Long Path Fourier Transform Spectroscopy (LPFTS) for Qualitative Approach to Development of Quantitative Knowledge Regarding Anthropogenic GHG Emissions.

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Background

The Kyoto Protocol states that participating industrialized countries are required to reduce their GreenHouse Gas (GHG) emissions by an average 5.2 % of the 1990 emissions during the time period of 2008-2012. These GHG's include CO_2, CH_4, N_2O, SF_6, HFC and PFC's. Protocol implementation has stimulated a new market where practices that reduce GHG emissions are "traded" for dollars with companies or countries that do not meet their target emission reductions.

One practice that has the potential to generate trades is the use of anaerobic digesters for processing of surplus organic materials and surplus manures from agricultural sources. The digester or biogas reactor processes raw manure from livestock to generate methane and fertilizer. The methane is harnessed and then used to generate electricity. The GHG emission savings are two fold from this process.

The first GHG saving is incurred by producing electricity from a hydrocarbon that does not originate from a fossil source. Therefore every kilowatt-hour of electricity produced by using biogas as a generator fuel reduces our dependence on fossil sources and potentially offsets a corresponding fraction of a kilowatt-hour of electricity that might otherwise have to be generated by a process that results in 'additional' GHG emissions. The fraction is present since not all electricity generation results in CO_2 emission (hydro, nuclear, wind etc.). The quantity of this fraction is directly related to the fraction of electricity, which generates CO_2. The carbon emitted as a result of burning biogas can be considered part of a closed loop as the CO_2 generated had been 'sequestered' previously during photosynthesis.

The second GHG reduction occurs when digester output (digestate) is land applied rather than 'raw manure'. Considering that a portion of the carbon originally present in the manure has been volatized and converted to methane and CO_2 during the digestion process, the potential of the digestate to emit CO_2 and CH_4 has been reduced accordingly. N_2O emissions are also potentially reduced as shown in related studies (Chatigny et al, 2003 as cited in MPTWG, 2005). Since the global warming potential of CH_4 and N_2O are respectively 21 and 296 times that of CO_2, a one-tone reduction in N_2O is equal to a 296-tone reduction in CO_2 (IPCC, 2001). Therefore there is great potential for direct mitigation of GHG's as well as generation of CO_2 equivalent credits downstream of the process. Currently, there is a significant research gap in this area as to how to properly first qualify all potential emissions and subsequently quantify verifiable reductions of pertinent GHG and precursor gases. Presented here is a detailed description of a measurement technique for qualitative understanding and then quantify these reductions in the downstream emissions.

Methodology

This section is split into two subsections, which describe how to measure the difference in GHG emissions between digested and raw manure qualitatively and quantitatively.

Qualitative – In order to accurately understand the GHG and precursor GHG emission it is important to observe all the emitted constituents without interfering with the natural conditions. Natural conditions include temperature, wind, rainfall, solar radiation etc. This is accomplished by using a Long Path Fourier Transform Spectroscopy (LPFTS) technique. A Fourier Transform Spectrometer (FTS) measures the amount of light at each frequency across a predetermined spectral interval. The common spectral interval utilized here is InfaRed (IR) radiation at 400 – 4000 wave numbers (cm^{-1}). Since molecules posses unique absorption features of IR radiation (or any radiation) the spectrometer is able to detect these constituents by monitoring the transmission of light across a predetermined path. The more molecules within the path, the more radiation absorbed within the molecules own unique region as seen in Figure 2.

In order to qualitatively measure the difference in GHG emissions between the raw and digested manure, the FTS is placed in between a field spread with raw manure and a field spread with digested manure as seen in Figure 1. Two mirrors are placed at the end of both fields. A broad band IR source sends light to the mirror where it is then reflected back into the spectrometer. The spectrometer measures the spectrum of light and the subsequent absorption features of every constituent present that absorbs light in this region. The path length is the distance to the mirror and back. Measurements are taken for both fields nearly simultaneously. The measurements are then divided as in Figure 2 to demonstrate the percent difference in transmitted light and the corresponding difference in concentration. Ideal conditions are when the wind direction will be perpendicular to the path in which the light travels. This allows us to see in near real time the difference in concentration of the two fields without disturbing the natural parameters outlined above. Path lengths are typically 200 m or more, which give a solid average concentration and remove the variability associated with spread manure. It is essential that the two fields are level and that the two light paths be at the same distance and height above ground.

Quantitative – In order to quantify the emission rates of the various GHG gases and GHG precursors, the same methodology is conducted as in the qualitative configuration only the micrometeorological parameters such as vertical and horizontal wind direction and speed are simultaneously logged (Greatorex, 2000) and paths at different heights and horizontal positions must also be monitored by other FTSs. This essentially gives a solid understanding of the movement of air, which is transporting the GHG's and also gives a gradient of concentrations. With all this data it is then possible to accurately determine the emission rates associated with each gas, without disturbing any of the natural parameters.

Abstract

LPFTS is a new evolving air pollution measuring technique with potential application in determining source GHG and precursor emissions. When monitoring any air pollution source, it is ideal to detect every emitted constituent. LPFTS is capable of detecting multiple gas absorption signatures simultaneously by measuring light transmittance across a predetermined path. Presented here is a detailed description of LPFTS methodology as well as protocols developed for simultaneous detailed field data acquisition of multiple gases to permit insights into qualitative and quantitative emission differences and relationships between land applied raw manure versus land applied anaerobically digested manure.
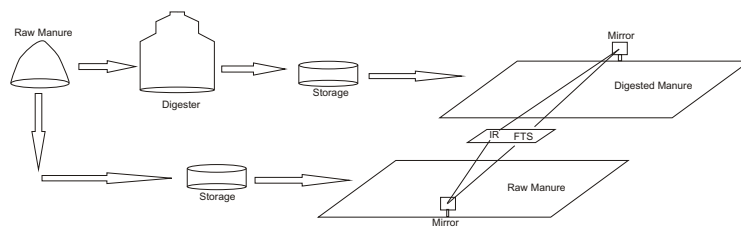
Figure 1: The above Figure shows an overview of the entire process and the configuration of the field measurement setup for qualitative analysis.
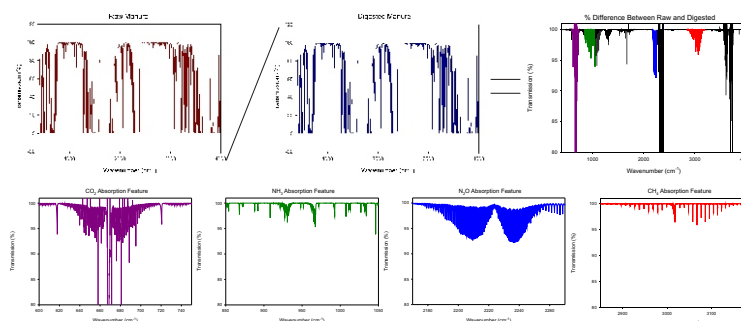

Figure 2: The above figure demonstrates how the two initial FTS measurements are used to determine the qualitative difference between the digested and raw manure. The two measurements are divided together to yield the percent difference in light transmission between the two measurements. The bottom four plots show the unique absorption features of CO_2, NH_3, N_2O and CH_4 found within the percent difference plot (colour coded).

Conclusion

In order to accurately quantify CO_2 equivalent credits generated by anaerobic digesters it is important to understand the downstream GHG reductions. Considering the global warming potential factors of some of the gases in question, generation of CO_2 equivalent credits in this area due to the process is potentially significant. The above literature demonstrates that the use of the LPFTS measurement technique has the potential to give a near real time qualitative picture of the GHG and Precursor GHG concentration differences between digested and raw manure emission without disturbing any natural parameters and can then subsequently provide the data required to quantify the emission rate of each individual gas when coordinated with micrometeorological techniques.

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Results and Discussion

The measurements will commence in the spring of 2006 at the Lynn Cattle Farm, located just north of London, Ontario, Canada. The landscape at this location is ideal as it is consistent and level. Since there are not any field data yet, what is presented here is a simulated result of what is expected. Figure 2 shows a FASCD3 simulation of a transmission measurement over a digested manure spread field. The path length used in the simulation is 200 m and the concentrations entered for CO_2, NH_3, N_2O and CH_4 are 365 ppmv, 100 ppbv, 320 ppbv and 1.8 ppmv respectively. These values are slightly higher than the accepted Northern Hemisphere average background concentration. Within the raw manure simulation the values for CO_2, NH_3, N_2O and CH_4 were increased by 1ppmv, 50 ppbv, 50 ppbv and 50 ppbv respectively. These two measurements were then divided to give the percent difference in the transmission of light between the two measurements. Figure 2 also shows a colour-coded display of the unique absorption features of CO_2, NH_3, N_2O and CH_4. The concentrations of these constituents will be determined by matching the measured transmission difference to a simulated transmission difference. The concentrations required to make the simulation match the measured values will be equal to the concentration difference between the two fields. The plots in Figure 2 demonstrate that these constituents are easily detected and that lower concentration differences will also be seen. The limiting factor for lower limit of detection is the noise of the instrument, which is illustrated in the error section.

LPFTS Error

The three significant sources of error in LPFTS are present in the instrument calibration, instrument noise and in the cross sectional data used by the FASCD3 model (Clough et al, 1995). Table 1 quantifies the amount of error associated with each source.

Error Sources	Error (%)
Instrument Calibration	3.0
Instrument Noise	0.6 - 100
Cross sectional data	2.2
Total Error *	**3.8**

Region (cm^{-1})	0.125 cm^{-1}	0.25 cm^{-1}	0.5 cm^{-1}
900-1100	1.055 %	0.665 %	0.295 %
2700-2900	0.592 %	0.373 %	0.165 %
4500-4700	0.563 %	0.355 %	0.158 %

Table 1 & 2: (1) Shows the contribution of the various error sources to the total error. Since each error source is independent of one another the total error is calculated by taking the square root of the sum of the squared error sources. * This total error is based on 0.6 % instrument noise and a 5-minute 0.125 cm^{-1} measurement.(2) Shows the noise values at different spectral resolutions.

The instrument noise contribution varies due to length of time and spectral resolution. The noise for two complete 5-minute measurements (digested and raw manure) equals 0.5921 % peak to peak at a resolution of 0.125 cm^{-1}. Now if the depth of the absorption feature is only 0.5% then the noise contributes 100 % error. Obviously the LPFTS method would not use such a peak. Figure 3 shows a typical absorption feature where the noise in this case would only contribute 2 %. The noise value can also be improved by reprocessing the measurement at a lower resolution if the absorption feature in question does not require a high resolution to measure it accurately. Table 2 shows the various noise values for each part of the spectrum under different spectral resolutions. The error can be improved further by repeating the analysis procedure on multiple absorption features belonging to the atmospheric constituent in question. This will reduce the error by a factor of $1/\sqrt{N}$ where N is the number of absorption features
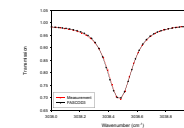

Figure 3: Shows the agreement between the measurement and the model for a single CH_4 absorption feature.

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