AQRP project 10-006: Quantification of Industrial Emissions of VOCs, NO_2 and SO_2 by SOF and Mobile DOAS

John Johansson*, Johan Mellqvist, Jerker Samuelsson and Brian Offerle

Chalmers University of Technology, Gothenburg, Sweden

Bernhard Rappenglück, Darrell Anderson, Barry Lefer, Sergio Alvarez and James Flynn

University of Houston

* email:john.johansson@chalmers.se

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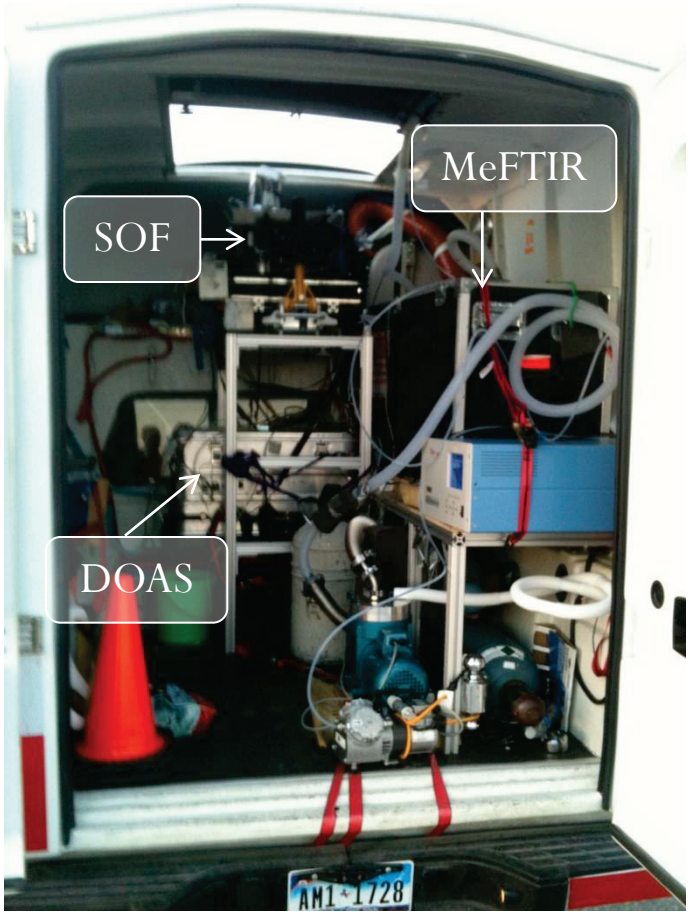
Mobile Atmospheric Lab



Mobile Atmospheric Lab

SOF: alkanes, alkenes, (methane)

MeFTIR: methane, CO, alkanes, alkenes,

Mobile DOAS: SO2, NO2, HCHO

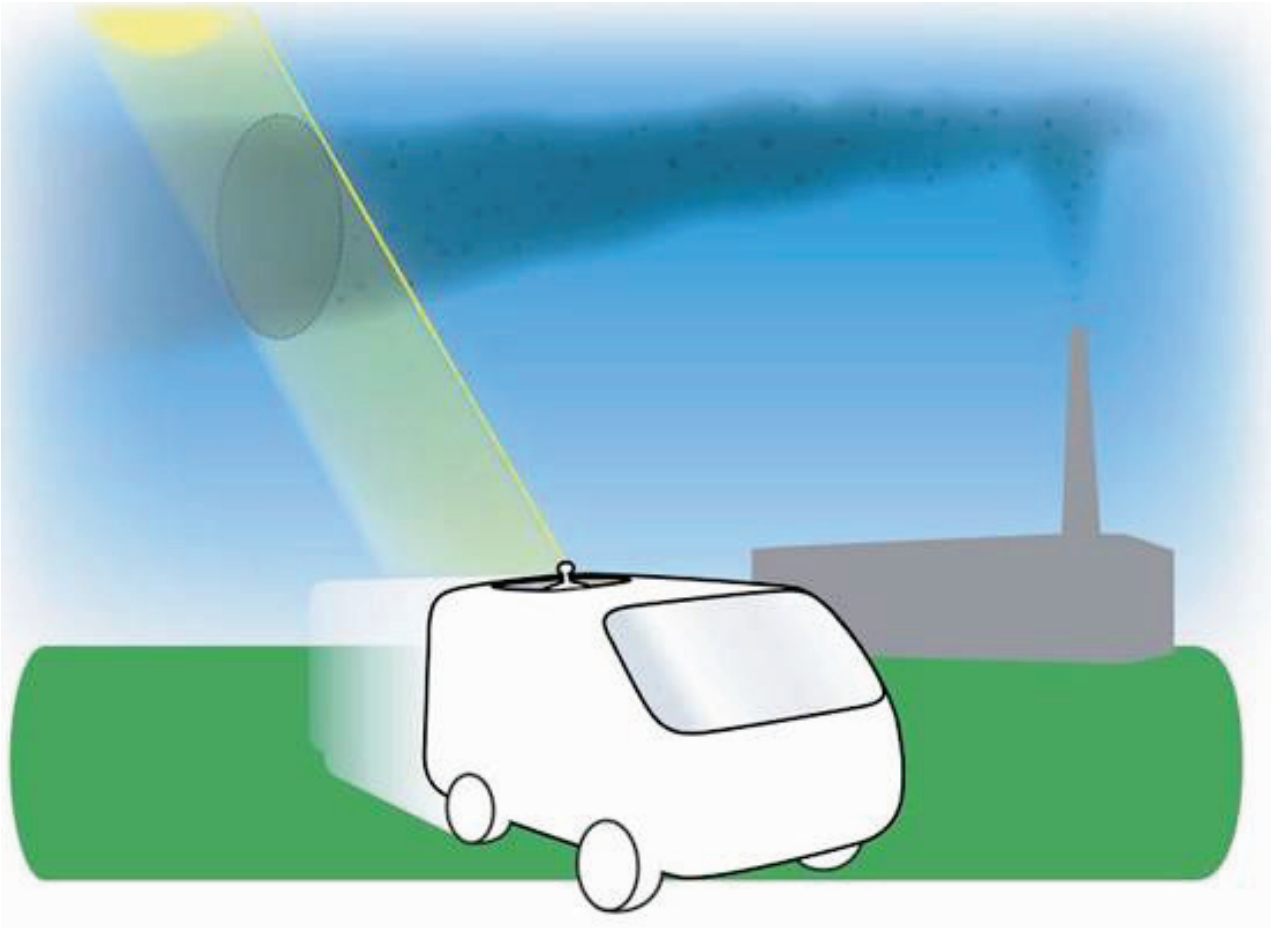
Thermo (Chemi) : NO

Canister sampling

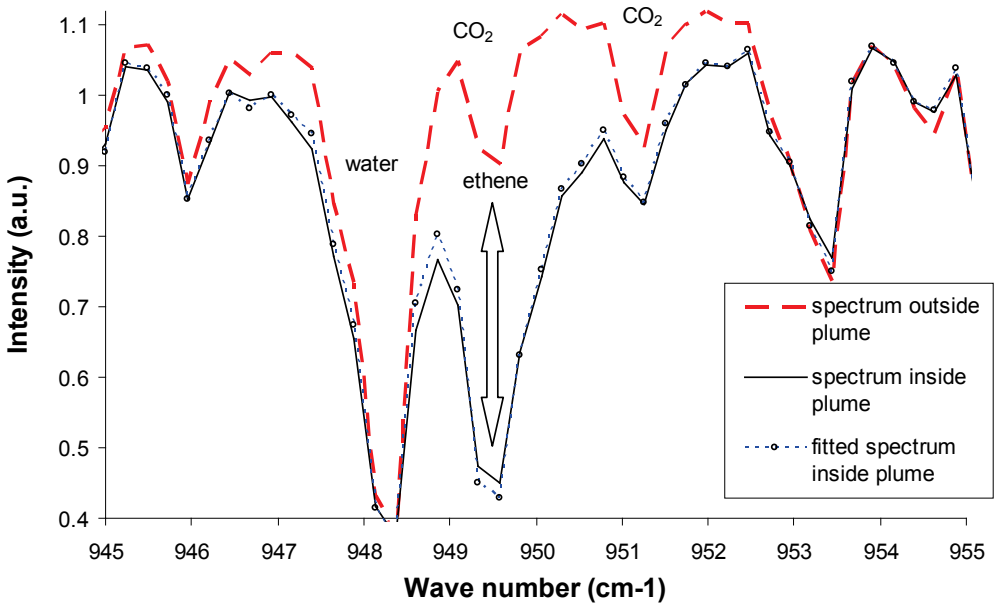
Mobile Atmospheric Lab

Method	**Measurement principle**	**Species measured**	**Type of quantity**	**Auxiliary measurements**	**Derived quantity**
SOF (Solar Occultation Flux)	Molecular absorption of direct sun light, Mid-IR 3–15 µm	Alkanes and alkenes	Column	GPS-coordinates, wind velocity	Mass flux
Mobile DOAS	Molecular absorption of scattered sun light, UV 310–350 nm	Formaldehyde, SO_2 and NO_2	Column	GPS-coordinates, wind velocity	Mass flux
MeFTIR	Molecular absorption of light from active source in multi-pass cell, Mid-IR 3–15 µm	Methane, other alkanes and N_2O	Concentration	Tracer gas release rate (N_2O)	Mass flux
Thermal FTIR	Molecular thermal emission of light, Mid-IR 8–15 µm	Ethene and Propene	Column	GPS-coordinates, telescope heading,	-
Canisters/GC-FID	Gas chromatography and flame ionization detection	59 different NMHCs (non-methane hydrocarbons)	Concentration	-	-

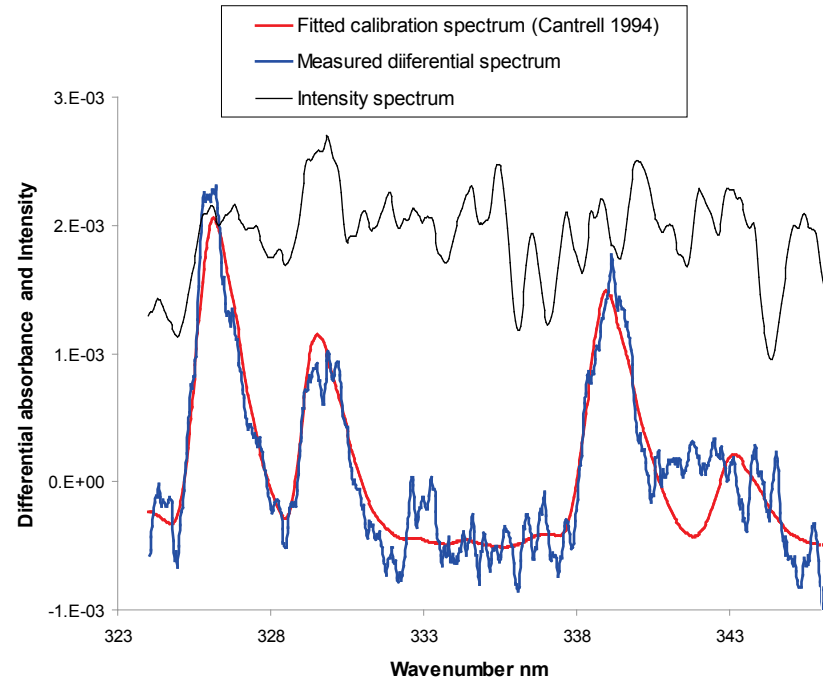
SOF/Mobile DOAS



SOF

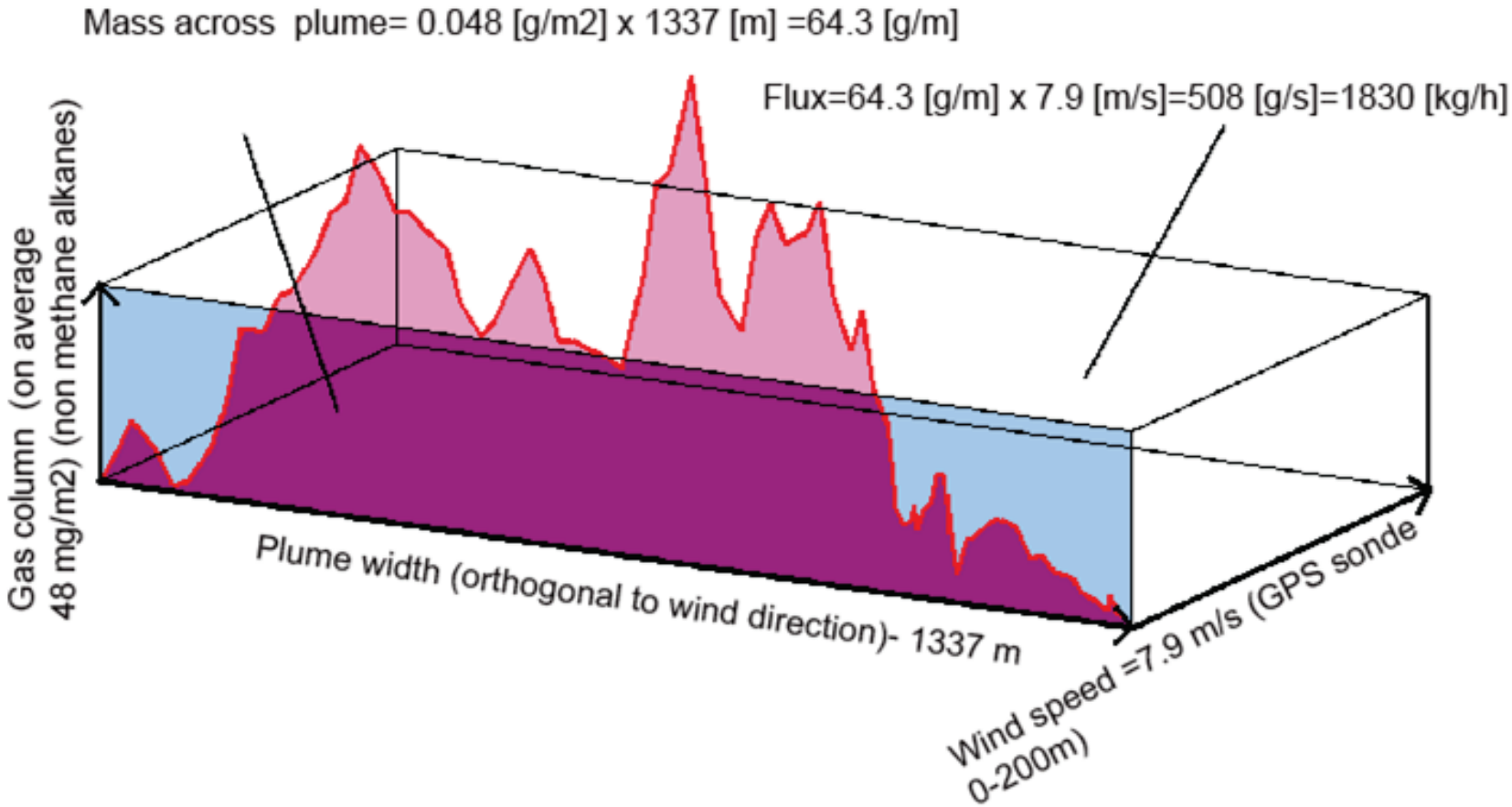


Mobile DOAS



Spectral evaluation

Absorption relative to a reference spectrum is fitted to a linear combination of crossections of species absorbing in the wavelength region of interest

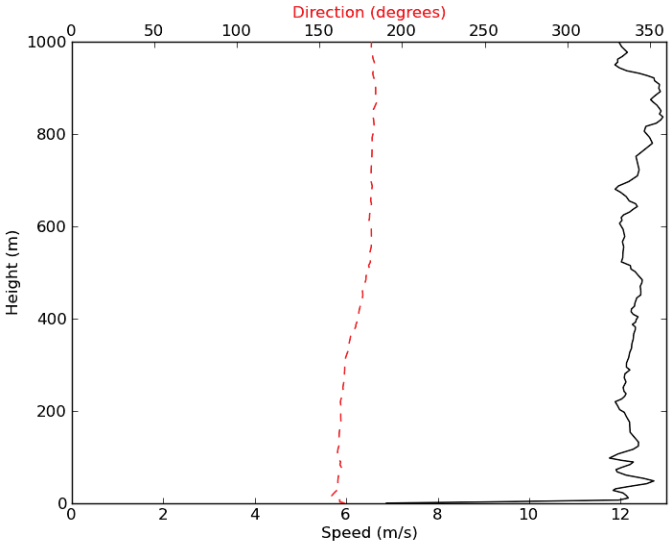


Flux calculation

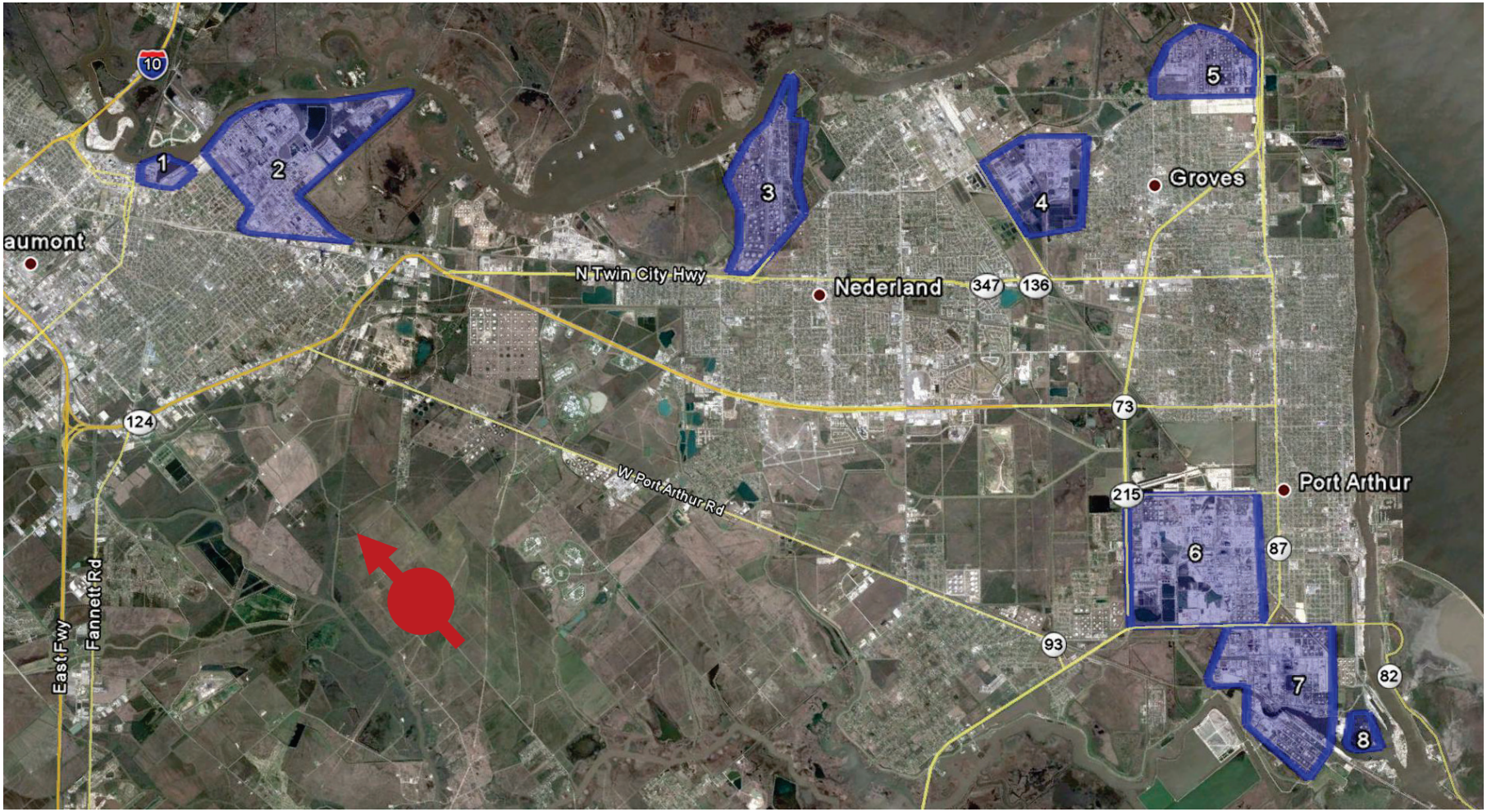
Vertical column concentrations are integrated alon measurement path and multiplied by wind speed. Geometrical corrections are made to compensate for path not being orthogonal to the wind direction.

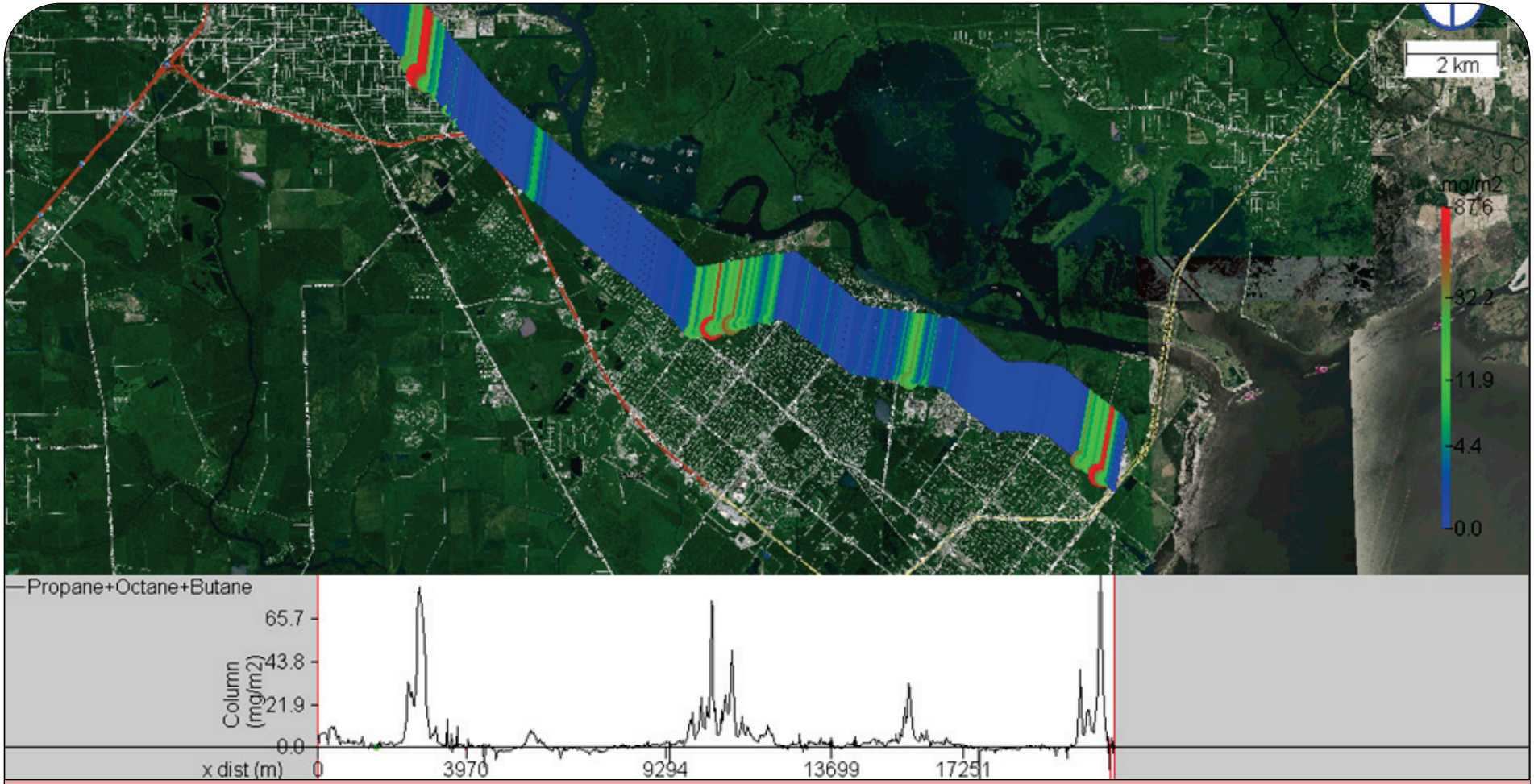
MeFTIR

Wind measurements



Beaumont / Port Arthur

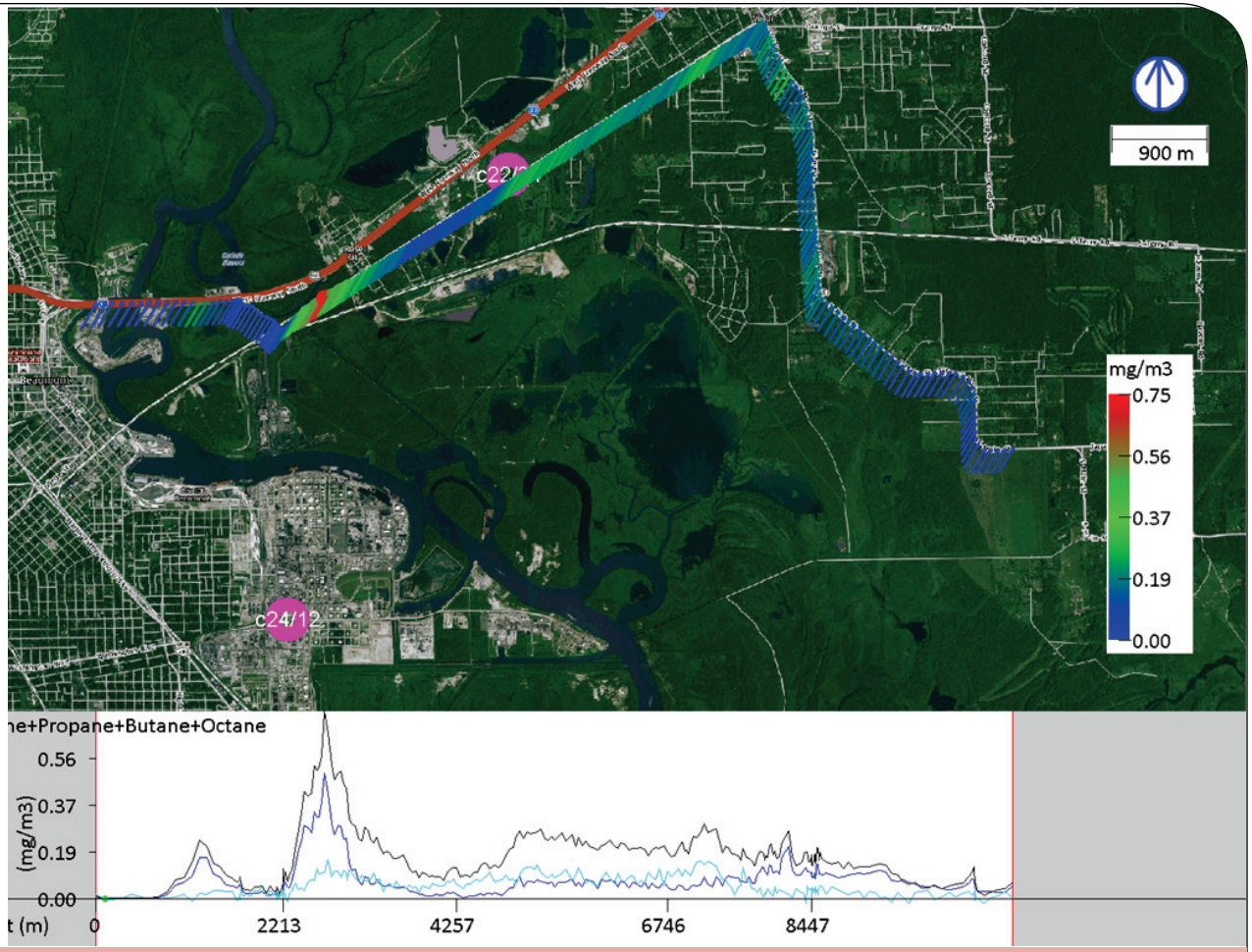




Alkanes in Beaumont / Port Arthur

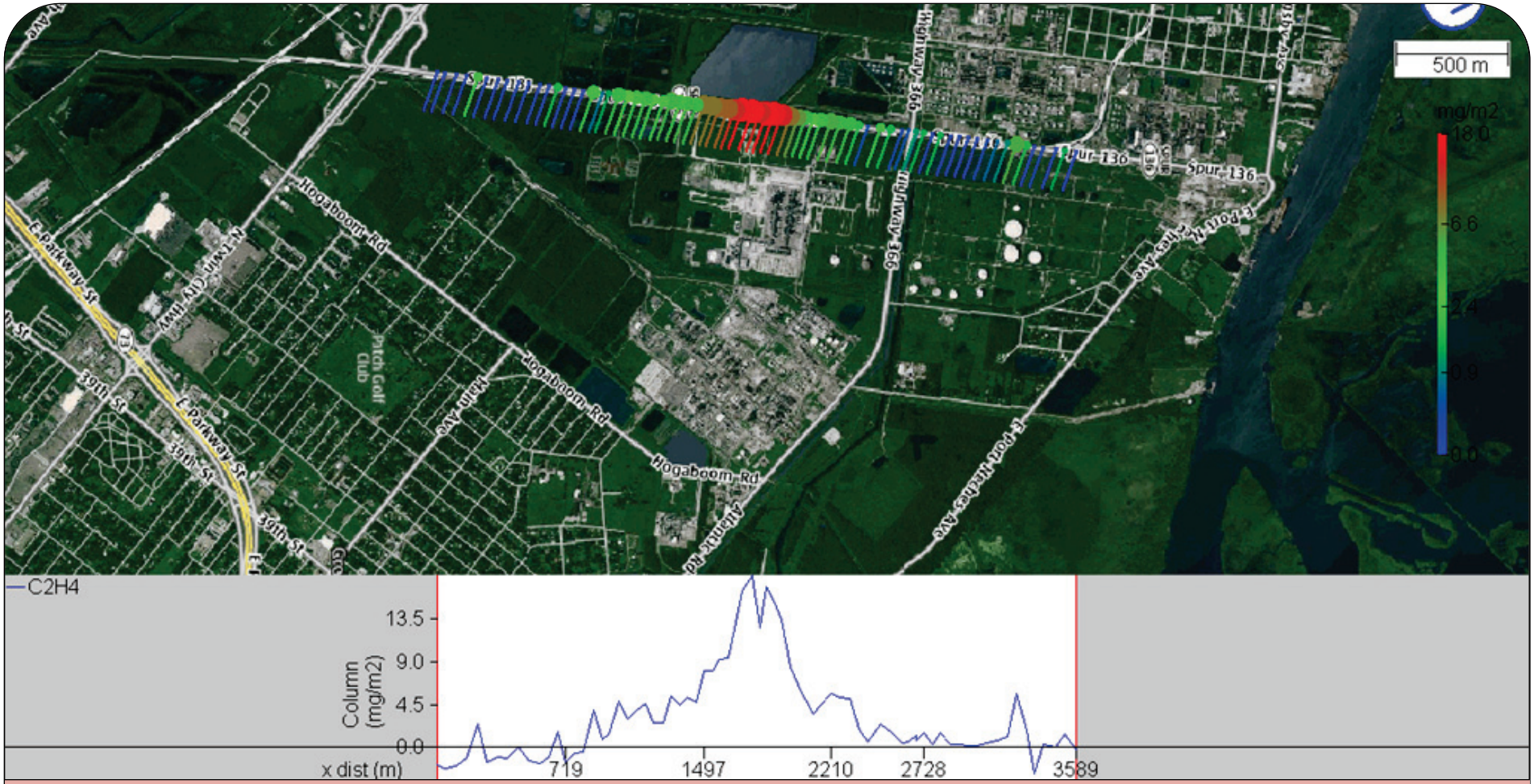
Total average emissions: 7412 kg/h

10 most abundant NMHCs[1] (at downwind site)	Inside Beaumont source (can#12)[2] (01:38-01:40 CDT)	Downwind (can#22,34)[3] (03:07-03:09 CDT)
i-butane	65.08	5.45 (±0.20)
ethane	45.48	10.67 (±0.10)
propane	27.72	8.88 (±0.22)
n-butane	15.17	4.48 (±0.10)
i-butene	12.26	0.81 (±0.10)
c-2-butene	8.81	0.01 (±0.00)
t-2-butene	8.40	0.05 (±0.02)
1-butene	6.97	0.09 (±0.00)
propylene	5.01	0.52 (±0.08)
i-pentane	4.35	7.12 ((±0.01)



Canister sampling

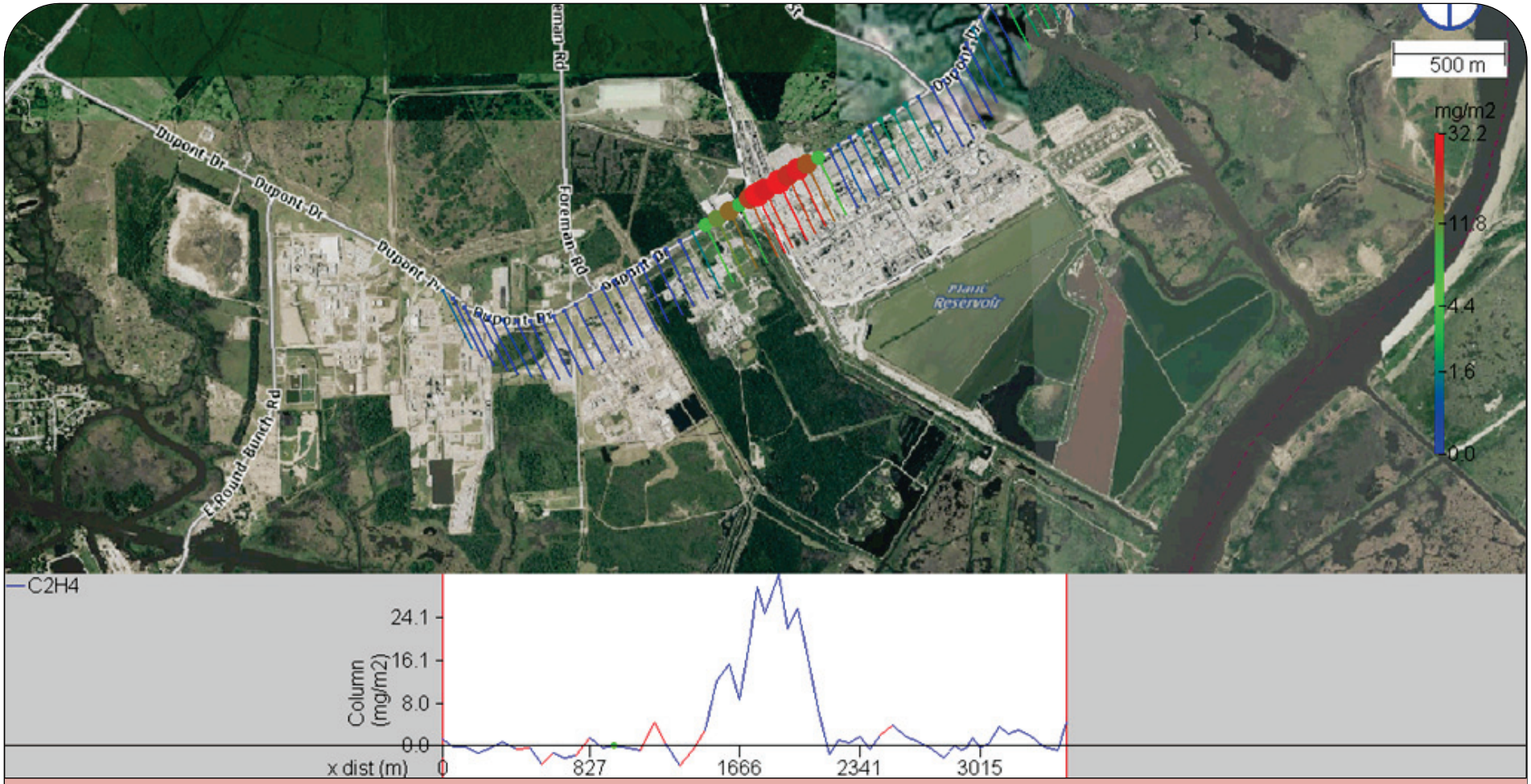
Example of canister sampling in Beaumont



Ethene in Beaumont / Port Arthur

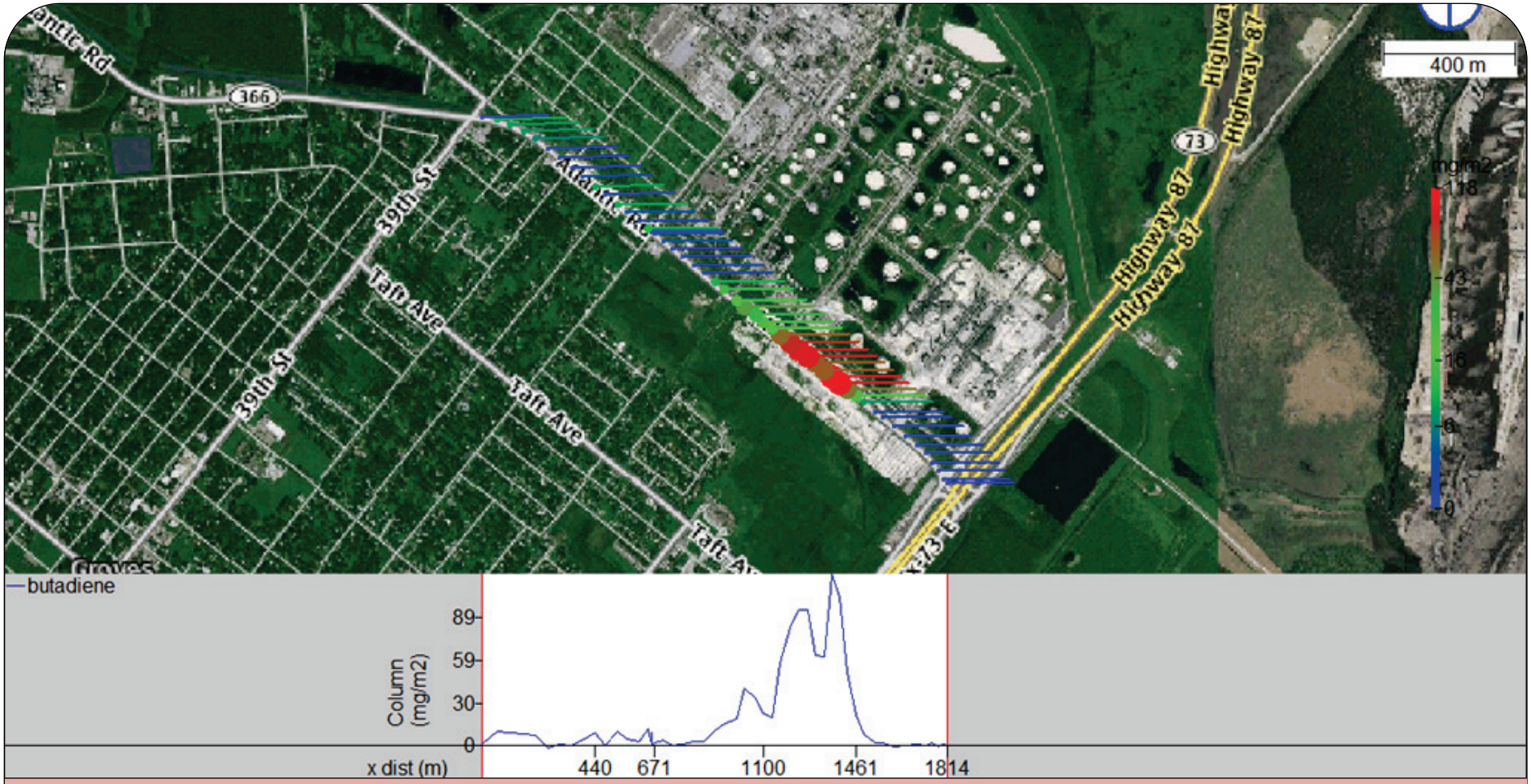
Largest source was Area 4: 93 kg/h

Total emissions: 179 kg/h



Ethene in Orange

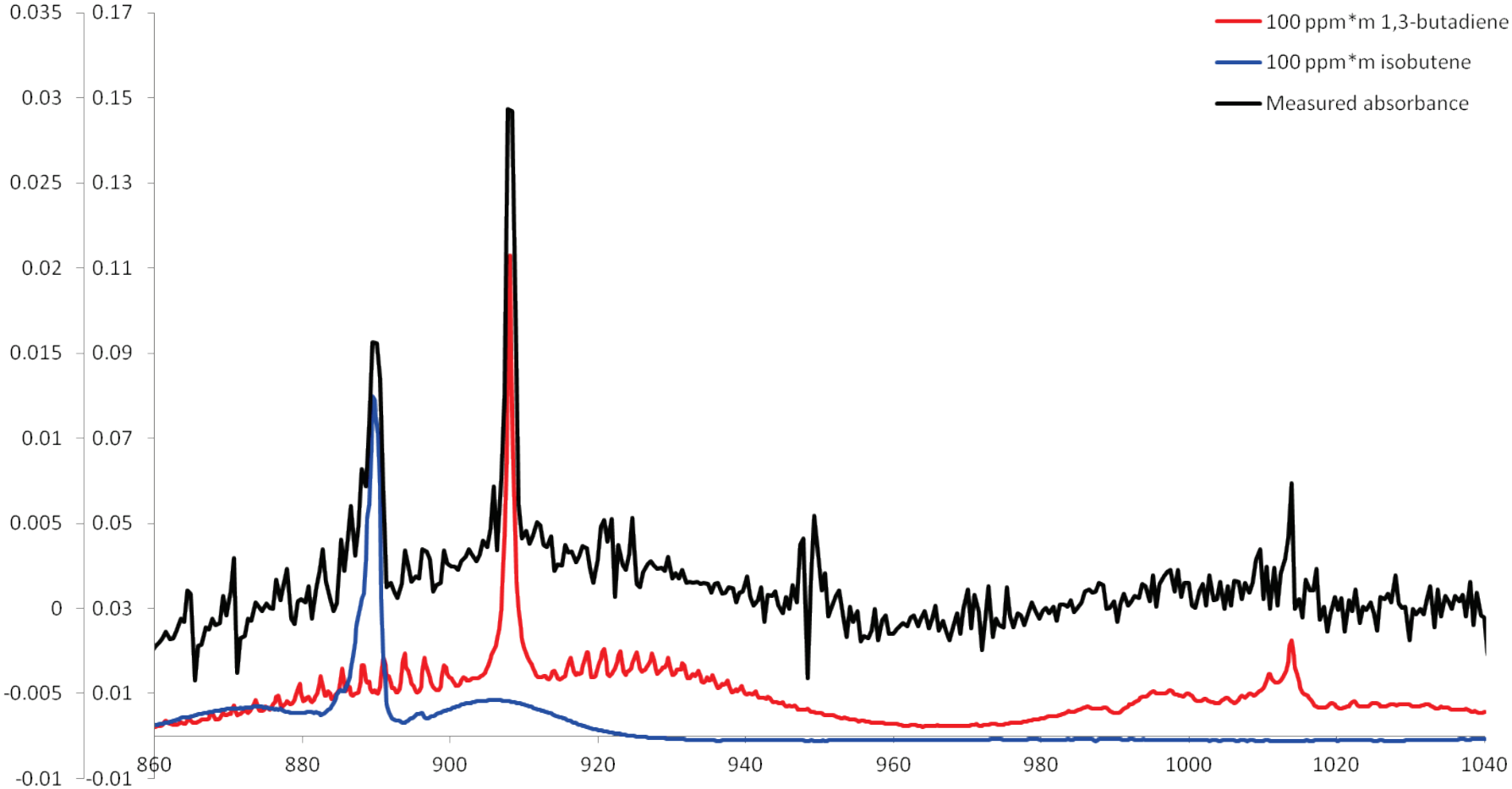
Average emission: 197 kg/h



1,3-butadiene and isobutene from Area 5

1,3-butadiene: 235 kg/h

Isobutene: 48 kg/h



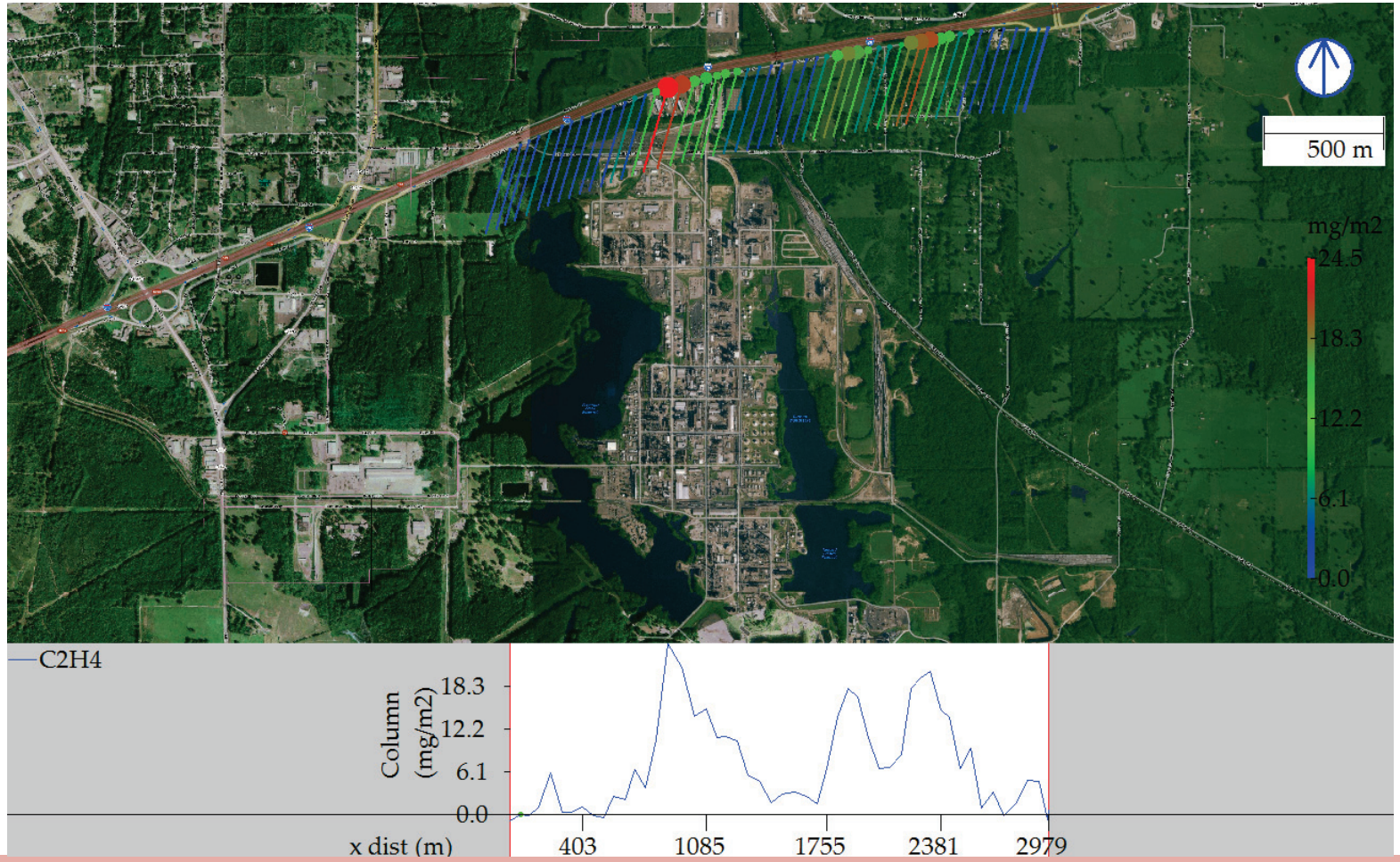
Spectral fit for 1,3-butadiene and isobutene

Normally hard to evaluate but large column concentration makes for a very clear signal

SO_2 from Coker Plant in Port Arthur

BPA area 8: 904 kg/h SO_2

BPA area 7: 354 kg/h SO_2

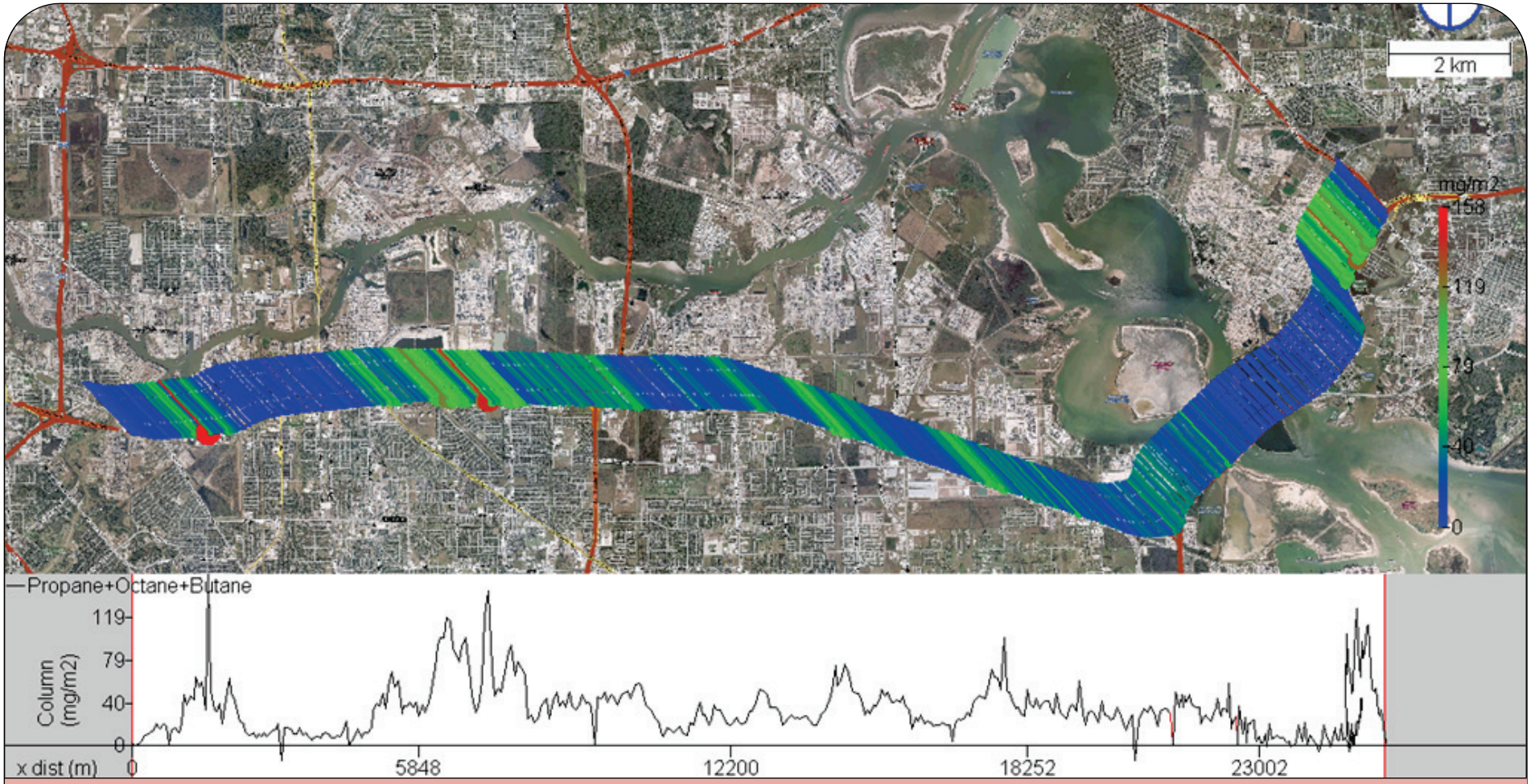


Longview

Ethene: 452 kg/h

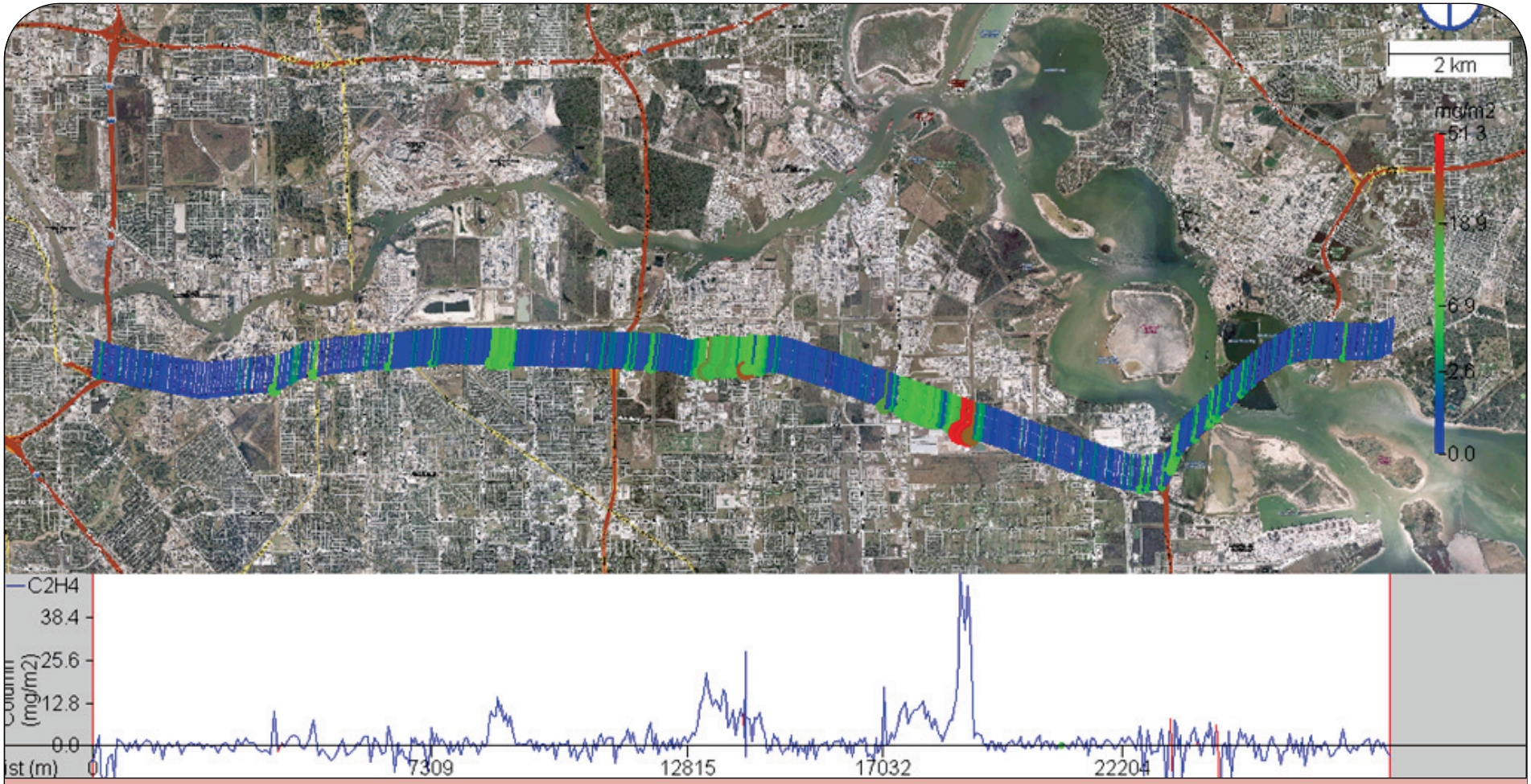
Propene: 282 kg/h

Alkanes: 841 kg/h



Alkanes in Houston Ship Channel

Total emissions 11 569 kg/h



Alkenes in Houston Ship Channel

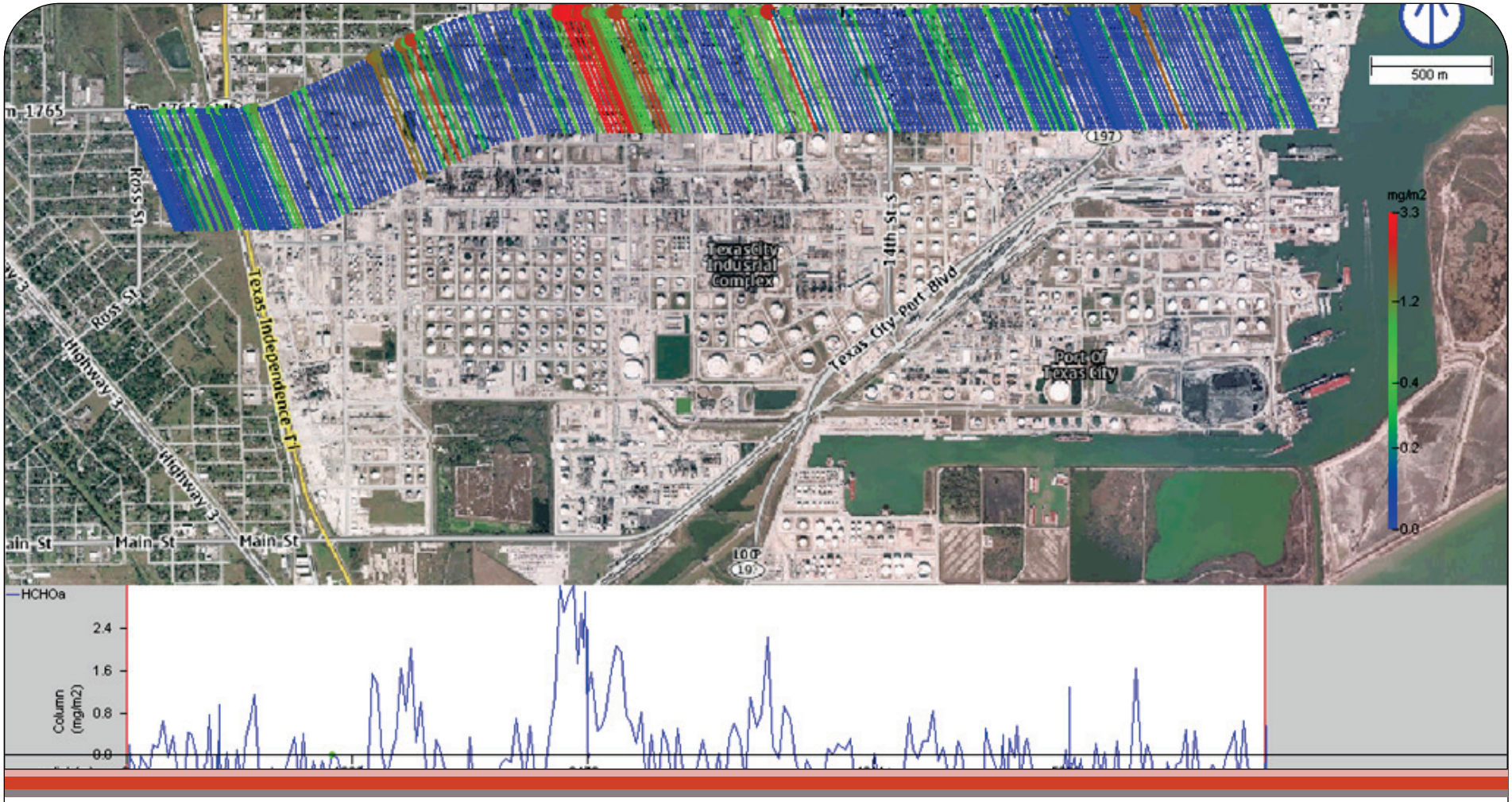
Ethene: 612 kg/h

Propene: 563 kg/h

Summary flux measurements

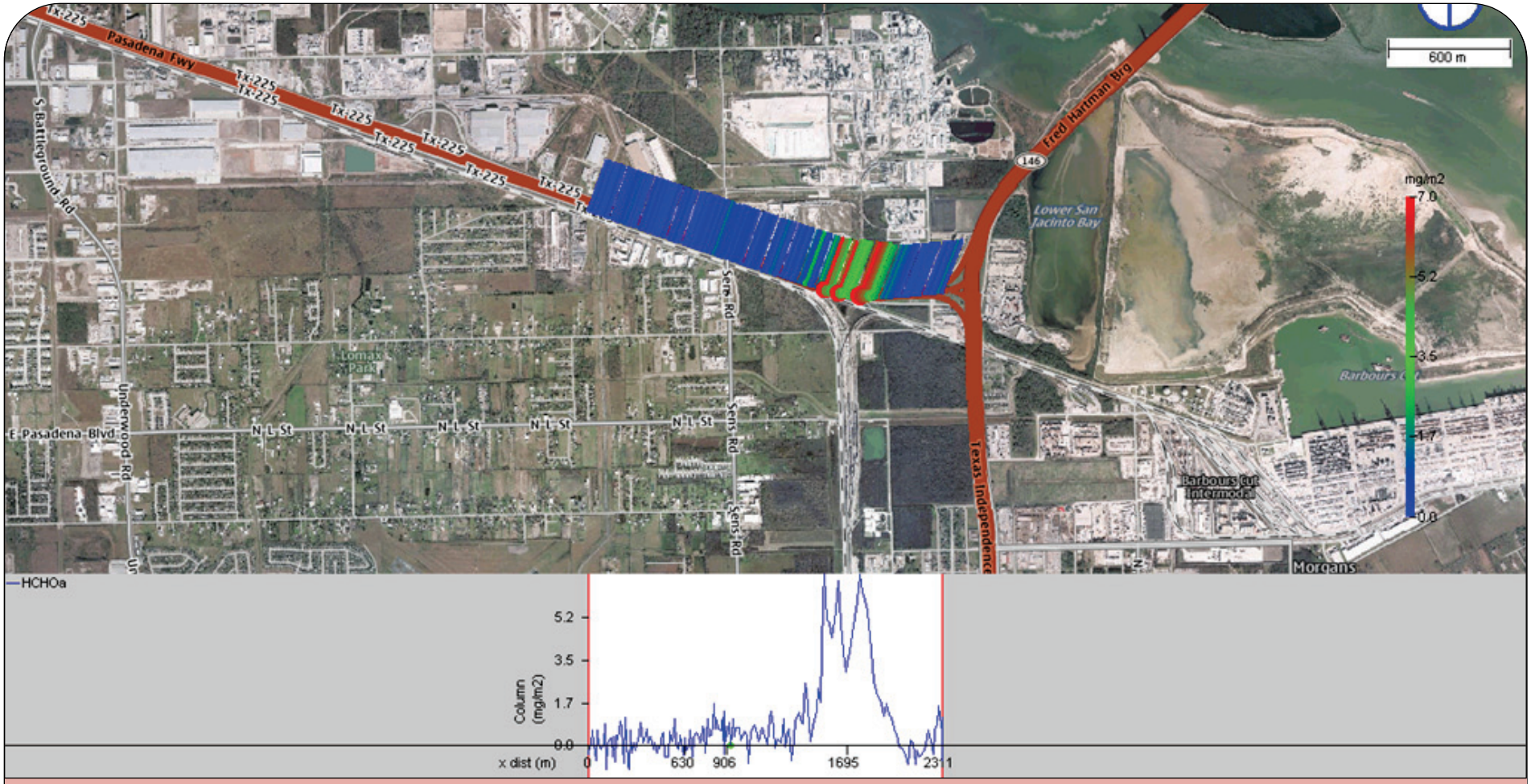
Source region	Species	SOF/DOAS 2011 (kg/h)	SOF/DOAS 2009 (kg/h)	SOF/DOAS 2006 (kg/h)	Inventory 2009 (kg/h)	Inventory 2006 (kg/h)	Inventory 2004 (kg/h)
Total HSC	Ethene	612	580	804	74	64	60
	Propene	563**	624	1653	77	140	80
	Alkane	11569	10134	11528	851	1483	1500
	SO_2	2328	3364		1967	2585	2552
	NO_2	1829			1297*		
Mont Belvieu	Ethene	545	429	443	65	81	45
	Propene	58**	310	488	28	35	12
	Alkane	1319	1837	863	244	190	261
	NO_2	305	168		192*	189*	268*
Texas City	Ethene	177	118	83	4	7	9
	Propene	56**	54	ND	8	9	11
	Alkane	2342	2598	2889	318	372	240
	SO_2	1209	834		327	596	613
	NO_2	492	283		387*	452*	883*
Beaumont / Port Arthur	Ethene	179			24		
	Propene	54**			20		
	Alkane	7412			457		
	SO_2	1611			1114		
	NO_2	1421			1145*		
Longview	Ethene	452			113		
	Propene	282			32		
	Alkane	841			87		
	NO_2	176			207*		

* NO_x is reported, ** degraded measurement quality



Formaldehyde in Texas City

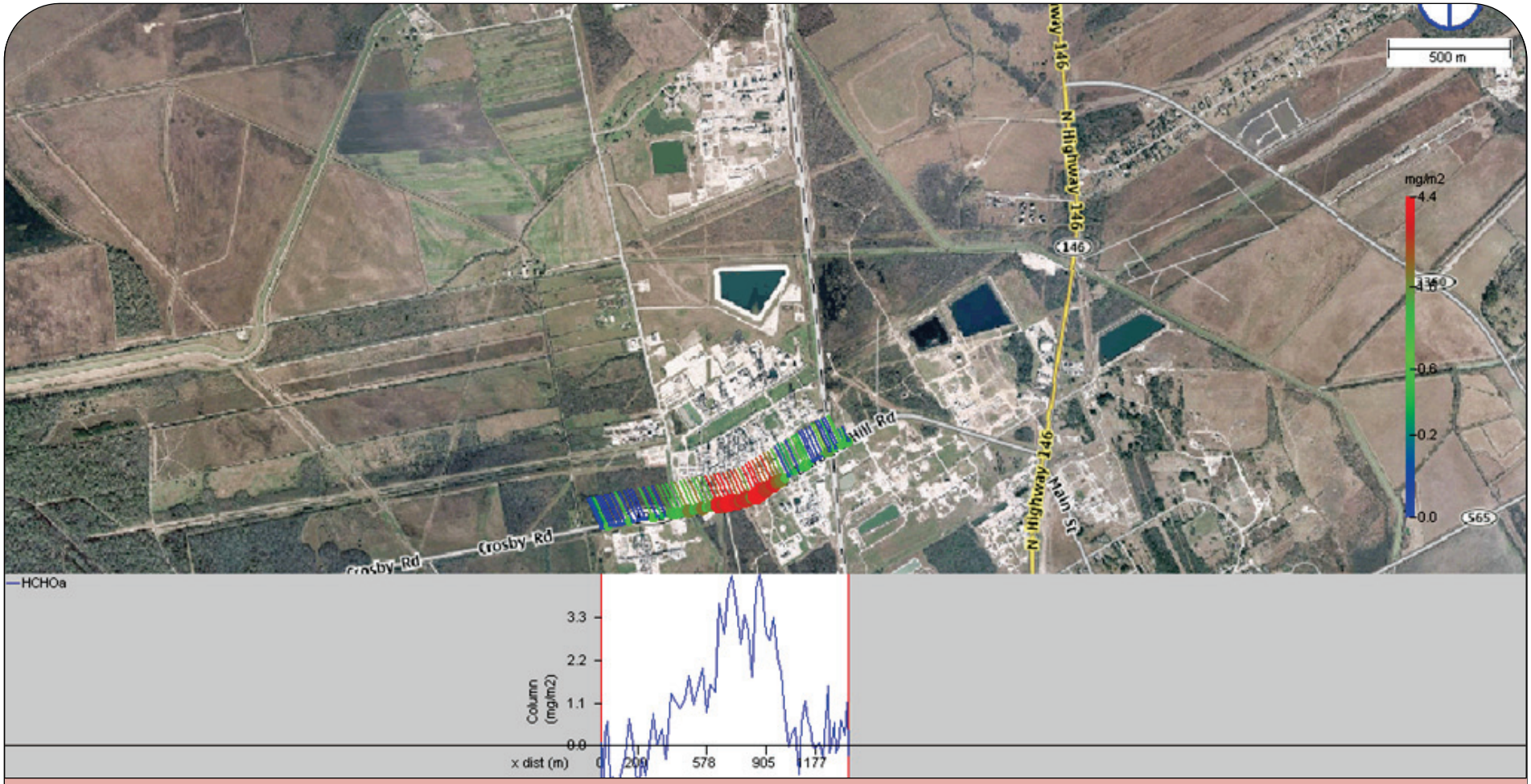
Three sources: 26, 15 and 10 kg/h respectively. All measurements from a single day.



Formaldehyde in Houston Ship Channel

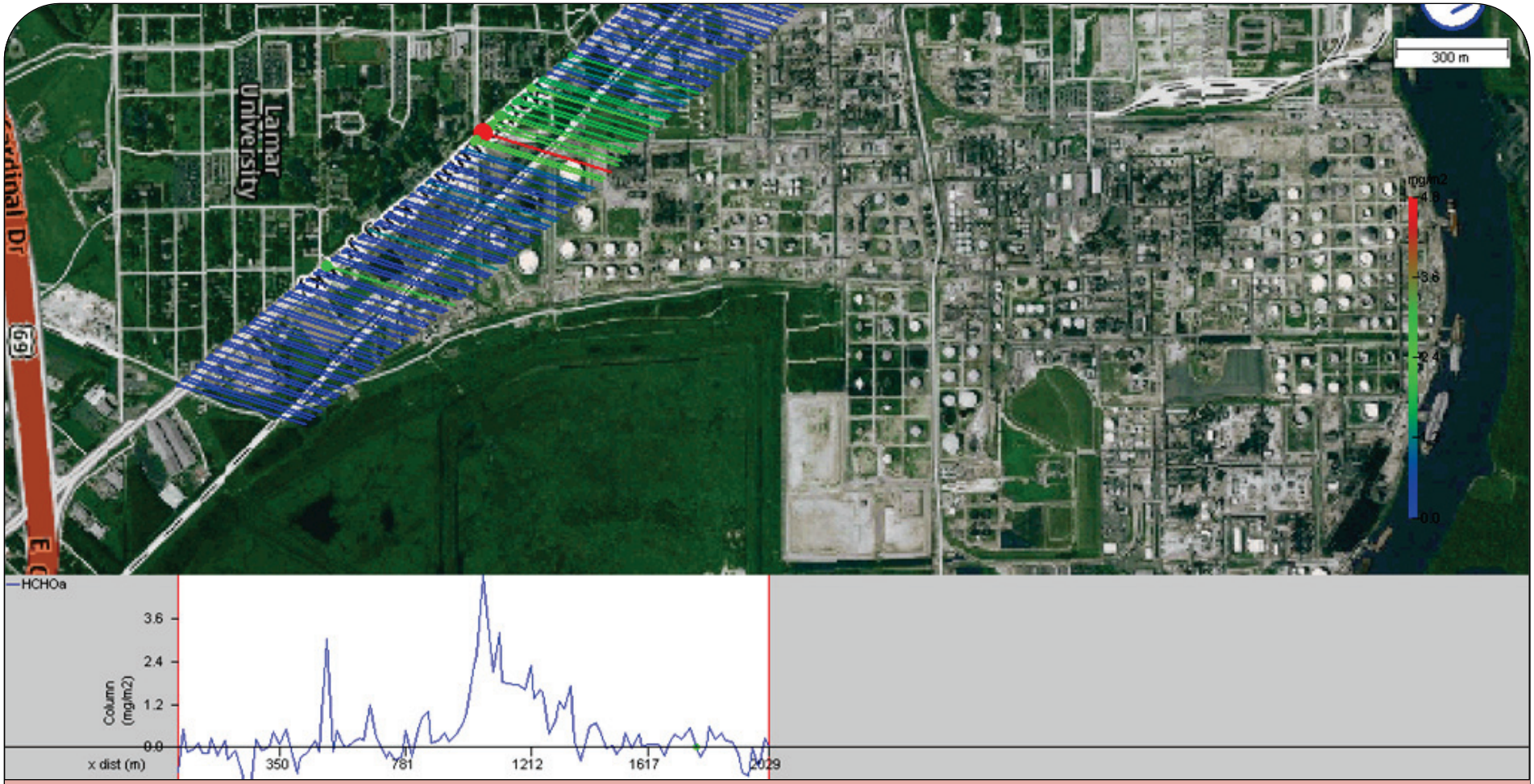
Large source close toJefferson Road seen again: 39 kg/h

New source found close to the Fred Hartman Bridge: 30 kg/h



Formaldehyde in Mont Belvieu

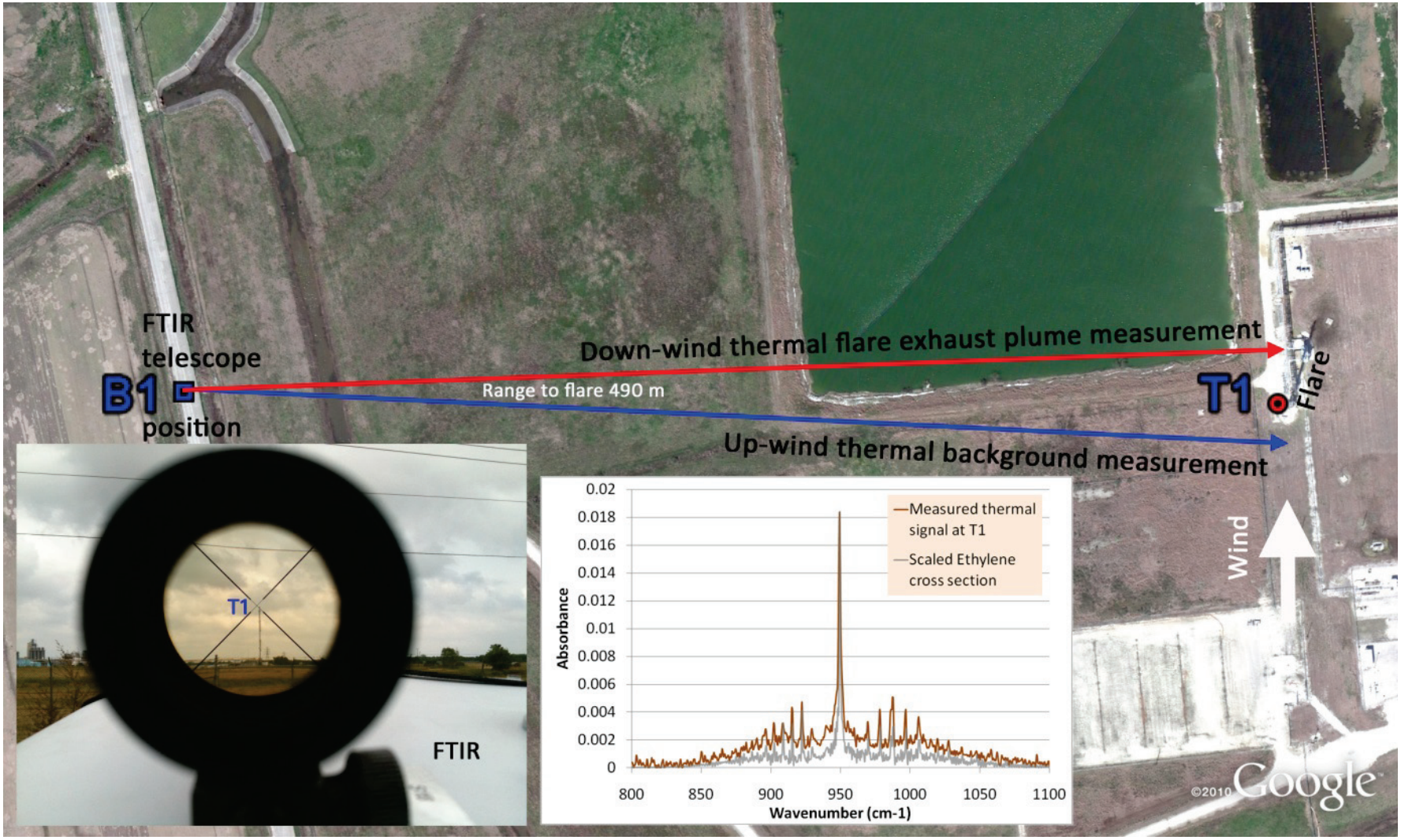
One source in northern Mont Belvieu: 19.5 kg/h



Formaldehyde in Beaumont / Port Arthur

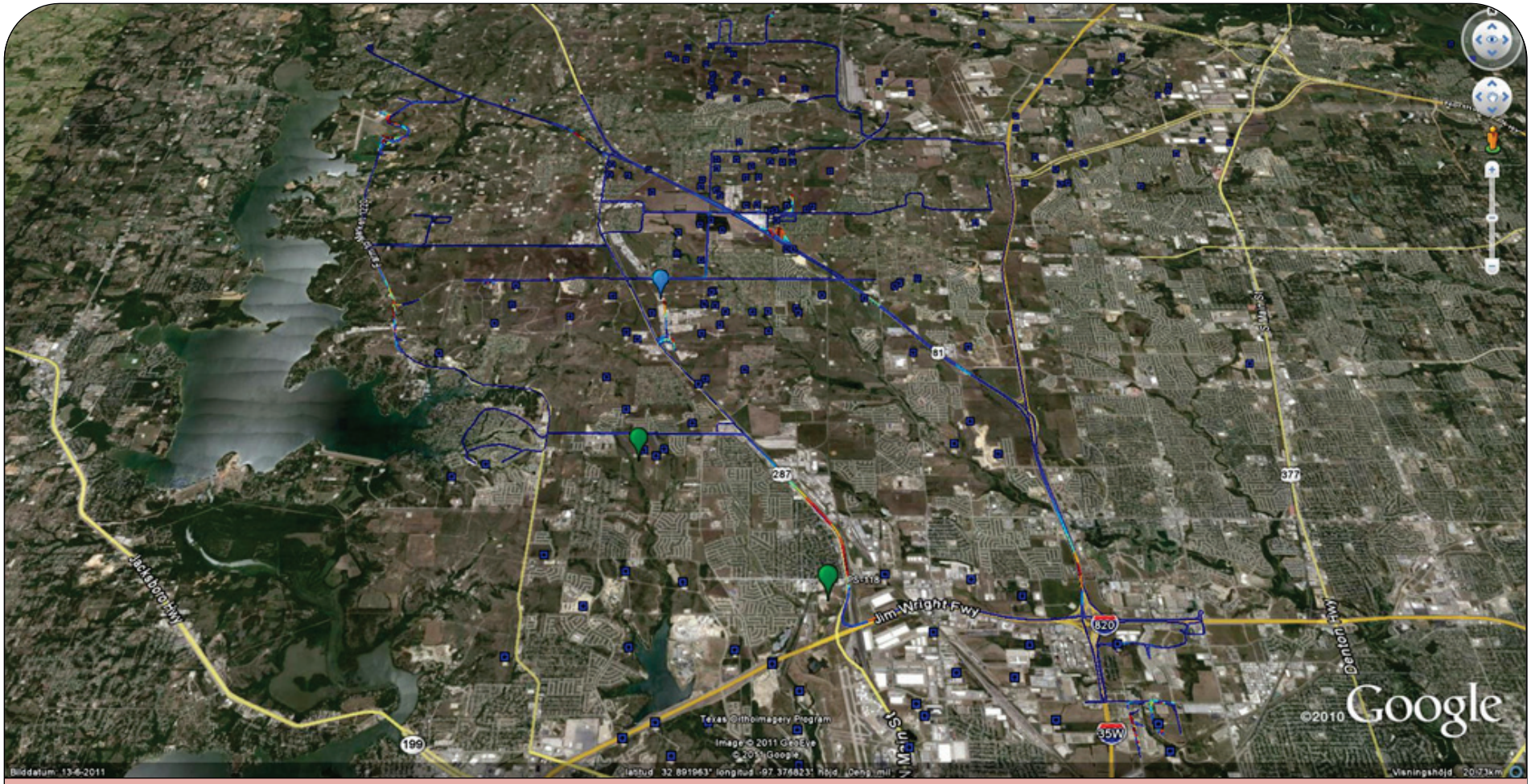
Three sources of formaldehyde: 27, 10 and 9 kg/h respectively.

Thermal emission FTIR



Thermal emission FTIR

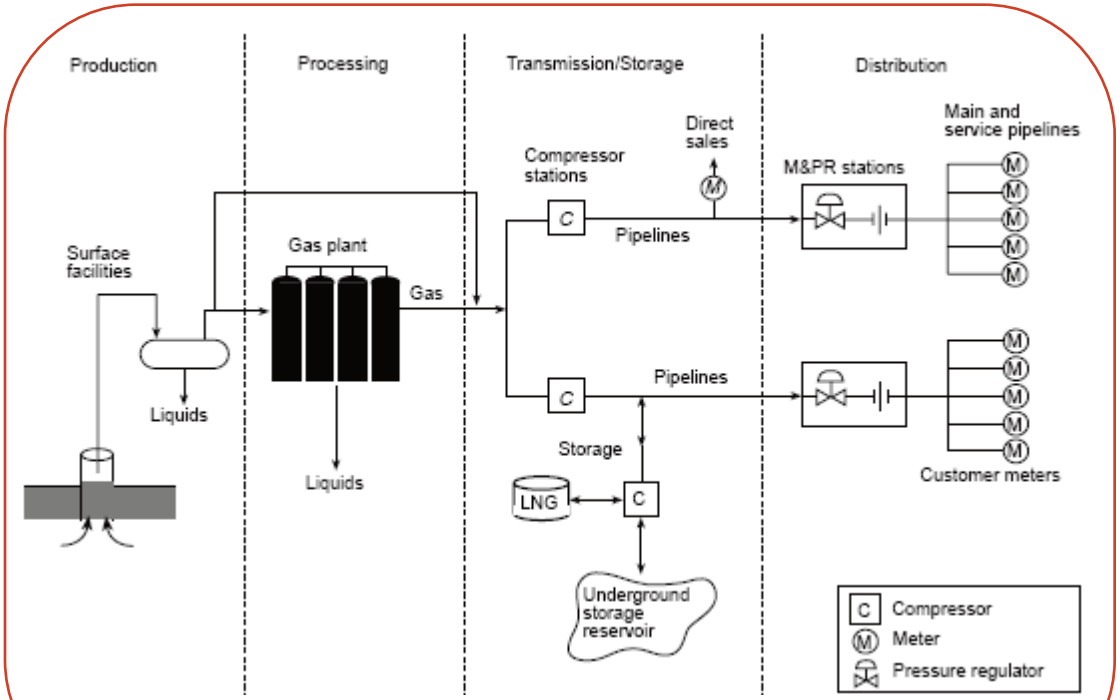
- 25 different sources studied, mostly flares
- 5 sources showed distinct ethene content and 2 showed distinct propene content
- 6 sources showed weak or ambiguous ethene content and 3 showed weak propene content



Overview of meFTIR measurements

Also shown: Sampling sites from FWAQS. General classification as wellheads (blue square), other (light blue) or compressor stations (green).

Location of sites

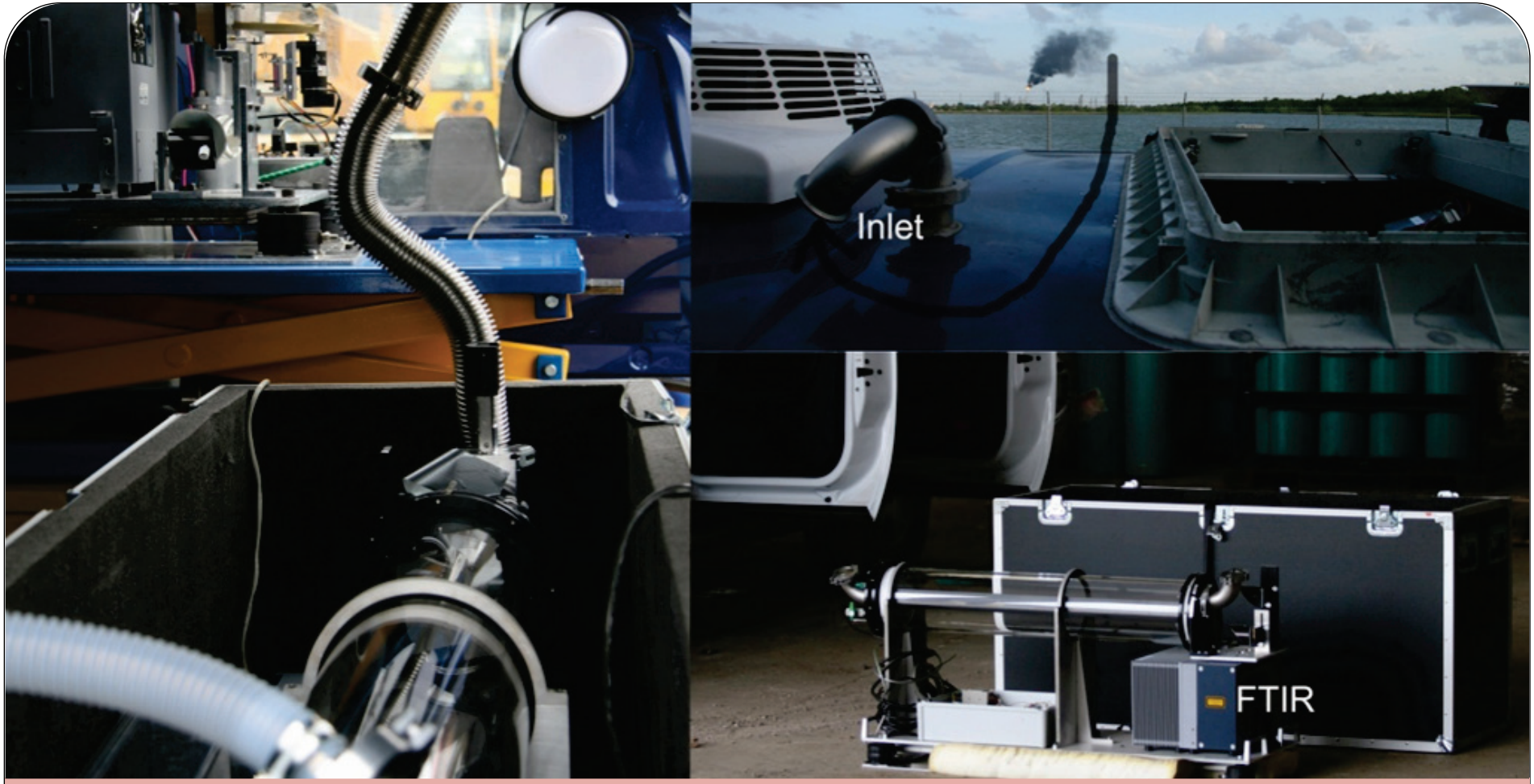


Adapted from Armendariz, 2008

- Drilling
- Wellhead Production (4-5 sites)
  - separators
  - on-site storage
  - compressors
- Processing Plant (Hicks RD)
- Transmission/Storage (2 – 3 sites)
  - compressor station
  - condensate
- Distribution
  - Broken gas main

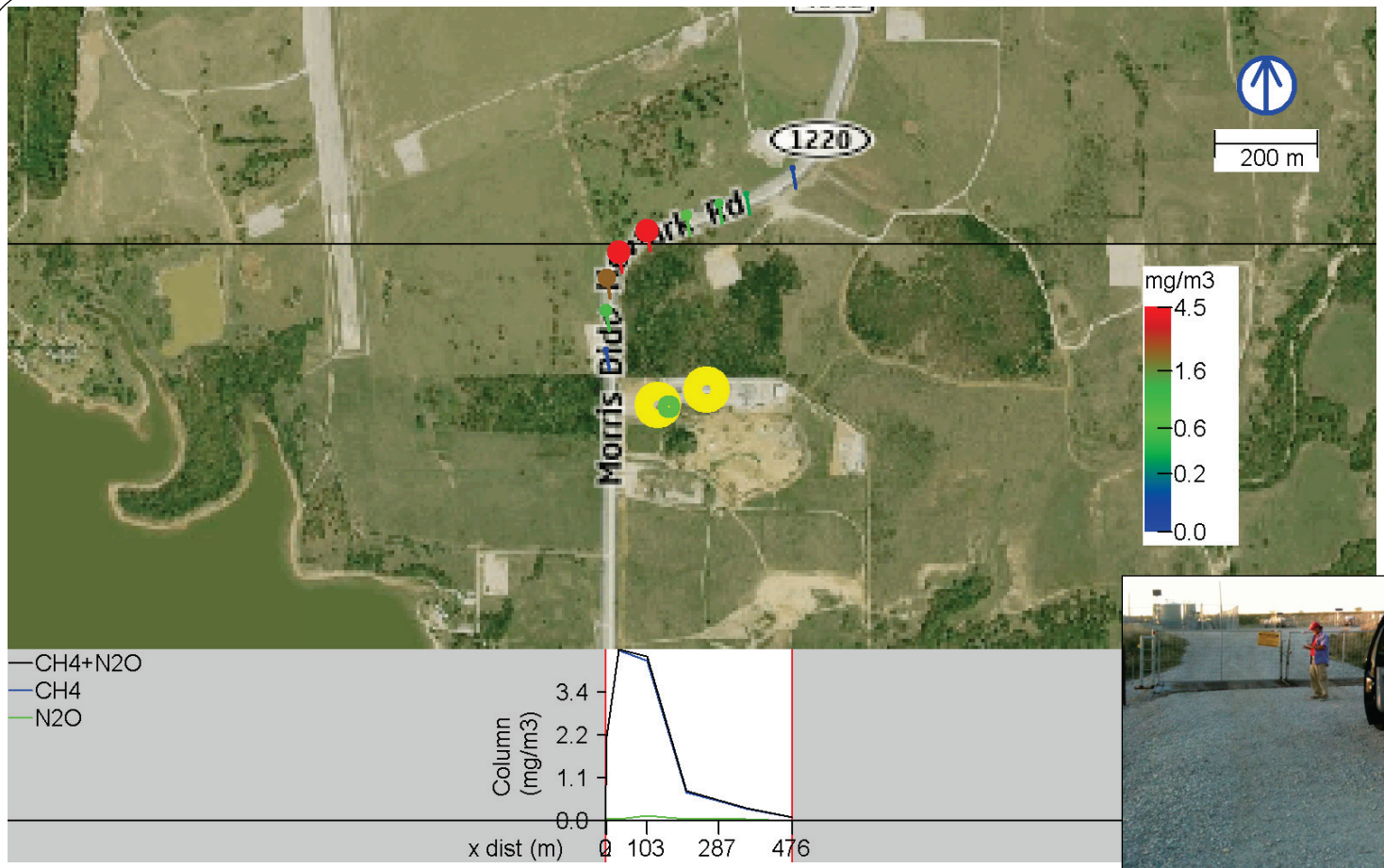
Natural gas production VOC emission sources

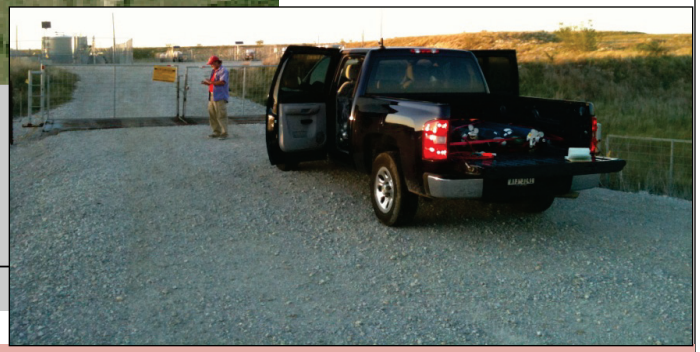
The main processes involved in the natural gas production in the Barnett Shale. Emissions were measured from all sectors during the week long campaign.



Mobile Extractive FTIR and Tracer (N_2O)

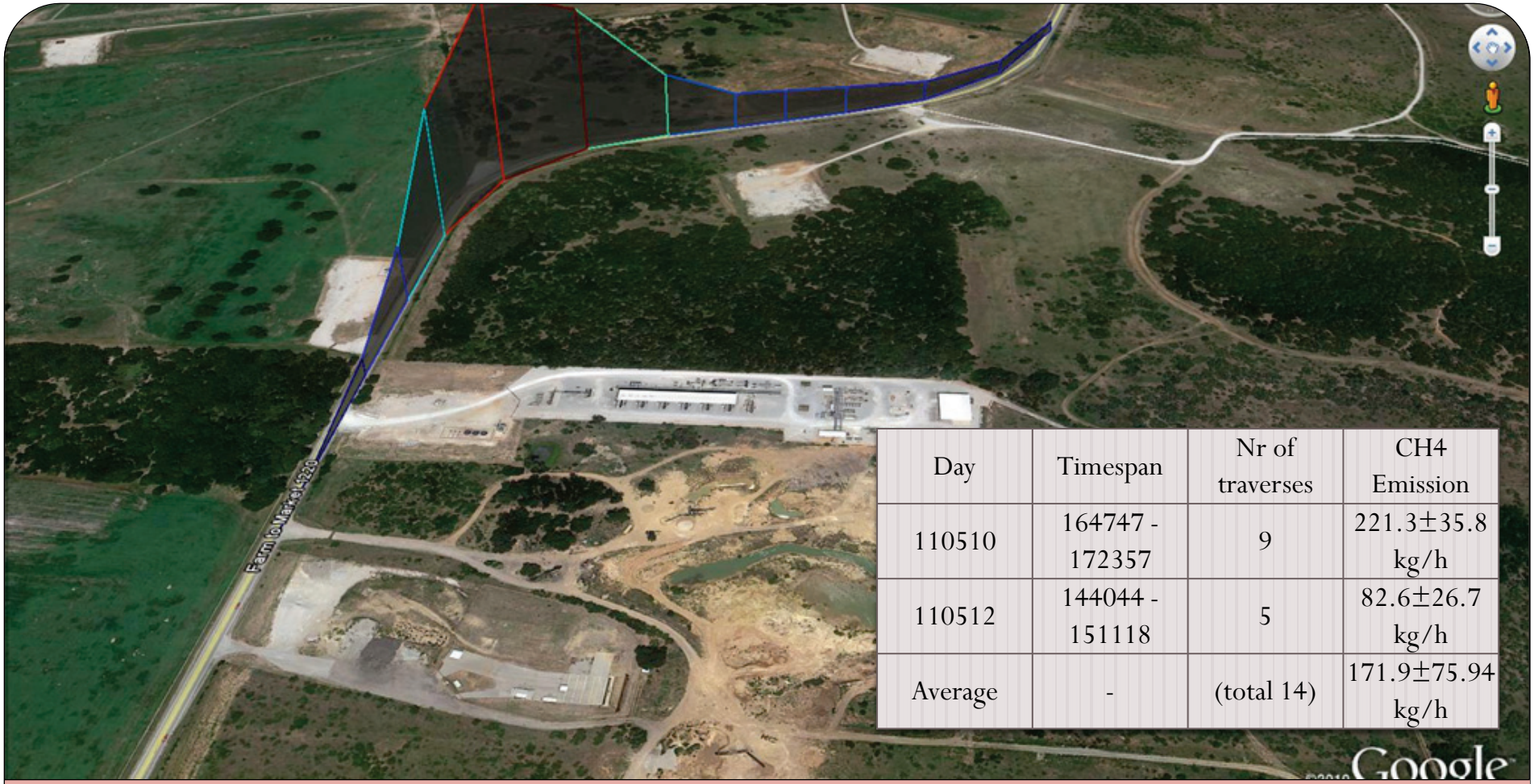
Bruker Matrix FTIR Spectrometer with InSb and MCT detectors coupled to optical cell with variable path length.





Example of a tracer measurement

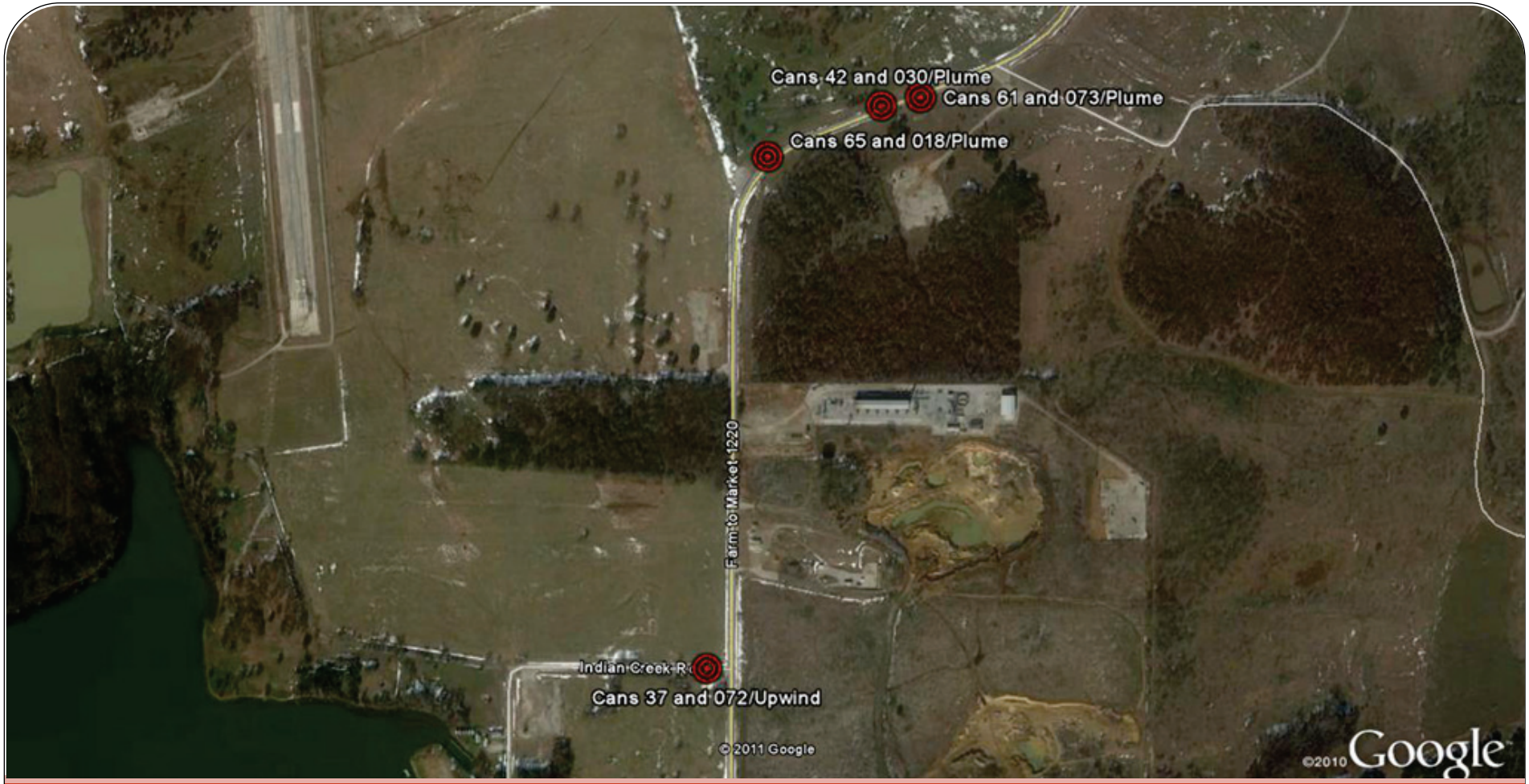
Tracer was released from a stationary location as near to the emissions source as access permitted. Mass rate of tracer was set depending on meteorology and distance.



Day	Timespan	Nr of traverses	CH4 Emission
110510	164747 - 172357	9	221.3±35.8 kg/h
110512	144044 - 151118	5	82.6±26.7 kg/h
Average	-	(total 14)	171.9±75.94 kg/h

FM 1220 – Compressor station

On one of the days storage tanks (west of compressor area) were a large source of emissions.

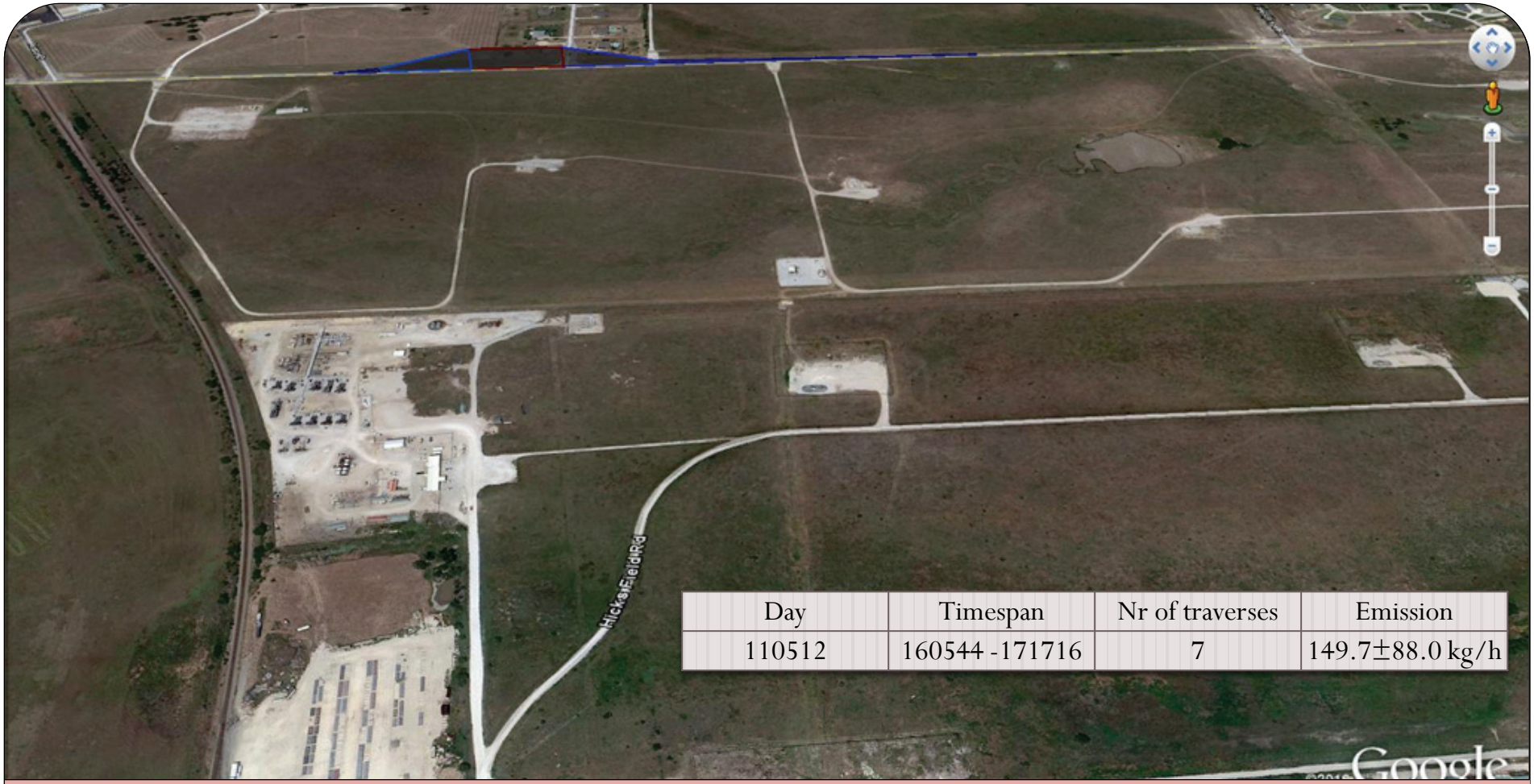


Canister Result FM 1220

10 most abundant NMHCs[1] (at downwind site)	Downwind (can#65,18)[2] (17.53-17:55 CDT)	Upwind (can#37,72)[2] (19:25-19:27 CDT)	Difference (downwind - upwind)
ethane	308.21 (±4.15)	13.49 (±0.26)	+294.72
ethylene	61.72 (±2.31)	1.12 (±0.01)	+60.60
propane	11.11 (±0.41)	3.49 (±0.06)	+7.62
n-butane	1.10 (±0.05)	1.12 (±0.09)	-0.02
propylene	1.01 (±0.10)	0.27 (±0.03)	+0.74
i-butane	0.81 (±0.01)	0.68 (±0.01)	+0.13
i-pentane	0.49 (±0.04)	0.59 (±0.01)	-0.10
acetylene	0.41 (±0.01)	0.41 (±0.01)	0.0
n-pentane	0.31 (±0.01)	0.43 (±0.01)	+0.12
isoprene	0.31 (±0.04)	0.29 (±0.03)	-0.02

Meacham Blvd & Long Rd – Compressors, Separators,Well head

Very high concentrations noted from Meacham or Long site on 9 May.



Day	Timespan	Nr of traverses	Emission
110512	160544 -171716	7	149.7±88.0 kg/h

Hicks Field Rd – Processing Plant

Tracer released south of site at bottom of image.

#	Name	Site	Comment	CH4 emission kg/h	C2H4/CH4 (m/m)	CO kg/h
1	FM 1220	Compressor station, well pad and treatment facility	2 meas. days. Large emissions from well on May 11, potentially due to regeneration. 6 compressors	172	5.4%	8
2	Hicks Field Rd	Treatment plant and compressor station	12 compressors	150	9%	37±23
3	Blue Mound Rd	Treatment plant and compressor station	6 compressors	120	3%	
4	Northern cross Rd	Well pads and mobile compressor	2 condensate tanks, 1 compressor	8	6.6%	0.4±0.4
5	Meacham Blvd	Compressor station, and gas separators and well pad	1 compressor	17	6.5%	0.6±0.4
6	Long Avenue	Compressor station	3 compressors	8	11%	10±2
7	Eagle Mt Rd	Well pads, distribution pipes	In the vicinity of compressor station and power station	6	3%	1.1±1.1
8	E Peden Rd (1)	Well pad	2 condensate tanks	~1	NA	0.1±0.05
9	E Peden Rd 2	Well pad	3 condensate tanks and potentially leaking pipeline	~1	12.5% (pipeline)	0.1±0.0
10	Bonds Ranch Rd	Well pad	2 tanks	~1	NA	0±0.17

Summary of Results

Largest emissions were seen from compressor and processing operations and storage tanks. For many well pads without aboveground storage, compressors or separators, emissions were below detection limits measured from the road. Measurements would have required site access. Or more nighttime measurements.

Emission category	Comment	Emission (kg/h)
Compressor station, and treatment facility	6–12 compressors	CH_4: 80-150 CO: 0-40 C_2H_6: 5-10 C_3H_8: 0.03-0.8 C_2H_4: 0-0.4
Small Compressor station, and gas separators and well pad	1–3 compressor	CH_4: 8-17 CO: 0.4-10 C_2H_6:1
Well pads	2–3 condensate tanks	CH_4: 1 CO: 0.1±0.05 C_2H_6: 0-0.12
Well pad	Flashing emission from condensate tank with open valve	CH_4: 138.7 CO: 0 C_2H_6: 10.6 C_3H_8: 0.40 C_2H_4: 2.04 C_3H_6:0.04 C_5H_6: 0.01

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