Quality Assurance Project Plan

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

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Summary of Project

QAPP Category Number: III
Type of Project: Secondary Data Project

QAPP Requirements: This QAPP contains sections detailing the project description and objectives; organization and responsibilities; scientific approach; sampling and measurements procedures; quality metrics; data analysis, interpretation, and management; reporting; and references

QAPP Requirements:
Audits of Data Quality: 10% Required
Report of QA Findings: Required in final report

May 29, 2014

General Requirements

Distribution list

John Jolly - TCEQ Project Liaison

David W. Sullivan - AQRP project manager University of Texas

Johan Mellqvist - Principal Investigator, Chalmers University of Technology

Barry Lefer - Co-Principal Investigator. University of Houston

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1. PROJECT DESCRIPTION AND OBJECTIVES

1.1 Process and environmental system to be evaluated.

Mobile remote sensing measurements by the SOF (Solar Occultation Flux) and mobile DOAS (Differential Optical Absorption Spectroscopy) methods were carried out in the Houston area during twenty days in September 2013 as part of the NASA (National Aeronautics and Space Administration) Discover AQ (Air Quality) experiment. During ten of these days, column measurements of sulfur dioxide (SO_2), nitrogen dioxide (NO_2), formaldehyde (HCHO) and volatile organic compounds (VOCs) in a box around the Houston Ship channel (HSC) 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 addition 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 (Fourier Transform InfraRed) to map ratios of the ground concentration of alkanes and aromatic VOCs downwind of various industries.

The data collected has great value of its own to be applied for future ozone modeling since emissions and atmospheric columns of key species related to tropospheric ozone formation have been measured. These data will be compared similar studies in 2006, 2009 and 2011 [Mellqvist 2007; 2009; 2010 and Rivera 2010.
Equally important, the measurements compliment the NASA Discover campaign that was running in the HSC area during September 2013. NASA flew a high altitude aircraft (B200) equipped with optical sensors measuring columns of SO2, NO2, HCHO and aerosol profiles with LIDAR (LIght Detection And Ranging). In addition a low flying airplane (P-3) made spirals in the vicinity of two ground stations in the HSC, to validate the high altitude measurements. Since the mobile DOAS measures the same species as the NASA aircraft there is a good data set available for comparison, to assess the quality of the information obtained by the high altitude airborne measurements.

1.2 Purpose of the project and specific project objectives.

The objective is to demonstrate the usefulness of geostationary satellites for providing environmental data by comparative studies. A second objective is to improve the understanding of tropospheric ozone formation and the impact of industrial emissions by providing emission data.
The main aim of this study is to compare the measured NO2, SO2 and HCHO around the Houston ship channel with similar data from the NASA aircraft and in situ measurements. This will require improving the quality of the column measurements of NO2, SO2, HCHO and VOCs obtained using mobile DOAS and SOF-
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 demonstrate a new instrument for aromatic VOC measurements by comparison of the data to other measurements and to derive aromatic VOC emissions from some isolated industries using a combination of SOF , mobile extractive FTIR and mobile White cell DOAS.

2. ORGANIZATION AND RESPONSIBILITIES

2.1 Project personnel, including QA, and related responsibilities for each participating organization, as well as their relationship to other project participants.

Principal investigator
Johan Mellqvist, Chalmers University of Technology
• Primary contact person at Chalmers University of Technology for contract and budget issues related to the project.
• Provides general oversight of project activities.
• Prepares project specific reports and maintains QA Project Plan
• Participates in planning teleconferences.
• Participates in data analysis, reporting and paper writing

Research Scientist
Pontus Andersson, Chalmers University of Technology
• Responsible for data analysis and paper writing of the MWDOAS data .

Doctoral Student
John Johansson, Chalmers University of Technology
• Responsible for data analysis of the mobile DOAS and SOF measurements, radiative transfer modeling and writing of scientific paper.

Co Principal Investigator
Barry Lefer - University of Houston (UH)
• Primary contact person at University of Houston for contract and budget issues related to the UH part of the project.
• Provides general oversight of UH project activities.
Will manage the project data analysis and interpretation as supervisor of other UH personnel.

Research Assistant Professor, James Flynn - University of Houston
Project data analysis and interpretation

Doctoral Student
Sergio Alvarez, University of Houston
Project data analysis and interpretation

2.2 Project schedule and key milestones.

Table 1. Time schedule of the main tasks

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***

3. SCIENTIFIC APPROACH

3.1 Secondary data needed to meet the project objective(s).

3.1.1. *Column and in situ data of NO2, SO2, HCHO and VOCs*

The weather during the AQ DISCOVER campaign was relatively poor with few really clear days. 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 NO2 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. The data will be compared to measurements by NASA from aircraft and ground sites. More details can be found in the workplan.

Data needed:
a) Column data of NO2, SO2 and HCHO from mobile DOAS (reanalysis)
b) Column data of VOCs from SOF (reanalysis)
c) Column data of NO2, SO2 and HCHO from NASA B300 aircraft
d) Column data of NO2, SO2 and from Pandora instrument at ground sites,
e) In situ data of NO2, SO2, HCHO and VOCs from NASA P-3 aircraft.
f) In situ data of NO2, SO2, HCHO and VOCs from ground sites.
Time period: September 2013
Geographical area: HSC

3.1.2 Emission data of VOCs SO2, NO2, HCHO.
We will compare the derived emission 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.

Data needed:
a) Emission data of VOCs from SOF (reanalysis)
b) Emission data of SO2 and NO2 from mobile DOAS (reanalysis)
c) Continuous Emission monitoring (CEM) data of SO_2 and NOx
d) Emission inventory data.
Time period: September 2013
Geographical area: HSC

3.1.2 Aromatic VOC data

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 ultraviolet (UV) multiple reflection cell connected to a DOAS spectrometer, here called MW-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.

In this study we want to compare the MW-DOAS data to correlative data obtained with PTR-MS (Proton Transfer Mass Spectrometer) by Aerodyne lab. We will also infer aromatic emissions from industrial sites using the measured ratios of aromatic VOCs and alkanes combined with SOF.

Data needed: reanalyzed SOF emission data of VOCs, reanalyzed mobile DOAS data of SO2 and NO2 emissions, CEM data of SO2 and NO2, emission inventory data from STARS (State of Texas Air Reporting System) 2011 or later.

Data needed:
a) In situ data of aromatic VOCs from MW-DOAS(reanalysis)
b) In situ data of aromatic VOCs from PTR-MS
c) In situ data from UH
Time period: September 2013
Geographical area: HSC

3.2 Sources for the secondary data.

Table 2. Sources for the secondary data.

Species	**Data**	**Technique**	**Source**	**Time**	**Location**
NO2	column	Mobile DOAS	Chalmers	Sep 2013	HSC
SO2	column	Mobile DOAS	Chalmers	Sep 2013	HSC
HCHO	column	Mobile DOAS	Chalmers	Sep 2013	HSC
VOCs (alkane, alkene)	column	SOF	Chalmers	Sep 2013	HSC
NO2	Emission	Mobile DOAS	Chalmers	Sep 2013	HSC
SO2	Emission	Mobile DOAS	Chalmers	Sep 2013	HSC
HCHO	Emission	Mobile DOAS	Chalmers	Sep 2013	HSC
VOCs (alkane, alkene)	Emission	SOF	Chalmers	Sep 2013	HSC
NO2	Emission	Acid Rain Data Base	TCEQ	Sep 2013	HSC
SO2	Emission	Acid Rain Data Base	TCEQ	Sep 2013	HSC
VOCs (alkane, alkene)	Emission	Inventory	TCEQ	Sep 2013	HSC
NO2	column	B200/Pandora	NASA	Sep 2013	HSC
SO2	column	B200/Pandora	NASA	Sep 2013	HSC
HCHO	column	B200/Pandora	NASA	Sep 2013	HSC
VOCs	column	B200/Pandora	NASA	Sep 2013	HSC
NO2	concentration	P3/ground site	NASA	Sep 2013	HSC
SO2	concentration	P3/ground site	NASA	Sep 2013	HSC
HCHO	concentration	P3/ground site	NASA	Sep 2013	HSC
VOCs	concentration	P3/ground site	NASA	Sep 2013	HSC
Aromatic VOCs	concentration	MW-DOAS	Chalmers	Sep 2013	HSC
Aromatic VOCs	concentration	PTR-MS	Aerodyne, University of Montana	Sep 2013	HSC

4. QUALITY METRICS

Here the quality criteria for the main instruments used by the Chalmers group are shown.

The quality of the comparative data that also will be used will be assessed during the project as well as the quality of the MW-DOAS data.

4.1 Quality requirements of the secondary data.

The QA objectives for the spectroscopic measurements (SOF, Mobile DOAS) are given in Table 3 below. As part of the QA procedure we will actively look for opportunities to compare the emissions estimates of SO2 and NO2 with a stack emission monitored by CEM.

Table 3. Quality requirements of the secondary data

Measurement Parameter	**Analysis Method**	**Accuracy**	**Precision**	**Completeness***
1) SOF column concentrations of alkanes, ethene and propene	QESOF** spectral retrieval	±10%	±5%	70-90%
2) Mobile DOAS column concentration of NO_2, SO_2 and HCHO	DOAS spectral retrieval	±10%	±5%	70-90%
3) Ambient Wind Speed	R.M. Young Wind monitor	±0.2 m/s	±0.2 m/s	95%
4) Ambient Wind Direction	R.M. Young Wind monitor	±5º	±3º	95%
5) GPS position	GPS*** receiver	±2m	±2m	95%
6) SOF mass flux of alkanes, ethene and propene	SOF flux calculations	±30%	±10%	80% (in suitable weather conditions)
7) Mobile DOAS mass flux of NO_2, SO_2 and HCHO	Mobile DOAS flux calculations	±30%	±10%	80% (in suitable weather conditions)

* For the optical measurements conducted in this project data completeness is difficult to estimate since the measurements are dependent on external parameters such as weather conditions.
****** Quantitative Evaluation of SOF (QESOF)
*** Global positioning System (GPS)

Accuracy of measurement parameters is determined by comparing a measured value to a known standard, assessed in terms of % bias using the following equation:

$$\left[1-\left(\frac{\text{Measurement}}{\text{Standard}}\right)\right]\times 100 \qquad (1)$$

Precision is a measure of the repeatability of the results. The precision for the SOF and mobile DOAS system is difficult to measure when inside the gas plumes. However it is assumed that the precision of the instrument corresponds to the 1sigma noise when measuring in clean air background. Precisions of the instrumentations used in the project are listed in Table 3.

Data completeness is calculated on the basis of the number of valid samples collected out of the total possible number of measurements. Data completeness is calculated as follows:

$$\% \text{ Completeness} = \frac{\text{Number of valid measurements} \times 100}{\text{Total possible measurements}}$$

Detection Limits

Estimates of the detection limit of various parameters measured in this study are shown in Table 4, determined from the typical absolute precision for column measurements in earlier studies when driving 40 km/h downwind of industries in Houston:

Table 4. Detection Limits

Parameter	**Detection Limit**
air temperature	n/a
Atmospheric Pressure	0.01 mb
Relative Humidity	n/a
Wind direction	1 degrees
Wind speed	0.5 m/s
SOF: alkanes (C3-C8)	3 mg/m^2
SOF:ethene	1 mg/m^2
SOF:propene	2 mg/m^2
mobile DOAS:SO2	1 mg/m^2
mobile DOAS:NO2	1 mg/m^2
mobile DOAS:HCHO	0.2 mg/m^2

Accuracy

The accuracy of the SOF and mobile DOAS systems is estimated as the square root sum of the precision and the systematic spectroscopic uncertainties. Accuracies of the instrumentations used in the project are listed in Table 5, Table 6 and Table 7.

Table 5 Accuracy of SOF and mobile DOAS.

Parameter	**Accuracy**
SOF: alkane column(C3-C8)	±10%
SOF:ethene column	±10%
SOF:propene column	±10%
mobile DOAS:SO2 column	±10%
mobile DOAS:NO2 column	±10%
mobile DOAS:HCHO column	±10%

Table 6. Meteorological parameters (weather mast)

Parameter	**Accuracy**
Air temperature	±1 degrees C
Atmospheric Pressure	±2 mb
Relative Humidity	±4 % RH
Wind direction	±1 degrees
Wind speed	±0.5 m/s for winds 0-5 m/s ±1 m/s for winds 5-40 m/s

Table 7. Meteorological parameters (radiosonde)

Parameter	**Accuracy**
Air temperature	±0.2 degrees C
Atmospheric Pressure	±0.5 mb
Relative Humidity	±5 % RH
altitude	±15 m
position	±5 m
velocity	0.1 m/s

Comparability

Comparability is achieved when the results are reported in standard units to facilitate comparisons between the data from this network and other similar programs. In order to accomplish this objective, the reporting units for the ambient monitoring measurements are listed as in Table 8.

Table 8 Comparability

Parameter	**Units**	**Conditions**
air temperature	deg C	Ambient
Atmospheric Pressure	mb	Ambient
Relative Humidity	%	Ambient
Wind direction	degrees	Ambient
Wind speed	m/s	Ambient
SOF columns	mg/m2	Ambient
mobile DOAS columns	mg/m2	Ambient

5. DATA ANALYSIS, INTERPRETATION, AND MANAGEMENT

5.1 Data reporting requirements,

A Draft and Final Report will be delivered to the TCEQ Project Manager electronically (i.e., via file transfer protocol (FTP) or e-mail) in Microsoft Word format no later than the established deliverable due date.
After post-processing, validation and analysis, the data will be delivered to the UT AQRP and to the TCEQ Project Manager at the time of the final report.

5.2 Data validation procedures to ensure the reporting of accurate project data.

Project personnel will maintain records that include sufficient information to reconstruct each final reported measurement from the variables originally gathered in the measurement process. This includes, but is not limited to, information (raw data, electronic files, and/or hard copy printouts) related to sampler calibration, sample collection, measurement instrument calibration, quality control checks of sampling or measurement equipment, "as collected" or “raw” measurement values, an audit trail for any modifications made to the "as collected" or “raw” measurement values, and traceability documentation for reference standards.
Difficulties encountered during sampling or analysis has been documented in narratives that clearly indicate the affected measurements. All electronic versions of data sets reflect the limitations associated with individual measurement values.
The reanalyzed data used in the project will made available in electronic format at the time of the final report. For all data we will produce ASCII tables with the geo-positioning and time. In addition KML (Keyhole Markup Language) files will be produced for the best looking data for Google Earth viewing.

- Instrument calibration data forms
- Electronic and manual daily and activity logs
- Electronic and manual data processing and validation logs
- Records of assessment, such as performance evaluation records

To ensure high quality data an internal audit procedure of the data is carried out. In the project gas columns obtained from SOF and mobile DOAS measurements are used to calculate gas fluxes through a procedure which includes manual checking of each measurement transect and manual choices of baselines etc. In the audit procedure 10% of the completed transects will be gone through by a person that was not involved in the actual data evaluation.

5.3 Data summary and analysis

The data will be post processed with the spectral retrieval programs QESOF (SOF. MeFTIR) and QDOAS (mobile DOAS, MW-DOAS). This will give time series of column concentrations, positions and solar angles stored in ASCII-files. These files are loaded into another custom software, Sofsuite which is used to calculate fluxes.
Radio sonde data is being processed using the iMetOS meteorological operating system. Data files are saved as ASCII text files.
The weather mast will be connected to a data logging computer. The data logger computer sample the analog output voltage of each instrument at a set time interval, digitizes it, and stores the data sequentially into a record.
ASCII tables with time stamped geo-positioned data will be produced. In addition KML files will be produced for the best looking data for Google Earth viewing. The data will also be retained for a minimum of 3 years at Chalmers University of Technology in Göteborg.

5.4 Data storage requirements

The spectra from the spectroscopic measurements (SOF and mobile DOAS) are already saved corresponding to approx. 2 GB data will be produced.

5.5 Audits of Data Quality.

In this section for the data generated by the analyses performed in this project, what data will audited, how much of it will be audited, and who will perform these audits.

John Johansson and Pontus Andersson will derive the column and concentration data from the various instruments. Johan Mellqvist will audit approx. 10+% of these.

6. REPORTING

6.1 Deliverables

Monthly Status Report

A monthly report will be delivered to the AQRP project manager electronically (i.e., via file transfer protocol (FTP) or e-mail) in Microsoft Word format. The report will cover activities for the previous month detailing the project status and the percentage of valid data produced for each monitor at each monitoring site. The report will be delivered by Chalmers on or before the 15th of each month.

6.2 *Final Project Report*

A Final Report shall be delivered to the TCEQ Project Manager electronically (i.e., via file transfer protocol (FTP) or e-mail) in Microsoft Word format no later than the deliverable due date shown below. The Final Report will include the following components:

1. An executive summary or abstract.
2. A brief introduction that discusses background and objectives. Include relationships to other studies if applicable.
3. A discussion of the pertinent accomplishments, shortfalls, and limitations of the work completed under each Grant Activities Description task, including the findings of the audits of data quality
4. Recommendations, if any, for what should be considered next as a new study.

The final report will include geopositioned column and concentration data of the various target species. These data will be compared to column and concentration measurements by NASA in various appropriate manners, such as tables, graphs and KML plots.

Part of the column data for VOCs, NO_2 and SO_2 will be converted to mass fluxes for certain isolated industrial areas in the HSC using available wind information. The mass flux measurements from various industrial areas will be shown in a table together with corresponding emission inventory data. However, the precise industrial areas in the HSC are not yet well defined since they depend on the data. The emission inventory data are usually reported on an annual basis so therefore a discussion about the influence of wind, temperature and solar radiation will be included.

7. REFERENCES

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