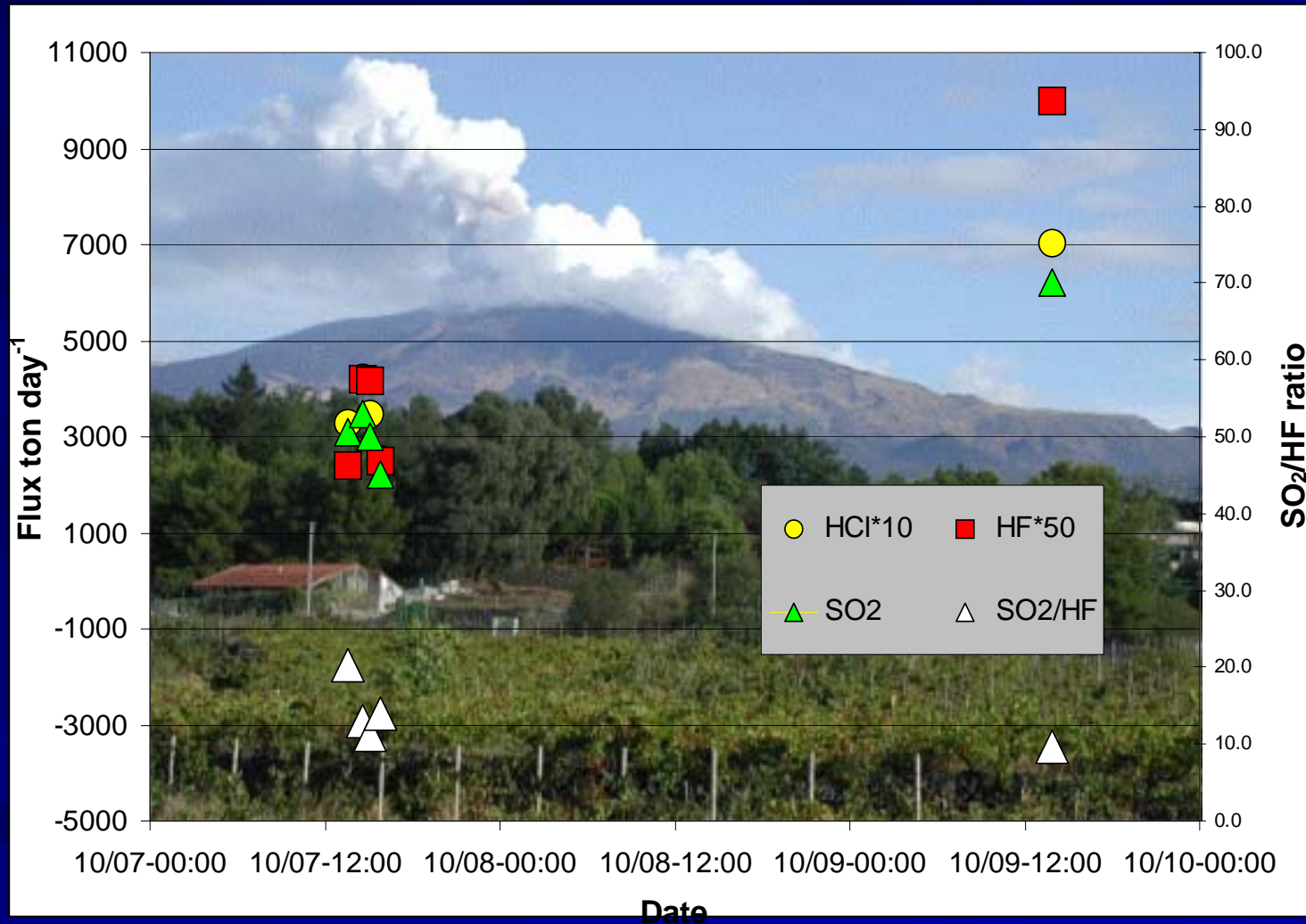
Principle of SOF:

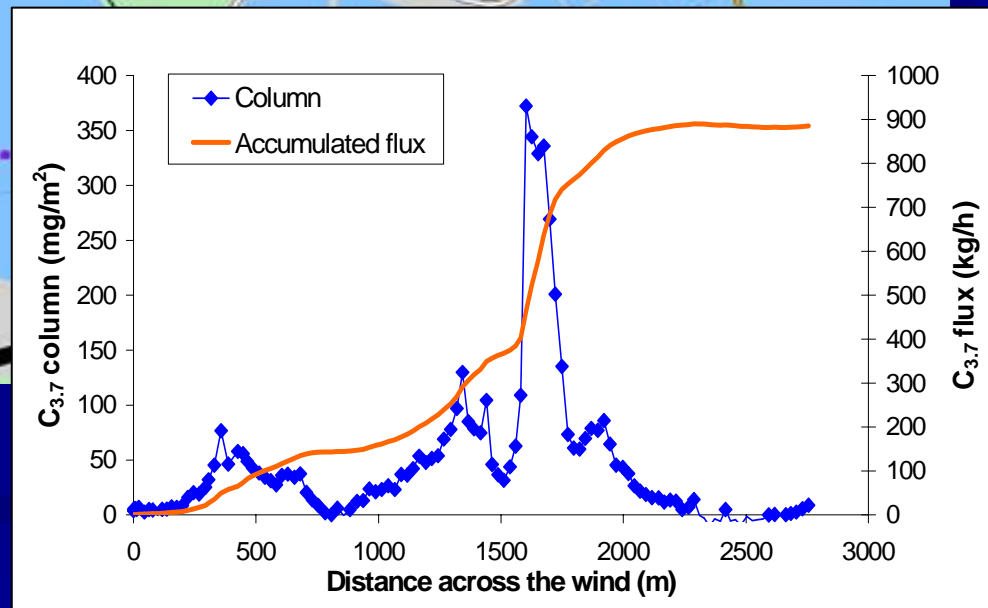
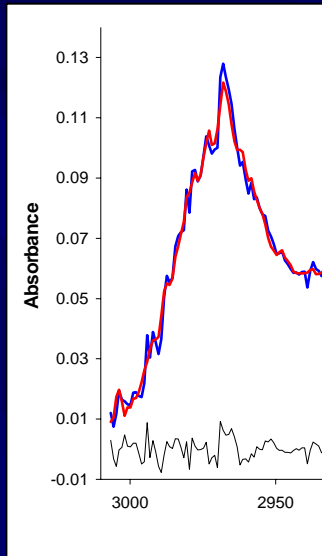
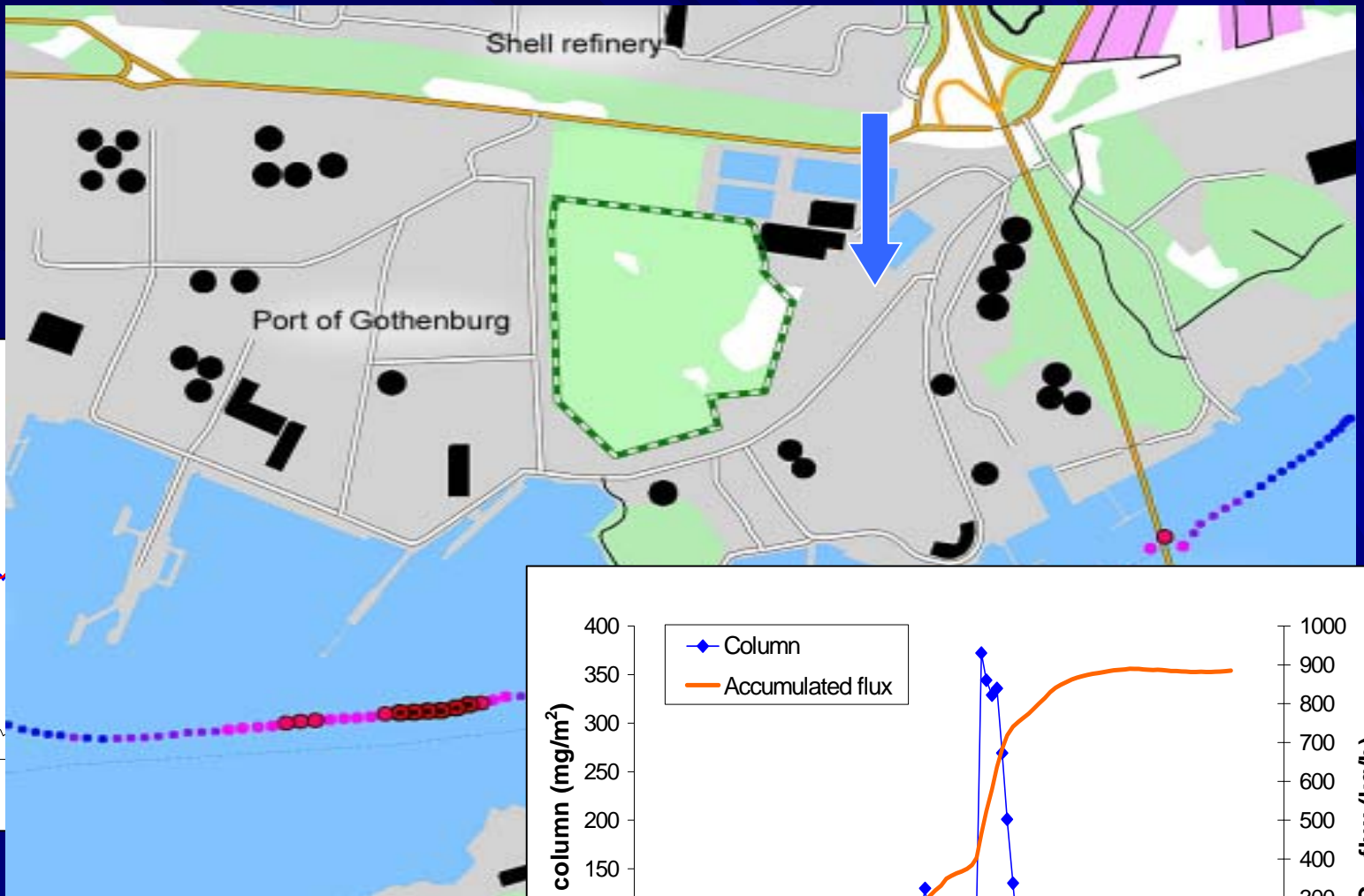
- Mobile measurements are conducted so that the solar light transects a cross section of the emission plume in study
- A clean air reference taken outside the plume is used in the retrieval
- The amount of forinstance hydrocarbons (in mg/m²) is retrieved over the cross section of the emission plume, by nonlinear fitting of reference spectra to the measured spectral features .
- The values are multiplied by the windspeed, yielding the **flux of the hydrocarbons** through the cross section of the plume. (mg/m²*m*m/s=mg/s)

Mt Etna 2000



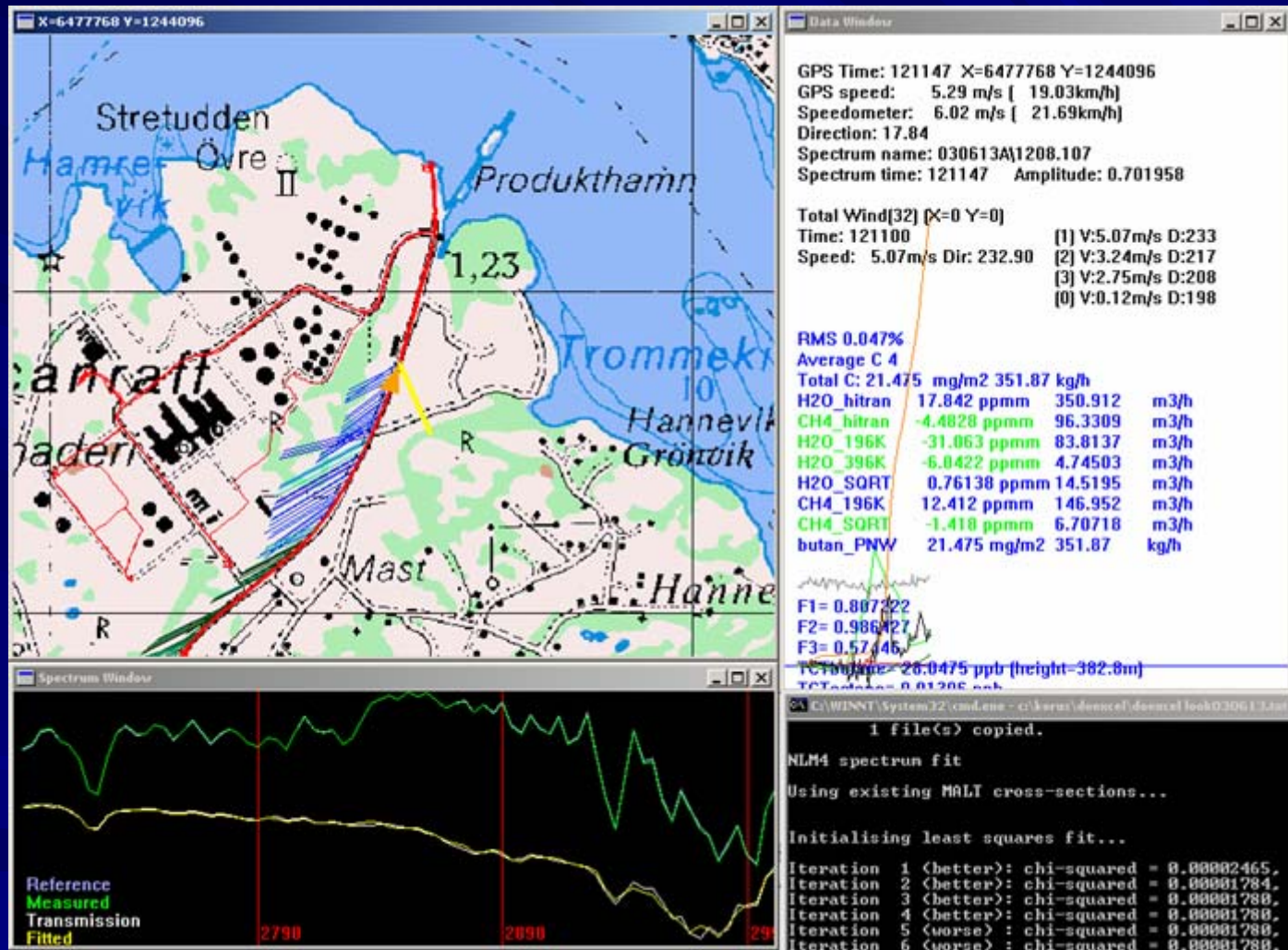
Flux rate from Mt Etna





SOF-measurement of butane from a ship in the Göteborg harbor

Automatic retrieval, QESOF



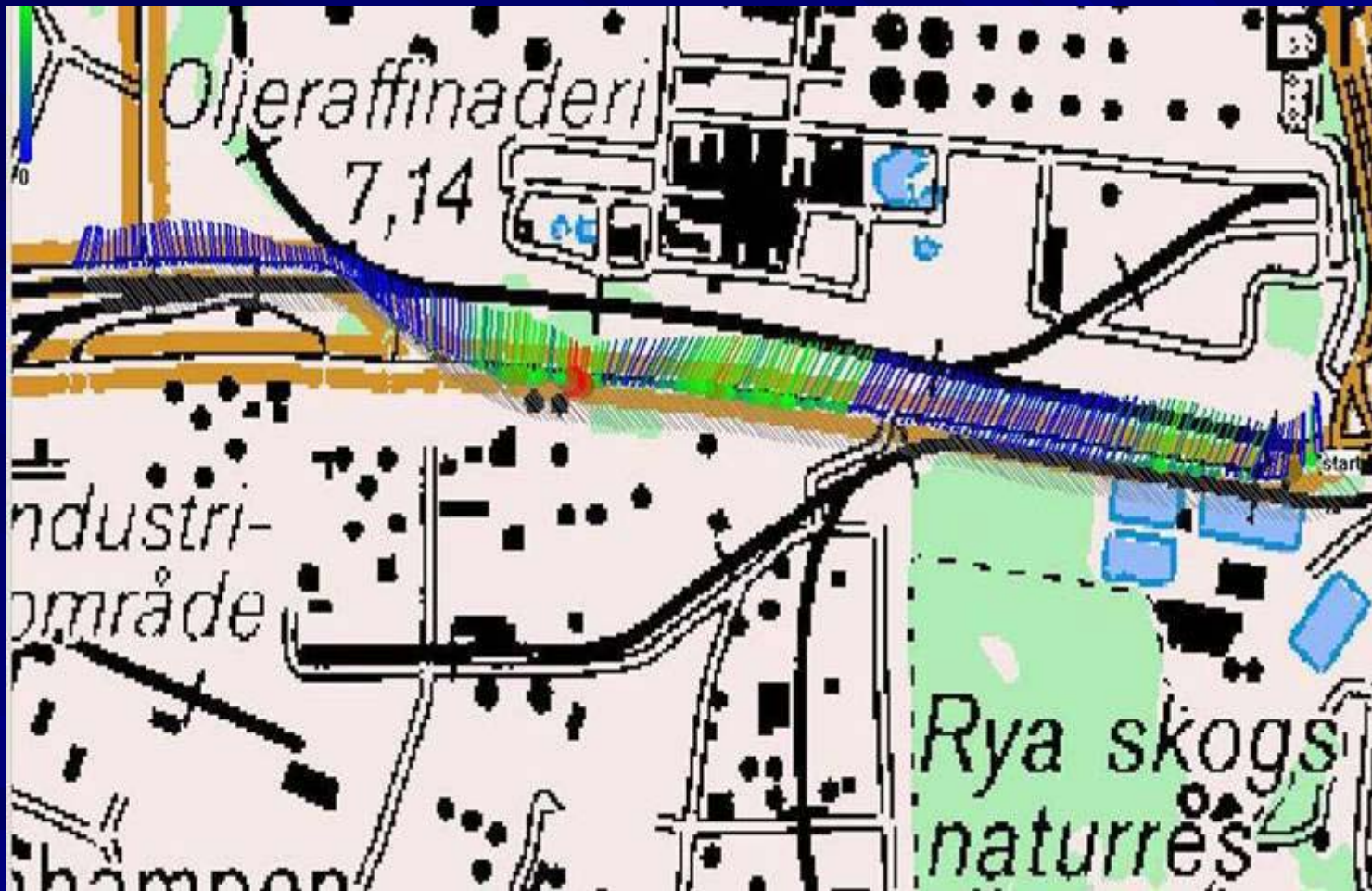
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2004/040907 excel.txt

IRCube, 10/15/2004

Refinery measurement



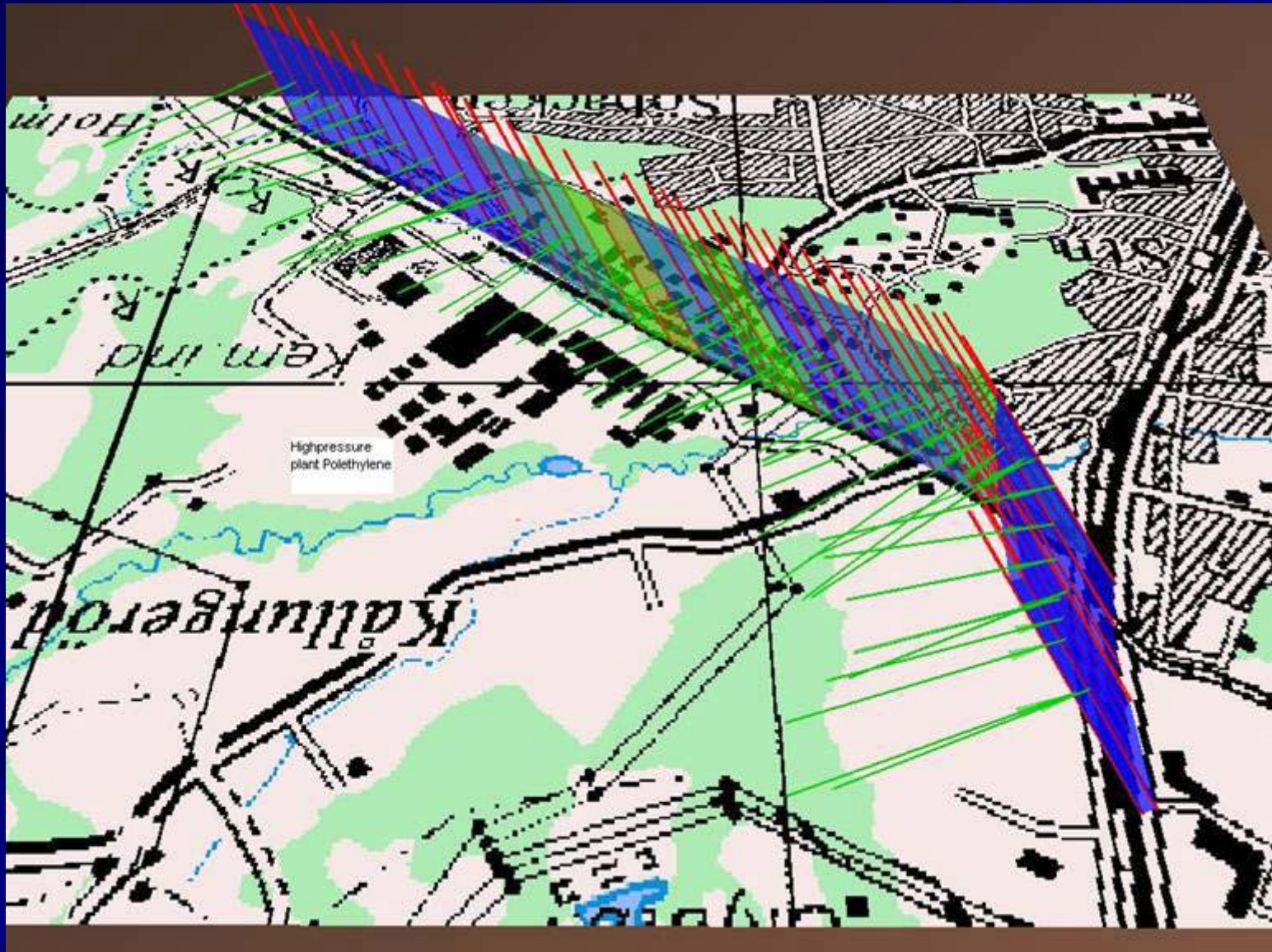
Leakage search, in Göteborg oilharbor

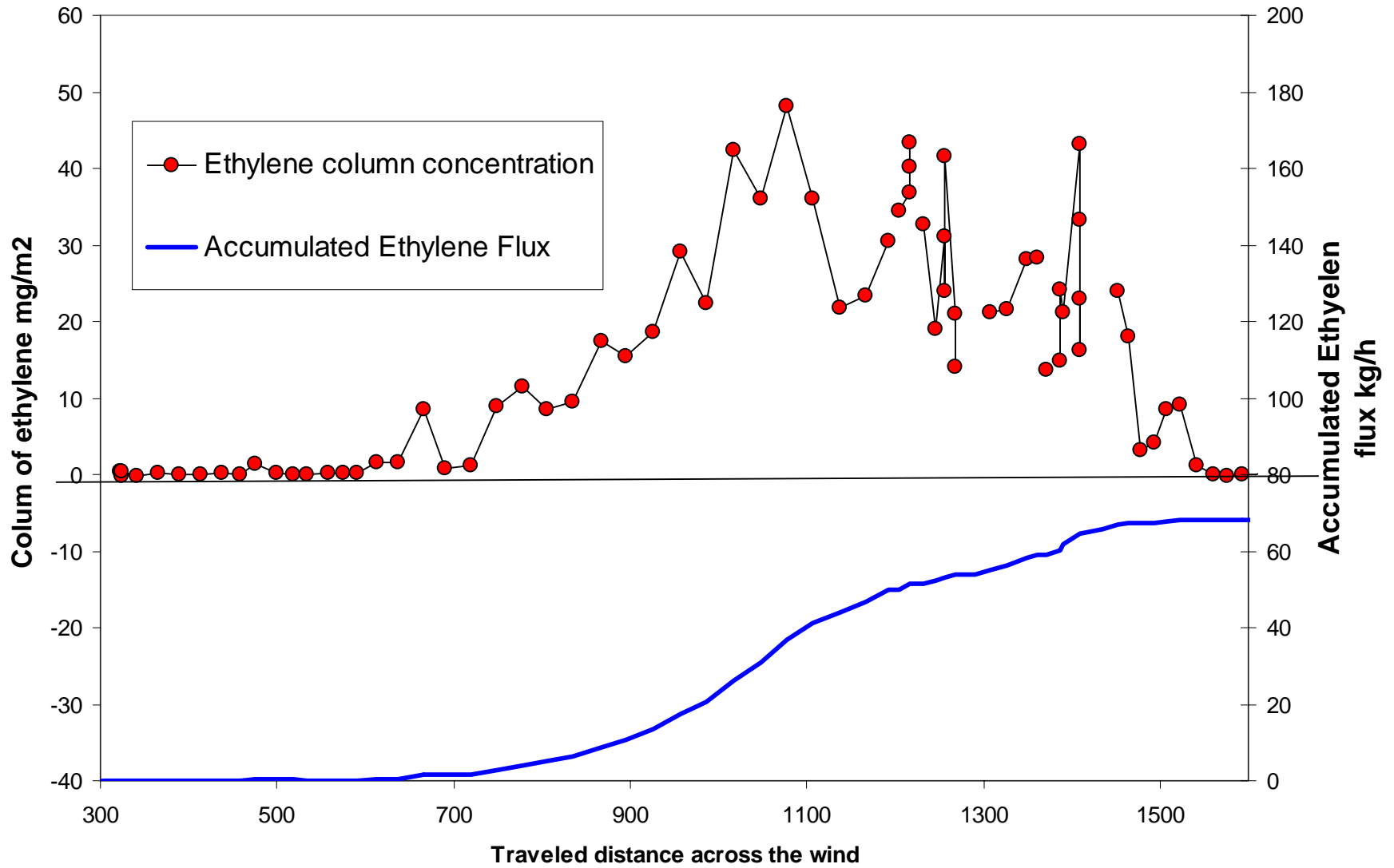


Typical emissions measured at Swedish refinery

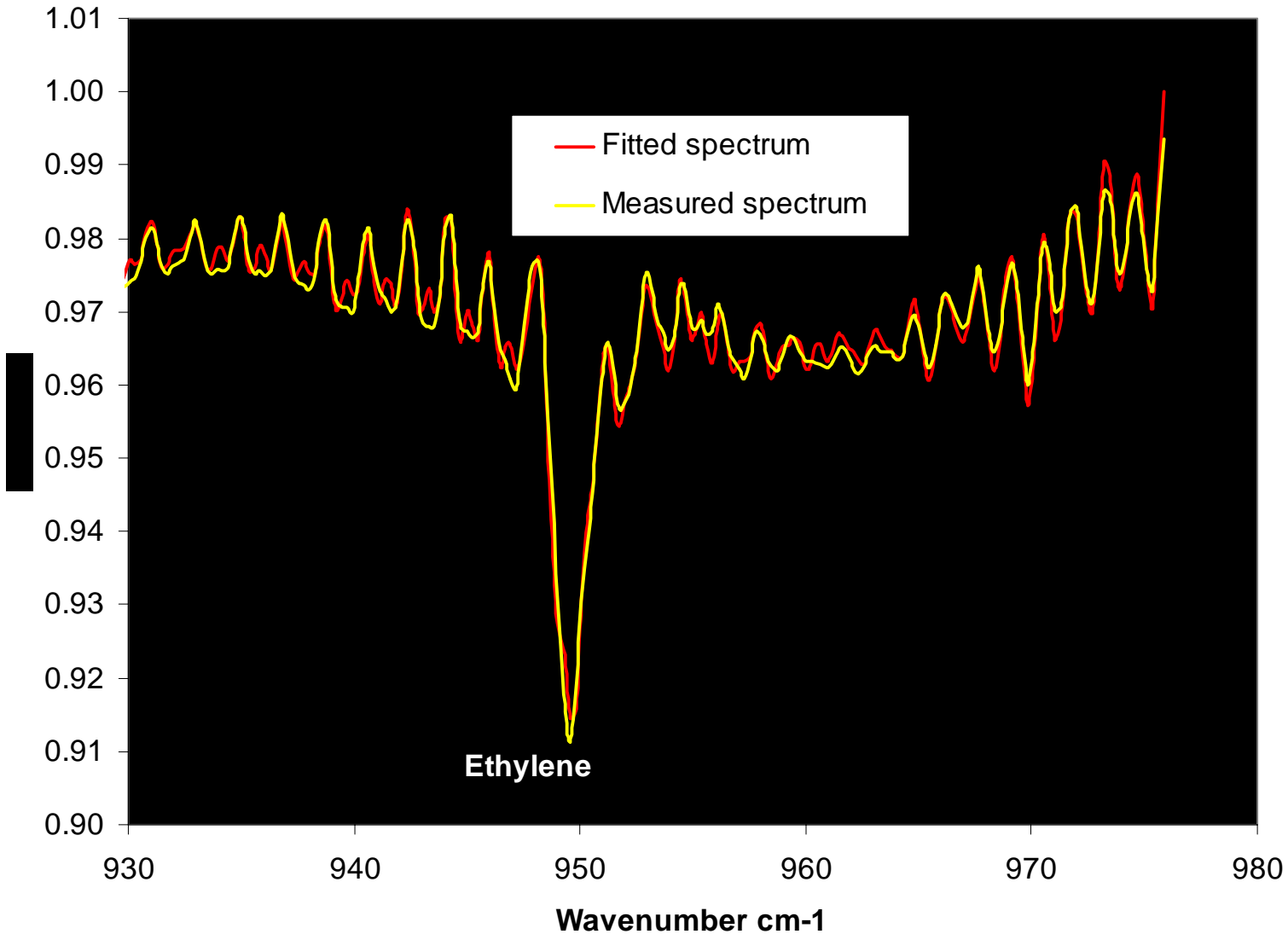
Source	Emission	Fraction
<u>Process</u>	54.3 kg/h	17.1%
<u>Crude Oil Tankpark</u>	73.5 kg/h	23.1%
<u>Black Components Tankpark</u>	96.9 kg/h	30.5%
<u>White Components Tankpark</u>	26.6 kg/h	8.4%
<u>Gasoline Components Tankpark</u>	12.7 kg/h	4.0%
<u>Water Treatment</u>	14.4 kg/h	4.5%
<u>Preskimmer</u>	8.4 kg/h	2.7%
<u>Cave Vent</u>	31.3 kg/h	9.8%
Sum of parts:	318.0 kg/h	100%

Ethylene measurement

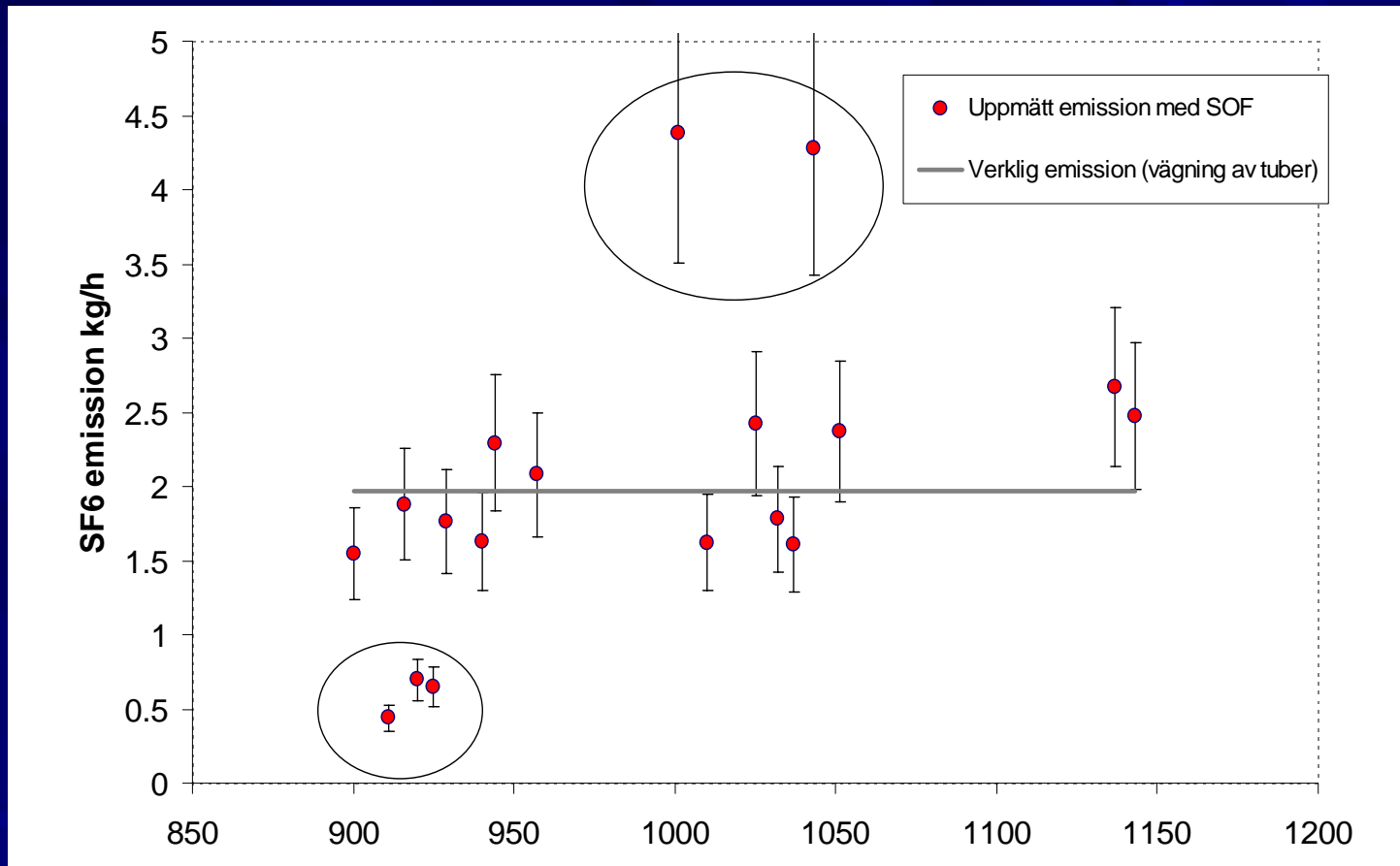




Ethylene spectrum and fit



How uncertain are the measurements?

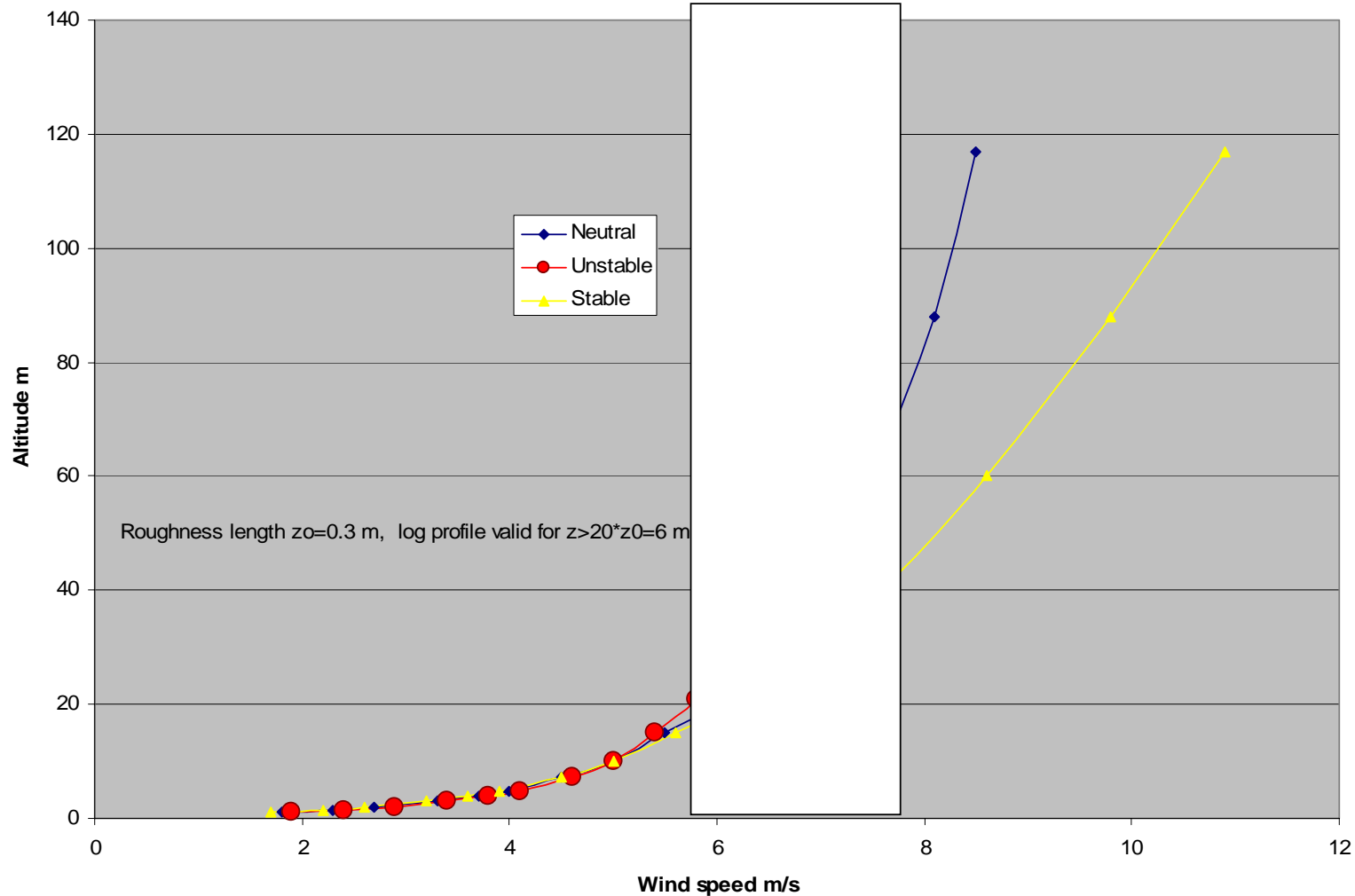


For simple sources and several traverses, the accuracy is better than 10%. For a single measurement worse than 20%.

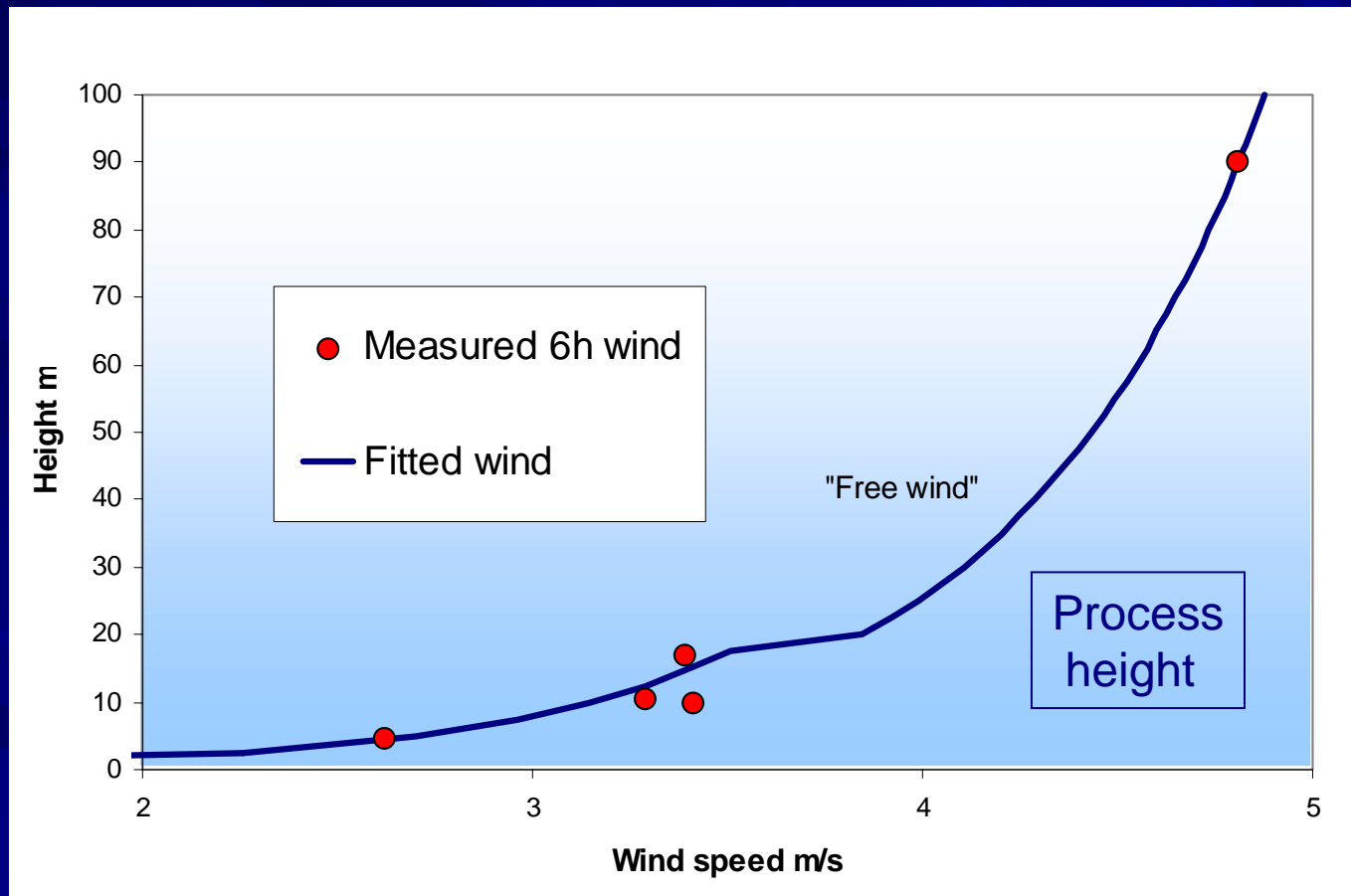
In the SOF measurement we can not distinguish at what height the plume is at.

Which systematic uncertainty may this cause if the wrong windspeed is used ?

Typical wind speed variation with height. Very small for unstable (convective) conditions



Measurement in Göteborg shows that the wind varies within 30% between 20 m and 90 m.



How well do the SOF method correspond to other methods?

Measurement on the Preem refinery with SOF and DIAL

Area	SOF (no of scans) 2001	DIAL 1999	DIAL 1995
Crude oil tanks	56 ±16	56 (wind normalised 4 m/s)	62 (wind normalised 4 m/s)
Process plant E	54 ±19	52	56
Process plant W	20 ±5	35	7.5
Water treatment	19 ±3	25	11

Validation experiment

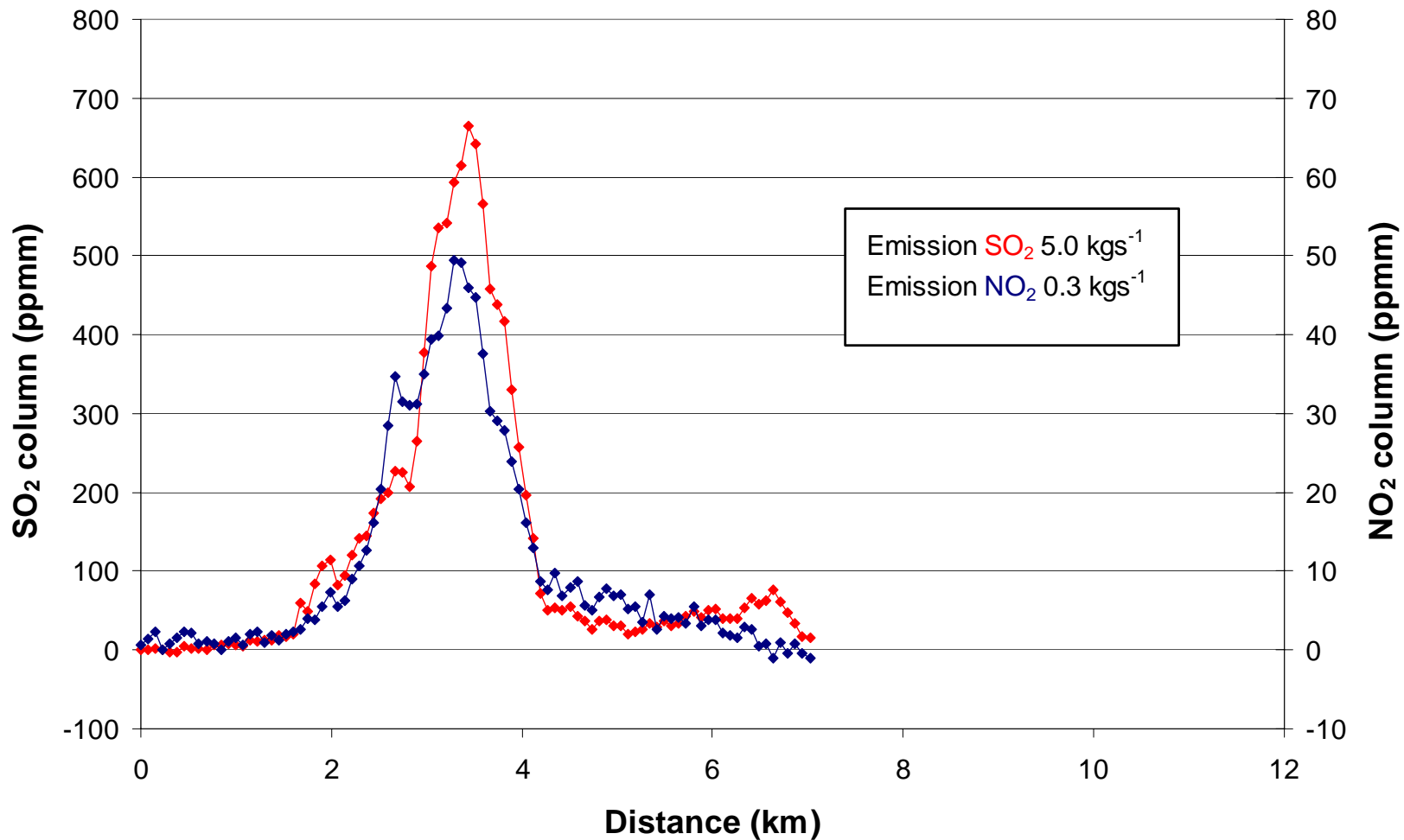
- This summer a rather extensive validation campaign of SOF will be conducted at a bitumen plant in Sweden

UV measurements

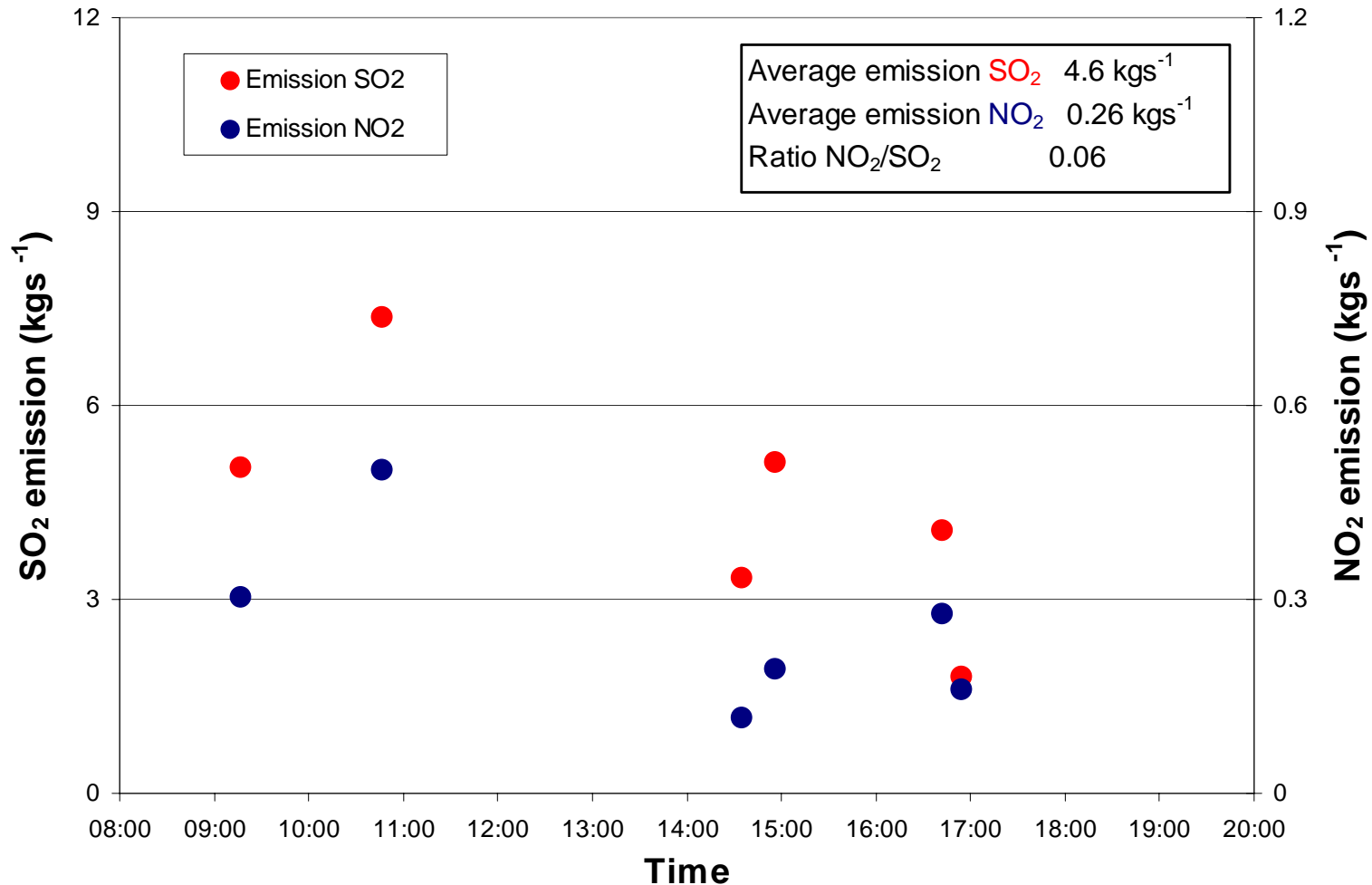
- Zenith sky DOAS for measuring NO₂ and SO₂



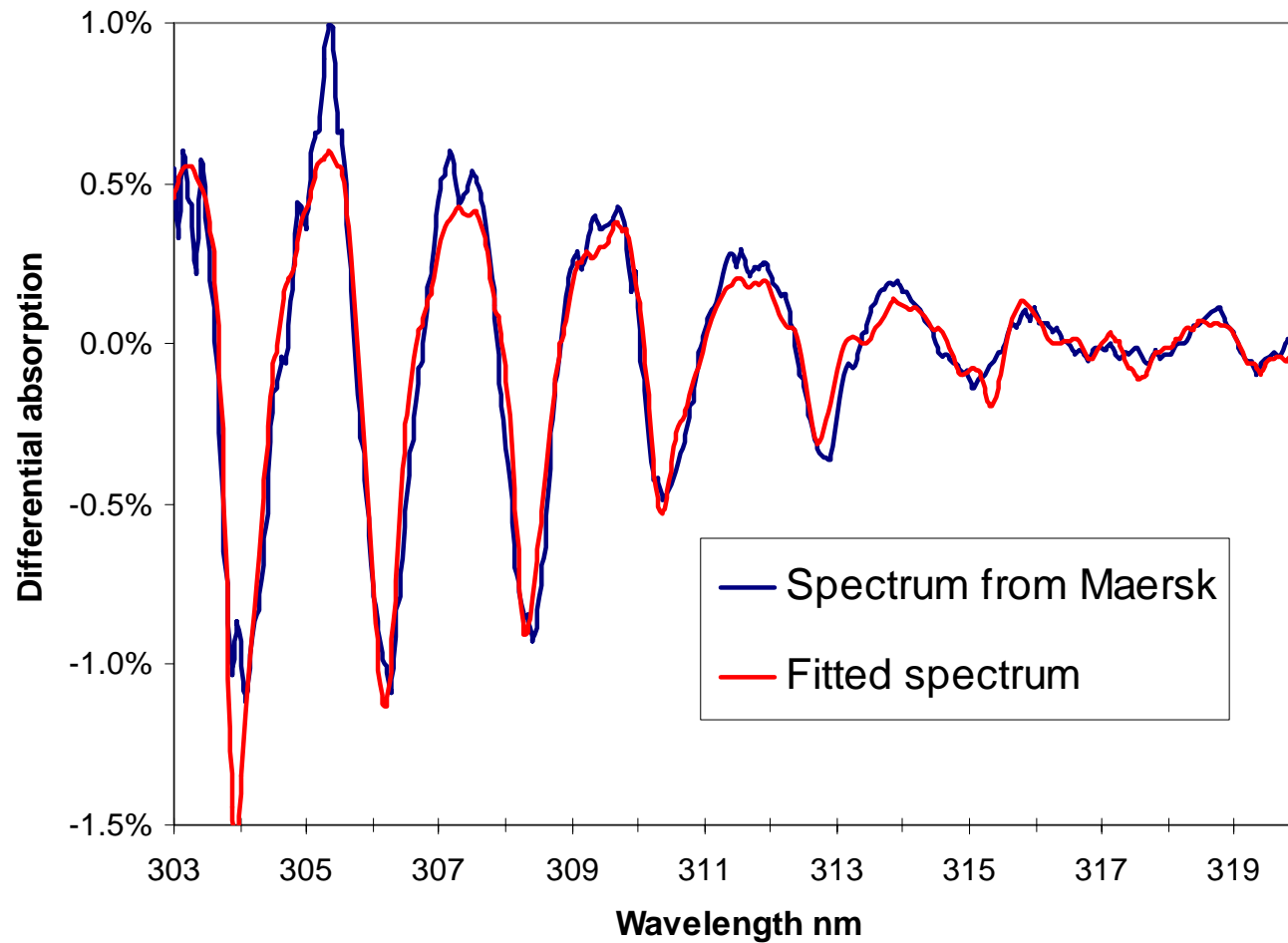
Mobile UV measurements at the Tula refinery and powerplant



Gas emissions measured with zenith sky DOAS, Tula 1 May 2003



Typical SO₂ spectra and fit



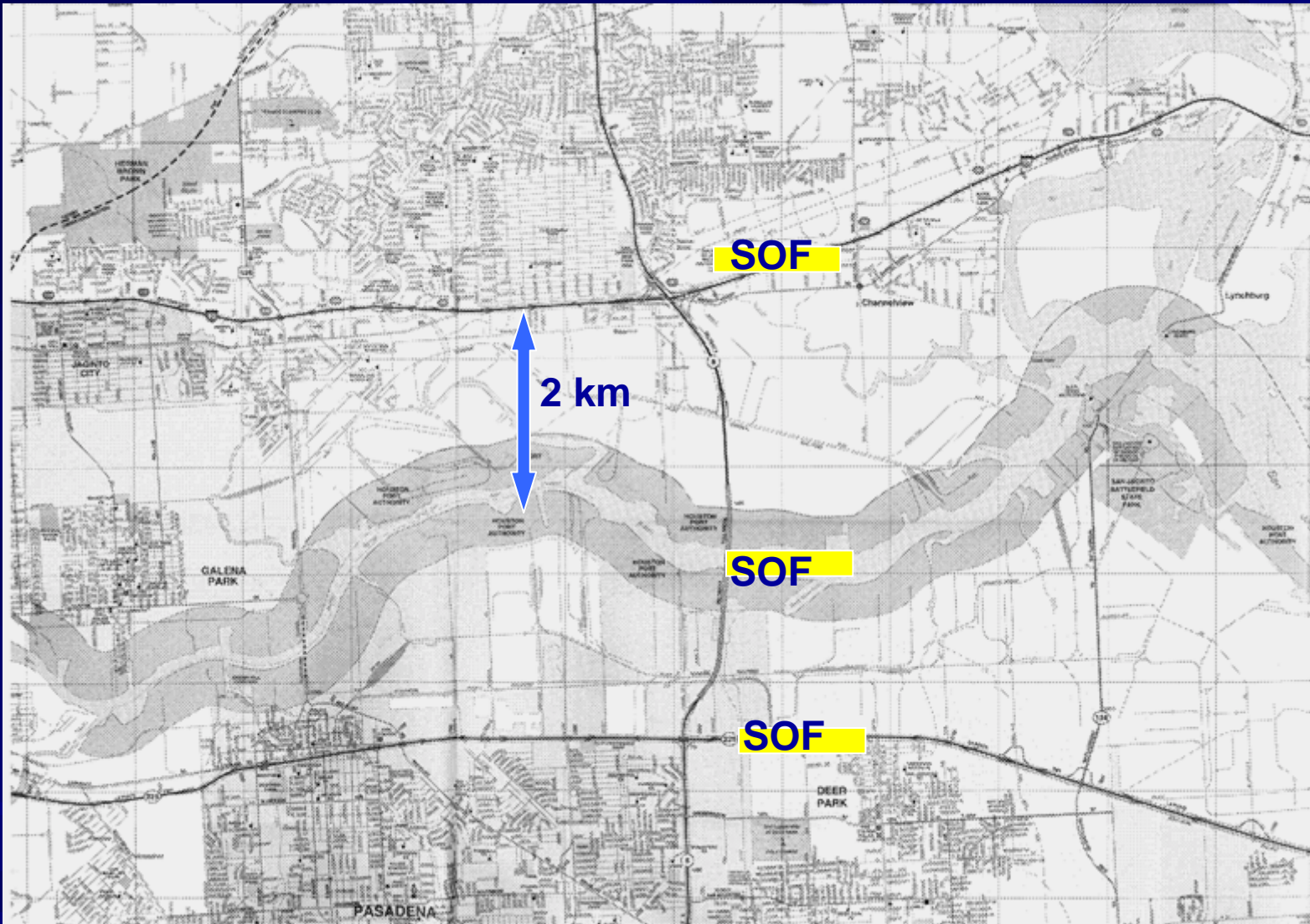
Main Activity during TEXAQII 05

- Many measurements around the shipchannel, at different distances from the sources and different windconditions.
- This will give more representative values and systematic errors

0 1000 2000 3000 4000 5000 Meters

Primary aim TEXAQ 1(3)

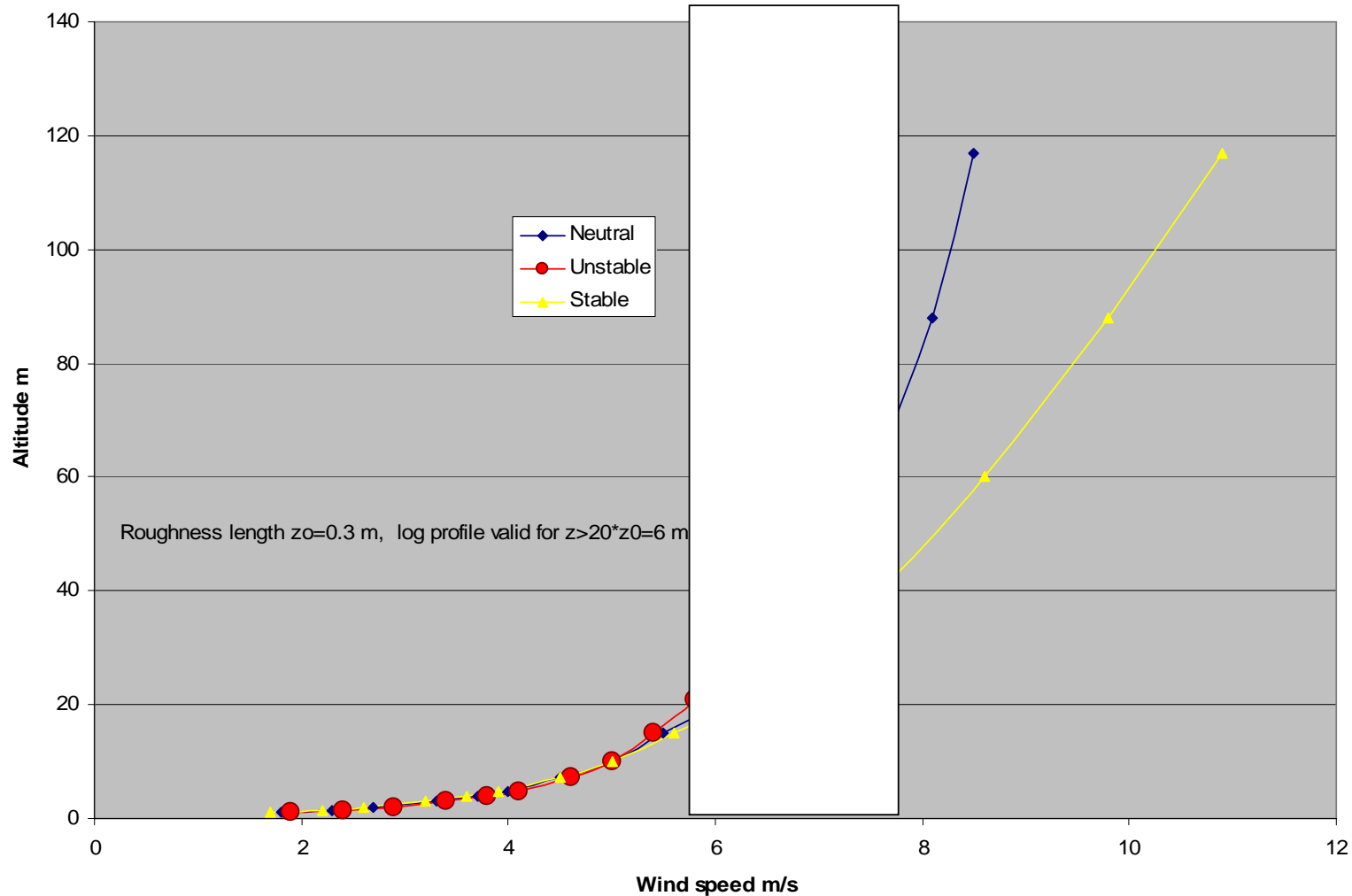
- To estimate the total emissions (tons/day) of VOCs, primarily alkanes and olefines, that are emitted from the Houston Ship Channel, including the Baystown complex). (Also NO₂, SO₂, CO, formaldehyde will be measured.) This will shed some light on the 500% discrepancies reported
- The measurements will be conducted using SOF from a pickup car or a small boat which is moved is such away that the solar light traverses over a cross section of the HSC plume, and the total mass, in the plume will thus be obtained.



Primary aim TEXAQ 2(3)

- In order to convert the SOF measurements to VOC fluxes, the wind profile is needed from for instance wind meters on the bridges, SODAR and balloons.
- For southerly wind the measurements will be done from highway 10, which is a few kilometers northward (2-5km) of the emission sources. For 5 m/s this would correspond to measuring 5-15 minutes downwind the plume
- For a convection rate of 0.5 m/s the plume would raise 200-400 m. Over part of the channel it is possible to get closer by other roads, this will also be tested.

Wind speed variation with height. Very small for unstable (convective) conditions



Primary aim 3(2)

- We will also measure with a small boat in the Houston Ship Channel (are there potential legal problems?).
- For northerly wind the measurements could be done from the ship channel and from highway 225, which is closer to the emission sources.
- Complimentary VOC profile measurements with airborne measurements or with a tethered balloon would improve the SOF measurement uncertainty.
- Possibly, conduct more detailed measurements at a more isolated plant (Sweeney)

Second aim

- To locate the emission sources, down to plant level, and furthermore down to process area level within the industries. Difficult in the HSC area since many roads are private.
- Generic measurements on a typical plant. Is it possible to get site access somewhere ?
- For southerly winds the measurements in the HSC and the highway 10 will give information in which segment of the channel that most emissions emanate from. In other wind directions, easterly or westerly will give even further information

Third aim

- Study the evolution of VOCs, formaldehyde, NO₂ SO₂ and CO in the plume further away, measuring at the same time as the airplanes.
- Study ratios of the species mentioned above

Time plan

- A 4 week campaign will be conducted in the period Sep to Nov 2005 and the choice will depend on the most favorable weather pattern. Fair weather with predominant wind around N or S, but as cold as possible to minimize plume lift and convection. This has to be investigated.
- This will be done with a smaller SOF equipment
- We are very keen on participating also 2006 during the large campaign (financing?)

Needs

- Meteorological measurements/model
 - Windprofile
 - Stability, vertical wind
- Local host
 - assistance with logistics, such as car, ship rental,
 - Legal aspects (permits), road, ship channel
 - Reciever of equipment
 - Lab facility/garage
- HSC site knowledge (which industries are there, what are they emitting ?)
- Typical Concentration profile measurements.