

Executive summary

The Solar Occultation Flux (SOF) method and mobile DOAS technique were used to measure industrial emissions of volatile organic compounds, formaldehyde, NO₂ and SO₂ in the vicinity of Houston during the time period April 15 to June 11, 2009. The measurements were conducted as part of the campaign FLAIR (Formaldehyde and alkenes from Large Industrial Releases), funded by the Texas Environmental Research Consortium. This measurement study was performed with the aim to study direct emission of formaldehyde and its precursors (mainly alkenes), in order to better quantify the number of the radicals available for tropospheric ozone production. The SOF technique is an optical method utilizing the absorption of direct solar infrared radiation in the 1.8-14 μm range for retrieval of total columns of various species such as ethene, propene, ammonia and alkanes. Mobile DOAS utilizes scattered light in the ultraviolet spectral region for measurements of HCHO, SO₂ and NO₂.

The SOF and mobile DOAS measurements are carried out from a moving vehicle, making it possible to traverse the emission plume downwind of an industry, and thus integrate all the molecules of the plume cross section in real time. By multiplying with the plume wind speed, the total mass flux emerging from the source can be obtained. This technique provides a direct measurement of the emissions. The spectroscopic measurements are based on documented retrieval procedures applied in atmospheric research. The SOF and mobile DOAS calibrations are traceable to published spectroscopic databases with uncertainties of 3-5%. In addition to the two main techniques, a third instrument was used, i.e. mobile extractive FTIR (meFTIR), to measure distributed concentrations of alkenes, alkanes and other tracer species such as CO, CO₂ and methane on the ground.

The main focus in the campaign was on the Texas City and the Mont Belvieu industrial areas, but also the Houston Ship Channel (HSC) was surveyed. The measurements were typically conducted at 0.5 to 3 km distance from the sources and emissions were obtained for various sectors in the Houston ship channel and various sources in the Texas City and Mt Belvieu area. During the campaign about 20 measurement days were conducted during which all instruments were running simultaneously. Primary wind information was obtained from Global Positioning System (GPS) sondes launched within the project in the near vicinity of the emissions measurements. Additional data were obtained from wind masts operated by Texas Commission on Environmental Quality (TCEQ). Data from these were upscaled to be consistent with the balloons. The various wind measurements were consistent within 30%, which was established as the main uncertainty for the actual SOF and mobile DOAS measurements, since the wind estimation is the largest source of uncertainty in these techniques. The overall uncertainty is estimated to about 35%.

Flux estimates were obtained for the refining and petrochemical complexes in Texas City, Mt Belvieu and the Houston Ship Channel, with abridged results shown in the tables below. Here also similar measurements during a previous campaign in 2006 are shown as well as comparisons to two emission inventories derived by TCEQ and NOAA (National Oceanic and Atmospheric Administration). It can be seen that for the HSC the alkene emissions are generally lower in 2009 than in 2006, but still much higher than in the emission inventories (discrepancy factor 5-10). For the other two industrial areas studied, the alkene emissions are similar between the two studies. For alkanes the 2009 emission values are similar to the 2006 values for the HSC and Texas City and higher for Mont Belvieu, with a discrepancy factor of around 7. For SO₂ the measured emissions in the HSC are about 30% greater than the inventories and for Texas City they are about 40% greater. For NO_x the measured emissions at Mont Belvieu are close to the inventory values, while they are 40% lower for Texas city. For NO_x, about 10-20% of the discrepancy can be explained by the fact that only NO₂ is

measured but it should also be noted that the discrepancies for both SO₂ and NO₂ are close to the measurement uncertainty. In addition, it should be considered that the inventories are 3 years old and therefore will not reflect that the emissions have been improved over the last years.

Mont Belvieu is a large alkene emitter. One source area in the northwest part of Mt Belvieu and another one in the southwest part make up the larger part of the ethene emissions while for propene the dominant source is in the central, eastern part of Mt Belvieu. In the HSC there are several large alkene sources. In Texas City there are three distinct sources of alkenes. Measurements conducted with the meFTIR system showed consistently elevated alkene values on the ground at all sites downwind of the main alkene sources identified by SOF. These values did not correlate, in general, with CO which was also measured by the meFTIR, hence it is likely that the emission are not coming from combustion related processes such as flaring but rather from fugitive emissions from within the process areas. However, this has to be investigated further since the CO is variable, and the extra CO may be relatively small so it is hidden in the variability of the background. By comparing the meFTIR and the SOF measurements it was possible to estimate a rough plume height of a few hundred meters in Texas City. This will be further compared to airplane measurements when available.

In Texas city two distinct sources of formaldehyde was found with emissions of 16±4 kg/h and 7±4 kg/h, measured over 4 different days. In Mont Belvieu three sources were observed with 10±4 kg/h and 7±4 kg/h and 36±20 kg/h, respectively. The third source often overlapped with other industries, and is probably a combination of several sources. In the Houston Ship Channel one distinct source at Jefferson Rd was measured with an emission rate of 45±20 kg/h and then large emissions were on several occasions detected from the Baytown area (around 150 kg/h). On one occasion the full plume from the Houston Ship Channel was traversed , and potentially the Mont Belvieu one, with a corresponding formaldehyde flux of 1200 kg/h. This flux could theoretically be explained by secondary production from alkenes emitted in the Houston shipchannel and Mont Belvieu (2000 kg/h), but this requires further, more advanced modelling. An interesting observation is that the observed formaldehyde fluxes are associated with alkene fluxes, in all cases except one. This could point towards the fact that all formaldehyde is secondary produced by degradation of alkenes. However, modelling, taking into account also the measured alkene fluxes, shows that a significant fraction of the formaldehyde fluxes that were measured during the campaign should be due to primary emissions.

Further work includes more comprehensive calculations based on the observed emissions, comparison to other measurements available within FLAIR and further use of the obtained data set.

Source region	Species	SOF/DOAS 2009 (kg)	SOF/DOAS 2006 (kg)	Inventory 2006 (kg/h)	Inventory 2004 (kg/h)
Total HSC	Ethene	580	804	64	60
	Propene	624	1653	140	80
	Alkane	10134	11528	1483	1500
	SO ₂	3364		2585	2552
Mt. Belvieu	Ethene	429	443	81	45
	Propene	310	488	35	12
	Alkane	1837	863	190	261
	NO ₂	168±38		189*	268*
Texas City	Ethene	118	83	7	9
	Propene	54	ND	9	11
	Alkane	2598	2889	372	240
	SO ₂	834		596	613
	NO ₂	283±35		452*	883*

- NO_x is reported,