Scope of Work For

Project 14-007
Analysis of VOC, NO2, SO2 and HCHO data from SOF, mobile DOAS and MW-DOAS during DISCOVER-AQ

Prepared for

Air Quality Research Program (AQRP)
The University of Texas at Austin

by

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1. Scope of work

1.1. Objective and Aim

The objective is to demonstrate the usefulness of geostationary satellites for providing environmental data. A second objective is to improve the understanding of tropospheric ozone formation and the impact of industrial emissions

The main aim of this study is to improve the quality of the column measurements of NO_2, SO_2, HCHO and VOCs obtained using mobile DOAS and SOF around the Houston ship channel during the NASA Discover aircraft flight and then compare these data to aircraft and in situ measurements.

A second aim is to improve the industrial emission measurements of VOCs, NO_2, SO_2 and HCHO and to compare these to emission inventories.

A third aim is to derive aromatic VOC emissions from some isolated industries using a combination of SOF , mobile extractive FTIR and mobile White cell DOAS.

1.2 Background

The Solar Occultation Flux method (SOF) and mobile DOAS technique has been applied in eastern Texas in several collaborative projects between Chalmers University of Technology and University of Houston during the last 6 years [Mellqvist 2007; 2009; 2010 and Rivera 2010, Johansson 2011] to measure emissions of VOCs, NO2, SO2 and formaldehyde. In September 2013 measurements were carried out in the Houston area during twenty days as part of the NASA Discover AQ experiment. 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 in parallel with flights by two aircraft from NASA. During the rest of the days more focused industrial measurements were carried out. In thus study the measured data will be refined and compared to the measurements by NASA.

The SOF (Solar Occultation Flux) [Mellqvist 1999; Kihlman 2005a] method is based on the recording of broadband infrared spectra of the sun with a Fourier transform infrared spectrometer (FTIR) that is connected to a solar tracker. The latter is a telescope that tracks the sun and reflects the light into the spectrometer independent of its position. Using multivariate optimization it is possible from these solar spectra to retrieve the path-integrated concentrations (referred to as column concentrations), in the unit mg/m2, of various species between the sun and the spectrometer. The system to be used in this project consists of a custom built solar tracker, transfer optics and a Bruker EM27 FTIR spectrometer with a spectral resolution of 0.5 cm-1, equipped with an MCT (Mercury Cadmium Telluride) detector.

The principle for Mobile DOAS (Mobile Differential Optical Absorption Spectroscopy) measurements is very similar to that of SOF. Instead of measuring direct sun light in the infrared region, scattered light in the UV and visible region is measured in zenith angle with a telescope connected with an optical fiber to a Czerny-Turner spectrometer with a CCD camera. Column concentrations are retrieved from spectra in a similar way as with the SOF, although absorption is generally weaker. The system used for this project consists of a quartz telescope (20 mrad field of view, diameter 7.5 cm) connected with an optical fiber (liquid guide, diameter 3 mm) to a 303 mm focal length Czerny-Turner spectrometer with a 1024 by 255 pixels, thermoelectrically cooled CCD camera.

During the NASA Discover campaign, column measurements with SOF and mobile DOAS of VOCs, NO_2, SO_2 and HCHO were carried out during 10 days in the Houston Ship Channel, in parallel with flight measurements from two aircraft and groundbased measurements . The Discover AQ has the objective to demonstrate that geostationary satellites can provide useful environmental data. NASA flew a high altitude aircraft (B200) equipped with optical sensors, measuring columns of SO2, NO2, HCHO and aerosol profiles (LIDAR). To validate these measurements they also carried out in situ measurements with a low flying airplane (P3) that did spirals above two ground stations in the Houston ship channel, equipped with optical (Pandora) and in-situ sensors.

The column data of NO_2, SO_2, HCHO obtained from the mobile DOAS is a very similar data product to the one obtained by the high altitude NASA B200 airplane and the Pandora instruments on the ground sites which uses very similar sensors. The different data sets can therefore be compared directly for various locations around the HSC. However, the weather during the campaign was rather variable and most days were partially cloudy. For such conditions the spectral retrieval and interpretation of column results from the mobile DOAS technique is challenging and to be able to compare these data to other measurements cloud effects have to be minimized. We will therefore work with radiative transfer and utilize multi angle measurements.

During the September 2013 campaign, SOF and mobile DOAS measurements were carried out to study industrial emissions in for instance Mt Belvieu and Texas city and elsewhere on non flight days.
During the campaign an additional mobile White cell DOAS (MW-DOAS) was used with the objective to quantify aromatic VOC emissions from industry. The MW-DOAS was used together with an extractive FTIR to map ratios of the ground concentration of alkanes and aromatic VOCs downwind of various industries. In this project we will refine the spectral analysis for measurements of the aromatic VOCs from the MW-DOAS and compare the data to parallel measurements with PTR-MS.

1.3. Work schedule and project task description

Below we describe and motivate the activities of this study in more detail.

Task 1: Improving measured columns obtained with mobile DOAS (Responsible Chalmers)
The weather during the AQ DISCOVER campaign was relatively poor with 4 good clear days, 10 moderate days and 6 days which were rather cloudy with only partial sun. For cloudy conditions the spectral retrieval and interpretation of column results from the DOAS techniques is challenging. The clouds scatter the light and the optical path through the atmosphere of the observed light is hence changed causing variations in the measured columns. In addition there may be optical interference effects. Hence column measurements of for instance NO_2 carried out around the Houston ship channel over 1 hour in partly cloudy conditions will have a variability (baseline drift) caused by this effect.

We will work with this problem in several ways: a) comparison of the optical data to other data b) calculation of columns from multiple angle data c) applying radiative transfer calculations, d) implementing a cloud filter and e) spectroscopic sensitivity analysis

1a) Comparison to other data, such as in situ sensors at the ground sites and P3 aircraft and optical sensors (Pandora, and imaging DOAS) will help to interpret whether observed baseline changes in the retrieved columns of SO2, NO2 and HCHO around the HSC are real, or caused by cloud artifacts.

1b) A scanning mirror was installed during the third half of the campaign and then UV measurements at three angles (zenith and ± 30^o) were carried out in sequence while driving. This was not part of the original project and there is no automatic procedure to evaluate the spectra and we will therefore implement this in our retrieval software. The principle is actually to calculate the difference between each consecutive zenith and 30^o measurement, respectively, to obtain the absolute tropospheric column (with some assumptions). This should make the cloud impact smaller, due to less change of optical path. In addition, it will be possible to obtain the absolute tropospheric column instead of a relative column, which will be very useful for the comparison with the NOAA sensors.

1c) In the DOAS measurements carried out over the last years we have assumed the geometric approximation, which assumes that the major fraction of the light is not scattered when passing the gas plume of interest; this is appropriate for isolated industrial emission plumes and for clear weather conditions but not for large plumes such as the Houston ship channel in varying cloudy conditions. To study the uncertainties involved, and possible remedies, it is useful to carry out radiative transfer modeling. This will be done with the Sciatran model (Rozanov, 2005) which is developed in Bremen.

1d) For clear sky conditions the measurement situation is much better than for cloudy conditions. We will therefore develop and implement a cloud filter, i.e. an algorithm that, based on the light intensity of the spectrum and perhaps additional parameters, determines whether the measurements were cloud-free or not, making it possible to flag the data for clouds.

1e) Based on task 1a, b and c above, we will carry out a sensitivity analysis on the used spectroscopic retrieval. Various wavelength intervals will be tested, in particular for formaldehyde to see if baseline artifacts can be removed during cloudy conditions by appropriate choices of wavelength interval. We will also carry out measurements over a few days in Sweden, in partly cloudy conditions, but in remote clean air site, to test the spectroscopic impact of clouds.

Task 2: Retrieving industrial emissions of VOCs SO_2, NO_2, HCHO and comparison to emission inventories. (Responsible Chalmers/UH)
This task has partly been carried out in the AQRP Project 13-005 but given the short time available for data retrieval since and a significant number of days with difficult measurement situation we will reevaluate the present data set for VOCs and make sensitivity analyses on the spectroscopy. The same applies for the SO_2, NO_2 and HCHO data obtained from the mobile DOAS measurements, but this is included in task 1 above. We will compare the data to available emission inventories and previous measurements. We will also compare our So2 and NO2 data to any available CEM data for the measurement period.

Task 3: Comparison of mobile DOAS and SOF data to data from ground sites and the two airplanes within NASA DISCOVER-AQ. (Responsible Chalmers/UH)
This task includes
a) Compilation of comparative data and comparison to mobile DOAS and SOF data.
b) Writing of a scientific paper.

Task 4: Estimating aromatic VOC emissions from refineries. (Responsible Chalmers/UH)
During the DISCOVER-AQ campaign a new instrument was brought along as an extra device to complement the SOF instrument with ground concentration measurements of aromatic VOCs, i.e. benzene, toluene, etc. This system is based on an open UV multiple reflection cell connected to a DOAS spectrometer, here called MW-DOAS (mobile White cell DOAS).
In addition, a mobile extractive FTIR (meFTIR) was used to measure the concentration of alkanes on the ground. This instrument is based on a closed IR multiple reflection cell connected to a FTIR spectrometer and it has been employed in previous campaigns.
The combination of the MW-DOAS and the meFTIR makes it possible to map ratios of the ground concentration of aromatic VOCs and alkanes downwind of various industries and by multiplying these ratios with the alkane emission obtained from the SOF also the aromatic emissions can be inferred. During the campaign we carried out side by side measurements with MW-DOAS and a PTR-MS (Aerodyne lab) in the Houston ship channel. The MW-DOAS and meFTIR instruments were not part of the project and therefore only some preliminary data are available in the final report of the present AQRP Project 13-005. Four tasks will be carried out:

4a) Reevaluation of aromatic VOCs from the MW-DOAS and alkanes from the meFTIR system

4b) Calculation of Aromatic emissions by combining SOF, MW-DOAS and meFTIR.

4c) Comparison of MW-DOAS and PTR-MS

4d) Writing of a Scientific paper

Table 1. Time schedule.

Time schedule	*Month 2014/2015*												
Activity	*06*	*07*	*08*	*09*	*10*	*11*	*12*	*01*	*02*	*03*	*04*	*05*	*06*
T1:, Improving measured columns obtained with mobile DOAS													
a Comparison to other data				***x***	***x***	***x***							
b Multiple angles	***x***	***x***	***x***	***x***									
c Radiative transfer	***x***	***x***	***x***	***x***	***x***								
d Cloud filter	***x***	***x***	***x***	***x***									
e Spectroscopic sensitivity analysis	***x***	***x***	***X***										
T2: Retrieving industrial emissions of VOCs SO2, NO2, HCHO and comparison to emission inventories].													
T 3: Comparison of mobile DOAS and SOF data to data from ground sites and two airplanes within NASA discover													
a Data compilation and comparison	***x***	***x***	***x***	***x***	***x***	***x***							
b Scientific paper					***x***	***x***	***x***	***x***	***x***	***x***			
T 4: Estimating aromatic VOC emissions from refineries													
a Reevaluation of aromatic VOC	***x***	***x***											
b Calculation of Aromatic emissions			***x***	***x***									
c Comparison of MW-DOAS and PTR-MS				***x***	***x***								
d Scientific paper						***x***	***x***	***x***	***x***	***x***	***x***		
Key milestones													
Final workshop													***X***
Draft Final report												***X***	
Final report													***X***

1.4 Deliverables

Deliverables

Executive Summary

At the beginning of the project, an Executive Summary will be submitted to the Project Manager for use on the AQRP website. The Executive Summary will provide a brief description of the planned project activities, and will be written for a non-technical audience.
Due Date: Friday, May 30, 2014

Quarterly Reports

The Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the Project Manager as a Word doc file. It will not exceed 2 pages and will be text only. No cover page is required. This document will be inserted into an AQRP compiled report to the TCEQ. Due Dates:

Report	***Period Covered***	***Due Date***
Quarterly Report #1	*June, July, August 2014*	*Friday, August 30, 2014*
Quarterly Report #2	*September, October, November 2014*	*Monday, December 1, 2014*
Quarterly Report #3	*December 2015, January & February 2015*	*Friday, February 27, 2015*
Quarterly Report #4	*March, April, May 2015*	*Friday, May 29, 2015*
Quarterly Report #5	*June, July, August 2015*	*Monday, August 31, 2015*
Quarterly Report #6	*September, October, November 2015*	*Monday, November 30, 2015*

Technical Reports

Technical Reports will be submitted monthly to the Project Manager and TCEQ Liaison as a Word doc using the AQRP FY14-15 MTR Template found on the AQRP website.

Due Dates:

Report	***Period Covered***	***Due Date***
Technical Report #1	*Project Start – July 31, 2014*	*Friday, August 8, 2014*
Technical Report #2	*August 1 - 31, 2014*	*Monday, September 8, 2014*
Technical Report #3	*September 1 - 30, 2014*	*Wednesday, October 8, 2014*
Technical Report #4	*October 1 - 31, 2014*	*Monday, November 10, 2014*
Technical Report #5	*November 1 - 30 2014*	*Monday, December 8, 2014*
Technical Report #6	*December 1 - 31, 2014*	*Thursday, January 8, 2015*
Technical Report #7	*January 1 - 31, 2015*	*Monday, February 9, 2015*
Technical Report #8	*February 1 - 28, 2015*	*Monday, March 9, 2015*
Technical Report #9	*March 1 - 31, 2015*	*Wednesday, April 8, 2015*
Technical Report #10	*April 1 - 28, 2015*	*Friday, May 8, 2015*
Technical Report #11	*May 1 - 31, 2015*	*Monday, June 8, 2015*

Financial Status Reports

Financial Status Reports will be submitted monthly to the AQRP Grant Manager (Maria Stanzione) by each institution on the project using the AQRP FY14-15 FSR Template found on the AQRP website. Due Dates:

Report	***Period Covered***	***Due Date***
FSR #1	*Project Start – July 31, 2014*	*Friday, August 15, 2014*
FSR #2	*August 1 - 31, 2014*	*Monday, September 15, 2014*
FSR #3	*September 1 - 30, 2014*	*Wednesday, October 15, 2014*
FSR #4	*October 1 - 31, 2014*	*Monday, November 17, 2014*
FSR #5	*November 1 - 30 2014*	*Monday, December 15, 2014*
FSR #6	*December 1 - 31, 2014*	*Thursday, January 15, 2015*
FSR #7	*January 1 - 31, 2015*	*Monday, February 16, 2015*

FSR #8	*February 1 - 28, 2015*	*Monday, March 16, 2015*
FSR #9	*March 1 - 31, 2015*	*Wednesday, April 15, 2015*
FSR #10	*April 1 - 28, 2015*	*Friday, May 15, 2015*
FSR #11	*May 1 - 31, 2015*	*Monday, June 15, 2015*
FSR #12	*June 1 - 30, 2015*	*Wednesday, July 15, 2015*
FSR #13	*Final FSR*	*Wednesday, August 15, 2015*

Draft Final Report

A Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will include an Executive Summary. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.
Due Date: Monday, May 18, 2015

Final Report

A Final Report incorporating comments from the AQRP and TCEQ review of the Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.
Due Date: Tuesday, June 30, 2015

Project Data

All project data including but not limited to QA/QC measurement data, databases, modeling inputs and outputs, etc., will be submitted to the AQRP Project Manager within 30 days of project completion. The data will be submitted in a format that will allow AQRP or TCEQ or other outside parties to utilize the information.
AQRP Workshop
A representative from the project will present at the AQRP Workshop in June 2015.

2. References

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