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Emissions Test Plan for Solar Occultation Flux Testing at Indiana Harbor Coke Company

Developed in accordance with Paragraph 30.a of Consent Decree, Case No. 2:18-cv-00035 (Oct. 25, 2018)

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Table of Contents

Table of Contents	2
List of Tables	3
List of Figures.....	3
1. INTRODUCTION	4
1.1 Test Plan Summary	4
1.2 Test Program Organization.....	5
2. Source Description	6
2.1 Process Description	6
2.1.1 General Overview	6
2.1.2 Plant Description	6
2.1.3 Production Activity Description.....	8
2.2 Control Equipment Description.....	10
2.2.1 Negative pressure and complete combustion	10
2.2.2 Coke Shed	10
2.2.3 Quench tower baffles	11
2.2.4 Flue Gas Desulfurization	11
3. TEST PROGRAM	11
3.1 Objectives	11
3.2 Test Matrix.....	12
4. SAMPLING LOCATIONS	14
5. SAMPLING AND ANALYTICAL PROCEDURES.....	15
5.1. Test methods.....	15
5.2. Process data	17
6. QA/QC ACTIVITIES	18
7. Reporting and data reduction requirements	21
7.1. Report format.....	21
7.2. Data reduction and summary.....	21
8. Plant entry and safety	23
8.1. Safety responsibilities.....	23
8.2. Safety program	23
8.3. Safety requirements	24
9. Personnel responsibilities and test schedule	25

9.1. Test site organization	25
9.2. Test preparations	26
9.3. Test personnel and responsibilities and detailed schedule	27
APPENDIX 1 – Measurement methods.....	28

List of tables

Table 1. Approximate height of main plant installations.	7
Table 2. Test matrix of main measurement targets.	12
Table 3. Test method overview and detection limits.....	13
Table 4. Summary data reduction table.....	22
Table 5. Test preparations.....	26
Table 6. Time schedule.....	27

List of Figures

Figure 1. Plant overview	6
Figure 2. Approximate heights of main buildings and installations.	7
Figure 3. Overview of the site and main measurement routes	15
Figure 4. Overview of the FluxSense mobile lab main instruments.....	16

1. INTRODUCTION

1.1 Test Plan Summary

This test plan relates to an emissions test at Indiana Harbor Coke Company (IHCC) located at 3210 Watling Street, East Chicago, Indiana. Measurements will be conducted by FluxSense Inc. (113 W G St #757, San Diego, CA 92101). Testing will be conducted to satisfy the requirements of paragraph 30 of the consent decree among the United States, the State of Indiana, SunCoke Energy, Inc., IHCC, and Cokenergy LLC entered in the U.S. District Court for the Northern District of Indiana on October 25, 2018 (Case No. 2:18-cv-00035).

The main objectives of the test are to attempt to quantify overall emissions of VOCs (volatile organic compounds) and SO₂ (sulphur dioxide) from the plant, and identify major sources of the emissions.

SOF (Solar Occultation Flux) will be used to measure emissions of VOCs, combining measured slant vertical columns with wind speed and direction measurements.

SkyDOAS (zenith-sky Differential Optical Absorption Spectroscopy) will be used to measure vertical columns of SO₂ combined with wind speed and direction measurements.

Plume concentration ratios of benzene and BTEX (benzene, toluene, ethylbenzene and xylene) to alkanes and SO₂ will be characterized both at the fenceline and closer to sources, for indirect emission assessment. Mobile and stationary extractive Fourier Transform InfraRed spectroscopy (MeFTIR) and ultraviolet DOAS (Mobile Whitecell DOAS) will be used for the concentration measurements of VOCs and SO₂.

Wind speed and wind direction will be measured at multiple locations by means of wind masts and a moveable vertical wind profiler (LIDAR, light detection and ranging) on a continuous basis.

The test is planned to be conducted during the period 25 May – 12 June, 2020.

The IHCC plant produces metallurgical coke from coal in heat-recovery coke ovens as detailed in section 2.1 below. In the heat recovery process, VOCs evolved from the pyrolyzed coal are combusted to completion within a negative pressure system. Residual heat in the combusted flue gas is extracted by heat recovery steam generators (HRSGs). Flue gas sulfur dioxide is treated by a flue gas desulfurization (FGD) system. The test will measure fenceline emission plumes and characterize emissions closer to potential sources (such as coke ovens, HRSGs, and flue gas treatment systems).

1.2 Test Program Organization

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2. Source description

2.1 Process Description

2.1.1 General Overview

IHCC operates an advanced heat-recovery process to transform coal into metallurgical coke. In the process, coal is charged into a high temperature oven. A portion of the coal pyrolyzes and produces volatile matter (VM). The remaining fixed carbon polymerizes into coke. The VM is combusted within the oven to provide the heat to continue the coking process. The combusted flue gas is directed through heat recovery steam generators (HRSGs) where the residual heat is extracted and steam is produced. The steam can be used to generate electricity supplied to the steel plant. The cooled flue gas is scrubbed in a flue gas desulfurization (FGD) system and exhausted. The finished coke is pushed from the oven, quenched with water, screened to remove fine material and delivered to the customer.

2.1.2 Plant Description

As shown in Figure 1, The IHCC plant is arranged in four batteries (A, B, C, & D) of 67 ovens each. There are two quench towers (one shared by batteries A&B and one shared by batteries C&D). Each battery has four HRSGs and emergency vent stacks. The HRSGs are owned and operated by Cokenergy. The combusted and cooled flue gas is directed to the FGD system in the Cokenergy facility comprised of a spray dry absorber (SDA), baghouse and main stack. There are two parallel induced draft fans at the base of the main stack that draw the flue gas through the entire system.

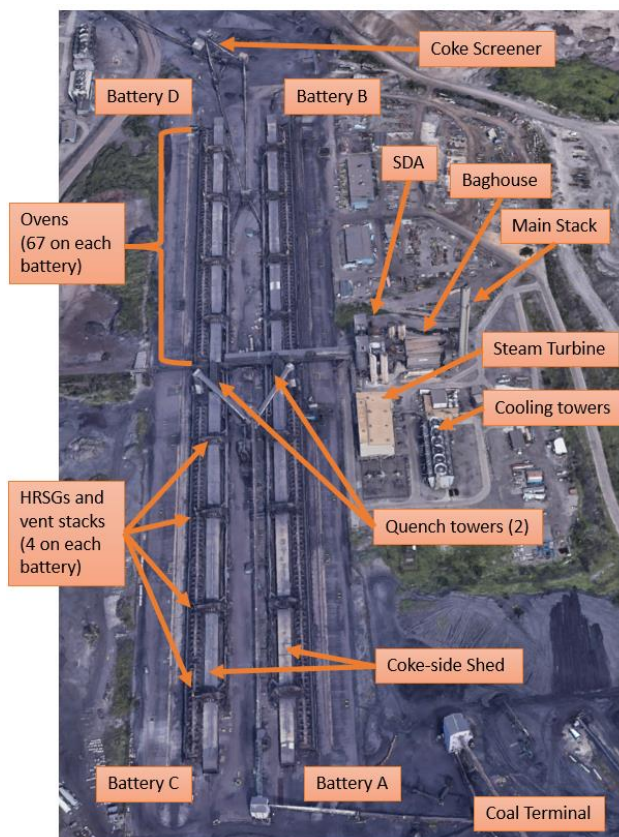


Figure 1. Plant overview.

For the purposes of an atmospheric plume detection trial, it is important to determine the approximate heights of various structures and potential sources. These heights and locations are described in Table 1 and Figure 2.

Table 1. Approximate height of main plant installations.

Site part	Approximate height above ground (feet)
Main stack	300'
Top of the SDA penthouse	150'
Bypass vent stacks	81'
Top of the common flue gas tunnel	29'
Top of the ovens	15'
Top of HRSG	55'
Quench tower	60'
Shed	42'
STG building and cooling towers	60'
Coal surge bin	118'

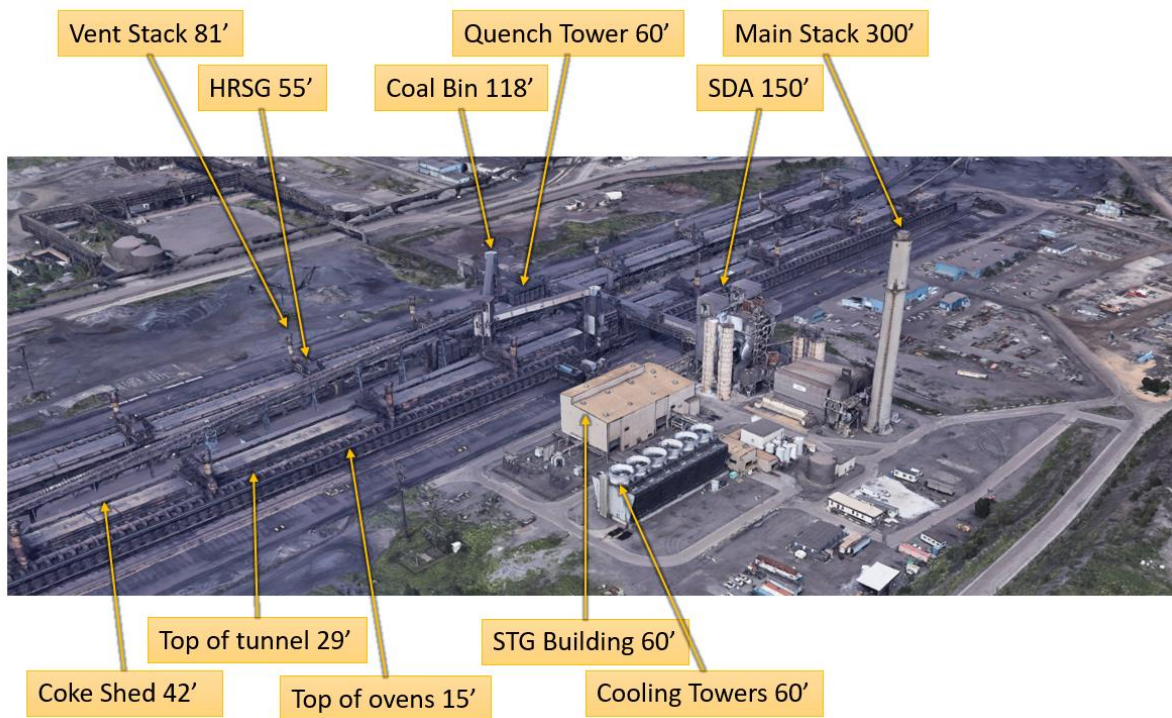


Figure 2. Approximate heights of main buildings and installations.

2.1.3 Production Activity Description

Figure 3 illustrates the generic process for heat-recovery coke making.

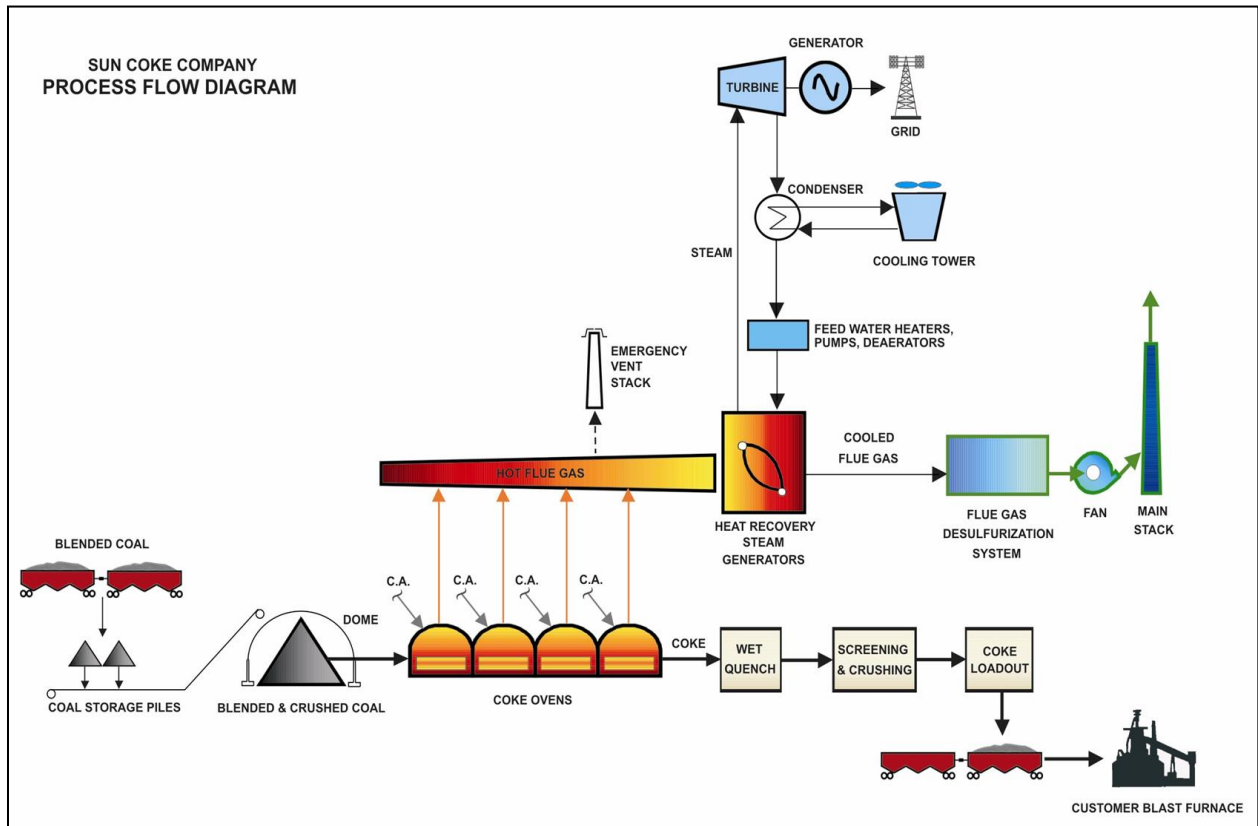


Figure 3. Heat Recovery Coke Making Process Flow Diagram.

In the normal production process at IHCC, crushed and blended coal is brought into the plant from the terminal via conveyor belt and temporarily stored in two coal bins. During the daily production cycle (1PM to 6AM), 134 ovens (half of the plant) are pushed and charged. The timing of the pushing of individual ovens is determined by when they are deemed fully coked (ready to push) in accordance with regulatory requirements and by minimizing the adjacency of freshly charged ovens to spread out the gas generation load within the flue gas system.

To push an oven, the Pusher-Charger-Machine (PCM) removes the oven door on the push side of the battery and aligns the pusher ram with the oven. On the coke side, the door machine removes the oven door and aligns the coke chute. The hot car is positioned under the coke chute. The PCM then rams the coke through the oven into the hot car. The hot car then trams to the quench tower. The distance from the quench tower to the furthest oven is 1,100 ft. The hot car tramping to the quench tower is done within a coke shed enclosure that has a dust removal system. In the quench tower, the coke is drenched in water to cool the coke down to a safe level. The quench process takes about 90 seconds. The hot car then dumps the coke onto the wharf. The coke is then metered onto the coke conveyor belt. The belt transports the coke to the screening deck where the waste small coke (breeze) is removed. The final product coke (known as furnace coke) is then transported by conveyor belt to the adjacent customer facility.

After the coke is pushed out, fresh coal is charged into the empty oven. On the coke side, the door machine replaces the door. On the push side, the PCM removes the ram and then aligns the leveling conveyor. A specific amount (typically 35-42 tons) of coal is then transferred by conveyor belt from

the coal bins to the PCM. The PCM then loads the coal charge into the oven via the leveling conveyor through the push side opening. The PCM then replaces the door. The pushing/charging process takes approximately 10 minutes to complete.

The coal in the oven carbonizes to coke over a period of approximately 48 hours. Each day, half the ovens in the plant are pushed and charged. To even out the mass flow in the flue gas system, the oven pushes are spread out over the time of the production shift, spread out over the batteries and spread out over the ovens under individual HRSGs. Both sides of the plant (A&B batteries and C&D batteries) operate at the same time. Thus, potential fugitive emission sources from the pushing/charging process are distributed over 17 hours and the length of the plant (2,300 ft).

In the oven, the pyrolyzing coal releases volatile matter (VM). Air is drawn into the oven which then combusts the VM in the crown space above the bed and in the flue below the bed, as illustrated in Figure 4.

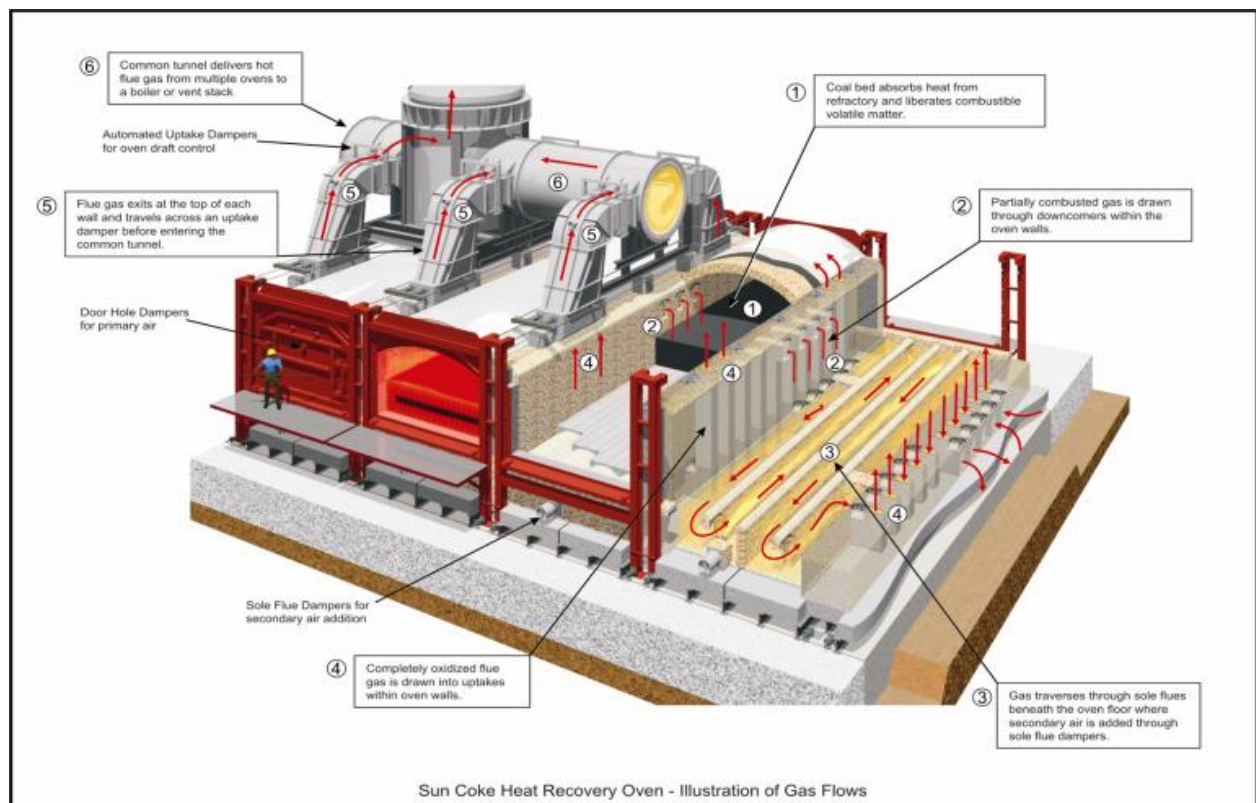


Figure 4. Heat Recovery Coke Oven Detail.

Heat recovery ovens are designed to operate under negative pressure during the coking cycle to minimize fugitive emissions compared with ovens at byproduct coke plants that operate under positive pressure. The VM is combusted completely, resulting in comparatively low VOCs. The flue gas generated by the coking process is conducted into a common tunnel which is designed to act as an afterburner. The common tunnel carries the flue gas to the heat recovery steam generators (HRSGs), which produce steam for use in the process or generating electricity.

After passing through the HRSGs, the flue gases are cleaned and filtered by a flue gas desulfurization (FGD) unit before being exhausted through the main stack by an induced draft fan. The induced draft fan creates the negative pressure throughout the system all the way back to the ovens. The FGD

consists of a spray dry absorber (SDA) that contacts lime slurry ($\text{Ca}(\text{OH})_2$) with the flue gas and a baghouse for collection of particulate matter (CaSO_4 particles).

Each HRSG is matched with an emergency vent stack. During normal facility operations, the vent stack lids remain closed. In the event of a process upset or outage of a HRSG that does not allow the oven exhaust to be sent to the FGD and the main stack, the vent stack lid will open to allow the flue gas from the associated ovens to exhaust to the atmosphere through the vent stack while maintaining negative pressure in the system.

2.2 Control Equipment Description

2.2.1 Negative pressure and complete combustion

The primary mechanism for emission control in heat recovery coke making is that the flue gas system is under negative pressure (known as draft) relative to the atmosphere. The induced draft (ID) fans provide a fraction of an inch of water column vacuum relative to atmospheric pressure at the ovens, which is designed to keep the VM and combustion gases inside the system. Additionally, the VM is combusted within the flue ductwork and common tunnel, which minimizes VOCs in the flue gases exiting the stacks.

2.2.2 Coke Shed

During pushing, the coke from the oven is transferred into a hot car and transported to the quench tower. In order to control any dust during this process, the hot car rail is enclosed in a coke shed shown in Figure 5. The coke shed includes a dust removal system which employs an induced draft fan and a baghouse.



Figure 5. Coke-side shed.

2.2.3 Quench tower baffles

When the coke in the hot car is quenched with water, a large volume of steam is rapidly created. The quench steam cloud is vented through a quench tower which directs the steam up into the atmosphere. Internal baffles (chevrons in the steam path) in the quench tower control particulate matter.

2.2.4 Flue Gas Desulfurization

The cooled flue gas is directed to a flue gas desulfurization system that consists of a spray dry absorber (SDA) and a baghouse. In the SDA, atomizers create a fine mist of droplets of lime slurry (aqueous calcium oxide or $\text{Ca}(\text{OH})_2$). The SO_2 in the gas diffuse into the droplets and react to ultimately form CaSO_4 . The droplets dry out in the SDA leaving solid particles of CaSO_4 and unreacted lime. These particles are collected by the baghouse and sent off site for disposal.

3. TEST PROGRAM

3.1 Objectives

The objectives of the proposed test plan and measurements are to attempt to quantify overall emissions of VOCs (volatile organic compounds) and SO_2 (sulphur dioxide) from the plant, and identify major sources of the emissions.

- Measure emissions of VOCs (alkanes, alkenes) emerging from the plant by Solar Occultation Flux (SOF) measurements of slant vertical columns combined with wind speed and direction measurements.
- Measure emissions of SO_2 from the plant by zenith-sky Differential Optical Absorption Spectroscopy (SkyDOAS) of vertical columns combined with wind measurements.
- Characterize plume concentration ratios of benzene and BTEX (benzene, toluene, ethylbenzene and xylene) to alkanes and SO_2 both at fenceline and closer to sources, for indirect emission assessment. Mobile and stationary extractive Fourier Transform InfraRed spectroscopy (MeFTIR) and ultraviolet DOAS (Mobile Whitecell DOAS) will be used for the concentration measurements of VOCs and SO_2 . MeFTIR will measure concentrations of total VOCs as observed by C-H-stretch absorption in the $2700\text{--}3100\text{ cm}^{-1}$ wavenumber region. Canister samples will be collected in parallel (at the back of the extractive optical cells) with the MeFTIR and MWDOAS instruments for QA-QC purposes. An analyte list of $\text{C}_6\text{--C}_{10}$ alkanes and $\text{C}_6\text{--C}_9$ aromatic compounds will be used for comparison.
- Measure wind speed and wind direction at multiple locations by means of wind masts and a moveable vertical wind profiler (LIDAR, light detection and ranging) on a continuous basis.
- Measure fenceline concentrations and vertical columns in order to attempt to understand any effects of neighboring site emissions on the observed emissions at IHCC.
- Obtain GPS time and location stamps for all measurements.
- Measure concentrations and fluxes of VOCs and SO_2 in the main stack by extractive sampling from the CEMS line and tracer injection (N_2O). Tracer gas will be injected upstream or in the base of the stack at a known rate (typical 10 liters/minute), and the tracer concentration as well as SO_2 and VOC concentrations are then sampled downstream higher up in the stack at the CEMS line intake. The concentration ratio between target gas and tracer gas combined with the tracer injection rate gives the flux.

- During the test period, obtain production rates and times for pushing and charging of the different ovens, and obtain time log for the quenching episodes. Obtain coal usage rates and % sulphur content in the used coal.
- Obtain logs for any deviations from normal production, specifically any bypass venting or other events that might affect observed emissions, also with regard to the service and maintenance window (6 AM – 1 PM).

3.2 Test Matrix

Table 2. Test matrix of main measurement targets.

Sampling location	No. of days	No. of runs	Pollutant / entity	Sample type	Sampling Method	Analytical method
Fenceline, overall site plume, route 1&2 ^{a)}	5+	25+	VOCs	Vertical columns	SOF	FTIR
Fenceline, overall site plume, route 1&2 ^{a)}	5+	25+	SO ₂	Vertical columns	SkyDOAS	DOAS
Fenceline, overall site plume, route 1&2 ^{a)}	5+	25+	VOCs, SO ₂ , BTEX, Benzene	Concentration	MeFTIR, MWDOAS	FTIR, DOAS
Fenceline, overall site plume, route 1&2 ^{a)}	2	10	VOCs ^{b)}	Concentration	Canisters	GC-FID, external lab
Main stack	2+	10+	VOCs	Vertical columns	SOF	FTIR
Main stack	2+	10+	SO ₂	Vertical columns	SkyDOAS	DOAS
Main stack, CEMS line	2	2+	VOCs, SO ₂ , BTEX, Benzene	Concentration	MeFTIR, MWDOAS	FTIR, DOAS
Main stack, CEMS line	1	4	VOCs ^{b)}	Concentration	Canister samples	GC-FID, external lab
Coke ovens, close-by screening along route 1&3 ^{a)} . Detailed screening min. 4 ovens per battery.	2	16	VOCs, SO ₂ , BTEX, Benzene	Concentration	MeFTIR, MWDOAS	FTIR, DOAS
Coke conveyance, close-by screening along route 1&3 ^{a)}	1	2	VOCs, SO ₂ , BTEX, Benzene	Concentration	MeFTIR, MWDOAS	FTIR, DOAS
Vent stacks, Detailed screening min. 1 vents per battery.	1	4	VOCs, SO ₂ , BTEX, Benzene	Concentration	MeFTIR, MWDOAS	FTIR, DOAS
Quench towers, Detailed screening	1	2	VOCs, SO ₂ , BTEX, Benzene	Concentration	MeFTIR, MWDOAS	FTIR, DOAS

HRSs, min. 1 per battery, Detailed screening	1	4	VOCs, SO ₂ , BTEX, Benzene	Concentration	MeFTIR, MWDOAS	FTIR, DOAS
Charging/Pushing unit, detailed screening	2	5+	VOCs, SO ₂ , BTEX, Benzene	Concentration	MeFTIR, MWDOAS	FTIR, DOAS
Charging/Pushing unit, detailed screening	1	4	VOCs ^{b)}	Concentration	Canister samples	GC-FID, external lab
All site	All days	All runs	Wind field	Wind speed and wind direction	Wind LIDAR and tower monitor	Wind induced doppler shift, rotational RPM and direction

a) See Figure 3.

b) Canister samples will be collected in parallel to the extractive FTIR and DOAS instruments (at the back of the optical cells) for QA-QC purposes. Sampling will be done to Silonite coated evacuated canisters, and the samples will be analyzed for C₆-C₁₀ alkanes and C₆-C₉ aromatic compounds (hexane, cyclohexane, heptane, octane, nonane, decane, benzene, toluene, ethylbenzene, xylene, trimethylbenzene).

Table 3. Test method overview and detection limits.

Method:	SOF	Sky DOAS	MeFTIR	MWDOAS
Compounds	Alkanes: (C _n H _{2n+2}) Alkenes: C ₂ H ₄ , C ₃ H ₆ NH₃	SO₂ NO₂	CH₄ Alkanes: (C _n H _{2n+2}) Alkenes: C ₂ H ₄ , C ₃ H ₆ NH₃ N₂O (tracer)	BTEX, Benzene SO₂
Detection limit	0.1-5 mg/m ²	0.1-5 mg/m ²	1-10 ppbv	BTEX 0.5-4 ppbv
Column				Benzene 0.5 ppbv, SO ₂ 4 ppbv
Detection limits	0.2-1 kg/h	1 kg/h	0.2-2 kg/h	Benzene: 0.15 kg/h
Direct Flux (SOF and SkyDOAS)* or inferred flux from concentration ratios by MeFTIR/MWDOAS combined with direct flux from SOF/SkyDOAS				BTEX: 0.25 kg/h
Detection limits with tracer release and			CH ₄ : 0.1 kg/h	Benzene: 0.1 kg/h

MeFTIR+MWDOAS nearby (20-100 m) localized source			Alkanes: 0.25 kg/h Alkenes: 0.4 kg/h	SO ₂ : 0.15 kg/h BTEX: 0.2 kg/h
Wind Speed Tolerance	1.5-12 m/s	1.5-12 m/s		
Sampling Time Resolution	1-5 s	1-5 s	5-15 s	8-10 s
Measured Quantity [unit]	Integrated vertical column mass [mg/m ²]	Integrated vertical column mass [mg/m ²]	Mass concentration at Vehicle height [mg/m ³]	Concentration at Vehicle height [mg/m ³]
Inferred Quantity [unit]	Mass Flux [kg/h]	Mass Flux [kg/h]	1) Alkane ratio of ground plume combined with SOF gives mass flux [kg/h] and plume height information [m] 2) Alkane and CH ₄ flux [kg/h] via tracer release	Combined with MeFTIR and SOF gives Mass Flux [kg/h] or combined with MeFTIR + tracer [kg/h]
Complementary data	Vehicle GPS- coordinates, Plume wind speed and direction	Vehicle GPS- coordinates , Plume wind speed and direction	Vehicle GPS- coordinates Plume wind direction	Vehicle GPS- coordinates, Plume wind direction

4. SAMPLING LOCATIONS

Measurements will be conducted both in a mobile mode, where the mobile lab is driven alongside near the facility installations and further away at the fenceline, and in a stationary mode where detailed concentration screening is made near the sources.

Figure 3 displays some planned main routes for the mobile measurements pending approval based on operational and safety constraints. The mobile measurements are conducted both upwind and downwind of the facility in order to observe if any incoming emissions from neighboring sites might interfere with the observations.

The close-by measurement route no. 1 will be driven slowly in order to obtain good spatial resolution in the continuous measurements, and hence gain knowledge of specific hotspots, if any. This also applies for the intermediate route no. 3 in between the oven batteries.

The fenceline route no. 2 will be used to screen the overall site emissions as well as to attempt to identify any interfering emissions from neighboring sites.

The prevailing wind direction is expected to be from lakeside (N-SE sector), but winds can be variable and change over the course of the day. Care needs to be taken for any inflow from the steelworks nearby for NW winds and for refinery background emissions for SW winds.

The wind will be monitored by a moveable vertical wind profiler (LIDAR) that will be placed near the location of the measurements. The wind LIDAR will monitor the wind in the 10 m – 200 m vertical range. This will be complemented by a stationary wind mast (~10 m) and wind meter mounted on the mobile lab.

Sampling will also be conducted by the main stack, both by vertical column measurements using SOF and SkyDOAS, and by concentration sampling utilizing the CEMS line at the main stack. The CEMS line sampling part will be associated with tracer injection (N_2O) into the stack for flux retrieval.

Concentration measurements for screening and concentration ratios will be done both from the mobile lab platform on routes 1-4, and for stationary extractive sampling assisted by inlet tubing attached to a sky-lift for elevated access to the plume from selected sources. The sky-lift will not carry any persons, but will be used to lift tubing to different positions for sampling. This sampling procedure will be used to obtain concentration ratios of BTEX and benzene versus other VOCs as measured by DOAS and FTIR in the cross section of different plumes, if identified.



Figure 3. Overview of the site and approximate planned measurement routes (subject to change).

5. SAMPLING AND ANALYTICAL PROCEDURES

5.1. Test methods

The FluxSense measurement vehicle or “mobile lab” is equipped with four optical instruments for gas monitoring and they will all be used during the survey: SOF (Solar Occultation Flux), SkyDOAS

(Differential Optical Absorption Spectroscopy), MeFTIR (Mobile extractive Fourier Transformed Infrared spectrometer) and MWDOAS (Mobile White cell DOAS). The individual measurement methods are described in Appendix 1.

SOF and SkyDOAS both measure gas columns through the atmosphere by means of light absorption. SOF utilizes infrared light from the direct sun whereas SkyDOAS measures scattered ultraviolet light from the sky. MeFTIR and MWDOAS both measure ground level concentrations of alkanes and BTEX respectively. Both instruments are used in extractive mode where ambient air is pumped from attached inlet tubing through the optical cell while being analyzed in real time.

Accurate wind data is necessary in order to compute emission fluxes. Wind information is derived from several different sources. A moveable wind LIDAR is used to measure vertical profiles of wind speed and wind direction from 10-200+ m height. The LIDAR data is combined with data from several wind masts. Figure 4 gives a general overview of the measurement setup and the data flow.

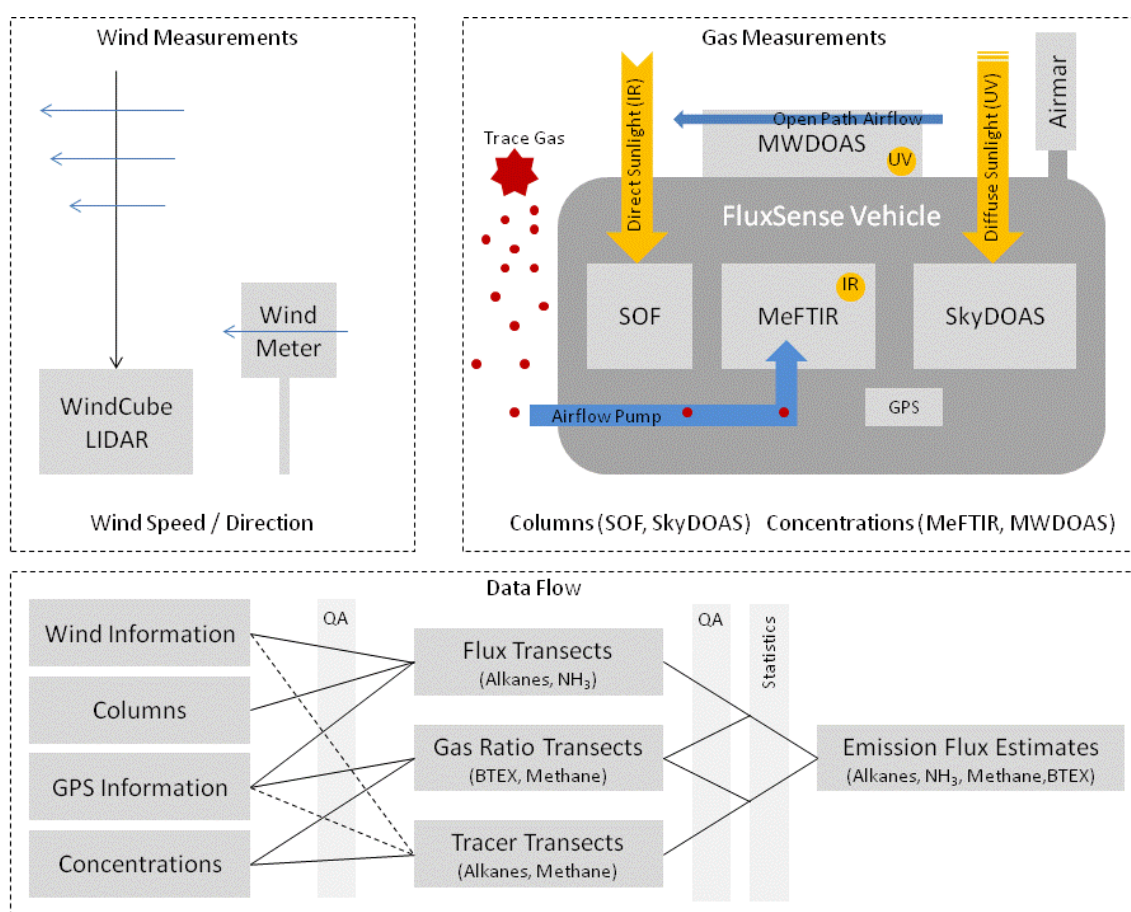


Figure 4. Overview of the FluxSense mobile lab main instruments; SOF, MeFTIR, MWDOAS and SkyDOAS (upper right panel) and wind measurements (upper left panel) and simplified data flow diagram (lower panel). SOF and SkyDOAS are column integrating passive techniques using the Sun as the light source while MeFTIR and MWDOAS sample local air concentrations using active internal light sources. The data flow describes what information that goes into the flux emission estimates. Direct flux emissions are given from measured columns (SOF and SkyDOAS) of alkanes and SO₂ while indirect fluxes are calculated via gas concentration ratios (MeFTIR and MWDOAS) of BTEX and benzene. See appendix 1 for principal equations. All emission flux estimates are based on statistical analysis of measured data. Q.C. = Quality Control, S.A.= Statistical Analysis (see Appendix for details).

In order to derive final emission flux estimates, the GPS-tagged gas column measurements by SOF and SkyDOAS are combined with wind data and integrated across plume transects at the various source locations. Gas mass ratio measurements by MeFTIR and MWDOAS are then used to indirectly estimate the emissions for BTEX.

The overall uncertainty for emission estimates based on optical remote sensing methods, such as proposed SOF and SkyDOAS for this survey, is dominated by uncertainties in the wind field. In the flux calculation, the measured (vertical or slant) concentration columns are associated with an average plume transportation speed. In this process the wind speed and direction are first measured, and in the next stage the concentration profile, e.g. the plume allocation by height, is addressed in order to attribute a plume transportation speed.

Each measurement location has its own layout and challenges, and as part of the emission survey uncertainties in the wind field and flux calculation will need to be investigated and discussed. For the particular survey of IHCC, there are a few challenges:

- The site is located at a peninsula in Lake Michigan with potential for rapidly changing wind during the course of the day.
- There are neighboring facilities with potential impacts, and care must be taken to avoid sampling if inflow of pollutants is judged to affect the observations at IHCC at a significant level, e.g. certain wind sectors might need to be omitted.
- The SOF and SkyDOAS methods require sunny weather conditions, which in combination with wind direction require flexibility in measurement planning on a day to day basis.
- The IHCC plant operates a hot process with potentially significant plume lift, and the site is comprised of many parts with potential emission points at different heights.
- The terrain near the site comprises high slag heaps that will contribute to a complex wind field at the site.
- The IHCC heat recovery coking process creates a potential emission source composition profile that changes over time during the coking cycle and over location as each of the 268 ovens is at a different point in the coking cycle, and some sources (such as the hot car) are actually in motion during operation. In addition, the quenching process is intermittent (90 seconds every 10 minutes for each tower during production).
- Integrating a constant source with a constant wind field is challenging enough. Integrating a variable source in time and location with a rapidly varying wind field in speed and direction will add a substantial uncertainty to the quantitative plume measurement.

5.2. Process data

In order to cross-correlate observed emission plumes with plant operation activities, during the test period IHCC will obtain pertinent process data and maintain detailed logs including:

- production rates and times for pushing and charging of the different ovens.
- time log for the quenching episodes.
- coal usage rates and % sulfur content in the used coal.
- logs for any deviations from normal production, specifically any bypass venting or other events that might affect observed emissions, also with regard to the service and maintenance window (6 AM – 1 PM).

6. QA/QC ACTIVITIES

6.1 SOF

- Verify that detector is cooled
- Verify that FTIR spectrometer is operational, (e.g. that all internal operational check flags are in order, such as laser amplitude, interferometer block etc.)
- Verify that GPS is operational and has sufficient amount of satellites (3+)
- Check that data storage disc has sufficient space
- Check that amplification for the solar tracker is properly set so that the tracker can lock properly on the sun without oscillating
- Check that vibration mounts are sufficiently filled with air
- Check light intensity so that the ADC (analog-digital converter) receives more than 1500 for the InSb (indium antimonide) detector
- Check interferogram for any abnormal oscillations
- Check that an RMS of $<0.15\%$ can be achieved in stationary mode
- Check retrieved concentration columns in different vehicle orientations to verify that the tracker is properly aligned (alkane column offsets $<2.5 \text{ mg/m}^2$)
- Check stationary stability in retrieved concentration columns to verify operation and stable background
- Check for consistent background columns at the plume edges before and after the plume scan and note significant deviations
- Check spectral fit to observe any interfering absorption not handled by the evaluation retrieval

6.2 SkyDOAS

- Verify that detector is cooled
- Verify that DOAS spectrometer is operational, (e.g. that all internal operational check flags are in order, such as shutter, slit width, grating etc.)
- Verify that GPS is operational and has sufficient amount of satellites (3+)
- Check that data storage disc has sufficient space
- Check that telescope is open and pointed vertically to the sky without obstruction
- Check that vibration mounts are operational
- Check light intensity and adjust exposure so that the detector does not get saturated at any wavelength (e.g. less than 65000 counts for a single spectrum at all columns of the CCD)
- Check that an RMS of $<0.01\%$ can be achieved in stationary mode
- Check stationary stability in retrieved concentration columns to verify operation and stable background
- Check for consistent background columns at the plume edges before and after the plume scan and note significant deviations
- Check spectral fit to observe any interfering absorption not handled by the evaluation retrieval

6.3 MeFTIR

- Verify that detector is cooled
- Verify that FTIR spectrometer is operational, (e.g. that all internal operational check flags are in order, such as laser amplitude, interferometer block etc.)
- Verify that GPS is operational and has sufficient amount of satellites (3+)
- Check that data storage disc has sufficient space
- Check that amplification for the sandwich detector is properly set so that both channels are operational without saturation
- Check that vibration mounts are sufficiently filled with air
- Check that light intensity is sufficient
- Check interferogram for any abnormal oscillations
- Verify pump operation and pressure in the gas cell (a few mbars below ambient in normal operation)
- Check that an RMS of $<0.2\%$ can be achieved in stationary mode
- Check stationary stability in retrieved concentration to verify operation and stable background
- Check for consistent background concentrations at the plume edges before and after the plume scan and note significant deviations. Consistent concentrations at the plume edges along with upwind measurements will indicate if significant interfering inflow of the target species is taking place.
- Check spectral fit to observe any interfering absorption not handled by the evaluation retrieval
- Check background concentrations for consistency (CH_4 , N_2O)
- Verify pathlength with laser/halogen lamp
- Conduct spike tests with methane gas ($\sim 5\text{-}15$ ppmv concentration)

6.4 MWDOAS

- Verify that detector is cooled
- Verify that DOAS spectrometer is operational, (e.g. that all internal operational check flags are in order, such as shutter, slit width, grating etc.)
- Verify that GPS is operational and has sufficient amount of satellites (3+)
- Check that data storage disc has sufficient space
- Check that vibration mounts are operational
- Verify pump operation and pressure in the gas cell (a few mbars below ambient in normal operation)
- Check light intensity and adjust exposure so that the detector does not get saturated at any wavelength (e.g. less than 65000 counts for a single spectrum at all columns of the CCD)
- Check that an RMS of $<0.01\%$ can be achieved in stationary mode
- Check stationary stability in retrieved concentrations to verify operation and stable background
- Check for consistent background concentrations at the plume edges before and after the plume scan and note significant deviations. Consistent concentrations at the plume edges along with upwind measurements will indicate if significant interfering inflow of the target species is taking place.

- Check spectral fit to observe any interfering absorption not handled by the evaluation retrieval
- Verify pathlength with laser/halogen lamp
- Conduct spike tests with p-xylene (or corresponding BTEX compound) (~ 100 ppbv range)

6.5 Wind LIDAR

- Verify that the LIDAR is aligned towards true north (e.g. compensate for the magnetic declination at the site)
- Verify that the instrument has a free field of view within a ± 17 degree cone from zenith
- Verify that power supply is operational and battery capacity sufficient
- Check that backscatter signal is sufficient for wind data retrieval in the 10-200 m range
- Check that data storage disc has sufficient space
- Observe wind LIDAR data output at start-up
- Backup wind data on a daily basis

6.6 Wind tower

- Verify that the wind tower is aligned towards true north (e.g. compensate for the magnetic declination at the site)
- Verify that the wind meter is not obstructed
- Verify that power supply is operational and battery capacity sufficient
- Check that wind speed and direction data are reasonable
- Check that data logger has sufficient space
- Observe wind logger data at start-up
- Backup wind data on a daily basis

6.7 Canisters

- Maintain chain of custody
- Check canister for vacuum prior to sampling
- Flush any sample restrictors/nozzles prior to sampling
- Record time from vacuum to full canister for consistency check
- Note initial and final canister pressure
- Label canister with location, time (start and stop), date and operator

7. Reporting and data reduction requirements

7.1. Report format

TABLE OF CONTENTS

- 1.0 Introduction
 - 1.1 Summary of Test Program
 - 1.2 Key Personnel
- 2.0 Source and Sampling Location Descriptions
 - 2.1 Process Description
 - 2.2 Control Equipment Description
 - 2.3 Flue Gas and Process Sampling Locations
- 3.0 Summary and Discussion of Results
 - 3.1 Objectives and Test Matrix
 - 3.2 Field Test Changes and Problems
 - 3.3 Summary of Results (one for each objective)
- 4.0 Sampling and Analytical Procedures
 - 4.1 Emission Test Methods
 - 4.2 Process Test Methods
 - 4.3 Sample Identification and Custody
- 5.0 QA/QC Activities

APPENDICES

The report will include electronic copies of the spreadsheets used to derive emissions estimates, and copies of the laboratory analytical results for the canisters.

7.2. Data reduction and summary

The test plan comprises several measurement instrumentations from which data will be combined to cover the test plan objectives. The main objectives are to attempt to quantify overall emissions of VOCs (volatile organic compounds) and SO₂ (sulphur dioxide) from IHCC, and identify major sources of the emissions. The measurements include:

1. Optical remote sensing techniques (SOF and SkyDOAS) with main data output being geo-tagged vertical mass columns of VOCs and SO₂.
2. Wind measurements, resulting in wind speed and wind direction data at various positions and altitudes.
3. Geotagged concentration measurements (MeFTIR, MWDOAS and canisters), providing leak search mapping, mass concentration and mass concentration ratios of VOCs and SO₂ at various positions and heights.

The measurements (according to section 4) are mobile in nature, hence concentration and column data are associated with a GPS position (rather than a static location), and related to current wind speed and wind direction at the time of the measurement.

The measurements integrate the cross section of the emission plume from the site, and on the upwind side for any background influence respectively. The data reduction, resulting in the emission estimates, include assessment of any upwind fluxes interfering with the measured flux on the downwind side of the source(s). Table 4 summarizes the data reduction steps and units.

Table 4. Summary data reduction table.

Method	Component	Unit	Associated data	Resulting data and unit
SOF	Vertical integrated concentration column: VOCs	[mg/m ²]	GPS positions, wind speed and direction, mass concentration ratios	Emission estimate, kg/h [(mg/m ²) x (m) x (m/s) => kg/h]
SkyDOAS	Vertical integrated concentration column: SO ₂	[mg/m ²]	GPS positions, wind speed and direction, mass concentration ratios	Emission estimate, kg/h [(mg/m ²) x (m) x (m/s) => kg/h]
MeFTIR	Mass concentrations: VOCs	[µg/m ³]	GPS positions, MWDOAS	Mass concentration ratios, [(µg/m ³) / (µg/m ³) => unitless]
MWDOAS	Mass concentrations: SO ₂ , BTEX, Benzene	[µg/m ³]	GPS positions, MeFTIR	Mass concentration ratios, [(µg/m ³) / (µg/m ³) => unitless]
Canisters	Mass concentrations: VOCs	[µg/m ³]	GPS positions, MeFTIR, MWDOAS	Mass concentration ratios, [(µg/m ³) / (µg/m ³) => unitless]
GPS	Latitude, Longitude, Time	[Deg N], [deg W], [s]		
Wind LIDAR	Wind speed and wind direction at different heights	[m/s], [deg 0-359]		
Wind tower	Wind speed and wind direction	[m/s], [deg 0-359]		

8. Plant entry and safety

8.1. Safety responsibilities

Safety Personnel

IHCC:	Elizabeth Moore, IHCC Health & Safety Manager
FluxSense:	Jerker Samuelsson, Test Director
SunCoke representative:	Jonathan Perkins, SunCoke project coordinator

FluxSense personnel are responsible for working according to local regulations and instructions on site, as well as following FluxSense general internal safety precautions and protocol for emissions testing work. FluxSense is responsible for providing IHCC all pertinent information regarding methods and materials used in the test that could interfere with normal plant operations. This is to ensure the health and safety of both visitors and site employees alike.

The IHCC Health & Safety Manager will provide on-boarding training for FluxSense personnel including general site and task specific information. The IHCC Health and Safety Manager will be available throughout the visit to answer any questions and/or address any safety concerns that may arise. The SunCoke representative will act as the escorting host and as a point of communication contact for FluxSense.

In any case, where a variance from following any site-specific safety protocol is requested, Pat Nigl (General Manager) and Elizabeth Moore (Health and Safety Manager) will have final approval.

8.2. Safety program

FluxSense Inc. has a comprehensive health and safety program that satisfies Federal OSHA requirements. The basic elements include:

- Written policies and procedures,
- Routine training of employees and supervisors,
- Medical monitoring,
- Use of personal protection equipment,
- Hazard communication,
- Pre-mobilization meetings with IHCC personnel and FluxSense test team personnel, and
- Routine surveillance of the on-going test work.

SunCoke's vision is zero incidents and injuries in the workplace. Safety is a core value; every job can and should be done safely every day. This vision can only be accomplished by

- Site and corporate leadership making a commitment to safety as the paramount value within the company.
- Site leadership practicing visible safety leadership on a daily basis.
- All team members and contractors taking responsibility for their own safety and the safety of those around them.
- All team members and contractors taking the time necessary to properly identify and mitigate all hazards and safely do each job.
- Complying with all applicable laws and regulations.

8.3. Safety requirements

While on-site, all visitors must abide by all federal, state and local regulations as well as all site specific policies and procedures. FluxSense personnel are required to follow all internal safety precautions and protocols for emissions testing work.

Prior to arriving at the site, full names of all visitors must be provided to the IHCC contact in order to ensure gate access from site security.

Upon first arrival to the site, all visitors will be shown a 1-hour safety orientation video. The orientation video will explain in detail all pertinent site safety policies and procedures. This includes but is not limited to: emergency preparedness/response, collision avoidance practices, required PPE, required work permits, etc. If the testing being performed requires the use of Lockout/Tagout or Confined Space entry, IHCC will provide this additional training as well as any needed related materials.

All visitors must sign into and out of the facility located in the lobby upon entry and exit each day.

The following PPE is required:

- FR – Category II with high-visibility reflective on the outer layer clothing
- Steel/composite-toed boots with metatarsal guarding
- Hard hats, gloves, hearing protection in applicable areas and safety spoggles/goggles
- Visitors to bring any needed task specific PPE

Visitors will either be provided a plant communication radio or the escorting host will have a radio on their person at all times while inside the facility.

Any equipment (such as manlifts) apart from that belonging to FluxSense will be operated by qualified IHCC personnel only. All safety policies and procedures pertaining to moving equipment shall apply to the operation of the mobile lab, including but not limited to: daily inspections, the use of spotters where needed, no use of electronic devices (phones) while driving, and seatbelts worn at all times while in motion.

In the cases where FluxSense personnel are operating in an area under the control of an adjacent entity (Cokenergy or ArcelorMittal), specific Health & Safety requirements set by those entities will be adhered to in addition to the IHCC requirements and those sites will be notified in advance.

9. Personnel responsibilities and test schedule

9.1. Test site organization

The key tasks and task leaders for the test are:

Management:	Jonathan Perkins, SunCoke, M: (610) 858-7706, jhperkins@suncoke.com Marianne Ericsson, FluxSense Inc., M: 775-830-5272, marianne.ericsson@fluxsense.com
Test- and site preparations:	Jonathan Perkins, SunCoke Jerker Samuelsson, FluxSense Inc., M: +46-70-3099669 / 619-806-4644, jerker.samuelsson@fluxsense.se Nancy Estrada, SunCoke, M: (219) 895-5976, nestrada@suncoke.com
Sampling site accessibility:	Nancy Estrada, SunCoke
Safety Coordination:	Elizabeth Moore, SunCoke, M: (270) 556-5268, ewmoore@suncoke.com Jerker Samuelsson, FluxSense Inc.
Sample Recovery and Data Management:	Brian Offerle, FluxSense Inc., M: +46-72-7296994 / 619- 806-4644, brian.offerle@fluxsense.se Jerker Samuelsson, FluxSense Inc.
Daily Sampling Schedule:	Jerker Samuelsson, FluxSense Inc.

9.2. Test preparations

Table 5 addresses the main preparation stages needed prior to the survey.

Table 5. Test preparations.

Item No.	Preparation measure	Timing	Responsible party	Comments
1	Prepare and test Mobile Lab instrumentation prior to shipping	April-May, 2020	FluxSense	
2	Order wind LIDAR and have it delivered to IHCC site in due time	February / May 2020	FluxSense	Book instrumentation in Feb. Ship in May.
3	Reserve a pick-up truck for deployment of the wind LIDAR	March/April	FluxSense	
4	Mount LIDAR and battery power source on pick-up truck	May	FluxSense	Ship/bring hardtop/softshell from San Diego
5	Order tracer gas and secure delivery to site	March/April	FluxSense	
6	Receive and store tracer gas prior to and during the survey	May-June	IHCC	
7	Collect liquid nitrogen for FTIR, 30L dewar	May	FluxSense	Local supplier
8	Order sample canisters from external lab	March/April	FluxSense	Local supplier
9	Receive and maintain Chain of Custody for the canisters during the full period of the survey until analysis.	May-June	FluxSense/IHCC	
10	Order supply of sky-lift for the survey and arrange operator	March-May	IHCC/FluxSense	
11	Set up local wind towers on site	May	FluxSense/IHCC	Identify secure locations and prepare necessary permits
12	Prepare logs of production parameters and how this and any deviations are retrieved during the survey	March-May	IHCC / FluxSense	Consider making 1-2 test days prior to the survey to set the protocol.
13	Arrange housing for the survey	March-April	FluxSense	
14	Secure parking on site with power access for Mobile Lab (115V, 20A)	May	IHCC	For power supply when not in operation.
15	Preparatory permitting work	March-May	IHCC / FluxSense	Identify any specific permits that the survey will require and prepare

9.3. Test personnel and responsibilities and detailed schedule

The emissions test measurements are planned to be conducted in late May and first half of June. This period is chosen to make use of the high solar angles that enable measurements with SOF and SkyDOAS into the early evening. Ambient temperatures are also warm but not extreme in general, with limited condensation plumes compared to earlier in spring and winter. Historic wind patterns in this time of year are also favorable.

FluxSense mobile lab and the wind LIDAR will be shipped to IHCC in the week of 20-24 May 2020, and the FluxSense team will also arrive in the end of this week for instrumentation work. The survey will commence on 25 May with safety orientation, planning meeting on site, and installation of met tower and wind LIDAR on site, see Table 6.

Main measurement period is planned for the period of 25 May – 12 June 2020, with the following weeks as a backup period in case of inclement weather or other events affecting the survey.

Table 6. Time schedule.

Date (2020)	Activity
April-May 2020	Mobile lab preparations
20-24 May, 2020	Transport of instrumentation and personnel to the IHCC site
25 May – 12 June, 2020	Measurement survey, main period
13 June – 26 June, 2020	Backup period in case of bad weather or unforeseen deviations
June, 2020	Instruments and personnel shipped out after measurements finished according to plan
June/July/Aug/Sep, 2020	Data analysis and preparation of draft test report and final test report

APPENDIX 1 – Measurement methods

The SOF method

The SOF method [Mellqvist 1999, 2008a, 2008b, 2009, 2010; Kihlman 2005a; Johansson 2014] 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 the orientation of the vehicle. 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/m^2 , of various species between the sun and the spectrometer. The system used in this project consists of a custom-built solar tracker, transfer optics and a Bruker IRCube FTIR spectrometer with a spectral resolution of 0.5 cm^{-1} , equipped with a dual InSb (Indium Antimonide) / MCT (Mercury Cadmium Telluride) detector. A reference spectrum is taken outside the plume so that atmospheric background concentrations are removed. This means that all measured SOF columns are analyzed relative to the background column concentrations.

The system is installed in a measurement vehicle which allows consecutive column concentration measurements to be performed while driving. The flux of a species in a plume from an industry is measured by collecting spectra while driving the vehicle so that the light path from the sun to the instrument gradually cuts through the whole plume, preferably as orthogonally as possible to the wind direction, see Figure A 1.

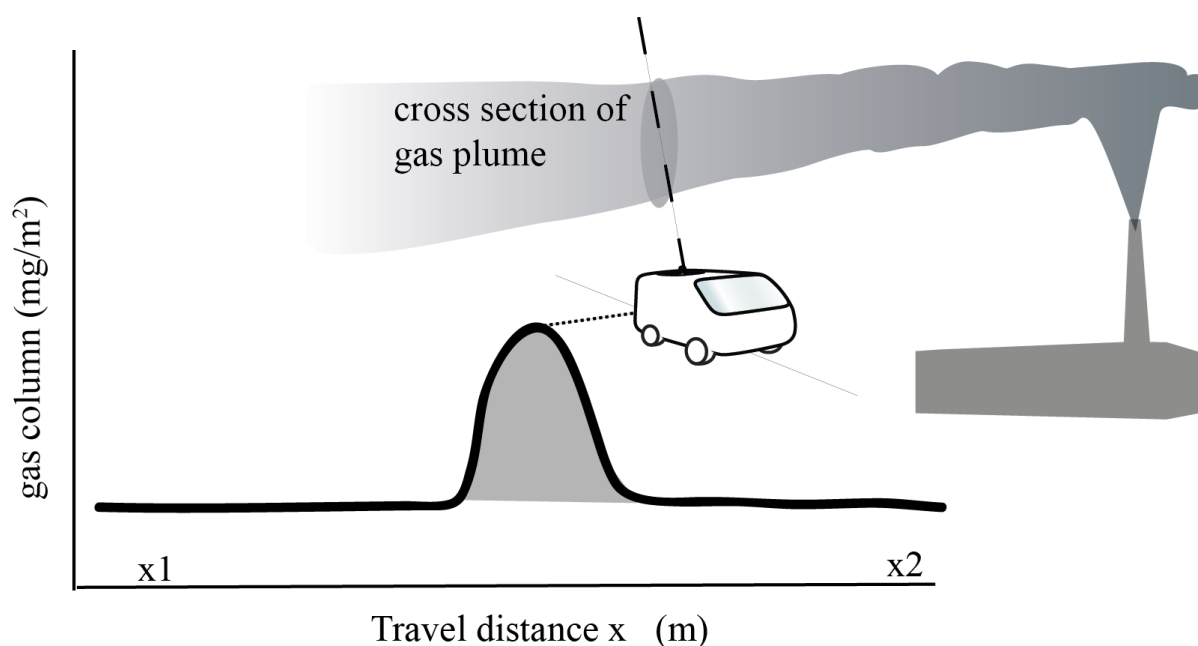


Figure A 1. Schematic of the SOF measurement where the vehicle is driven across the prevailing wind so that the solar beam cuts through the emission plume while the sun is locked into the FTIR spectrometer by the solar tracking device on the roof. The VOC mass (or other compound of interest) is integrated through the plume cross section.

For each spectrum a column concentration of the species is retrieved using custom software (QESOF, i.e. *Quantitative evaluation of SOF*) [Kihlman 2005b]. These column concentrations, together with positions recorded with a GPS (Global Positioning System) receiver and the solar angle calculated from the time of the measurements, are used to calculate the area integrated column of the species in the intersection area between the plume and the light path. The flux of the species is then obtained by multiplying this area integrated concentration with the orthogonal wind speed vector component.

The IR spectra recorded by the SOF instrument are analyzed in QESOF by fitting a set of spectra from the HITRAN infrared database [Rothman 2003] and the PNNL (Pacific Northwest National Laboratory) database [Sharpe 2004] in a least-squares fitting procedure. Calibration data from the HITRAN database is used to simulate absorption spectra for atmospheric background compounds present in the atmosphere with high enough abundance to have detectable absorption peaks in the wavelength region used by SOF. Spectra, including water vapor, carbon dioxide and methane, are calibrated at the actual pressure and temperature and degraded to the instrumental resolution of the measurements. The same approach is applied for several retrieval codes for high resolution solar spectroscopy developed within Network for the Detection of Atmospheric Composition Change (NDACC) [Rinsland 1991; Griffith 1996] and QESOF has been tested against these with good agreement, better than 3%. For the retrievals, high resolution spectra of ethylene, propene, propane, n-butane and n-octane were obtained from the PNNL database and these are degraded to the spectral resolution of the instrument by convolution with the instrument line shape. The uncertainty in the absorption strength of the calibration spectra is about 3.5% for all five species.

In this project, the SOF method is used to measure VOCs in two different modes. Most VOCs with C-H bonds absorb strongly in the 3.3-3.7 μm (2700-3005 cm^{-1}) spectral region. This region is mainly used for alkane measurements using a spectral resolution of 8 cm^{-1} . Alkenes (including ethylene and propylene) and ammonia are instead measured in the spectral region between 910 and 1000 cm^{-1} using a spectral resolution of 0.5 cm^{-1} . In the alkane mode – the IR light absorption is essentially sensitive to the total alkane mass (number of alkane C-H bonds) present in the plume. The absorption structures (cross sections) for the various alkane compounds are rather similar, with the absorption strength scaling to the mass of the alkane species. Hence, the actual mix of alkanes in the plume does not affect the retrieved total alkane mass flux much, although only cross sections from a subset of all alkanes (propane, n-butane and octane) are fitted in the spectral analysis. Typically, the rare event of significant absorption from other species in the plume shows up as elevated residuals and is further investigated in the re-analysis. For the alkene mode the specificity of the measurements is good, since the absorption of different species is rather unique in this so called “fingerprint region” and absorption features are often sharp and well separable from each other at 0.5 cm^{-1} resolution.

SOF is a technique employed by FluxSense in over 100 fugitive emission studies around the world. In Europe the SOF technique is considered one of the Best Available Technology [European Commission 2015] for measurements of fugitive emission of VOCs from refineries; and in Sweden it is used together with tracer correlation and optical gas imaging for annual screening of all larger refineries and petrochemical plants. The estimated uncertainty for the SOF emissions measurements is typically 30 % for the total site emissions. This uncertainty has been calculated from several controlled release experiments (blind and non-blind) and side-by-side measurements with other measurement techniques.

Mobile SkyDOAS

The principle for Mobile SkyDOAS (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 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, see Figure A 2.



Figure A 2. The mobile SkyDOAS system: Telescope, optical fibre, spectrometer and control computer.

The system was installed in the same measurement vehicle as the SOF system. Plumes were transected in the same way as with the SOF system and the retrieved column concentrations used to calculate fluxes exactly the same way, except that the SkyDOAS measurement direction is always zenith.

In this project, mobile SkyDOAS is used to measure SO_2 , NO_2 and H_2CO . NO_2 is retrieved in the wavelength region between 324 and 350 nm and SO_2 in the region 310-325 nm. H_2CO is measured in the region 322-350 nm. Apart from SO_2 , NO_2 and H_2CO the spectral analysis also includes other atmospheric compounds such as O_3 and O_4 . The rare event of significant absorption from other species in the plume than those included in the spectral fit shows up as elevated residuals and is further investigated in the re-analysis. The absorption line parameters of the retrieved compounds are well established in published databases, stating an uncertainty of 4% (Vandaele *et al.* 1998) for the UV cross section of NO_2 and less than 2% for the SO_2 cross sections (Bogumil *et al.* 2003).

The DOAS technique was introduced in the 1970's (Platt *et al.* 1979) and has since then become an increasingly important tool in atmospheric research and monitoring both with artificial light sources and in passive mode utilizing the scattered solar light. In recent time the multi axis DOAS technique (scanning passive DOAS) has been applied in tropospheric research for instance measuring formaldehyde (Heckel *et al.* 2005; Pikel'naya *et al.* 2007).

Passive DOAS spectroscopy from mobile platforms has also been quite extensively applied in volcanic gas monitoring (Galle *et al.* 2003) for SO_2 flux measurements and for mapping of formaldehyde flux measurements in megacities (Johansson *et al.* 2009). Mobile SkyDOAS has been used in several studies for measurements of industries i.e. SO_2 , NO_2 and H_2CO for several campaigns in Texas including NO_2

measurements at Longview in 2012 (Johansson *et al.* 2014a; Johansson & Mellqvist 2013). (Rivera 2009) did SO₂ measurements on a power plant in Spain for validation purposes. They also made measurements at an industrial conglomerate in Tula in Mexico (Rivera *et al.* 2009a) and measurements of SO₂, NO₂ and H₂CO during the TexAQS 2006 campaign (Rivera *et al.* 2009b; Rivera *et al.* 2010).

Mobile extractive FTIR (MeFTIR)

Mobile Extractive FTIR (MeFTIR) [Galle 2001, Börjesson 2009] in combination with tracers has been used to quantify VOC emissions from refinery and petrochemical sources in Europe and in the U.S. Alkanes and alkenes are typically measured, but also methane and other climate gases can be retrieved. In the present project MeFTIR will measure both concentrations of total VOCs (as observed by C-H-stretch absorption in the 2700-3100 cm⁻¹ wavenumber region) and methane.

MeFTIR is an optical technique capable of monitoring gas concentrations at ppb-sensitivity in mobile field operations. It is used both independently for concentration mapping and flux measurements, but often combined together with simultaneous SOF flux measurements to provide more detailed VOC speciation of plumes and for plume height assessments [Johansson *et al.* 2013a]. The plume height can be estimated by dividing measured columns (mg/m²) with ground concentrations (mg/m³), assuming that the plume is evenly distributed up to the plume height (and zero above).

The MeFTIR system contains a mid-infrared spectrometer with medium resolution (0.5 cm⁻¹). It utilizes an internal glow bar as an infrared radiation source, and by customized optics this light is transmitted through an optical multi-pass measurement cell with path-length of typically 56-110 meters. The system is mounted on a vibration dampening platform to allow for real time plume mapping from a mobile platform, such as a vehicle or boat, see Figure A 3.



Figure A 3. The MeFTIR instrumentation consisting of a Bruker FTIR spectrometer connected to an optical multi-pass cell.

The transmitted light is detected simultaneously with an InSb-detector in the 2.5–5.5 μm (1800–4000 cm⁻¹) region and an MCT detector in the 8.3–14.3 μm (700–1200 cm⁻¹) region. Temperature and pressure in the cell are averaged over the duration of each measurement. Atmospheric air is

continuously pumped at high flow rate through the optical cell from the outside, taking in plume air from the roof of the vehicle (2.5 m height) through a Teflon tube. A high flow pump is used to ensure that the gas volume in the cell is fully replaced within a few seconds. Spectra are typically recorded with an integration time of 10-15 seconds. A GPS-receiver is used to register the position of the vehicle every second. Extended Teflon tubing can be attached to the system for elevated sampling or leak search purposes.

The concentration in the spectra is analyzed in real time by fitting a set of calibrated spectra from the HITRAN infrared database [Rothman 2003] and the PNNL database [Sharpe 2004] in a least-squares fitting procedure. Compounds being analyzed include ethylene, propylene, total alkane mass (based on fitting cross sections of ethane, propane, n-butane, i-pentane, n-octane), water, methane, CO, CO₂ and N₂O. The analysis routines are very similar to the ones for SOF, but less complex because strong absorption by atmospheric trace gases (water, methane, CO₂) has less consequence at the shorter path length in the MeFTIR measurement cell.

The MeFTIR tracer approach has been tested in a so-called gas release “blind test” together with other techniques in U.S. [EREF 2011]. In that test, methane was released from an area-distributed source in four different configurations and flow rates ranging from 1.1-3.3 g/s. At a downwind distance of 400 meters MeFTIR retrieved the fluxes within 6% in 3 cases and 19% in the fourth. This is consistent with other validation experiments, showing a flux estimate accuracy of better than 20%. Concentration measurement by FTIR is a widely used procedure, and the main uncertainties are associated with the absorption cross sections (typically < 3.5%) and spectral retrieval, with an aggregate uncertainty better than 10% in the analysis.

Concentrations are monitored in real time in order to detect emission plumes and to judge whether any interfering sources are being sampled. Unwanted signals from local traffic exhaust or from the measurement vehicle itself could be filtered out by looking at exhaust compound signatures like carbon monoxide concentrations. Measurements of ambient concentrations of methane and carbon dioxide (with known atmospheric concentrations) are used for consistency check.

Mobile White Cell DOAS (MWDOAS)

The mass concentrations of benzene, toluene, ethylbenzene, m- and p-xylene (BTEX) are measured using a mobile real-time system: Mobile White cell DOAS (MWDOAS). The MWDOAS system consists of a long optical White cell that is mounted on the measurement vehicle (see Figure A 4). By multiple reflections in the White cell mirror system an overall path length of 110-210 m is obtained depending on configuration, resulting in low detection limits (ppb). The light from the internal lamp is transmitted through the White cell and then analyzed in a DOAS spectrometer, using the UV wavelength region 255 - 285 nm. The system comes in two versions – one open path model and one extractive gas cell model (similar to the MeFTIR system), dependent on application.

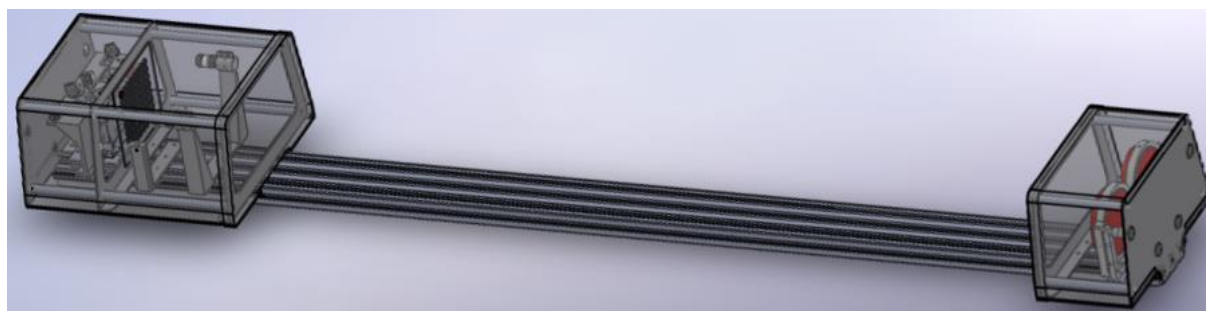


Figure A 4. The MWDOAS cell having an overall optical path-length of 110-210 m.

A measurement begins by acquiring a reference spectrum outside the plume, usually upwind of the facility. Spectra are then sampled and averaged continuously while driving through emission plumes. The averaging time is set to around 6 seconds in order to achieve acceptable SNR (see below). The spatial sampling is also dependent on the vehicle's velocity. A typical driving speed for MWDOAS measurements is 10-20 km/h for sufficient plume sampling. The spectra are geo-tagged and evaluated online using the standard DOAS technique, giving information of plume locations and constituents. Published absorption cross-sections included in the DOAS evaluation routine are tabulated in Table A. 1.

The MWDOAS data is later merged with the corresponding MeFTIR data to produce a plume specific BTEX/Alkane mass ratio. The mass ratio of BTEX/Alkanes is then used to calculate the aromatic flux from individual sub areas where alkane fluxes have been measured by SOF, assuming they have the same source. Specific area plumes are ideally probed at several times, and an overall average of all plume transect BTEX/Alkane ratios is made. The method requires in situ access to the plume of the studied source.

Table A. 1. The UV-cross-sections used in the evaluation of the MWDOAS spectra.

Chemical compound	Origin of reference cross section
O ₃	[Burrows 1999]
SO ₂	[Bogumil 2003]
O ₂	[Bogumil 2003]
Toluene	[Fally 2009]
Benzene	[Etzkorn 1999]
1,3,5-Trimethylbenzene	[Etzkorn 1999]
1,2,4-Trimethylbenzene	[Etzkorn 1999]
Styrene	[Etzkorn 1999]
Phenol	[Etzkorn 1999]
p-Xylene	[Etzkorn 1999]
m-Xylene	[Etzkorn 1999]
Ethylbenzene	[Etzkorn 1999]

The MWDOAS technique has been validated in various surveys by comparison with canister samples acquired at several different locations and which were subsequently analyzed by gas chromatography (GC-FID). The validation shows that the result from MWDOAS lies well within 10% of the result of the certified canister results for BTEX. Due to an absorption cross-section too weak to be used with reliability in the MWDOAS analysis, the ortho isomer of the xylene has been omitted in this

comparison. Hence, the xylene concentration from MWDOAS is defined as the sum of the measured m- and p-isomers and the inferred o-isomer from associated MeFTIR or canister speciation.

The MWDOAS system has been used in previous campaigns with good results. For instance, during the 2013 DISCOVER-AQ campaign [Johansson, 2013b] in Houston, Texas, the system was run in parallel to a mobile Proton Transfer Mass spectrometer (PtrMS) lab as a validation check. The results of benzene, toluene and styrene was compared and showed good agreement, with the PtrMS showing slightly elevated benzene concentrations compared to the MWDOAS. The sensitivity of MWDOAS is better than 1 ppb for benzene, better than 3 ppb for toluene, ethylbenzene and m-xylene and 0.5 ppb for p-xylene.

Since the distribution of the BTEX constituents varies with source we will also present the benzene to alkane ratio to facilitate the calculation of benzene flux and identify specific benzene sources.

Note that all concentrations are enhancements above the reference/background.

Wind Measurements and Auxiliary Data

Wind LIDAR

A wind LIDAR (Light Detection and Ranging, ZephIR ZX300) is used to measure vertical wind profiles of wind speed and direction. The LIDAR provides wind profiles in the vertical range of 10 m up to 200+ m above ground, and wind speed accuracy of 0.1 m/s. The system records 1-s data, and 1-minute averages are typically used for flux calculations. The principle of detection is based on the Doppler shift of the infrared pulse that the instrument sends out and retrieves.

Wind Masts

Meteorological parameters are also measured at selected sites using a portable 3-10 m mast. This mast is equipped with a calibrated RM Young 05108 “prop and vane” anemometer and a Campbell Scientific CR5000 data-logger, see Figure A 5.



Figure A 5. The FluxSense mobile wind mast with an RM Young anemometer mounted on top. The mast could be erected from 3 to 10 m.

Airmar (Mobile Weather Station)

A sonic wind meter (Airmar WeatherStation 200 WX) is installed on the roof of the measurement vehicle to complement the other wind measurements and give local ground winds at the vehicle. The wind information from the car-based Airmar is not used for flux calculation since the wind field can be heavily disturbed and turbulent. The Airmar is only used as a real-time aid to keep track of the plume directions when making the gas emission measurements. The Airmar provides wind speed and direction relative to true north (compensating for vehicle position), as well as air temperature, pressure and relative humidity. It also provides GPS positions that may be used as a backup for the other GPS-antenna.

GPS

The FluxSense vehicle is equipped with two standard USB GPS-L1 receivers (GlobalSat BU-353S4) hooked up to the SOF and MWDOAS-computers. They are placed horizontally on the roof and by the windscreen for optimal reception. The receivers give the position at a rate of 1 Hz.

Principal Equations

The primary methods in this project is the direct flux measurements from SOF and SkyDOAS. In the secondary method BTEX fluxes are measured indirectly from MWDOAS/MeFTIR gas mass ratios.

DIRECT FLUX MEASUREMENTS:

The emission mass flux (Q) of species (j) measured by SOF for a single transect (T) across the plume (P) along path (l) can be expressed by the following integral (SI-units in gray brackets):

$$Q_T^j [\text{kg/s}] = \bar{v}_T [\text{m/s}] \cdot \int_P C_l^j [\text{kg/m}^2] \cdot \cos(\theta_l) \cdot \sin(\alpha_l) dl [\text{m}]$$

Where,

\bar{v}_T = the average wind speed at plume height for the transect,

C_l^j = the measured slant column densities for the species j as measured by SOF or SkyDOAS,

θ_l = the angles of the light path from zenith ($\cos(\theta_l)$ gives vertical columns),

α_l = the angles between the wind directions and driving directions

dl = the driving distance across the plume

Note that SOF and SkyDOAS have different light paths, where the SkyDOAS telescope is always looking in the zenith direction while the SOF solar tracker is pointing toward the Sun. Hence, the measured SOF slant column densities will vary with latitude, season and time of day.

To isolate emissions from a specific source, the incoming/upwind background flux must be either insignificant or subtracted. If the source is encircled, the integral along l is a closed loop and the flux calculations are done with sign.

INDIRECT FLUX MEASUREMENTS:

The indirectly measured flux (indirectly measured emission, IME) is computed using a combination of SOF and MeFTIR/MWDOAS measurements. The indirect mass flux (\hat{Q}^i) for species (i) are calculated from MeFTIR and/or MWDOAS gas mass ratios integrated over the plume (P) along path (l) are given by (SI-units in gray brackets):

$$\hat{Q}^i [\text{kg/s}] = \bar{Q}^j [\text{kg/s}] \cdot \frac{1}{k} \sum_k \frac{\int_P N_l^i [\text{kg/m}^3] dl [\text{m}]}{\int_P N_l^j [\text{kg/m}^3] dl [\text{m}]}$$

Where,

\bar{Q}^j = the average flux of species j from multiple transects as measured by SOF,

N_l^i = the number density concentrations of species i as measured by MWDOAS or MeFTIR,

N_l^j = the number density concentrations of species j as measured by MeFTIR,

k = the number of gas ratio measurements

Note that the IME operates on average values since simultaneous SOF, MWDOAS and MeFTIR measurements are generally not performed and because individual gas ratios are more variable and uncertain than the average. Although not necessarily simultaneously measured, SOF and MeFTIR/MWDOAS measurements must represent the same source plumes. Note also that gas ratios do not intrinsically depend on complete plume transects (like for direct flux methods) as long as the emission plume is well mixed at the sampling distance.

TRACER GAS FLUX MEASUREMENTS:

The third method to conduct flux measurements is by tracer correlations using only MeFTIR measurements or simultaneous MeFTIR and MWDOAS measurement and a known tracer gas release. These fluxes are given for each transect (T) by the following equation (SI-units in gray brackets):

$$Q_T^j [\text{kg/s}] = Q^{tracer} [\text{kg/s}] \frac{\int_P N_l^j [\text{kg/m}^3] dl [\text{m}]}{\int_P N_l^{tracer} [\text{kg/m}^3] dl [\text{m}]}$$

Where,

Q^{tracer} = the release mass flux of the tracer gas from bottle,

N_l^{tracer} = the number density concentrations of the tracer as measured by MeFTIR,

N_l^j = the number density concentrations of species j from MeFTIR or MWDOAS,

Note that tracer gas correlation fluxes do not intrinsically depend on complete plume transects (like for direct flux methods) as long as the emission plume and the tracer gas is well mixed at the sampling distance. Complete plume transects are, however, recommended since the tracer gas release point might not completely match at the sampling distance.

Uncertainties and Error Budget

A summary of the typical performance of the FluxSense measurements is presented in Table A. 2.

In addition, for each site the statistical error is calculated. It corresponds to the random error but in addition there could be systematic errors. For instance, in the used wind speed due to the errors in estimated height of the plume and spectral calibration errors. The statistical error is given by the 95 % Confidence Interval (CI) for the mean, \bar{x} , according to:

$$CI = \bar{x} \pm t_{.025} \frac{s}{\sqrt{N}}$$

Here t is Student's T distribution and s corresponds to sample standard deviation:

$$s_x = \sqrt{\frac{\sum_{i=1}^N (x - \bar{x})^2}{N - 1}}$$

Table A. 2. Performance of FluxSense measurement methods.

Measurement Parameter	Analysis Method	Accuracy	Precision
SOF column concentrations alkanes, alkenes, NH ₃	QESOF spectral retrieval	±10%	±5%
SkyDOAS column concentrations NO ₂ , SO ₂ , H ₂ CO	DOAS spectral retrieval	±10%	±5%
MeFTIR concentrations CH ₄ , VOC*, NH ₃ , N ₂ O	QESOF spectral retrieval	±10%	±5%
MWDOAS concentrations BTEX, Benzene	MWDOAS spectral retrieval	±10%	±5%
Wind Speed (10 m)	R.M. Young Wind monitor	±0.3 m/s or 1%	±0.3 m/s
Wind Direction (10 m)	R.M. Young Wind monitor	±5°	±3°
LIDAR Wind Speed (10-200+ m)	Doppler LIDAR	±0.1 m/s	-
GPS position	USB GPS receiver	±2m	±2m
SOF mass flux Alkanes, alkenes, NH ₃	SOF-Report flux calculations	±30%	±10%
SkyDOAS mass flux NO ₂ , SO ₂ , H ₂ CO	SkyDOAS flux calculations	±30%	±10%

* MeFTIR measures concentrations of total VOCs as observed by C-H-stretch absorption in the 2700-3100 cm⁻¹ wavenumber region.

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