Executive summary

In a previous project, mobile remote sensing measurements of atmospheric gas column measurements of sulfur dioxide (SO_2), nitrogen dioxide (NO_2), formaldehyde (HCHO) and Volatile Organic Compounds (VOCs) were carried out in a box around the Houston Ship channel (HSC), in parallel with flights by two aircraft from National Aeronautics and Space Administration (NASA). In this project the collected data was reanalyzed, improved and compared to other data, as part of the NASA DISCOVER-AQ (Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality) experiment. The data were obtained using mobile optical remote sensing measurements by the Solar Occultation Flux (SOF) and Mobile Differential Optical Absorption Spectroscopy (DOAS) techniques, which were carried out in the Houston area during September 2013.

The DISCOVER-AQ campaign had the objective to demonstrate that geostationary satellites can provide useful environmental data. NASA operated a high altitude aircraft (B200) equipped with optical sensors, measuring columns of SO_2, NO_2, HCHO and aerosol profiles. To validate these measurements they also carried out in situ measurements with a low flying airplane (P3B) that did spirals above two ground stations in the Houston ship channel, equipped with optical (Pandora) and in-situ sensors.

During the 2013 field campaign a new VOC sensor was used to map ratios of the ground concentrations of alkanes and aromatic VOCs downwind of various industries. The sensor is an open path Differential Optical Absorption Spectroscopy (DOAS) system coupled to a custom made multiple-pass cell working in the ultraviolet (UV) region between 250-280 nm. In this project we have refined the spectral analysis for measurements of aromatic VOCs from this sensor and compared its data to parallel data from a proton transfer mass spectrometer (PTRMS) and canister sampling with subsequent Gas Chromatography-Flame Ionization Detector (GC-FID) analysis. The instrument shows a detection limit (1σ) of 0.3-1 ppb of for the Benzene, Toluene, Ethylbenzene and Xylene (BTEX) species. For a number of transects through plumes from real emission sources in the HSC, the ratio of time-integrated benzene concentrations measured by the Mobile White-cell DOAS (MW-DOAS) and a PTRMS operated by Montana State University was 1.00 on average, indicating very good agreement, while for toluene the PTRMS was 11% lower on average. In a corresponding experiment, canister sampling carried out downwind of several refineries in the Middle East and subsequent GC-FID analysis showed 32 % and 43 % lower values, respectively, for the same species compared to MW-DOAS. This will be further investigated. Ground data measured with MW-DOAS, downwind of a Texas City refinery shows that the BTEX to alkane mass rations were 0.10±0.04, corresponding to a mass emission 134 kg/h for the 2013 data. Here it is assumed that the aromatic VOCs and alkanes were well mixed in the emission plume at the measurement position. An additional uncertainty is the few amount of measurements carried out in 2013.

During the campaign, mobile remote sensing by the SOF method and Mobile DOAS were carried out in the Houston area on twenty days in September 2013 together with frequent balloon launches. During ten of these days, column measurements of SO_2, NO_2, HCHO and VOCs in a box around the Houston Ship channel were carried out synchronized with science flights by the NASA aircrafts. During the rest of the days more focused industrial measurements were carried out. The weather during the campaign was relatively poor with 4 good clear days, 10 moderate days and the rest rather cloudy.

A small measurement study was carried out in Sweden in September 2014 to investigate the effects of clouds on the Mobile DOAS measurements. During the course of this study, a so far undetected instrumental effect was discovered which was seen to affect the quality of evaluation negatively. A drift in instrumental lineshape was determined to be the cause of this and a method was developed to compensate for it. This method was successfully applied to the measurements during the DISCOVER-AQ campaign and was seen to improve spectral fit quality and give more stable baselines in some cases.

The measurement study also concluded that the changes in evaluated columns experienced due to clouds are most likely real changes in the actual column due to changes in radiative transfer rather than some form of spectral artifacts. Because of this, development of cloud indicator was determined to be the best way to deal with cloud effects. A cloud indicator based on the principle of a color index, a simple ratio between the spectral intensity at two different wavelengths, was developed and applied to the measurement series in order to allow more data to be used for flux calculations.

Multi-angle Mobile DOAS measurements performed during the last days of the DISCOVER-AQ campaign were evaluated using a new scheme designed to enable absolute columns to be derived. As part of this scheme radiative transfer simulations were performed using in-situ data from the airborne measurements in order to derive direction dependent differential air mass factors needed to convert the evaluated columns to absolute mixing layer columns. After some averaging and filtering, this data could be used to establish an absolute offset for the relative columns from the standard evaluation and control for baseline drift. This gave a better absolute column product that is suited for comparisons with other data from the DISCOVER-AQ campaign.

Table 1 was shows the final emission rates for the 2013 campaign together with corresponding results from previous studies and reported annual routine emissions from the STARS (State of Texas Air Reporting System) emission inventory for 2013.

Table 1 Emission fluxes (kg/h) measured with SOF and Mobile DOAS for different sites, as reported after the measurement campaign. Results from earlier campaigns and Emission inventory data for 2013 [Johansson, 2014b] are also shown.

Area	Species	2006	2009	2011	2013	2013Emission Inventories
HSC	Ethene	878 ± 152	614 ± 284	612 ± 168	475 ± 79	53
	Propene	1511 ± 529	642 ± 108	563 ± 294*	394 ± 245	48
	Alkanes	12276 ± 3491	10522 ± 2032	11569 ± 2598	13934 ± 4321	818
	SO_2	2277 ±1056	3364 ± 821	2329 ± 466	1683 ± 223	1153
	NO_2	2460 ± 885	-	1830 ± 330	2242 ± 684	1103
Mont Belvieu	Ethene	443 ± 139	444 ± 174	545 ± 284	271 ± 33	29
	Propene	489 ± 231	303 ± 189	58*	220 ± 115	21
	Alkanes	874	1575 ± 704	1319 ± 280	2854 ± 1212**	146
	NO_2	-	168 ± 39	305 ± 29	245 ± 102	138
Texas City	Ethene	83 ± 12	122 ± 41	177 ± 48	-	2
	Propene	ND	54 ± 22	56 ± 9*	-	4
	Alkanes	3010 ± 572	2422 ± 288	2342 ± 805	1340 ± 140	276
	SO_2	-	834 ± 298	1285 ± 428	414 ± 172	128
	NO_2	460 ± 150	283 ± 30	492 ± 71	408 ± 93	331

* Propene retrievals were of poor quality throughout much of this campaign

** Only a single day of measurements with variable emissions.