

# Quantification of industrial emissions of VOCs, NO<sub>2</sub> and SO<sub>2</sub> by SOF and mobile DOAS during DISCOVER AQ

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# Objective

- Column measurements of  $\text{NO}_2$ , and  $\text{SO}_2$  and HCHO in the Houston ship channel, for future comparisons with Airborne NASA data.
- Measurements of VOC emissions using SOF in Houston Ship Channel for added value to ozone modelling.

# Methods

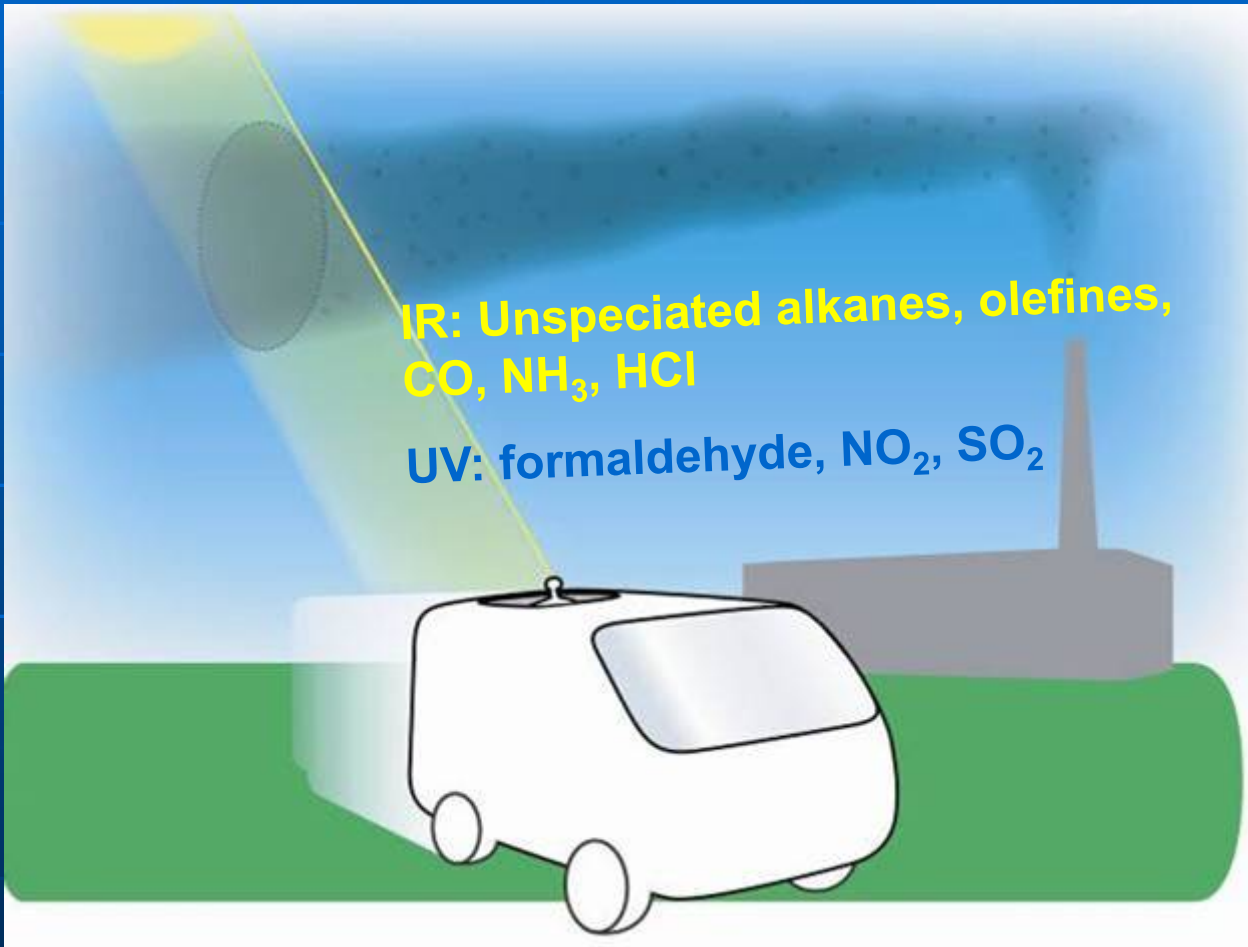
- SOF (alkanes, alkanes)
- Mobile DOAS ( $\text{NO}_2$ ,  $\text{SO}_2$ , HCHO)
- Meteorological balloons

# Additional measurements, (outside the project)

- Alkane concentration measurements using Mobile extractive FTIR (meFTIR)
- Aromatic VOC concentration measurements using a UV multi reflection cell (MAC DOAS)

# Method . The Solar Occultation Flux method (SOF)

<http://www.youtube.com/watch?v=6cre9q8YAzE>



1) The number of various molecules above the SOF vehicle are estimated from spectroscopic analysis of direct solar IR light and zenith scattered UV light.

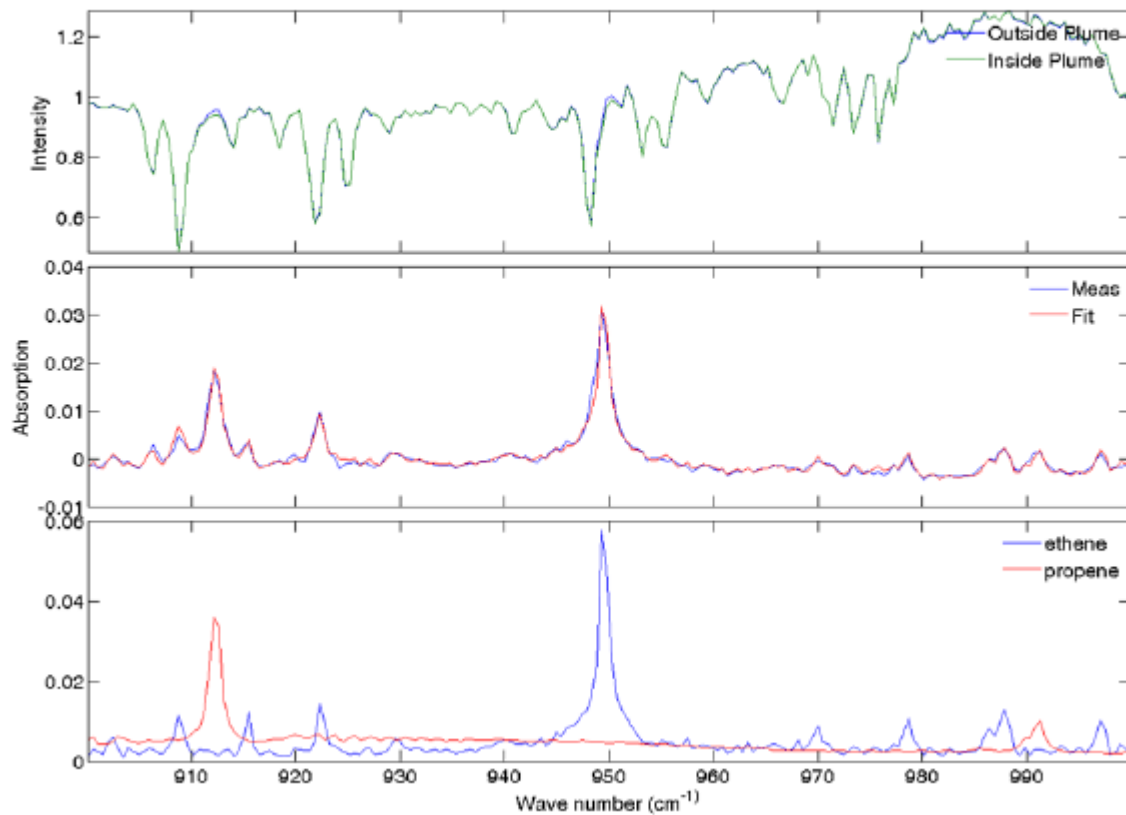
2) The measurements are conducted while driving and hence is it possible to **measure the total mass of molecules along the roads traveled.**

3) The total mass is multiplied by the wind which yields the flux in kg/s.

N.B Methane and aromatic VOCs not measured directly by SOF (yet) BUT by meFTIR and canister sampling

# SOF spectral fit

Example of spectral fit:



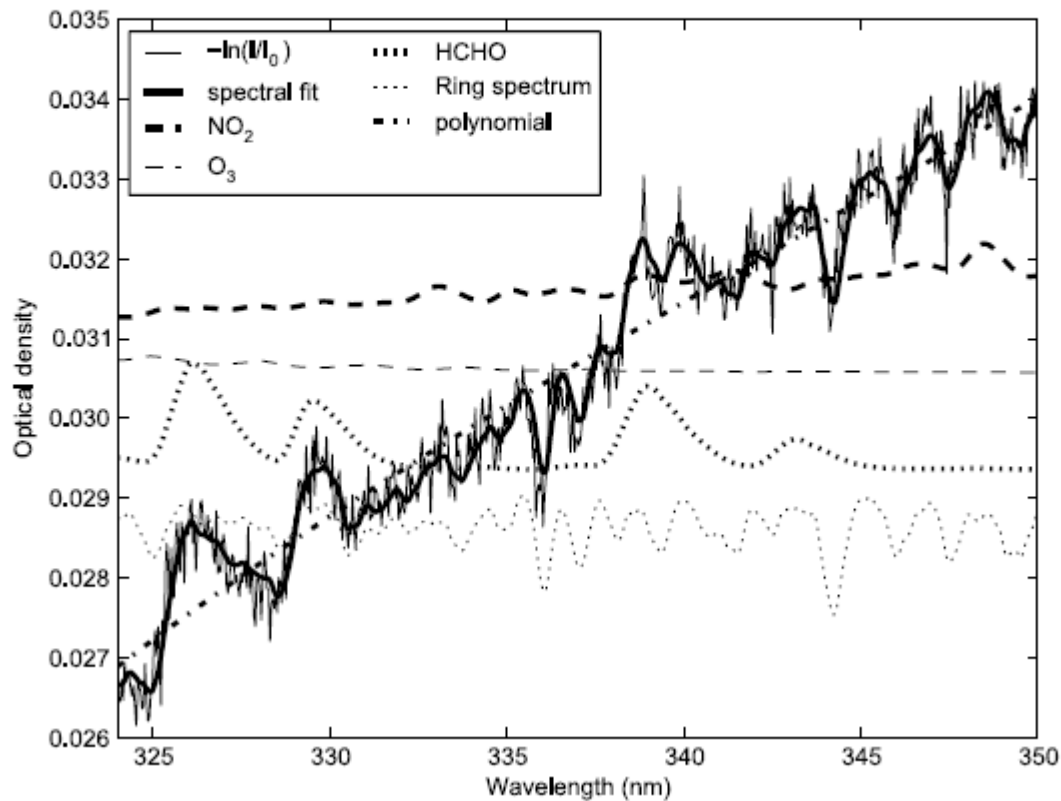
# Mobile DOAS

Mobile DOAS (Differential Optical Absorption Spectroscopy):

- Passive open path differential spectroscopy of **scattered** sun light
- Visible-UV light measured with a Czerny-Turner spectrograph and a thermo-electrically cooled CCD
- Spectral evaluations of  $\text{NO}_2$ ,  $\text{SO}_2$  and HCHO in the 310–350 nm wavelength window

# Mobile DOAS spectral fit

Example of spectral fit:





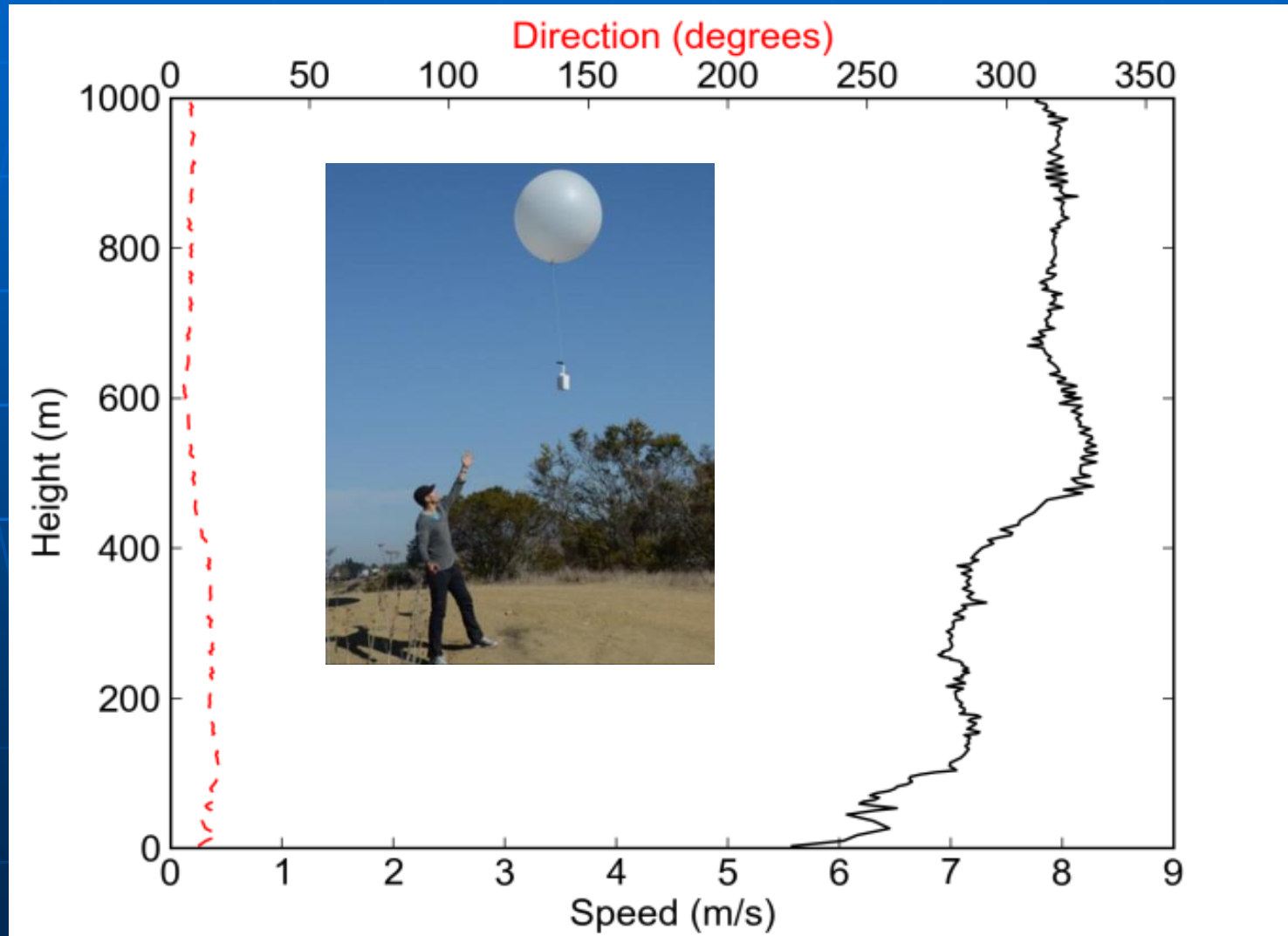
# Measurement van



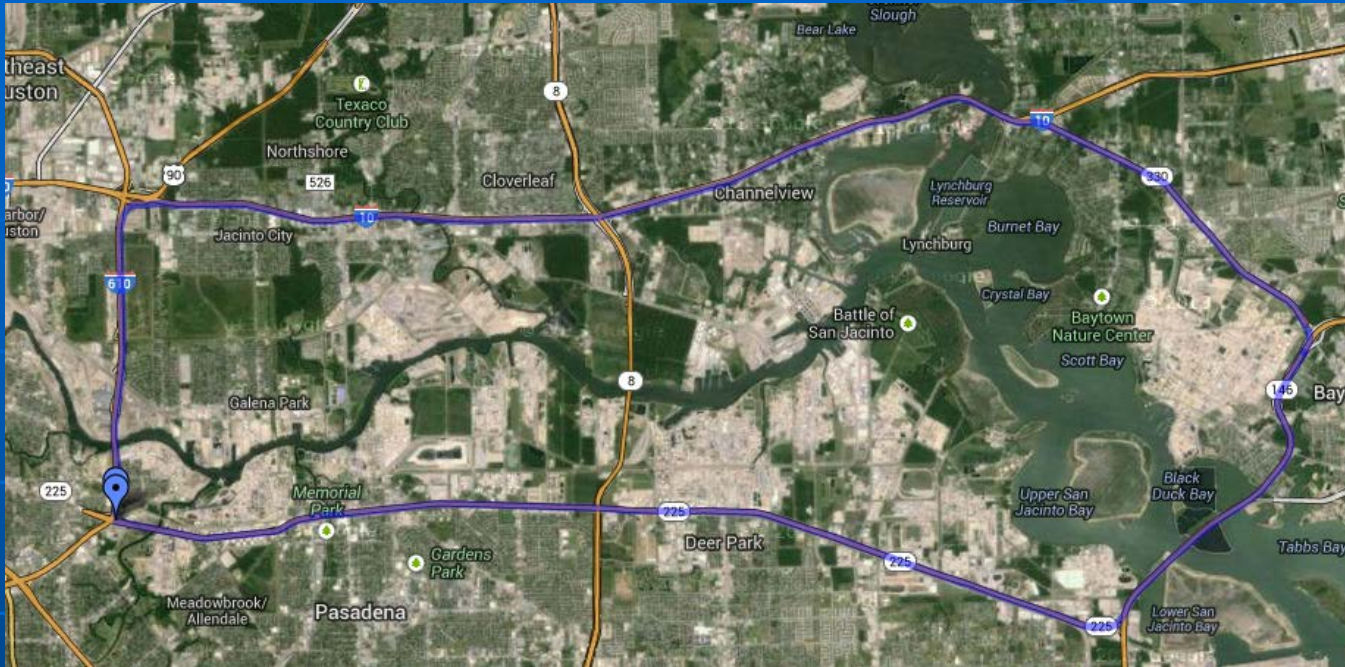
# Measurement van



Wind: Radio sonde launches will be combined with data from TCEQ wind masts to obtain wind speed and direction. Here Lynchberg ferry crossing on Sep 26.



# Measurement strategy



- SOF box measurements around the Houston ship channel were carried out on all flight days, 10 days
- Winds balloons were released from the Battleground area
- On non flight days more focused industrial measurements were carried out.

# Measurements

20 measurements days have been carried out, in varying meteorological conditions. Data evaluation is on going

Date	DISCOVER-AQ flight day	Independent SOF day	Weather conditions
Sep 3		X	Moderate
Sep 4	X		Poor
Sep 6	X		Poor
Sep 8		X (afternoon)	Moderate
Sep 9		X	Moderate
Sep 10		X	Poor
Sep 11	X		Moderate
Sep 12	X		Moderate/good
Sep 13	X		Moderate/poor
Sep 14	X		Poor

# Measurements (cont.)

Date	DISCOVER-AQ flight day	Independent SOF day	Weather conditions
Sep 15		X	Poor
Sep 16		X	Poor
Sep 18		X	Moderate
Sep 22		X	Moderate
Sep 23		X (afternoon)	Moderate
Sep 24	X		Moderate/good
Sep 25	X		Good
Sep 26	X		Good
Sep 27	X		Poor
Sep 28		X	Poor

# Measurements

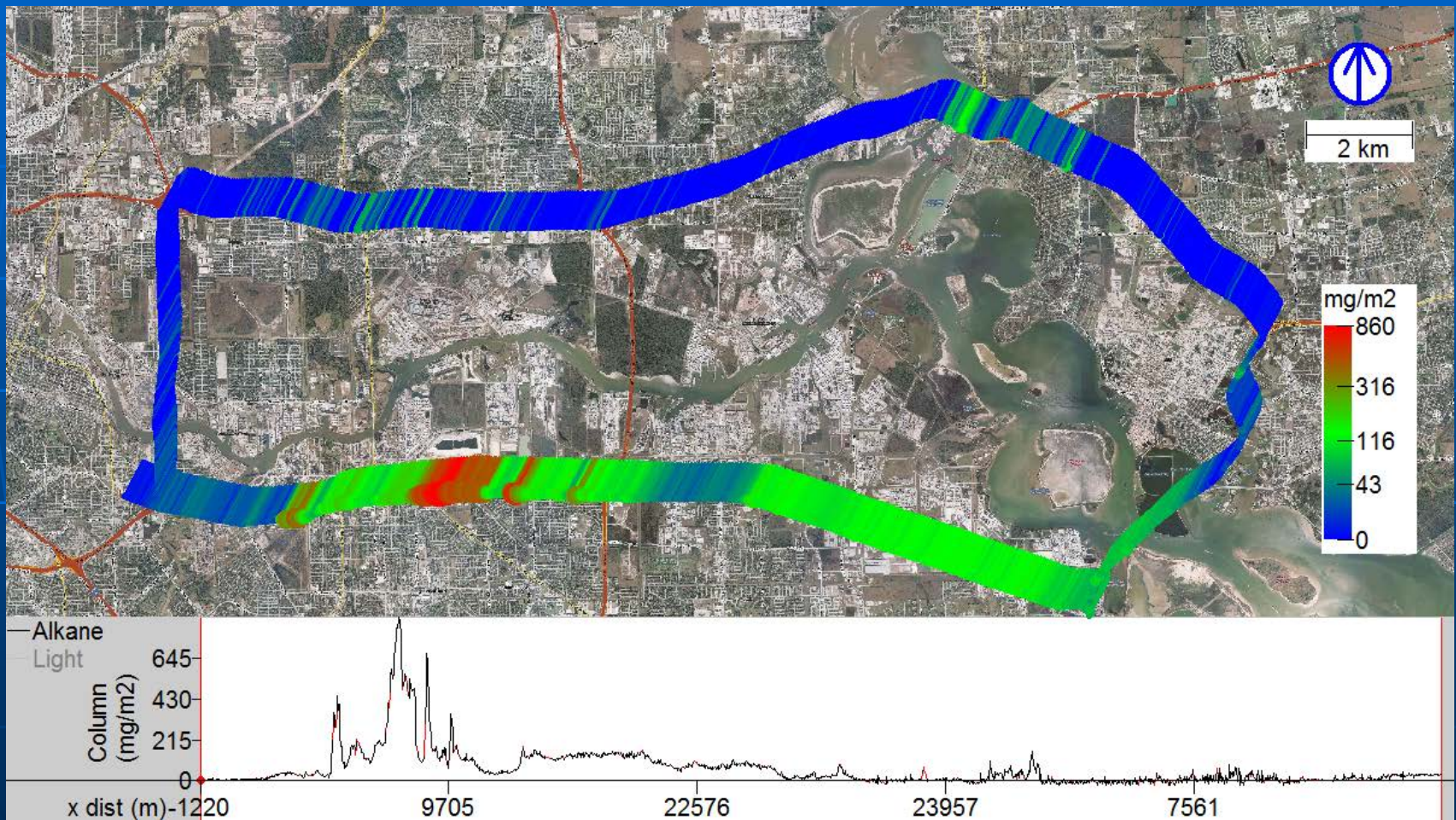
- The campaign period was dominated by cloudy weather and prevailing easterly wind, as seen in the measurement tables above.
- These weather conditions made SOF and Mobile DOAS measurements difficult. However, a frontal passage at the later part of the campaign brought improved weather conditions with mostly clear skies.
- The two objectives of the campaign were conflicting for easterly winds, i.e. coordinated column measurements with NASA in the large SOF box around HSC and industrial emission measurements of VOCs and other species. On flight days, which had the best weather, the first objective was prioritized and few good days were therefore available for the latter objective.
- The data are still being analysed and will be made available for the final report.

# Column measurements to support NASA Discover flights

- Some examples (data analysis on going)

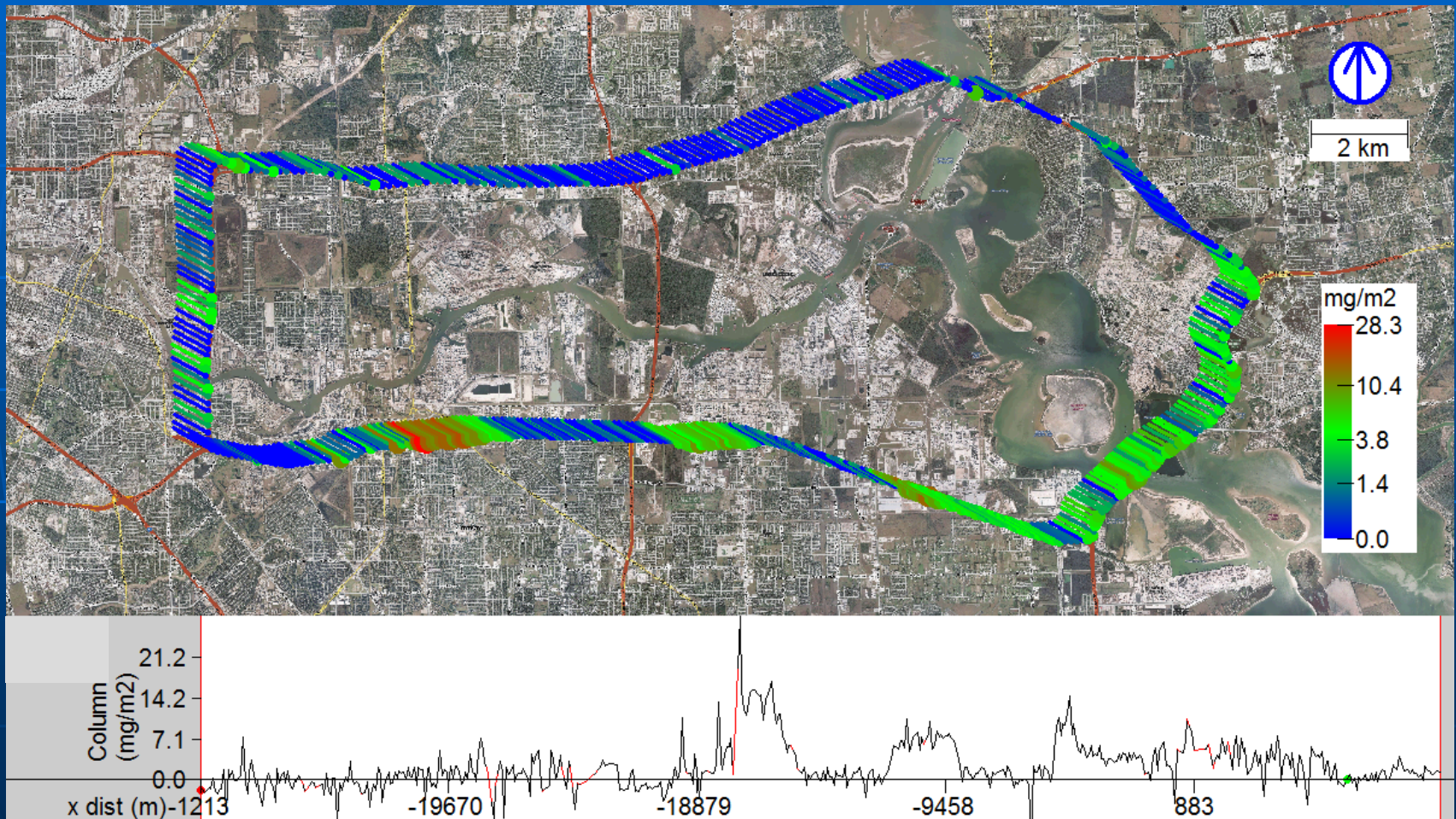


# Alkanes 13-09-25 15:40



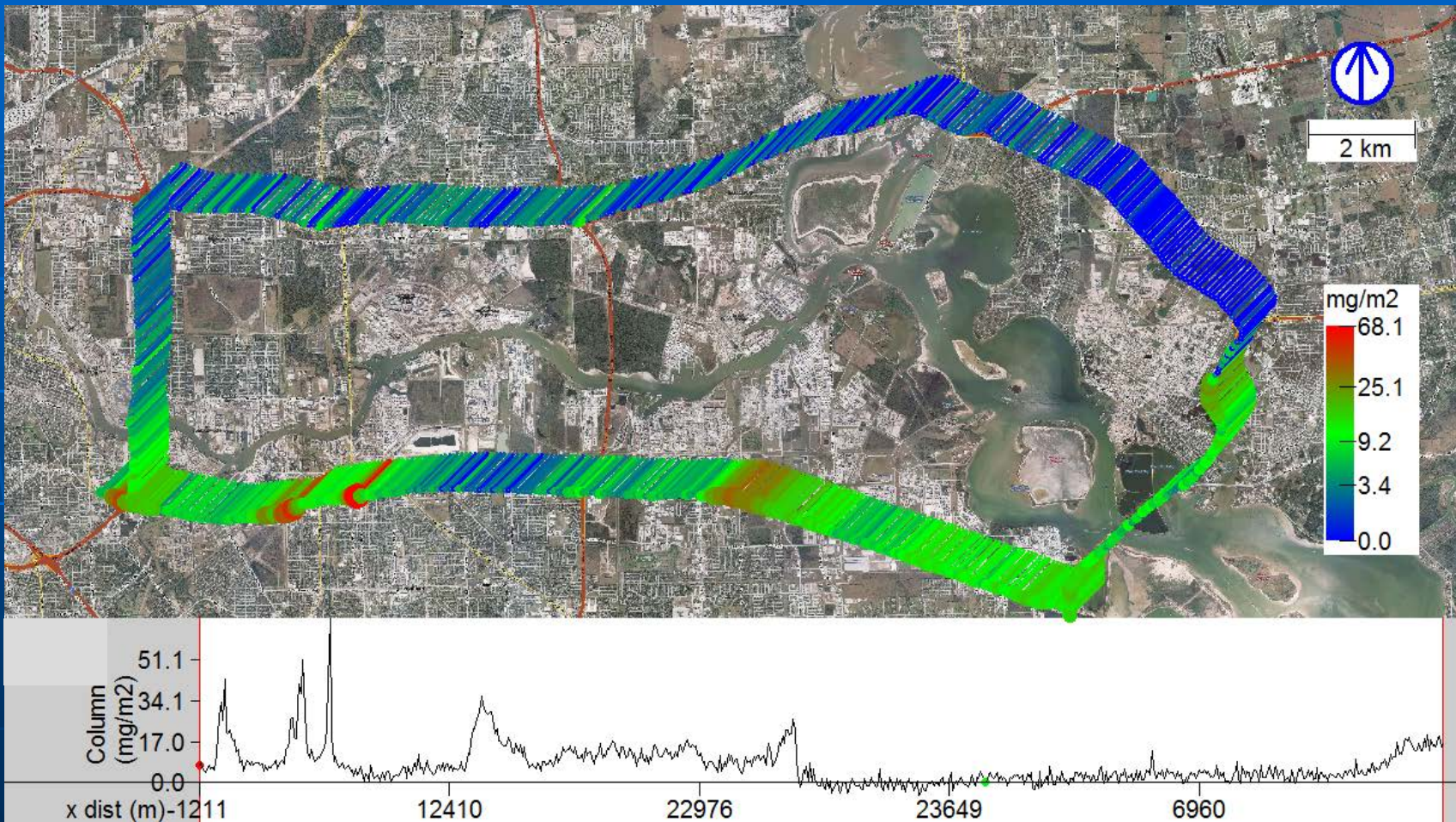
n.b. logarithmic color map

# Ethene 13-09-25 10:20



n.b. logarithmic color map

# SO<sub>2</sub> 13-09-25 15:40



n.b. logarithmic color map

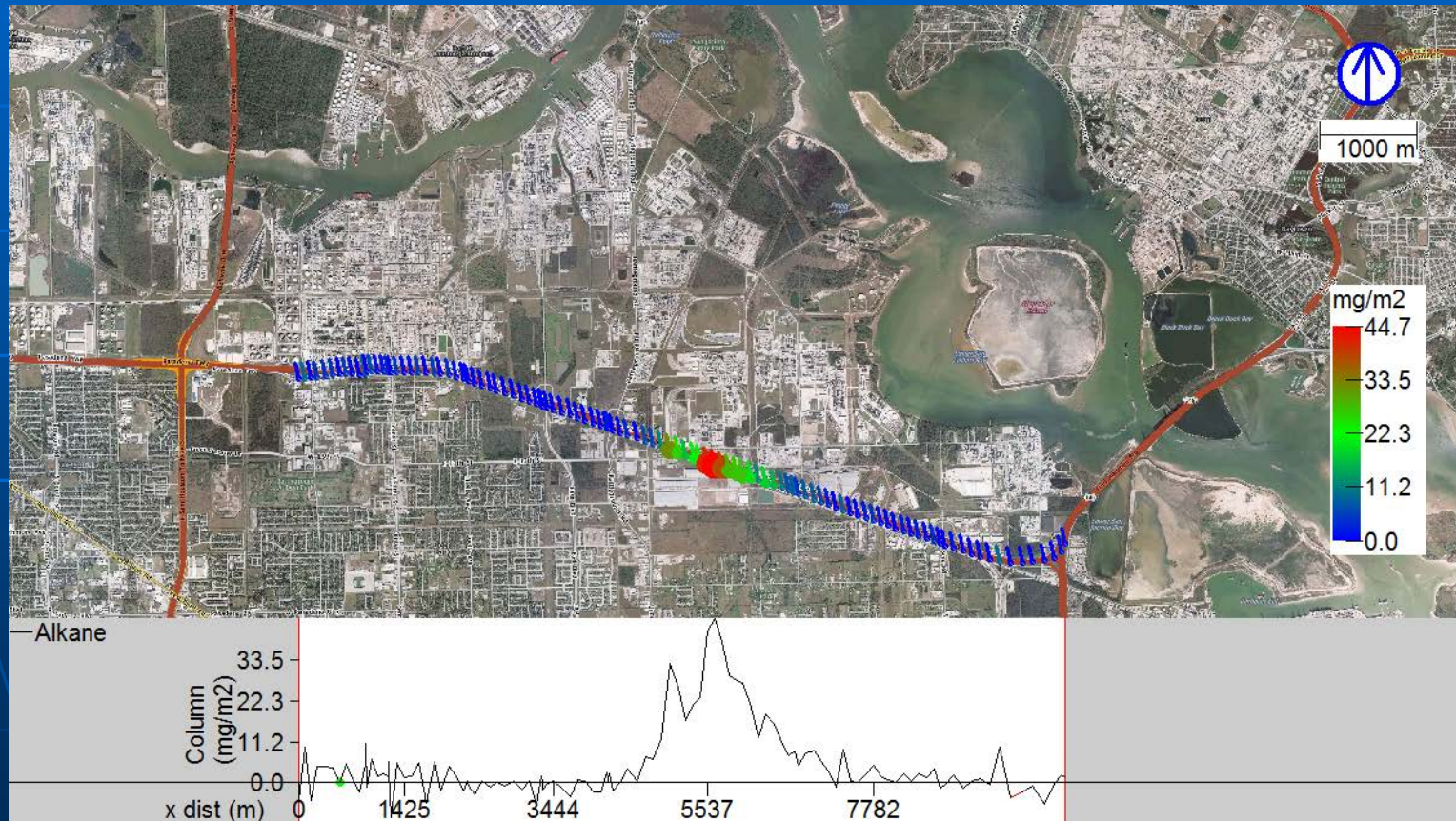
# Emission measurements

Data analysis is on going. Here emission data for a few days are shown. Measurements in HSC, Mt Belvieu, Channelview and Texas City have been carried out.

	Alkanes (kg/h)	Ethene (kg/h)	Propene (kg/h)	SO2 (kg/h)	NO2 (kg/h)
HSC	14550 ± 5294 (2 days)	568 ± 98 (2 days)	391 ± 110 (3 days)	1726 ± 443 (3 days)	2053 ± 209 (2 days)
Bayport			580 ? (1 day)		
Mt Belvieu N	3000 ? ( 1 day)	100	120		
Mt Belvieu E			100		

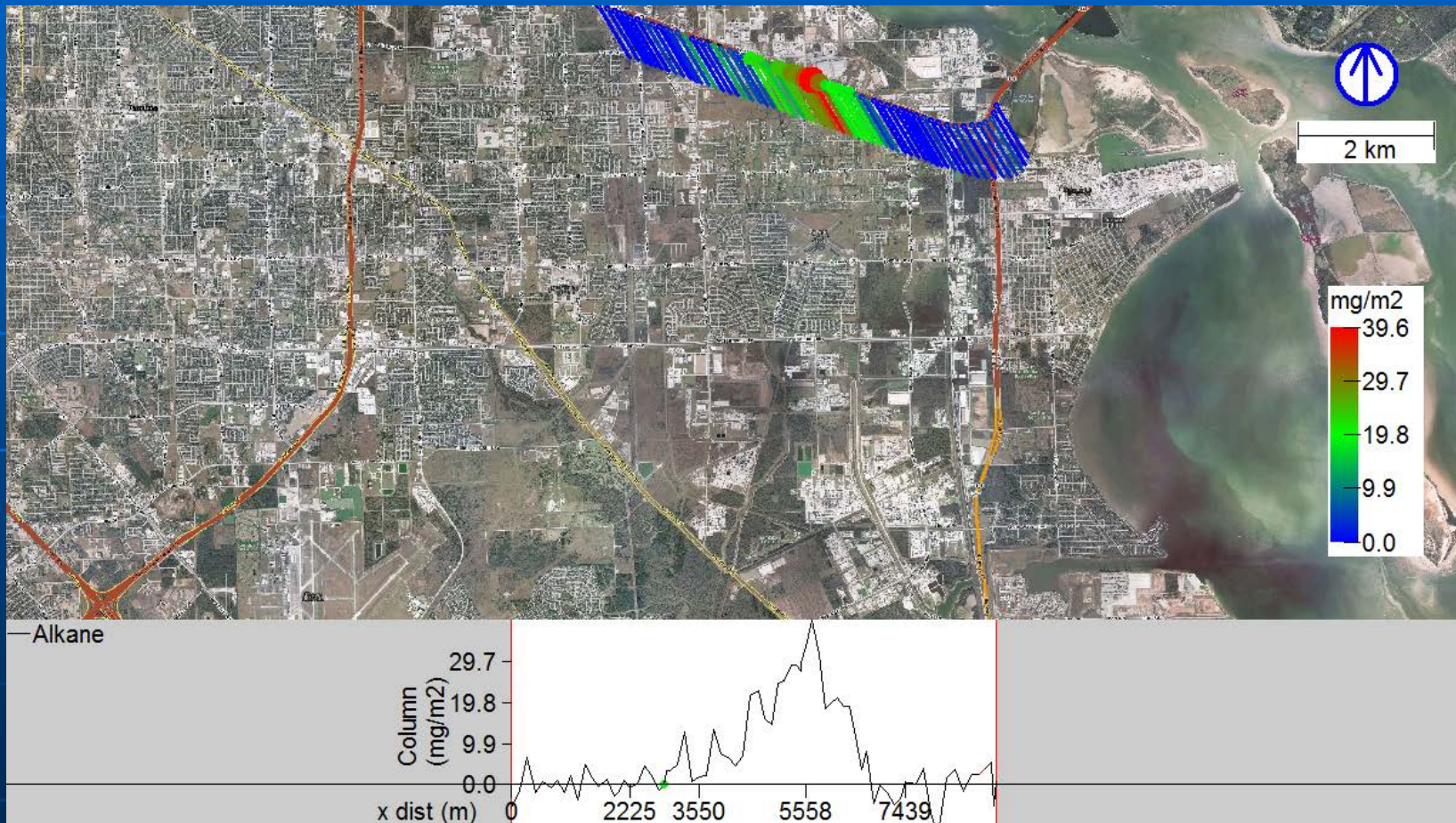
# Largest propene source in HSC

Between Battleground Road and Miller Cutoff Road  
Preliminary emissions 100-250 kg/h



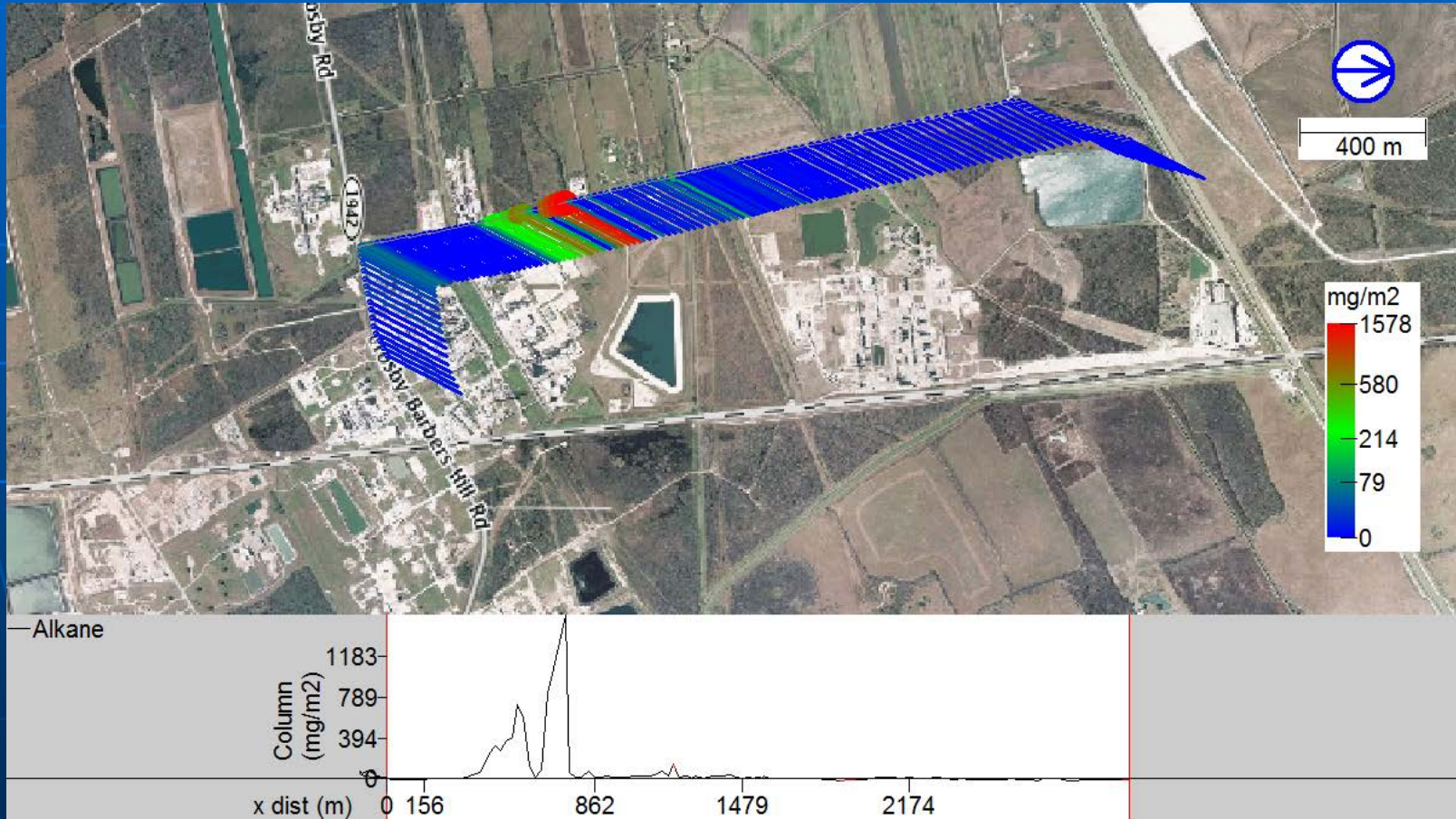
# Bayport propene 13-09-26

New source: Preliminary emissions 580 kg/h



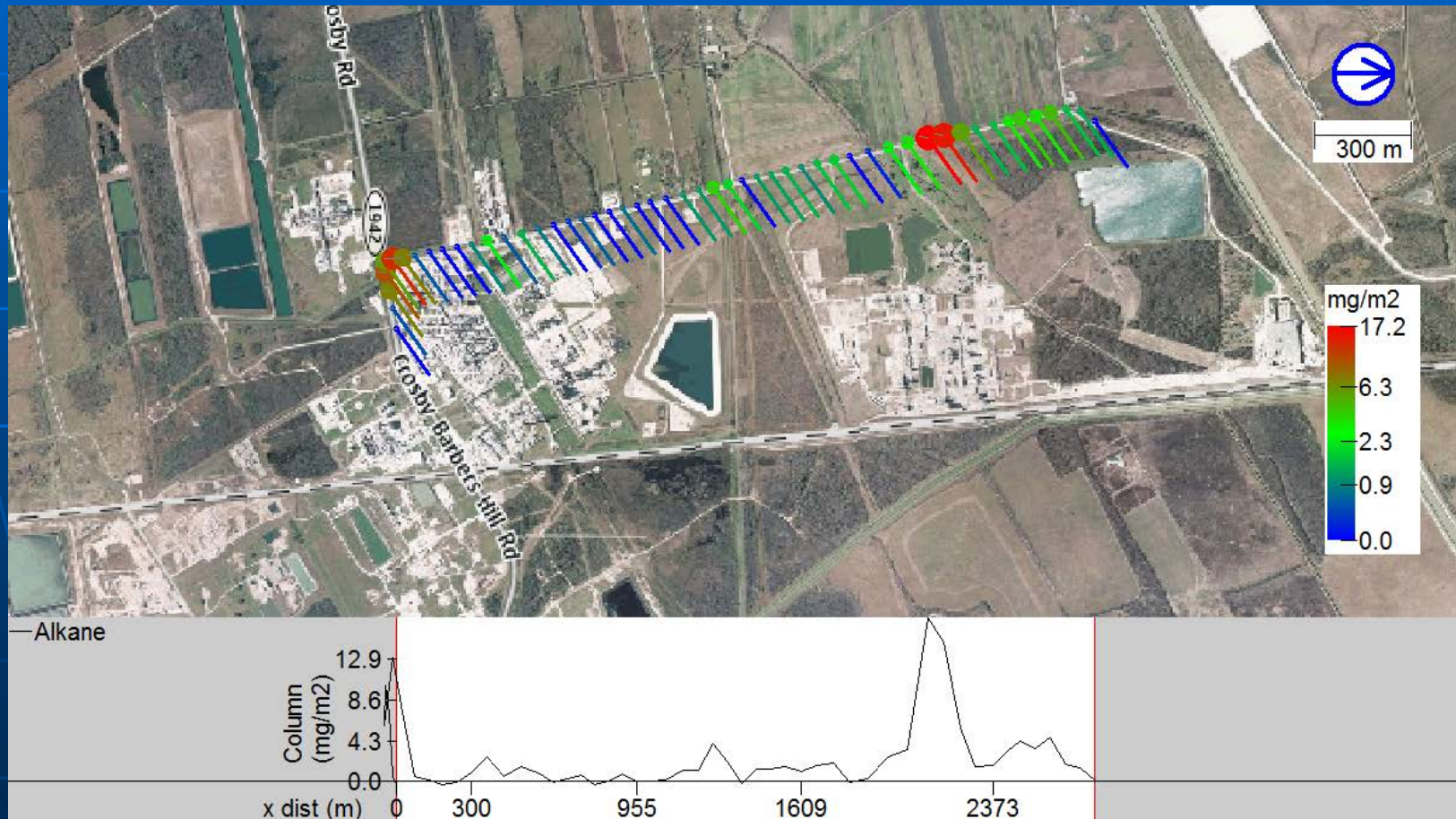
# Northern Mont Belvieu

Large alkane emissions: ~3000 kg/h one day



# Northern Mont Belvieu

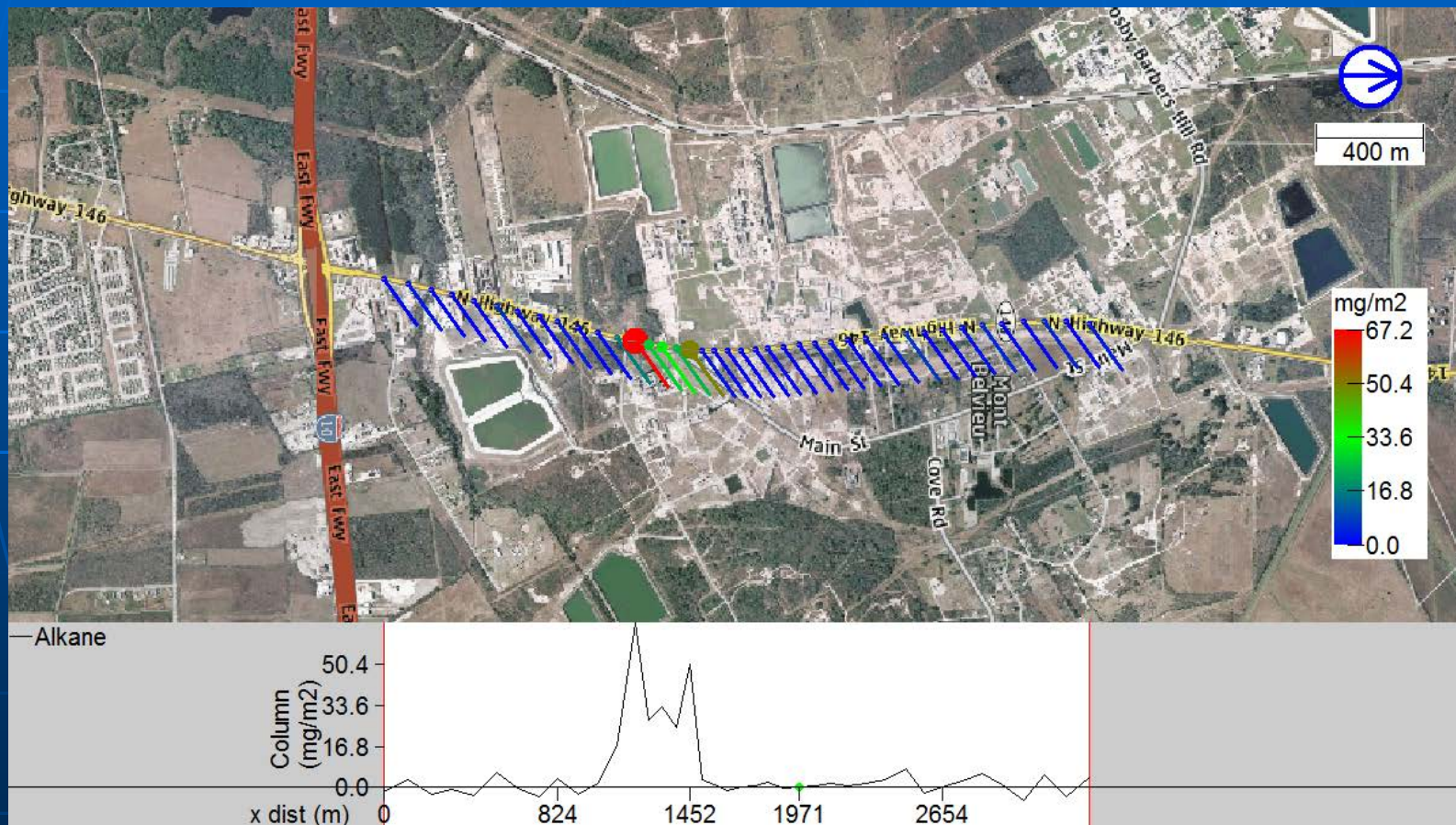
Less alkenes than previous years: Preliminary emissions:  
~100 kg/h ethene and ~120 kg/h propene (different sites)





# Eastern Mont Belvieu

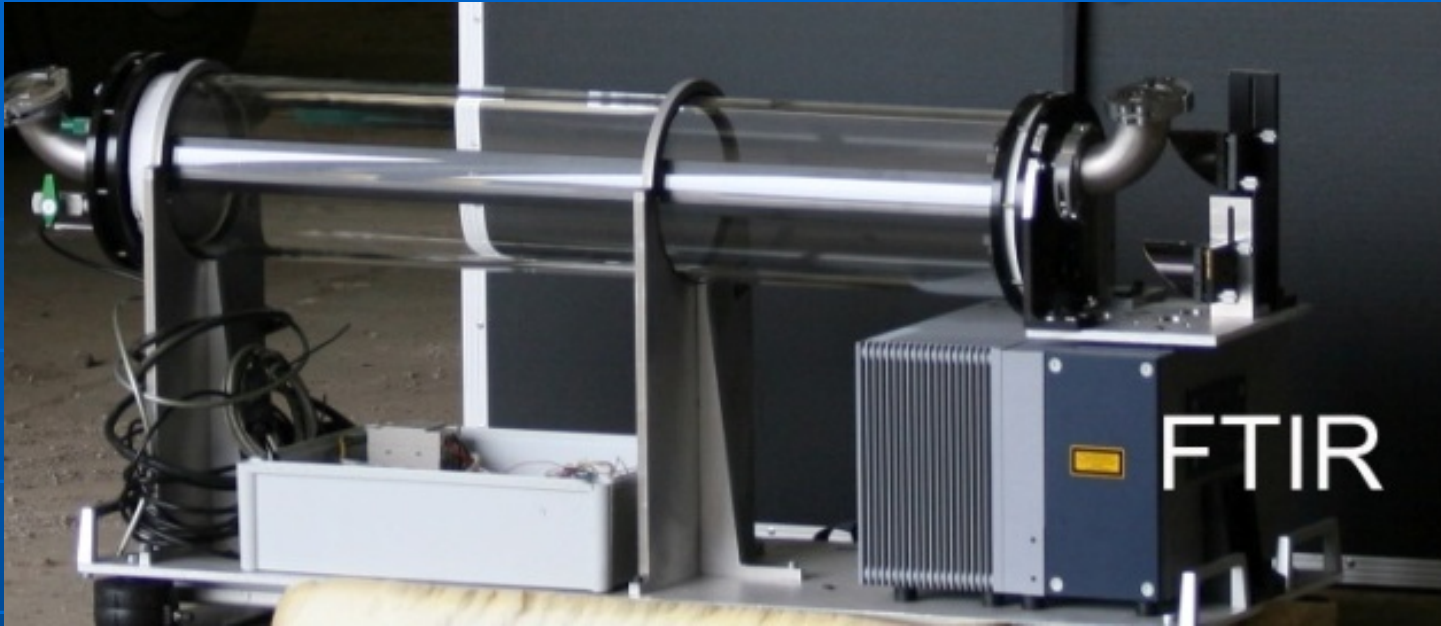
Propene emissions similar to previous year: ~100 kg/h



# Extra measurements

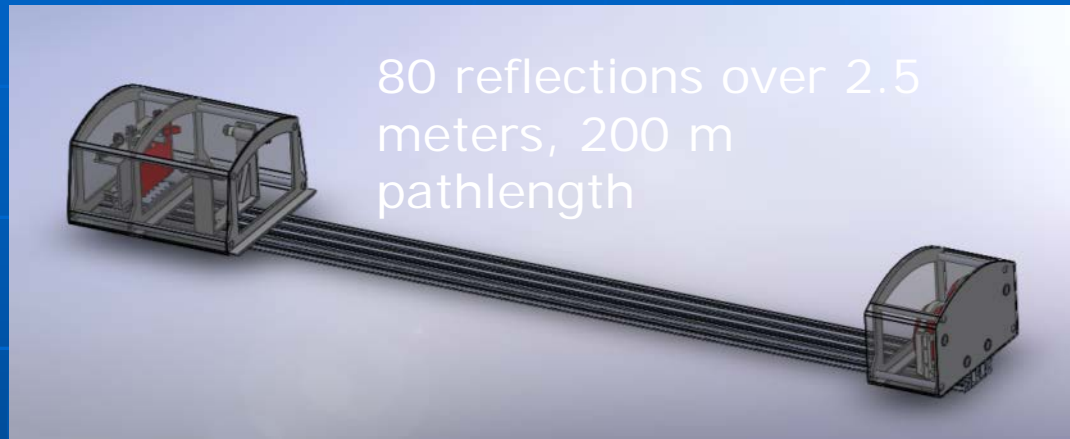
- Mobile ground concentration measurements of aromatic and straight chained VOC's.
- Objective to measure ratios of aromatic VOCs and alkanes from various facilities to obtain emissions values of aromatic VOCs by multiplying with SOF alkane emissions.
- Comparison to PTR-MS

# Mobile extractive FTIR (meFTIR)

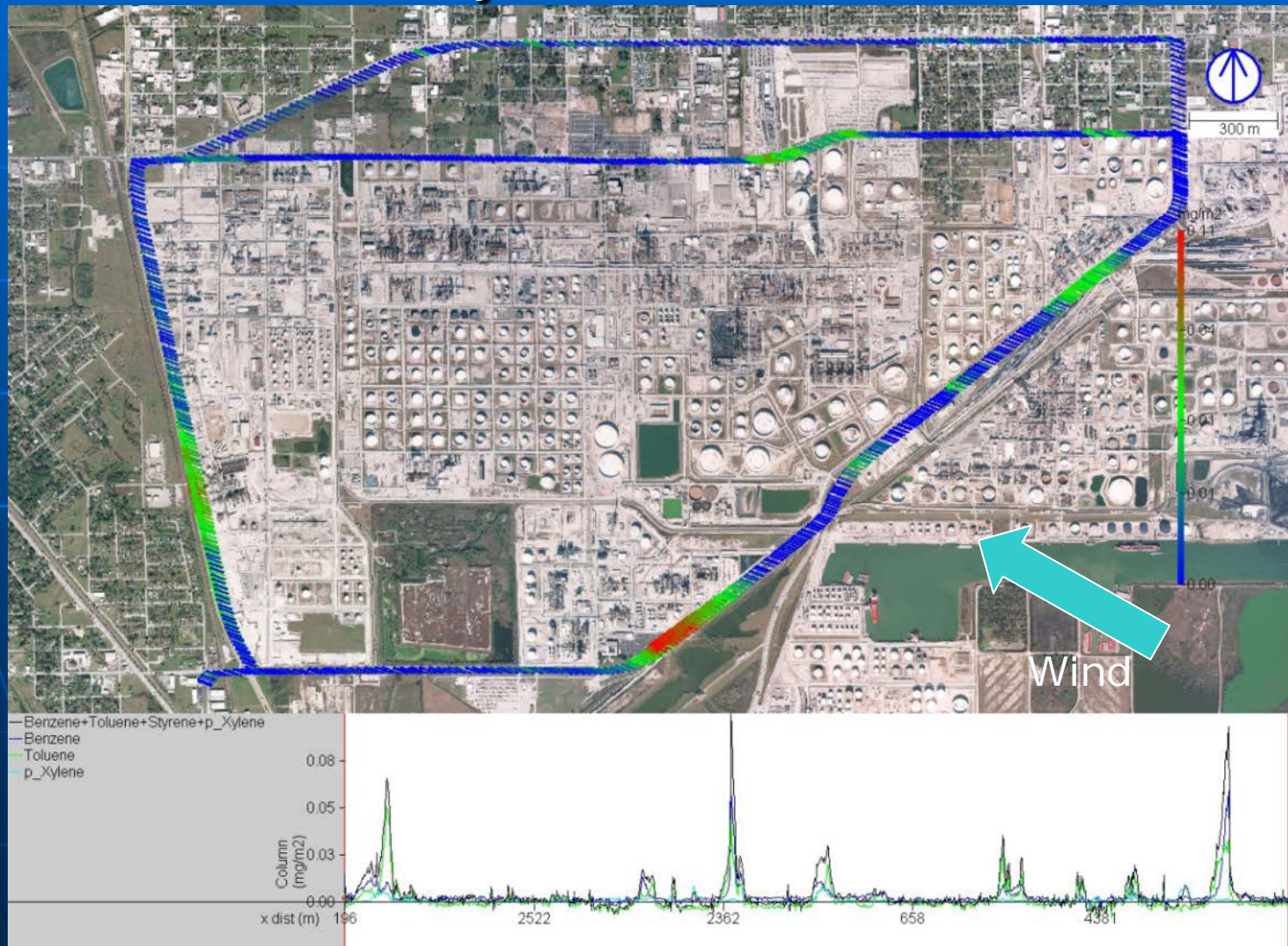


- FTIR coupled to a multi-reflection cell
- Concentration measurements of alkanes, alkenes, methane CO, CO<sub>2</sub> and NH<sub>3</sub> with 15s time response, 1ppb detection limit.

# Measurements of aromatic VOCs using a UV multi-reflection cell and DOAS (MAC DOAS)



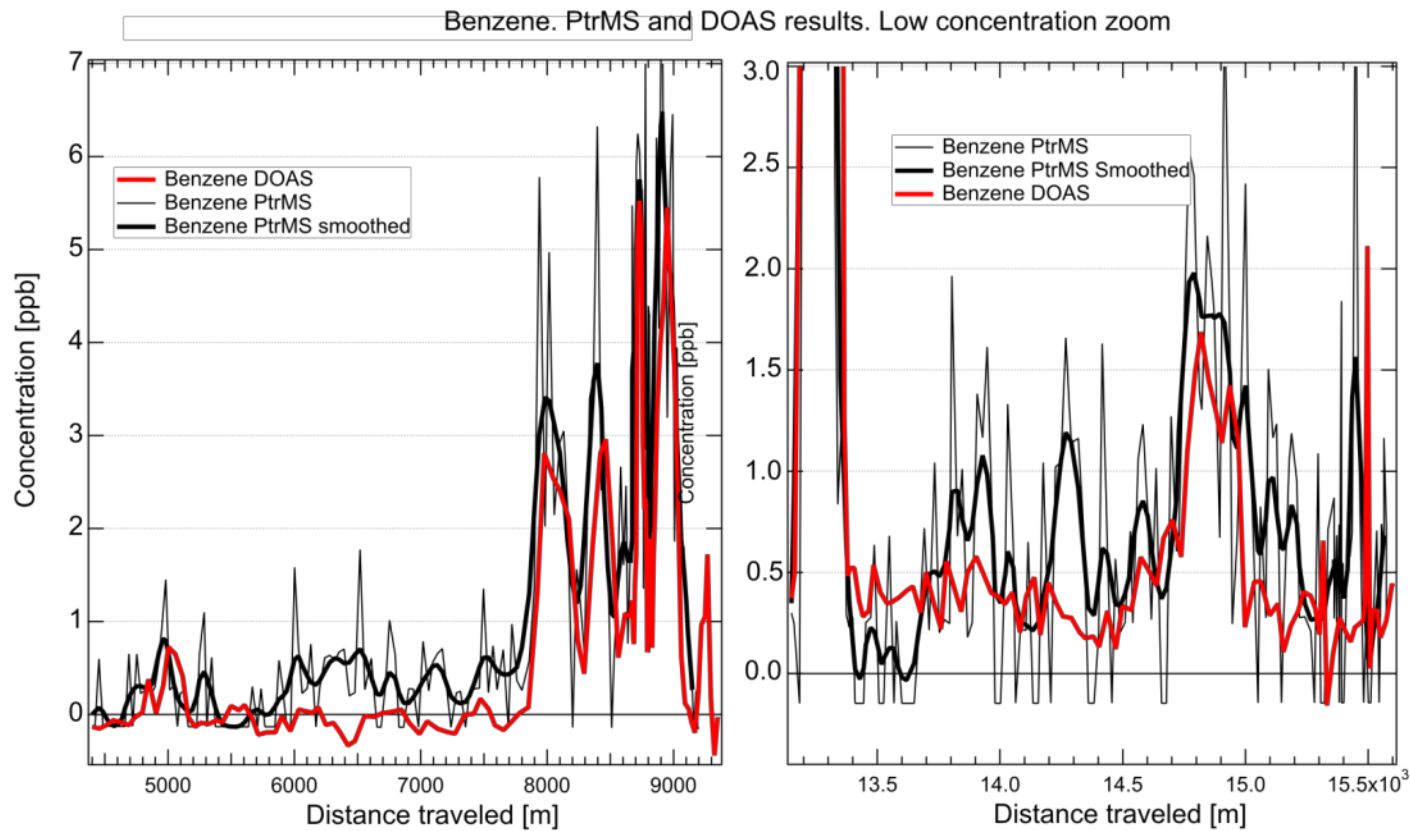
# Concentration of aromatic VOCs (benzene, toluene, p-xylene) around the Texas City refinery, from MAC DOAS



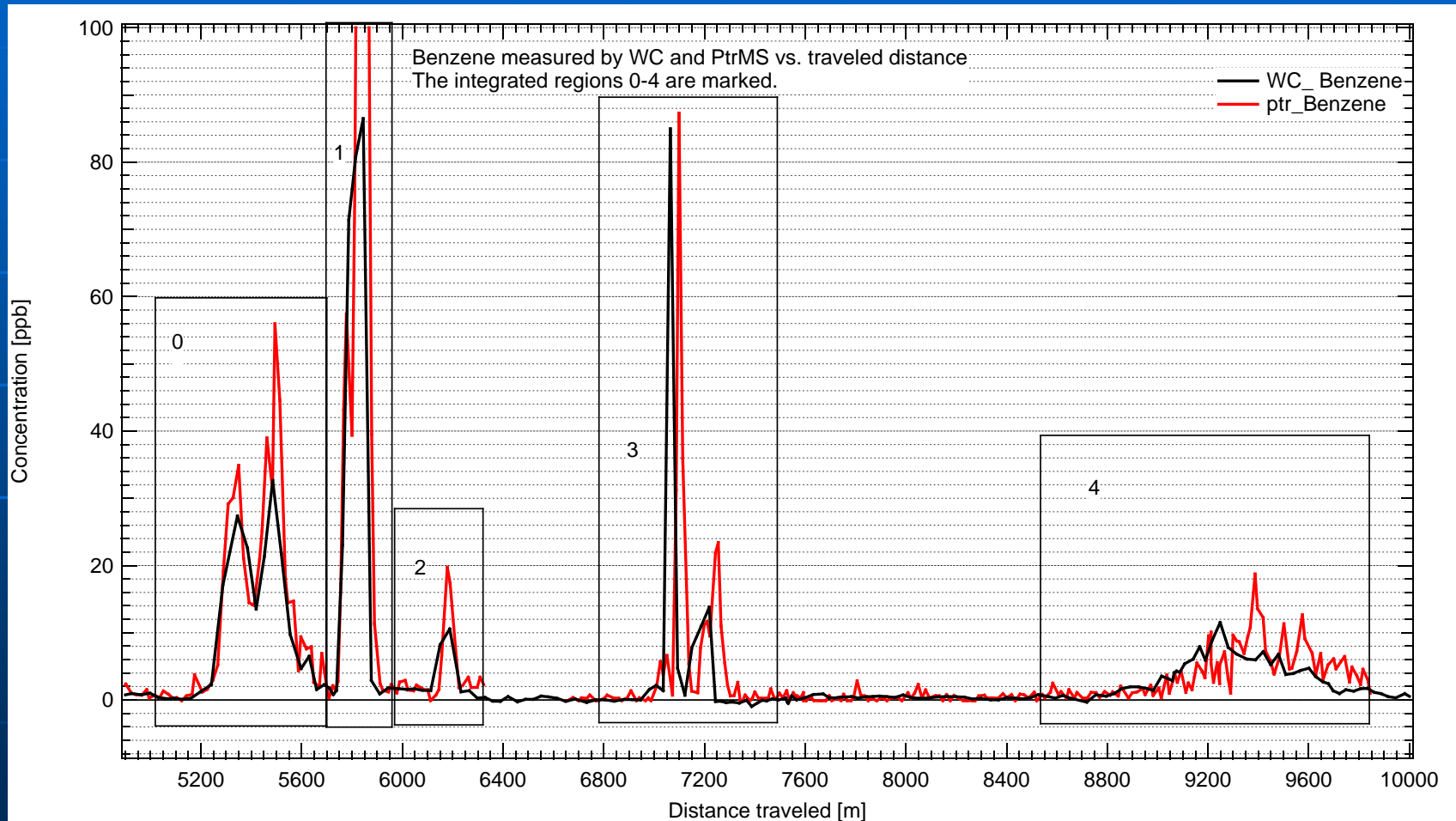
# Comparison between MAC DOAS and meFTIR to PTR-MS



# Comparison MAC DOAS to PTR-MS for Benzene measuring Channelview

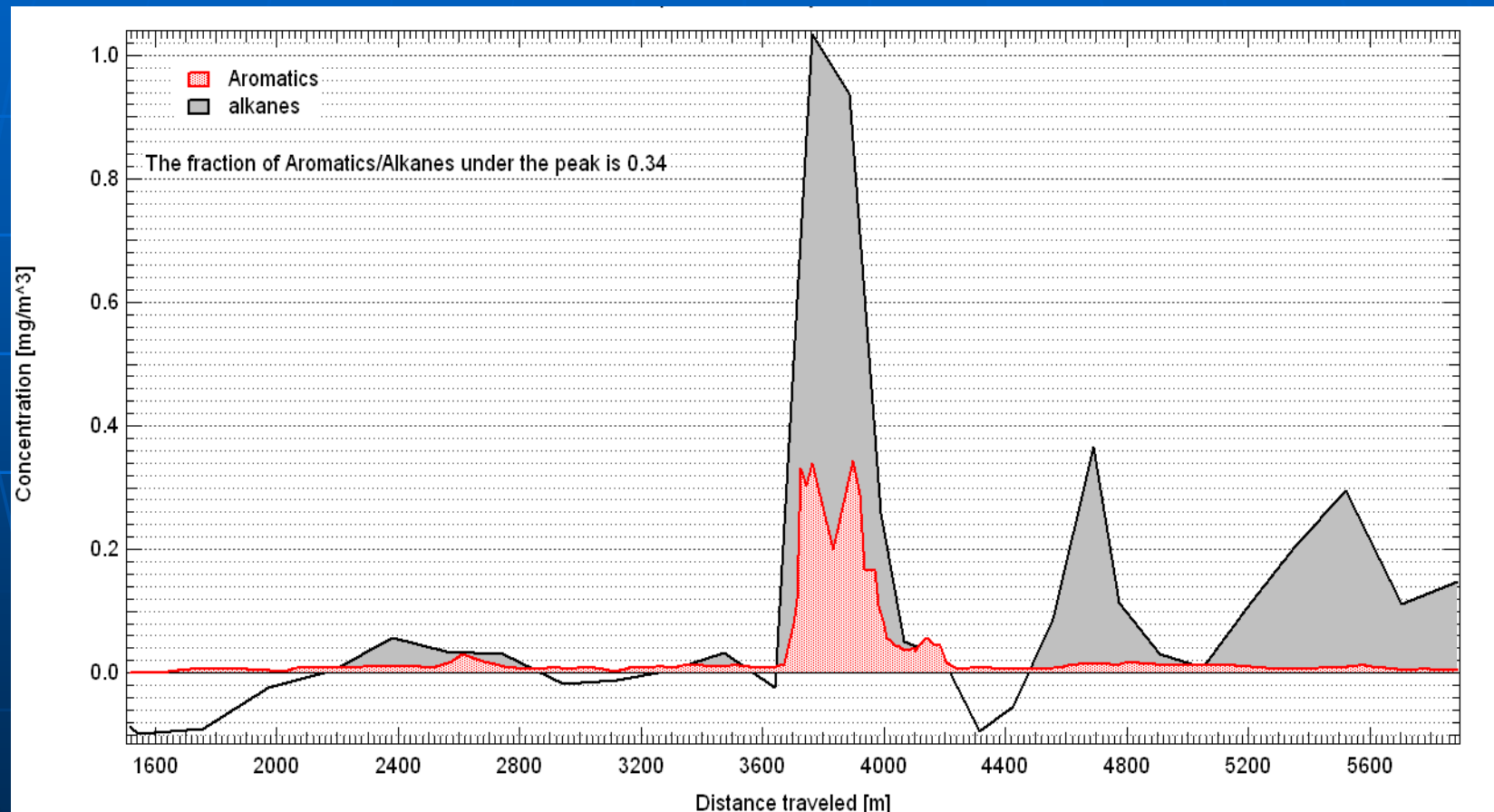


# Comparison MAC DOAS (WC-benzene) to PTR-MS





# Alkanes (meFTIR) and aromatics (MAC DOAS) in an emission plume downwind of the La Porte plant (Independence Parkway)



# Conclusions

- Ten days of column measurements of SO<sub>2</sub>, NO<sub>2</sub>, HCHO, alkanes and alkenes were carried out during the Discover flights in varying meteorological conditions. From some of these column measurements also emissions from individual plants can be estimated.
- Six days of independent SOF emission measurements were carried out at various sites in moderate meteorological conditions. Potentially less VOC emissions than previous years from Mt Belvieu
- Ratios between aromatic and VOVs and alkanes have been measured downwind of various facilities. Possibility to infer aromatic emissions.
- Good agreement between PTR-MS and MAC DOAS
- Analysis still on going.