Trace Detection of Nitrous Oxide in Soils Using Infrared Spectroscopy Method

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Introduction

According to NOAA's Global Greenhouse Gas Reference Network, the atmospheric concentrations of nitrous oxide (N_2O) increased from 270 ppb to 328 ppb between 1750 - 2015. Whereas soil and manure management practices are regarded as major contributors to N_2O emissions, emissions from natural agricultural soils plays a major role in the total N_2O emission budget. Emissions of N_2O from agricultural lands can vary depending on the soil type. According to the 2012 census data, Putnam County has a total of 31,445 acres of agricultural land. As the most common type of soil in these agricultural lands, loam soils can contain N_2O mole fractions ranging from 0.04 to 0.78, depending on whether the land is already cultivated with growing crops or is just manured. In this poster, the viability of Gas Chromatography and Fourier Transform infrared (FTIR) spectroscopic techniques in detecting and quantifying trace concentrations of N_2O from Putnam County agricultural soils is being investigated.

Why N_2O?

- N_2O is the 3rd largest anthropogenic contributor to GHG emissions.
- N_2O has a higher radiative forcing of about 300 times that of CO_2.
- Average atmospheric lifetime of N_2O is 150 years.
- Breakdown of N_2O in to NO in the stratosphere results in Ozone (O_3) layer depletion.

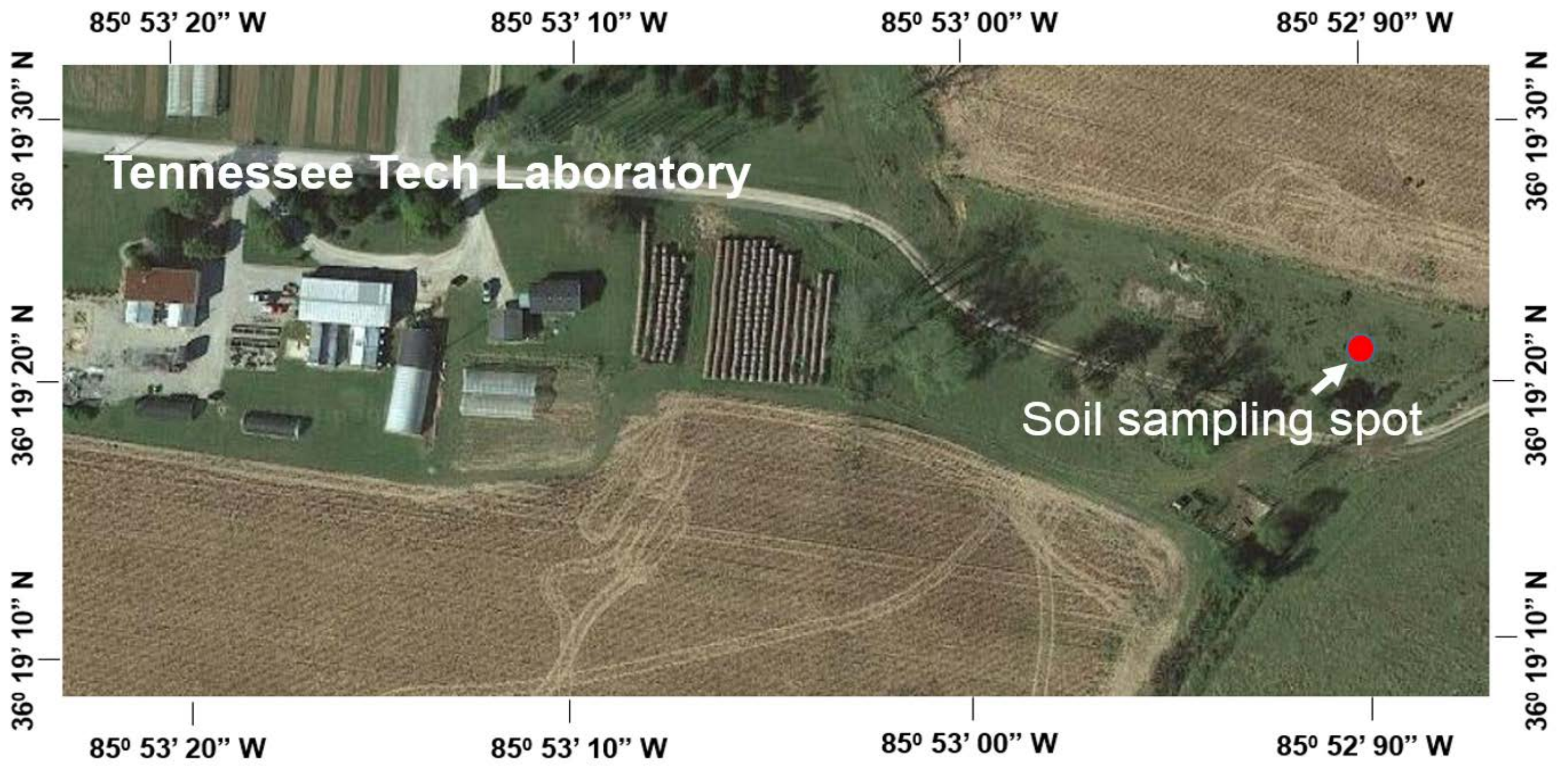
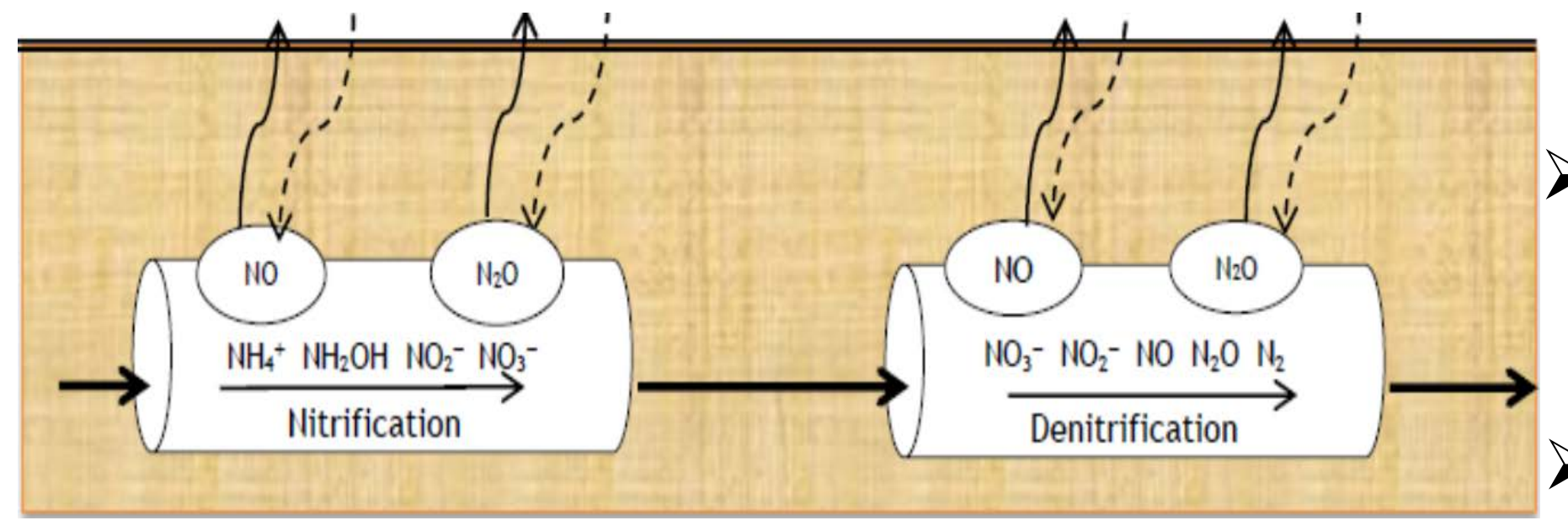


Fig 1: Map of the soil sampling site, Cookeville, TN.

Table 1: Different soil types and the annual N_2O emissions

Location (ref.)	Soil type (Loam)	Annual N_2O emission kg ha^{-1}	N_2O emission ppb
North China (Wang et al.2014)	Silt loam	0.093 - 0.470	62 - 313
California (Bouwman et al., 1996)	Yolo loam	0.100 - 9.900	66 - 6,600
Iowa (Bouwman et al., 1996)	Clay loam	0.330 - 19.600	220 - 13,066
Texas (Bouwman et al., 1996)	Sandy loam	0.070 - 1.370	46 - 913
Iowa (Bouwman et al., 1996)	Silty clay loam	0.380 – 1.920	0.380 – 1.920
Germany (Bouwman et al., 1996)	Sandy clay loam	0 - 0.380	0 - 0.253
California (Bouwman et al., 1996)	Fine loam	7.680 – 41.800	5,200 – 27,866



$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

- Denitrification (wet conditions, and in slowly draining soils)

$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow N_2O$

- Nitrification (well drained and during drier period)

Ref. Firestone and Davidson (1989) and Davidson et al. (2000)

Fig 2: Nitrification and denitrification of soils

Factors that influence N_2O production and emissions in soils

- Organic matter inputs
- Ammonium and Nitrate based fertilizer
- Soil moisture
- Soil pH
- Microbial activity
- Soil temperature
- Tillage, residue inputs
- Irrigation

Experimental techniques and Methods

Static Chamber method in N_2O sampling

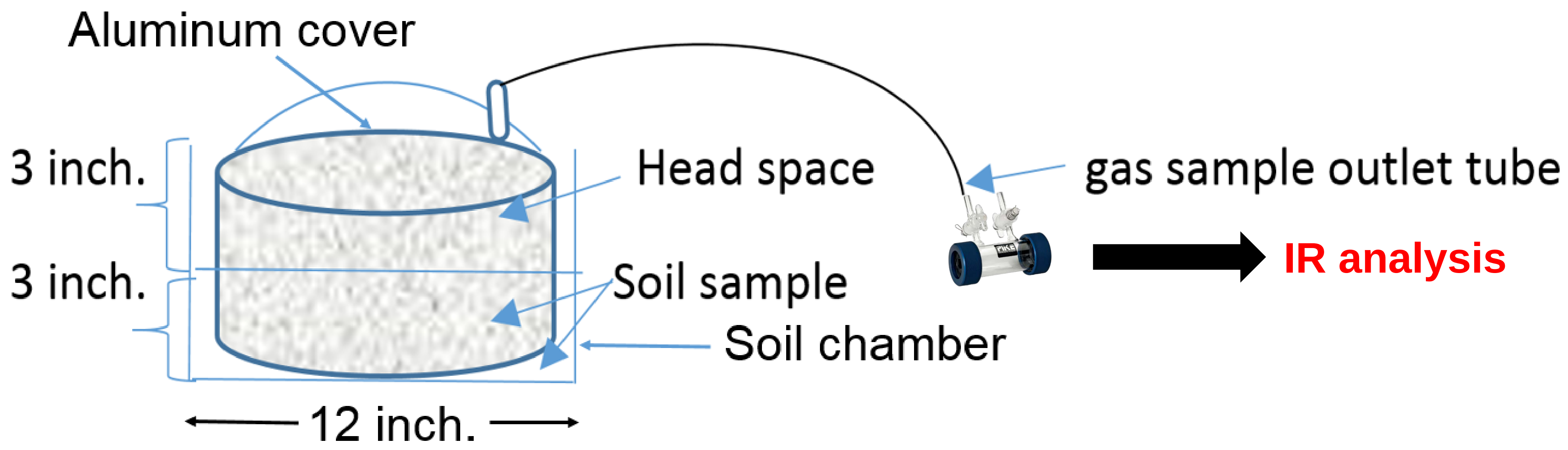


Fig 3: Schematic diagram of soil chamber, chamber parameters and the gas cell

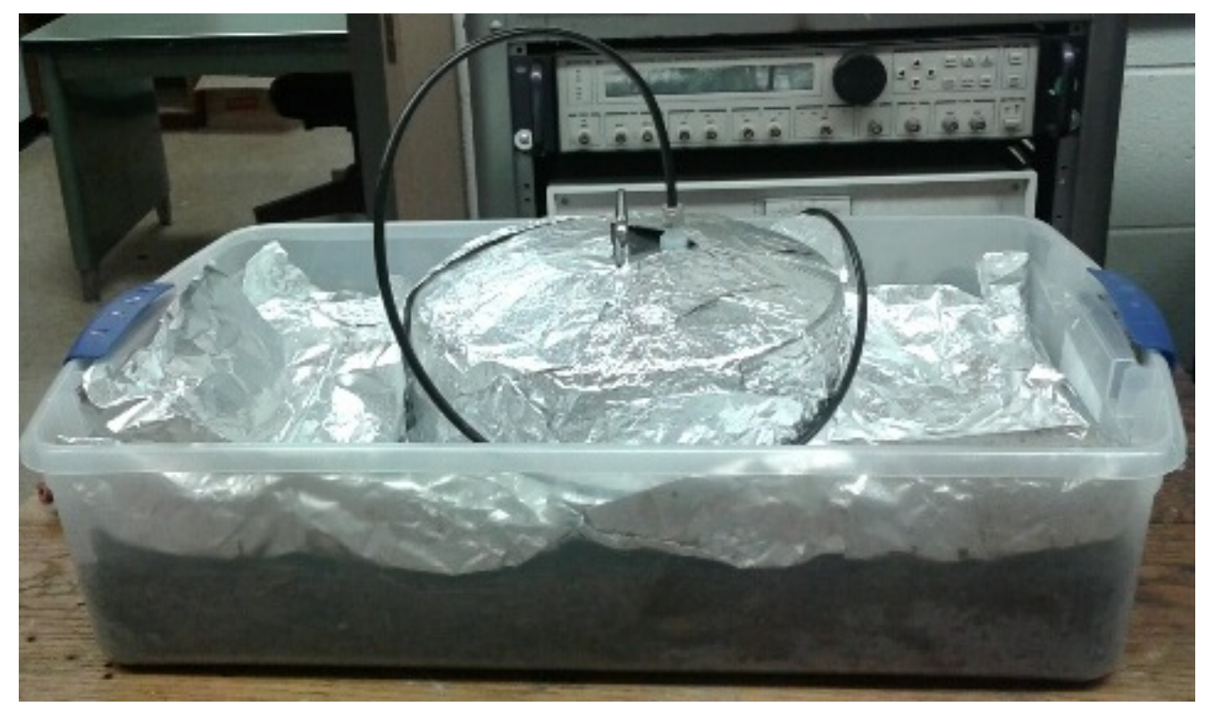


Fig 4: Soil sample in the lab.

- Half of the soil chamber is buried in the soil sample and covered at least 2 hours prior to the gas sampling from the head space.
- Volume of the soil sample inside the chamber and the headspace volume of the chamber is approximately similar.
- Gas samples from the chamber headspace were collected in 30 minutes intervals after covering the soil sample.

N_2O flux measurements

- Determine the area/height of known N_2O samples and prepare a calibration curve, then determine the concentration of unknown N_2O samples by using the calibration curve.
- Convert gas concentration from volumetric to mass using the Ideal Gas Law ($PV = nRT$).
- Plot time vs concentration graph and perform linear regression.
- Use the slope of the regression to calculate flux: $F = S \cdot V \cdot A^{-1}$

F = N_2O flux, S = slope of the regression, V = chamber volume, A = chamber area.

Results and Discussion

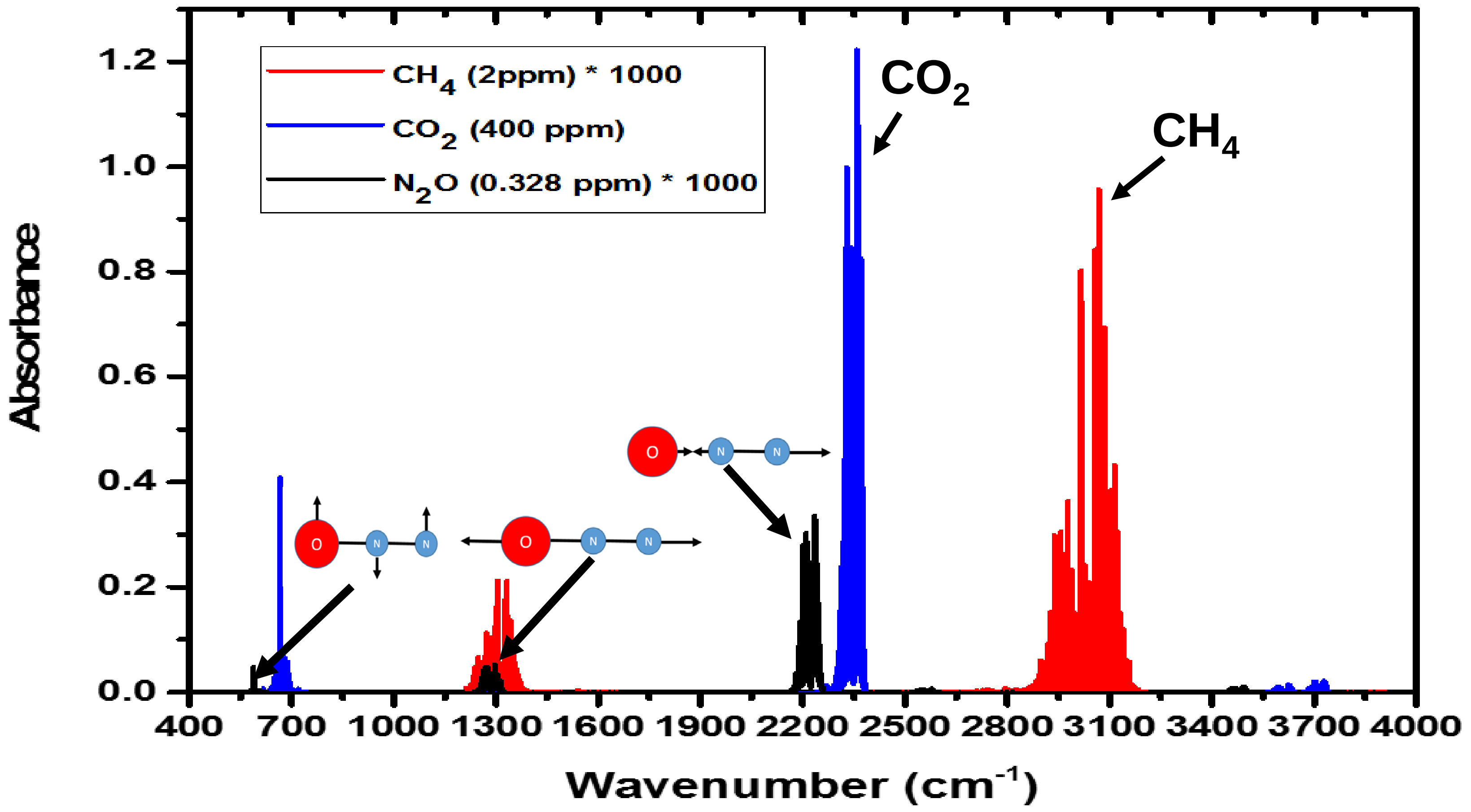


Fig 5: Simulation plot of CO_2, CH_4 and N_2O at 25⁰C temperature, 760 torr pressure, 0.25 cm^{-1} resolution and 10 cm path length of the gas cell.

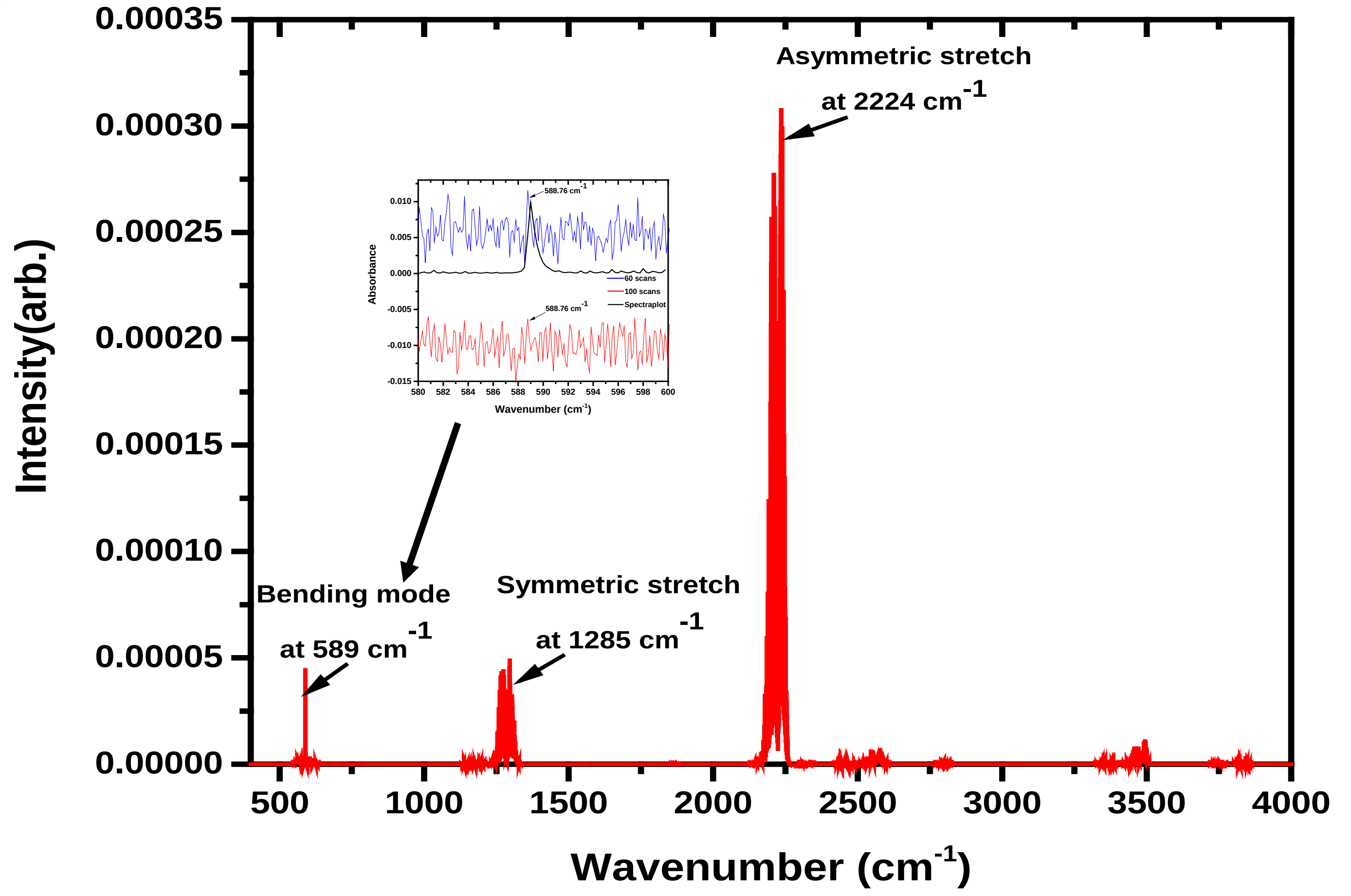


Fig 6: Atmospheric simulations of N_2O mid IR spectra with an experimental N_2O bending mode inserted at the top

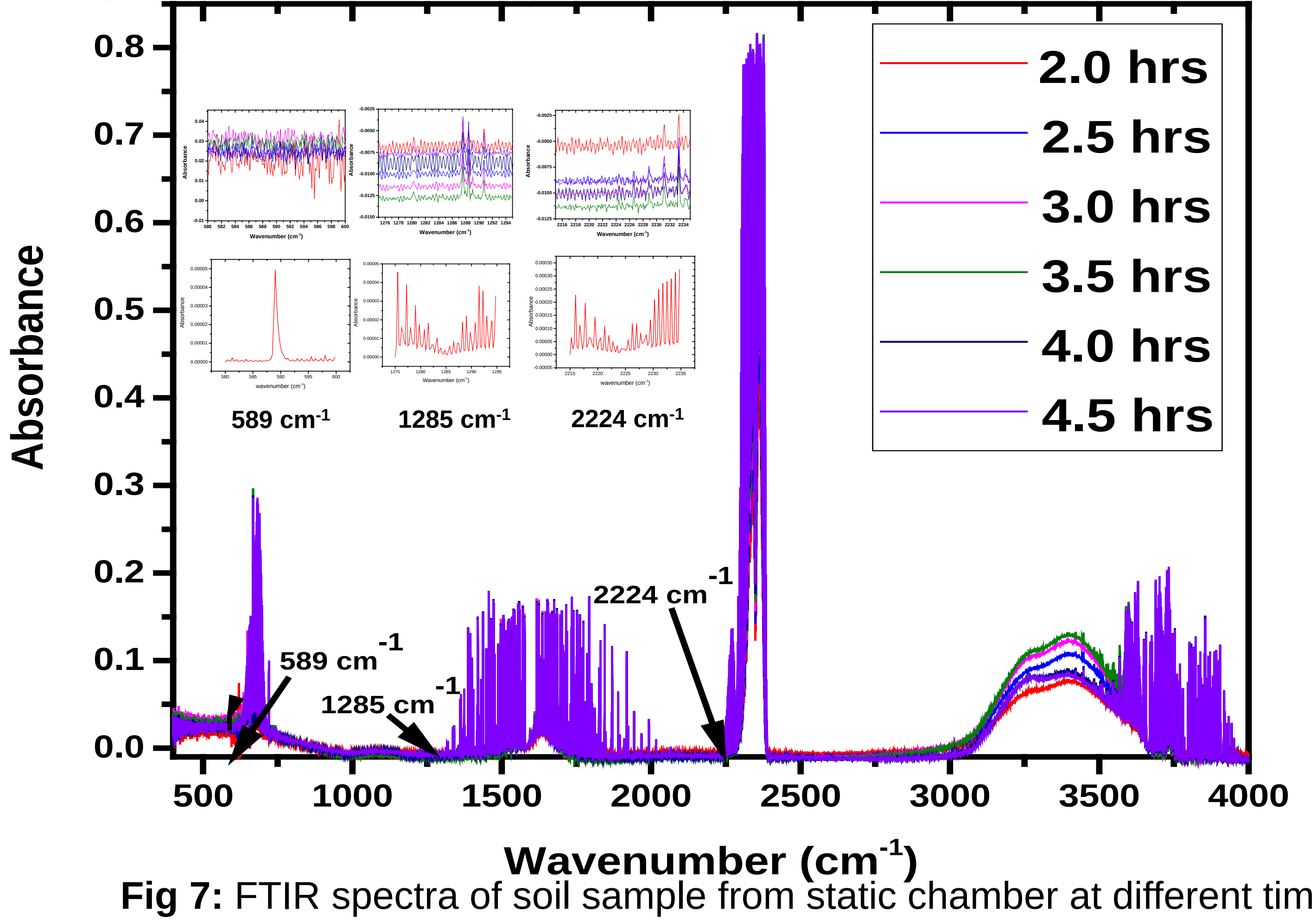


Fig 7: FTIR spectra of soil sample from static chamber at different times

Conclusions and future directions

- N_2O flux measurements are difficult to quantify using FTIR due to low signals (ppb levels) and overlap with CO_2, CH_4 and other hydrocarbons at region of interest.
- Longer time measurements in a static chamber may allow for accumulation of appreciable N_2O signals.
- Future plans in to quantify N_2O using GC and IR techniques (after carefully calibration with known N_2O standards)

References

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