Solar Occultation Flux (SOF) Measurements during TexAQS II

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Activities

Direct emission measurements of olefines, alkanes, NH3, NO_2 and SO_2 have been conducted to pin-point and quantify the largest emission sources in the vicinity of Houston during TexAQS 2006

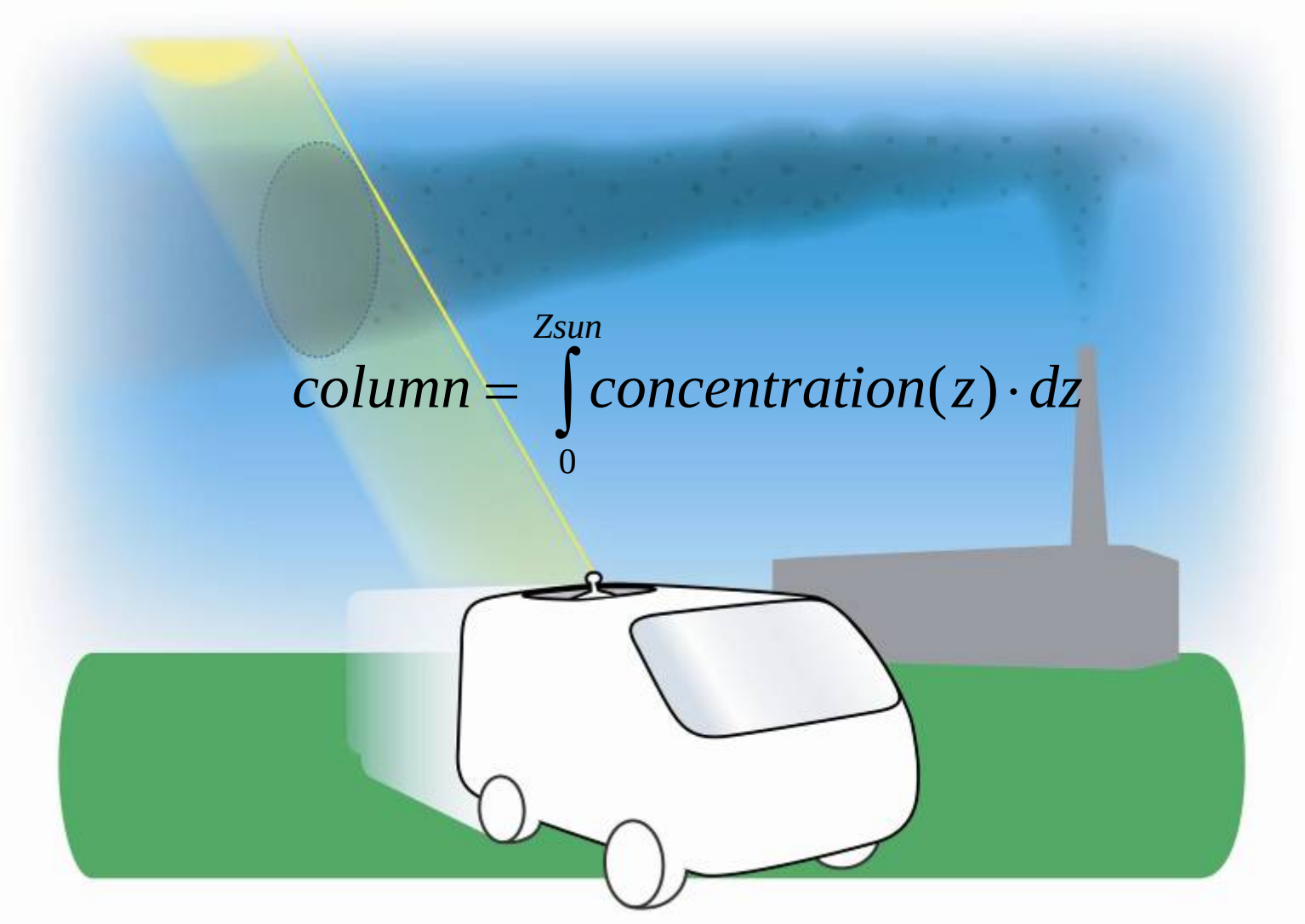
Posters

- *Johan Mellqvist al.,* Measurements of industrial emissions of HRVOCs in Texas using the SOF method
- *Claudia Rivera, et al.,* Measurements of industrial emissions of NO2 and SO2 in Texas using mobile DOAS
- Jerker Samuelsson et al., Measurements of industrial emissions of alkanes in Houston and southeastern Texas using the Solar Occultation Flux method

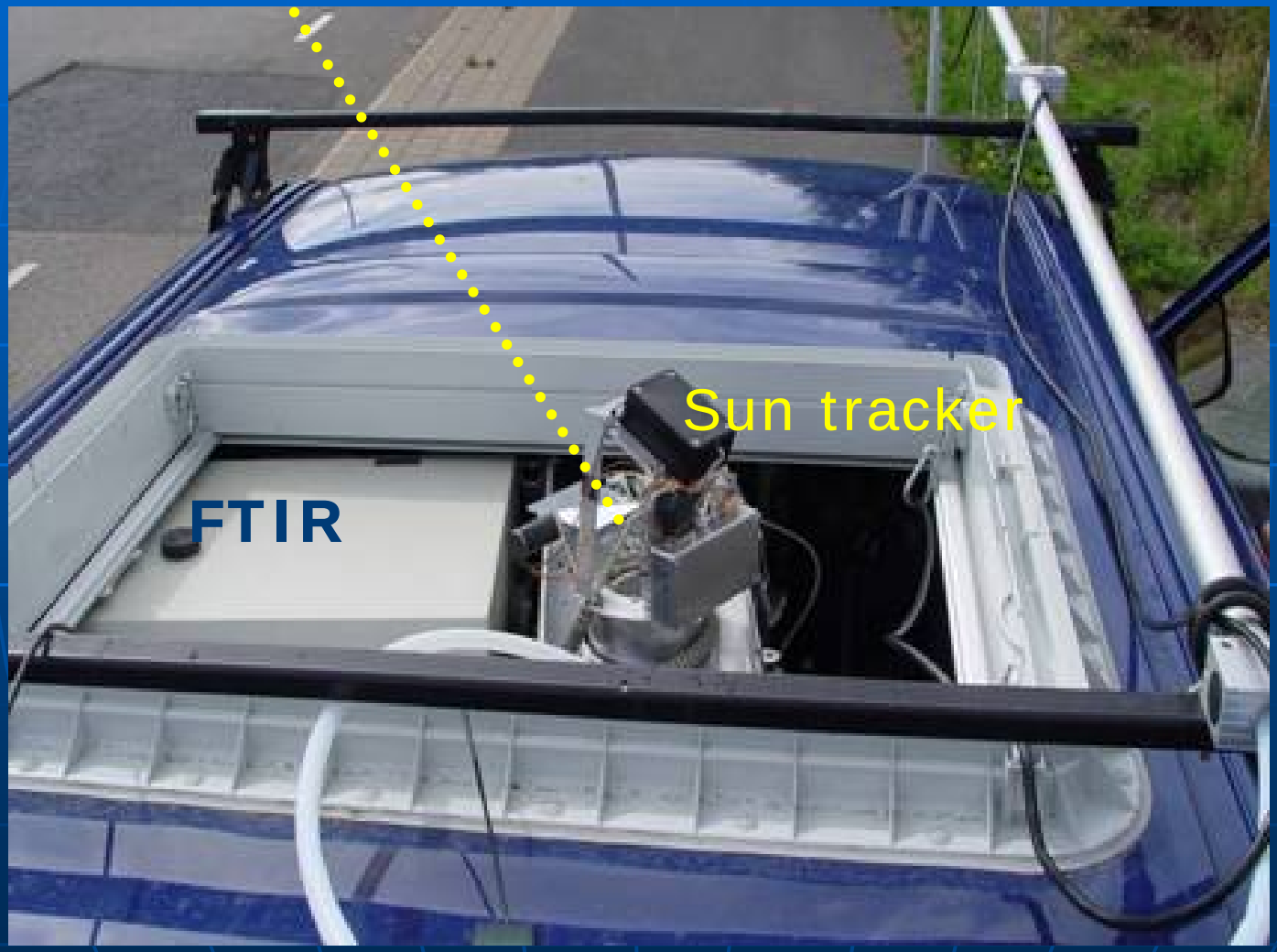
Method

Solar Occultation Flux

Direct infrared solar measurements for retrieval of VOCs, ammonia etc.

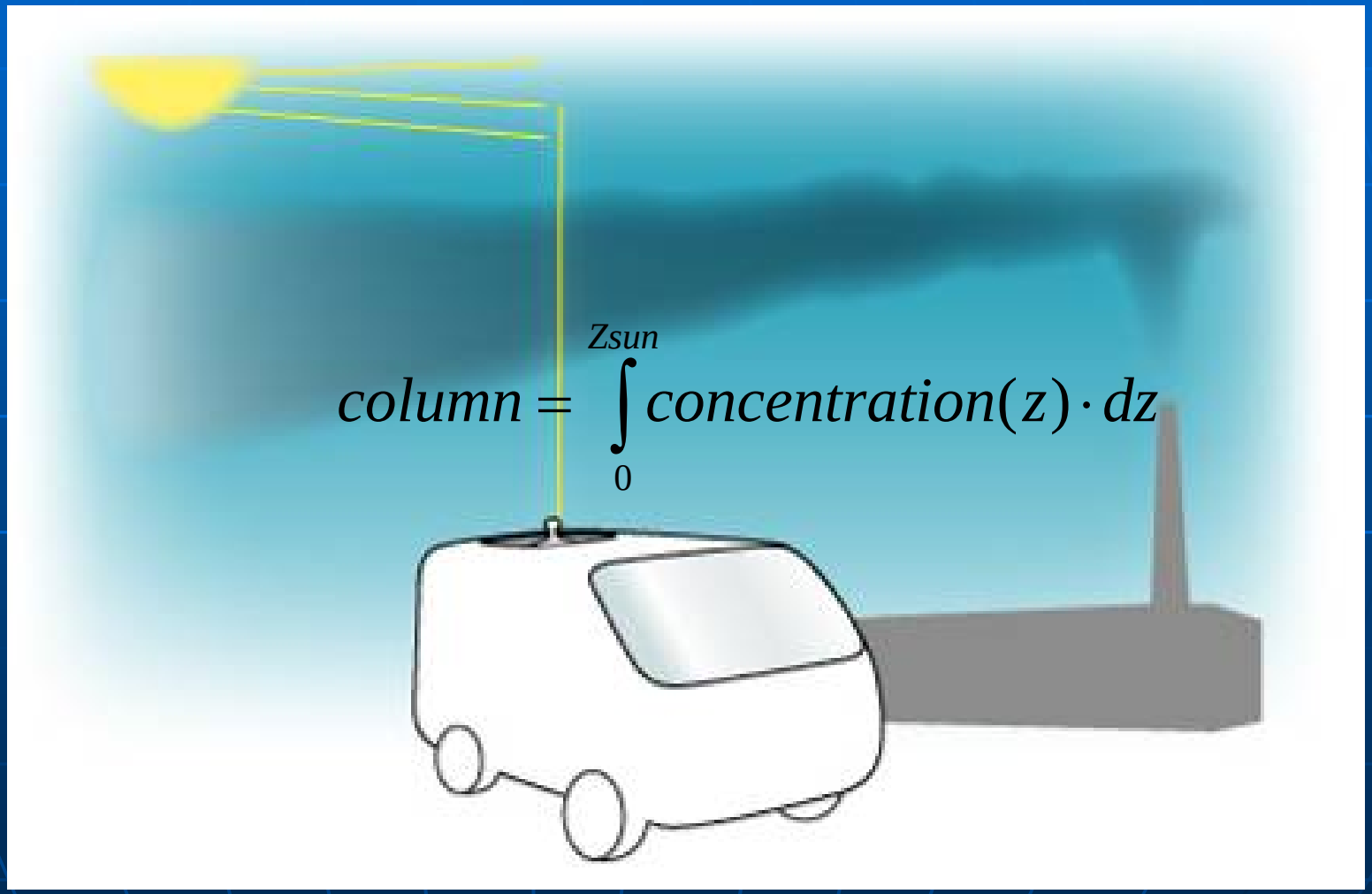


SOF



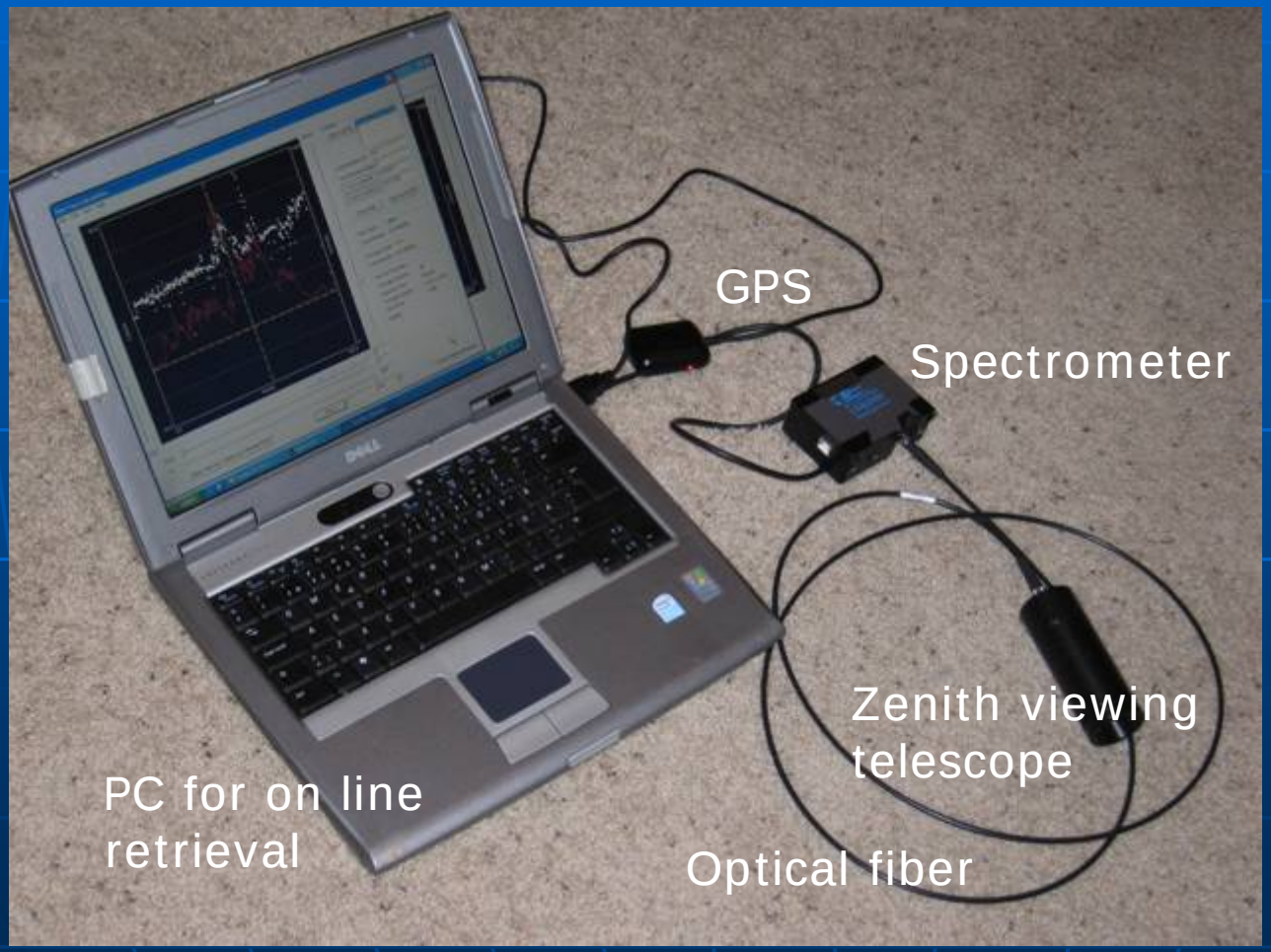
Mobile DOAS,

Scattered UV/visible solar light for NO2 and SO2



Mobile DOAS,

Scattered UV/visible solar light for NO2 and SO2. Developed for volcanic measurements



SOF Column Retrieval

- The retrieval is based on multivariate analysis in which calibration spectra recorded in the laboratory are fitted to the measured spectra

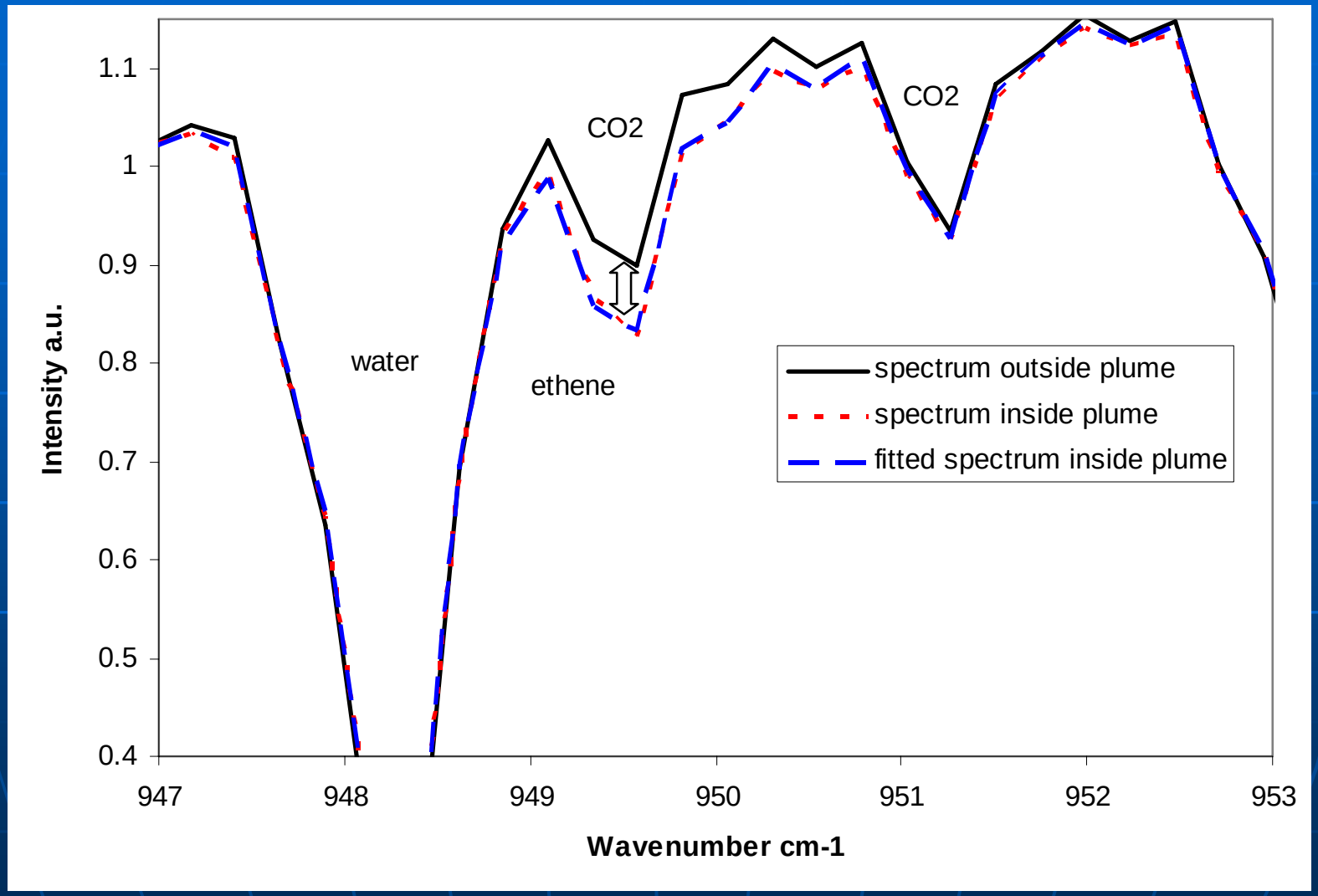
$$\ln\left[I_{fit}(v)\right] = \ln\left[I_{backgr}(v)\right] - \sum_i \sigma_i(v) \cdot \int conc_i(x) \cdot dx$$

- The code QESOF is used. It has been tested against other established codes, < 5% differences
- Calibration data are taken from reference libraries (HITRAN and PNL), ~3% uncertainty
- The measurents of alkenes and ammonia at 10µm are more specific than for alkanes at 3µm (see next slides)

Mobile DOAS Column Retrieval

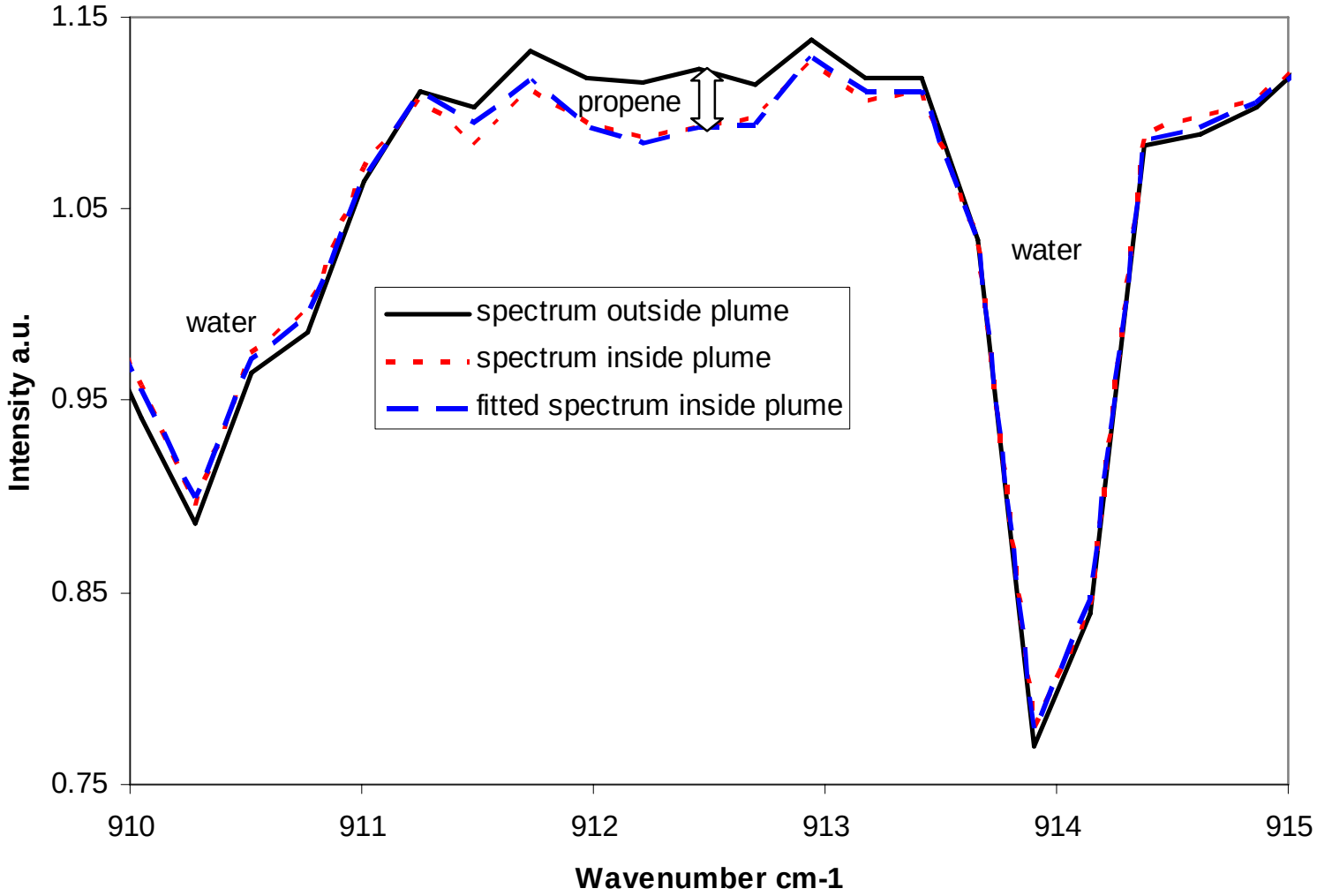
- The UV/visible spectra are filtered according to standard DOAS algorithms and then fitted to calibration spectra using multivariate analysis
- The retrieval code mobile DOAS is used . It has been tested against other established DOAS codes,
- Calibration data are taken from Vandale [1994]

SOF retrieval, ethene

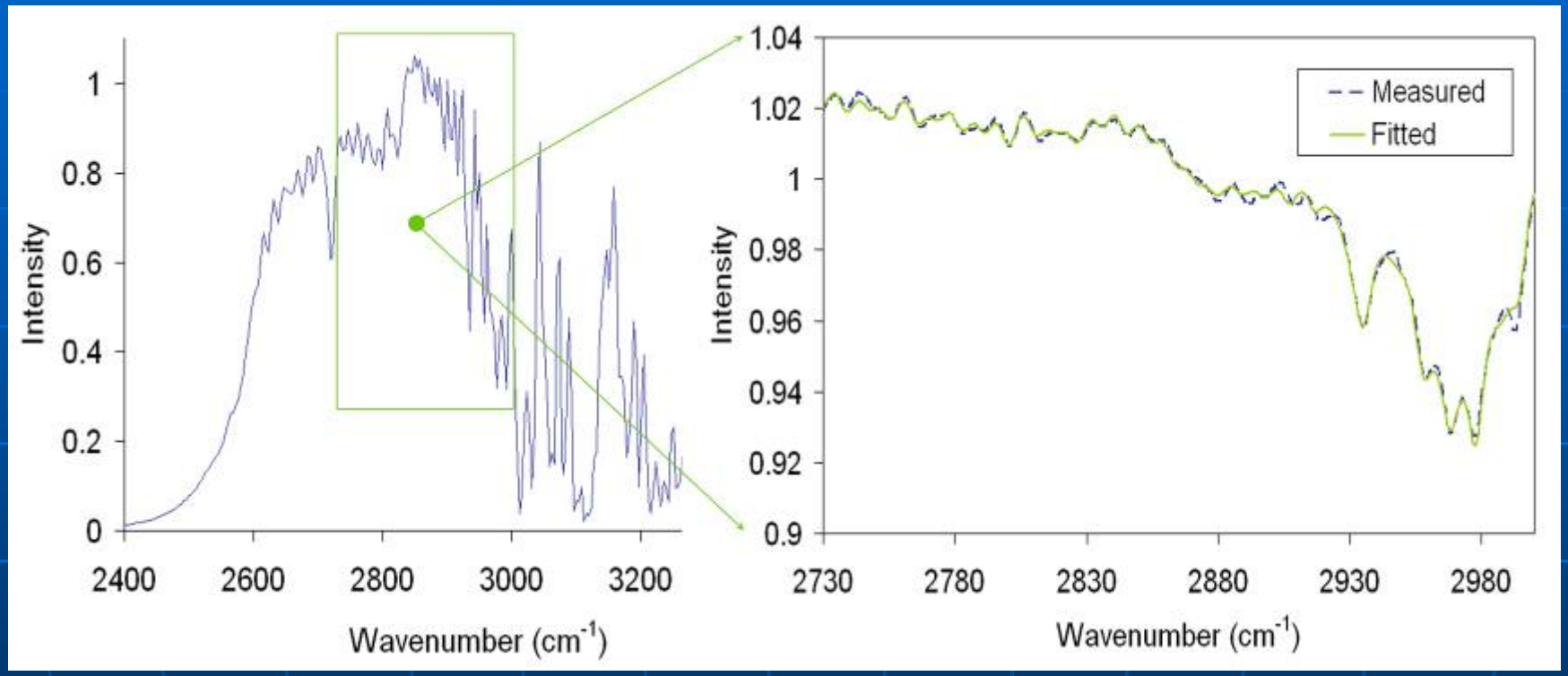


$$\ln\left[I_{fit}(v)\right] = \ln\left[I_{backgr}(v)\right] - \sum_i \sigma_i(v) \cdot \int conc_i(x) \cdot dx$$

SOF retrieval -propene



SOF retrieval - alkanes



The alkane channel is sensitive to various VOC species , but this only causes 5% overestimation

Cross sensitivity of the alkane channel, causes 5% overestimation in HSC

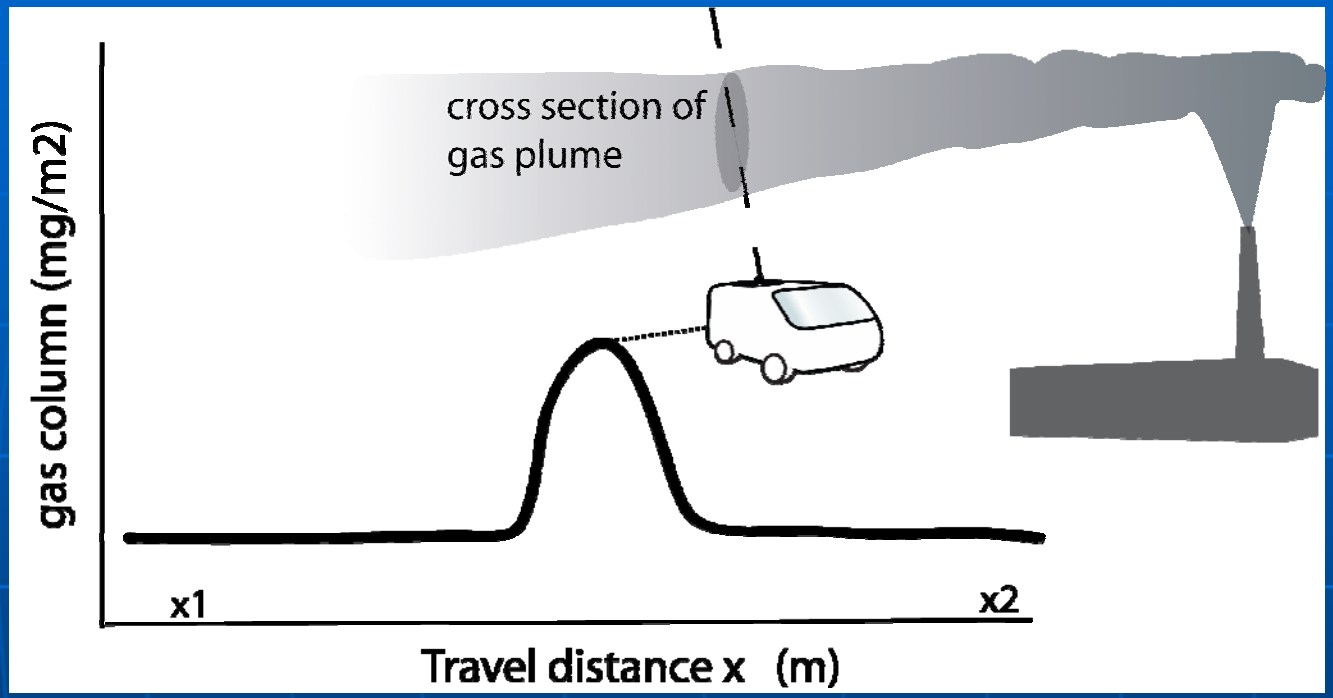
Alkanes	***Cross sensitivity (alkane mass)***	**Alkenes**	***Cross sensitivity (alkane mass)***
ethane	***1.000***	ethylene	***0.078***
propane	***1.000***	propylene	***0.202***
n-butane	***1.000***	acetylene	***0.001***
i-butane	***1.176***	1,3-butadiene	***0.007***
cyclo-pentane	***1.037***	2-butene (c+t)	***0.290***
i-pentane	***1.000***	1-butene	***0.283***
n-pentane	***1.003***	i-butene	***0.305***
2m-pentane	***1.015***	isoprene	***0.100***
3m-pentane	***0.840***	t-2-pentene	***0.464***
cyclo-hexane	***1.239***	1-pentene	***0.330***
2,2-dimethyl-butane	***1.084***	c-2-pentene	***0.316***
n-hexane	***0.984***	styrene	***0.000***
3m-hexane	***0.848***	**Aromatics**	
n-heptane	***0.990***	benzene	***0.000***
n-octane	***1.000***	toluene	***0.064***
i-octane	***1.082***	m-xylene	***0.118***
n-nonane	***1.048***	p-xylene	***0.095***
n-decane	***1.051***	o-xylene	***0.170***
		ethyl-benzene	***0.184***

70-87%

5-15%

5-16%

Flux measurements



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

Where:

$$u'_{average} = \frac{\int_{o}^{Hmix} u' \cdot dz}{\int_{o}^{Hmix} dz}$$

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

The wind

- To obtain the flux the measured mass of the plume ($\int column(x)dx$) is multiplied by the average **wind speed of the plume** (u')
- Hence, to understand the uncertainty in the wind (u') derived from observations one need to know:
  - **the height distribution of the plume**
  - **the height and spatial variation of the wind**

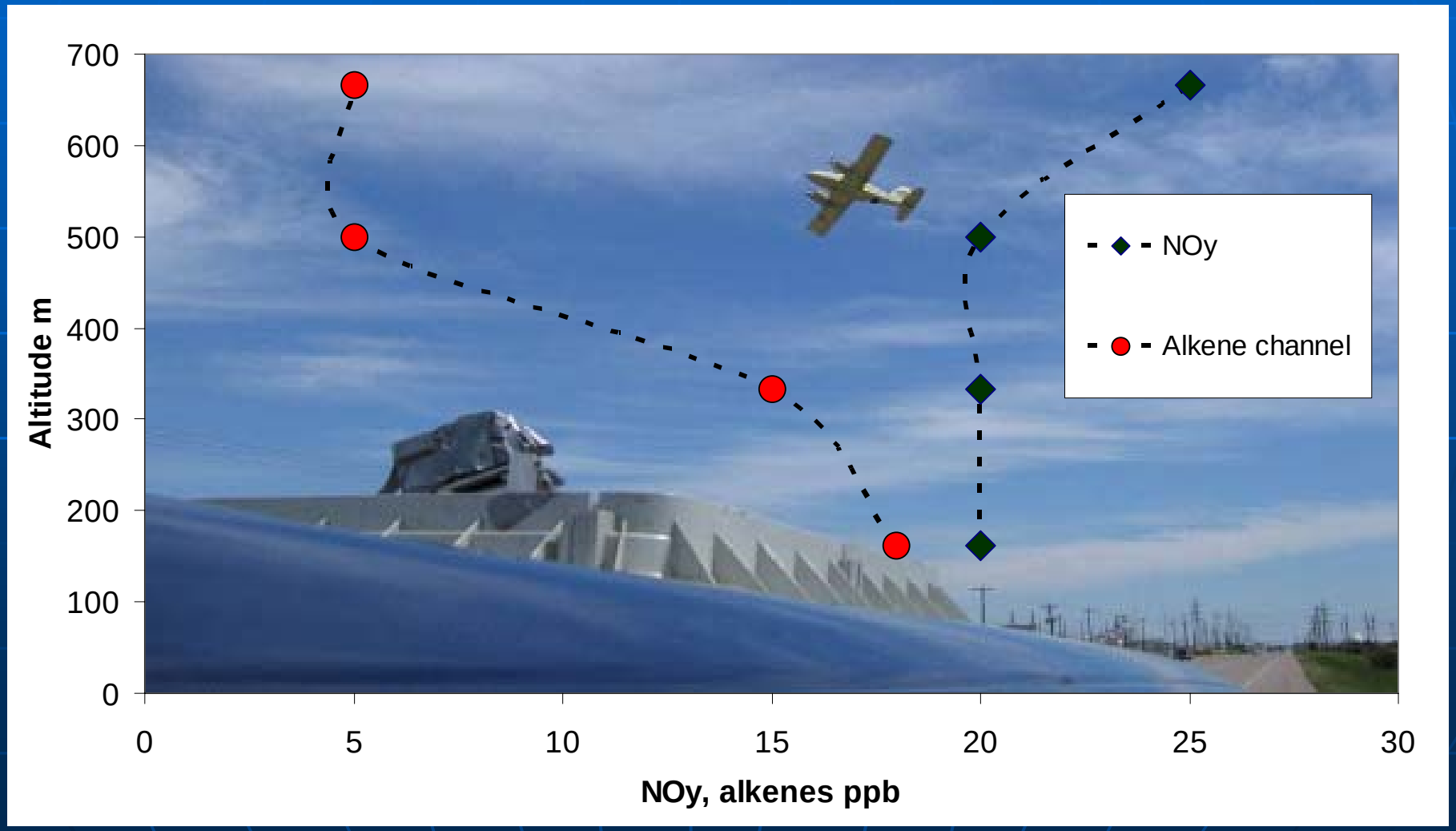
Height distribution of the plume

- The NOAA WP3 measurements shows that the emission plume from the industries are distributed within the full mixing layer within 1000-2000s transport time , i.e. indicating vertical mixing velocities of ±(0.5- 1) m/s [pers comm J. de Gouw]

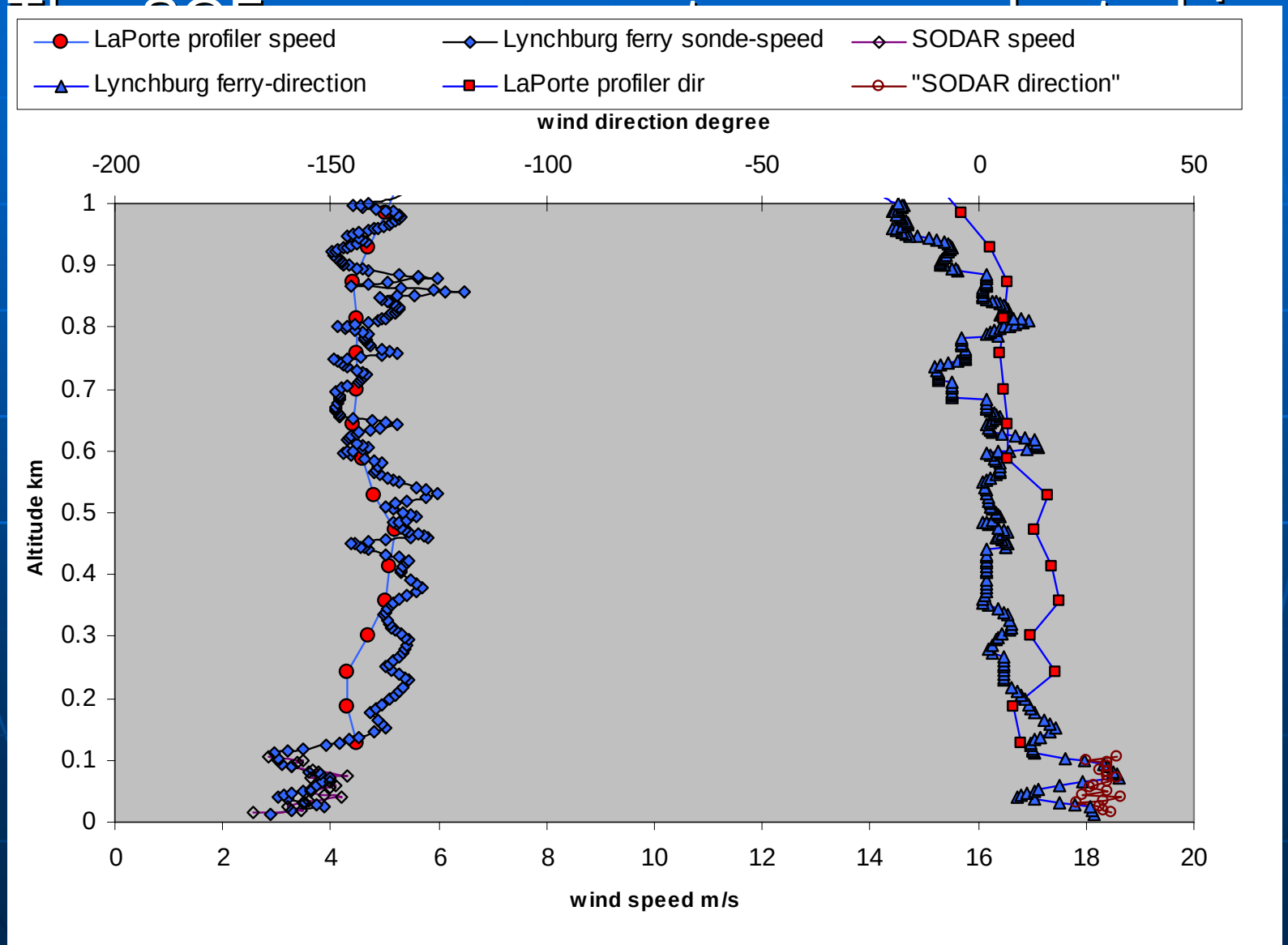
- The NOAA Doppler LIDAR (Ron Brown) shows typical vertical mixing velocities of ±(0.5-1.5) m/s over land [pers comm S. Tucker]

- The Baylor University Twin Otter shows alkene plumes distributed upto 300 m, 250 s downwind, again indicating ± 1 m/s vertical mixing speed .

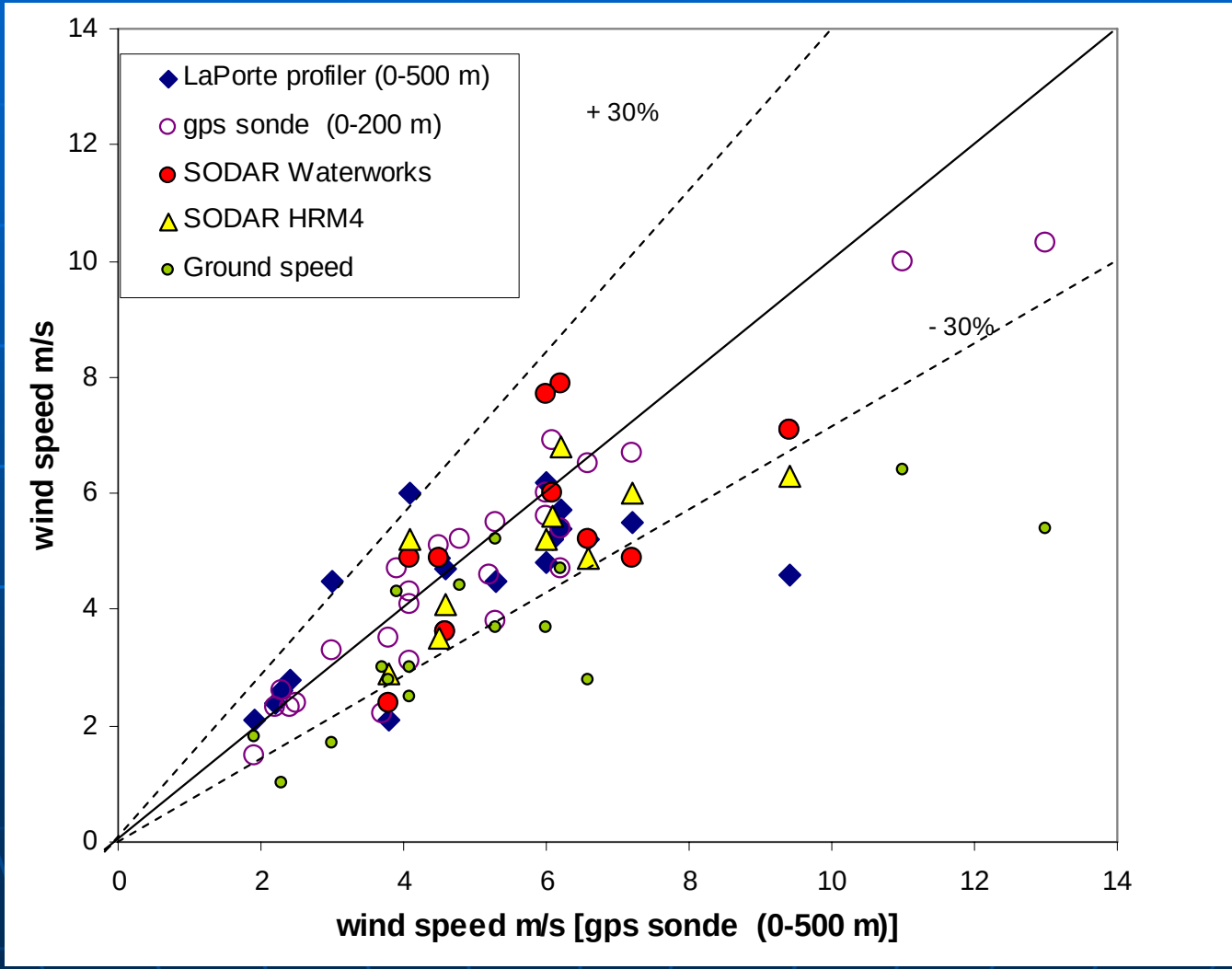
Airborne measurements by Baylor twin Otter 250 s transport time down wind the Freeport area. Crude plot from data presented by Buhr, et al. at the Rapid Science synthesis workshop, 2006.



Height Variation of the wind



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



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

Wind measurement	Wind speed	Wind direction
Laporte wind profiler (0-500 m)	(-3±27)%	(2±15)^{o}
GPS sonde (0-200 m)	(-6±15)%	(2±9)^{o}
SODAR waterworks (0-100 m)	(-7±24)%	(7±16)^{o}
SODAR HRM4 (0-100 m)	(-12±18)%	(2±18)^{o}
Ground stations (CAMS, 10 m)	(-29±21)%	(12±21)^{o}

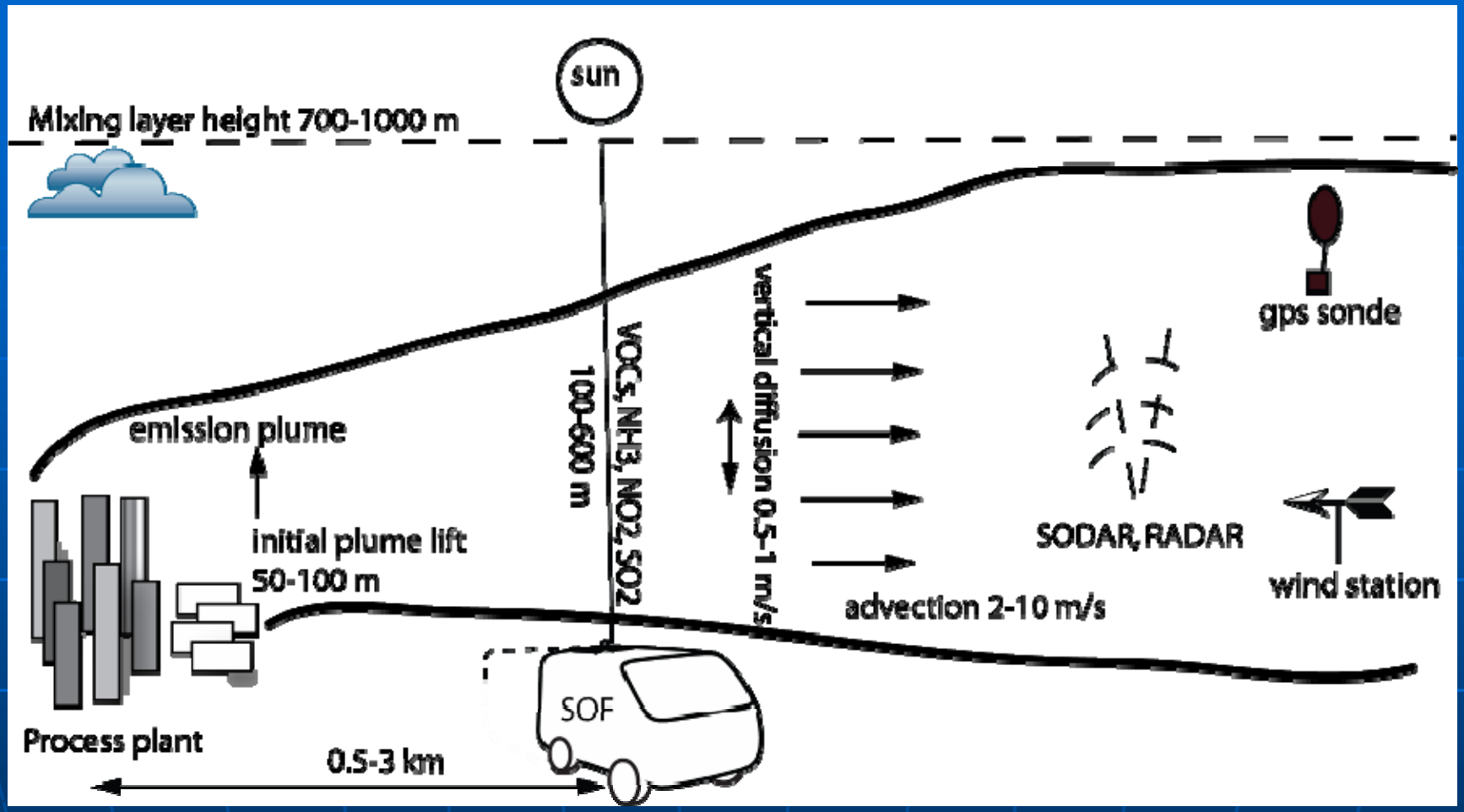
Error budget

- Retrieval method-interference: 10%
- Lineparameters 3%
- Wind speed 27%
- Wind direction 10%

Overall error= 30%

The SOF measurement during TexAQS 2006

- In Sep 2006 about 10 days of measurements were conducted in the vicinity of the Houston ship channel area (HSC), 2 days in Texas City, 1 day in Choc bayoU and Freeport and 2 days in Sweeny
- On a given day multiple measurements of the emission sources were conducted and the source were if possible enclosed in a “measurement box”
- GPS soundings were carried out in the vicinity of the measurements (4 per day).
- Coordinated measurement with NOOA WP3 and Baylor Twin Otter

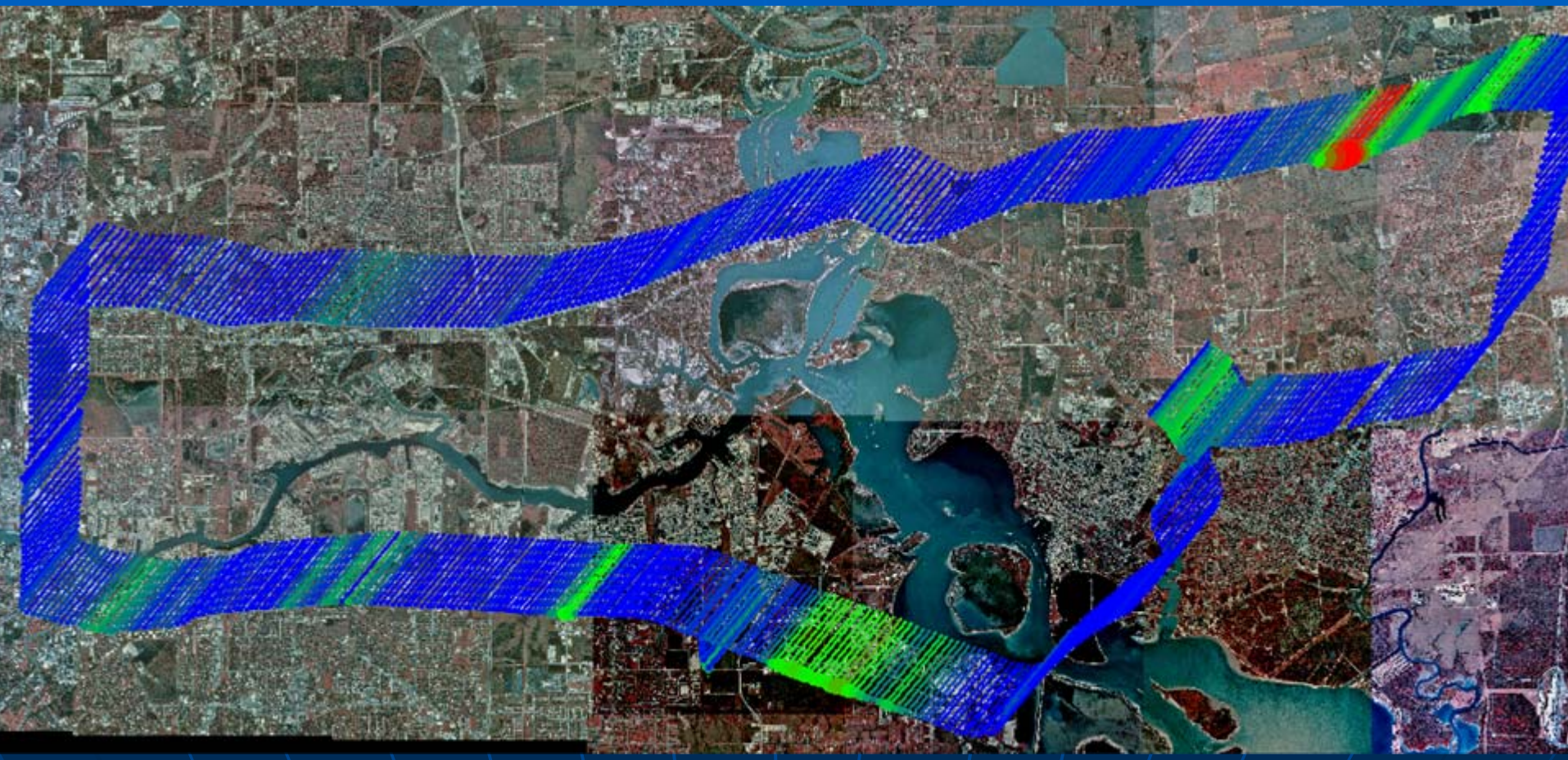


The measurements were typically conducted at 0.5 to 3 km distance from the sources 100-600 s. The assumption is then that the plume is distributed from the ground up to several hundred meters height and that the wind varies little with height. The average wind [0-200] m or [0-500] m was used , obtained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

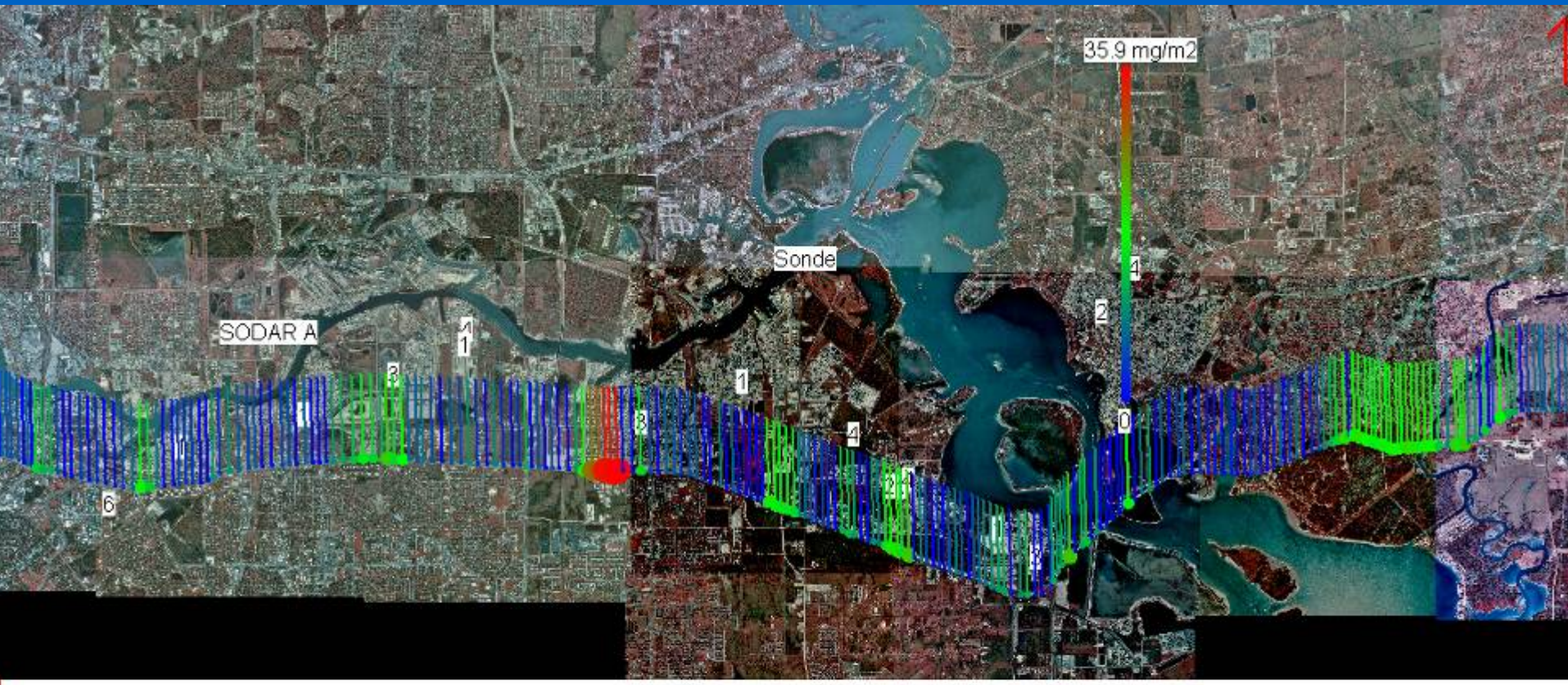
Meteorological sites and North-south sectors into which the emissions data was divided into.

”SOF box” of ethene around the HSC on Sep 19, 12-1400

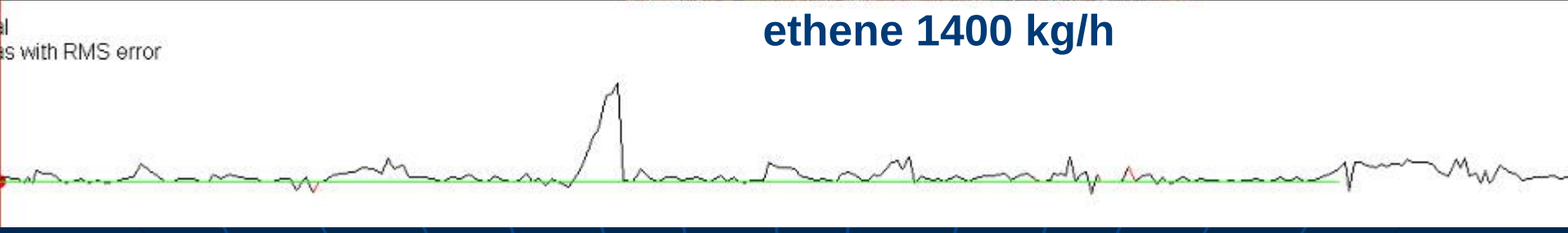
Here the colorcode correspond to the mass of ethylene measured in the solar light. The lines point towards the wind



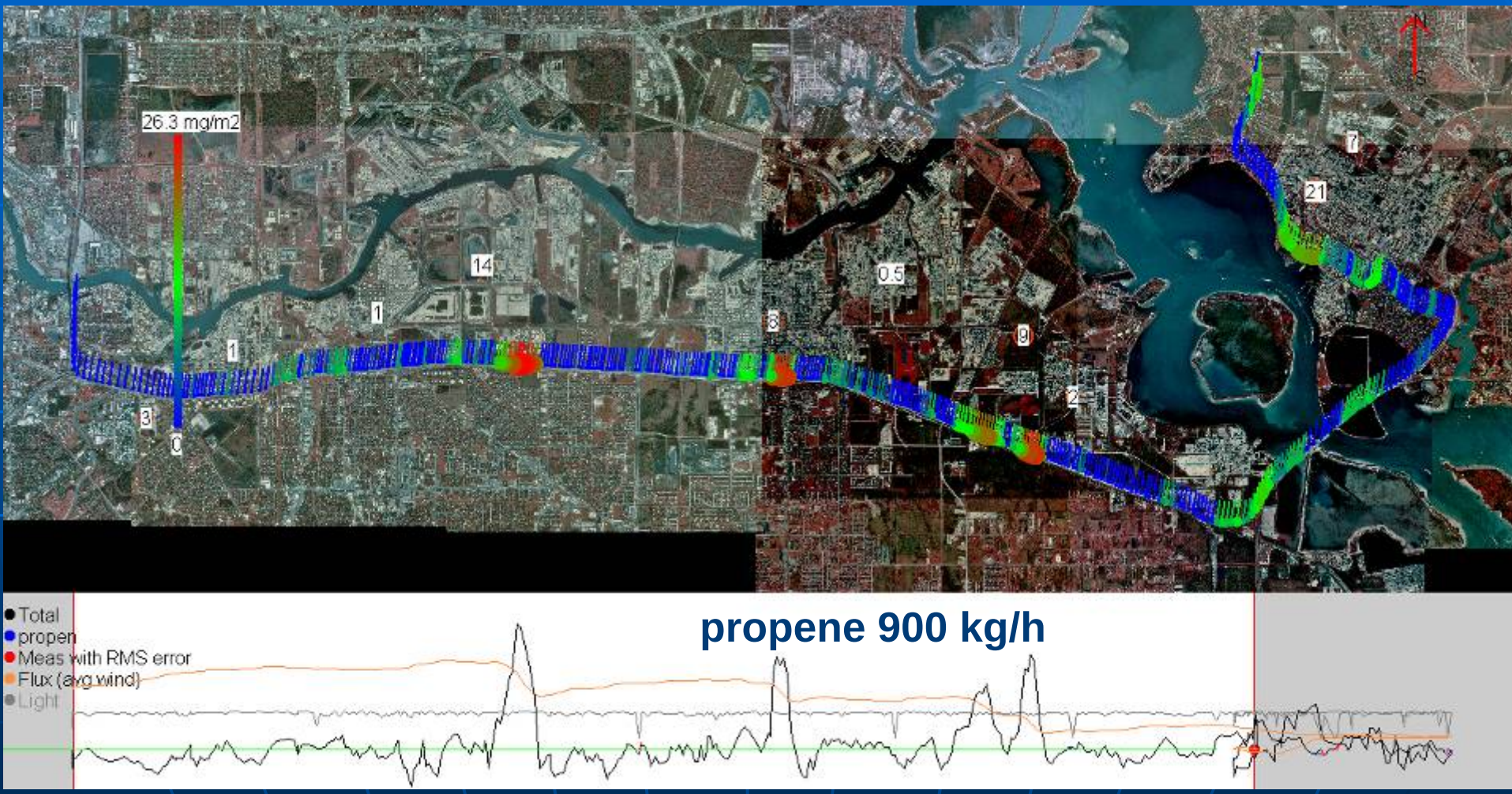
HSC Aug 30, ethene,



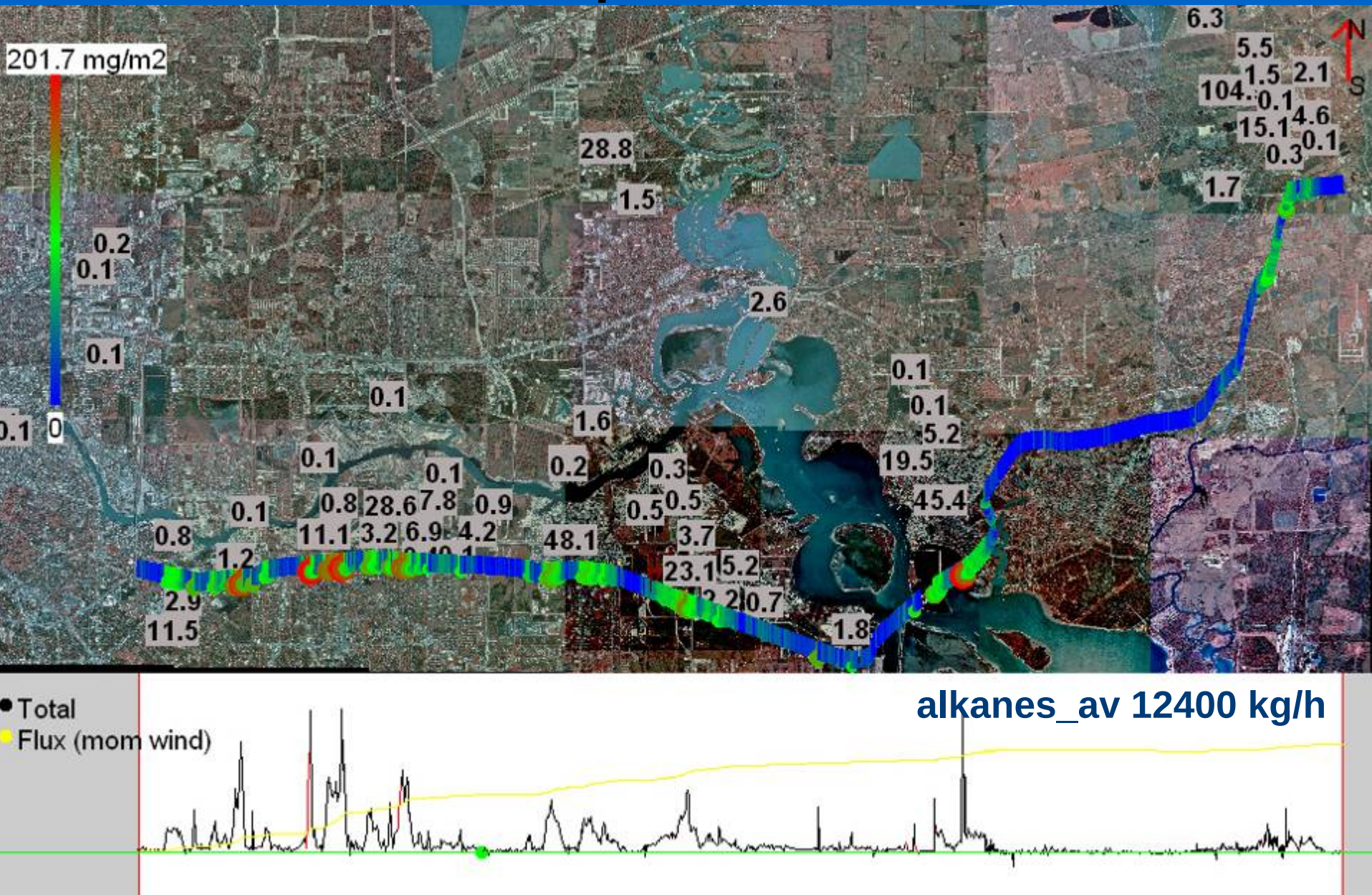
ethene 1400 kg/h



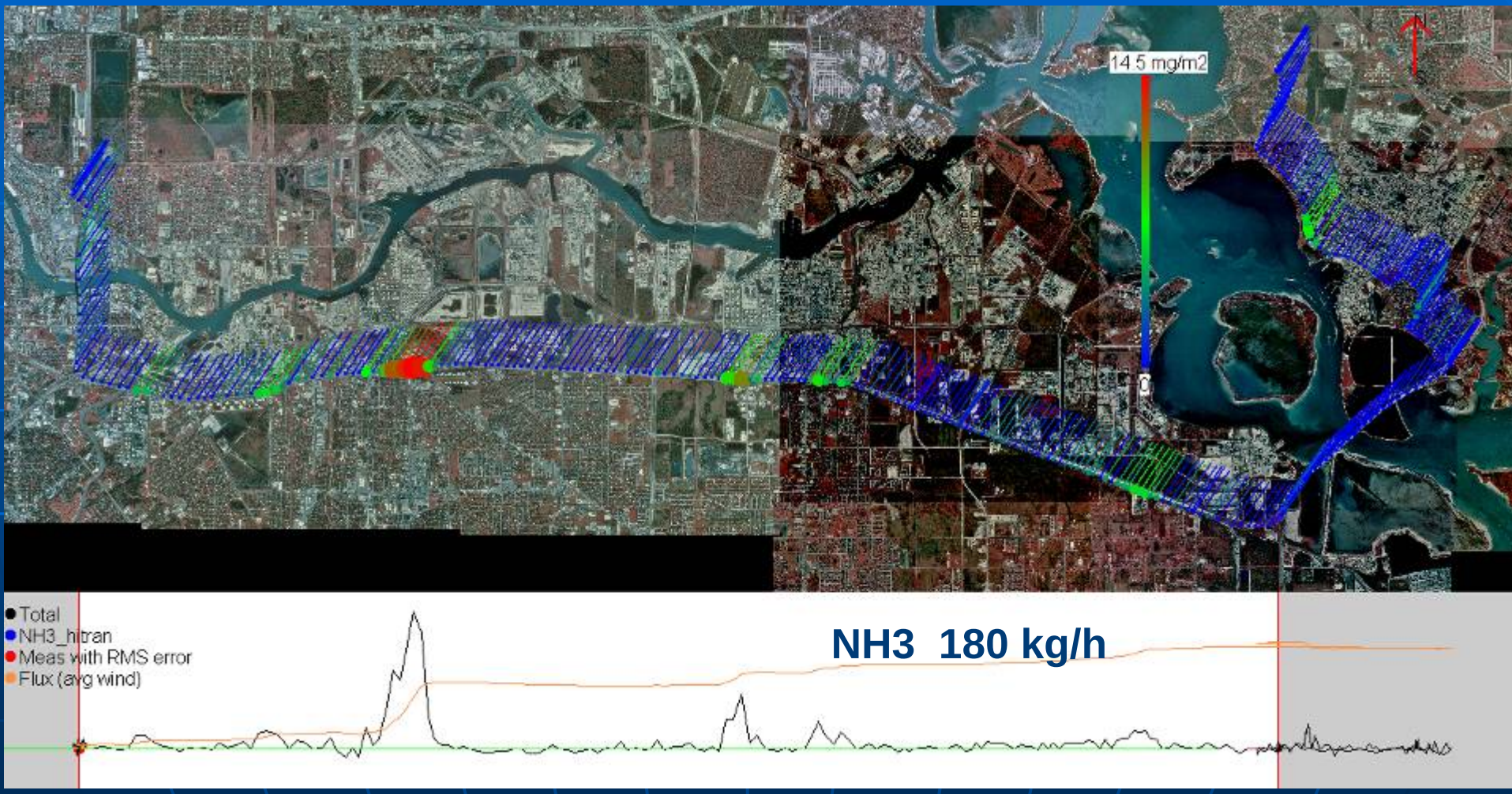
HSC Sep 25, propene,



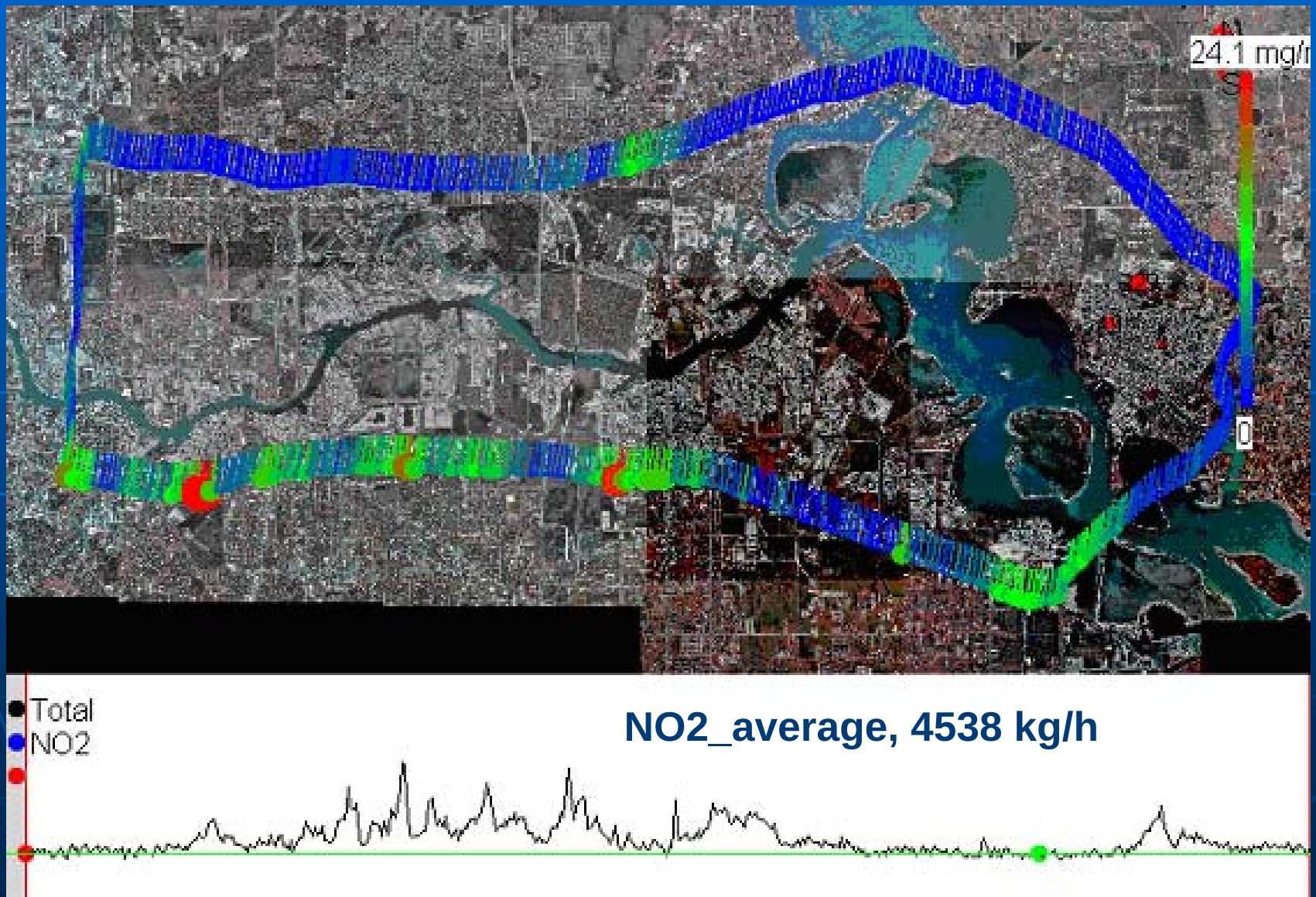
HSC Sep 25,alkanes,



HSC Sep 19, Ammonia



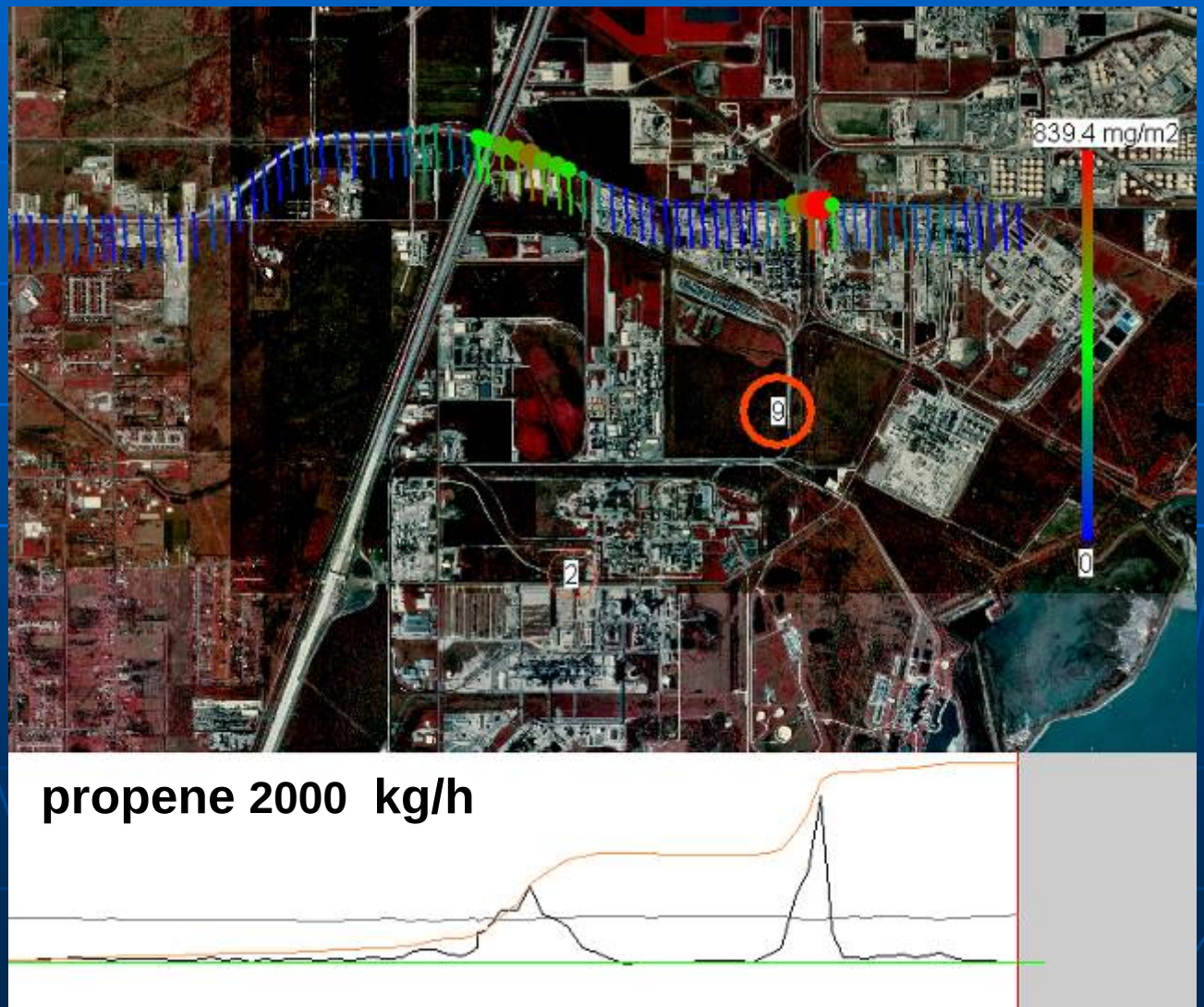
HSC Sep 19, NO2



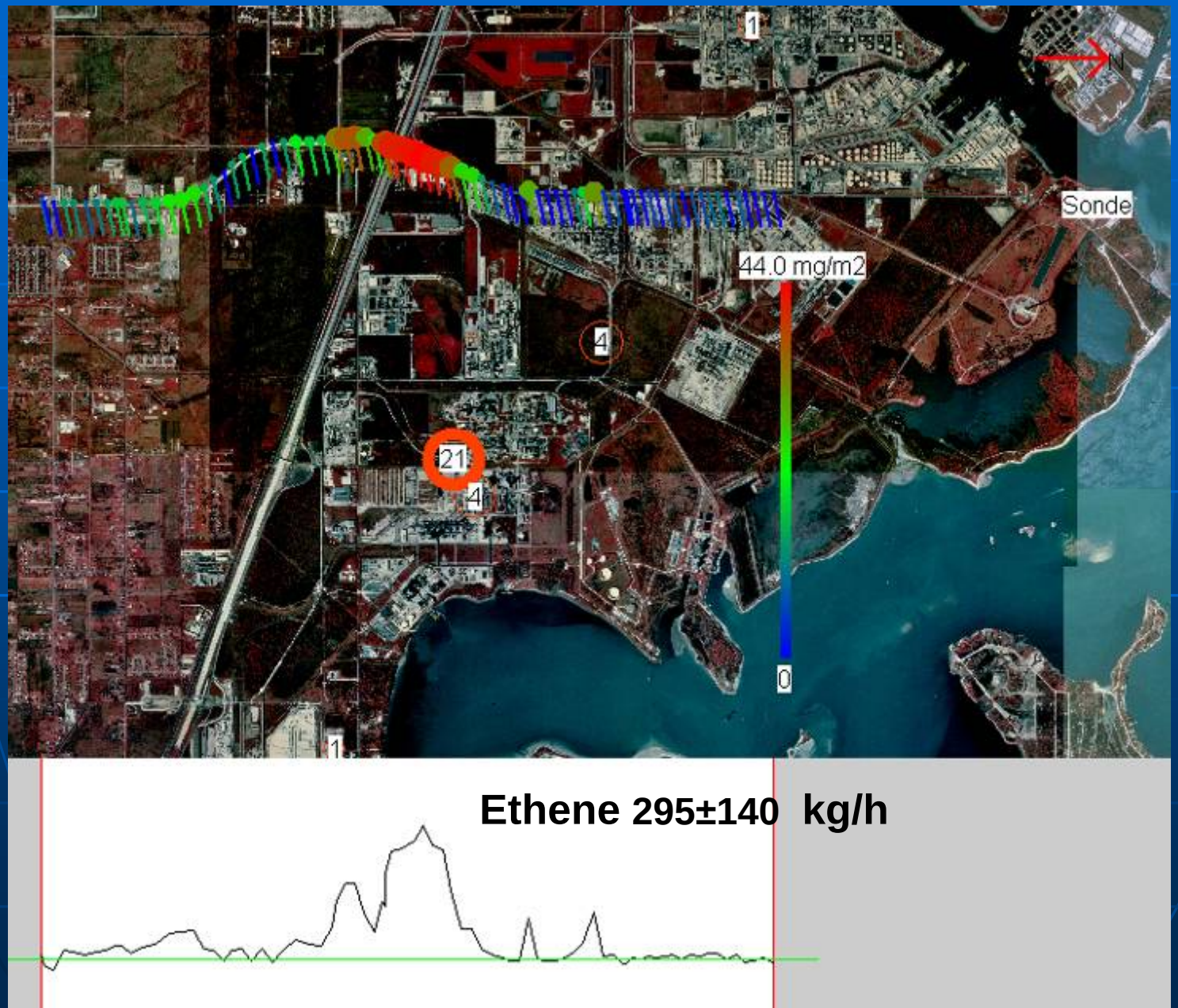
Intermediate emissions

- Propene varied more than ethene!
- Is this due to differences in sources causing more upset emissions for propene, for instance flaring ?

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



N-S Transect on Battleground road, Aug 31



HSC Sep 06, Average emissons in kg/h

Species	Meas	Inventory
ethene	860±180	47
propene	1500±500*	60
alkanes	12400	372
NH3	190 ±20	
NO2	4500±1900	3089
SO2	5200 ±2400	2752

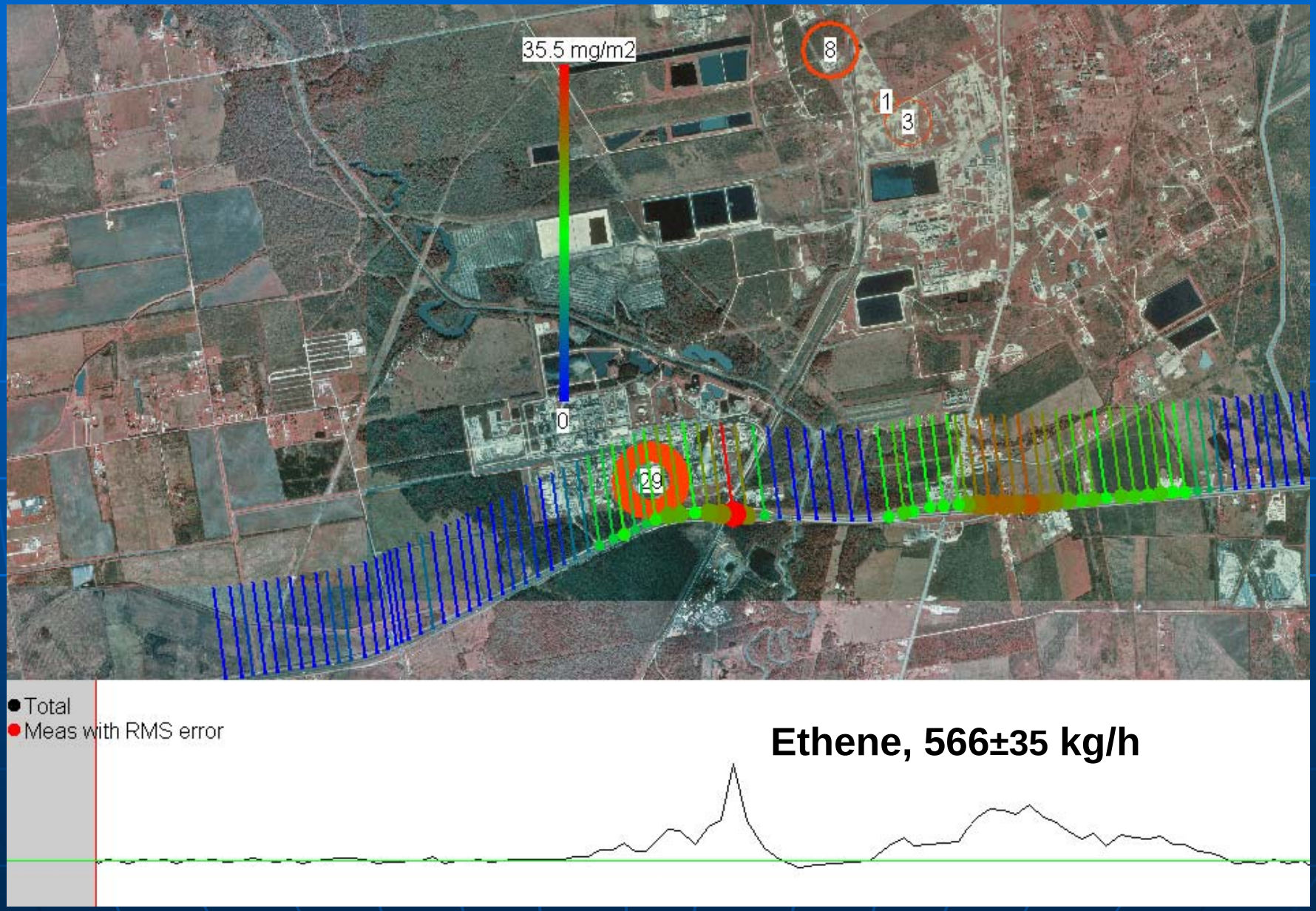
* Uncertain due to large variability in the emissions

Emission inventory

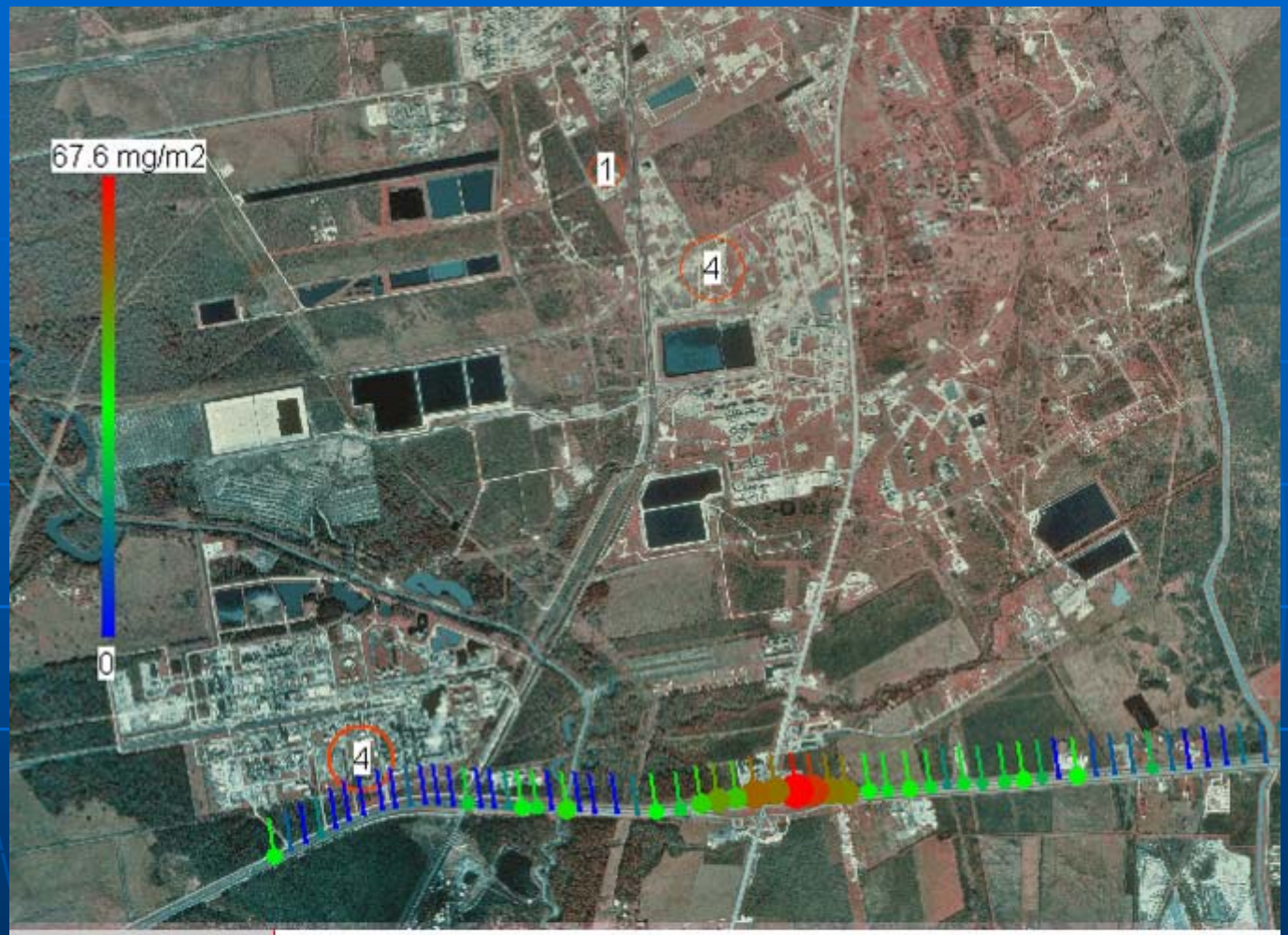
- The data has been derived by NOAA [Frost 2006] for the state of Texas including emissions of NOx, SO2, CO, total and selected speciated VOCs, PM2.5, and PM10 from 1858 fixed-location pollution sources statewide.
- The data are based on TCEQ's 2004 annual totals
- The 2004 ethylene, propylene and alkane emissions for each point source have been derived from the 2004 total VOC emissions by assuming the same speciation at that point source as in 1999,

More details

Mt Belvieu Sep 25, ethene

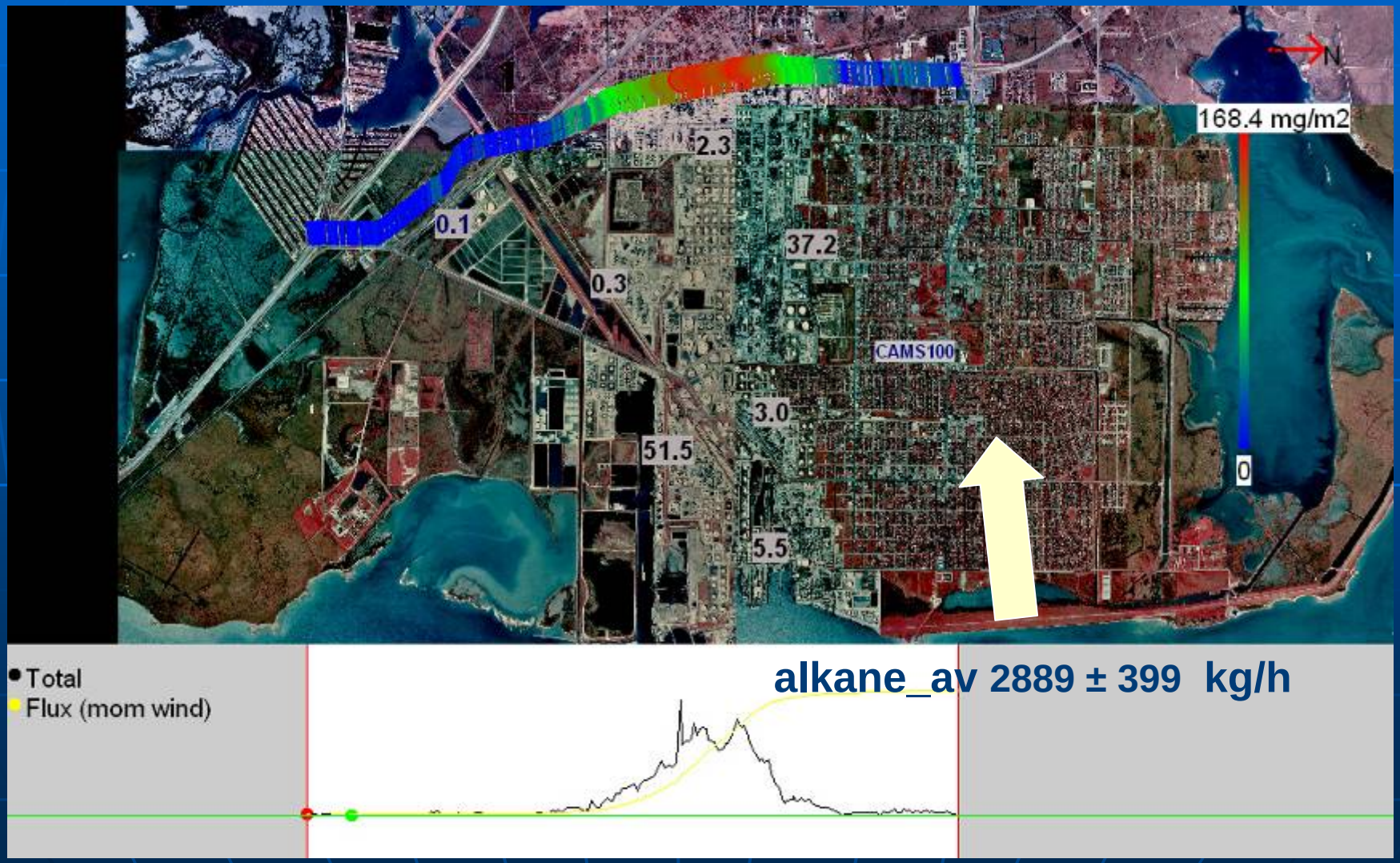


Mt Belvieu, Sep 25, propen

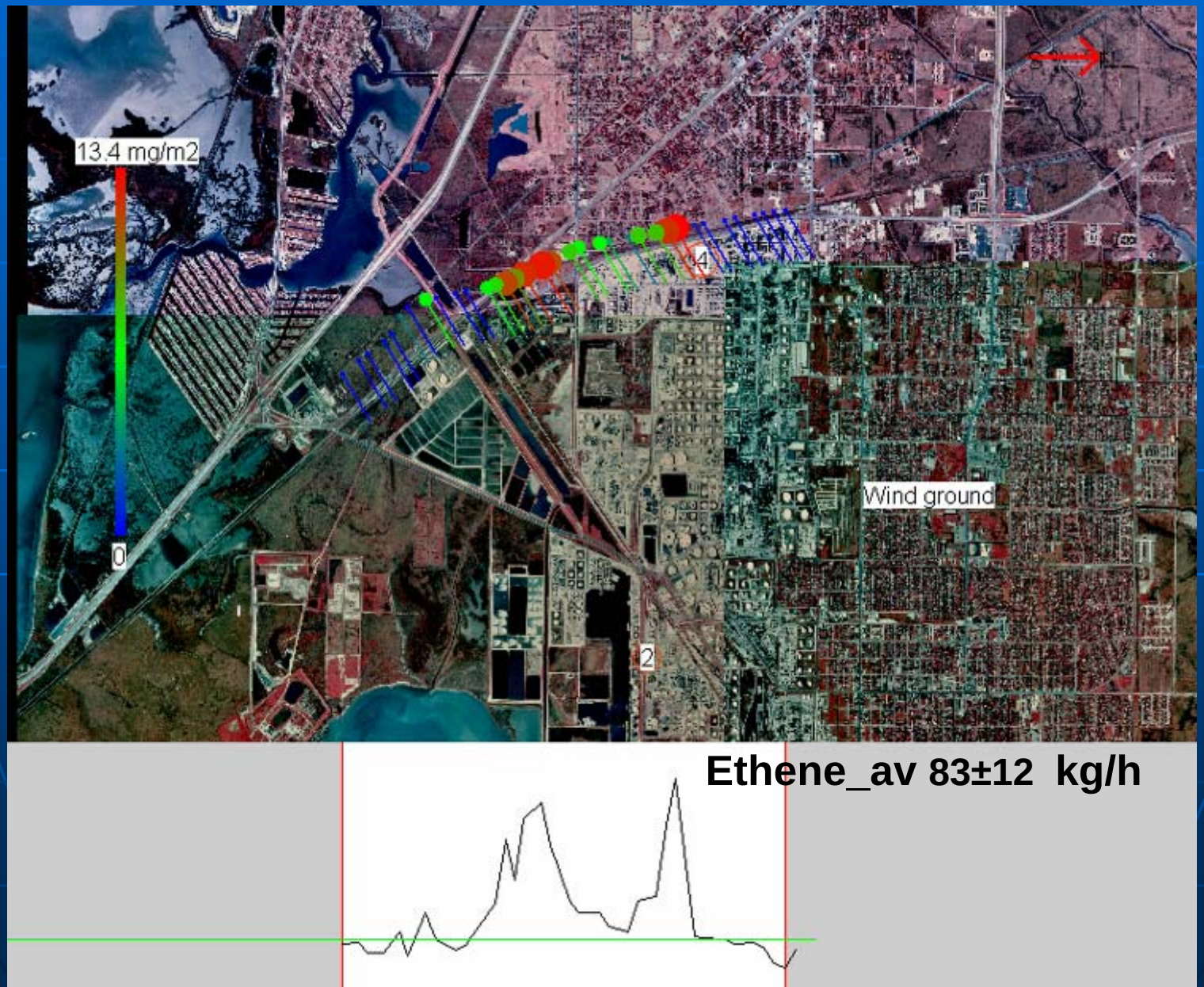


propene 646 kg/h

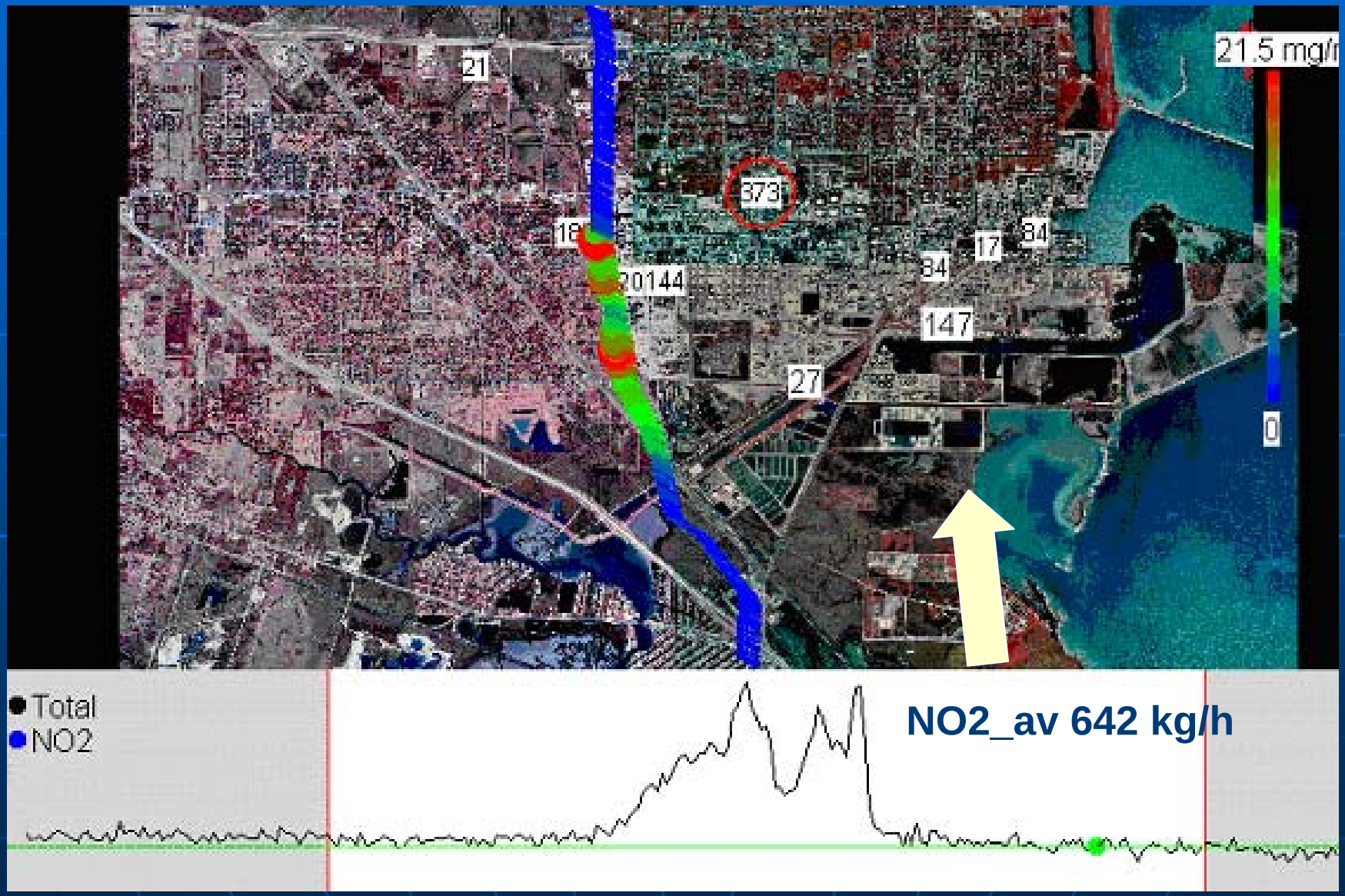
Texas city Sep 20, alkanes



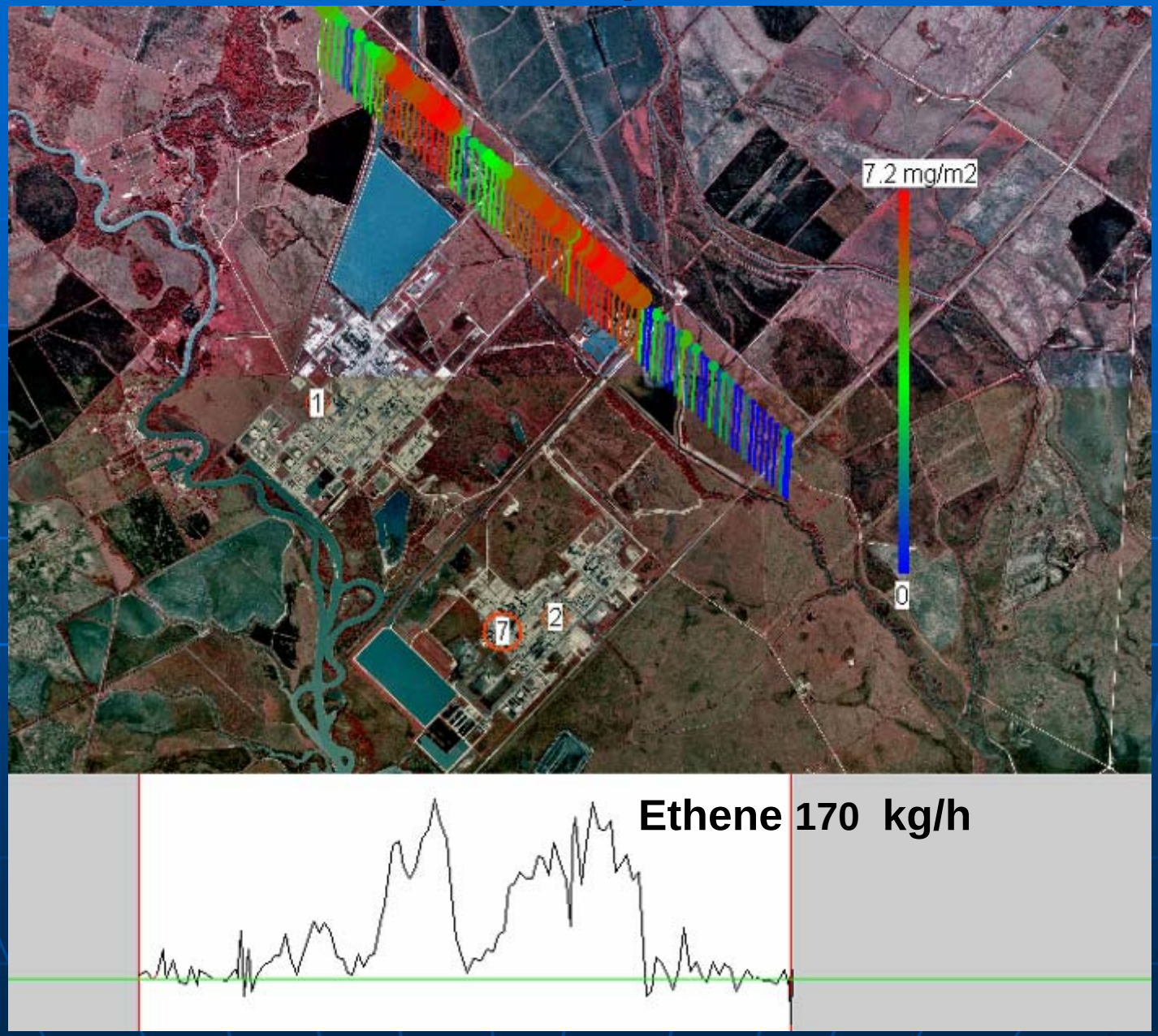
Texas city Sep 20, ethene



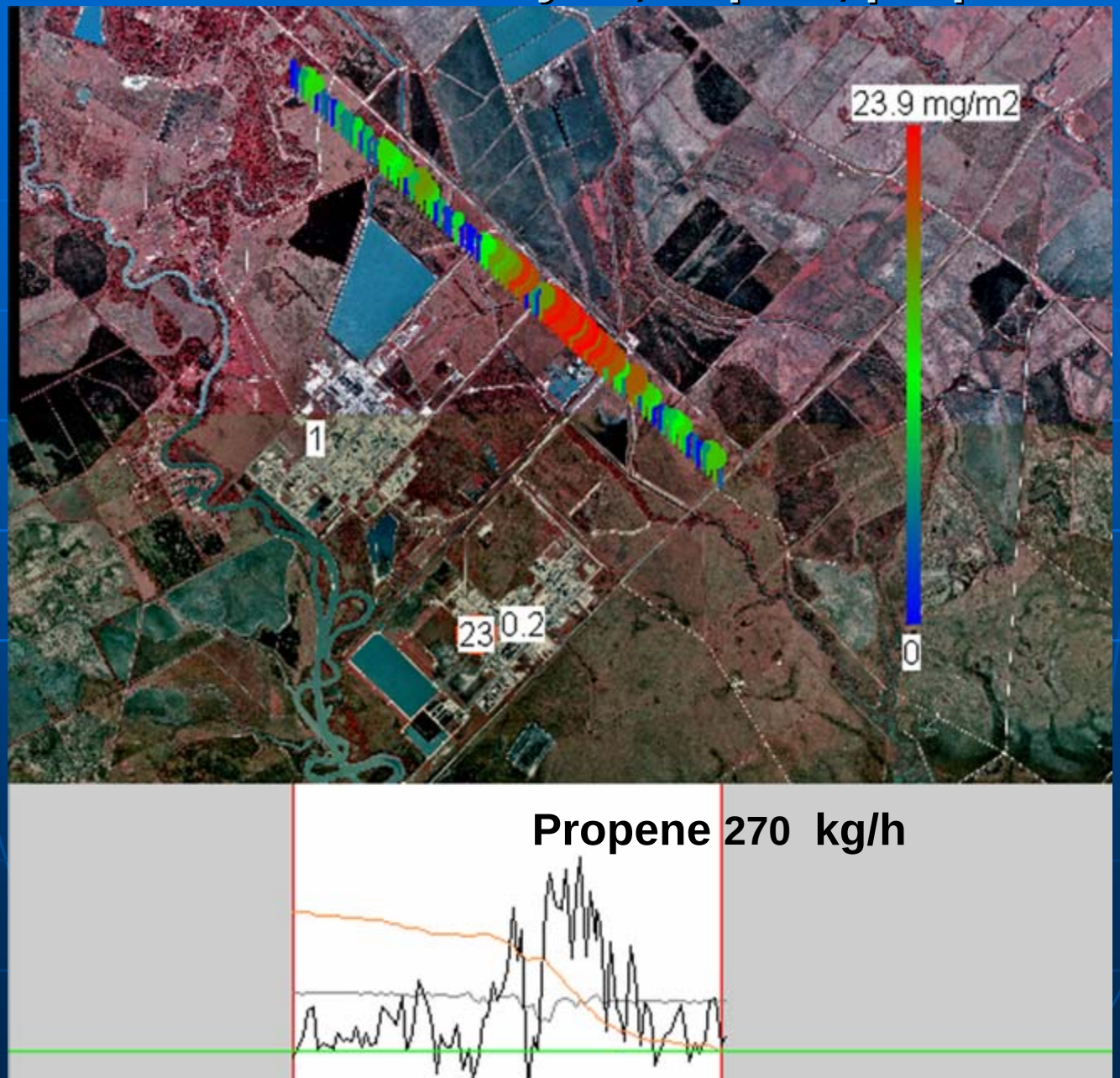
Texas city Sep 20, NO2



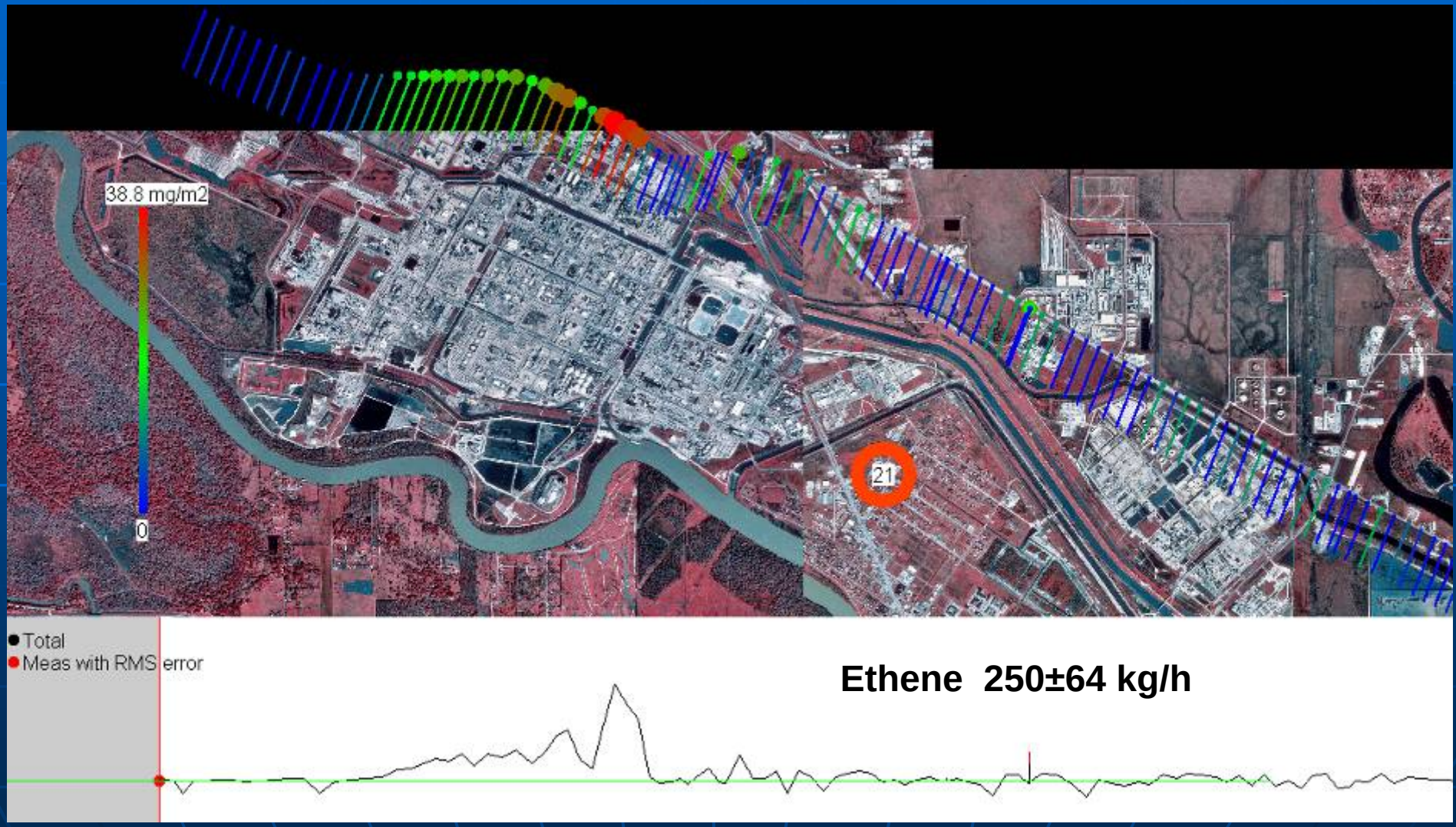
Chocolate Bayou, Sep 26, ethene



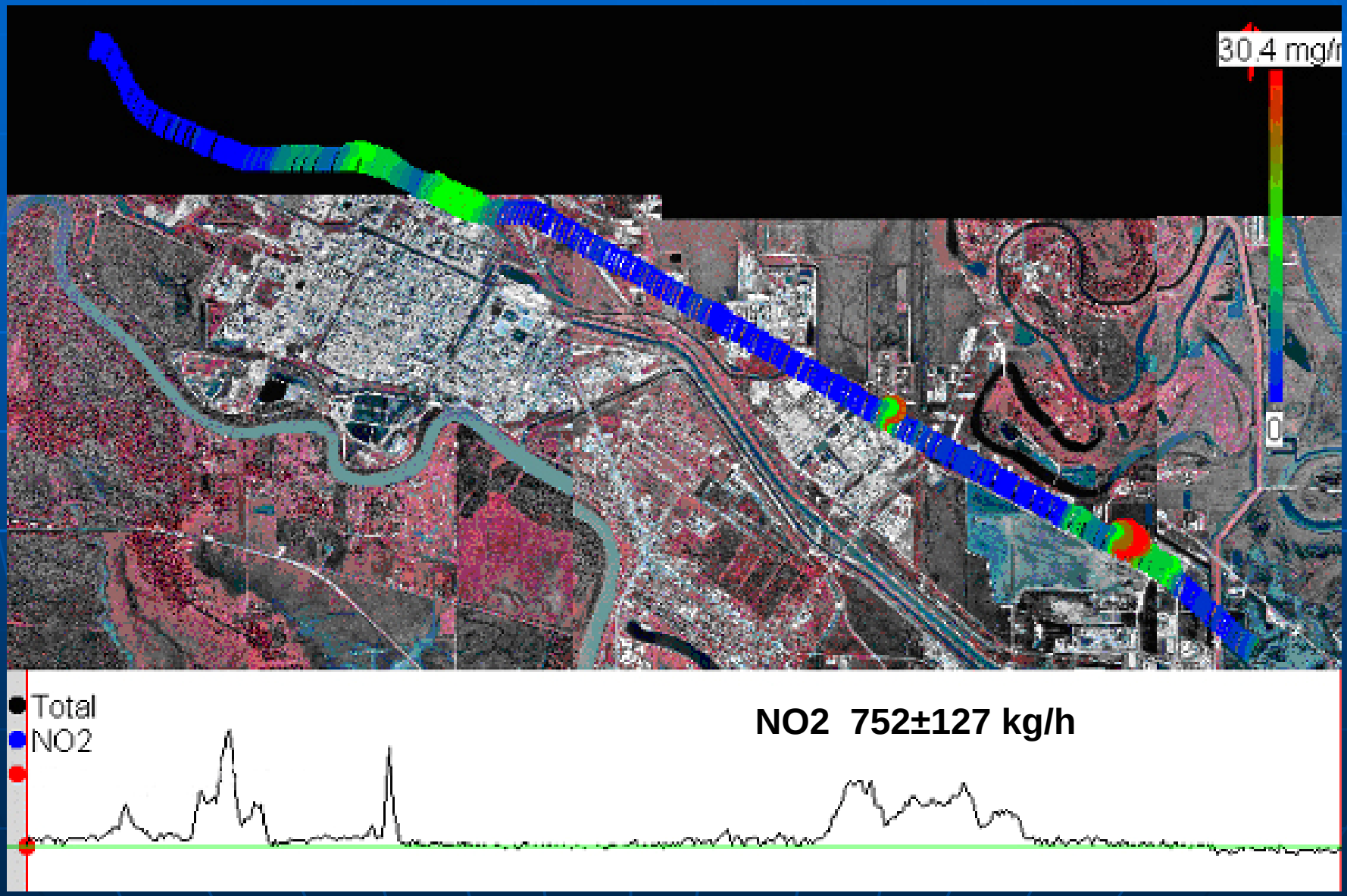
Chocolate Bayou, Sep 26, propene



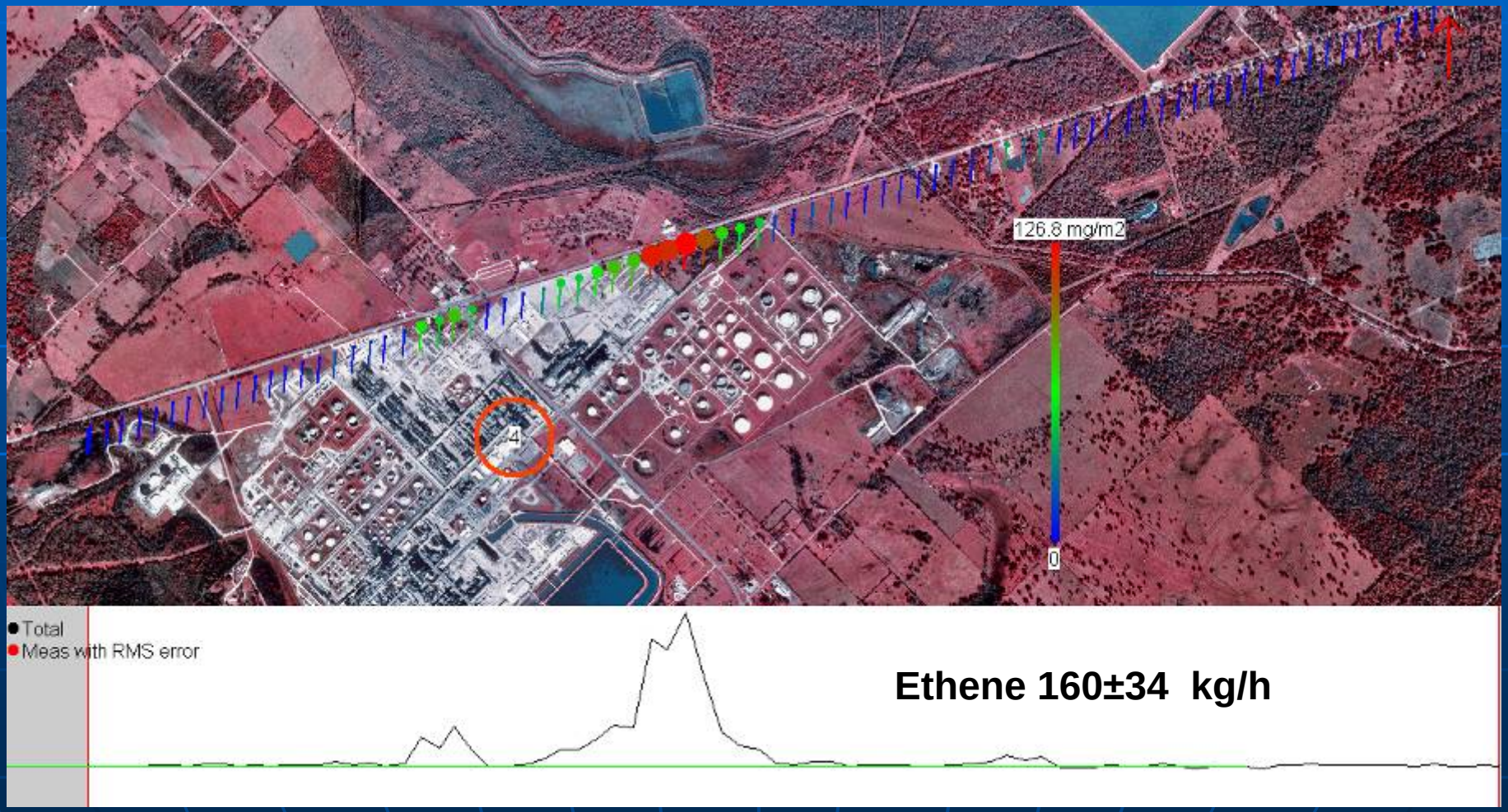
Freeport, Sept 26, ethene



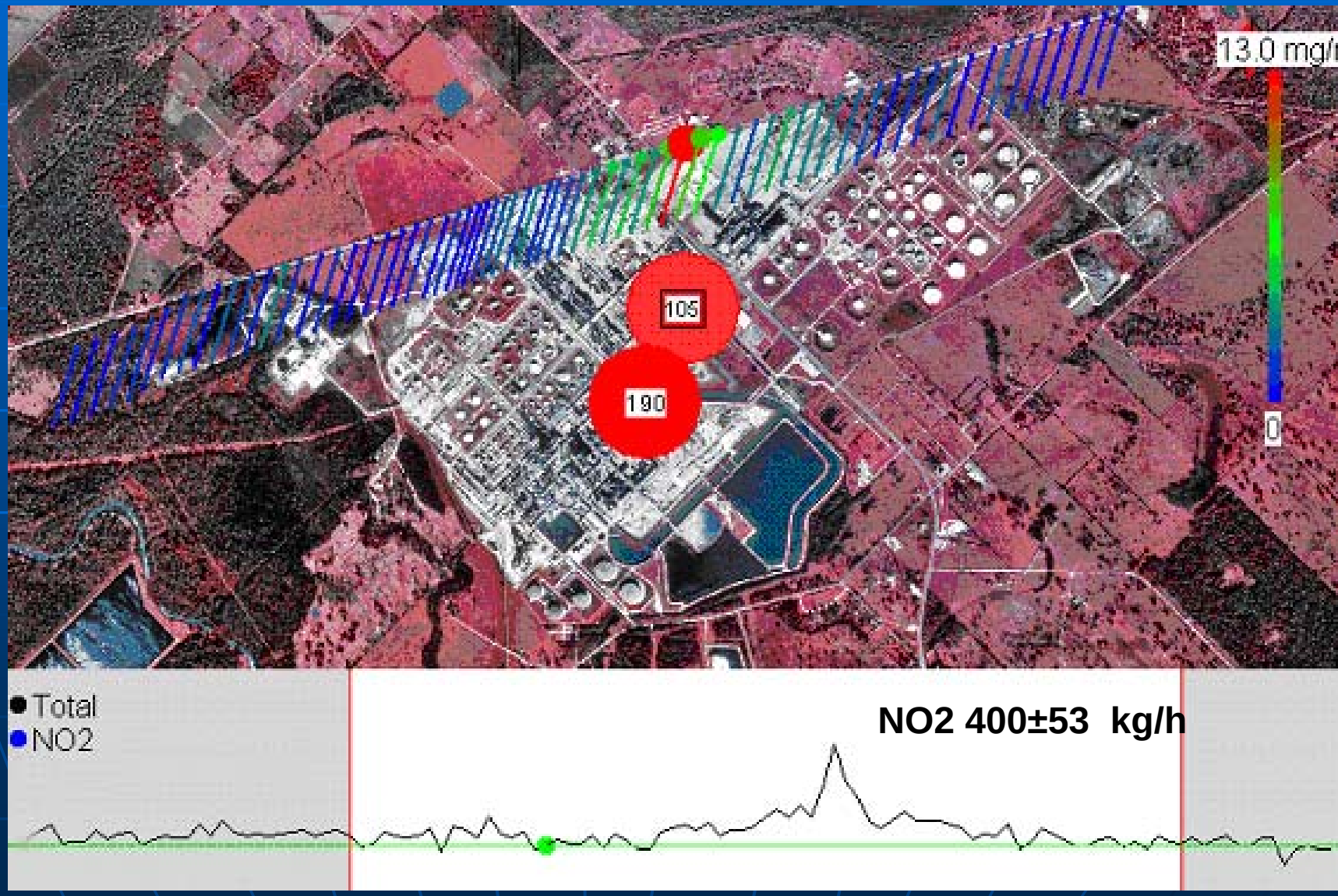
Freeport, Sept 26, NO2



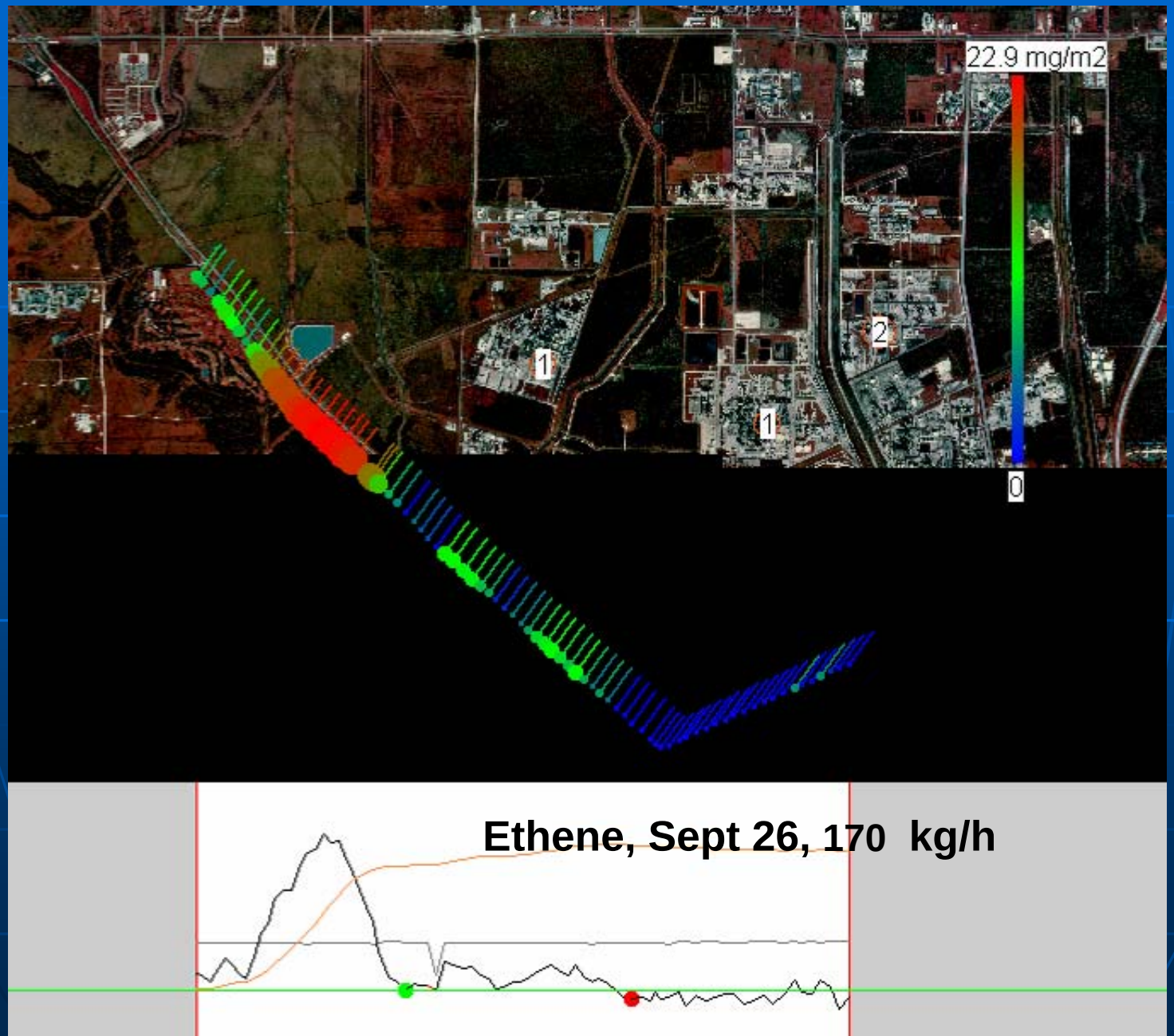
Sweeny, sept 26, ethene



Sweeny, sept 26, NO2



Bayport, Sept 26, ethene



Summary of results

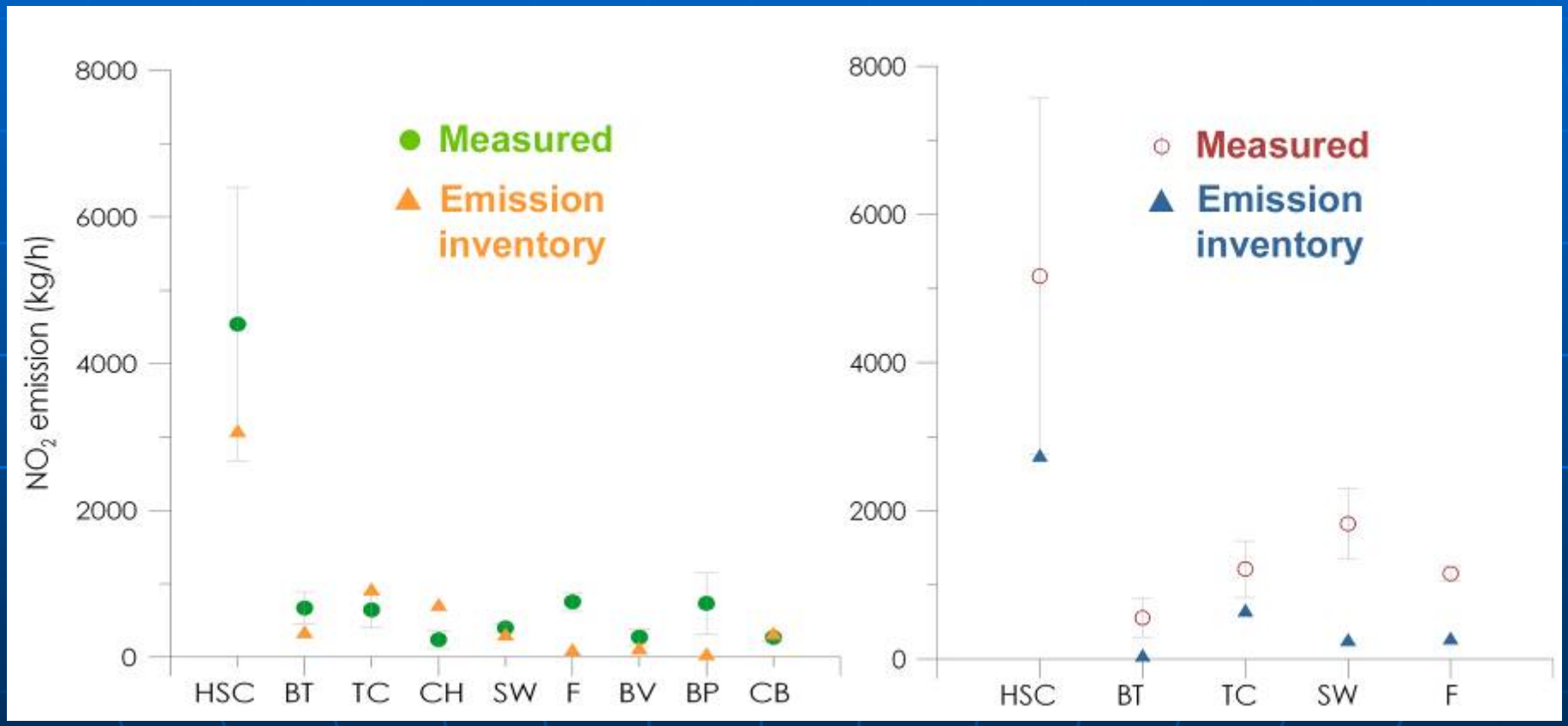
VOC emissions in Sep 2006, with SOF

Sector/Region	ethene	propene	alkanes
1. Allen Genoa Rd	96±15	1	1739 ± 759
2. Davison street	120±24	144±75	3678 ± 1165
3. Deer-Park	187±110	282±282	2983 ± 1424
4. Battleground road	92± 47	380±390	1264 ± 343
5. Miller cutoffroad	184± 156	211±70	420 ± 123
7. Baytown	72 ± 24	260±95	976 ± 113
8. Mt Belvieu	404±41	420±280	863
Bayport	170*		
Channelview	64±32		
Chocolate-Bayou	136*	273.0*	
Freeport	250±65	21	
Sweeny	163±5	126±64	3633
Texas-City	83±12		2889 ± 399

VOC emissions compared to inventory

Species	Ethene kg/h		Propene kg/h		Alkanes kg/h	
Area	**Meas**	**Invent**	**Meas**	**Invent**	**Meas**	**Invent**
HSC	860	47	1500	60	12400	372
Mt Belvieu	404	44	400		860	142
Baytown	72	6			980	75
Texas City	83	8			2890	100
Channelview	64	11				
Sweeny	163	4	126	4	3630	56
Freeport	250	21				
Bayport	170*	4				
Choc. Bayou	136*	10	273	24		

NO2 and SO2 compared to inventory



NO2

SO2

Ethene and NO2

Area	Ethene (kgh^{-1})	NO_2 (kgh^{-1})	Meas Ethene/ NO_2	inventory Ethene/ NO_2	Other ethene/NO_x
HSC (sec. 1-7)	859	4538	0.19	0.02	
Mt Belvieu (8)	404	271	1.49	0.35	
Baytown (7)	72	668	0.11	0.02	
Texas City	83*	642	0.13	0.01	
Channelview	64	237	0.27	0.02	
Sweeny	163	398	0.41	0.01	3.6[1], 3.7[2], 1.5[3]
Freeport	250*	752	0.33	0.20	1.5[1], 2[2], 0.26[3]
Bayport	170*	731	0.23	0.09	
Choc. Bayou	136*	268	0.51	0.03	2[1]

* Uncertain, few measurements or other, [1]Ryerson [2003]-2000, [2]Buhr [2001], [3]Buhr [2006].

More information

- A report has been finalized and will be put on the HARC website (www.HARC.edu):

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

- Contact: johan.mellqvist@chalmers.se

- Reports: www.fluxsense.se

Acknowledgement

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- This work was funded by the Houston Advanced Research Center (HARC) under project no H53.