

Investigation of VOC radical sources in the Houston ship channel by the Solar Occultation Flux (SOF) method and mobile/scanning DOAS

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- This project is a continuation of a previous HARC project (H53):

Mellqvist, J, Samuelsson, J., Rivera, C. Lefer, B. and M. Patel, Measurements of industrial emissions of VOCs, NH₃, NO₂ and SO₂ 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>)

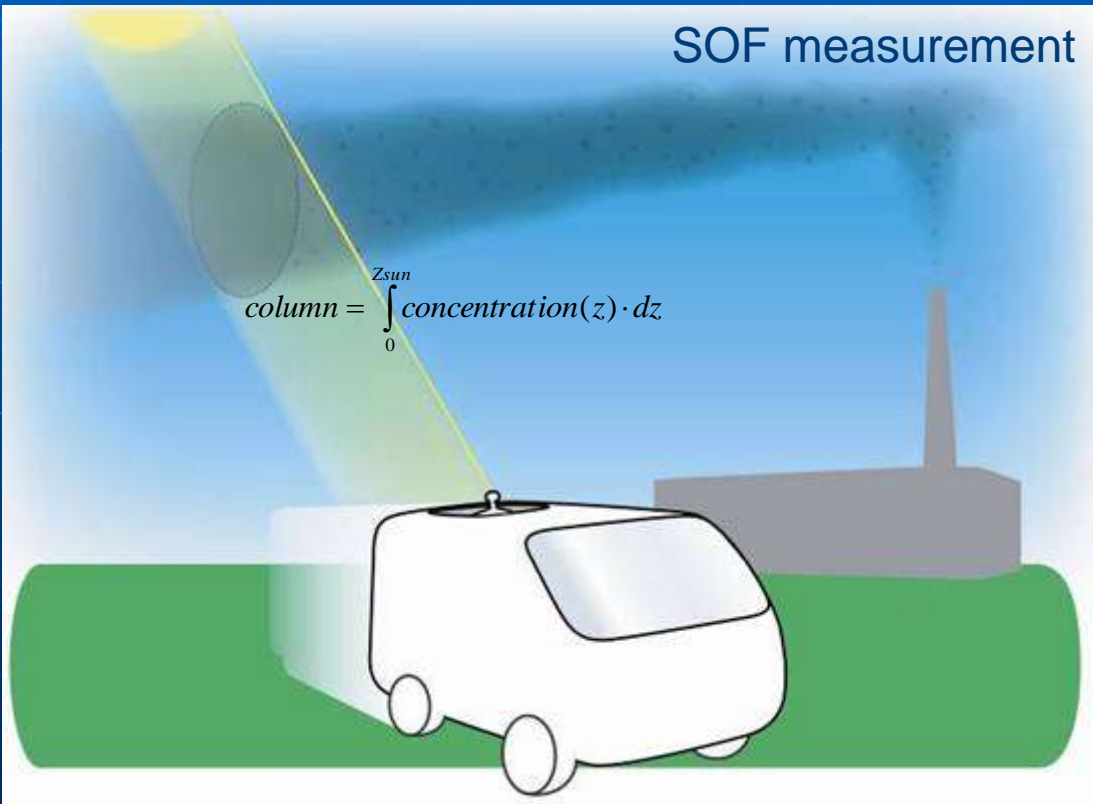
Technique

The Solar Occultation Flux method (SOF): mobile direct infrared solar measurements for retrieval of VOC's, CO and NH₃

DOAS: mobile and scanning UV/visible measurements of scattered solar light for retrieval of HCHO, NO₂ and SO₂

SOF measurement

$$column = \int_0^{z_{sun}} concentration(z) \cdot dz$$



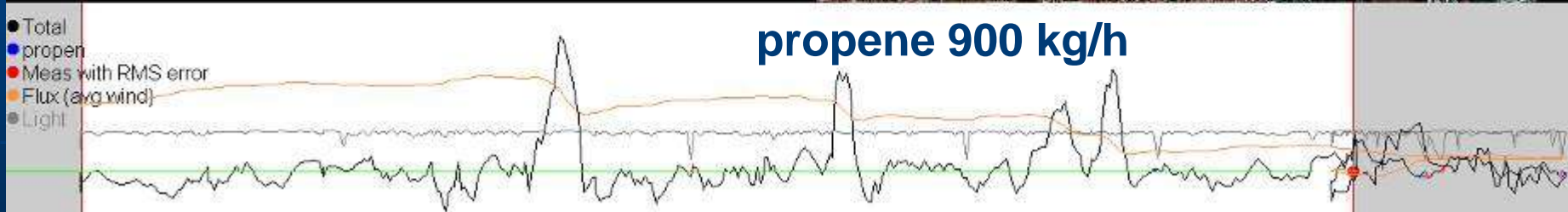
$$flux = F \cdot u'_{average} \int_{x1}^{x2} column(x) dx$$

u' =mass averaged wind

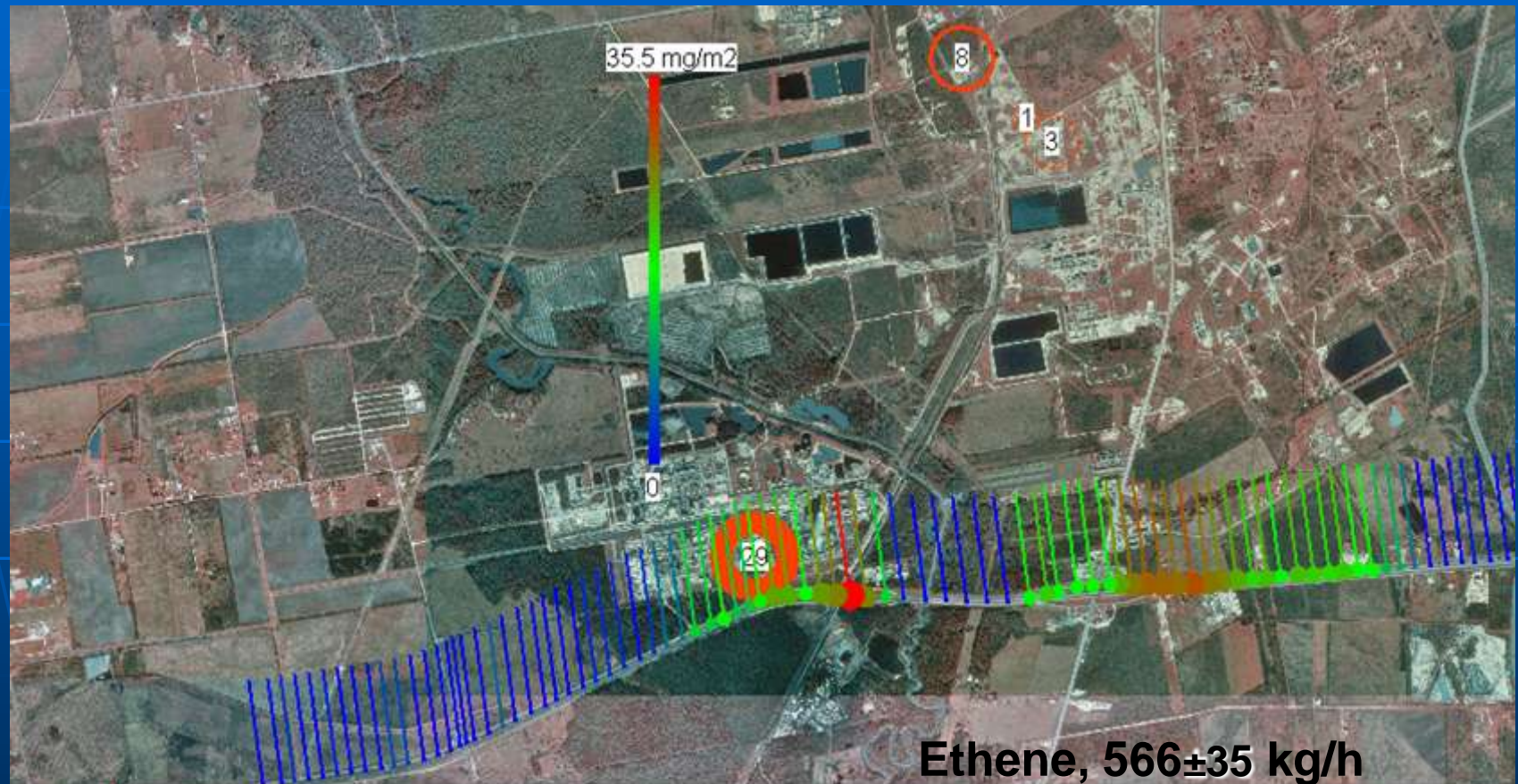


HSC Sep 25, propene,

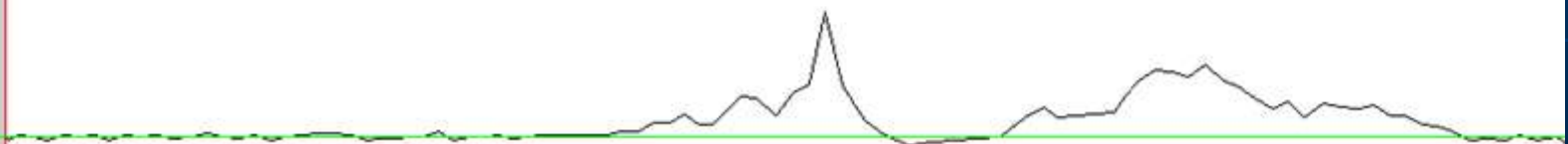
Here the colorcode corresponds to the mass of propene measured in the solar light. The lines point towards the wind



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). The measurement correspond to 566 kg/h, compared to the inventory yielding 44 kg/h.



● Total
● Meas with RMS error



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.Belvieu	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

Summary of H53 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 NH₃ and about 5 tons of SO₂ and NO₂ each.
- For the VOCs this corresponds to 5-50 times greater emissions than reported in the 2004 TCEQ inventory. For NO₂ and SO₂ 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 larger variability than alkanes with some cases of extreme short term variability, 100-2000 kg/h possibly due to flaring or other upset emissions

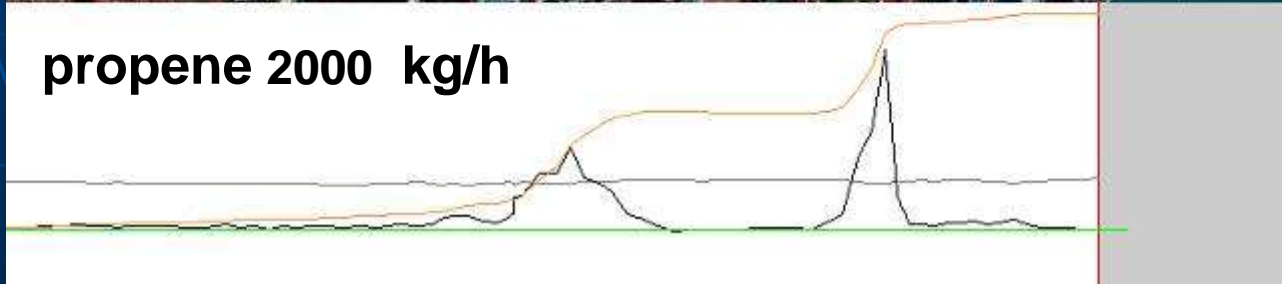
Aim and scope of new study 1(2)

- The H53 study was aimed at getting an overview of the VOC emissions at several sites. In this new study we will zoom in on the highest olefin emitters and study the variability of the emissions and try to understand from where the emissions originates.
- A comparison will be conducted with the latest TCEQ inventory.
- We suspect that part of the variability of the olefins emitted from the chemical plants may be caused by inefficient flaring. To investigate this, VOCs will be measured together with CO and NO₂ to investigate whether high olefins are associated with combustion.
- Formaldehyde measurements will be conducted to investigate primary emissions using a new DOAS system, that will be modified to work both in scanning and mobile mode. Complimentary SOF measurements of formaldehyde will be done as well, but with lower sensitivity

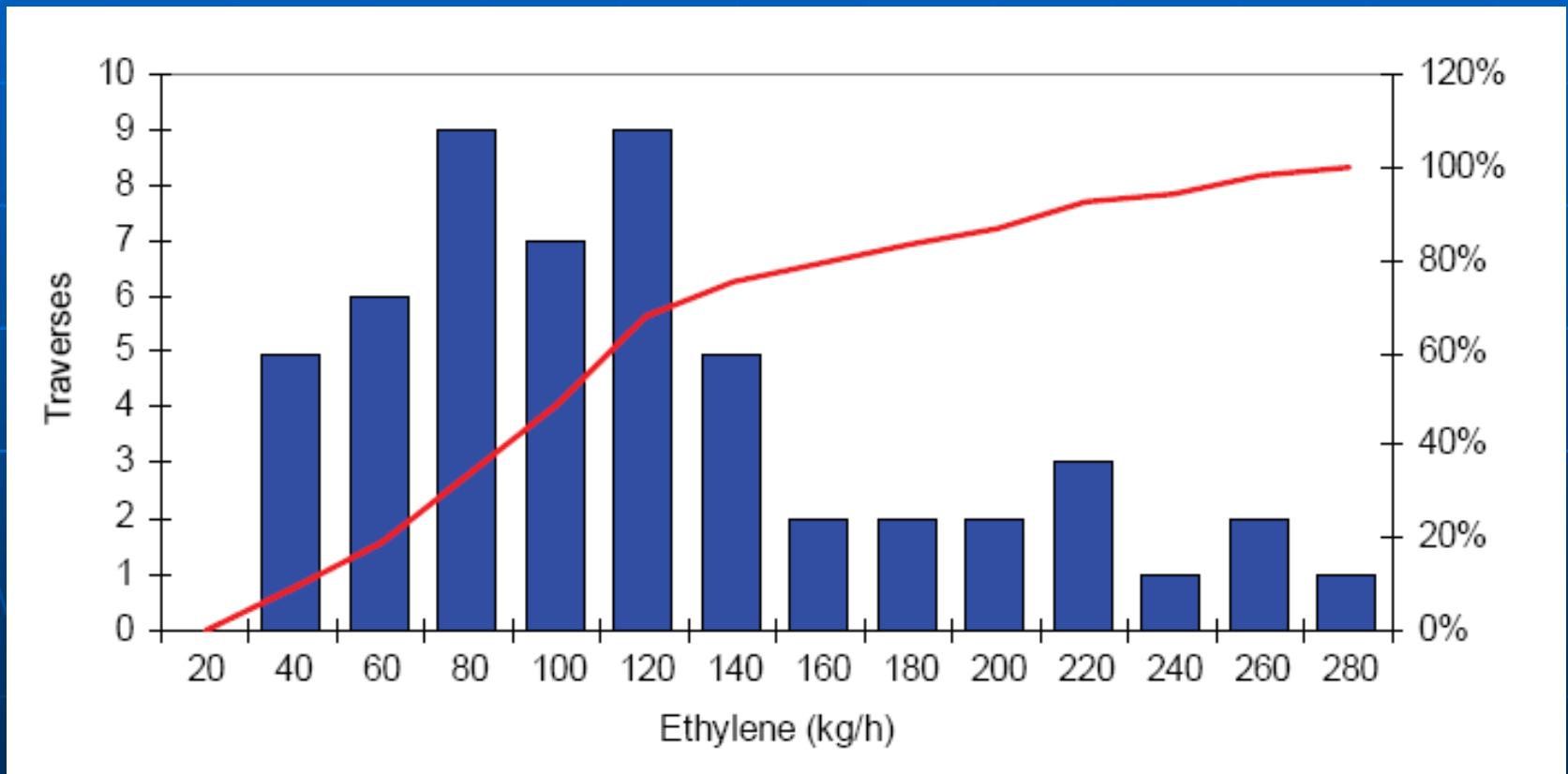
N-S Transect on Battleground road Aug 31.
On Aug 31 & Sep 14 the measurements vary between 200-2000 kg/h) (upsets, flares?)



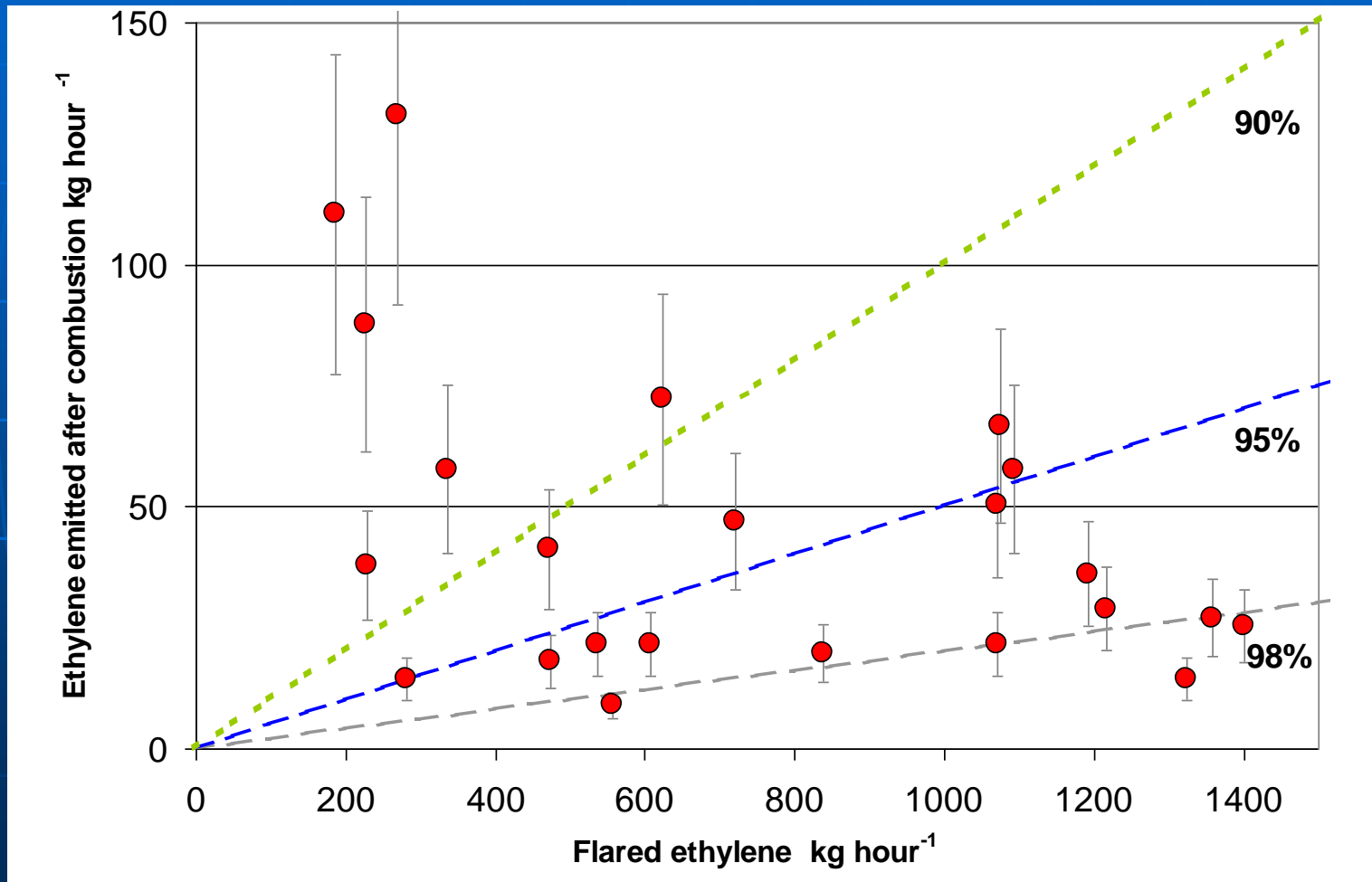
propene 2000 kg/h



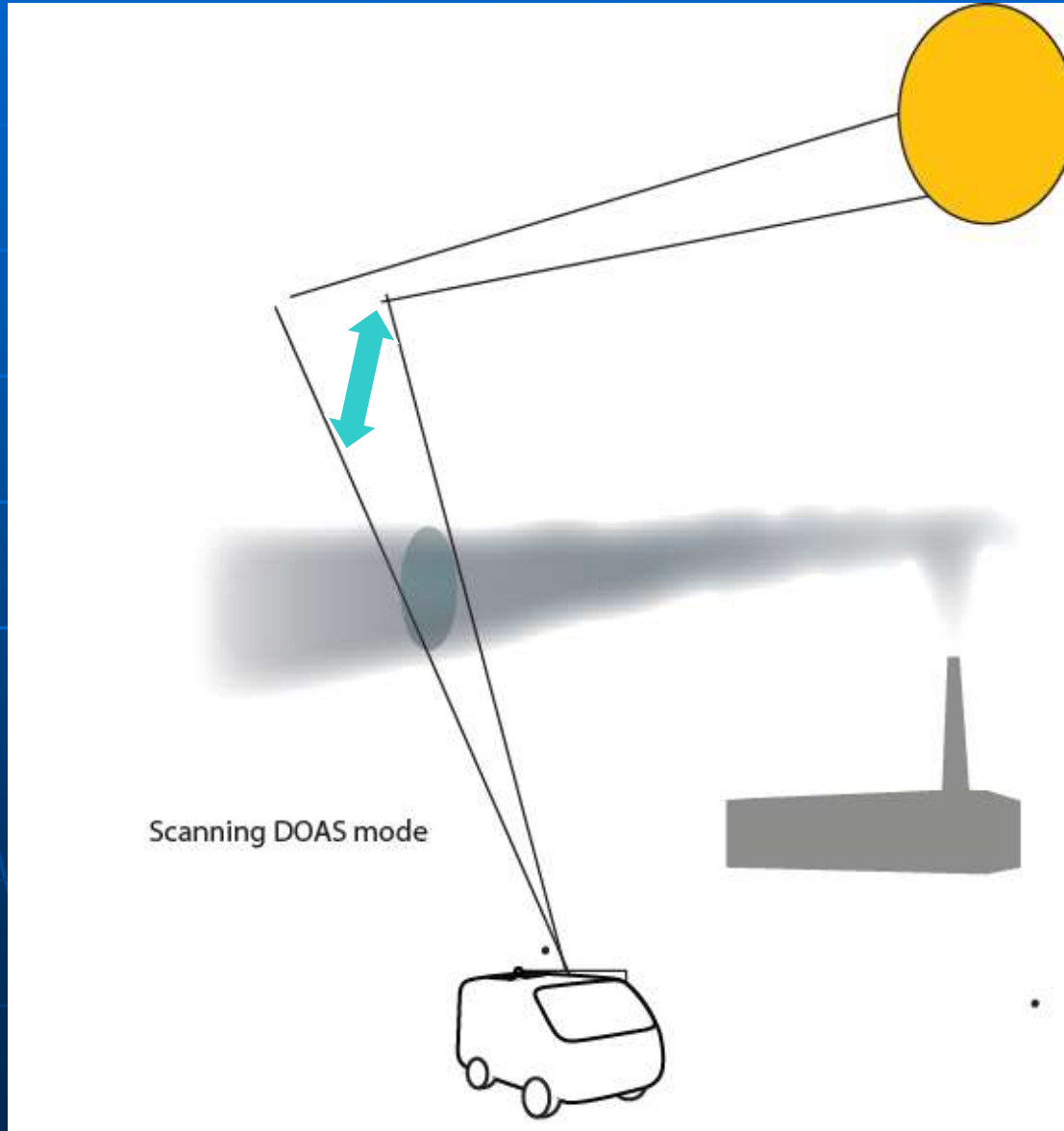
Distribution of total facility ethene emission from an olefine plant in Sweden. The skew distribution is due to variability in flaring



Ethylene emission versus flared amount measured by SOF, from a Swedish olefine plant



Scanning DOAS mode, a telescope views in different directions while standing still



Aim and scope 2(2)

- In parallel with the SOF measurements canister sampling on the ground (or airplane if available) will be conducted by university of Houston to investigate the gas matrix.
- UH will conduct wind measurements using gps sounders, anemometers and possibly SODAR
- During part of the measurements a FLIR camera may be used.

Organisation

- Chalmers University of Technology
 - PI: Johan Mellqvist, Role: SOF measurements of olefins/formaldehyde/CO UV/visible measurements of formaldehyde, NO₂ and SO₂, both in scanning stationary mode and mobile mode.
- University of Houston
 - PI: Bernhard Rappengluck, Role: Wind measurements, using wind profilers, SODAR and windmeter. Canister sampling (20-50 samples) in certain relevant plumes. Logistical support. Participate in the data interpretation and reporting

Time

- 1 month field campaign in October 2008, or optionally during the spring of 2009, preferably with other research activities. Dry and fair weather is preferred.