Review of Technologies for the Characterization and Monitoring of VOCs, Reduced Sulphur Compounds and CH_4

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OSRIN
Oil Sands Research and
Information Network

Oil Sands Research and Information Network

OSRIN is a university-based, independent organization that compiles, interprets and analyses available information about returning landscapes and water impacted by oil sands mining to a natural state and provides knowledge to those who can use it to drive breakthrough improvements in reclamation regulations and practices. OSRIN is a project of the University of Alberta's School of Energy and the Environment (SEE). OSRIN was launched with a start-up grant of $4.5 million from Alberta Environment and a $250,000 grant from the Canada School of Energy and Environment Ltd.

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REPORT SUMMARY

The overall goal of this project is to better understand the advantages and limitations of air emission pollutant characterization and monitoring techniques from area sources. This will allow for the selection of current technologies that are most suitable for measuring fugitive emissions of air pollutants from oil sands tailings ponds.

The project consists of the following tasks:

> Task 1: Review concentration measurement technologies for volatile organic compounds (VOCs) reduced sulphur compounds (including H_2S), and CH_4.
>
> Task 2: Review flux measurement technologies that are used or can be used to measure air pollutant emissions from oil sand tailing ponds.

Task 1: Review concentration measurement technologies for volatile organic compounds (VOCs), reduced sulphur compounds, and CH_4

Methodology

A review was conducted to determine the available technologies for characterizing and measuring the flux of each of the three groups of pollutants (VOCs, reduced sulphur compounds, and CH_4). The review of the technologies included the following: a short description of the technology and its operating principle; instrument sensitivity (detection limit); advantages and limitations of the technique (performance, versatility, reliability); and cost, whenever possible. Costs do not include the labour to collect samples or the costs involved in running the analyses at other laboratories, as these are variable. However, such costs should be weighed when considering the application of the different technologies. Sample collecting procedures are important as they may affect the accuracy and precision of the technologies; these techniques are generally standard and have not been focused on for this report.

Technologies for VOC Characterization

The technologies for VOC characterization were classified into conventional analytical technologies (based on laboratory and field techniques) and remote sensing monitoring technologies (based on field techniques).

The following technologies have been reviewed and assessed:

- Conventional Analytical Technologies
    - Flame Ionization Detection (FID)
    - Infrared (IR) Absorption Spectroscopy
    - Photo Ionization Detection (PID)
    - Gas Chromatography-Mass Spectrometry (GC-MS)
    - Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)
    - Fourier Transform Infrared (FT-IR) Spectroscopy

- Remote Sensing Monitoring Technologies
    - Open Path Fourier Transform Infrared (OP-FTIR) Spectroscopy
    - Differential Optical Absorption Spectroscopy (DOAS)
    - Tunable Diode Laser Absorption Spectroscopy (TDLAS)
    - Differential Absorption LIDAR (DIAL)
    - Solar Occultation Flux (SOF)

Technologies for Reduced Sulphur Compound Characterization

The technologies for reduced sulphur compound characterization were classified into conventional analytical technologies (based on laboratory techniques and field techniques) and remote sensing monitoring technologies (based on field techniques).

The following technologies have been reviewed and assessed:

- Conventional Analytical Technologies
    - Flame Photometric Detection (FPD)
    - Pulsed Flame Photometric Detection (PFPD)
    - Sulphur Chemiluminescence Detection (SCD)
    - Photo Ionization Detectors (PID)
    - Ultraviolet (UV) Spectrometric Detection
- Remote Sensing Monitoring Technologies
    - Tunable Diode Laser Absorption Spectroscopy (TDLAS)
    - Image Multi-Spectral Sensing (IMSS)
    - Differential Absorption LIDAR (DIAL)
    - Open Path Fourier Transform Infrared (OP- FTIR) Spectroscopy

Technologies for CH_4 Characterization

The technologies for CH_4 characterization were classified into conventional analytical technologies (based on laboratory and field techniques) and remote sensing monitoring technologies (based on field techniques).

The following technologies have been reviewed and assessed:

- Conventional Analytical Technologies
    - Infrared (IR) Absorption
    - Mid-Infrared Polarization Spectroscopy
    - Photoacoustic Absorption Spectroscopy (PAS)

    - Solid State (SS) sensor
    - Wavelength Modulation Spectroscopy (WMS)
- Remote Sensing Monitoring Technologies
    - Radial Plume Mapping (RPM)
    - Differential Optical Absorption Spectroscopy (DOAS)
    - Correlation Spectroscopy (CS)
    - Airborne Natural Gas Emission Lidar (ANGEL)

Task 2: Review flux measurement technologies that are used or can be used to measure emissions from air pollutant emissions and greenhouse gases from oil sand tailing ponds.

The technologies for measuring concentration fluxes of fugitive emissions within the atmosphere were also classified into conventional analytical techniques and remote sensing monitoring technologies (all based on field techniques).

The following technologies have been reviewed and assessed:

- Conventional Analytical Techniques
    - Chamber Methods
    - Eddy Covariance (EC)
    - Eddy Accumulation and Relaxed Eddy Accumulation
    - Flux Gradient Techniques
    - Mass Balance Techniques
    - Tracer Gas Method
- Remote Sensing Monitoring Technologies
    - Solar Occultation Flux (SOF)
    - Nocturnal Boundary Layer Box Method
    - Radial Plume Mapping (RPM)

The report concludes with recommendations for technologies to use for monitoring air emissions from oil sands tailings ponds based on the following factors: spatial coverage, quantification of the pollutants, determination of emission factor, characterization of VOC speciation, and frequency of monitoring. For a variety of reasons there may not be one technology that is best suited for emission measurements across the oil sands region, and it is important to understand the different advantages and limitations of the technologies when selecting an option and interpreting the resulting data.

DISCLAIMER

The mention of names of individual instruments and/or methodologies is not to be taken as an endorsement of the instrument or technology by OSRIN, the University of Alberta, or Alberta Environment and Water.

SUMMARY OF EMISSION MONITORING TECHNOLOGIES

The following four tables summarize the characteristics of the emission monitoring technologies that are described in more detail in the body of the report. Costs in the tables are in C$ unless otherwise specified.

Table 1. Review of technologies for characterizing VOCs.

Methods	**Minimum Detection Limits**	**Advantages**	**Limitations**	**Purchasing Cost (C$)**	**Operation Costs**	**Technology Application**
Conventional Analytical Methods						
Flame Ionization Detection (FID)	~ 0.05 ppm for most VOCs ~ 2 ppmv for benzene	- Quantitative measurement of most organic compounds - Can be used for hot and wet samples - High temperature prevents dropout of heavy hydrocarbons along sample line - Continuous concentration monitoring and fast response time	- Only responds to carbon atoms - Provides total non-methane VOCs (no speciation) - Sample cannot be re-used	~ 8,000 to 15,000	- Power consumption, combustion gases	- Ambient air monitoring, emission monitoring, measurement of industrial gas impurities
Infrared (IR) Absorption Spectroscopy	~ 0.3 to 9.2 ppm at 3.4 to 13.89 µm wavelengths for non-methane VOCs	- IR absorbed is directly related to the number of gas molecules - Measures specific VOC species - Minimal sample preparation with no sample destruction	- Requires expensive optical components - Overlapping peaks for various gases produce an additive response (concentrations appear greater than their actual value)	NA	- Power consumption	- Emission monitoring (industrial), personal gas monitoring - Bitumen solvent characterization
Photo Ionization Detectors (PID)	< 0.1 ppm for most VOCs	- Compact, accurate, affordable, and reliable real-time VOC monitoring - Non-destructive sample analysis	- Cannot detect methane - Above a few thousand ppm, self-quenching effects occur - Affected by humidity	~ US3,000 to US10,000	- Power consumption/ battery packs, calibration gases/ kits, sensor/ lamp replacement	- Fugitive emission monitoring, indoor air quality monitoring, personal monitoring

Methods	Minimum Detection Limits	Advantages	Limitations	Purchasing Cost (C$)	Operation Costs	Technology Application
Gas Chromatography-Mass Spectrometry (GC-MS)	~ 5 µg/L for most VOCs in full scan mode ~ 0.5 ppb using MS in SIM mode	- Provides a finer degree of substance identification - Useful for measuring multiple compounds at the same time	- Requires sufficient training and time for analysis - Accuracy is controlled by the analytical method of calibration	~ US75,000 to US150,000+	- Power consumption, carrier gases, maintenance costs (replacement tubing, septa, liners, fittings, valves, pump oils and grease), performance standards	- Rapid in-field air sampling, indoor air exposure assessment, characterization/ quantification of naphthenic acids
Proton Transfer Reaction Mass Spectrometry (PTR-MS)	~ 10 to 100 ppt	- No sample preparation required - Low detection limits (alternative to GC-MS) - Fast response time - No gas supply required - Insensitivity to water molecules	- Sensitivity is dependent upon the efficiency of H_3O^+ ions - Interpretation of the mass spectra can be complicated - Different isomers of the same compound cannot be separated	~99,540 to 186,900 Euro	- Power consumption, distilled water, calibration gases	- Emission monitoring, on-line ambient air monitoring, continuous VOC monitoring
Fourier Transform Infrared (FTIR) Spectroscopy	~ 2 ppb for methane	- Multi-compound analysis - Rapid analysis reduces noise - Sample spectra can be stored for post-measurement analysis - Some instruments can account for water interference	- Cannot detect compounds outside of the library of spectra accurately - H_2O and CO_2 spectra can interfere with measurements	~ 20,000 to 100,000	- Power consumption, purge gases, desiccant packs, solvents	- Ambient air monitoring, characterization of industrial emissions and naphthenic acids
Remote Sensing Monitoring Methods						
Open Path Fourier Transform Infrared (OP-FTIR)	~ 1 to 30 ppb for various VOCs	- Capable of simultaneous quantitative measurements - Continuous operation with real-time data - Design is optimal for field use - Detection sensitivity decreases with increasing path length	- Sensitivity to humidity - Unable to detect homo-nuclear diatomic species - Requires cryogenic cooling - May need to be deployed at multiple sites to obtain an accurate representation of VOCs present	~ 125,000	- Power consumption, liquid nitrogen, compressed air, optical fibre cables, transportation	- Ambient air monitoring, characterization of industrial emissions, motor vehicle emission assessment, atmospheric gas detection

Methods	Minimum Detection Limits	Advantages	Limitations	Purchasing Cost (C$)	Operation Costs	Technology Application
Differential Optical Absorption Spectroscopy (DOAS)	~ 0.3 to 6 ppb for VOCs (including BTEX)	- Large areas can be monitored from one station, providing rapid measurements with high temporal resolution - Allows for non-contact real-time measurements - Lower minimum detection limit for BTX than OP-FTIR	- Requires frequent calibration - Fog and haze can scatter sunlight into the receiving telescope	~ 100,000 to 150,000	- Power consumption, purge air gases, transportation	- Ambient air monitoring, industrial emission monitoring, long-term air quality monitoring, climate research
Tunable Diode Laser Absorption Spectroscopy (TDLAS)	~ 0.05 to 10 ppbv	- Lightweight with low level detection limits - Capable of performing direct calibration with air sources - Generates real-time, path-averaged concentration data in-situ - No post-field data analysis necessary	- Multiple target compounds cannot be measured simultaneously - Requires use of fibre optic cables which can be difficult to deploy over terrain - Requires use of remote reflector mirrors	~ 75,000	- Power consumption, transportation, calibration gases	- Ambient air monitoring, remote vehicle exhaust emission sensing, leak detection of hydrocarbons
Differential Absorption LIDAR (DIAL)	~ 10 to 200 ppb for VOCs 50 ppb for methane	- Can measure up to 2 km - Can be tuned to measure specific classes of species - Add wind speed for mass flux - Can determine the profile of a gas concentration profile along the length of the light beam	- Only one compound or class of compounds can be measured at once - Expensive and complex to operate	~ US500,000	- High power consumption, transportation, calibration gases	- Hydrocarbon emission detection and surveying, leak detection from industrial sources
Solar Occultation Flux (SOF)	~ 0.3 to 0.5 mg/m^2	- Cost effective, mobile, easier to operate, and faster than DIAL - Can be used to measure diffusive emissions - Moving mirrors compensate for the relative movement of the sun - Can obtain total flux	- Unable to measure plume height - Aromatics have weaker absorption of IR light and cannot be measured - Measurements can only be taken in sunny conditions - Systematic errors are difficult to estimate	NA	- Power consumption, transportation costs + select FTIR operating costs	- Emission inventories and screening, ambient air quality measurements, characterization of volcanic emissions

Table 2. Review of technologies for characterizing reduced sulphur compounds.

Methods	**Minimum Detection Limits**	**Advantages**	**Limitations**	**Purchasing Cost ($)**	**Operation Costs**	**Technology Application**
Conventional Analytical Methods						
Flame Photometric Detection (FPD)	~ 10 ppb	- Filters can remove interferences - Dual flame burner eliminates interfering emissions providing a more reproducible response and increasing instrument sensitivity	- Phosphorous compounds can interfere with measurements - Filters must be exchanged between runs if other compounds are to be detected - Quenching by co-elution of hydrocarbons	~ 4,000 to 9,300	- Power consumption, hydrogen gas, carrier gases, wavelength filters, maintenance costs (seals, fittings)	- Pollution monitoring, emission monitoring, detection of compounds in crude oil and natural gas
Pulsed Flame Photometric Detection (PFPD)	~ 2.4 to 9.8 ppbv	- Long-term flame stability and increased sensitivity in comparison to FPD - Increased optical signal - Reduced hydrogen and air consumption	- Temperature variation effects detection limit - Large sample volumes are required to reach low ppb detection limits (can lead to overloading and quenching)	unknown	- Power consumption, hydrogen gas, photo-multiplier tube, maintenance costs (seals, fittings)	- Emission monitoring, ambient air monitoring, detection of compounds in crude oil and natural gas
Sulphur Chemi-luminescence Detection (SCD)	~ 0.13 ppbv	- Linear response with low detection limits - Free of interferences from water vapour and CO - Hydrocarbon interferences are minimized by adjustment of the residence time of the sample in the flame - No quenching from other compounds in the sample matrix	- Interference from metal ions - Flame temperature can shorten lifetime of the probe - Lack of selectivity of compounds that do not include sulphur	~ 10,000 to 30,000	- Power consumption, replacement of pump oil, reaction cell, oil filter, and chemical trap + select GC operating costs	- Ambient air monitoring of natural and industrial sources, water monitoring

Methods	**Minimum Detection Limits**	**Advantages**	**Limitations**	**Purchasing Cost ($)**	**Operation Costs**	**Technology Application**
Photo Ionization Detectors (PID)	- Single figure ppmv	- Compact, accurate, affordable, and reliable real-time VOC monitoring - Non-destructive sample analysis	- Cannot detect methane - Above a few thousand ppm, self-quenching effects occur - Affected by humidity	~ 3,000 to 10,000	- Power consumption/ battery packs, calibration gases/kits, sensor/ lamp replacement	- Fugitive emission monitoring, indoor air quality monitoring, personal monitoring
UV Spectrometric Detection	~ 5 mg/m^3	- Robust and straightforward optical technique - Free of interferences from water vapour and CO_2	- Method is inappropriate for multi-gas analysis - Limited to single pure species analysis - Potential for interference with other gases due to the absorbance additivity law	~ 1,000 to 20,000	- Power consumption, reference and sample cell holders, standards and solvents	- Fugitive emission detection and monitoring, risk assessment
			Remote Sensing Monitoring Methods			
Tunable Diode Laser Absorption Spectroscopy (TDLAS)	~ 8.0 ppbv	- Lightweight with low level detection limits - Capable of performing direct calibration with air sources - Generates real-time, path-averaged concentration data in-situ - No post-field data analysis necessary	Multiple target compounds cannot be measured simultaneously - Requires use of fibre optic cables which can be difficult to deploy over terrain - Requires use of remote reflector mirrors	~ 75,000	- Power consumption, transportation, calibration gases	- Ambient air monitoring, remote vehicle exhaust emission sensing, leak detection of hydrocarbons
Image Multi-Spectral Sensing (IMSS)	- Capable of measuring various sulphur compounds at the ppm level	- Uses a single element to perform imaging and throughput - Does not require spatial scanning - Small, lightweight, and robust	- Requires image processing to sharpen the resulting spectrum - Gas image can be affected by scattering by solar activity	~ US125,000	- Power consumption, performance testing	- Pollution monitoring, gas leak detection, comparison with modeling predictions
Differential Absorption LIDAR (DIAL)	~ 20 ppb at 299 nm (for SO_2)	- Can measure up to 2 km - Can be tuned to measure specific classes of species - Add wind speed for mass flux - Can determine the profile of a gas concentration profile along the length of the light beam	- Only one compound or class of compounds can be measured at a time - Expensive and complex to operate - Requires retro-reflectors	~ US500,000	- High power consumption, transportation, calibration gases	- Hydrocarbon emission detection and surveying, leak detection from industrial sources

Methods	Minimum Detection Limits	Advantages	Limitations	Purchasing Cost ($)	Operation Costs	Technology Application
Open Path Fourier Transform Infrared (OP-FTIR) Spectroscopy	~ 400 ppb	- Capable of simultaneous quantitative measurements - Continuous operation with real-time data - Design is optimal for field use - Detection sensitivity decreases with increasing path length	- Sensitivity to humidity - Unable to detect homo-nuclear diatomic species - Requires cryogenic cooling - May need to be deployed at multiple sites to obtain an accurate representation	~ 125,000	- Power consumption, liquid nitrogen, compressed air, optical fibre cables, transportation	- Ambient air monitoring, characterization of industrial emissions, motor vehicle emission assessment, atmospheric gas detection

Table 3. Review of technologies for characterizing CH_4.

Methods	Minimum Detection Limits	Advantages	Limitations	Purchasing Cost (C$)	Operating Cost	Technology Application
Conventional Analytical Methods						
Infrared (IR) Absorption	<10,000 ppm (0.1 s detection speed)	- IR absorbed is directly related to the number of gas molecules - Measures specific VOC species - Minimal sample preparation with no sample destruction	- Requires expensive optical components - Overlapping peaks for various gases produce an additive response (concentrations appear greater than their actual value) - Calibration with 100% pure CH_4 may cause false alarms	unknown	- Power consumption	Emission monitoring (industrial), personal gas monitoring - Bitumen solvent characterization
Mid-Infrared Polarization Spectroscopy	< 10,000 ppm	- Provides coherent, laser-like beam signals which rids background noise from luminous environments - Capable of focusing the signal on a small area - Simple set-up	- Limited to the ultraviolet/ visible spectral region by exciting electronic transitions - Less sensitive than visible radiation detectors	unknown	- Power consumption, liquid nitrogen, carrier gases	- Ambient air monitoring and emission control, detection of CH_4 in harsh environments
Photoacoustic Absorption Spectroscopy (PAS)	~ 13 ppb	- Capable of detecting target gases at low levels due to its inherent stability and reduced cross-sensitivity - Can detect small pressure pulses before the concentration reaches the threshold limit - Eliminates the need to adjust for zero drift - Precise, low-cost, reliable, and high-performance monitoring - Additional sensors can be added to monitor IR detectable gases - Direct analysis without sample preparation/ alteration	- Thermal wave is reflected back to the sample where it decays, making it difficult to obtain an adequate signal-to-noise ratio - Signal saturation can affect the modulation frequency - Sensitivity is limited by the pressure sensor and microphone - Corrosive gases can impact the monitor	unknown	- Power consumption, purge gases, calibration gases	- Ambient air monitoring and detection of air pollutants or toxic/ combustible gases

Methods	**Minimum Detection Limits**	**Advantages**	**Limitations**	**Purchasing Cost (C$)**	**Operating Cost**	**Technology Application**
Solid State (SS) Sensors	~ 1.7 ppm for atmospheric CH_4 (SnO_2 layered SS sensor)	- Sensors provide real-time data - Small in size, portable, and automated providing fast analyses of real-time measurements - Long operating life and reasonable parameter stability with low maintenance - Feasible and easy to handle - High reliability with good resistance to corrosive gases - Allows the rapid replacement of the detector without having to change the whole device - Provides the most robust and versatile solution to fieldwork	- Sensitive to ambient humidity and to multiple chemicals showing cross sensitivities - Semiconductors have to be heated (physical limitation) - Long sensor stabilization time after energization based on the field ambient air condition - Suffers from limited measurement accuracy over the operating lifetime	unknown	- Power consumption, monthly or three-month calibration intervals	- Commercial gas sensors (fire and leak detection), indoor air quality, ambient air quality - Monitoring of geologic emissions and landfill gases
Wavelength Modulation Spectroscopy (WMS)	~ 1.15 to 50 ppm	- Powerful technique with a high signal-to-noise ratio - Simple setup - Optoelectronic set-up has been implemented in a fully controlled manner for the detection and monitoring of CH_4 - The detection bandwidth is shifted from DC to higher frequencies to rid excess noise - Low instrument error	- Problems with the stability of the laser and the introduction of noise with increasing life-span	unknown	- Power consumption, calibration costs	- Trace gas emission monitoring from natural and anthropogenic sources (industry)

Methods	**Minimum Detection Limits**	**Advantages**	**Limitations**	**Purchasing Cost (C$)**	**Operating Cost**	**Technology Application**
Remote Sensing Monitoring Methods						
Open Path Fourier Transform Infrared (OP-FTIR)	~ 6.63 ppb	- Capable of simultaneous quantitative measurements - Continuous operation with real-time data - Design is optimal for field use - Detection sensitivity decreases with increasing path length	- Sensitivity to humidity - Unable to detect homo-nuclear diatomic species - Requires cryogenic cooling - May need to be deployed at multiple sites to obtain an accurate representation of VOCs present	~ 125,000	- Power consumption, liquid nitrogen, compressed air, optical fibre cables, transportation	- Ambient air monitoring, characterization of industrial emissions, motor vehicle emission assessment, atmospheric gas detection
Differential Optical Absorption Spectroscopy (DOAS)	~ 0.12 ppm	- Large area sources can be monitored from one station with rapid measurements and high temporal resolution - Allows for simultaneous measurements of multiple wavelengths	- Requires frequent calibration - Fog and haze can scatter sunlight into the receiving telescope	~100,000 to 150,000	- Power consumption, purge air gases, transportation	- Ambient air monitoring, industrial emission monitoring, long-term air quality monitoring, climate research
Correlation Spectroscopy	~ 20 ppmv over a 30 m path length	- Comparison of gases acts as a perfect filter to identify the target gas - Low cost method/ simple to use - High selectivity	- Sensitive to water vapour - If all light at the absorbing wavelength is absorbed, the method will not work	unknown	- Power consumption, calibration costs	- Emission detection, monitoring and mapping greenhouse gases, indoor monitoring/ surveillance/ exposure assessments
Airborne Natural Gas Emission LIDAR (ANGEL)	- Measures concentration path length (CPL) in ppm/m	- Can survey up to 1,000 miles per day - Eliminates all accessibility issues and terrain conditions - Sensor accounts for plane position and orientation- Accounts for background emission levels - Can provide 3-D coverage - GIS-ready data sets available	- Provides a passive measure of the contaminant in a slow and expensive fashion - Complex system design, integration and data analysis	unknown	- Power consumption, aircraft costs (fuel, pilot, etc.)	- Leak detection and mapping of natural gas pipelines - Detection of hazardous liquid emissions from broad area sources

Table 4. Review of flux measurement technologies for VOCs, reduced sulphur compounds and CH_4.

Methods	**Minimum Detection Limits**	**Advantages**	**Limitations**	**Cost of the System (C$)**	**Technology Application**
Conventional Analytical Methods					
Chamber Methods	- ppbv	- Simple, portable, low in cost - Can measure multiple gases simultaneously at low flux levels - Continuous/ long-term monitoring is possible - Measurement can be taken rapidly and precisely - Static closed chambers require no power consumption	- Pressure differences and turbulence can create artefact gas fluxes - Solar radiation exposure can expand contained gases - Venting of closed chambers can generate errors - Build-up of water internal water vapour can displace chamber air - Small areas are measured over a short term - Flat and homogeneous terrain is required	unknown	- Oil sands mining sites and upgrading facilities - Floating chambers over freshwater bodies
Eddy Covariance (EC)	< 0.1 mg/m^2·h for most VOCs and 22 ng/m^2·s for CH_4	- Minimal system disturbance - Provides direct and simple measurements - Good temporal resolution - Instruments can be housed in controlled environments - Can be used over long sampling periods	- Issues surrounding correct mounting height, flow distortion, and sampling frequencies - Variability in data with temporal variations - Heat and water vapour fluxes must be taken simultaneously - Instrument surfaces may become contaminated by rain/ dust - Delays between sonic anemometer and gas analyzer can cause flux estimate errors - Varying sampling heights may have different footprint characteristics	unknown	- Surface energy fluxes atop overburden piles at mining facilities, and over forests/ lakes

Methods	**Minimum Detection Limits**	**Advantages**	**Limitations**	**Cost of the System (C$)**	**Technology Application**
Eddy Accumulation (EA) Relaxed Eddy Accumulation (REA)	~ 0.2 µg/m^2·s for REA ~ 1 ppb for most VOCs	- Does not require a rapid response sensor for the covariate - Directly measures gas flux at a point - Samples can be measured online or offline - Offline: samples can be dried and brought to uniform temperature to remove heat and water vapour effects	- EA: Difficult to measure proportionally to updrafts and downdrafts - EA: Requires an accuracy of 0.1% - REA: Difficult to measure empirical coefficients - Density fluctuations can affect flux measurements - Wind speed can produce measureable noise	NA	- Biogenic and anthropogenic flux measurements over forest ecosystems
Flux Gradient Techniques	- measured as µmol/m^2·h; dependent on the instrumentation used	- Can also measure net exchange of momentum, sensible/latent heat flux - Straightforward methodology - Can be teamed with highly sensitive instrumentation	- Flux relationships are complex over tall vegetation and forests - Changes in heat and water vapour affect gradient measurements - Requires suitable and stable atm. conditions - Weather conditions can affect sampling - Flux gradients break down near rough surfaces	NA	- Flux monitoring over boreal forests, wetlands and peat lands
Mass Balance Techniques	- measured as mg/m^2·s; dependent on the instrumentation used	- Allows for continuous measurements within small areas and point sources - Non-disturbing and independent of atm. stability - Theoretical assumptions of profile shape are not required - Can measure heterogeneous and elevated sources - Extrapolation of gas concentration and wind speed profiles are not required - Simple instrumentation	- Requires extensive interpretation and high-precision analytical techniques - Can overestimate the flux by 5% to 20% if the turbulent flux component is ignored - Changes in wind direction affect flux measurements - Instrumentation requires an unobstructed fetch - Uncertainty imbedded in the magnitude of the diffusive flux	NA	- Fugitive emission fluxes around liquid manure storages, and oil systems

Methods	**Minimum Detection Limits**	**Advantages**	**Limitations**	**Cost of the System (C$)**	**Technology Application**
Tracer Gas Methods	- ppbv range with an associated error of ± 10 ppbv	- Not dependent on wind speed or direction - Does not require vertical profiling - Tracer and target gases can be measured in the same air sample - Samples can be measured in-situ in real-time	- Issues surrounding spatial heterogeneity during integration of the flux - Confined to point sources or finite boundary locations - High cost - Interfering sources can affect flux measurements - Time consuming and elaborate sampling procedure required	NA	- Flux measurements from landfills, large area sources, and difficult to measure point sources
Remote Sensing Monitoring Methods					
Solar Occultation Flux (SOF)	~ 0.3 to 0.5 mg/m^2	- Cost effective and faster than the DIAL technique - Easier to automate	- Aromatics cannot be measured - Systematic errors are difficult to estimate - Measurements can only be taken in sunny conditions	NA	- Emission inventories from flares, cooling towers, tank areas, and water treatment areas - Volcanic flux emissions
Nocturnal Boundary Layer Box Method	- Can be measured to µmol/m^2·h and is dependent on the characterization instrumentation used	- Simple sampling technique and mathematical conversion - Balloon techniques can be used at higher altitudes - Can be teamed with high detection level characterization instrumentation	- Only suitable for emission profiles showing a step change in concentration over a small change in altitude - Difficulties in representing flux at the landscape scale - Turbulent conditions can affect concentration measurements - Error in steady state assumptions	NA	- Landscape scale flux measurements over wetlands - Regional scale measurements over extensive areas
Radial Plume Mapping (RPM)	~ 1.75 ppmv for methane gas. Flux often varies from 10% to 25% of the actual emission source	- Capable of characterizing emissions from large area sources - Methodology has been well developed, evaluated, demonstrated, and peer reviewed by the US EPA - Can prepare 3-D pollutant profiles	- Single point emission sources cannot be measured - Requires the operation and co-ordination of a number of instruments and components - Flux calculations are time consuming and complex requiring trained persons	NA	- Hot spot and flux concentration mapping over landfills - Flux measurements over large area sources

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1 INTRODUCTION

The Canadian oil sands deposits, within the Athabasca oil sands region (North of Fort McMurray, Alberta) represent one of the largest unconventional hydrocarbon reserves in the world (Department of Energy, Government of Alberta 2011). Over the past 30 years, surface and in-situ mining operations have increased, resulting in the production of large quantities of waste by-products. Approximately 3 m^3 of water is required for the extraction of 1 m^3 of oil sands, producing around 4 m^3 of tailings waste (comprised of sand, water, clay, residual bitumen, and inorganic and organic contaminants (Allen 2008). Due to the zero discharge approach adopted throughout the region, the tailings are stored on site, in manufactured tailings ponds, allowing for the solids to settle out of solution and water to be re-used throughout the extraction and upgrading processes. It has been estimated that over 843 million m^3 of tailings are currently stored in tailings ponds (Pembina 2007).

During the extraction phase, organic solvents (diluents) are added to the bitumen to lower its viscosity, allowing it to be transported through pipes (Gan et al. 2009, Simpson et al. 2010). It has been observed that the small proportion of diluent that enters the ponds serves as a desirable carbon source (or substrate) for the growing bacterial communities residing within the ponds (Siddique et al. 2006). Through the stimulation of microbial activity, methane gas has been found to bubble to the surface of tailings ponds (Penner and Foght 2010) and the precipitation of iron sulphides (Fedorak et al. 2003) have indicated the release of reduced sulphur compound emissions from the ponds. It is also expected that the use of diluents (comprised of n-alkanes and BTEX components) may indicate the emission of volatile organic compounds (VOCs) during tailings deposition.

Current issues surrounding the emissions of VOCs, CH_4 (methane), and reduced sulphur compounds include the impacts on air and land resources with respect to pollution, climate change as well as the impact on human health to exposure. The oil sands industry currently accounts for 23% of Canada’s greenhouse gas emissions (CAPP 2011) and 3% to 7% of Canada’s nitrogen oxide, VOC, and sulphur dioxide emissions (Birn and Khanna 2010). The emissions released from the large tailings pond area sources has not been well defined due to the heterogeneity ranging across the region. The complexity is further enhanced by the variation and size amongst ponds within the Athabasca region and the lack of accessibility for assessment. However, it is expected that the fugitive sources contribute to the increasing growth of total annual emissions.

The goal of this project was to examine and review the literature, available instrumentation and product information to review current methodologies and technologies for measuring fugitive emissions of air pollutants from the oil sands tailings ponds. This will allow for a better overall understanding of the advantages and limitations of air pollutant characterization from tailings ponds, and lead to the most optimal selection of technologies for emission measurements. This was completed through the following two tasks:

- Task 1: Review concentration measurement technologies for volatile organic compounds (VOCs), reduced sulphur compounds and CH_4. This task will investigate the available characterization technologies for conventional and analytical techniques including: a short description of the technology and its operating principle; instrument sensitivity (detection limit); advantages and the limitations of the technique (performance, versatility, reliability); and cost, whenever possible. *Costs are provided in Canadian dollars unless otherwise specified.*

- Task 2: Review flux measurement technologies that are used or can be used to measure air pollutant emissions and greenhouse gases from oil sand tailing ponds. This task will outline conventional analytical and remote sensing technologies used for the measurement of VOC, reduced sulphur compound and CH_4, and fluxes.

Recommended technologies for the characterization and monitoring of fugitive emissions from oil sands tailings ponds will be made at the end of the report based on the following factors: spatial coverage, determination of emission factors, characterization of VOC speciation, and frequency of monitoring.

2 REVIEW OF TECHNOLOGIES FOR CHARACTERIZATION OF VOCS

Volatile organic compounds (VOCs) represent a class of highly reactive and unstable gaseous pollutants, which are precursors to smog and pose a significant risk to human health (some are well-known carcinogens) (Kumar and Viden 2007). As a result, it is important to understand which VOCs are present within a fugitive emission source for both environmental and human health protection. Simpson et al. (2010) detected the presence of 53 VOCs over the Athabasca oil sands region from both evaporative emissions and mining effort emissions by airborne whole sampling. Therefore, it is important to be able to characterize which components are volatilizing from the tailings ponds to understand how it may be influencing the atmosphere, as well as to discriminate emissions and identify the cumulative effects from stacks, upgraders, and vehicles.

The technologies for VOC characterization were classified into conventional analytical technologies and remote sensing monitoring technologies.

The following technologies have been reviewed and assessed:

- Conventional Analytical Technologies
    - Flame Ionization Detection (FID)
    - Infrared (IR) Absorption Spectroscopy
    - Photo Ionization Detection (PID)
    - Gas Chromatography-Mass Spectrometry (GC-MS)
    - Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)
    - Fourier Transform Infrared (FT-IR) Spectroscopy
- Remote Sensing Monitoring Technologies
    - Open Path Fourier Transform Infrared (OP-FTIR) Spectroscopy
    - Differential Optical Absorption Spectroscopy (DOAS)
    - Tunable Diode Laser Absorption Spectroscopy (TDLAS)
    - Differential Absorption LIDAR (DIAL)

- Solar Occultation Flux (SOF)

2.1 Conventional Analytical Methods

2.1.1 *Flame Ionization Detection (FID)*

2.1.1.1 Methodology

FID is a universal detector for organic compounds allowing for the measurement of hydrocarbon concentrations in air. Measured samples are ionized within a burning hydrogen flame in two stages: the organic compounds are primarily cracked forming CH_1, CH_2, and CH_3 radicals; afterwards, contact with oxygen causes chemical ionization producing a measureable electric current. Electric currents vary depending on the various physical and chemical properties of the compounds. The positively charged ionized fragments (CHO^+) are driven by an electric field generated by both the burner jet (cathode) and a negatively charged electrode. The current produced through the ionization of the carbon atoms is measured with an electrometer (in amp), which can be related to the ‘total’ and ‘non-methane’ hydrocarbons within the sample – a function of the number of ionizable carbon atoms and the concentration of atoms within the initial sample (Berezkin and Drugov 1991, McDermott 2004). FIDs are known for their ability to respond to most organic carbon compounds, while having no capacity to respond to inorganic compounds (for example, H_2S) (Guiochon and Guillemin 1988). Portable hand-held FIDs can be used for direct in-field detection of unsaturated, saturated and aromatic hydrocarbons.

FIDs can also be integrated with gas chromatographs (GC) in the laboratory to resolve a broad range of VOC concentrations at higher resolutions (Murphy and Morrison 2007). For this application, samples are required to be obtained from the field using either sorption tubes, canisters, or sampling bags. If sorption tubes are selected, then a desorption system is required to be integrated into the GC system to desorb the adsorbed compounds for analysis. Samples from canisters and/or sampling bags can either be attached to the GC system through a gas sampling valve or can be directly injected into the inlet using glass syringes.

2.1.1.2 Special Features

FID hydrocarbon analyzers are highly versatile instruments with a well-rounded expandability allowing for system integration (Rosemount Analytical 2008). Some manufactured FID systems have the ability to combine with a photo ionization detector (PID) for simultaneous and dual detection of both saturated and unsaturated hydrocarbons and VOCs. This increases the original FIDs resolution, sensitivity and range of compound detection capabilities (O.I. Analytical 2011a).

2.1.1.3 Sensitivity / Limits

FIDs are highly sensitive instruments. Independent FIDs have a minimum detection limit of 0.05 ppm for most VOCs and a response time of 1.5 to 70 s, depending on the manufacturer (Thermo Scientific [Model 55C]; Signal Instruments [Model 3000HM]). Other models have the ability to detect hydrocarbons at a minimum detection limit of 0.1 nanogram (Cole-Parmer 2010). A fast response of 90% full-scale within 1 s has been measured with an Emerson hydrocarbon FID (Rosemount

Analytical 2008). FIDs can measure concentrations over a wide range. For instance, benzene has a dynamic range of 0 to 50,000 ppm and a minimum detection limit of 2 ppmv (McDermott 2004). The sensitivity of the FID is as follows: Hydrocarbons > Esters > Alcohols > Acids. The associated detection limit for VOCs within a GC-FID is approximately 10 ng/L, indicating an increased sensitivity when paired with a gas chromatograph unit (Murphy and Morrison 2007).

2.1.1.4 Advantages

- The high sensitivity and linearity of the instrument has led to the increased reliability of the technique (Guiochon and Guillemin 1988).
- One of the most common quantitative measurements for organic compounds and can often be found paired with gas chromatographs and photo ionization detectors (Murphy and Morrison 2007, O.I. Analytical 2011a).
- Can be used in the measurement of hot and wet samples as the instrument is not influenced by humidity and elevated temperatures (Signal Instruments Inc. 2007).
- Continuous elevated temperatures within the FID unit prevent the dropout of heavy hydrocarbons along the sample line (Signal Instruments Inc. 2007).
- The detection method has a fast response time, making it effective for alarm status monitoring applications, real-time reporting, and continuous concentration monitoring (Signal Instruments 2007).
- Can detect and measure methane.
- Insensitive to water, inert gases and inorganic compounds, while having a negligible response to carbon monoxide and carbon dioxide (Guiochon and Guillemin 1988).

2.1.1.5 Limitations

- Does not respond to fully oxidized carbons or inorganic compounds; response also decreases with increasing substitutions of halogens, amines and hydroxyl groups (Zachowshi and Paleologos 2009).
- Independent FID models cannot differentiate between specific hydrocarbon species as it measures ‘total hydrocarbons’ (Spectra Scientific 2005). This can be overcome with the use of a GC-FID, where individual compounds can be resolved.
- There are operation and safety hazards as hydrogen gas is used as a burner.
- Sample cannot be re-used as it is burned (Zachowshi and Paleologos 2009).

If interested in individual VOCs emitted, the use of an independent FID may not be suitable as multiple hydrocarbon compounds is expected from the oil sands tailings ponds. The laboratory application of the GC-FID may require large sample volumes since the samples cannot be re-used. Transportation of large quantities of samples may limit the effectiveness of the technique.

2.1.1.6 Maintenance

A dirty FID may lead to the production of poor detector sensitivity (Supelco 1998). High purity hydrogen gas (99.9995%) should be used and monitored for gas leaks, and the jets should be routinely cleaned (Supelco 1998). The temperature of the FID should also be monitored during measurements to ensure that it is above dewpoint; such monitoring will ensure that condensation does not occur inside of the instrument affecting the sensitivity of the results.

2.1.1.7 Technology Application

- Ambient air monitoring of hydrocarbon contaminants (landfills), emission monitoring (motor vehicle emissions), and monitoring of industrial sources (exhaust emissions from internal combustion engines, and leak detection and control) (Rosemount Analytical 2008, Zielinska et al. 1996).
- Measurement of industrial gas impurities and hydrocarbons in cryogenics/air liquefaction processes (Rosemount Analytical 2008).
- GC-FIDs have been used in the analysis of gaseous streams of solvent refined coal to characterize the liquid fraction, as well as to isolate hydrocarbons and aromatic compounds (Grob and Barry 2004).

2.1.1.8 Cost

- The cost of the detector ranges from approximately $8K to $15K (Cole-Parmer 2010, EQUIPCO 2011). Costs will increase with the addition of a gas chromatograph system.
- Direct operation costs include power consumption and combustion gas (air and hydrogen) usage.

2.1.2 *Infrared (IR) Absorption*

2.1.2.1 Methodology

Infrared (IR) refers to a range within the electromagnetic spectrum between visible light and microwave radiation (Nakamoto 2009); from 0.7 µm in the near infrared range to 1000 µm in the far infrared range. The wavelength of IR radiation absorbed by a compound is unique to each gas or vapour molecule, producing varying spectral scans or spectral ‘fingerprints’ (Herres 1989). More specifically, when IR radiation is absorbed by organic compounds, it is converted into varying degrees of vibrational and rotational energy (Nakamoto 2009). IR absorption spectroscopy passes a known spectrum of IR radiation through a sample, and measures the resulting light reaching a detector. The instrument then compares the detected light to the energy emitted by the source, to obtain the quantity of IR light absorbed by the sample. The difference in the energy levels indicates the gas concentration level (Lodge 1988, McDermott 2004). For methane gas, the absorption line is detected by sweeping a wavelength of 1,300 nm (emitted from a laser diode light source) across the sample (Noda et al. 2005). There are different IR configurations of sensors that may be suited to specific application use and specific gas detection. Configurations can include: fixed focusing mirrors, entrance and exit slits;

filter systems controlled by a microprocessor; or acousto-optical tunable frequencies used to overcome mechanical issues surrounding multi-wavelength filter instruments (Globalspec 2011). IR spectrometers have been integrated with Fourier transform technology to achieve higher sensitivity and detection of VOCs (see Section 2.1.6).

2.1.2.2 Special Features

IR spectrometers are known to come in a variety of sizes to suit a user's needs. Models tend to be rugged and portable allowing for both field and laboratory measurements. Instruments are also designed to be simple for the user. Consequently, theoretical knowledge of the instrument and methodology is not required for instrument use. Some instruments have the ability to automatically compensate for any contamination of the optical components as well as emission source intensity changes, by using electronic signal ratios imbedded within the on-board microprocessor (Galvanic Applied Sciences 2000). IR combustible gas detectors can be utilized for numerous commercial and industrial applications, as they often monitor other conditions such as supply voltage and optical path integrity (General Monitors 2011).

2.1.2.3 Sensitivity / Limits

The detection limits for many organic compounds varies from 0.1 to 20 ppm. For non-methane VOCs, the minimum detectable concentration ranges from 0.3 to 9.2 ppm at wavelengths between 3.4 µm to 13.9 µm.

The resolution for a Buck Scientific IR spectrometer nominally ranges from 600 to 2,000 cm^{-1} (≤ 2 cm^{-1}) and 2,000 to 4,000 cm^{-1} (≤ 3 cm^{-1}) with a sensitivity of 1 V/mW (Buck Scientific 2011). For this instrument, scan speeds of 3, 6, 12, and 24 min are possible depending on the amount of data points required over the full wavelength range (Buck Scientific 2011). An accuracy of ±2% of range has been measured with a Galvanic IR spectrometer when operated within a temperature range of 0 to 45°C (Galvanic Applied Sciences 2000). This may not be ideal for the oil sands application since temperatures are often below 0°C north of Fort McMurray, Alberta for more than six months of the year.

2.1.2.4 Advantages

- The amount of IR radiation absorbed is directly related to the number of the gas molecules in the sample – providing a good reliability behind the measurement of concentration (General Monitors 2011).
- Measures specific VOC species since the characteristic absorption of wavelengths is specific for certain compounds (Galvanic Applied Sciences 2000).
- Minimal sample preparation and no sample destruction (Painter et al. 2010).

2.1.2.5 Limitations

- Requires expensive optical components, such as light sources, photo detectors, and lenses (Envirotech Engineering 2007).

- The usefulness of IR analyzers for monitoring complex mixtures is limited since overlapping peaks for various gases produce an additive response, making concentrations appear higher than actual (McDermott 2004).
- Requires very sensitive and properly tuned instruments (McDermott 2004).
- Calibration with 100% pure methane may cause the IR sensor to overstate the concentration of other hydrocarbons, because it is least sensitive to single bonded methane, resulting in false alarms (Zéninari et al. 2003).

This technique may not be optimal for monitoring tailings ponds since the emissions are expected to contain complex mixtures, leading to overlapping peaks and uncertainty in the data.

2.1.2.6 Maintenance

Due to the rugged and fixed parts design, IR spectrometers require minimal maintenance. With limited or no included moving parts, the instrumentation requires no optical realignment by the user. The spectrometer parts are typically contained within a sealed enclosure to prohibit contamination by water vapour, CO_2 and dust. Specific parts, such as the light source or detector, can often be replaced by the manufacturer if malfunctioning occurs. The instrument requires only periodic cleaning of the optical windows as well as a re-zeroing to maintain dependable performance (General Monitors 2011).

2.1.2.7 Technology Application

- Emission monitoring (natural gas and landfill gas) (Galvanic Applied Sciences 2000).
- Industrial emission monitoring: chemical plants, compressor stations, drilling and production platforms, fuel loading facilities, oil well logging, refineries, wastewater treatment facilities (General Monitors 2011).
- Personal gas monitoring (confined space entry, industrial plants, underground utility/ electricity ducts, engine rooms) (Honeywell Analytics 2008).

2.1.3 *Photo Ionization Detectors (PID)*

2.1.3.1 Methodology

Photo ionization detectors (PID) contain an ultraviolet (UV) lamp that ionizes organic compounds (such as VOCs) within an air sample. UV radiation contains higher energies than visible light and infrared radiation due to its shorter wavelengths and higher frequencies. Generally, three different lamps of 9.5 eV, 10.6 eV and 11.7 eV are used as the UV source within the PID (McDermott 2004). Within the PID, the UV lamp is filled with a low pressure inert gas (such as krypton) that is excited or energized by a high voltage electric current. The PID instrument converts the concentration of ionizable organic compounds into an electric signal, producing an ion current. The ion current produced is proportional to the mass of the sample, number of atoms, or concentration, allowing for the determination of concentration (displayed as ppm). This technique is used for direct in-situ field measurements.

2.1.3.2 Special Features

There are various PID instrument configurations that can be used to measure other sources depending on the application of the technology and the types of gases monitored. For instance, a MiniRAE 2000 PID can measure between 0 and 10,000 ppm allowing for the delineation of a range of chemicals (Rae Systems 2009). A MiniRAE 3000 PID can measure between 0 and 15,000 ppm. PIDs are not selective and can measure a range of VOCs instantaneously. PIDs can also detect and measure some inorganic compounds such as hydrogen sulphide and ammonia. For instance, a MultiRAE PID can detect H_2S with 0.1 ppm, with detection limits ranging from 0 to 200 ppm.

2.1.3.3 Sensitivity / Limits

VOC sensors have the capability of measuring between 0 to 999.9 ppm with a resolution and response time of 0.1 ppm and < 3 s, respectively. For VOCs ranging from 1,000 to 15,000 ppm, the associated resolution and response time is 1 ppm and < 3 s, respectively (Rae Systems 2007b). Methane has an ionization potential of 12.6 eV, and cannot be detected using a PID, even with an 11.6 eV lamp. Hydrogen sulphide can be detected by a PID by using a 10.6 eV lamp, since it has an ionization potential of 10.45 eV (McDermott 2004). Typical minimum detection limits are on the order of single figure ppmv (Environment Agency 2001). Newer PID models can have a minimum detection limit in the ppb range. PIDs can have a measurable response time of < 20 s (T_{90}) when operated within 0 to $50^{o}C$ (Global Detection Systems 2006). For high accuracy, sensors should initially be allowed to stabilize for 10 to 20 min after calibration with a known target gas; stabilization is not necessary for applications where high accuracy is not necessary (Global Detection Systems 2006). PID instrumentation has a low ppb resolution when measuring both flammable and non-flammable gases and vapours, while providing a ± 10% reading accuracy (Rae Systems 2009).

Advantages:

- Does not require a carrier or combustion gas (Kahn 2009).
- Compact, accurate, affordable, and reliable real-time VOC monitoring (Rae Systems 2007b).
- Non-destructive analysis of the sample (Rae Systems 2004).
- Small and portable models are available for field measurements (Rae Systems 2004).
- Consistent calibration will ensure reliability of the measurements (Global Detection Systems 2006).

Limitations:

- Cannot detect methane (Rae Systems 2004).
- Above a few thousand ppm, some of the gas molecules become blocked from the UV light sources, leading to ‘self-quenching’ effects (Rae Systems 2007a).
- For some PIDs (11.7 eV probe), concentration measurement is greatly affected by humidity reducing the instrument response up to 50% (Rae Systems 2007a).

For the oil sands tailings pond application, it is not expected that the hydrocarbon emissions will exceed a few thousand ppm. However, humidity may influence the accuracy of the data in the field limiting the efficiency of the technology.

2.1.3.4 Maintenance

The PID instrumentation is enclosed to prevent contamination, thereby allowing for little to no maintenance. However, ambient air contaminants can reduce the sensitivity of the sensor by building up on the UV window; routine calibration can compensate for this effect (Global Detection Systems 2006). The PID lamp should also be replaced after 5,000 h of operation (typical lifespan) (Global Detection Systems 2006). The electrode stack has the potential to be contaminated if exposed to acidic gases at high levels of humidity and temperature; the stack can be carefully removed and replaced (Burt 2008). The lamp can also be cleaned with α-alumina powder (Burt 2008).

2.1.3.5 Technology Application

- Continuous emission monitoring applications of fugitive emission (scrubber efficiency, carbon bed breakthrough detection, well logging, etc.).
- Indoor air quality monitoring (indoor VOC sources), solvent detection, air treatment system monitoring, VOC emissions from incinerators, and refinery analyzer shelter emissions (Rae Systems 2006).
- Personal monitoring, workplace exposure limits monitoring.

2.1.3.6 Cost

- The cost of the system ranges from approximately US$3,000 to US$10,000 (Mid-State Instruments 2011, U.S. Environmental Protection Agency 2007b).
- Operating costs: portable models require the use of lithium-ion and alkaline battery packs which are typically rechargeable units (Rae Systems 2005). Calibration gases are also necessary for routine maintenance. Gas types required depend on the user and usage of the instrument. Calibration kits can be obtained from the manufacturer containing mixtures of gases at specific concentrations (Rae Systems 2005).
- Sensors and lamps may require replacement after 1 to 3 years; replacement lamps can cost between $200 and $900 (Brown 2006).

2.1.4 *Gas Chromatography-Mass Spectrometry (GC-MS)*

2.1.4.1 Methodology

Gas chromatography-mass spectrometry (GC-MS) is used for the identification and quantification of complex mixtures of VOCs and semi-VOCs. More specifically, the GC component separates VOCs and semi-VOCs into individual molecules depending on their atomic mass, and the MS component provides structural information on the masses of particles for the determination of elemental composition based on the mass to charge ratio for parent and daughter ions (Settle 1997). The separation of molecules occurs at different retention times within the GC capillary columns which are used by the MS to capture and pass the molecules through an electric field (where the molecules are then ionized). Ionized molecules are directed into a magnetic field, perpendicular to the ion beam causing the ions to scatter and be collected based on their mass number. The ions in the detectors are counted as electrical signals (McDermott 2004, McEwen et al. 1996). The results are presented as a spectrum of peaks that can be compared to peaks of authentic compounds for identification and classification. GC-MS instruments can be integrated with thermal desorption technology to desorb VOCs and semi-VOCs from sample matrices and canisters. This technique is used for laboratory applications and measurements, where samples are required to be obtained from the field using either sorption tubes, canisters, or sampling bags. Samples can be collected within sorbent tubes (filled with carbonaceous material) and thermally desorbed (with a thermal desorber), where characterization and quantification of the components are then measured through GC-MS technology. Samples from canisters and/or sampling bags can either be attached to the GC system through a gas sampling valve or can be directly injected into the inlet using glass syringes. Smaller and portable GC-MS models may be taken to the field for in-situ measurements (see Technology Application).

2.1.4.2 Special Features

GC-MS instruments have the capacity to identify multiple VOC components (as well as other gases) within the same sample stream. Integrated software programs allow for the comprehensive quantification and characterization of these components. Some commercially available software generates pseudo-color 3-D image maps of single and multiple traditional two-dimensional peak chromatographs to aid in resolving compounds (Hübschmann 2008). These digital image processing techniques provide insight to analytical samples, improving the speed of analysis (Hübschmann 2008).

2.1.4.3 Sensitivity / Limits

Using the MS in full scan mode allows for the quantification of VOC concentrations between 2 to 5 µg/L. Detection limits of approximately 0.5 ppb are possible using the MS in Selective Ion Monitoring (SIM) mode. To maintain accuracy of the results, high purity carrier gases are required in addition to the use of blanks and calibration standards for quality assurance and quality control. Consistent calibration standards will ultimately increase the reliability of the technique. A Varian GC was reported to have an injector accuracy of ± 0.1 psi (5% full scale flow) and a resolution of 0.1 mL/min (Agilent Technologies 2010a). The instrument has an associated MS scan rate of 5,000 to 10,000 amu/s for a unit mass resolution (Agilent Technologies 2010a). Another Agilent GC was reported to have a pressure range of 0 to 150 psi with a 0.01 psi resolution; the MS component has the capability of identifying masses ranging from 1.6 to 800 amu (Agilent Technologies 2004).

2.1.4.4 Advantages

- Identifies individual VOC species (Loconto 2006), providing a finer degree of substance identification.
- Especially useful when compounds emerge at the same time from the GC column (U.S. Environmental Protection Agency, 2001).

2.1.4.5 Limitations

- Can only measure compounds with vapour pressures exceeding 1.32×10^{-13} atm (Settle 1997).
- Accuracy is controlled by the analytical method of calibration (Settle 1997).
- Requires sufficient training and time for analysis (Agilent Technologies 2011a).
- Difficulty in resolving compounds with similar mass to charge ratios.

If experienced users are available, the GC-MS technology will allow for accurate individual compound detection at low levels for the oil sands tailings application.

2.1.4.6 Maintenance

Contaminated gas delivery tubing can lead to noise within the results. Therefore, proper cleaning of the tubing with the use of suitable detergents, solvents and purgeable nitrogen within an oven can increase the quality and the lifetime of the GC-MS system through the limitation of contamination (Agilent Technologies 2005). GC-MS maintenance should also consist of periodic checking of fittings and connections with a gas leak detector to prevent contaminants from entering the gas stream; skewing the results (Agilent Technologies 2005). The carrier and support gas flows should be monitored on a regular basis to ensure instrument accuracy and sensitivity (Agilent Technologies 2005).

Additional parts such as septum and syringes used within the analysis should be cleaned before use and proper sizes and material types (teflon, glass, stainless steel, etc.) should be used to prevent reactions with the sample of interest and leaks into the system.

The addition of water, gas, oxygen, and hydrocarbon traps for carrier and detector gas purification and the removal of detrimental impurities will improve the quality of the gas and preserve columns, prevent column bleed, and extend the lifetime of the instrument (Agilent Technologies 2005). These traps can be replaced over time as they become concentrated with impurities to ensure the quality of the gases.

2.1.4.7 Technology Application

- Rapid in-field air sampling of VOCs, pesticides, and polychlorinated biphenyls with solid-phase micro-extraction fibres (clinical, forensic, food and environmental applications) (Hook et al. 2002).
- Assessment of indoor exposure and air characterization of VOCs and semi-VOCs (Yoshida et al. 2004).
- Characterization and quantification of naphthenic acids in oil sands tailings water, groundwater, and sediment before and after use of treatment technologies (Del Rio et al. 2006, Holowenko et al. 2002, Merlin et al. 2007).

2.1.4.8 Cost

- The cost of the system ranges from approximately US$75,000 (U.S. Environmental Protection Agency 2001) to US$150,000+.
- Major operating costs include power consumption and carrier gas supply. Shimadzu (2010) has developed an energy-saving GC unit (GC-2025) which consumes 30% less power than other models with included automatic shutdown functions reducing power consumption from 280 kWh to 190 kWh for a single analysis.
- The following parts can also be included within the operating and maintenance costs over the lifetime of the instrument: GC-MS tubing, reference/tuning/performance standards, inlet septa, MS certified liners, fittings and ferrules, valve supplies, and pump oils and grease (Agilent Technologies 2011b).

2.1.5 ***Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)***

2.1.5.1 Methodology

Proton transfer reaction-mass spectrometry (PTR-MS) is a recently developed technique for measuring trace amounts of VOCs within the atmosphere, by combining chemical ionization and drift tube technologies. The PTR-MS system consists of the following components: an ion source that produces H_3O^+ ions; a drift tube allowing for non-reactive collisions between the H_3O^+ ions and the trace gases; and, an ion detection system which measures the count rates between the H_3O^+ ions and the organic reactants (Hansel et al. 1999). Continuous pumping of air throughout the reactor allows for any VOCs to be ionized by proton transfer reactions with the H_3O^+ ions (Sprung et al. 2001). The use of the drift tube provides great advantages for this method over other conventional analytical methods. More specifically, an electric field is applied in the axial direction within the drift tube allowing for the ion kinetic energy to increase, reducing the tendency of clustering between the reagent and the produced ions (De Gouw et al. 2003). The simplified ion chemistry facilitates the detection of multiple compounds within the same air sample. A quadruple mass spectrometer attached to the ion detection system analyzes the masses of the H_3O^+ ions and the organic reactants separately, identifying the organic species present (De Gouw et al. 2003).

PTR-MS has been recently integrated with time of flight (TOF) analyzers to create commercially available PTR-TOF-MS instruments (Cappellin et al. 2010). The PTR-TOF-MS instrument combines the sensitivity and speed of the PTR-MS with new features which allow for the determination of the exact elemental composition of the measured peaks and improved mass accuracy (Cappellin et al. 2010).

These techniques are currently used for laboratory real-time measurements, but some models allow for the instrument to be operated in nearly any environment as no gas supply is necessary for sample measurements (Ionicon Analitik 2008).

2.1.5.2 Special Features

PTR-MS provides real-time quantitative analysis due to constant and well defined conditions in the drift tube. The simplistic nature of the PTR-MS ion chemistry allows for the determination of relative concentrations of primary ions, minimizing fragmentation within the spectrum (Hewitt et al. 2003). The instrument ion mass precision is governed by the ion signal strength and the integration period and is described by Poisson statistics (Hewitt et al. 2003). Therefore, the precision behind low VOC concentrations can be increased by increasing the integration period between successive measurements (Hewitt et al. 2003).

2.1.5.3 Sensitivity

PTR-MS method allows for the measurement of VOCs at low detection limit ranges from 10 to 100 pptv with a fast response time nearly 1 s (Ionicon Analitik 2011a). A high sensitivity PTR-MS has a detection limit of 5 pptv with an associated resolution and response time of <1 amu and 100 ms, respectively (Ionicon Analitik 2008). The Ionicon PTR-TOF 2000 model has a detection limit of less than 5 pptv averaged over 1 min, and an associated resolution of 2000 amu (Ionicon Analitik 2011b).

2.1.5.4 Advantages

- No sample preparation necessary; whole air samples can be introduced directly to the drift tube for analysis (Ionicon Analitik 2008).
- Low detection limits make it an alternative to GC-MS (Ionicon Analitik 2008).
- Fast response time, high sensitivity, compact design (Hansel et al. 1999).
- The instrument can be operated in nearly any environment as no gas supply is necessary for sample measurements (Ionicon Analitik 2008).
- Only one product ion species will occur for each neutral reactant since the primary H_3O^+ ions have many non-dissociative proton transfer processes (Lindinger et al. 1998).
- Insensitivity to water molecules (Lindinger et al. 1998).

2.1.5.5 Limitations

- The electric field and pressure within the drift tube limits the reaction time of the H_3O^+ ions (De Gouw et al. 2003).
- The sensitivity of this system depends on the conversion efficiency of the H_3O^+ ions (De Gouw et al. 2003).
- The interpretation of the mass spectra can be complicated by the fragmentation of the product ions (leading to mass overlap) (De Gouw et al. 2003).
- Different isomers of some compounds cannot be separated (Lindinger et al. 1998).

If experienced users are available, this technology will allow for accurate compound detect at low levels for the oil sands tailings application.

2.1.5.6 Maintenance

To achieve the accuracy required for VOC measurements, the PTR-MS instrument has to be calibrated based on the known exact mass of ions regularly and consistently (Cappellin et al. 2010, Taipale et al. 2008). For instances where there are no calibration gas standards available for the specific VOC of interest, qualitative results can be utilized from calibration curves of other close compounds (Taipale et al. 2008). After sample measurement, the following suite of options can be performed in order to reduce any observable noise and drift within the signal: subtraction of the VOC background signals; normalization of the product ion count; smoothing of the primary and water cluster ion count rates; and the inclusion of fragmentation in the measured sensitivities (Taipale et al. 2008).

Instrument fasteners, connections, and seals should be monitored consistently for leaks, distortions, and overheating. Such parts should be replaced if overheating and/ or deterioration are evident. The instrument should also be placed in a clean area of low humidity to prevent contamination and noise within the measurements.

2.1.5.7 Technology Application

- Emission monitoring (motor vehicle emissions) (Rogers et al. 2006), ambient air mixing ratio monitoring of VOCs in urban, rural and remote areas (Taipale et al. 2008).
- On-line ambient air monitoring (diurnal variation detection) and indoor air characterization and control of mixtures of organic compounds (Lindinger et al. 1998).
- Continuous VOC monitoring of air pollution events within Alberta’s oil sands (Borrego and Miranda 2008).
- Various medical (endogenous VOCs in human breath), environmental (vehicle and biomaterial emissions, characterization of partially oxidized VOCs) and food chemistry (aromatic compounds) applications of VOC monitoring (Lindinger and Hansel 1997, Lindinger et al. 1998).

2.1.5.8 Cost

- The capital costs for a Standard PTR-MS, High Sensitivity PTR-MS, and Compact PTR-MS model is approximately 186,900 Euro, 209,790 Euro and 99,540 Euro, respectively (Ionicon Models) (Ionicon Analytik, personal communication, March 25 2011).
- The PTR-MS only consumes electrical power and small quantities of laboratory-grade distilled water. Calibration gases are also required for instrument use.

2.1.6 *Fourier Transform Infrared (FT-IR) Spectroscopy*

2.1.6.1 Methodology

Within the FT-IR spectrometer, a beam splitter divides an incoming IR source into two equal beams before directing the beams of light to both a fixed and rotating mirror creating interference and producing maximum amplitude of the signals. These reflections are then recombined in a Michelson interferometer and passed through the sample cell, creating an interferogram of unique encoded sample information. The Fourier transform function converts the signal strength back to an IR light frequency response (IPTL 2009). The data are then collected by a detector where the identity and concentration of the gases is interpreted. For multi-component gas molecules, computer software retrieves calibration data from its database to compare the sample spectrum to background data (Gosz et al. 1990, McDermott 2004).

This technique is commonly used in laboratory applications; however, some models allow for in-situ field ambient monitoring (see Section 2.1.6.7).

2.1.6.2 Special Features

Newer FT-IR instruments can include an automatic water vapour compensation option which eliminates the need for purge gases by using calibration-free algorithms, thereby reducing operating costs (Perkin Elmer 2009). Instruments also have the capability of adding liquid and solid sampler accessories to characterize a range of materials. Most software includes a large high-resolution spectral library (including a wide range of inorganic and organic volatile compounds) that can be used for material characterization; this library can also be updated with calibration standards and sample peaks which can be used for future reference (Thermo Scientific 2008). The reproducibility of the interferogram data using the reference laser not only increases the degree of reproducibility of the instrument, but also the reliability of the spectral signatures. FT-IR instruments can also be integrated with near infrared, mid-infrared, and far-infrared technologies expanding its range of spectral sensitivity (Perkin Elmer 2009).

2.1.6.3 Sensitivity / Limits

For methane, the minimum detection limit is 2 ppb at a frequency of 3,018 cm^{-1} (Sigrist 1994). The Nicolet iS10 FT-IR spectrometer has a non-apodized spectral resolution of 0.4 cm^{-1}, and a wavelength precision of 0.01 cm^{-1} at 2,000 cm^{-1} which is suitable for slow responsivity within materials as well as high-sensitivity detectors (Thermo Scientific 2008). The accuracy of the instrument is dependent upon its response to known calibration standards. Perkin Elmer (2008) developed an IR spectral reflection set for their FT-IR instruments with a reproducibility of < 0.001 and accuracy of < 0.007 with respect to instrument performance.

2.1.6.4 Advantages

- Can identify both organic and inorganic gaseous compounds allowing for multi-compound analysis (MKS Instruments Inc. 2004).
- Rapid analysis reduces noise (Gosz et al. 1990).
- Can store sample spectra for post-measurement analysis (Perkin Elmer 2009).
- Systems can be battery operated ensuring a truly portable solution (Gasmet Technologies 2009).

- Some instruments have the capacity to generate water vapour spectra to account for water vapour interference during mid-infrared measurements (Perkin Elmer 2009, U.S. Environmental Protection Agency 1999a).

2.1.6.5 Limitations

- To detect any compounds accurately, it requires an extensive library of spectra containing multiple spectra for each compound over a range of concentrations. Compounds without any spectra cannot be determined accurately (U.S. Environmental Protection Agency 1992).
- Can only measure compounds which absorb IR radiation; consequently, the spectra for H_2O and CO_2 within the IR range can interfere with compounds of interest (Chambers 2001).

This method may allow for accurate low level detection for the oil sands tailings application if the system can be adjusted to remove spectra interferences from H_2O and CO_2.

2.1.6.6 Maintenance

FT-IR spectrometers require little maintenance due to design of the instrument. The spectrometer parts are typically contained within a sealed enclosure to prohibit contamination by water vapour, CO_2 and dust. The sample chamber can be purged with N_2 before analysis to remove any water vapour or CO_2.

Specific parts such as the windows, desiccant pack, light source and detector can often be replaced by the manufacturer if malfunctioning occurs. Desiccant packs should be replaced every 4 to 6 months depending on the use of the instrument, or when the indicator turns pink (Perkin Elmer 2009).

2.1.6.7 Technology Application

- Ambient air monitoring of numerous atmospheric gases and vapours around or over industrial facilities, workplace environments, hazardous waste sites (spills, releases), remediation operations, and agro-ecosystems (agricultural fields) (Gosz et al. 1990).
- Characterization of steady-state or batch emissions, high concentration gas streams, compliance studies, inlet and stack measurements, and emissions from industrial and combustion processes (example, chemical manufacturing) (General Electric Company 2006b).

2.1.6.8 Cost

- The cost of the system ranges from approximately $20,000 (Perkin Elmer, personal communication, June 22, 2009) to $100,000 (U.S. Environmental Protection Agency 2009) depending on the accessories and parts required for analysis.

- Routine operating costs of the instrument are quite low, as it mainly requires power consumption, the occasional gas purge of the sample chamber (typically N_2), and cleaning of the sample cell with solvents (for example dichloromethane).
- Sample cells and reusable desiccant packs can both range from $200 to $600 depending on the supplier as well as the material required for analysis (Perkin Elmer, personal communication, June 22, 2009).

2.2 Remote Sensing Monitoring Methods

2.2.1 *Open Path Fourier Transform Infrared (OP-FTIR) Spectroscopy*

2.2.1.1 Methodology

Open path Fourier transform infrared (OP-FTIR) spectroscopy is the most versatile among open path technologies, as it measures the presence of multiple VOCs simultaneously at relatively low detection limits (ppb levels). For this technique, data is analyzed based on Beer's law, where the wave intensity on an absorbing medium diminishes exponentially with the number of absorbers in the beam (U.S. Environmental Protection Agency 2007a).

OP-FTIR measurements can be made using either an active or passive approach. For the active approach, the instrument focuses a light beam before passing it through an interferometer. The interferometer converts the light beam into a modulated signal (interferogram) as a function of the optical path difference. The encoded light beam then passes from the sending optics, through the sample, to the receiving optics before being recorded by a detector. The recorded signal is mathematically manipulated using a Fourier transformation to produce a spectrum that can be used to identify specific airborne contaminants and their concentrations. The passive approach does not utilize a sending optical unit; instead, the instrument uses an external energy source to provide IR light (such as the sun). Receiving optics focus the light into the interferometer that encodes them into an interferogram format before directing it through the sample, and towards the detector. The recorded signal also undergoes mathematical manipulation using a Fourier transformation to produce a spectrum that can be used to identify specific contaminants and their concentrations (Bauer et al. 1996, Chambers 2001, Gosz et al. 1990, Martin 2002, McDermott 2004). For both methods, IR light absorption by the VOCs is converted to concentrations, integrated over the entire optical path length (Todd et al. 2001).

2.2.1.2 Special Features

OP-FTIR instruments have the ability to detect and measure multiple compounds from the same data set, including VOCs, CH_4, H_2S and ammonia from a variety of area sources (Modrak et al. 2009). For this reason, OP-FTIR can be used for monitoring non-homogenous sources and dispersed plumes (Todd et al. 2001). OP-FTIR can be integrated with computer-assisted tomography to create two-dimensional concentration maps of gases over a surface (Todd et al. 2001). The chemical imaging system allows for the user to visualize snapshots of the contaminant flow over both space and time (Todd et al. 2001).

2.2.1.3 Sensitivity / Limits

OP-FTIR provides a minimum detection limit of 1 to 30 ppb for various VOCs within a common industrial monitoring distance of 300 m (U.S. Environmental Protection Agency 2007a). Data can be collected at the following resolutions 0.125, 0.25, 0.5, 1, 2, 4, and 8 cm^{-1} (Modrak et al. 2009). A VOC study conducted by Smith et al. (2010) retrieved a 6% accuracy using the OP-FTIR, where path length concentrations ranged four orders of magnitude. The minimum detection limit for H_2S is 400 ppb at a frequency of 1,200 to 1,300 cm^{-1} (Sigrist 1994). The minimum concentration obtained for methane during an assessment of OP-FTIR for ambient air quality monitoring was 6.63 ppb (Barnack and Jones, 2004). Routine calibration with known gases will increase the reliability of the data.

2.2.1.4 Advantages

- Capable of quantitative simultaneous measurements of multiple chemicals along the line of site (Smith et al. 2010).
- Detection sensitivity decreases with increasing path length (Gosz et al. 1990).
- Rapid analysis at low detection limits (Chambers 2001).
- Continuous operation with real-time data (Smith et al. 2010).
- Design is optimal for field use, as it has only one moving part (Gosz et al. 1990).

2.2.1.5 Limitations

- Instrument is sensitive to relative humidity (Chambers 2001).
- Unable to detect homo-nuclear diatomic species (Cl_2, N_2, etc.) (Gosz et al. 1990).
- Requires cryogenic cooling (for example, with liquid nitrogen) to reduce detector noise allow for better detection limits and a better overall sensitivity (Barnack and Jones 2003).
- OP-FTIR may need to be deployed in multiple locations at a site to obtain an accurate representation of the target gas present. Setting the instrument up again requires additional mirror alignment and maintenance (Modrak et al. 2009).

2.2.1.6 Maintenance

OP-FTIR requires maintenance for accurate data collection. The liquid nitrogen reservoir needs to be refilled daily; newer OP-FTIR models have cryogenic coolers which eliminate the need for liquid nitrogen and still allow for a reduction in detector noise (Barnack and Jones 2004).

Operators should also check the beam alignment on the retroreflector daily to ensure that it reliably holds its position. This requires communication between the signal voltage located on the computer as well as the telescope on the instrument (Barnack and Jones 2003).

Telescope mirrors and retroreflector lenses should be cleaned with compressed air; scratching can occur if cloths are used (Barnack and Jones 2003). Routine calibration can also be conducted by placing a known gas of a specific concentration into the chamber of the telescope (Barnack and Jones 2003).

2.2.1.7 Technology Application

- Ambient air monitoring of numerous atmospheric gases and vapours around or over industrial facilities, workplace environments, hazardous waste sites (spills, releases), remediation operations, and agro-ecosystems (agricultural fields) (Gosz et al. 1990).
- Characterization of steady-state or batch emissions, high concentration gas streams, compliance studies, inlet and stack measurements, and emissions from industrial and combustion processes (example, chemical manufacturing) (General Electric Company 2006b).
- Assessment of motor vehicle emissions (Bradley et al. 2000).
- High altitude atmospheric pollution detection, toxic cloud auto-detection, hot gases detection (aircraft exhaust, smoke plumes, and volcano emissions), and cloud temperature detection (Zhang et al. 2005).
- Air quality studies of refineries, power stations, petrochemical plants, biomass burning, agricultural emissions, roadway emissions, and metropolitan locations (Lin et al. 2008).

2.2.1.8 Cost

- The cost of the system is approximately $125,000 USD including the scanner and retro-reflecting mirrors (Modrak et al. 2009, U.S. Environmental Protection Agency 2007b).
- Daily operating costs include: power consumption, optical fibre cables (connecting OP-FTIR to a computer), liquid nitrogen, and compressed air.

2.2.2 *Differential Optical Absorption Spectroscopy (DOAS)*

2.2.2.1 Methodology

Differential optical absorption spectroscopy (DOAS) has been demonstrated to have high practical performance, as it is well suited for the detection of multiple atmospheric trace gases (including CH_4) (Pundt et al. 2005). Based on the UV to visible molecular absorption of atmospheric gases, DOAS has the ability to measure (and average) the optical absorption of gases over path lengths from several hundreds of metres to several kilometres (Edner et al. 1993, Hönninger et al. 2004). In doing so, less local disturbances, which are typical within point measurements, are observed within the collected data. As light passes through an air mass, attenuation (of different forms) occurs leaving a specific molecular absorption imprint. The imprint can be mathematically extracted and fitted to a reference to calculate the concentration of a light-absorbing species, indicating the VOC species present (Jimenez et al. 2000).

The principle is as follows: from a continuous light source (e.g., a xenon lamp) a light beam is directed from the telescope towards retroreflectors (Pundt et al. 2005). The retroreflectors reflect the light precisely back in the direction of its origin (Pundt et al. 2005). After travelling twice through the atmosphere, the same telescope collects the light and conducts it into the entrance slit of a spectrograph (usually via optical fibres which transmit the light to the spectrometer). The incoming light carries the absorption structures of the trace gases that are present along the light path; these structures can be detected with high sensitivity (Pundt et al. 2005).

A typical DOAS system consists of the following components: light emitter, telescope to collect attenuated light beams, spectrograph, either a single channel or a multi-channel light detection system, and a computer for hardware control, data acquisition and processing (Edner et al. 1993, Hönninger et al. 2004, Jimenez et al. 2000). The multi-axis DOAS (MAX-DOAS) is comprised of novel technology which allows it to utilize scattered sunlight received from multiple viewing directions to measure the spatial distribution of trace gases (Hönninger et al. 2004). This geometric approach analyzes the distribution of the paths taken by registered protons within the atmosphere providing information on the mixing layer (Hönninger et al. 2004).

2.2.2.2 Sensitivity / Limits

Detection limits for VOCs (including BTEX) range from 0.3 to 6 ppb (North American Research Strategy for Tropospheric Ozone 1999b). The minimum detection limit for CH_4 is 0.12 ppm (Qu et al. 2006)

2.2.2.3 Advantages

- Trace gas concentrations are averaged over a several kilometre long light path (more representative data) (Edner et al. 1993, Hönninger et al. 2004).
- A large area can be monitored from one station providing rapid measurements with high temporal resolution (Edner et al. 1993).
- Allows for the simultaneous measurement of multiple wavelengths (Jimenez et al. 2000).
- Allows for non-contact, real-time measurements of multiple trace gas species (Chambers 2001, Jimenez et al. 2000).
- Has a lower minimum detection level for BTEX than OP-FTIR (Modrak et al. 2009).

2.2.2.4 Limitations

- Frequent calibration is necessary due to the sensitivity between pixels over time (Edner et al. 1993).
- Fog and haze have the ability to scatter sunlight into the receiving telescope (Edner et al. 1993).

2.2.2.5 Maintenance

DOAS instruments are low maintenance, as the sensors are sealed and not subject to poisoning or contamination. However, the instruments require routine calibration checks to ensure reliability of the data. The alignment of the projector and receiver may also be necessary at the time of calibration.

The instrument also needs to be mounted on a stable platform which may need to be adjusted with time.

2.2.2.6 Technology Application

- Ambient air monitoring of air pollutants in densely urbanized/industrialized sites; commercial monitoring of urban pollutants (ozone, NO_2, aromatic hydrocarbons, SO_2) for the monitoring of air quality and air pollution-related research (Platt and Stutz 2008).
- Long-term observation and monitoring of air quality, including the continuous evaluation of photochemical pollution episodes (smog and pollution plumes) (Jimenez et al. 2000, Platt and Stutz 2008). This may be ideal for tailings pond applications as long term measurements are preferred to understand spatial, temporal, and seasonal variations.
- Measurement of industrial emissions using a zenith scattered light path arrangement (Platt and Stutz 2008).
- Climate research (radiative transport in clouds) (Platt and Stutz 2008).

2.2.2.7 Cost

- The cost of the instrument is $100K to $150K.
- Operating costs include the following: power consumption, purge air gases, and shelter costs if required.

2.2.3 *Tunable Diode Laser Absorption Spectroscopy (TDLAS)*

2.2.3.1 Methodology

Tunable diode laser absorption spectroscopy (TDLAS) is operated within th**e** infrared region, generally between 2 to 15 µm under low pressures. Some special characteristics such as: non-intrusive, high sensitivity, high selectivity, and fast response time make TDLAS handier than conventional analytical point sensors for VOC and H_2S detection. Molecules of interest must have an IR line-spectrum resolvable at the Doppler limit (must be comprised of up to five atoms together) to be accurately measured (Werle 1998). TDLAS systems are designed to focus on single absorption wavelengths, specific to compounds of concern. To achieve this, the instrument uses a diode to generate light within a narrow frequency range corresponding to a unique absorption wavelength. The laser frequency is tuned either by heat or by altering the incoming current until it matches the spectral absorption line of interest. The degree of absorption is then used to calculate the concentration. To calculate several compounds at once, multiple diodes are necessary (Sigrist 1994, Werle 1998). Rather than measuring the absorption of a spectrum of light, TDLAS measures the absorption of the specific wavelength produced. During the measurement, the TDLAS compares the relative absorption of the reflected beam in the atmosphere to that in a reference cell, thereby calculating the average concentration of the target gas (Chambers 2001, Chen et al. 2006).

2.2.3.2 Special Features

Ametek (2009a) developed a TDLAS instrument with a built-in sealed moisture reference cell containing a moisture vapour within a buffer gas that does not absorb into the desired spectral range. These aids in analyzer verification and performance by constantly comparing the analyzer response to the value of the moisture concentration within the reference cell; also contributing to the reliability of the instrument (Ametek 2009a). Some commercially available instruments contain multiple channels which use multiple telescopes (up to 8 beams) to collect path-integrated concentration data along the multiple beam paths (Modrak et al. 2009).

2.2.3.3 Sensitivity / Limits

TDLAS systems have an adequate resolution and a low signal-to-noise ratio which allows the spectrometer to measure target gases at low levels (Spectra Sensors 2011). The minimum detection limit ranges from 0.05 to 10 ppbv (U.S. Environmental Protection Agency 2006a). The Ametek (2009b) portable gas analyzer has a natural gas measuring range of 5 to 2,500 ppmv with an accuracy and speed of response of ± 2% and 90% in less than 15 s, respectively within ambient air. The TDLAS device produced by Physical Sciences Inc. has demonstrated a detection limit of 20 ppm for H_2S in the atmosphere (Chen et al. 2006). Other instruments have the capability of measuring concentrations within the ppb range over an open path up to 1,000 m for gases such as H_2S, CO, CO_2, and CH_4 (Modrak et al. 2009).

2.2.3.4 Advantages

- Lightweight, portable and easy to use with low detection limits (Ametek 2009b, U.S. Environmental Protection Agency 2006a).
- Capable of performing direct calibration by sequentially attaching the calibrant and zero air sources to the instrument inlet (Werle 1998).
- Generates real-time, path-averaged concentration data in-situ where no post-field data analysis is required (Modrak et al. 2009).

2.2.3.5 Limitations

- Measures one compound of interest at a time; multiple compounds cannot be detected within the same dataset or with the same hardware (Modrak et al. 2009).
- Each telescope must be connected to a control box with fibre optic cables which can be difficult to deploy, depending on the topography of the source area (Modrak et al. 2009).
- Requires the use of remote reflector mirrors positioned at the end of the column of gases to be analyzed and monitored (Chambers 2001).

2.2.3.6 Maintenance

Non-contact measurements and built-in moisture reference cells lead to low maintenance of the instrument (Ametek 2009b). Periodic calibration with a known external gas can also be introduced to ensure the performance of the instrument; adjustments can be made to the calibration parameters at any time (Ametek 2009c). The instrument does not require the use of filters or dryers, which also decreases the maintenance needs.

2.2.3.7 Technology Application

- Ambient air monitoring and concentration profile development (greenhouse gases and ozone depletion) (Martin 2002).
- Detection of species in hostile environments of high temperatures and pressures (Martin 2002).
- Remote vehicle exhaust emission sensing (hydrocarbons, oxygenated hydrocarbons, CO, CO_2, NO_x, water) (Martin 2002).
- Leak detection of hydrocarbons (oil pipelines, underground storage systems).

2.2.3.8 Cost

- The cost of the instrument is approximately $75,000 including the costs for the scanner and retro-reflecting mirrors (U.S. Environmental Protection Agency 2007b). The cost for a TDLAS unit with retroreflector can be US$20,000 to US$40,000.
- Operating costs will include power consumption, transportation, and calibration gases.

2.2.4 *Differential Absorption Light Detection and Ranging (DIAL)*

2.2.4.1 Methodology

Differential absorption light detection and ranging (DIAL) is a laser-based optical method used to detect and measure concentrations of target species remotely within the atmosphere. The instrument uses pulsed lasers operated at two wavelengths: one strongly absorbed by the gas species of interest and the other weakly absorbed (Chambers et al. 2006). The use of mirrors and lenses directs the powerful lasers towards a specific air mass of interest, and detects/measures the concentrations in the air mass area by collecting any back-scattered light (Chambers et al. 2006). Attached telescope equipment at the receiver end of the instrument analyzes the strength and ratio of the back-scattered signals and translates the data into an estimate of the concentration of species (Chambers et al. 2006, Sigrist 1994). The pulsing of the laser light source enables a distance determination from the speed of light and the time taken to receive the reflection. Using a time series of laser pulses and reflections, the change in gas concentration along the line of sight can be calculated. When combined with meteorological measurements of wind, pressure and temperature, these concentration maps can also be used to calculate mass emissions of gas species from a point source; such as a flare (Chambers 2001, Hatchell et al. 2006, Shewchuk and Spellicy 2002, Strasburg and Harper 2005). Fugitive gas measurements using DIAL technology depend on the wind direction to achieve accurate results. In the case of measuring a particular gas of interest, DIAL is used to scan through a plume and produce a 2-D concentration profile (Chambers 2004). When measuring a class of compounds, sorption tubes are mounted on a tower within a plume in order to gather concentration data which can be specifically analyzed for detailed hydrocarbon composition.

DIAL systems also have the capacity to be operated within the IR and ultraviolet regions. However, for lower troposphere gas measurements, the IR spectral region is the most suitable DIAL technique for quantifying target species (Ambrico et al. 2000, Sigrist 1994).

2.2.4.2 Special Features

DIAL has the ability to gather trace gas data sets of diurnal cycles for a number of heights up to the cloud level due to its high temporal resolution and narrow field of view (Ertel 2004). The laser system can come in a variety of complex forms, emitting multiple wavelengths or specific wavelengths within the emission spectrum. These systems can be integrated on to mobile platforms such as aircraft and ships depending on the location of the emission source (Ertel 2004).

2.2.4.3 Sensitivity / Limits

The sensitivity for methane and VOCs is approximately 50 ppb and 10 to 200 ppb, respectively at 200 m. DIAL has also been used to measure SO_2; converted from H_2S. The minimum detection limit for SO_2 is 20 ppb at a 299 nm wavelength (Sigrist 1994). The maximum measurement distance varies from approximately 500 to 1,000 m (Modrak et al. 2009, NPL 2009, Spectrasyne 2009). Ikuta et al. (1999) designed a compact DIAL system for gas leak detection of CH_4 with a resolution of 15 m within a radius of 500 m. Other DIAL instruments have the ability to measure other sources, such as ozone concentrations down to 1 ppb using powerful lasers (Kipp and Zonen 2011). DIAL is capable of completing measurements in approximately 1 s (Ertel 2004).

2.2.4.4 Advantages

- Can measure emissions remotely, up to 2 km distant with low (ppb) detection limits (Chambers 2004).
- The instrument can be tuned to measure specific classes of species (Chambers 2004).
- Can incorporate wind speed measurements to obtain mass fluxes (Chambers and Strosher 2006).
- Instead of obtaining an integrated average concentration, DIAL has the ability to determine the profile of a gas concentration profile along the length of a light beam (Chambers 2003).

2.2.4.5 Limitations

- Only one compound (or a class of compounds) can be measured at a time as the laser has to be tuned to the particular compound of interest (Modrak et al. 2009, North American Research Strategy for Tropospheric Ozone 1999a).
- Expensive and complex to operate (Chambers 2001).

2.2.4.6 Maintenance

Telescopes should be contained within optical grade quartz windows to shield the interior of the instrument from dust, rain, moisture, etc. as well as to maintain the laser and sensors at a consistent temperature (Ertel 2004). The level of maintenance required to operate DIAL is high, and consistent monitoring of the instrument is necessary.

2.2.4.7 Technology Application

- Fugitive hydrocarbon emission detection and characterization of coker areas, refineries and cooling towers (Chambers and Strosher 2006).
- Hydrocarbon emission surveying of sour gas processing plants, and leak detection at upstream oil and gas facilities (Chambers 2004).
- Tracking of SO_2 plumes from incinerator stacks and combustion efficiency of well test gas flares (Chambers 2004).
- Leak detection and preparation of concentration profiles from refineries and industrial tanks (Chambers and Strosher 2006).

2.2.4.8 Cost

- There are no domestic suppliers of DIAL technology, and equipment must be mobilized from Europe costing approximately US$500,000 for a typical 28 to 35 day field study (Modrak et al. 2009).
- Truck-mounted systems with tracking optics can cost between $1,000,000 to $1,500,000 (Chambers 2001).
- The system consumes a high level of energy adding to the overall operation costs (Ertel 2004). Operation costs also include: transportation costs, calibration gases, and high instrument monitoring costs (Chambers 2001).

2.2.5 *Solar Occultation Flux (SOF)*

2.2.5.1 Methodology

Solar occultation flux (SOF) is a newly developed technique used for the quantification of fugitive VOC emissions within the atmosphere. This technology uses IR solar spectra instead of laser pulses, and is comprised of the following components: a solar tracker, FT-IR spectrometer, and a global positioning system (Mellqvist et al. 2007). The solar tracker is a mirror device that is used to track the sun and reflect the incoming radiation into an FT-IR spectrometer which measures the IR spectra (Mellqvist et al. 2007, 2010). An absorbance spectrum is produced from the IR solar spectra, which can be translated to the average concentration of recoverable VOCs (in mg/m^2). The instrument is typically mounted on a vehicle, allowing for the measured solar light to traverse the cross-section of the emission plume of interest (Fransson and Mellqvist 2002, Mellqvist et al. 2007). In doing so, the number of molecules within the plume cross-section can be determined, and the mass flux can be calculated by multiplying the measured number of molecules by the wind speed at the site (Mellqvist et al. 2010). The path-averaged concentration of a number of species absorbing IR solar radiation along the light of the sun can also be determined using multivariate analysis with a fitted calibration spectrum. Calibration spectra can be obtained from published reference libraries such as the HITRAN (www.hitran.com), NIST and PNL databases (Mellqvist et al. 2005, 2007).

2.2.5.2 Special Features

SOF has the ability of measuring not only VOC concentrations, but also a wide range of other species including: NO_2, HCl, HF, ammonia, aldehydes, vinyl-chloride, terpenes, ethylene-oxide, SO_2, propane, and propylene (Mellqvist et al. 2006). Using the calibration spectra provided by the HITRAN database and multivariate analysis, these compounds can be measured in real-time (Mellqvist et al. 2006).

2.2.5.3 Sensitivity / Limits

Minimum detection limits of 0.3 to 0.5 mg/m^2 can be achieved when measuring a point source at 0.5 kg/h at a distance of 50 m (with 3% precision) (Sigrist 1994). Accuracy of 10% has been recorded by researchers using SOF technology using an FTIR spectrometer with a spectral resolution of 0.5 cm^{-1} (Mellqvist et al. 2009).

2.2.5.4 Advantages

- Cost effective, mobile, easier to operate, and faster than the DIAL technique (Fransson and Mellqvist 2002, Mellqvist et al. 2006).
- Can be used in the measurement of diffusive emissions (Fransson and Mellqvist 2002).
- Moving mirrors compensate for the relative movement of the sun, allowing for the measurement vehicle to follow a non-straight path as it transverses a plume (Beecken and Borgentun 2007).
- Total flux can be obtained by simply multiplying the plume by the wind speed (Beecken and Borgentun 2007, Mellqvist et al. 2007).

2.2.5.5 Limitations

- Measurements can only be taken in sunny conditions (Mellqvist et al. 2009).
- Aromatics have a weaker absorption of infrared light and cannot be measured.
- Unable to measure plume height, adding uncertainty to derived fluxes (Mellqvist et al. 2006).
- Systematic errors such as local changes in the wind field due to buildings and industrial structures, and turbulence effects leeward of oil tanks are difficult to estimate (Fransson and Mellqvist 2002, Mellqvist et al. 2010).

2.2.5.6 Maintenance

The instrument must be shielded from overheating by sun rays as well as from moisture. Surface cleaning of the optical windows should be completed regularly to remove any dust particles. The maintenance practices for FTIR spectrometers also apply (see Section 2.1.6).

2.2.5.7 Technology Application

- Emission inventories from fixed location pollution sources (flares, cooling towers, tank areas, process areas, and water treatment areas) (Fransson and Mellqvist 2002, Mellqvist et al. 2010), and rapid emission screening over industrial facilities under sunny conditions (conducted over 40 plant surveys within the USA and Europe) (Mellqvist et al. 2009).
- Ambient air quality measurements (Mellqvist et al. 2010).
- Characterization and quantification of volcanic emissions (Beecken and Borgentun 2007).

3 REVIEW OF TECHNOLOGIES FOR CHARACTERIZATION OF REDUCED SULPHUR COMPOUNDS

The emission of reduced sulphur compounds (ranging from simple gases to complex polycyclic aromatics) can lead to a complex series of both chemical and physical transformations, resulting in the production of acidic precipitation and increases in aerosol particle populations (Bates et al. 1992). Reduced sulphur compounds are not only a source of malodorous conditions, but also contribute to the atmospheric sulphur flux; influencing the global sulphur cycle and contributing to global air pollution. Low levels of reduced sulphur ambient odours may be associated with health symptoms occurring at the time of exposure, with odour thresholds typically in the ppb range, where mucous membrane irritation typically occurs at 10 to 20 ppm for hydrogen sulphide, mercaptans, and thiophenes (Schiffman et al. 2000).

Hydrogen sulphide (H_2S) is of most concern due to its corrosivity to industrial infrastructure, as well as its toxic effect to human health during exposure; leading to unconsciousness or death. H_2S is a common toxic co-pollutant within reduced sulphur compound odours, where non-irritant concentrations are often associated with health symptoms (Schiffman and Williams 2005). Consequently, low level exposure to H_2S concentrations within reduced sulphur compound emissions may cause detrimental health effects. Ambient H_2S emissions have increased from 15% to 68% north of Fort McMurray, Alberta between 1999 and 2006 (Timoney and Lee 2009). Airborne whole sampling has also estimated the release of 204 tonnes of SO_2 per day over the Athabasca oil sands region (Simpson et al. 2010).

It is important to characterize fugitive emissions of reduced sulphur compounds from the oil sands tailings ponds to understand how they may influence both human health and the environment. The H_2S concentrations from the ponds can be translated into emission rate estimations, which can further be used in atmospheric dispersion models (Gostelow and Parsons 2000). This information would allow for a larger scale idea of how the tailings ponds may be impacting the surrounding environment.

The technologies for reduced sulphur compound characterization were classified into conventional analytical technologies and remote sensing field monitoring technologies. Due to the reactivity of H_2S, it is difficult to obtain low level concentrations of the compound. Low level detection of H_2S is essential for the characterization of reduced sulphur compounds, as it is not expected to be biologically produced in ponds emitting high concentrations of methane. H_2S is known to react with stainless steel, therefore canisters, sample bags, and instrument pathways may require a sulphur-inert coating to ensure measurement accuracy within both the laboratory and the field.

The following technologies have been reviewed and assessed for reduced sulphur compound analysis conducted in both the laboratory as well as in the field. Conventional analytical technologies are based on laboratory techniques; however, field applications are specified where applicable. The remote sensing monitoring technologies are based on in-situ field applications.

- Conventional Analytical Technologies
    - Flame Photometric Detection (FPD)
    - Pulsed Flame Photometric Detection (PFPD)
    - Sulphur Chemiluminescence Detection (SCD)
    - Photo Ionization Detectors (PID)
    - Ultraviolet (UV) Spectrometric Detection
- Remote Sensing Monitoring Technologies
    - Tunable Diode Laser Absorption Spectroscopy (TDLAS)
    - Image Multi-Spectral Sensing (IMSS)
    - Differential Absorption LIDAR (DIAL)
    - Open Path Fourier Transform Infrared (OP- FTIR) Spectroscopy

3.1 Conventional Analytical Methods

3.1.1 *Flame Photometric Detection (FPD)*

3.1.1.1 Methodology

The flame photometric detector (FPD), otherwise known as a flame emission photometer, is used to detect and measure atmospheric sulphur containing gases (Poole 2002). The FPD is typically paired with a gas chromatograph (GC) to identify and quantify the sulphur species present within the air sample (Patterson 1978). The FPD can also be integrated with an FID detector for sulphur, hydrocarbon, and phosphorus detection and characterization.

For the FPD method, sulphur-containing gaseous compounds are burnt in a hydrogen enriched flame within the gas chromatographic column allowing for the sulphur atoms to convert to a higher energy state (Poole 2002). When the atoms return to their ground state, they emit a characteristic radiation signature between 300 and 425 nm. The emitted light passes through a narrow optical filter, before it is detected by a photomultiplier which produces an associated current. The produced current is amplified by an electrometer, and the magnitude of the response is recorded (Poole 2002). Levels of H_2S within the atmosphere are usually lower than detection limits and require a pre-concentration by an $AgNO_3$ impregnated filter tube (Braman et al. 1978, Brunner et al. 1995, Kalontarov et al. 1995).

Originally, the FPD was available as a single flame detector; however, recent advances have led to the development of the dual flame and pulsed flame versions (Poole 2002).

FPDs are commonly connected to a GC unit and utilized in laboratory applications. However, portable instruments are available for field use, directly drawing samples in-situ without the requiring sample preparation (Sun and Ong 2004). Samples can be collected within sorbent tubes (filled with carbonaceous material) and thermally desorbed (with a thermal desorber), where characterization and quantification of the components are then measured through GC-FPD technology. Samples from canisters and/or sampling bags can either be attached to the GC system through a gas sampling valve or can be directly injected into the inlet using glass syringes.

3.1.1.2 Sensitivity / Limits

Sulphur sensitivity for FPD is approximately 10 ppb (Khandpur 2006). SRI Instruments (2011) developed an FPD for simultaneous sulphur and phosphorus detection capable of detecting sulphur compounds to 200 ppb.

3.1.1.3 Advantages

- The development of filters has led to the capability to remove interferences from hydrogen sulphide and other organic sulphur compounds (Khandpur 2006).
- The dual-flame burner also eliminates any interfering emissions providing a more reproducible response, increasing instrument sensitivity (Patterson 1978, Poole 2002).

3.1.1.4 Limitations

- Phosphorous compounds produce similar wavelengths creating interference with the desired sulphur compounds. Consequently, different optimum conditions are required for phosphorous and sulphur detection as well as for different compound classes determined with the same detector (Poole 2002).
- Filters must also be exchanged between runs if multiple compounds are to be detected (Khandpur 2006).
- Problems associated with FPD response quenching by the co-elution of large amounts of hydrocarbons (Katz 1977, Poole 2002).

Since the emission of multiple compounds of hydrocarbons is expected from the oil sands tailings ponds, interferences may limit the effectiveness of this technology. Consequently, it may not be suitable for the measurement of reduced sulphur compounds for this application.

3.1.1.5 Maintenance

The FPD's photomultiplier tube is a consumable part periodically requiring replacement (SRI Instruments 2010). The associated hydrogen, air and gas flows should be occasionally and independently measured with a flow meter to ensure correct flow to the FPD (Rood 2007). The FPD uses two optical wavelength filters which should be replaced once they age; however, the user should wear gloves and use a soft tissue when replacing the filters to avoid fingerprints and scratching (Agilent Technologies 2000). The following parts should also be periodically checked for leaking as this will affect the performance of the FPD: septum, swage-type fittings, detector block o-ring or vespel seals and fittings (Agilent Technologies 2000). Contamination of any of the seals (fingerprints, dust, atmospheric contaminants) can reduce the detector sensitivity and should be carefully replaced as necessary (Agilent Technologies 2000).

3.1.1.6 Technology Application

- Atmospheric pollution monitoring (source detection, chemical fate, and characterization in urban and rural areas) (Black et al. 1978, Inomata et al. 1999).
- Anthropogenic air (kraft paper mills, fossil burning generators, combustion, and petrochemical industries) and natural air (volcanic activity, sea spray, organic matter decomposition, and bacterial sulphate reduction) emission monitoring (Black et al. 1978).
- Detection of sulphur compounds in crude oil, sulphur contaminants in natural gas, volatile sulphur compounds in food analysis, and sulphur in chemical warfare agents (Agilent Technologies 1997).

3.1.1.7 Costs

- The cost of the system ranges from approximately $4,000 to $9,300, depending on the number of detectors required for analysis (Quadrex Corp. 2011).
- Operating costs include: power consumption, wavelength filters, septum, seals, fittings, hydrogen gas, and carrier gases (when paired with GC) required for analysis (Agilent Technologies 2000).
- If paired with a GC, GC operating costs apply (see Section 2.1.4).

3.1.2 *Pulsed Flame Photometric Detection (PFPD)*

3.1.2.1 Methodology

The pulsed flame photometric detector (PFPD) is a member of the flame photometric detector (FPD) family. The PFPD can be integrated with a GC unit for better identification and quantification of sulphur species within the measured air sample (Khandpur 2006). The operation of the PFPD is based on a pulsed-flame instead of a continuous flame for the generation of chemiluminescense (Cheskis et al. 1993). The ignited flame is transmitted through the detector, where it self-terminates when the combustible gaseous mixtures (typically hydrogen and air heated on a Ni/Cr wire igniter) are burnt and consumed (Cheskis et al. 1993, Khandpur 2006). The whole system propagates in periodic cycles, repeating every one or a few hundred milliseconds. The PFPD is characterized by several important properties such as: low flow rate of gases (necessary for flame propagation), and pulsed periodic ignition (for pulsed flame production). As a result, the PFPD is differentiated by the pulsed nature of the emitted light. The instrument can be coupled with a pulsed flame ionization detector (PFID) to form a combined pulsed flame photometric ionization detector (PFPID) (Amirav and Jing 1995, Cheskis et al. 1993, Kim 2005).

PFPDs are commonly connected to a GC unit and utilized in laboratory applications. Samples can be collected within sorbent tubes (filled with carbonaceous material) and thermally desorbed (with a thermal desorber), where characterization and quantification of the components are then measured through GC-PFPD technology. Samples from canisters and/or sampling bags can either be attached to the GC system through a gas sampling valve or can be directly injected into the inlet using glass syringes.

3.1.2.2 Special Features

When combined with a GC, the GC-PFPD has a better resolution and separation of sulphur compounds, eliminating any quenching that may have been observed with the PFPD alone (Agilent Technologies 2010b). The equimolar response of the instrument simplifies calibration and increases its sensitivity to detect carbonyl sulphide, hydrocarbons, and other sulphur compounds at ppb levels (Chambers 2009). The PFPD has a 10-fold increase in sensitivity, sulphur-hydrocarbon selectivity and long term flame stability than FPD technology making it a reliable technique for ASTM methods (Chambers 2009).

3.1.2.3 Sensitivity / Limits

The minimum detection limit for H_2S gas varies from 2.4 to 9.8 ppbv (Catalan et al. 2006).

3.1.2.4 Advantages

- Long-term flame stability and a 10-fold increase in sensitivity from FPD models (Chambers 2009).
- Due to the increased brightness of the PFPD analyzer, the optical signal is increased (Amirav and Jing 1995).
- The consumption of hydrogen and air is reduced (Agilent Technologies 2010b).
- The PFPD has an enhanced sensitivity due to a coloured glass-broadband optical filter, resulting in increased selectivity through the collection of a broader spectral band width (Amirav and Jing 1995, Chambers 2009).

3.1.2.5 Limitations

- Temperature variation has an effect on the detection limits. At low temperatures, the sensitivity of the analyzer is reduced becoming species dependent (Amirav and Jing 1995).

- Large sample volumes are required to reach the low ppb detection limits which can lead to sample overloading and signal quenching effects (Agilent Technologies 2010b).

If seasonal measurement is desired, this method may not be ideal for reduced sulphur compound characterization due to the effect on detection limits. Large sample volumes may also be difficult to obtain and transport, effecting the accuracy of the data. Therefore, this method may not be ideal for oil sands tailings emission measurements.

3.1.2.6 Maintenance

The PFPD uses a photomultiplier tube which must be periodically replaced, as it is consumable. Seals and fitting should be routinely checked for leaks as well as deterioration. The gas flow should also be checked to ensure correct flow rate to the instrument. The PFPD requires less maintenance than most detectors as it avoids the build-up of soot deposits which can interfere with the transmission of sulphur signals (O.I. Analytical 2011b).

3.1.2.7 Technology Application

- Emission monitoring of strongly polluted areas (landfill vent systems and industrial facilities) (Kim 2006).
- Ambient air monitoring in urban and rural areas (Kim 2006).
- Detection of sulphur compounds in crude oil, sulphur contaminants in natural gas, volatile sulphur compounds in food analysis, and sulphur in chemical warfare agents (Agilent Technologies 1997).

3.1.2.8 Costs

- Operation costs include cost of hydrogen gas, power consumption, replacement of the photomultiplier tube, seals and fitting.

3.1.3 *Sulphur Chemiluminescence Detection (SCD)*

3.1.3.1 Methodology

Chemiluminescence is a chemical reaction where an energetically excited species produced within a chemical reaction emits photons of light as it decays to a lower state of energy. Sulphur chemiluminescense detector with gas chromatography (GC-SCD) is a quantitative analytical method which is used to detect low levels of sulphur compounds within atmospheric samples (Sye and Chen 2000). For GC-SCD, the analytes eluting from a column are directed into a reaction chamber, where chemiluminescence takes place (Sye and Chen 2000). This chamber is maintained at low pressure, allowing for minimum energy loss from gas-phase collisions and maximum excitation of analyte molecules. The resulting emission of protons is detected by a photomultiplier tube, allowing for selective sulphur detection. The GC component provides fast quantification and identification of the sulphur compounds (Choi et al. 2004). For standardization, a commercially available standard gas mixture (H_2 or He) is used as a carrier gas within the GC unit (Choi et al. 2004, Rauhut et al. 1998, Sye and Chen 2000).

This technique is restricted to laboratory applications. Samples can be collected within sorbent tubes (filled with carbonaceous material) and thermally desorbed (with a thermal desorber), where characterization and quantification of the components are then measured through GC-SCD technology. Samples from canisters and/or sampling bags can either be attached to the GC system through a gas sampling valve or can be directly injected into the inlet using glass syringes.

3.1.3.2 Special Features

Sulphur chemiluminescence detectors have an inherently linear and equimolar response which is less susceptible to hydrocarbon interference; this eliminates the need for linearization of the data or the determination of separate response factors for individual sulphur compounds (Agilent Technologies 2007).

3.1.3.3 Sensitivity / Limits

In the real-time mode, the detector has a linear response from sub parts per billion by volume (ppbv) to sub parts per million by volume of sulphur. The GC-SCD has a detection limit of about 0.13 ppbv with a time constant of 2 s (Benner and Stedman 1989), but current models have detected low level sulphur at 5 to 10 ppb (Agilent Technologies, 2001). For a retention time of 0.94 min, the detection limit for H_2S is 1.6 to 8.2 µg/L at 240 ºC within a GC-SCD (Benner and Stedman 1989). Calibration with SO_2 proved an accuracy of ± 10% with a GC SCD model (Benner and Stedman 1989).

3.1.3.4 Advantages

- The SCD has a linear response with a low detection limits (ppbv) (Agilent Technologies, 2001). It also provides nearly equimolar response to a wide variety of sulphur compounds (Agilent Technologies 2007, Choi et al. 2004).
- No interferences from water vapour or CO (Benner and Stedman 1989).
- Hydrocarbon interference is minimized by the adjustment of residence time of the sample in the flame (Agilent Technologies 2007, Benner and Stedman 1989).
- No quenching from other compounds in the sample matrix (Choi et al. 2004, Sye and Chen 2000).

3.1.3.5 Limitations

- Interference problems with other species such as metal ions (Maya et al. 2007, Rauhut et al. 1998).
- Flame temperature can shorten the lifetime of the probe (Tuan et al. 1995).
- Lack of selectivity of compounds that do not include sulphur (Tuan et al. 1995).

For the oil sands tailings pond application, it is not expected that there will be the co-elution of metal ions. If the user's interest is to monitor reduced sulphur components only this method allows for low level detection.

3.1.3.6 Maintenance

Maintenance includes changing of the vacuum pump oil and reaction cell, and the replacement of the oil filter and chemical trap (General Electric Company 2006a).

3.1.3.7 Technology Application

- Identification and quantification of sulphur compounds in petroleum feed, petroleum products (for example, ethylene, propylene, paraffins, and natural gas), and food and beverage products (General Electric Company 2006a , Sye et al. 2000).
- Ambient air monitoring of natural (animals, vegetation, soils, and volcanoes) and industrial sources (refineries, smelters, kraft paper pulpers, food processors, and power generators) (General Electric Company 2006a).
- Monitoring of sulphide in water (for example, lagoon biological wastewater treatment stations and leachates from wastewater plants) (Maya et al. 2007).
- Detection of sulphur compounds in beverages (including wines) (Rauhut et al. 1998).

3.1.3.8 Costs

- $30K (Agilent 355 Sulphur Chemiluminescence Detector; Agilent Technologies, personal communication, June 28, 2011).
- Operating costs include power consumption, and the replacement of pump oil, reaction cell, oil filter, and chemical trap. When paired with a GC, associated operating costs apply.

3.1.4 *Photo Ionization Detectors (PID)*

Refer to Section 2.1.3 for details.

3.1.5 *Ultraviolet (UV) Spectrometric Detection*

3.1.5.1 Methodology

The ultraviolet (UV) spectrometric detection technique involves the spectroscopy of photons in the UV to visible light spectral region (200 to 300 nm for H_2S and 285 nm for SO_2) (Dupuit et al. 2000). Like IR absorption spectroscopy, the instrument passes a known spectrum of UV light through a sample, and measures the intensity of resulting light reaching a detector. The instrument then compares the detected light to the energy emitted by the source to obtain the quantity of UV light absorbed by the sample. The difference in the energy levels is compared to the electromagnetic spectrum, where the concentration of the target gas is determined. Methods of evaluation are based on the Beer Lambert law[1], stating that a compound's concentration is proportional to its measured absorbance (Dupuit et al. 2000).

This technique is commonly used for laboratory applications. Compact, battery operated models may be utilized in the field for in-situ measurements (Ocean Optics 2012).

3.1.5.2 Special Features

UV spectrometers are typically integrated with visible and even near infrared light detectors to increase the application of the technology and the sensitivity of the instrument. Galvanic Applied Sciences (2011) developed a UV spectrometer that separates the electronics from the measurement cell and uses fibreoptics to connect the sample cell to the light source and detectors. As a result, the cell requires no optical alignment, where automatic calibration ensures accuracy within the instrument (Galvanic Applied Sciences 2011).

3.1.5.3 Sensitivity / Limits

The minimum detection limit is 5 mg/m^3 (Dupuit et al. 2000). Shimadzu's UV-3600 instrument has a resolution of 0.1 nm with a UV-visible wavelength accuracy of ± 0.2 nm and a sampling pitch of 0.01 to 5 nm (Shimadzu 2011).

3.1.5.4 Advantages

- Robust and straightforward optical technique (Dupuit et al. 2000).
- Free from the interference of water vapour and CO_2 (Dupuit et al. 2000).

3.1.5.5 Limitations

- Method is inappropriate for multi-gas analysis due to the superposition of some spectra broad bands (Dupuit et al. 2000).
- Limited to single pure species analysis (Dupuit et al. 2000).
- Potential for interference with other gases due to the absorbance additivity law (Dupuit et al. 2000).

Due to the potential limitations of the technique, this method may not be suitable for oil sands tailings pond characterization due to the co-elution of multiple species of VOCs and greenhouse gases that may interfere with the analysis.

3.1.5.6 Maintenance

The Galvanic UV spectrometer requires minimal maintenance since it has no moving parts (Galvanic Applied Sciences 2011). Optical windows can be cleaned by rinsing the sample cells with a solvent,

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[1] See http://en.wikipedia.org/wiki/Beer%E2%80%93Lambert_law

and calibration can be completed through the use of external standards (Galvanic Applied Sciences 2011).

3.1.5.7 Technology Application

- Detection and monitoring of the following fugitive emissions from wide area sources (for example, industrial plants): hydrocarbon paraffins (methane, ethane, propane, and pentane), aromatics (benzene, toluene, and xylene), and toxic hydrogen sulphide)(Danker et al. 1995).
- Emission characterization/quantification and risk assessment (Dupuit et al. 2000).
- Detection of flammable or toxic gases (such as SO_2), medical diagnosis, detection of chemical warfare agents, and monitoring of combustion efficiency in automobile engines (Gondal and Dastageer 2008).

3.1.5.8 Costs

- The cost of the instrument typically ranges from $1,000 (US Bio Solutions 1999) to $20,000 depending on the sample holders used and the detection spectrum required for analysis (Perkin Elmer, personal communication, February 6, 2011).
- The cost of a UV-Vis spectrometer typically ranges from $6,000 to $27,000 (Perkin Elmer, Lamda Series Models) (Perkin Elmer, personal communication, February 7, 2011).
- Operating costs include cost of reference and sample cell holders and of standards and solvents (Perkin Elmer, personal communication, February 7, 2011).

3.2 Remote Sensing Monitoring Methods

3.2.1 *Tunable Diode Laser Absorption Spectroscopy (TDLAS)*

Refer to Section 2.2.3 for details.

3.2.2 *Image Multi-Spectral Sensing (IMSS)*

3.2.2.1 Methodology

Image multi-spectral sensing (IMSS) follows the principals of diffractive optics, and can be categorized as an optical imaging technique. IMSS uses a combination of a diffractive imaging spectrometer and an adaptive tunable filter, which performs real time imaging of fugitive emissions through image processing algorithms with field programmable gate arrays (FPGAs) (Hinnrichs 2002). Typically made up of a small, hand held Sherlock® camera, the device disperses light along the optical axis by the diffractive optical element (GIT 2009, Hinnrichs 2002, Hinnrichs and Piatek 2004). The dispersed light array as well as the focal length of the lens is scanned to produce images made up of different wavelengths or colors (Hinnrichs and Piatek 2004). The entire instrument contains an infrared camera, computer, video data recording capabilities, data logger, imaging spectrometer, and a real time image processing unit in a small and light weight design (Envirotech Engineering 2007, GIT 2009, Hinnrichs 2002).

3.2.2.2 Special Features

IMSS uses a single element to perform both imaging and throughput allowing for little optical alignment which can be controlled remotely (Hinnrichs 2002). The Pacific Advanced Technology IMSS has the capacity of measuring either mid- or long-wave IR which can be used for a variety of applications including: threat warning, surveillance, clutter rejection, target identification, pollution monitoring, and for the collection of signatures of targets and backgrounds (Pacific Advanced Technology 2011).

3.2.2.3 Sensitivity / Limits

Capable of measuring different sulphur compounds at the ppm level (Robinson and Luke-Boone 2009). The Sherlock IMSS has the sensitivity of detecting gas leaks as low as 1 g/h (GIT 2009). Pacific Advanced Technology (2011) has developed an IMSS instrument with a nominal spectral resolution of 0.01 µm between 4 and 9 µm within the mid- and long-wave range. Other IMSS instruments have a spectral resolution on the order of 6 wave numbers with a low noise equivalent spectral response (Envirotech Engineering 2007, GIT 2009, Hinnrichs 2002).

3.2.2.4 Advantages

- IMSS uses a single element to perform both imaging and throughput (Hinnrichs and Piatek 2004).
- Does not require spatial scanning (Hinnrichs 2002)
- Ideal for field applications that require small, lightweight, and robust instruments (Hinnrichs 2002, Hinnrichs and Piatek 2004).
- Can be operated in the necessary number of spectral bands to detect a specific gas saving time and processing power (Hinnrichs 2002).

3.2.2.5 Limitations

- The image must be processed to sharpen the resulting spectrum (Hinnrichs 2002).
- The gas image can be affected by scattering and reflection by solar activity (Hinnrichs 2002).

3.2.2.6 Maintenance

IMSS sensors require minimal maintenance. Lenses can be cleaned of fingerprints, dust, etc. with a soft non-scratch cloth. Operators should check the beam alignment periodically to ensure that it reliably holds its position. With limited or no included moving parts, the instrumentation requires no optical realignment by the user. The spectrometer parts are typically contained within a sealed enclosure to prohibit contamination by water vapour, CO_2 and dust. Specific parts, such as the light source or detector, can often be replaced by the manufacturer if malfunctioning occurs.

3.2.2.7 Technology Application

- Collection of signatures from target emissions and background data, pollution monitoring, and drug interdiction. Uses in threat warning, surveillance, clutter rejection, and target pollutant identification (Pacific Advanced Technology 2011).
- Real-time gas leak detection from oil refineries, gas processing plants, petrochemical plants, and pharmaceutical plants (Hinnrichs 2002).
- Comparison of plume images with plume dispersion model predictions and point sampling data (Chambers 2001).

3.2.2.8 Costs

- The market price for IMSS technology with a Sherlock® camera unit is approximately US$125,000 (GIT 2009).
- Performance testing of an IMSS plume imaging system for one month can cost approximately $75,000 (Chambers 2001).

3.2.3 *Differential Absorption Light Detection and Ranging (DIAL)*

Refer to Section 2.2.4 for details.

3.2.4 *Open Path Fourier Transformed Infrared (OP- FTIR) Spectroscopy*

Refer to Section 2.2.1 for details.

4 REVIEW OF TECHNOLOGIES FOR CHARACTERIZATION OF CH_4

Methane (CH_4) emissions are of interest as it is considered to be one of the major contributors of greenhouse gas emissions, due to natural biological reactions occurring within the tailings ponds. It was estimated that the cumulative release of methane gas from Syncrude's MLSB and West In-Pit tailings ponds was approximately 43 million L/ day (Holowenko et al. 2000; Penner and Foght 2010). The potency of this greenhouse gas on the environment is 25 times that of CO_2 (Yeh et al. 2010). Therefore, it is important to monitor and identify the rate of CH_4 entering the environment to understand how the tailings ponds are influencing Canadian greenhouse gases emissions.

The technologies for CH_4 characterization were classified into conventional analytical technologies and remote sensing monitoring technologies. Each section mentions if CO_2 can be simultaneously be measured by the individual technologies.

The following technologies have been reviewed and assessed:

- Conventional Analytical Technologies
  - Infrared (IR) Absorption

  - Mid-Infrared Polarization Spectroscopy
  - Photoacoustic Absorption Spectroscopy (PAS)
  - Solid State (SS) sensor
  - Wavelength Modulation Spectroscopy (WMS)
- Remote Sensing Monitoring Technologies
  - Radial Plume Mapping (RPM)
  - Differential Optical Absorption Spectroscopy (DOAS)
  - Correlation Spectroscopy (CS)
  - Airborne Natural Gas Emission Lidar (ANGEL)

4.1 Conventional Analytical Methods

4.1.1 *Infrared Absorption (IR)*

Refer to Section 2.1.2 for details

4.1.2 *Mid-Infrared Polarization Spectroscopy (PS)*

4.1.2.1 Methodology

Mid-infrared polarization spectroscopy is one of the most sensitive ‘Doppler-free’ spectroscopic techniques used for the detection of CO_2, CH_4 and C_2H_2 (Li et al. 2004). The high sensitivity and resolution within the mid-IR spectral region can be attributed to the availability of a high-power line width, and a tunable IR quantum cascade laser source (Bartalini et al. 2009). In a typical polarization spectroscopy (PS) set-up, a strong pump beam and a weak probe beam, with a common ground or excited state, are tuned to the optical transition of the target species and crossed at a sample. The optical pumping of a target species through a polarized pump beam produces a birefringence, while inducing detectable polarization changes in the weak probe beam (Li et al. 2007). The PS technique has the unique ability to distinguish spectral transitions belonging to P, R or Q branches by an evaluation of the J-dependence of an absorption cross-section (Li et al. 2004). Being a coherent technique with the signal created in a laser-like beam, PS is efficient in the collection of signals and the discrimination against background noise from scattered light and flame emission (Li et al. 2005, Richard and Ewart 2009).

This technique is commonly used in the field for direct in-situ sampling.

4.1.2.2 Special Features

PS has the capacity to detect CH_4 in both cold flows and flames at atmospheric pressure, showing a good two-dimensional visualization of the signal (Li et al. 2005). The technology can also be further applied to other sources such as hydrocarbon fuels and combustion intermediated species (such as CH_3 and CH_2) which are difficult to detect with conventional electronic excitation techniques (Li et al.

2005). PS uses beam-like coherent signals of infrared light, which can be detected remotely, where the scattering of light can be properly filtered spatially (Sun et al. 2010).

4.1.2.3 Sensitivity / Limits

The minimum detection limit is approximately ≤10,000 ppm for methane (CH_4). PS is among the highest sensitivity Doppler-free spectroscopic techniques available with a better signal-to-noise ratio than standard saturation spectroscopic methods (Bartalini et al. 2009).

4.1.2.4 Advantages

- Provides signals in the form of a coherent, laser-like beam facilitating discrimination against background noise from luminous environments (such as flames or hot plasmas) (Richard and Ewart 2009).
- Capable of focusing the signal on a small area (Richard and Ewart 2009).
- Provides a stringent test of the laser system in terms of the amplitude and frequency stability of the output (Richard and Ewart 2009).
- Simple setup makes it more feasible for application in combustion diagnostics (Richard and Ewart 2009).

4.1.2.5 Limitations

- Limited to the ultraviolet / visible spectral region by exciting electronic transitions (Li et al. 2004).
- Less sensitive than visible radiation detectors (Richard and Ewart 2009).

This technique may be limited to specific times of the day when sunlight is optimal, which may not be practical for the winter months in the Athabasca oil sands region. The technique is also less sensitive than other visible radiation detectors which may not be efficient for tailings pond emission measurements.

4.1.2.6 Maintenance

Gas flows should be continuously measured and maintained with flow meters (Li et al. 2005). To maintain an acceptable signal-to-noise ratio of >100:1, users should use high concentrations of methane and high partial pressures (ranging from 1 to 5 Torr) in mixtures with N_2 (Richard and Ewart 2009). The alignment of the polarizers is critical in maintaining the signal-to-noise ratio; ensure a maximum extinction of 2.6×10^{-7} (Richard and Ewart 2009). Any drift in the polarizer alignment due to beam steering optics or changes in the optomechanical mounts can lead to leakage of the probe light which will complicate the spectral fitting (Richard and Ewart 2009). Consequently, the beam alignment should be regularly monitored in order to ensure high sensitivity within the measurements.

4.1.2.7 Technology Application

- Ambient air monitoring and emission control (Li et al. 2005).

- Determination of intermediate species in hydrogen combustion processes (Li et al. 2007).
- Detection and quantification of methane and other toxic molecular species in harsh environments, which are otherwise hardly detectable at trace levels (Sun et al. 2009).

4.1.2.8 Cost

- Operational costs include the cost of continuous liquid nitrogen required for housing the laser (Bartalini et al. 2009), as well as carrier gases.

4.1.3 *Photoacoustic Absorption Spectroscopy (PAS)*

4.1.3.1 Methodology

Photoacoustic absorption spectroscopy (PAS) with infrared technology is the latest innovation for ambient gas monitoring (Mine Safety Appliances Company 2001). For this technique, the instrument exposes a gas sample to a radiation source and then monitors what happens to the gas after the absorption of IR light by taking direct measurements. Instrument set-up is typically comprised of the following components: a radiation source, modulator, photoacoustic cell, and signal processing device (or pressure sensor) (Uotila et al. 2005). The use of an IR laser instead of a black body radiation source can increase the sensitivities and selectivity of the system. When a sample of gas is introduced into the measurement chamber, it is exposed to a radiation source of a specified IR wavelength. If the sample contains the target gas species of interest (CH_4), the IR light will be absorbed, where the concentration of the target gas is proportional to the quantity of IR light absorbed (Mine Safety Appliances Company 2001). After the target gas has absorbed the IR light, the molecules begin to move around within the measurement chamber more rapidly, generating an increased temperature and pressure; the pressure produces audible pulses detectable by a sensitive microphone located within the photoacoustic IR monitor (Mine Safety Appliances Company 2001). The magnitude of the pressure pulses indicates the level of target gas species present, or lack thereof.

PAS is commonly used in the field for direct in-situ sampling since it does not require sample preparation (McClelland 2007).

4.1.3.2 Special Features

PAS technology can be integrated with solid-state lasers which add sufficient power, high efficiency, and broad and continuous tuning to the methodology (Liang et al. 2000). PAS can also be integrated with FTIR technology to produce a higher sensitivity of the photoacoustic detectors (McClelland et al. 2002). For this method, the PAS signal is generated when an FTIR beam (oscillating in intensity) is absorbed by a sample; the temperature oscillations decay as they move through each light-absorbing layer providing spectral information (McClelland et al. 2002). The PAS FTIR can be applied to other sources including solid and liquid samples. Overall, PAS can be used for the detection of multiple gases including: CH_4, H_2O, CO_2, C_2H_4, and N_2O (Besson 2006).

4.1.3.3 Sensitivity / Limits

The minimum detection limit for ambient methane gas is 13 ppb with a 0.37 s measurement time, and approximately a 1 m effective absorption path (Uotila et al. 2005). With the use of solid-state lasers, PAS has the ability to detection methane with a sensitivity of 20 to 30 ppb and a resolution of 80 cm^{-1} (Liang et al. 2000). Lack et al. (2006) detailed an experiment for which they found the accuracy and precision for PAS to be 5% and 6 %, respectively.

4.1.3.4 Advantages

- Can detect gases at extremely low levels (ppb) due to its inherent stability and reduced cross-sensitivity (Mine Safety Appliances Company 2001).
- Has the ability to detect small pressure pulses before the concentration reaches the threshold limit value using a highly sensitive microphone (Mine Safety Appliances Company 2001).
- Offers zero stability as it eliminates the need to adjust for zero drift; no zero points involved (Mine Safety Appliances Company 2001).
- This method provides a precise, low-cost, reliable, and high-performance monitoring for a variety of gases (Besson 2006).
- Photoacoustic infrared monitoring systems can be expanded to observe up to eight separate locations (Mine Safety Appliances Company 2001).
- Additional sensors can be added to the instrument to monitor IR detectable gases (Mine Safety Appliances Company 2001).
- PAS is suitable for direct analysis of most samples without sample preparation or sample alteration (McClelland 2007).

4.1.3.5 Limitations

- Most of the thermal wave amplitude generated in the sample is never transmitted into the gas where the pressure signal evolves, but rather the thermal wave is reflected back into the sample where it decays, making it difficult to obtain an adequate signal-to-noise ratio (McClelland 2007).
- Signal saturation can affect the modulation frequency, causing the signal amplitude to sink into the noise floor (McClelland 2007).
- The sensitivity of the system is limited by the pressure sensor and microphone (Kauppinen et al. 2004).
- The radiation source is directly exposed to the gas sample; corrosive gases can impact the monitor (Mine Safety Appliances Company 2001).

If H_2S emissions are high over individual tailings ponds, then corrosive gases may impact the instrumentation ultimately affecting the accuracy of the technique. However, tailings ponds with high

CH_4 emissions are not expected to also have high H_2S emissions and corrosivity will not be a limitation to the technique.

4.1.3.6 Maintenance

PAS instruments require minimal maintenance. A study by Besson (2006) found that continuous measurements over two weeks for 24 h a day allowed for successful measurements without any maintenance of the sensor. However, maintenance of the instrument should include the purging with N_2 before use and during intermittent measurements to ensure that no impurities are introduced to the sensor (Besson 2006).

4.1.3.7 Technology Application

- Ambient air monitoring and detection of air pollutants or toxic gases by anthropogenic sources (motor vehicle and industrial exhaust, large-area damages to nature, and the generation of photochemical smog) (Meyer and Sigrist 1990).
- The following application areas for targeting specific gases: polymers development, pharmaceuticals, paints, textiles, forest and agricultural products, paper treatments, and nano- and other synthesized materials (composites, biomedical samples, and fuels) (McClelland 2007).
- Detection and monitoring of combustible gases.
- Detection and monitoring of CH_4, CO_2, NH_3 and N_2O gas emissions from livestock manures (Osada et al. 1998).

4.1.3.8 Cost

- Operational costs include the costs of power and purge/ calibration gases.

4.1.4 *Solid State (SS) Sensors*

4.1.4.1 Methodology

The detection of methane with Solid State (SS) is based on the reversible interaction between the gas and the SS sensor. Metal oxides deposited as thick or thin films on the SS sensor are used as active layers in gas sensing devices (Opekar and Stulik 2002). For methane gas sensing, the chemical SS sensor is manufactured with a metal oxide semiconductor, either SnO_2 or ZnO_2, as they can measure small levels of toxic or flammable gases (including hydrocarbons, NO_x, and O_2) within the atmosphere (Garcia and Masson 2004). The potential of this technique is based on the low conductivity of the SS sensor in clean air, which increases with increasing available methane gas within the atmosphere (Capone et al. 2003, Garcia and Masson 2004).

SS sensors are commonly used in the field for direct in-situ sampling, providing real-time data where no post-laboratory analyses are required (Garcia and Masson 2004).

4.1.4.2 Sensitivity / Limits

A minimum detection limit of 1.7 ppm of atmospheric methane gas is available with the use of a SnO_2 layered SS semiconductor sensor (Garcia and Masson 2004). However, the resistive-type sensors have undesirable aging effects (drift in sensor response and baseline signal) leading to poor reproducibility; more than one sensor should be used to obtain a higher sensitivity in the concentration levels (Capone et al. 2003). The typical accuracy and response time for an SS sensor is ±3% to 10% of full scale and 20 to 90 s (T_{80}), respectively for temperatures ranging from -20^{o}C to 50^{o}C (International Sensor Technology 2008).

4.1.4.3 Advantages

- SS sensors provide real time data, where no laboratory analyses are required (Garcia and Masson 2004).
- SS sensors are small (with good mechanical strength), portable, user-friendly and automated providing fast analysis (Capone et al. 2003, Garcia and Masson 2004).
- Long operating life and reasonable parameter stability with low maintenance (Opekar and Stulik 2002).
- High reliability with good resistance to corrosive gases (Comini et al. 2005).
- SS sensors allow for the rapid replacement of the detector without having to change the whole device (Garcia and Masson 2004).
- SS sensors provide robust and versatile solution for fieldwork at low costs (Garcia and Masson 2004).

4.1.4.4 Limitations

- Sensitivity to ambient humidity (water vapour) leads to the limited selectivity of the target species (Garcia and Masson 2004).
- Sensitive to multiple chemicals showing cross-sensitivities (Capone et al. 2003).
- Semiconductors have to be heated (Comini et al. 2005) adding a physical limitation.
- Sensors may have a long stabilizing time after energization based on the field ambient air conditions (Garcia and Masson 2004).
- SS sensors suffer from limited measurement accuracy with their operating life causing long-term stability issues (Capone et al. 2003).

This technology may not be practical for emissions measurements from tailings ponds due to the expected humidity and emissions of multiple chemicals which may affect the accuracy of the results as well as the efficiency of the technique. Limited measurement accuracy with respect to the SS sensor operating life may increase the overall costs of the application, also reducing the practicality.

4.1.4.5 Maintenance

Calibration of the SS sensor can compensate for any influences of varying oxygen or humidity levels. More specifically, a correction factor for oxygen can be introduced and the sensors can be calibrated at different humidity levels to correct the signal of the detector (Garcia and Masson 2004). Pre-aging thermal treatments and cycle calibration checks should also be periodically conducted to observe any sensor drifts or contamination effects and to increase reliability (Capone et al. 2003).

4.1.4.6 Technology Application

- Commercial gas sensors – fire detectors, leakage detectors, controllers of car and plane ventilation, alarm devices (warning of reaching threshold concentrations) (Capone et al. 2003).
- Indoor air quality and industrial air quality detection and characterization (Capone et al. 2003).
- Ambient air quality detection and pollution monitoring (Capone et al. 2003).
- Monitoring of geologic emissions of methane from petroliferous sedimentary basins through micro-seepage surveys, and flux conditions in soil and wetlands (Garcia and Masson 2004).
- Detection and monitoring of landfill gases through the decomposition of municipal solid waste (Comini et al. 2005).

4.1.4.7 Cost

- Sensor lifetime ranges between 3 to 5 years, where replacements costs are typically around $200.

4.1.5 ***Wavelength Modulation Spectroscopy (WMS)***

4.1.5.1 Methodology

Wavelength modulation spectroscopy (WMS) is a new optoelectronic technique for the detection and monitoring of gases, including methane. For this method, the wavelength of a continuous laser is modulated at a certain frequency before scanning through the gas absorption line (Magalhães et al. 2008). Here, the wavelength modulation becomes an amplitude modulation, allowing its highest amplitude to pass through the highest slope points of the absorption peak (Magalhães et al. 2008). The amount of light absorbed as the laser scans through the absorption line is proportional to the concentration of the target gas (following the Lambert-Beer law); the absorption information is retrieved by a synchronous detection system, the voltage output measured is proportional to the target gas concentration (Magalhães et al. 2008).

WMS is commonly used in the field under harsh environmental conditions for direct absorption measurements.

4.1.5.2 Special Features

WMS uses laser diodes which allow the detection bandwidth to be shifted from DC to higher frequencies, ridding excess noise and increasing the signal-to-noise ratio (Cubillas et al. 2005, Magalhães et al. 2008). Semi-conductor lasers are most typically used in trace gas detection adding flexibility to the modulation of the input injection current (Dzikowski 2009).

4.1.5.3 Sensitivity / Limits

The minimum detection limit varies from 1.15 to 50 ppm for methane gas (Cubillas et al. 2005). Silveira and Grasdepot (1996) developed a WMS sensor using a distribution feedback laser, achieving a methane concentration ranging from 0.2% to 100% with a 0.1% resolution for an optical path of 30 cm.

4.1.5.4 Advantages

- WMS is a very powerful technique with a high signal-to-noise ratio (Magalhães et al. 2008).
- The system has relatively a simple setup (Magalhães et al. 2008).
- The optoelectronic setup has been implemented in a fully controlled manner for the detection and monitoring of CH_4 (Magalhães et al. 2008).
- The detection bandwidth is shifted from DC to higher frequencies to rid any excess noise (Magalhães et al. 2008).
- An error of 2.8% between experimental and theoretical values was obtained which validated the technology, indicating high reliability of the instrument (Magalhães et al. 2008).

4.1.5.5 Limitations

- Issues regarding the stability of the laser and the introduction of noise with increasing life-span (Cubillas et al. 2005).

The limitations of this technology are few and the stability of the laser may be increased with calibration. Due to the sensitivity of the technology and the simple set-up, this application may be effective for CH_4 measurement over oil sands tailings ponds.

4.1.5.6 Maintenance

Auto-calibration should be done regularly to enable the sensor to be only sensitive to the absorption of CH_4 and not to the spurious variations of the beam energy to amplitude variations, screening by dust particles or changes in the optical window transmission (Silveira and Grasdepot 1996).

4.1.5.7 Technology Application

- Trace gas emission monitoring from natural or anthropogenic sources (Magalhães et al. 2008, Silviera and Grasdepot 1996).

- Environmental monitoring and methane detection in water treatment plants and industrial wastelands (Cubillas et al. 2005).
- Industrial monitoring and methane detection in chemical plants and mines (Cubillas et al. 2005).

4.1.5.8 Cost

- Operation costs arise from power consumption and calibration.

4.2 Remote Sensing Monitoring Methods

4.2.1 *Open Path Fourier Transform Infrared (OP-FTIR) Spectroscopy*

Refer to Section 2.2.1 for details.

4.2.2 *Differential Optical Absorption Spectroscopy (DOAS)*

Refer to Section 2.2.2 for details.

4.2.3 *Correlation Spectroscopy (CS)*

4.2.3.1 Methodology

The correlation spectroscopy method uses two micro-optic cells with Gradient-Index (GRIN) lenses to collimate and collect light beams undergoing absorption (Zhang et al. 2008). One cell contains the air sample to be measured, and the other cell is referred to as the 'reference cell' containing the pure target gas (or CH_4). Reflections are introduced into the micro-optic devices (or GRIN lenses) creating interference signals that produce harmonics distinguishable from the gas signal (Zhang et al. 2008). These interference signals can be reduced by coating the lenses with an anti-reflection coating. During measurement, a broadband light source (of light emitting diodes) ranging from 1,100 to 1,700 nm is used (Zhang et al. 2008). The spectrums of the target gas and reference cell are measured and correlated to obtain the total amount of CH_4 within the air sample. Another reference cell can be used to eliminate other gas interferences such as CO_2 (Zhang et al. 2008). A space-borne correlation spectroscopy sensor named 'measurement of pollution in the troposphere' or MOPITT has been deployed as a remote sensing technique to measure total column amounts of methane (Larsen and Stamnes 2006, Zhang et al. 2008).

4.2.3.2 Special Features

The absorption spectrum of a gas of interest can be either directly or indirectly pressure, Stark, or phase modulated to produce a desired signal (Edwards and Dakin 1993). Correlation spectroscopy has been integrated with satellite sensors to measure emitted and reflected infrared radiance within an atmospheric column, relating to total column CH_4 (Kramer 2001). Software can translate the data into three-dimensional maps to model the global tropospheric chemistry of multiple gases, including the spatial distribution of CO and CH_4 (Kramer 2001).

4.2.3.3 Sensitivity / Limits

Minimum detection limits of approximately 20 ppmv over a 30 m path length at the 1.65 μm band is possible with the use of a gas correlation filter wheel and a fast response InGaAs detector (Chapman and Hilton 2006). The sensor has a coarse spatial resolution of 22 km at nadir (Larsen and Stamnes 2006, Zhang et al. 2008). Satellite CS has the capacity of measuring CH_4 with an accuracy of 1% within a 4 km layer and a spatial resolution of 22 x 22 km (Kramer 2001).

4.2.3.4 Advantages

- The comparison of gases acts as a perfect filter. Unless interfering gases have spectral lines at almost exactly the same wavelength as the target gas, they will not be observed (Chapman and Hilton 2006, Zhang et al. 2008).
- Low cost method and relatively simple to use (Chapman and Hilton 2006).
- The technique is advanced in the field of optical gas sensors, where optical fibres are used as the transmission medium. As a result, the sensor part and measurement circuit can be isolated completely, enhancing the safety of the technique (Edwards and Dakin 1993, Zhang et al. 2008).

4.2.3.5 Limitations

- During methane detection, the sensor starts to become significantly sensitive to water vapour when optical filter bandwidths of 100 nm are used (Zhang et al. 2008).
- If all of the light at the absorbing wavelength is absorbed by the correlation cell, the method will not work. For optimal results, a transmission of 30% to 80% is essential (Chapman and Hilton 2006).

4.2.3.6 Maintenance

All of the measurements can be referenced to internationally recognized calibration gases; samples should be compared to the standards regularly. Since the instrument is operated remotely less maintenance is required. The spectral components are enclosed within a casing to prevent contamination by dust, particles, etc.

4.2.3.7 Technology Application

- Emission detection and characterization of trace gases in industrial areas (Chambers et al. 2004).
- Monitoring and global mapping of greenhouse gases within the atmosphere over natural (decay of organic matter, wetlands) and anthropogenic (landfills, sewage, leakage due to the mining of fossil fuels, natural gas pipeline leakage, and biomass burning) sources (Chapman and Hilton 2006, Larsen and Stamnes 2006, Sandsten et al. 1996).
- Indoor monitoring, surveillance, and exposure assessment of hazardous gases (Sandsten et al. 1996).

4.2.3.8 Cost

- Correlation spectroscopy is the least expensive remote sensing optical technique for identifying and tracking plumes (Chambers 2001). Operation costs mainly consist of power consumption and calibration costs.

4.2.4 *Airborne Natural Gas Emission LIDAR (ANGEL)*

4.2.4.1 Methodology

The airborne natural gas emission LIDAR (ANGEL) technique uses three separate sensors: a differential absorption LIDAR (DIAL) sensor, a high-resolution mapping camera, and a color digital video camera (Murdock et al. 2008). The ANGEL system remotely detects, quantifies, and allows for precise detection and reporting of natural gas leak sources. The airborne platform (containing the ANGEL system) is a fixed wing aircraft that is typically flown at approximately 300 m at speeds up to 240 mph (Murdock et al. 2008). From here, it can measure emissions from pipelines, facilities, etc. The included DIAL sensor uses laser wavelengths to illuminate the source with mid-wave infrared (MWIR) laser pulses. These laser pulses are scattered from the ground and detected by a receiver package on the aircraft. The sensor itself contains three separate laser benches which are accurately tuned to emit co-aligned pulses at slightly different wavelengths of mid-wave infrared (MWIR) at a 1 kHz rate (Murdock et al. 2008). The DIAL sensor has been designed to detect both methane and ethane - the two major components of natural gas. The methane bench produces two “online” emissions of laser energy. The first laser bench emits energy which is absorbed specifically by methane molecules along the light path; ethane molecules absorb energy at a specific wavelength from the second laser bench (Murdock et al. 2008). Lastly, an “offline” laser bench emits energy which is not absorbed by common gases within the atmosphere to provide a ratio of “online” and “offline” signals (Murdock et al. 2008). These ratios can then be combined with information regarding the path between the aircraft and the ground, allowing for algorithmic calculations of the target gas of interest (Murdock et al. 2008).

4.2.4.2 Special Features

ANGEL has been used for pipeline surveying to detect, quantify, and report the precise location of gas leaks from a quarter-mile above (Brake et al. 2004). Datasets supplied by ANGEL can then be used for the maintenance of potentially dangerous scenarios, low priorities, and nuisance emissions (Brake et al. 2004).

4.2.4.3 Sensitivity / Limits

The system measures the concentration path length in units of parts per million per metre (ppm/m) (Murdock et al. 2008). The DIAL system (including a high-resolution digital mapping camera) maintains its sensitivity while operating at altitudes of approximately 460 m and at airspeeds of 240 kph, collecting up to 1,600 km of data per day (Brake et al. 2004). The collection of data from 200 to 230 m will result in a swath width of approximately 30 m (Murdock et al. 2008).

4.2.4.4 Advantages

- Can survey up to 1,600 km per day (100 times faster than other conventional analytical methods) (Brake et al. 2004).
- Virtually eliminates all accessibility issues, such as terrain conditions and property access (Lenz et al. 2004).
- Utilizing GPS data and a computer-controlled optical scanning system, the sensor automatically accounts for plane position and orientation (Lenz et al. 2004).
- The ANGEL services capture data and mapping to within 3 metres (Lenz et al. 2004).
- Utilizing field-tested algorithms, ANGEL Services eliminates false alarms by accounting for background emission levels (Lenz et al. 2004).
- As an outsourced service, direct and indirect operating cost savings can be achieved (Lenz et al. 2004).
- Can provide 3-D coverage (Lenz et al. 2004).
- GIS-ready data sets available providing information on existing pipelines and facilities (ITT Industries, Inc. 2008).

4.2.4.5 Limitations

- Provides a passive measure of the contaminant in a slow and expensive fashion (Brake et al. 2004).
- Complex system design, integration and data analysis (Lenz et al. 2004).

4.2.4.6 Maintenance

During instrument use, breaks should be scheduled every 90 to 120 min to back up the data and to check the alignment of the system. Checking the data will infer whether there have been power failures or whether the flash lamp has to be replaced (indicated by gaps in the datasets) (Ertel 2004).

The level of maintenance required to operate DIAL is high and consistent monitoring of the instrument is necessary for the following additional reasons: numerous optical surfaces can lead to optical damage; small fluctuations in the pump pulse energy can lead to large fluctuations in the rod refractive index; and, the length of the resonator may lead to issues surrounding the mechanical stability (Ertel 2004). Camera lenses should be cleaned with a soft non-scratch cloth.

4.2.4.7 Technology Application

- Leak detection, gas characterization, and imaging (GIS) of natural gas pipelines (natural gas or refined liquids) (Murdock et al. 2008).
- Detection of hazardous liquid emissions from broad area sources (Murdock et al. 2008).

4.2.4.8 Cost

- Operational costs include the high amount of energy required for illuminating a target, as well as the aircraft costs (including fuel, pilot, etc.).

5 REVIEW OF FLUX MEASUREMENT TECHNOLOGIES FOR VOCS, REDUCED SULPHUR COMPOUNDS AND CH_4

This section outlines the approaches and methodologies for measuring fugitive emission fluxes from area sources. These methods and micrometeorological techniques are mostly based on in-situ field measurements (though applications can represent macro- and micro-scales) and often require the use of previously outlined VOC, reduced sulphur compounds and CH_4 characterization instrumentation. Along with the methodology, the sensitivity, advantages, limitations will be discussed, whenever possible.

The following technologies have been reviewed and assessed:

- Conventional Analytical Techniques
    - Chamber Methods
    - Eddy Covariance (EC)
    - Eddy Accumulation and Relaxed Eddy Accumulation
    - Flux Gradient Techniques
    - Mass Balance Techniques
    - Tracer Gas Method
- Remote Sensing Monitoring Technologies
    - Solar Occultation Flux (SOF)
    - Nocturnal Boundary Layer Box Method
    - Radial Plume Mapping (RPM)

5.1 Conventional Analytical Methods

5.1.1 *Chamber Methods*

5.1.1.1 Methodology

Chambers are frequently used as an in-situ technique for measuring atmospheric fugitive emission fluxes of various trace gases at the ground surface (including VOCs, reduced sulphur compounds and CH_4). The chambers themselves differ depending on whether they are open or closed, as well as static or dynamic and can be classified into the following categories: non-steady-state non-through-flow (closed static), non-steady-state through-flow (closed dynamic), and steady-state through-flow (open dynamic) chambers (Norman et al. 1997, Pumpanen et al. 2004). Open flow-through chambers determine the flux by monitoring the incoming and outgoing trace gas concentrations as well as the rate of air flow through the chamber (Welles et al. 2001). For this method, wind speed cannot be controlled and may affect the flux measurements through dilution. Within a closed chamber, the trace gas flux is measured through monitoring both the chamber volume and the rate of increase of the trace gas concentration with an attached gas analyzer (Welles et al. 2001). These chambers are open on the bottom to measure fluxes released from the ground (or pond) surface, and sealed on the top to contain the trace gas concentrations (Tillman and Smith 2004). Static chambers provide no air circulation within the enclosure, whereas dynamic chambers circulate the air samples allowing for the rate of concentration increase to be monitored within the head space of the chamber (Denmead 2008). For both the open and closed chamber methods, flux calculations require the following measurements: surface area covered by the chambers, and the gas concentration within the air entering the chamber (Denmead 2008). Chamber designs can be altered to better fit the specific trace gas of interest. For example, carbon adsorbent traps can be attached to a closed dynamic chamber to collect VOC vapours from the air stream to be later analyzed using a thermal desorption/ gas chromatograph system (Tillman and Smith 2004). Closed chambers can also be equipped with lids that open and close automatically for venting and pressure control; be measured via continuous syringe sampling or automatic sampling by gas detector; contain a time controller; and/or a data acquisition system increasing the reliability of the emission data (Van Cleemput and Boeckx 2006).

The US EPAs compendium method TO-14A (U.S. Environmental Protection Agency 1999b) outlines the use of an initially evacuated positively pressurized canister for sample collection prior to analysis with gas chromatography. Air is drawn into the canister via a sampling train comprised of components regulating the rate and duration of sampling; once obtained, the sampling valve is closed and transported to a predetermined laboratory for analysis and characterization (U.S. Environmental Protection Agency 1999b).

5.1.1.2 Sensitivity / Limits

The sensitivity of the method is dependent upon the chamber technique. When discrete samples are taken and stored in gas canisters, the analytical detection limit is on the order of ppbv (U.S. Environmental Protection Agency 1985). Larger concentration changes are detectable at ppb levels with the use of closed chambers (Denmead 2008). For benzene, the analytical detection limit is 0.01 ppbv with an estimated emission rate sensitivity of 0.001 $\mu g/m^2 \cdot min$ (Eklund 1992).

5.1.1.3 Advantages

- Simple operating principles; portable in size; and low in cost, requiring minimal space for measurements (Denmead 2008).
- Static closed chambers require no power consumption (Denmead 2008).
- Multiple gases can be measured simultaneously at low fluxes (Van Cleemput and Boeckx 2006).
- Continuous and long-term monitoring is possible (Van Cleemput and Boeckx 2006).
- The chambers themselves have little influence on microclimatic variables (Yim et al. 2002).

- Measurements can be taken rapidly and precisely over a short period of time (Kabwe et al. 2005, Yim et al. 2002).

5.1.1.4 Limitations

- Differences in pressure between the chamber and the outside atmosphere (produced by wind or air pressures) can create artefact gas fluxes through the production of viscous flows (Denmead 2008, Pumpanen et al. 2004, Welles et al. 2001).
- Turbulence due to wind speed within the chamber can affect flux measurements (Denmead 2008).
- Chambers readily exposed to direct solar radiation may experience an expansion of contained gases, affecting flux measurements (Pumpanen et al. 2004).
- Closed chambers may build up water vapour disturbing the ground flux by displacing some of the chamber air (Welles et al. 2001).
- Venting of closed chambers can generate large measurement errors (Van Cleemput and Boeckx 2006).
- Non-steady-state chambers may underestimate fluxes by 10% due to an altered diffusion gradient of trace gases (Pumpanen et al. 2004).
- Small areas are typically measured over a short term (Van Cleemput and Boeckx 2006).
- Flat homogeneous terrain is required (Van Cleemput and Boeckx 2006).

5.1.1.5 Technology Application

- Trace gases (VOCs, CH_4, and SO_2) were measured and characterized by canister/chamber sampling methods near surface oil sands mining sites and upgrading facilities within the Athabasca region (Simpson et al. 2010).
- Floating static chambers were deployed over surface freshwater bodies in Quebec to monitor greenhouse gas emission fluxes over aquatic systems (PP Systems 2008).

5.1.2 ***Eddy Covariance (EC)***

5.1.2.1 Methodology

Eddy Covariance (EC) is a micrometeorological technique to directly measure the rate of vertical transport of trace gases, including VOCs and CH_4, providing a measure of average flux (Denmead 2008). More specifically, EC measures the statistical covariance between the concentration of a trace gas (or number of molecules) as well as the vertical wind speed within eddies (the speed of the molecules moving up and down). The air density, vertical wind speed, and mixing ratio of the trace gas can be directly translated into the gas flux (Denmead 2008). For this technique, instruments are placed at some height above the ground surface (depending on atmospheric stability and surface roughness) within the internal boundary layer, where the flux is estimated to be constant with height

(Kabwe et al. 2005). The wind speed component is typically measured by way of a 3-D sonic anemometer, while the trace gas concentrations can be measured with a gas analyzer, such as a proton transfer reaction mass spectrometer (PTR-MS) or a trace gas analyzer (Karl et al. 2002, Leuning and Judd 1996). Consequently, the measurement system requires the turbulent transportation of air requiring specific meteorological conditions.

5.1.2.2 Sensitivity / Limits

The response time for resolving VOC fluctuations with a PTR-MS system is less than 0.8 s, where instrument noise is independent of concentration measurements (Karl et al. 2001). This system has a minimum detection limit of less than 0.1 $mg/m^2 \cdot h$ for most VOCs (Karl et al. 2001). The minimum detection limit for CH_4 measurements has been estimated at 22 $ng/m^2 \cdot s$ using a Fast Methane Analyzer (FMA, Los Gatos Research) (Smeets et al. 2009). Typical errors of the eddy covariance system range from 10 to 20% (Norman et al. 1997).

5.1.2.3 Advantages

- Minimal system disturbance (Welles et al. 2001).
- Provides a direct and simple measurement independent of atmospheric stability, and does not require common simplifying assumptions (Denmead 2008).
- Greater temporal resolution than other techniques (Kabwe et al. 2005).
- Instruments may be housed in a controlled environment to aid in maintaining the stability of the calibrations (Leuning and Judd 1996).
- Can be used over long sampling periods within a variety of ecosystems (Leuning and Judd 1996, Smeets et al. 2009).

5.1.2.4 Limitations

- Issues surrounding correct mounting height, alignment of the sonic anemometer, flow distortion from neighbouring instruments, appropriate sampling frequencies and averaging times, and the need to account for the effects of simultaneous heat and water vapour fluxes (Denmead 2008).
- Variability in the data may stem from temporal variations (Kabwe et al. 2005).
- Heat and water vapour fluxes must be taken simultaneously for density corrections (Leuning and Judd 1996).
- Instrument surfaces may become contaminated by rain or dust (Leuning and Judd 1996).
- Delay between signals from the sonic anemometer and gas analyzer can cause variable error in flux estimates (Leuning and Judd 1996).
- Varying sampling heights may have different footprint characteristics (Karl et al. 2002).

5.1.2.5 Technology Application

- Used at Syncrude Canada Ltd., Fort McMurray to measure surface energy fluxes (momentum, sensible heat, and latent heat) atop overburden piles to compare energy partitioning between reclaimed soil cover to a natural boreal forest (Carey 2008).
- Continuous measurements of water vapour, heat and momentum fluxes were taken by eddy covariance over the Siberian forest to determine the fate and transport of biogenic VOCs (Katrynsti 2008).
- Eddy covariance was used to measure evaporative fluxes over Great Slave Lake, North West Territories, to determine the magnitude of seasonality with inter-annual meteorological conditions (Blanken et al. 2000).

5.1.3 *Eddy Accumulation and Relaxed Eddy Accumulation*

5.1.3.1 Methodology

The eddy accumulation method (or conditional sampling method) allows the user to overcome some of the limitations within the eddy covariance technique. Like the eddy covariance technique, eddy accumulation measures the turbulent transportation of trace gases within a sampling area. However, when air is drawn in by the anemometer (measuring vertical wind speed), it is diverted to an analyzer where the trace gas concentrations are measured separately within updrafts and downdrafts over time (Baker et al. 1992). The gas sampling system must be capable of switching between air samples during up and down drafts (Fowler et al. 1995). The averaged updraft concentrations are subtracted from the averaged downdraft concentrations to obtain the net flux (Baker 2000, Baker et al. 1992, Fowler et al. 1995, Katul et al. 1996). To measure the trace gases, a fast solenoid valve is substituted for the fast-response gas sensor used in the eddy covariance technique (Denmead 2008). For this method, sampling must be proportional to the strength of the updrafts and downdrafts (Baker et al. 1992, Katul et al. 1996).

The relaxed eddy accumulation method involves sampling at a constant flow rate, where the updrafts are also sampled separately from the downdrafts (Baker et al. 1992). In doing so, the technique relaxes the sampling requirements that are proportional to the wind velocity (Fowler et al. 1995). The net flux is then obtained through the subtraction of the averaged updraft and downdraft concentrations (Baker 2000, Baker et al. 1992, Katul et al. 1996). The relaxed method requires the evaluation of an empirical constant, β, which has been previously simulated to be 0.6 ± 10% from wind, humidity, and temperature signals obtained from an historical eddy correlation data set (Baker et al. 1992). This value can either be assumed or determined by measuring similar scalars within the atmospheric surface layer (Katul et al. 1996). Both eddy accumulation and relaxed eddy accumulation techniques have been demonstrated to capture CH_4 and VOC fluxes within the atmosphere.

5.1.3.2 Sensitivity / Limits

During conditional sampling, the resolution is approximately 0.1 s for the gas sampling system (Fowler et al. 1995). The minimum detection limit for the relaxed eddy accumulation system is approximately 0.2 µg/m^3, where it is capable of resolving fluxes greater than 20 ng/m^2·s (Nemitz et al. 2001). The minimum detection limit for most VOCs is approximately 1 ppb for relaxed eddy accumulation systems (Bowling et al. 1999).

5.1.3.3 Advantages

- Does not require a rapid response sensor for the covariate (Baker 2000).
- Directly measures gas flux at a point (Denmead 2008).
- Samples can be measured online or offline within a laboratory using gas chromatography or high precision mass spectrometer (Denmead 2008).
- Air samples can be dried and brought to uniform temperature before measuring offline, removing any heat and water vapour effects (Denmead 2008).

5.1.3.4 Limitations

- Difficult to measure proportionally to the updrafts and downdrafts, making it difficult to sample small changes in flux using eddy accumulation (Baker et al. 1992, Katul et al. 1996).
- Eddy accumulation requires the accuracy in a sampled gas volume measurement to be 0.1% (Baker et al. 1992).
- Difficult to evaluate empirical coefficients within the relaxed eddy accumulation technique (Baker et al. 1992).
- Fluctuations in density caused by sensible or latent heat transport can affect flux measurements (Baker 2000).
- Wind speed measurement has the potential to produce random measurement error (or noise) within the sampling data (Baker 2000).

5.1.3.5 Technology Application

- Relaxed eddy accumulation methods were used to develop an aircraft based VOC flux measuring system over a boreal forest in Manitoba (Zhu et al. 1999).
- Emission and deposition fluxes of biogenic and anthropogenic VOCs and methane were evaluated by relaxed eddy accumulation with gas chromatography over a Mediterranean forest ecosystem subject to forest management (Ciccioli et al. 2003).

5.1.4 ***Flux Gradient Techniques***

5.1.4.1 Methodology

The flux gradient technique is a micrometeorological method used to measure the site-specific vertical transport of trace gases through the atmosphere. Using an equation analogous to Fick’s law of molecular diffusion[2], calculations simply require the vertical gradient of trace gas concentration and either the eddy or turbulent diffusivity coefficient (K) (Denmead 2008, Fowler et al. 1995, Muller et al. 2009). By measuring the average concentration of trace gases at various heights above the surface, one can obtain the vertical gradient (Muller et al. 2009). The method assumes a well-mixed layer of air within the sampling profile, where the equation used can be altered to include a logarithmic wind profile and the friction velocity; termed the 'Aerodynamic Method' (Beswick et al. 1998, Denmead 2008). Consequently, the equations can be altered depending on the number of assumptions included and the analyses preformed. For example, it is assumed that the atmosphere is dominated by turbulent exchange (K_x) for all gases; however, in unstable conditions it is appropriate to apply the diffusion coefficient for momentum (K_m) (Fowler et al. 1995). The diffusivity coefficient is resolved in-situ at the time of measurement since it requires an understanding of the atmospheric stability, and can be determined by wind speed, height and aerodynamic stability (Denmead 2008). Instrumentation used is dependent on the sensors required to detect small concentration gradients of specific trace gases of interest (VOCs, CH_4, or reduced sulphur compounds) within the large background (Fowler et al. 1995). For the measurement of CH_4 emissions, flame ionization detectors have been successfully used to measure the vertical concentration gradient without destroying all of the non-methane hydrocarbons (Fowler et al. 1995). A combination of gas chromatography and flame ionization detectors have been used to measure VOC concentration gradients over a discrete area (Rinne et al. 2000). These methodologies have been described previously in Section 2.1.1and Section 2.1.4.

5.1.4.2 Sensitivity / Limits

It is common for fluxes to be measured as $\mu mol/m^2 \cdot h$ (Fowler et al. 1995). The diffusivity coefficient (K) is typically of order 0.1 m^2/s (Denmead 2008). The sensitivity of the method is dependent upon the type of instrumentation paired with the technique.

5.1.4.3 Advantages

- Flux-profiles can measure the net exchange of momentum, sensible and latent heat flux, and a range of trace gases (Fowler et al. 1995).
- Can be teamed with highly sensitive gas characterization instrumentation.
- Specific gas characterization instrument advantages are transferred to this technique.

5.1.4.4 Limitations

- Flux-profile relationships are complex over tall vegetation and forests leading to large systematic differences between measured fluxes (Fowler et al. 1995).
- Changes in heat and water vapour can affect the measured gradients (Fowler et al. 1995).
- Requires suitable and uniform atmospheric conditions (Fowler et al. 1995).
- May underestimate gas fluxes (Denmead 2008).

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[2] See http://en.wikipedia.org/wiki/Fick's_laws_of_diffusion

- Weather conditions during sampling can significantly affect the trace gas flux (Watt et al. 2004).
- Flux gradient laws tend to break down near very rough surface (such as forest canopies) (Rinne et al. 2000).
- Uncertainties imbedded within sampling and analysis and the turbulent exchange coefficient may lead to either random or systematic errors (Rinne et al. 2000).
- Specific gas characterization instrument limitations are transferred to this technique.

5.1.4.5 Technology Application

- VOC fluxes have been monitored over northern Boreal forests to observe changes in the ambient air with daily and temperature variations (Rinne et al. 2000).
- Flux gradient techniques have been used to determine the fate of CH_4 with in the atmosphere over wetlands and peatlands with changing water table depth and soil temperature (Fowler et al. 1995).

5.1.5 *Mass Balance Techniques*

5.1.5.1 Methodology

The mass balance technique is a meteorological flux measurement method used to calculate trace gas (most commonly CH_4) fluxes emitted from a source area. In general, the differences between flow rates of a gas are calculated as it moves, by the wind, into and out of a defined space (Denmead et al. 2000). More specifically, an emitted gas from a horizontal plane (source) will be carried by the mean wind flow and pass a vertical downwind plane (sampling location), where the flux from the surface can be inferred through the conservation of mass (Park et al. 2010). By vertically integrating the horizontal flux, using the horizontal wind speed and the trace gas concentration, the surface flux can be mathematically calculated (Park et al. 2010). For measurement and calculation purposes, the plume from an emitting source should extend to a height of approximately 1/10 of the upwind fetch (Denmead et al. 2000).

The mass balance technique can be separated into closed system and open system methods. Closed systems are often used for small, defined source areas with heterogeneous source distributions (Denmead 2008). During sampling, air is drawn in to an enclosed sampler via tubes (located at different heights within the test area) at equal rates along their lengths before reaching a gas analyzer; the mean gas concentration is obtained at each sampling height on each face of the test area (Denmead 2008). Wind measurements and concentrations are obtained and calculated between the integrated horizontal fluxes along the upwind and downwind boundaries. In contrast, open systems are typically utilized for uniform surface fluxes with an emitting area limited in upwind extent (Denmead 2008). Here, the trace gas concentrations are measured downwind of the emitting source at sufficient heights to define the shape of the concentration profile, extending through the top of the gas cloud (Denmead 2008). Both methods can be teamed with different concentration and wind measurement instrumentation, depending on the user’s needs.

5.1.5.2 Sensitivity / Limits

The sensitivity of the method is dependent upon the instrumentation utilized for the wind (open path laser, sonic anemometers, etc.) and trace gas concentration (gas chromatography, infrared analyzers, tunable diode lasers etc.) measurements. Flux gradient measurements are typically reported in $mg/m^2 \cdot s$, indicating the limits of the technique.

5.1.5.3 Advantages

- Allows for continuous measurements within small areas and distributed point sources (Denmead 2008, Denmead et al. 2000).
- Non-disturbing and independent of atmospheric stability (Denmead et al. 2000).
- Theoretical assumptions based on the shape of the profile are not necessary (Denmead et al. 2000).
- Method can be utilized in areas with heterogeneous source distributions and elevated sources (Park et al. 2010).
- Extrapolations of gas concentration and wind speed profiles are not necessary (Park et al. 2010).
- The closed system method does not require a uniform surface flux (Denmead 2008).
- Necessary instrumentation can be simple and of slow response (Denmead 2008).

5.1.5.4 Limitations

- Requires extensive interpretation. Each flux calculation requires the determination of many gas analyses (Denmead et al. 2000).
- Requires high-precision analytical techniques (Denmead et al. 2000).
- The method can overestimate the flux by 5% to 20% if the turbulent flux component is not considered (Park et al. 2010).
- Changes in wind direction will affect flux measurements and require constant monitoring (Denmead 2008). Method can be unreliable in light winds where wind direction may be variable (Denmead et al. 2000).
- Instrumentation requires an unobstructed fetch for accurate measurements (Denmead 2008).
- Uncertainty imbedded in the magnitude of the diffusive flux (Denmead 2008).

5.1.5.5 Technology Application

- Mass balance techniques have been used to measure CH_4 fluxes around liquid manure storage areas due to the heterogeneous distribution of the source as well as its varying elevation (Park et al. 2010).

- Techniques have also been used in the measurement of fugitive emission fluxes from oil systems where gases are typically vented or flared (Intergovernmental Panel on Climate Change 2002).

5.1.6 *Tracer Gas Method*

5.1.6.1 Methodology

The tracer gas method is typically used in the measurement of CH_4 fluxes within the atmosphere (Czepiel et al. 1996). For this technique, a tracer gas (commonly sulphur hexafluoride) is injected into the emitting edge of a sample area and the integrated concentrations of CH_4 and the tracer gas are measured downwind; depending on the average wind direction (Tregoures et al. 1999). The flux can then be calculated through a simple relationship involving the tracer release rate, the measured CH_4 mixing ratio above the background, and the measured mixing ratio of the tracer gas (Czepiel et al. 1996). Consequently, background measurements must be measured and quantified before tracer gas injection. Direct reading instruments can be set-up downwind from the source for real-time measurement and quantification of the fugitive emissions and tracer gas. Samples can also be remotely collected in canisters or bags placed along a transect perpendicular to the average wind direction (Czepiel et al. 1996, Galle et al. 2001, Tregoures et al. 1999). For other fugitive emission sources, water vapour or CO_2 can be used to measure the concentration flux (Denmead 2008).

5.1.6.2 Sensitivity / Limits

Detection limits have been demonstrated to be within the ppbv range with respect to a CH_4 mixing ratio above background with an associated error of ± 10 ppbv (Czepiel et al. 1996). Uncertainty ranges from 17% to 35% depending on the gas detector chosen (Czepiel et al. 1996, Tregoures et al. 1999).

5.1.6.3 Advantages

- Method is not dependent upon meteorological measurements, including changes in wind speed or direction. Measurements can be taken in most micrometeorological conditions (Griffith et al. 2006).
- Does not require vertical profiling (Griffith 2006).
- Tracer and target gases can be measured in the same air sample (Griffith 2006).
- Samples can be measured in-situ in real-time (Griffith 2006).

5.1.6.4 Limitations

- Issues surrounding spatial heterogeneity when integrating over the whole flux area (Czepiel et al. 1996).
- Confined to point sources or finite boundary locations (Czepiel et al. 1996).

- High cost and dependence on micrometeorological conditions (Czepiel et al. 1996, Tregoures et al. 1999).
- Interfering sources can affect flux calculations and method requires a strong enough source to be measured downwind (Czepiel et al. 1996).
- Time consuming and elaborate sampling procedure required (Galle et al. 2001).

5.1.6.5 Technology Applications

- Tracer gas methods have been utilized to measure CH_4 emission fluxes from landfills (Galle et al. 2001).
- Tracer gas methods of reduced sulphur compounds and VOC emissions are also performed by select companies to quantify large area and volume sources and difficult to measure point sources from a variety of industrial sources (for example, oil sands mining facilities, oil production tanks, disposal facilities, upgrading facilities, and hazardous waste treatment facilities) (Clearstone Engineering Ltd. 2002).

5.2 Remote Sensing Monitoring Methods

5.2.1 *Solar Occultation Flux (SOF)*

5.2.1.1 Methodology

Solar occultation flux (SOF) is a newly developed technique used for the quantification of VOC fluxes within the atmosphere. This technology uses IR solar spectra instead of laser pulses, and is comprised of the following components: a solar tracker, FT-IR spectrometer, and a global positioning system (Mellqvist et al. 2007). The solar tracker is a mirror device that is used to track the sun and reflect the incoming radiation into an FT-IR spectrometer which measures the IR spectra (Mellqvist et al. 2007, 2010). An absorbance spectrum is produced from the IR solar spectra, which can be translated to the average concentration of recoverable VOCs (in mg/m^2). The instrument is typically mounted on a vehicle, allowing for the measured solar light to traverse the cross-section of the emission plume of interest (Fransson and Mellqvist 2002, Mellqvist et al. 2007). In doing so, the number of molecules within the plume cross-section can be determined, and the mass flux can be calculated by multiplying the measured number of molecules by the wind speed at the site (Mellqvist et al. 2010). The path averaged concentration of a number of species absorbing IR solar radiation along the light of the sun can also be determined using multivariate analysis with a fitted calibration spectrum. Calibration spectra can be obtained from published reference libraries such as the HITRAN (www.hitran.com), NIST, and PNL databases (Mellqvist et al. 2005, 2007).

5.2.1.2 Sensitivity / Limits

Minimum detection limits of 0.3 to 0.5 mg/m^2 can be achieved when measuring a point source at 0.5 kg/h at a distance of 50 m (with 3% precision) (Sigrist 1994).

5.2.1.3 Advantages

- Cost effective and faster than the DIAL technique.
- Easier to automate.

5.2.1.4 Limitations

- Aromatics have a weaker absorption of infrared light and cannot be measured.
- Systematic errors such as local changes in the wind field due to buildings and industrial structures, and turbulence effects leeward of oil tanks are difficult to estimate.
- Measurements can only be taken in sunny conditions.

5.2.1.5 Technology Application

- Emission inventories from fixed pollution sources (flares, cooling towers, tank areas, process areas, and water treatment areas) (Fransson and Mellqvist 2002, Mellqvist et al. 2010).
- Rapid emission screening over industrial facilities under sunny conditions (conducted over 40 plant surveys within the USA and Europe) (Mellqvist et al. 2009).
- Ambient air quality flux measurements (Mellqvist et al. 2010).
- Quantification of volcanic flux emissions (Beecken and Borgentun 2007).

5.2.2 *Nocturnal Boundary Layer Box Method*

5.2.2.1 Methodology

The nocturnal boundary layer box method can be used to monitor the accumulation of un-reactive gases (such as methane) under a nocturnal temperature inversion from a source at the surface (Fowler et al. 1996). The top of the temperature inversion inhibits the upwards movement of fugitive emissions allowing for concentrations to be measured throughout the boundary layer (Beswick et al. 1998). The concentration flux is assumed to be horizontally homogeneous and can be mathematically deduced by obtaining measurements of the depth of the boundary layer, the concentration at a start time, as well as the concentration at a specified end time (Beswick et al. 1998, Choularton et al. 1995, Fowler et al. 1996). Consequently, the flux is simply the change in concentration with time over the extent of the boundary layer. This approach also assumes that the height of the nocturnal boundary layer is constant and well mixed throughout the observation period (Choularton et al. 1995). To test this assumption, the mixture of the boundary layer can be quantified through the comparison of the total heat balance of the layer with the rate of temperature change within the layer (Choularton et al. 1995). In the field, a stable nocturnal boundary layer is most likely to occur during the transition between day and night allowing for optimal nocturnal measurements (Beswick et al. 1998). Using a range of criteria, the height and extent of the nocturnal boundary layer can be estimated from Doppler sodar measurements or a balloon profile method where sampling of the height and concentration profile is conducted with a tethered balloon (Choularton et al. 1995, Fowler et al. 1996).

5.2.2.2 Sensitivity / Limits

Flux measurements can be measured to $\mu mol/m^2 \cdot h$ (Beswick et al. 1998). Minimum detection limits vary depending on the instrumentation used to measure trace gas concentrations.

5.2.2.3 Advantages

- Simple sampling technique and mathematical conversion to concentration flux.
- Balloon techniques can be used at greater altitudes than other techniques (Beswick et al. 1998).
- Methodology can be teamed with high detection level technologies to characterize and quantify fugitive emissions.

5.2.2.4 Limitations

- Only suitable for emission profiles that show a step change in concentration over a small change in altitude (Beswick et al. 1998).
- Difficulties in representing flux at the landscape scale since landscapes are not homogeneous (as represented within the equations) (Beswick et al. 1998).
- Turbulent conditions can affect boundary layer mixing, and ultimately, concentration measurements (Choularton et al. 1995).
- Error with respect to the steady state assumptions since the profile naturally varies with sampling height (Choularton et al. 1995).

5.2.2.5 Technology Application

- Landscape scale flux measurements have been assessed over peat wetlands to determine the fate and transport of CH_4. Using aircraft, flux measurements of methane gases have also been conducted on a regional scale over extensive pool areas of wetlands (Fowler et al. 1996).

5.2.3 ***Radial Plume Mapping (RPM)***

5.2.3.1 Methodology

Radial plume mapping (RPM) is a path integrated optical remote sensing (ORS) technique which can be configured as the following: horizontal radial plume mapping (HRPM), vertical radial plume mapping (VRPM), or one-dimensional radial plume mapping (1D-RPM) (Hashmonay 2008, U.S. Environmental Protection Agency 2004). For all of the possible configurations, several mirrors are placed at the survey site as path determining components (as mentioned in Section 4.2.1).

For VRPM, two different beam configurations (consisting of either five beams or more or three beams) are used for each outlined cell or grid, where estimates of the rate of emission from a fugitive source are measured providing a vertical scanning plane downwind of the source (Hashmonay et al. 2008). Beams sequentially scan over mirrors (retroreflectors) located along the ground-level as well as mirrors elevated on vertical structures to spatially define the plume within the crosswind direction (Kim and Platt 2007). Gaussian profiles are then used to retrieve concentration profiles of the vertical gradient, where concentration values are obtained for every square unit in the vertical plane (Kim and Platt 2007). VRPM can be used to directly calculate the mass flux of a trace gas of interest through a vertical plane downwind from an emission source by incorporating wind information (Hashmonay et al. 2008). The result is the trace gas flux rate upwind from an area source. More specifically, multiple non-intersecting beam paths are utilized in a vertical plane creating a mass-equivalent plume map, which can be integrated in conjunction with wind speed and direction to obtain the measured flux (Kim and Platt 2007). Concentration values (ppmv) are converted to g/m^3 by considering the molecular weight of the trace gas of interest allowing for the direct calculation of flux (g/s), using wind speed data (m/s) (Kim and Platt 2007).

5.2.3.2 Sensitivity

The detection of the gas flux often varies from 10% to 25% of the actual emission source (Hashmonay et al. 2008). The average minimum detection limit for methane gas is 1.75 ppmv (Hazardous Waste Consultant 2004).

5.2.3.3 Advantages

- Capable of characterizing fugitive emissions from large area sources with optical remote sensing-radial plume mapping (ORS-RPM) (Modrak et al. 2004a).
- Appropriate for characterizing emissions from ground level area sources and non-point fugitive emission sources such as landfills, lagoons and industrial complexes (Segall et al. 2005).
- RPM methodology has been well developed, evaluated, demonstrated, and peer reviewed by the U.S. Environmental Protection Agency.
- 3-D pollutant profiles can be created through the use of this method.

5.2.3.4 Limitations

- Single point emission sources cannot be evaluated through the use of this method.
- Requires the operation and co-ordination of a number instruments and components, making the system complex. Therefore, this method requires sufficient training and experience (Hashmonay et al. 2008).
- Flux calculations require the use of time consuming and complex mathematical relationships, sufficient training needed for data manipulation.

5.2.3.5 Technology Application

- Hot spot or fugitive emission source detection and flux concentration mapping over landfills (Hashmonay 2008, Hashmonay et al. 2008, Modrak et al. 2004a).

- Air quality flux concentration measurements of large concentration pollutant plumes over area sources (for example, forests) (Hashmonay et al. 2008).

6 RECOMMENDED TECHNOLOGY FOR THE CHARACTERIZATION AND MONITORING OF FUGITIVE EMISSIONS FROM OIL SANDS TAILINGS PONDS

Due to the current issues surrounding the emissions of VOCs, reduced sulphur compounds, and CH_4 it has become important to evaluate large area sources for their potential contributions to impacts on human health and the environment. Currently, fugitive emission data from oil sands tailings ponds are limited and non-specific due to the challenging nature of characterizing the emitting source. The size of the tailings ponds, accessibility limitations, and the heterogeneous nature of the ponds across the oil sands operations also present challenges for monitoring. Seasonal and temporal variations increase the variation in data, adding to the challenges of developing baseline data and annual emission factors. The tailings material differs between operations for the following reasons: (1) the geology of the oil sand deposits is complex and inconsistent across the region; (2) companies utilize different extraction and upgrading processes; and, (3) different organic (naphtha or paraffinic) solvents are used, where small percentages end up in the ponds. As new technologies are developed to increase solids settling within the ponds, companies may change their processing techniques. Consequently, emission measurements may differ within operations as well. Therefore, tailings ponds need to be measured separately and consistently over time to understand the different factors and parameters that may influence the emissions of different compounds. For that reason, there may not be one technology that is best suited for emission measurements across the oil sands region, and it is important to understand the different advantages and limitations of the technologies when interpreting data.

The selection of specific technologies is dependent upon the compounds measured, the sensitivity required, factors of interest, flux or concentration measurements, and the specific annual monitoring budgets. This is specific to the user and variable depending on the specific question one wishes to address. Though there have been numerous techniques and methodologies previously presented for the characterization and monitoring of VOCs, reduced sulphur compounds and CH_4, this section will outline recommendations based on the following factors: spatial coverage, quantification of the pollutants, determination of emission factor, characterization of VOC speciation, and frequency of monitoring. In doing so, appropriate technologies can be chosen which are best suited for the specific needs of the user which capture the unique benefits and advantages of the techniques.

6.1 Spatial Coverage

Fugitive emissions from area sources (such as oil sands tailings ponds) are difficult to measure with point-based air sampling techniques due to the spatial, daily, and seasonal temporal variability. Consequently, conventional analytical techniques are challenging methods as they require numerous data points over the desired spatial scale of the source to obtain an accurate representation of the target gases emitted. Obtaining access to the middle of the pond may also be complicated and pose safety concerns, limiting the extent of the sampling protocol over the source. Active tailings ponds are continuously changing as the dykes are built, which may affect annual interpretations of emissions based on spatial coverage. As a result, line-based or remote sensing monitoring techniques are recommended if a large spatial coverage is required, as they provide more representative data of an average concentration integrated over a larger measureable area (or light path).

- Recommended remote sensing techniques for achieving high spatial coverage include:
    - Open Path Fourier Transform Infrared (OP-FTIR)
    - Differential Optical Absorption Spectroscopy (DOAS)
    - Tunable Diode Laser Spectroscopy (TDLAS)
    - Differential LIDAR (DIAL)
    - Solar Occultation Flux (SOF)
    - Image Multi-Spectral Sensing (IMSS)
    - Radial Plume Mapping (RPM)
    - Correlation Spectroscopy (CS), and
    - Airborne Natural Gas Emission LIDAR (ANGEL).
- For high accuracy measurements, OP-FTIR, DOAS, and TDLAS are recommended.
- In time limited situations where no post-field data analysis can be conducted, DOAS and TDLAS are recommended.
- For the measurement of multiple compounds (or high versatility) OP-FTIR, DOAS, SOF, and IMSS are recommended.
- DIAL, RPM, and ANGEL are complicated and expensive techniques requiring a large team for the application of the technologies and are not recommended for the purpose of monitoring oil sands tailings ponds.

6.2 Determination of Emission Factors

The determination of emission factors is based on the quantity of a target gas released over the tailings ponds at a set point in time. Resolving the average concentration is necessary over a large spatial coverage to have an accurate representation of the emissions. Due to the challenges in obtaining point-based measurements remote sensing monitoring techniques are recommended. Some of these techniques (e.g., DIAL, SOF, eddy covariance) are able to provide emission fluxes of air pollutants, while other techniques (TDLAS, OPFTIR, DOAS) can only measure concentrations of air pollutants but can be used in measuring emission fluxes when combined with flux measuring techniques.

- For high accuracy measurements, OP-FTIR, DOAS, and TDLAS are recommended.
- In time limited situations where no post-field data analysis can be conducted, DOAS and TDLAS are recommended.
- For the measurement of multiple compounds (or high versatility) OP-FTIR, DOAS, SOF, and IMSS are recommended.

- For continuous monitoring of concentration fluxes, the following techniques are recommended: Eddy Covariance, Eddy Accumulation and Relaxed Eddy Accumulation.

6.3 Characterization of VOC Speciation

Due to the range of compounds embedded in volatile organic compounds (VOCs), technologies which can characterize a wide range of species are preferred. The following technologies are recommended for the characterization of VOC speciation:

- A GC-MS is recommended for its ability to identify and quantify complex mixtures of VOCs and semi-VOCs. Samples can be collected on-site in sorbent tubes, bags or canisters and analysed with a GC-MS.
- For higher precision, a PTR-MS is recommended for the quantification of VOCs at lower detection limits (pptv) with faster response times.
- For additional on-site measurement techniques, OP-FTIR, DOAS, and TDLAS are recommended for their ability to remotely characterize VOCs over an entire optical path length.

6.4 Frequency of Monitoring

Due to the difficulties in capturing daily and seasonal temporal variability, monitoring over longer periods of time is necessary to evaluate fugitive emission trends in concentration fluxes. Intermittent monitoring will allow for slower response instruments which may have the capability of monitoring several target gas species within the same air mass simultaneously. However, these instruments will not be able to pinpoint accurately when changes in concentration fluxes occurred. In this case, continuous monitoring using fast-response and highly sensitive instruments may be preferred.

- For intermittent monitoring of fluxes, chamber methods, flux gradient techniques, mass balance techniques, and tracer gas methods can be used.
- Intermittent monitoring of fluxes using TDLAS, DOAS, and OP-FTIR combined with other methods can also be conducted to measure fluxes from an area source.
- For continuous monitoring of concentration fluxes, the following techniques are recommended: Eddy Covariance, Eddy Accumulation and Relaxed Eddy Accumulation.
- Radial Plume Mapping is complicated and expensive requiring a large team for the application of the technology, and is not recommended for the purpose of monitoring oil sands tailings ponds.

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8 ACRONYMS, UNITS AND CHEMICAL FORMULAE USED IN THIS REPORT

8.1 Acronyms

1D-RPM	One dimensional Radial Plume Mapping
ANGEL	Airborne Natural Gas Emission Lidar
ASTM	American Society for Testing and Materials
CS	Correlation Spectroscopy
DIAL	Differential Absorption LIDAR
DOAS	Differential Optical Absorption Spectroscopy
FID	Flame Ionization Detection
FPD	Flame Photometric Detection
FPGA	Field Programmable Gate Arrays
FT-IR	Fourier Transform Infrared
GC-MS	Gas Chromatography-Mass Spectrometry
GIS	Geographical Information System
GRIN	Gradient Index
HRPM	Horizontal Radial Plume Mapping
IMSS	Image Multi-Spectral Sensing

IR	Infrared
MOPITT	Measurement of Pollution in the Troposphere
MWIR	Mid-wave Infrared
OP-FTIR	Open Path Fourier Transform Infrared
OSRIN	Oil Sands Research and Information Network
ORS	Optical Remote Sensing
ORS-RPM	Optical Remote Sensing Radial Plume Mapping
PAS	Photoacoustic Absorption Spectroscopy
PFPD	Pulsed Flame Photometric Detection
PID	Photo Ionization Detection
PS	Polarization Spectroscopy
PTR-MS	Proton-Transfer-Reaction Mass Spectrometry
RPM	Radial Plume Mapping
SOF	Solar Occultation Flux
SCD	Sulphur Chemiluminescence Detection
SEE	School of Energy and the Environment
SIM	Selective Ion Monitoring
SS	Solid State
TDLAS	Tunable Diode Laser Absorption Spectroscopy
TOF	Time of Flight
USD	United States Dollar
U.S. EPA	United States Environmental Protection Agency
UV	Ultraviolet
VOC	Volatile Organic Compound
VRPM	Vertical Radial Plume Mapping
WMS	Wavelength Modulation Spectroscopy

8.2 Units

amu	atomic mass unit
Da	Daltons
eV	electron volts

g/h	grams per hour
g/s	grams per second
K	eddy or turbulent diffusivity coefficient
K_m	diffusion coefficient for momentum
K_x	turbulent exchange coefficient
kg/h	kilograms per hour
m/s	metres per second
m^2/s	metre squared per second
mg/m^2	milligrams per square metre
$mg/m^{2}\cdot min$	milligrams per square metre per minute
mg/m^3	milligrams per cubic metre
mL/min	millilitre per minute
ms	milliseconds
ng/L	nanograms per litre
$ng/m^{2}\cdot s$	nanograms per square metre per second
nm	nanometres
ppb	parts per billion
ppbv	parts per billion by volume
ppm	parts per million
ppm/m	parts per million per metre
ppmv	parts per million by volume
pptv	parts per trillion by volume
psi	pounds per square inch
s	second
µg/L	micrograms per litre
$\mu g/m^{2}\cdot min$	micrograms per square metre per minute
$\mu g/m^3$	micrograms per cubic metre
$\mu mol/m^{2}\cdot h$	micromoles per square metre per hour
V/mW	volts per milliwatt

8.3 Chemical Formulae

$AgNO_3$	silver nitrate
BTEX	benzene, toluene, ethylbenzene and xylene
CH_2	methylene
CH_3	methylium cation
CH_4	methane
C_2H_2	acetylene
Cl_2	chlorine gas
CO	carbon monoxide
CO_2	carbon dioxide
H_2O	water
H_2S	hydrogen sulphide
HCl	hydrochloric acid
He	helium
HF	hydrogen fluoride
H_3O^+	hydronium
N_2	nitrogen gas
N_2O	nitrous oxide
NO_2	nitrogen dioxide
NO_x	oxides of nitrogen (often NO and NO_2)
O_2	oxygen
SF_6	sulphur hexafluoride
SnO_2	tin dioxide
SO_2	sulphur dioxide
ZnO_2	zinc peroxide

9 LIST OF OSRIN REPORTS

OSRIN reports are available on the University of Alberta's Education & Research Archive at https://era.library.ualberta.ca/public/view/community / uuid:81b7dcc7-78f7-4adf-a703-6688b82090f5. The Technical Report (TR) series documents results of OSRIN funded projects. The Staff Reports series represent work done by OSRIN staff.

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