Author's Response

Part-I: Point-by-point response

1. Two citations were suggested
    a. Errors in absorbance measurements in infrared Fourier transform spectrometry because of limited instrument resolution (R.J. Anderson and P.R. Griffiths, Anal. Chem., 47, 2339-2347 (1975).
    b. Extending the range of Beer's law in FTIR spectrometry. Part I: Theoretical study of Norton-Beer apodization functions (C. Zhu and P. R. Griffiths, Appl. Spectrosc. 52, 1403-1408, 1998.

Response:

"Zhu and Griffiths, Appl. Spectrosc. 52, 1403-1408, 1998" was included.

2. A discussion as why the effect of increasing the temperature above ambient and changing the relative humidity reduces the accuracy to which the concentration of the analytes can be predicted would have been useful.

Response:

We did simply mention temperature-broadening effect in the manuscript. More discussions are addressed in the modified manuscript.

3. Define zero-filling factor (ZFF)

Response:

In this study, the zero-filling factor (ZFF) stood for a power of two (i.e., 2^n, n = 1,2, …, m), so that 'ZFF of one' meant that one interpolated data points was artificially added within each resolution (0.5 cm^{-1}) to increase the resolution of instrument which was 0.25 cm^{-1}.

4. S-OPS abbreviation.

Response:

The term of the S-OPS was defined in the text at the page 6.

5. Clarify the physical paths that we used: not only 150 m, but 50 and 100 m.

Response:

Three path lengths (physical path = 50-, 100-, and 150-m) were used in the field OP-FTIR experiment. Only the path length of 150-m was used to study the effect of water vapour, temperature, and the wind speed on the quantification of N_2O and CO_2 concentrations in the field. The path lengths of 50-, 100-, and 150-m were used to investigate the effect of the path length on gas quantification. That would be a good idea to simplify the path length from three different paths to one path of 150-m in Figure-1.

6. How do the N_2O estimations quoted in the abstract reconcile with those from the companion paper (-4.9% for N_2O with CLS over 5,000-20,000 ppmv water from from 10-35 °C). In general, if there was discussion of how this study is distinct from the companion paper, which also presents calculated bias results, then I missed it and it needs to be highlighted more.

<u>Response</u>:

For both papers, quantitative biases of gas concentrations were calculated by comparing the path-averaged concentrations between the synthetic open path gas sampling system (S-OPS) and the open-path FTIR (Eq-1 at the P6L31). The main objective of the companion paper (Application of open-path Fourier transform infrared spectroscopy (OP-FTIR) to measure greenhouse gas concentrations from agricultural fields) was to optimize the methods, including the selections of single-bean backgrounds, analytical regions, and multivariate models (CLS vs PLS), for quantifying gas concentrations. The averaged N_2O bias of -4.9±3.1 % was calculated from ninety spectra which contained similar N_2O concentrations (338±0.3 ppbv) with different humidity (5,000-20,000 ppmv) and temperature (10-35 °C) using the CLS model. The PLS model was capable of improving the accuracy of gas quantification (i.e. bias =1.4±2.3 %). The main objective of this paper is to evaluate the sensitivities of CLS and PLS models to the ambient temperature and humidity for gas concentration calculations. The results showed that CLS was not only more sensitive to the ambient variables than PLS models for concentration calculations, but highly correlated to ambient temperature which likely resulted from the temperature broadening effect of the gas rotation-vibrational absorption features. This study showed that the CLS underestimated N2O concentrations by 3% from lab-FTIR experiment and by 12% from the OP-FTIR experiment when the reference and sample spectra were collected at the same temperature (no temperature variation), which is highlighted in the abstract.

7. Section 2.1.2: I found the descriptions of how CLS and PLS models are built and used to derive concentrations from lab absorption spectra (33 m path) unclear, with key method references not sign posted for the un-initiated reader. Why are the N2O reference spectra at 30, 35 and 40 C? Surely these are on the very high end of atmospheric temperatures during an Indiana summer?

<u>Response</u>:

The spectra containing single gas species (e.g. N_2O or water vapour only) were used to build CLS models, and the spectra containing mixed-gas species (e.g. N_2O mixed with water vapour) were used to build PLS models. Two CLS and one PLS models (CLS-1, CLS-2, and PLS shown in the following table) were built based on the source of reference spectra in this study. The CLS-1 model was created using five N_2O spectra (i.e. 310, 400, 500, 600, and 700 ppbv) and four water vapour spectra (i.e. 7K, 15K, 22K, and 28K ppmv) collected from the lab-FTIR spectrometer at 30 °C. The CLS-2 was created using twelve N_2O spectra and sixteen water vapor spectra generated from HITRAN database at 30 °C (see the table S1 in the supplement). The PLS model was created using a total of sixty mixed-gas spectra (N_2O mixed with water vapour) collected from the lab-FTIR spectrometer at 30 °C (see the table S1 in the supplement). Validation/wet sample spectra of the wet N_2O were both collected from the lab- and OP-FTIR spectrometers to evaluate model performances. The CLS-1 and PLS were used to calculate N_2O concentrations from the validation spectra (wet N_2O) collected from the lab-FTIR; the CLS-2 and PLS were used to calculate N_2O concentrations from the validation spectra collected from the OP-FTIR (see the following table). Since these quantitative models are temperature-specific (i.e. 30 °C), the temperature variation between reference and the validation/sample spectra lead to biased in gas quantification. For instance, the OP-FTIR validation spectra were collected at 10-35 °C in field experiment (9-19 June 2014) and a strong correlation between temperature and the CLS-quantified biases was observed from the field measurements (Fig-5d in the manuscript). A weak correlation between water vapour and biases, however, were also observed. It was difficult to isolate the effect of the temperature and humidity on quantitative biases from the field experiment, so that the validation spectra with the fixed concentrations of N_2O and water vapour (310 ppbv N_2O mixed with 21,500 ppmv water vapour) collected at 30, 35, 40 °C from the lab-FTIR to evaluate the sensitivity of CLS and PLS to temperature (Fig.4 in the manuscript). The increased water vapour content was not necessary to increase N_2O biases within the water vapour range of 5,000-20,000 ppmv (Fig.2 in the manuscript).

Table1. Multivariate models (i.e. CLS and PLS) used for N_2O and CO_2 quantification: 1) the CLS-1 model was built by five dry N_2O spectra (310, 400, 500, 600, 700 ppbv) and four water vapour spectra (7 000, 15 000, 22 000, 28 000 ppmv) collected from the lab-FTIR, 2) CLS-2 model was built by twelve dry N_2O, seventeen dry CO_2, and sixteen water vapour spectra generated from the HITRAN database (see Table S1), and 3) the PLS model was built by a total of sixty wet N_2O spectra collected from Lab-FTIR (see Table S2).

Model	Training/Reference spectra	Source	Validation/Wet Sample spectra	Source
CLS-1	Dry N_2O: 310-700 ppbv Water vaour: 7,000-28,000 ppmv	Lab-FTIR	N_2O	Lab-FTIR
CLS-2	Dry N_2O, CO_2, water vapour: see Table S1	HITRAN	N_2O, CO_2	OP-FTIR
PLS	Wet N_2O: see Table S2	Lab-FTIR	N_2O	Lab- and OP-FTIR

8. Section 2.2.2: I would like to see the specific rejection criteria used in this study for QA and QC listed, along with the proportion of resultant data loss. Again, not clear on why single-gas reference spectra were generated with HITRAN for CLS while PLS models were built from the lab FTIR measurements. Why not use HITRAN to generate PLS models, too? Also in this section, it is not clear how NLLS regression is used in the CLS model (P6L9) – please explain. Finally, what is the accuracy of the N2O and CO2 gas analyzers that OP-FTIR results are being bench marked against?

Response:

1) In this study, there were no specific rejection criteria for ambient temperature and water vapour content which variation between reference and sample spectra resulted in quantitative bias. Our study was more interested in the ‘delta concentration’ between two measurement points to calculate gas fluxes than the absolute concentrations measured from the measuring points. The delta concentration/fluxes were measured every thirty minute. Since ambient temperature and humidity presumably remained stationary within thirty minutes, the effect of temperature and humidity variation on the delta concentration can be negligible. The path length set-up and wind condition, however, significantly influence the calculation of delta concentrations and fluxes. For instance, a set-up of the short path length (e.g. physical length = 50 m) resulted in greater underestimations than a long path length (e.g. physical length = 100 m or 150 m). Difference path length set-ups (i.e. short and long) likely distorted the actuality of the delta concentration and led to biases in flux estimations. Thus, the criterion for path length is to make sure the same path length used in the measurement system, either short (i.e. physical length less than 100 m) or long (i.e. physical length greater than 100 m) path lengths. The poor-mixed air (wind speed < 2 m s^{-1}) also led to uncertainties in delta concentration, so that the concentrations collected under low wind condition (< 2 m s^{-1}) were excluded.
2) Ambient variables likely interfere with the quantification of gas concentrations from the OP-FTIR spectra, resulting in unknown bias. One of the advantages of using PLS models is that numerous ambient variables can be considered in PLS models simultaneously. For instance, reference spectra containing different gas species, concentrations, temperature, humidity, and pathlength, etc. can be considered in one PLS model for concentration calculations. The HITRAN database has been widely used to generate the single-gas spectra to create the quantitative model, mostly CLS and NLLS; so, we only generated the single-gas spectra using the HITRAN. Instead, the lab-FTIR were used to collect the spectra which both contained N_2O, water vapour, and temperature.
3) The third-degree polynomials were used for the NLLS regression applied in CLS model using the IMACC software (Industrial Monitoring and Control Corp., Round Rock, TX). More details are described in the IMACC manual (see the supplement materials).
4) Both N_2O analyzer (IRIS 4600, Thermo Fisher Scientific Inc., Waltham, MA) and CO_2 analyzer (LI20 840, LI-COR Inc., Lincoln, NE) provided high precision for N_2O (< 0.15 ppbv, 1σ) and CO_2 (< 1.0 ppmv, 1σ) concentration measurements and calibrated using the certified standard gas every four hour to insure the stability of analyzers as well as the accuracy for gas measurements.

9. Figure 3 shows that water vapour overlaps the N2O P-branch. How does it “compromise” the intensity of the N2O P-branch (P7L21)? The authors suggest that it is via resolution (P7L26), but given how systematic the “compromise is”, could it not result from the background correction? Please discuss.

Response:

The N_2O (310 ppbv) spectra were acquired in both dry and wet (28,000 ppmv water vapour content) conditions. Ideally, the N_2O absorbance/intensity should be identical because of the same concentrations (310 ppbv). The intensity of the N_2O P-branch in the wet N_2O spectra (red solid line) was observed to be lower than the dry N_2O spectra (black solid line) (Figure 3 in the manuscript). To resolve the strong overlap of water vapour in N_2O spectra, the inadequate resolution (0.5 cm^{-1} in this study) was considered as one of the possibilities that cause this issue (intensity reduction in wet conditions). The single-bean backgrounds were acquired before both dry and wet N_2O measurements.

10. ‘’greater interference at increased temperature” by water vapour (P8L13) presumably means increased line strength in highly temperature-sensitive water vapour lines? Can the worst offenders be avoided via spectral window selection?

Response:

Yes, the increased intensity of water vapour with increasing temperature was observed in Figure 4b. It is difficult to avoid the water vapour interference, but this interference could be mitigated via window selection (e.g. W_N1 vs. W_N3 in CLS models shown in Figure 4a in the manuscript).

11. Are water vapour and temperature really confounding variables (P8L21) or are their effects in spectra truly indistinguishable (more water vs. greater line strength)? In Figure 5, R2=0.20 (weak) with water and R2=0.86 (strong) with temperature. Furthermore, temperature and RH can be independently measured and in the NLLS approach with calculated HITRAN-based spectra RH and T can be specified independently. Please clarify.

Response:

Temperature is considered as a confounding variable influencing both humidity and quantitative bias. The higher temperature tends to have higher water vapour content in the air. In this study, the increased temperature increased biases ($R^2 = 0.86$), and the spurious correlation between water vapour content and bias ($R^2 = 0.20$) likely resulted from temperature effect (i.e. the confounder).

12. In explaining the excess bias in field values of N2O interferences by CO and CO2 are invoked as “presumable”. Can one not look at the spectral fit residuals to see if CO and CO2 interferences are being captured correctly?

Response:

N_2O concentrations were calculated from the analytical window of 2224-2170 cm^{-1} which includes the information of N_2O, water vapour, CO, and CO_2 (see the following Fig.2).

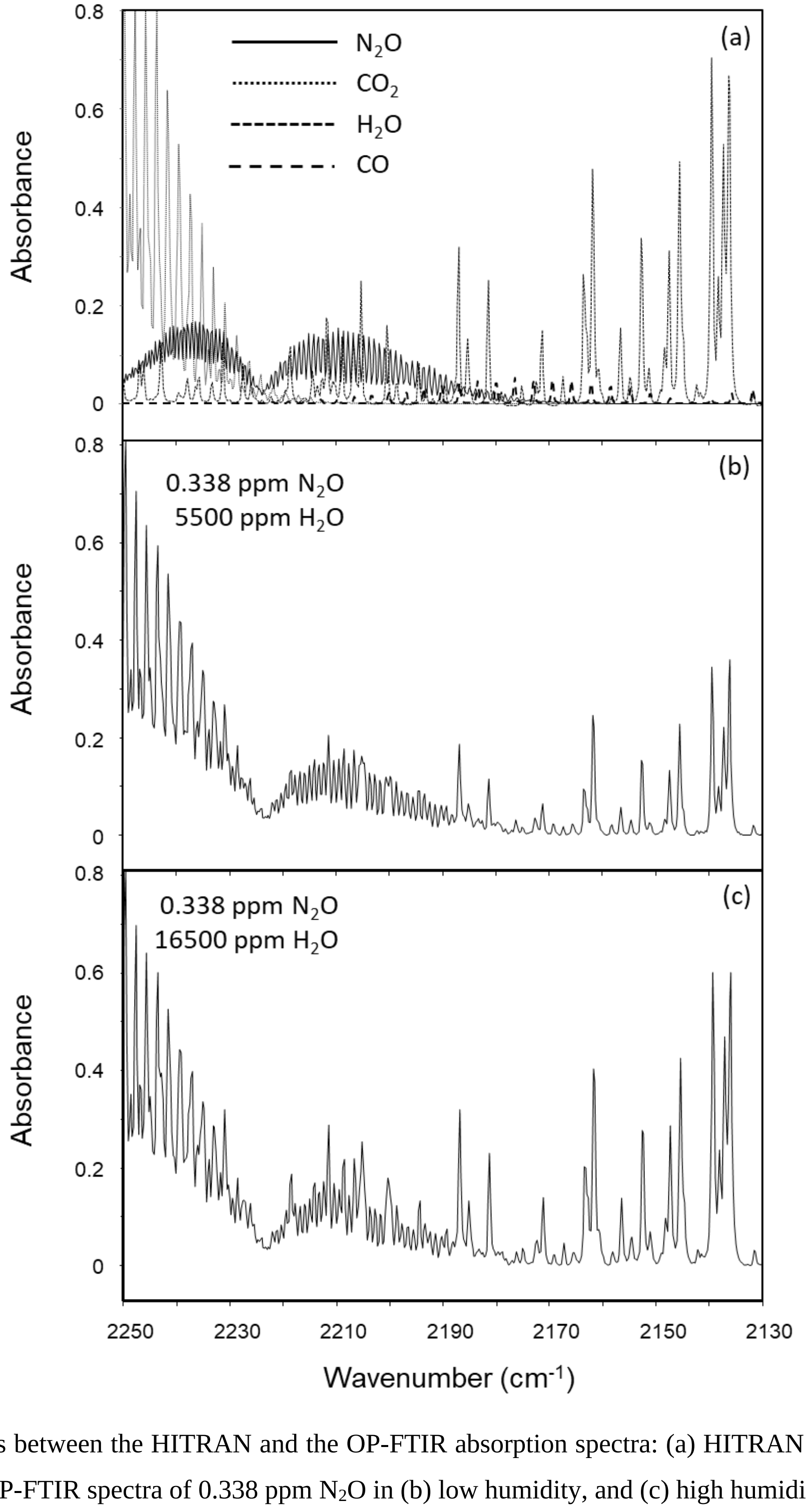

Fig.2 – Comparisons between the HITRAN and the OP-FTIR absorption spectra: (a) HITRAN N_2O, CO_2, CO, and water vapour, and OP-FTIR spectra of 0.338 ppm N_2O in (b) low humidity, and (c) high humidity conditions.

13. In explaining the short-path bias in field values of N2O, inadequate resolution is invoked as "presumable". Can this not be pinned down more firmly with some test retrievals on synthetic spectra? Is the N2O absorption depth greater than the spectral noise for the 50 m path? Why is the CO2 bias changing at all with path given the very strong absorption signals even at short paths?

Response:

The non-linear relationships between the path length and absorbance respond to different spectral resolution and analyte species (Russwurm and Phillips, 1999: Effects of a nonlinear response of the Fourier-transform infrared open-path instrument on the measurements of some atmospheric gases). For the OP-FTIR spectra, the overlap of multiple species in the spectra further complicated the non-linear responses between path length and absorbance to changing resolution, which might not be easily solved using the single-specie synthetic spectra. The physical length of 50-m/optical path length of 100-m couple with the 64 scans should give us the adequate ratio of single to noise for each spectrum. Compared with the absorption features of N_2O at 2170-2224 cm^{-1}, the less complicated features of CO_2 absorption make CO_2 quantification less sensitive to a short path length than N2O quantification using CLS model (Figure-6 in manuscript). CO_2 absorption was also overlapped by water vapour at 2075-2080 cm^{-1}, and the effect of water interferences on gas quantification became severe for the low CO_2 absorption spectra acquired from a short path. The 'stronger' absorption signal from a short path was attributed to a strong water vapour signal.

14. P10L14: In explaining the greater bias variability of CO2, the authors presume a greater environmental variation in CO2 than N2O. What would be the biogeochemical and/or physical reason for that? Is respiration (night) more variable than photosynthesis (day)? Do you mean here that 22% of all measurements are calm and at night while 36% of all measurements are calm and during the day? Please clarify.

Response:

1) Since quantitative bias was calculated by comparing the path-averaged concentrations between the S-OPS and OP-FTIR, the spatial distribution of gas concentrations in the atmosphere substantially influence the bias calculation. For instance, CO_2 can be produced from both soil and canopy respirations, and plant uptake via photosynthesis. N_2O was predominately produced from soil nitrification and denitrification. The CO_2 concentrations as well as their spatial distribution in the air were influenced by the variabilities of both soil properties and crop species (different sources). Thus, CO_2 concentrations in the air tended to have higher variabilities than N_2O and become highly heterogeneous if the air was poorly mixed in the low wind condition (< 2 m s^{-1}).
2) We do not know if the respiration or photosynthesis lead to more variation in CO_2 concentrations.
3) During 9-19th 2014, a total of 259 data point (30-min averages) was collected during the daytime measurements (06:00-20:00, LT) and a total of 130 data point was collected from the nighttime measurements (20:00-06:00, LT). The low wind conditions can occur during both day and night (it is more common to have a low wind condition at night). In this study, 22% of all daytime measurements are calm, and 36% of all nighttime measurements are calm.

Editor's comments

1. This paper provides a useful qualitative guide to practitioners of OP-FTIR spectroscopy for atmospheric analysis of the systematic errors and biases that arise with commercial low resolution spectrometers using commercial analysis packages based on CLS and PLS chemometric methods. However the authors provide no evidence that the quantitative errors observed and documented in detail here will translate to other instruments and field setups with different resolutions, instrument lineshapes, pathlengths and other conditions. I therefore do not agree with the last sentence of the abstract, which should be removed – this studies serves as a qualitative guide, but not a reference for other users (see also RC2 page C2).

   <u>Response</u>:

   The authors added more details and discussions as the editor and referrers requests in the manuscript. The last sentence in the abstract was rephrased to 'This study identified the most common interferences that affect OP-FTIR measurements of N_2O and CO_2, which can serve as a quality assurance/control guide for current or future OP-FTIR users'.

2. P10L13 (RC2 page C2 ref P3L17) This comment has not been addressed in the authors' response. It is essentially the same comment as made in my initial access review. This work demonstrates significant and complex biases in quantitation using CLS and PLS, including non-linearity and cross-dependency between variables – in this sense it is a useful contribution to the field for the users of commercial chemometric software packages. These sources of error are already well known and recognised from earlier studies. They are less prevalent in a least squares fitting approach to spectrum analysis as now referenced in the papers on L14. RC2's question "What advantage does CLS and PLS offer over NLLS as implemented in the works cited here?" should be addressed, perhaps by a short review paragraph which points out the pros and cons of each approach.

   <u>Response</u>:
   A short review paragraph was added in the introduction (the 5th paragraph) to describe the pros and cons of these methods.

3. P10L22: "The influences…" The meaning of this sentence is unclear. HITRAN provides a database of absorption line parameters from which an absorption spectrum for any combination of temperature, pressure and gas composition (including mixtures) can be calculated. This is the approach used in NLLS analysis in which the spectrum is iteratively calculated until a best fit to the measured spectrum is obtained. Please clarify.

   <u>Response</u>:
   The sentence was rephrased and the authors want to emphasize that only limited studies examined how the dynamics of environmental variables affect gas quantification using CLS and PLS models.

4. P11 section 2.1.1 and P12 section 2.2 – sample and atmospheric pressure: I cannot find any reference to pressure measurement or control, or pressures used in the CLS/PLS generation of calibration models or analysis of unknowns. Pressure has an important effect on the spectra, as does temperature (for example linewidths are proportional to pressure). In the lab measurements I presume the pressure has been measured and controlled to be the same for calibration and analysis measurements. If so, please state so. But how was pressure included in the open path analysis? Atmospheric pressure will change from hour to hour and day to day, yet the calibration models are presumably built

at a single pressure and temperature. Pressure and temperature have two separate effects on retrieved mole fractions in air: (1) the spectroscopic analysis fundamentally determines a concentration*pathlength product, from which the concentration (in mol/m3 or similar) is determined. To convert to a mole fraction (eg ppm or ppb) requires the density of air, P/RT. How is this done with the software used? (2) molecular lineshapes are both pressure and temperature dependent, leading to errors of the calibration spectra and unknown spectra are measured at different pressures and temperatures. This spectroscopic effect is independent of the density effect (1). The treatment of pressure and pressure variability should therefore be addressed.

<u>Response:</u>
In lab-FTIR experiment, gas samples were continuously introduced into the White cell with a constant flow rate and the sample pressure was controlled close to the room ambient pressure. The spectra (both training and sample spectra) were collected when the sample concentrations, temperature, humidity and pressure became constant. The training spectra from HITRAN were generated at the pressure of 760 torr. The barometric pressure in the experiment field was measured from 981 to 996 hPa. Compared with the wide ranges of temperature (10-35 °C) and water vapour content (5000 to 20 000 ppmv), the effect of this small variations in the pressure (989.3±3.2 hPa, n = 355) on linewidth as well as gas quantification was not examined and, the measured pressure was only used to adjust the model-calculated concentrations in this study. The potential errors driven by pressure broadening effect was addressed in the results (P10L25). The format of the HITRAN output was specified the product of molar fraction and path length (ppm*m). The HITRAN references were generated at 30 °C and 760 torr. The measured sample/field temperature and pressure can be imported in the quantitative software to adjust the model-calculated molar fraction to the air-density-corrected molar fraction, which was also addressed in P7L4.

5. P11L17: The synthetic reference mixtures were prepared using N2 as a buffer gas rather than air. Line-broadening coefficients for N2 and air are different, and this will add a systematic bias to the reference measurements of N2O relative to air. This error should be addressed and corrected, or included in the error analysis.

<u>Response:</u>
In lab experiment, N2 was used as the background gas to collect both training and sample spectra. Authors specified air as the buffer gas to generate HITRAN training spectra. Therefore, CLS-1 and PLS were based on N2 buffer, and CLS-2 was based on the air. The N2-induced error was addressed in P10L21 to explain the quantitative error of the N2O concentrations calculated from the OP-FTIR spectra using the PLS model.

6. P12 L21. Zero filling (RC1): Different FTIR manufacturers and users define “ZFF” differently and it is probably better to avoid this term. From Figure 3 it appears that the point spacing is approx. 0.25 cm-1 or half the 1/maxOPD resolution of 0.5 cm-1. This means the interferogram is minimally sampled and corresponds to NO zero filling, ie the interferogram is extended with zeros only up to the next power of 2 points beyond the highest OPD point (a filling factor of 1, but for example the Bruker and RC1 definition would call this ZFF=2). The best way to resolve this ambiguity is to say “no zero filling” rather than quoting a ZFF value. With no zero filling the point spacing is 0.5/maxOPD.

<u>Response:</u>
All zero filling was changed to no zero filling to avoid confusion (P6L14).

7. P11 2.1.2 (RC2) I agree with RC2's comment that the CLS and PLS calibration details are lacking and should be expanded in the paper along the lines in the response – it is not sufficient to respond only to RC2, but to make the methods used clear to all readers in the paper, with sufficient detail that they could repeat the analysis given the same set of data, or their own data. The respective software packages for quantitative analysis have only been presented as a "black box". The claim in the abstract that this paper can be a reference for future work could only stand up if all details of the analysis are presented.

   Response:
   More details were added in 2.1.2 (Data collections and gas quantification for lab-FTIR) and 2.2.2 (Data collections and gas quantification for OP-FTIR) along with the additional table 1. For the details of generating the synthetic background can be found in the companion paper.

8. How were the single gas reference spectra calculated from HITRAN data? This is a non-trivial calculation (see eg Griffith 1996), and it is very important to know details of both the molecular spectra and the convolution with the FTIR instrument function if these spectra are to be quantitatively compared with measured spectra (via the CLS/PLS models). It is also not clear exactly what the IMACC software has been used for, or how. In the manual provided in the supplement there is only a description of the user interface, not the underlying calculations or physics behind them. Was IMACC used to calculated SB spectra from Hitran data, or only to generate ABS spectra from measured spectra and background? If not, how were they calculated? None of this is clear. As above, the description should be in principle sufficient for another practitioner to follow your method and achieve the same results.

   Response:
   HITRAN: Training absorption spectra used in the CLS model were generated from the HITRAN database using E-trans (Ontar Corporation North Andover, MA). Briefly, high-resolution spectral lines of N_2O, CO_2, and water vapour output from E-trans were interpolated to generate spectra ranging from 500 cm^{-1} to 4000 cm^{-1} and convolved with a triangular apodization function. The convolved spectral lines were used to generate the reference spectra with the identical resolution and data point density matching the field spectra using Grams/32 (Childers et al., 2001). The HITRAN reference spectra were generated at the pressure of 760 torr and temperature of 30 °C.

   IMACC: The stray-light corrected field SB spectrum was converted to absorbance spectra by the synthetic SB background (syn-bkg) spectra using the IMACC Quantify package (Industrial Monitoring and Control Corp., Round Rock, TX). The syn-bkg was generated by selecting multiple points from the spectral interval of interest (i.e. six points within 2050.0–2500.0 cm^{-1} for N_2O and CO_2) to fit the curvature of the sample SB spectrum using a polynomial function (Lin et al., 2019). Three spectral windows (Table 2) and the HITRAN references were used to build the CLS model (CLS-2 shown in Table 1) in the IMACC software. The third-degree polynomial function was used to correct the non-linear response of the CLS-calculated concentration to the actual concentration. More details regarding the IMACC quantification package were described in the IMACC user manual attached as the supplementary material. The PLS models were built using lab-FTIR measurements and only used for estimating N2O concentrations. Since the molar fraction changes with changing air density which is the function of temperature and pressure, the measured temperature and pressure in the gas cell and experimental field were imported in the quantitative software to adjust the model-calculated concentrations.

   Both details were added in the section of 2.2.2 (Data collections and gas quantification for OP-FTIR)

9. P13 L16: What is the accuracy (not precision) of the IRIS and Licor analysers used to measure the S_OPS samples? How were they calibrated. Any systematic bias or error in these calibrations feeds directly into the biases calculated for OP measurements via Eq. 1. (This was answered in a response to RC2, please include in the manuscript)

   Response:
   Author included in P7L15.

10. On the same topic, gas concentrations along the open path will vary with time and location. If the S-OPS measurements are not coincident in time (ie simultaneous) or space (eg along the whole path rather than 150m OP vs 50m S-OPS) an estimate of the potential error needs to be made. At present S-OPS seems to be used as absolute truth without full justification. RC2 points out that this is potentially a very valuable feature of this study, but it cannot be fully exploited without this part of the error analysis.

    Response:
    This question has been addressed in author's response in companion paper. Briefly, the path-averaged concentrations of N_2O and CO_2 were measured from both S-OPS and OP-FTIR simultaneously, and the S-OPS-measured concentrations were used as benchmarks to examine the accuracy and the sensitivity of OP-FTIR on gas quantification. The surface layer of air tends to become homogeneous in a well mixing condition (i.e. wind speed > 1.7 m s^{-1} shown in Lin et al., 2019), and the well-mixed atmospheric condition can minimize spatial variations in the path-averaged concentrations from different measurement units (i.e., 50-m S-OPS vs. 150-m OP-FTIR).

11. P14 L26: Increasing resolution will decrease the non-linearity effects of Beer's Law breakdown, but at the cost of signal:noise and hence detection limits and precision. The optimal resolution is a trade-off – this should be included in the discussion here.

    Response:
    Authors included this resolution trade-off issue in P9L2.

12. P16L18: "Detector saturation at short distances was avoided…" The meaning is unclear. If higher signal levels at short open path distances resulted in saturation (as seen in signal below the detector cut-off), how was this addressed or corrected? Were these spectra rejected? Was the intensity reduced so the detector operated in the linear regime?

    Response:
    Detector saturation at short distances was avoided in this study by examinations of the IFG centre burst and SB spectra. For instance, the spectra were excluded if either the maximum or minimum signal of the centre burst exceeded the detector A/DC capacity (~ 2.5 V). Also, the elevated baseline below the detector cut-off, usually 600.0 cm^{-1}, in the SB spectrum was used as an indicator to inform the detector saturation (ASTM, 2013).

Part-II: A list of relevant changes

Summary – unclear, ambiguous content, and points that needed to be highlighted were rephrased and modified in this manuscript. Also, more discussions and clarifications that were suggested by the reviewers and editors were addressed. The mark-up version if this manuscript was attached (Part-III), and the list of the relevant changes is as follows:

1. **Abstract**

   P1L12 – the CLS underestimated N_2O concentrations by 3% (lab-FTIR) and by 12% (OP-FTIR) experiments when the reference and sample spectra were collected at the same temperature, which is highlighted in the abstract to differentiate the purposes of the companion paper and this article.

   P1L20 – the last sentence in the abstract was rephrased based on the suggestions from the editor and the anonymous referee#2.

2. **Introduction**

   P3L17 – A review paragraph was added in the introduction to describe the strengths and weaknesses these methods.

3. **Materials and experimental methods**

   P5L12 (2.1.2 Data collections and gas quantification for Lab-FTIR) – The entire section was rephrased and one more table (table-1) was added to clarify the methods used in the lab-FTIR experiment which was also suggested by the editor and the anonymous referee#2.

   P6L11 (Data collections and gas quantification for OP-FTIR) – The entire section was rephrased and more information was added to clarify the methods of 1) using the OP-FTIR to acquire spectra, 2) generating HITRAN training spectra, 3) correcting the model-calculated concentrations using the measured temperature and pressure, and 4) calibrating the N_2O and CO_2 analysers, which were suggested by the editor and referrers.

4. **Results and discussion**

   Section 3.1.1 Water vapour effect from lab-FTIR experiment

   - P8L21: Explain why the increased water vapour interferences compromised/reduced N2O absorption intensity.
   - P9L2: Increased optimal resolution is a trade-off for the S/N ratio which is along with detection limits as well as quantitative precision.

   Section 3.1.2 Temperature effect from lab-FTIR experiment

   - P9L16: respond to RC2 questions that the water vapour interference could be mitigated by selecting proper spectral windows.

   Section 3.2.1 Water vapour effect from the OP-FTIR experiment

   - P9L24: This section was rephrased to explained how water vapour was confounded by the ambient temperature.

   Section 3.2.2 Temperature effect for OP-FTIR

   - P10L16: the error analysis of the PLS-calculated concentrations was further discussed.

   Section 3.2.3 Wind speed effect

   - P12L7: the multiple sources of CO_2 and N_2O were explained to address the variabilities of CO_2 and N_2O, and the measurements during the low wind conditions were clarified.

   Section 3.2.3 Path length effect

   - Avoiding detector saturation was addressed in P11L10.

   Section 3.2.4 Wind speed effect

- More variations in CO2 than N2O concentrations were explained in P12L7, and the data collected from the low wind conditions were clarified in P12L12.

Sources of error in open-path FTIR measurements of N_2O and CO_2 emitted from agricultural fields

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Abstract. Open-path Fourier transform infrared spectroscopy (OP-FTIR) is susceptible to environmental variables which can become sources of errors for gas quantification. In this study, we assessed the effects of water vapour, temperature, path length, and wind speed on the uncertainty of nitrous oxide (N_2O) and carbon dioxide (CO_2) concentrations derived from OP-FTIR spectra. The presence of water vapour resulted in underestimating N_2O in both lab (−3 %) and field (−12 %) experiments~~ at 30 °C~~ using a classical least squares (CLS) model when the reference and sample spectra were collected at the same temperature (i.e. 30 °C). Differences in temperature between the sample and reference spectra also underestimated N_2O concentrations due to temperature broadening and the increased interferences of water vapour in spectra of wet samples. Changes in path length resulted in a non-linear response of spectra and bias (e.g. N_2O and CO_2 concentrations were underestimated by 30 % and 7.5 %, respectively, at the optical path of 100 m using CLS models). For N_2O quantification, partial least squares (PLS) models were less sensitive than CLS to the influence of water vapour, temperature, and path length, and provided more accurate estimations. Uncertainties in the path-averaged concentrations increased in low wind conditions (< 2 m s^{-1}). This study identified the most common interferences that affect OP-FTIR measurements of N_2O and CO_2, which can serve as a quality assurance/control guide ~~. The quantified errors can be used as references~~ for current or future OP-FTIR users.

1 Introduction

Agriculture substantially contributes greenhouse gases (GHGs), mostly N_2O and CH_4, to the atmosphere (IPCC, 2007). In 2010, emissions led by agricultural activities (e.g. crop production and livestock management) were estimated between 5.2 and 5.8 Gt of CO_2 equivalent per year, accounting for 10-12 % global anthropogenic emissions (IPCC, 2014). Estimations of gas fluxes over an extended period (e.g. growing seasons) is complicated due to the dynamic and episodic nature of gas emissions and measurement complexities. The integrated uses of fast-response gas concentration sensors and micrometeorological techniques were developed to measure long-term gas fluxes continuously (Baldocchi, 2003; Denmead, 2008; Flesch et al., 2016). Open-path Fourier transform spectroscopy (OP-FTIR) is capable of measuring concentrations of multiple gases simultaneously with high temporal and spatial resolution through real-time measurements and path-averaged concentrations (Russwurm and Childers, 2002). OP-FTIR has been applied to measure GHGs, and other trace gases (e.g. NH_3)

emitted from agricultural fields (Childers et al., 2001a and 2001b; Bjorneberg et al., 2009; Flesch et al., 2016; Lam et al., 2017). Using OP-FTIR to quantify gas concentrations, however, is a complicated process. Each step in data collection and spectral analyses influences the accuracy and precision of gas quantifications, including spectral resolution, apodization function, choice of background (e.g. zero-path or synthetic backgrounds), and chemometric models (Russwurm and Childers, 1999; Griffiths and de Haseth, 2007; Hart and Griffiths, 2000; Hart et al., 2000). Also, OP-FTIR spectra are sensitive to ambient environmental conditions (e.g. humidity, air temperature, optical distance, and wind speed), which interferes with spectral analyses and quantification of gas concentrations (Griffiths and de Haseth, 2007; Muller et al., 1999; Shao et al., 2007 and 2010).

Water vapour is a major interference in FTIR-derived trace gas quantification due to its strong absorption features within the mid-infrared region (400-4000 cm^{-1}) (Russwurm and Childers, 1999; ASTM, 2013). For the interference-free spectra, a single absorption line can be easily isolated to calculate gas concentrations (i.e. univariate methods). Using this method, however, is challenging to adequately isolate the absorption feature of the gas of interest from water vapour (Muller et al., 1999; Briz et al., 2007). Multivariate methods have been proposed to improve gas quantification from spectral interferences including water vapour by selecting broad spectral windows of gases of interest (Haaland and Easterling, 1980; Haaland and Thomas, 1988; Hart and Griffiths, 1998 and 2000; Hart et al., 1999 and 2000; Muller et al., 1999). The most common method in commercial quantification packages is the classical least squares (CLS) quantitative model (Griffiths and de Haseth, 2007). Studies showed that the interference of water vapour was mitigated by either considering reference spectra of water vapour or through selection of appropriate spectral windows in CLS models (ASTM, 2013; Haaland and Easterling, 1980; Hart and Griffiths, 2000; Horrocks et al., 2001; Jiang et al., 2002; Du et al., 2004; Briz et al., 2007; Lin et al., 2019). Other studies, however, found that CLS models resulted in substantial quantification errors of the targeted gas under the interference of the non-targeted gases (mostly water vapour) even if the reference spectra of all gas species and the optimal spectral window were considered (Hart et al., 1999; Briz et al., 2007; Shao et al., 2010; Lin et al., 2019). As a result, the partial least squares (PLS) algorithm was proposed to improve the accuracy of gas quantification (Haaland and Thomas, 1988; Hart et al., 2000; Shao et al., 2010; Lin et al., 2019).

The features of gas rotation-vibrational absorption bands are temperature dependent (Lacome et al., 1984; Rothman et al., 2005). Ideally, sample and reference spectra should be collected at the same temperature to avoid temperature-related bias (Russwurm and Childers, 1999; ASTM, 2013). Training spectra for building quantitative models, such as CLS, were generally collected at the same temperature. The non-linear responses of spectral absorbance to significant diurnal variations in temperature will lead to errors in gas quantification (Russwurm and Phillips, 1999; de Castro et al., 2007; Smith et al., 2011). For continuous field measurements, it is time-consuming to create piecewise models to cover the entire ranges of 1) the path-integrated concentrations of gases of interest and interferences, and 2) temperature. A PLS model was developed to cover the wide ranges of environmental variables, including concentrations, path lengths, humidity, and temperature (Bjorneberg et al., 2009; Griffiths et al., 2009; Shao et al., 2010 and 2011).

Besides changes in water vapour content and temperature, the experimental configuration and optical parameters also influence OP-FTIR spectra. Compared with extractive methods, one of the advantages of OP-FTIR is the ability to use different path lengths to measure gases from multiple sources (Russwurm and Childers, 1999; Bacsik et al., 2006). OP-FTIR measurements require electronic gain to fill the analogue-to-digital converter (A/DC) of the instrument. Consequently, short optical path lengths can over saturate the detector that introduces error in gas quantification (Bartoli et al., 1974; Chase, 1984; Griffiths and de Haseth, 2007). A long path length increases the sensitivity for gas quantification, but the increased length reduces the intensity of the incident signal and decreases the signal-to-noise (S/N) ratio (Griffith and Jamie, 2006; Nelson et al., 1996; Kosterev et al., 2008). Spectral resolution and apodization also affect the spectral linearity (Griffiths, 1994; Zhu and Griffiths, ~~1994~~1998; Russwurm and Phillips, 1999; Childers et al., 2002). Lower resolution spectra are incapable of resolving absorption features. Even though the apodized interferogram (IFG) can reduce noises (or spurious oscillations) of a single-~~bean~~ beam (SB) spectrum converted by Fourier transformation, different apodization functions affect spectrum linearity differently. The non-linear relationship between absorbance and concentrations disobeys Beer-Lambert Law and leads to biases in gas quantification (Haaland, 1987; Russwurm and Phillips, 1999; Childers et al., 2001a). ~~Thus, the non-linear least squares (NLLS) regression function was proposed to correct non-linear behaviour of the Beer-Lambert law and improve the quantitative accuracy (Smith et al., 2011; Griffith et al, 2012; Paton-Walsh et al., 2014; Phillips et al., 2019).~~

The CLS algorithm is subject to the nonlinearity induced by ambient interferences (e.g. multiple overlapping components) or instrumentation setup (e.g. low spectral resolution) which can be overcame by the PLS-based quantitative models (Hart et al., 2000). Alternatively, the non-linear least squares (NLLS) regression function was also proposed to correct non-linear behaviour of the spectrum to concentrations and improve the quantitative accuracy (Smith et al., 2011; Griffith et al, 2012; Paton-Walsh et al., 2014; Phillips et al., 2019). The NLLS coupled with a forward modelling approach named the Multi-Atmospheric Layer Transmission (MALT) method can model a transmission spectrum from the HITRAN database by selecting specific parameters (including temperature, pressure, path length, resolution, and apodization function) to fit the sampled SB spectrum for gas quantification (Griffith, 1996). One of the benefits of the MALT is that a ‘background’ SB spectrum (the spectra without gases of interest) is not required in the procedure for quantification, which can avoid the background-induced errors (e.g. zero-path background or the zapped background shown in Lin et al, 2019). Nevertheless, it is challenging to consider other sources of variables in the field (e.g. severe spectral overlap or wind-induced variations) using the MALT which is built upon the HITRAN library. Instead, the PLS-based approach can be trained empirically and consider the local environmental variables in quantitative models for field gas measurements (ASTM, 2013; Griffith et al., 2009).

Many OP-FTIR field studies used either CLS or PLS as frameworks for gas measurements. ~~For OP-FTIR measurements, many~~ Most of these studies minimized environmental interferences (e.g. water vapour or wind speed) by developing methods for spectral analyses and gas quantification (Hong and Cho, 2003; Hart et al., 1999 and 2000; Muller et al., 1999; Childers et al., 2002; Briz et al., 2007; Shao et al., 2007; Griffiths et al, 2009; Shao et al., 2010; Lin et al., 2019). Briz et al. (2007) examined the difference in water vapour content (0.5 % vs. 2.5 %) on trace gas quantification but their study did not include N_2O. Shao et al. (2007) investigated the effect of wind on spectrometer vibrations and spectra qualities but did not address its influence on gas quantification. ~~The influences of temperature~~Temperature effect on~~–~~ spectral parameters (e.g. ~~trace gas~~ absorption intensity and bandwidth) of single gas components have been well established ~~for some simple systems~~ (e.g. ~~single gas component shown in the~~ high-resolution transmission molecular absorption~~ (~~, HITRAN,~~)~~ database published by Rothman et al., 2005); however, only limited studies assessed influences of dynamic temperature ~~effect~~ on gas quantification using OP-FTIR. Horrocks et al. (2001) and Smith et al. (2011) used OP-FTIR spectrometer and a gas cell purged with dry samples to measure the temperature-related error in SO_2, CO, CO_2, and CH_4 quantification, but not for N_2O.

To the best of our knowledge, there has never been a study of exploring the influence of changing temperature and path length on N_2O quantification under interferences of water vapour in spectra. ~~It is challenging to~~To test the quality of OP-FTIR methods for multiple gas quantification is challenging due to interferences and the lack of proper measurement benchmarks. Also, the influence of water vapour is confounded by temperature and path length effects. In this study, the influence of water vapour, temperature, path length, and wind speed on N_2O and CO_2 quantification are examined using lab and field-based (OP-FTIR) methods.

2 Materials and experimental methods

2.1 Lab FTIR experiment

The lab FTIR experiment was used to assess the effects of water vapour and air temperature on N_2O quantification from spectra. An FTIR spectrometer equipped with a variable-path length gas cell was used to acquire reference spectra of N_2O, water vapour, and N_2O plus water vapour mixtures (i.e. wet N_2O) as shown in Fig. 1a.

2.1.1 Instrumentation setup

The lab FTIR spectrometer (Nexus 670, Thermo Electron Corporation, Madison, WI) was equipped with a KBr beam splitter, and a high-D* MCT detector was used to analyse gas samples using a multi-pass gas cell (White cell) (model MARS-8L/40L, Gemini Scientific Instruments, CA) with an optical path length of 33 m. Spectra range of 700.0-4000.0 cm^{-1}, optical velocity of 0.6 cm s^{-1}, and a resolution of 0.5 cm^{-1} were selected for spectra acquisition. Each spectrum was acquired by co-adding 64 IFGs using the OMNIC software package (Thermo Fisher Scientific, Inc.) A triangular function was applied to apodize an IFG for converting an SB spectrum using the Fourier transform. A sampled SB spectrum contained the visible information of gases of interest and interferences. A background SB spectrum was collected from pure N_2 and used to convert a sampled SB spectrum to an absorbance spectrum. The temperature of the gas cell was controlled and monitored (model 689-0005, Barnant Co., Barrington, IL). The spectrometer was purged with dry air (−20 °C dew point) from a zero air generator (model 701H, Teledyne, Thousand Oaks, CA). Gas samples were produced using a diluter (series 4040, Environics Inc, Tolland, CT). The mole fraction (ppbv) of N_2O was diluted with ultra-pure N_2 gas. Water vapour concentrations (ppmv) were controlled by a Nafion tube (Perma Pure, Lakewood, NJ) enclosed within a sealed container containing saturated water vapour. The concentration of saturated water vapour in the container was adjusted by controlling temperature of the water bath. Wet N_2O gas samples were produced by passing dry N_2O from the diluter through Nafion tube with a constant flow rate (4 L·min^{-1}). Gas samples were continuously introduced into the White cell with a constant pressure close to the room ambient pressure. Humidity and temperature probes (model HMT330, Vaisala Oyj, Helsinki, Finland) were used to monitor the humidity and temperature of the introduced gas samples. In this study, N_2O (dry and wet) was diluted from 30.0 ppmv (N_2O in N_2) to 310.0, 400.0, 500.0, 600.0, and 700.0 ppbv with various water vapour contents (a relative humidity of 20 %, 40 %, 60 %, and 80 % at 30 °C).

2.1.2 Data collections and gas quantification

Spectra were collected when the N_2O and water vapour concentrations and ~~and~~ temperature of the introduced samples were steady. ~~Concentrations of N_2O and water vapour were calculated from the mixed-gas (wet N_2O) absorbance spectra by CLS and PLS models using TQ Analyst software Version 8.0 (Thermo Fisher Scientific, Inc.)~~ A total of ~~9~~ nine single-gas absorption spectra~~-~~, five ~~of~~ dry N_2O spectra with concentrations of ~~(~~310.0-700.0 ppbv~~)~~ and four water vapour spectra with concentrations of ~~(~~7000-28 000 ppmv~~)~~ were used to ~~build~~ train CLS models (CSL-1 shown in Table 1). A total of ~~60~~ sixty mixed-gas (wet N_2O) spectra were used to build PLS models (see the table S1 in the supplement). Spectral windows (Table ~~1~~2) and linear baseline correction were applied in CLS-1 and PLS models to calculate concentrations of N_2O and water vapour from the mixed-gas spectra (the validation/wet sample spectra shown in Table 1) using TQ Analyst software Version 8.0 (Thermo Fisher Scientific, Inc.)~~.~~ The previous study showed that the integrated window of 2188.7-2204.1 and 2215.8-2223.7 cm^{-1} (W_N3) is less sensitive to changing environment (e.g. water vapour = 5000-20 000 ppmv; ambient temperature = 10-35 °C) and provides higher accuracy than the window of 2170.0-2223.7 cm^{-1} (W_N1) for N_2O quantification using either CLS or PLS models (Lin et al., 2019). These ~~Two~~ two windows (W_N1 and W_N3) ~~reported by Lin et al. (2019)~~ were used to calculate ~~for~~ N_2O ~~quantification~~ concentrations and examine the effect of water vapour, temperature, and path length on N_2O calculations in this study~~(W_N1: 2170.0-2223.7 cm^{-1} and W_N3: 2188.7-2204.1 + 2215.8-2223.7 cm^{-1})~~. In PLS models, optimum factors were determined by cross validation and justified by the prediction of residual error sum of squares (PRESS) function to avoid over-fitting issues (see Table S2 in the Supplement published by Lin et al., 2019). Since -it was difficult to isolate the effects of the temperature and humidity on quantitative biases from the field experiment, the validation spectra with the fixed concentrations of N_2O and water vapour (310 ppbv N_2O mixed with 21 500 ppmv water vapour) collected at 30, 35, 40 °C from the lab-FTIR to evaluate the sensitivity of CLS and PLS to temperature.~~The influence of air temperature on N_2O quantification using CLS and PLS was examined by collecting spectra at 30, 35, and 40 °C.~~

2.2 Open-path FTIR experiment

The OP-FTIR experiment was used to assess the effects of water vapour, air temperature, path lengths, and wind speed on the quantification of N_2O and CO_2 from field spectra. The field instrumentation and configuration were shown in Fig. 1b.

2.2.1 Site description and instrumentation setup

The field study was conducted at Purdue University Agronomy Center for Research and Education of West Lafayette, Indiana, the United States (86°56´ W, 40°49´ N). The predominant soil series at the study site was a Drummer silty clay loam (fine-silty, mixed, mesic Typic Endoaquoll). The bulk density of topsoil (0-10 cm) and organic matter (0-20 cm) was measured 1.6 g·cm^{-3} and 3.8 %, respectively. The experimental site (Purdue Field Trace Gas Flux Facility) was between two maize cropping fields (~10 m apart) with anhydrous ammonia applications. A monostatic OP-FTIR (IR source, interferometer, transmitting and receiving telescope, and detector combined in one instrument) spectrometer (model 2501-C, MIDAC Corporation, Irvine, CA) was used to collect field-IR spectra. A retroreflector with 26 corner-cubes (cube-length of 76 mm) was mounted on a tripod 150 m from the spectrometer corresponding to an optical path of 300 m. The experiment of varying path lengths was conducted using optical path lengths of 100, 200, and 300 m.

2.2.2 Data collections and gas quantification

The same sample collection parameters were used to collect both OP-FTIR and lab-FTIR spectra. OP-FTIR spectra were collected using the AutoQuant Pro4.0 software package (MIDAC Corporation, Irvine, CA). Each field spectrum was collected by co-adding 64 IFGs and a resolution of 0.5 cm^{-1}. ~~A zero-filling factor of one, t~~Triangular apodization, ~~and~~ Mertz phase correction, and no zero-filling were applied to convert an IFG into an SB spectrum. A stray-light SB spectrum was collected by pointing the spectrometer telescope away from the retroreflector and subtracted from sampled SB spectra for stray-light correction. Quality control and assurance procedures (Russwurm, 1999; ASTM, 2013; Russwurm and Childers, 1999; Childers et al., 2001b; Shao et al., 2007) were used to evaluate spectra qualities and the influence of wind-induced vibrations. ~~The corrected field SB spectra were converted to absorbance spectra using the synthetic SB background (syn-bkg) spectra shown by Lin et al. (2019).~~

Gas concentrations derived from the OP-FTIR ~~absorbance~~ spectra were also calculated by CLS and PLS models. ~~Single-gas reference~~Training absorption spectra used in the CLS model were generated from the HITRAN database using E-trans (Ontar Corporation North Andover, MA)~~and used to create CLS models~~. Briefly, high-resolution spectral lines of N_2O, CO_2, and water vapour output from E-trans were interpolated to generate spectra ranging from 500 cm^{-1} to 4000 cm^{-1} and convolved with a triangular apodization function. The convolved spectral lines were used to generate the reference spectra with the identical resolution and data point density matching the field spectra using Grams/32 (Childers et al., 2001). ~~Identical parameters, including resolution, apodization, zero-filling factor, were used to acquire both reference and field spectra.~~ The HITRAN reference spectra ~~, including N_2O, CO_2, and water vapour,~~ were generated at the pressure of 760 torr and temperature of ~~at~~ 30 °C ~~to calculate N_2O and CO_2 concentrations from field spectra~~.

The stray-light corrected field SB spectrum was converted to absorbance spectra by the synthetic SB background (syn-bkg) spectra using the IMACC Quantify package (Industrial Monitoring and Control Corp., Round Rock, TX). The syn-bkg was generated by selecting multiple points from the spectral interval of interest (i.e. six points within 2050.0–2500.0 cm^{-1} for N_2O and CO_2) to fit the curvature of the sample SB spectrum using a polynomial function (Lin et al., 2019). Three ~~using~~ spectral ~~optimum~~ windows ~~(W_N3 for N_2O and W_C2 for CO_2 (shown in~~ Table ~~1~~2) ~~published by Lin et al. (2019)~~ and the HITRAN references were used to build the CLS model (CLS-2 shown in Table 1) in the IMACC software.~~.~~ ~~Both processes of the absorbance spectra conversion (based on the syn-bkg spectrum) and CLS models were conducted using the IMACC software (Industrial Monitoring and Control Corp., Round Rock, TX).~~ The third-degree polynomial function was used to correct the non-linear response of the CLS-calculated concentration to the actual concentration. ~~The NLLS regressions between absorbance and the path-integrated concentrations of reference spectra were used in the CLS model.~~ More details regarding the IMACC quantification package were described in the IMACC user manual attached as the supplementary material. The PLS models were built using lab-FTIR measurements and only used for estimating N_2O concentrations. Since the molar fraction changes with changing air density which is the function of temperature and pressure, the measured temperature and pressure in the gas cell and experimental field were imported in the quantitative software to adjust the model-calculated concentrations.

Ambient temperature, ~~and~~ relative humidity, and barometric pressure in the field were measured using an HMP45C probe (Vaisala Oyj, Helsinki, Finland) and a pressure sensor (278, Setra, Inc., Boxborough, MA) at 1.5 m above ground level (a.g.l.). The mean wind speed was measured by a 3-D sonic anemometer (model 81000, RM Young Inc., Traverse City, MI) mounted at 2.5 m a.g.l. and recorded at 16 Hz. A 50-m synthetic open path gas sampling system (S-OPS) (Heber et al., 2006) was used to collect gas samples along the OP-FTIR optical path to analyse the path-averaged concentrations of N_2O and CO_2 using a difference frequency generation mid-IR (DFG-IR) laser-based N_2O gas analyser (IRIS 4600, Thermo Fisher Scientific Inc., Waltham, MA) and a non-dispersive IR (ND-IR) CO_2 gas analyser (LI-840, LI-COR Inc., Lincoln, NE), respectively. The N_2O and CO_2 analysers provided a high precision for N_2O (< 0.15 ppbv, 1σ) and CO_2 (< 1.0 ppmv, 1σ) measurements, and both analysers were calibrated using the certified standard gas every four hour to insure the instrumentation stability and the accuracy. ~~so the~~The path-averaged concentrations of N_2O and CO_2 were measured from both~~the~~ S-OPS and OP-FTIR simultaneously, and the S-OPS-measured concentrations were used as benchmarks to examine the accuracy and the sensitivity of OP-FTIR on gas quantification (Lin et al., 2019). The surface layer of air tends to become homogeneous in a well mixing condition (i.e. wind speed > 1.7 m s^{-1} shown in Lin et al., 2019), and the well-mixed atmospheric condition can minimize spatial variations in the path-averaged concentrations from different measurement units (i.e., 50-m S-OPS vs. 150-m OP-FTIR).

2.2.3 Path lengths experiment

A variable path length between an OP-FTIR spectrometer and a retroreflector resulted in different path-integrated concentrations and the depth of gas absorbance in SB spectra. The complexities of N_2O absorption features within the 2170.0-2224.0 cm^{-1} range required high spectral resolution (Fig. 3). For N_2O, the increased absorbance, resulting from a longer path length, likely improves its quantitative sensitivity and accuracy. Spectra were collected from physical lengths of 50, 100, and 150 m (Fig. 1b) using the same parameters. During the measurement (14:30-18:30, local time (LT) on 6 May 2016), background concentrations of N_2O (349.0 ± 0.5 ppbv) and CO_2 (400.0 ± 4.4 ppmv), ambient temperature and humidity (the relative humidity of 35.0 % at 25 °C) remained nearly constant. The spectra acquired from different path lengths were analysed by CLS-2 models for N_2O and CO_2 concentrations and by PLS models only for N_2O.

2.4 Quantitative accuracy

Quantitative accuracy/bias was determined by the relative error of the path-averaged concentrations between FTIR (x_i) and the true gas concentrations (x_t) of either the introduced gas (Lab) or the S-OPS measurements (Field), following Eq. (1):

$$\text{Bias} = [(x_i - x_t)/x_t] \times 100\ \% \qquad (1)$$

3 Results and discussion

Quantification of target gas concentrations from either lab- or field-based FTIR spectra requires knowledge of the optimum spectral window (the spectral region used for quantification). In general, broadening the spectral windows will contain more spectral features that can be used for quantification. At the same time, however, broader windows will also contain more contributions from interfering constituents (e.g. water vapour). The optimum window would have clean spectral features of the target species with minimal spectral interference from other gases. For N_2O quantification, our previous work showed that the optimum window was to integrate two intervals of 2215.8-2223.7 and 2188.5-2204.1 cm^{-1} (W_N3 shown in Lin et al., 2019). In this paper, two windows (W_N1 and W_N3) and models (CLS and PLS) from the previous study were used to predict N_2O concentrations.

3.1 Lab FTIR experiment

3.1.1 Water vapour effect

Water vapour interfered with spectral windows and resulted in underestimations of N_2O concentrations using CLS models; increased water vapour increased the bias (Fig. 2). The PLS model provided more accurate predictions for N_2O than the CLS. The CLS accurately predicted gas concentrations only when the water vapour was absent or limited in spectra (Hong and Cho, 2003; Esler et al., 2000; Shao et al., 2010; Smith et al., 2011). In open-path measurements, CLS was often observed to underestimate gas concentrations, as reported by Childers et al. (2002), Briz et al. (2007), Shao et al. (2010), and Lin et al. (2019). Absorbance spectra of dry and wet N_2O ~~(Fig. 3)~~ showed that the interference of water vapour likely compromised the intensity of the N_2O P-branch absorbance (Fig. 3~~P-branch~~). Ideally, the absorbance/intensity of the 310 ppbv N_2O should be identical in either dry or wet conditions. The wet spectrum (red solid line), however, showed lower N_2O intensity than the dry spectrum (black solid line) after the baseline correction (Fig. 3). The reduced N_2O absorbance in wet samples resulted in underestimations of N_2O concentrations using CLS models created based on references of dry N_2O samples and water vapour. PLS models, created by wet N_2O references, showed improved accuracy in wet samples but overestimated N_2O in dry samples (Fig. 2). It is still unclear how water vapour interfered with gas quantification. The N_2O underestimation (based on the CLS model predictions) resulting from the attenuated absorbance was hypothesized due to the inadequate spectral resolution. High resolution is required to resolve rotation-vibrational gas spectral features (e.g. full-width at half height ~ 0.2 cm^{-1}) to avoid spectral nonlinearity to concentrations (ASTM, 2013; Griffiths and de Haseth, 2007; Russwurm and Phillip, 1999; Muller et al., 1999). Absorption features of N_2O were strongly overlapped by water vapour within 2170.0-2224.0 cm^{-1}. In order to resolve absorbance spectra of multiple gases and spectral overlaps, spectral resolution higher than 0.2 cm^{-1} would be suggested. Increased optimal resolution, however, is a trade-off for the ratio of signal to noise which is along with detection limits as well as quantitative precision.

3.1.2 Temperature effect

The temperature-sensitivity of gas-phase FTIR spectra results in non-linearity of absorbance to temperature. Bias will be introduced if there is a temperature difference between reference and sample spectra (Russwurm and Phillip, 1999; Smith et al., 2011). The effect of this delta temperature on N_2O quantification is shown in Fig. 4a. Spectra of wet N_2O (310 ppbv N_2O blending with 21 000 ppmv water vapour) were collected at 30 °C, 35 °C, and 40 °C. Reference spectra of dry N_2O, water vapour, and wet N_2O were acquired at 30 °C and used to calculate N_2O concentrations from spectra collected at temperatures of 35 °C and 40 °C. The difference in temperature led to biases in N_2O calculations (Fig. 4a). Smith et al. (2011) calculated concentrations of CO_2, CH_4, and CO using the ~~Multi-Atmospheric Layer Transmission (~~MALT~~)~~ (Griffith, 1996) and showed that temperature-related error was approximately 3.0 % when the delta temperature was within 10 °C. As mentioned, water vapour present in spectra resulted in underestimations of N_2O by CLS models (Fig. 2), and this bias further increased with increasing the delta temperature. For instance, the bias increased from -3.0 to -5.0 % with increasing temperature from 30 to 40 °C using CLS models (Fig. 4a). Sources to this bias appeared to include 1) temperature-broadening of N_2O and 2) temperature-induced interference of water vapour (i.e. greater interference at increased temperature). Increased temperature tends to broaden the width of absorption lines in the rotation-vibration N_2O spectra and results in underestimations of gas concentrations. The increased strength of water vapour led to more interference in spectral analyses and great biases (Fig. 4b). Even though it is challenging to avoid interferences from water vapour, a proper window selection (e.g. W_N1 vs. W_N3) can mitigate the effect of water vapour on gas quantification. PLS methods also showed more accurate estimations and less sensitivity to temperature than CLS models (Fig. 4a).

3.2 Open-path FTIR experiment

3.2.1 Water vapour effect

In fields, water vapour ranged from 5000 to 20 000 ppmv during 9-19 June 2014.~~,~~ ~~and t~~The increased water vapour showed the increased N_2O biases using CLS~~ (Fig. 5a)~~. In the lab experiment, ~~the increased~~ water vapour increasing from 5000 to 20 000 ppmv at 30 °C only showed consistent underestimations of N_2O by approximately 3.0 % using CLS (Fig. 2). ~~Since water vapour and air temperature are confounding variables, it is difficult to isolate their contributions to quantitative errors in the field.~~ The positive ~~negligible correlation~~relationship ~~(R^2 = 0.20 shown in Fig. 5a)~~ between water vapour content and the N_2O bias (Fig. 5a) was because water vapour was confounded by temperature. The increased temperature (i.e. ~~temperature ranged from~~ 10~~ °C to~~-35 °C in fields) tends to increase humidity in the air. ~~and~~ This negligible correlation (R^2 = 0.20 shown in Fig. 5a) became insignificant when the calculated biases were categorized by temperature (~~i.e.~~e.g. R^2 = 0.01 at the interval of 25-30 °C, data not shown). CO_2 measured by CLS was less sensitive to changing water vapour content (R^2 = 0.05) than N_2O (Fig. 5b) in field measurements, presumably due to the less water vapour absorption features in 2075.5-2084.0 cm^{-1} than 2170.0-2224.0 cm^{-1} (Lin et al., 2019). For PLS calculations, N_2O biases became consistent but slightly increased with increasing water vapour (Fig. 5c).

3.2.2 Temperature effect

Increased air temperature increased both N_2O and CO_2 biases ~~estimations~~ from CLS models (Fig. 5d and 5e). ~~Since the temperature-dependent absorbance varied with species and wavelengths, gas quantification reacts differently to a changing environmental temperature (Smith et al., 2011). The~~ A strong correlation of air temperature to N_2O biases (R^2 = 0.86) showed the N_2O quantification was more sensitive to temperature effects than CO_2 (R^2 = 0.39). The lab experiment (Fig. 4) showed that CLS underestimated N_2O by 3.0 % in wet air for samples with a low delta-temperature. N_2O calculations from OP-FTIR spectra, however, were underestimated by 12.0 % (approximately 36 ppbv less than the true value) even if the HITRAN reference and sample spectra were collected at the same temperature (i.e. 30 °C). The excess bias (12.0 % minus 3.0 %) likely ~~presumably~~ resulted from interferences from CO and CO_2 in 2170.0-2224.0 cm^{-1} and inherent uncertainties in line intensities and bandwidths of gas absorbance from HITRAN database (Rothman et al., 2005). ~~-~~The CLS-calculated CO_2 values were less influenced by temperature ~~(R^2 = 0.39)~~ than N_2O (Fig. 5e), attributed to the reduced complexity of CO_2 absorption features in the 2075.0-2085.0 cm^{-1} region, and less interference of water vapour within this region (Lin et al., 2019). Since the temperature-dependent absorption lines vary with species and wavelengths, the resolution parameter and gas quantification react differently to a changing environmental temperature (Smith et al., 2011; Griffith et al., 2012).

The PLS model~~s~~ were not only less ~~influenced~~ affected by temperature ~~for N_2O quantification~~ ($R^2 = 0.05$) ~~and~~ but ~~also~~ provided better accuracy for N_2O estimations (Fig. 5f). For instance, N_2O bias was reduced from -12.0 % (the CLS-calculated ~~model underestimated~~ N_2O ~~concentration by approximately 8.5 % (~~shown in ~~i.e. -8.5±1.2 % shown in~~ Fig. 5d) to 2.2 % using the PLS model at 30 °C ~~, and the PLS model reduced the bias to 2.2 % (i.e. 2.2±0.8 % shown in (~~Fig. 5f)~~.~~ This slightly overestimated N_2O concentration (i.e. 2.2±0.8 % shown in Fig. 5f) was possibly due to 1) the limited information regarding other sources of environmental variables (e.g. wind-driven variables such as the homogeneity of the mixing air) in the PLS model, and 2) different background gases between training and field spectra. The pure N_2 was used as a buffer gas to generate reference mixtures (i.e. N_2O mixed with water vapour) to train the PLS model. For field spectra, however, only approximately 78 % N_2 is present in the spectra. Since the line-broadening coefficient is sensitive to the background compositions (~~ADD Refs~~Lacome et al., 1984), the discrepancy in backgrounds (i.e. N_2 vs. air) likely leads to errors in gas quantification. Furthermore, the linewidth of absorption bands is influenced by both temperature and pressure broadening effects (~~ADD Refs~~Loos et al., 2015). Variations in pressure between the reference and sample spectra also reduce the quantitative accuracy (Smith et al., 2011). In the control environment experiment, the pressure effect on bandwidth (or the associated error) was minimized due to the nearly constant pressure in the gas cell. The ambient air pressure was measured from 981.0 to 996.0 ~~hectopascals (~~hPa~~)~~ every thirty minute during the measurement period. Compared with the wide ranges of temperature and water vapour content, the effect of this small variations in the pressure (989.3±3.2 hPa, n = 355) on gas quantification was not examined and, the measured pressure was only used to adjust the model-calculated concentrations in this study.

3.2.3 Path length effect

OP-FTIR spectra containing N_2O concentrations of 349.0 ± 0.5 ppbv and CO_2 concentrations of 400.0 ± 4.4 ppmv were collected from optical lengths of 100, 200, and 300 m. As path lengths decreased, both N_2O and CO_2 concentrations were underestimated (Fig. 6a and 6b). For N_2O, CLS-derived concentrations were more sensitive to changing path lengths than PLS (Fig. 6a). The Beer-Lambert law should show a linear response of absorbance to the path-integrated concentration. Nevertheless, the path-averaged absorbance of N_2O and CO_2 (i.e. $\frac{\text{Absorbance}}{Path\ length(m)}$) did not conform to the Beer-Lambert law even though background concentrations of N_2O and CO_2 were consistent (Fig. 6c and 6d), showing that there was a non-linear response of OP-FTIR spectra to the path-integrated concentrations. Several reasons may have caused non-linearity issues, such as detector saturation, spectral resolution, and apodization (ASTM, 2013; Russwurm and Childers, 1999; Griffiths and de Haseth, 2007). Detector saturation at short distances was avoided in this study by examinations of the IFG centre burst and SB spectra ~~(i.e. the elevated baseline below the detector cut-off, usually 600.0 cm^{-1}) in this study (ASTM, 2013)~~. For instance, the spectra were excluded if either the maximum or minimum signal of the centre burst exceeded the detector A/DC capacity (~ 2.5 V). Also, the elevated baseline below the detector cut-off, usually 600.0 cm^{-1}, in the SB spectrum was used as an indicator to inform the detector saturation (ASTM, 2013).

~~Presumably~~Thus, this short-path-derived bias (Fig. 6a and 6b) likely resulted from the inadequate spectral resolution. Short path lengths reduced the absorbance depth in an SB spectrum and sensitivity for quantification. Poorly resolved absorbance spectra could lead to a spectral non-linear response with different path-integrated concentrations (Zhu and Griffiths, 1994; Russwurm and Phillips, 1999). Also, N_2O quantification was more sensitive to path lengths than CO_2. With increasing optical path lengths from 100 m to 300 m, the accuracy of N_2O calculated from CLS models increased by approximately 20.0 % (N_2O biases reduced from −30.0 % to −10.0 % shown in Fig. 6a). For CO_2, the accuracy only increased 2.5 % (CO_2 biases reduced from −7.5 % to −5.0 % shown in Fig. 6b). The difference in sensitivity between gas quantification and path length was attributed to the complexity of absorbance spectra. N_2O absorption features in 2170.0-2224.0 cm^{-1} were more complicated than CO_2 in 2075.0-2085.0 cm^{-1}; furthermore, more interfering gases (CO, CO_2, and water vapour in 2170.0-2224.0 cm^{-1}) interfered with N_2O quantification (Lin et al., 2019). A triangular apodization function applied in spectra results in a non-linear response (Russwurm and Phillips, 1999). The poorly-resolved spectra containing multiple gas species likely complicated the magnitude of the non-linearity led by apodization, which, however, was not evaluated by this study. The PLS methods reduced N_2O biases and showed less sensitivity to path length than CLS (Fig. 6a).

3.2.4~~3~~ Wind speed effect

Nitrous oxide is predominately produced via soil microbial activities (nitrification and denitrification) and CO_2 is from respirations from soil microbes and vegetation (Mosier et al., 1996). As a result of soil and crop heterogeneities, multiple sources, and intermittent fluxes of N_2O and CO_2 from soil and/or canopy result in inhomogeneous gas concentrations in the atmosphere under low winds. Since the path length of the S-OPS (50-m) was different from the OP-FTIR (the physical length of 150 m), the gas uniformity across the 150 m influenced their path-averaged concentrations. The difference in the path-averaged N_2O and CO_2 concentrations between the S-OPS and OP-FTIR was used to calculate quantification bias (Fig. 7). Variabilities of N_2O and CO_2 biases were small but increased when the wind speed was less than 2 m s^{-1} (Fig. 7c and Table ~~S1~~ S3 in the Supplement). This increased variability inferred the poorly-mixed air (< 2 m s^{-1}). Thus, decreasing wind speed and turbulent mixing tended to increase gas concentration differences between the S-OPS and OP-FTIR. During the low wind environment, CO_2 bias showed higher variability than N_2O presumably due to a greater environmental variation in CO_2 concentrations than N_2O (Lin et al., 2019). For instance, CO_2 can be produced from both soil and canopy respirations, and plant uptake via photosynthesis. N_2O was predominately produced from soil nitrification and denitrification. The CO_2 concentrations and their spatial distribution in the air were influenced by the variabilities of both soil properties and crop species (different sources). Thus, CO_2 concentrations in the atmosphere tended to have higher variabilities than N_2O and become highly heterogeneous if the air was poorly mixed in the low wind condition. Low wind conditions likely occurred during the night period. During 9-19th 2014, a total of 259 and 130 data point (30-min averages N_2O) was collected from the daytime (06:00-20:00, LT) and nighttime (20:00-06:00, LT) measurements, respectively. The low wind conditions can occur during both day and night even though a low wind condition is more common during the night. In this study, 22% (57 out of 259) of all daytime measurements and 36% (47 out of 130) of all nighttime measurements were collected from low winds (<

2 m s^{-1})~~For instance, 22.0 % (57 out of 259) of the collected data (30-min-averaged N_2O) collected from low winds (< 2 m s^{-1}) was from daytime measurements (06:00-20:00, LT), and 36.2 % (47 out of 130) was from nighttime measurements (20:00-06:00, LT)~~ (Fig. 7a).

4 Conclusion and recommendations

In this study, we have evaluated the effects of water vapour, temperature, path length, and wind speed on open-path FTIR measurements of N_2O and CO_2 quantified by CLS and PLS models. Water vapour in spectra underestimated N_2O concentrations by 3.0 % (lab experiment) and 12.0 % (field experiment) at 30 °C using CLS models. PLS models improved the accuracy of N_2O quantification (lab bias = −0.6 ± 0.4 % and field bias = 2.0 ± 0.8 %). Differences in temperature between reference and sample spectra led to errors in gas quantification. Increased air temperature significantly increased quantification bias using CLS models. For wet N_2O, 10 °C difference introduced 1.9 % (Lab) and 9.1 % (Field) more biases in gas concentrations. PLS models were less sensitive to temperature. Short path lengths reduced the sensitivity and accuracy for gas quantification, and CLS models were more sensitive to changing path lengths than PLS. These short-path-led biases were presumably due to the inadequate spectral resolution. CO_2 quantification using CLS model was less influenced by environmental variables than N_2O likely due to the less complex absorption features. The wind affected the mixings of gases and the low wind speed (< 2 m s^{-1}) led uncertainties in the path-averaged concentrations.

~~For the users who are interested in absolute gas concentrations and the associated accuracy, The t~~The partial least squares model generally provided more accurate measurements than CLS if the gas of interest is strongly interfered by water vapour (or other interferences) (e.g. strong overlap of water vapour absorbance features or broad spectral windows). PLS is also less sensitive to environmental variables than CLS. For OP-FTIR measurements, the CLS-calculated concentrations need to be verified carefully for quality assurance and to avoid substantial underestimations. Path lengths must be adequate, which can be checked by conducting a path length experiment before measurements. For the users interested in multi-source measurements, we suggested avoiding a great difference in path lengths if CLS models are used for gas quantification. High spectral resolution (< 0.5 cm^{-1}) is recommended to resolve complex spectral features of either gas of interest or interferences. A high resolution also introduces more noises and increasing the scan time is suggested to increase the ~~single~~signal-to-noise ratio (Griffiths and de Haseth, 2007).

Author contributions. CHL, CTJ, RHG, and AJH designed the lab- and field-FTIR measurement experiments. CHL and RHG conducted the field experiment. CHL conducted the lab experiment, spectral and data analyses, and prepared the manuscript with contributions from CTJ, RHG, and AJH.

Competing interests. The authors declare that they have no conflict of interest.

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References

ASTM International.: ASTM E1865-97(2013) Standard Guide for Open-Path Fourier Transform Infrared (OP/FT-IR) Monitoring of Gases and Vapors in Air, West Conshohocken, PA, https://doi.org/10.1520/E1865-97R13, 2013a.

ASTM International.: ASTM E1982-98(2013) Standard Practice for Open-Path Fourier Transform Infrared (OP/FT-IR) Monitoring of Gases and Vapors in Air, West Conshohocken, PA, https://doi.org/10.1520/E1982-98R13, 2013b.

Baldocchi, D. D.: Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future, Global Change Biology, 9, 479-492, https://doi.org/10.1046/j.1365-2486.2003.00629.x, 2003.

Bartoli, F., Allen, R., Esterowitz, L., and Kruer, M.: Auger-limited carrier lifetimes in HgCdTe at high excess carrier concentrations, J. Appl. Phys., 45, 2150-2154, https://doi.org/10.1063/1.1663561, 1974.

Bacsik, Z., Komlosi, V., Ollar, T., and Mink, J.: Comparison of open path and extractive long-path FTIR techniques in detection of air pollutants, Applied Spectroscopy Reviews, 41, 77-97, https://doi.org/10.1080/05704920500385494, 2006.

Briz, S., de Castro, A. J., Díez, S., López, F., and Schäfer, K.: Remote sensing by open-path FTIR spectroscopy. Comparison of different analysis techniques applied to ozone and carbon monoxide detection, J. Quant. Spectrosc. Radiat. Transf., 103, 314-330, https://doi.org/10.1016/j.jqsrt.2006.02.058, 2007.

Bjorneberg, D. L., Leytem, A. B., Westermann, D. T., Griffiths, P. R., Shao, L., and Pollard, M. J.: Measurement of atmospheric ammonia, methane, and nitrous oxide at a concentrated dairy production facility in southern Idaho using open-path FTIR spectrometry, Trans. ASABE, 52, 1749-1756, 2009.

Chase, D. B.: Nonlinear detector response in FT-IR, Appl. Spectrosc., 38, 491-494, https://doi.org/10.1366/0003702844555296, 1984.

Childers, J. W., Thompson, E. L., Harris, D. B., Kirchgessner, D. A., Clayton, M., Natschke, D. F., and Phillips, W. J.: Multi-pollutant concentration measurements around a concentrated swine production facility using open-path FTIR spectrometry, Atmos. Environ., 35, 1923-1936, https://doi.org/10.1016/s1352-2310(00)00545-8, 2001a.

Childers, J. W., Thompson, E. L., Harris, D. B., Kirchgessner, D. A., Clayton, M., Natschke, D. F., and Phillips, W. J.: Application of standardized quality control procedures to open-path fourier transform infrared data collected at a concentrated swine production facility, Environ. Sci. Technol., 35, 1859-1866, https://doi.org/10.1021/es001744f, 2001b.

Childers, J. W., Phillips, W. J., Thompson, E. L., Harris, D. B., Kirchgessner, D. A., Natschke, D. F., and Clayton, M.: Comparison of an Innovative Nonlinear Algorithm to Classical Least-Squares for Analyzing Open-Path Fourier Transform Infrared Spectra Collected at a Concentrated Swine Production Facility, Appl. Spectrosc., 56, 325-336, https://doi.org/10.1366/0003702021954917, 2002.

de Castro, A. J., Lerma, A. M., López, F., Guijarro, M., Díez, C., Hernando, C., and Madrigal, J.: Open-path Fourier transform infrared spectrometry characterization of low temperature combustion gases in biomass fuels, Infrared Phys. Technol., 51, 21-30, https://doi.org/10.1016/j.infrared.2006.11.005, 2007.

Du, Y. P., Liang, Y. Z., Jiang, J. H., Berry, R. J., and Ozaki, Y.: Spectral regions selection to improve prediction ability of PLS models by changeable size moving window partial least squares and searching combination moving window partial least squares, Analytica Chimica Acta, 501, 183-191, https://doi.org/10.1016/j.aca.2003.09.041, 2004.

Esler, M. B., Griffith, D. W. T., Wilson, S. R., and Steele, L. P.: Precision trace cas analysis by FT-IR spectroscopy. 1. Simultaneous analysis of CO_2, CH_4, N_2O, and CO in air, Analytical Chemistry, 72, 206-215, https://doi.org/10.1021/ac9905625, 2000.

Flesch, T. K., Baron, V. S., Wilson, J. D., Griffith, D. W. T., Basarab, J. A., and Carlson, P. J.: Agricultural gas emissions during the spring thaw: Applying a new measurement technique, Agric. For. Meteorol., 221, 111-121, https://doi.org/10.1016/j.agrformet.2016.02.010, 2016.

Denmead, O. T.: Approaches to measuring fluxes of methane and nitrous oxide between landscapes and the atmosphere, Plant Soil, 309, 5-24, https://doi.org/10.1007/s11104-008-9599-z, 2008.

Griffith, D. W.: Synthetic calibration and quantitative analysis of gas-phase FT-IR spectra, Appl. Spectrosc., 50, 59-70, https://doi.org/10.1366/0003702963906627, 1996.

Griffith, D. W. T., and Jamie, I. M.: Fourier Transform Infrared Spectrometry in Atmospheric and Trace Gas Analysis, in: Encyclopedia of Analytical Chemistry, https://doi.org/10.1002/9780470027318.a0710, John Wiley & Sons, Hoboken, 2006.

Griffith, D. W. T., Deutscher, N. M., Caldow, C., Kettlewell, G., Riggenbach, M., and Hammer, S.: A Fourier transform infrared trace gas and isotope analyser for atmospheric applications, Atmospheric Measurement Techniques, 5, 2481-2498, https://doi.org/10.5194/amt-5-2481-2012, 2012.

Griffiths, P. R.: "Fourier Transform spectrometry at low resolution: how low can you go?", Proc. SPIE 2089, 9th International Conference on Fourier Transform Spectroscopy, https://doi.org/10.1117/12.166563, 1994.

Griffiths, P. R., and de Haseth, J. A.: Fourier transform infrared spectrometry, John Wiley & Sons, Hoboken, 2007.

Griffiths, P., Shao, L., and Leytem, A.: Completely automated open-path FT-IR spectrometry, Analytical and bioanalytical chemistry, 393, 45-50, https://doi.org/10.1007/s00216-008-2429-6, 2009.

Haaland, D. M.: Methods to Include Beer's Law Nonlinearities in Quantitative Spectral Analysis, in, edited by: McClure, G. L., ASTM International, West Conshohocken, PA, 78-94, https://doi.org/ 10.1520/STP23164S, 1987.

Haaland, D. M., and Easterling, R. G.: Improved Sensitivity of Infrared Spectroscopy by the Application of Least Squares Methods, Appl. Spectrosc., 34, 539-548, https://doi.org/10.1366/0003702804731258, 1980.

Haaland, D. M., and Thomas, E. V.: Partial least-squares methods for spectral analyses. 1. Relation to other quantitative calibration methods and the extraction of qualitative information, Anal. Chem., 60, 1193-1202, https://doi.org/10.1021/ac00162a020, 1988.

Hart, B. K., and Griffiths, P. R.: Use of partial least squares regression for the multivariate calibration of hazardous air pollutants in open-path FT-IR spectrometry, AIP Conference Proceedings, 430, 241-244, https://doi.org/10.1063/1.55811, 1998.

Hart, B. K., Berry, R. J., and Griffiths, P. R.: Effects of resolution, spectral window, and background on multivariate calibrations used for open-path Fourier transform infrared spectrometry, Field Analytical Chemistry and Technology, 3, 117-130, https://doi.org/10.1002/(sici)1520-6521(1999)3:2<117::aid-fact7>3.0.co;2-v, 1999.

Hart, B. K., Berry, R. J., and Griffiths, P. R.: Effects of resolution on quantification in open-path Fourier transform infrared spectrometry under conditions of low detector noise. 2. Partial least squares regression, Environmental Science & Technology, 34, 1346-1351, https://doi.org/10.1021/es990439v, 2000.

Hart, B. K., and Griffiths, P. R.: Effect of resolution on quantification in open-path Fourier transform infrared spectrometry under conditions of low detector noise. 1. Classical least squares regression, Environ. Sci. Technol., 34, 1337-1345, https://doi.org/10.1021/es9904383, 2000.

Hong, D. W., and Cho, S. Y.: Improved methods for performing multivariate analysis and deriving background spectra in atmospheric open-path FT-IR monitoring, Applied Spectroscopy, 57, 299-308, 10. https://doi.org/1366/000370203321558218, 2003.

Heber, A. J., Ni, J. Q., Lim, T. T., Tao, P. C., Schmidt, A. M., Koziel, J. A., Beasley, D. B., Hoff, S. J., Nicolai, R. E., Jacobson, L. D., and Zhang, Y. H.: Quality assured measurements of animal building emissions: Gas concentrations, J. Air Waste Manage. Assoc., 56, 1472-1483, https://doi.org/10.1080/10473289.2006.10465680, 2006.

Horrocks, L. A., Oppenheimer, C., Burton, M. R., Duffell, H. J., Davies, N. M., Martin, N. A., and Bell, W.: Open-path Fourier transform infrared spectroscopy of SO2: An empirical error budget analysis, with implications for volcano monitoring, J. Geophys. Res.-Atmos., 106, 27647-27659, https://doi.org/10.1029/2001jd000343, 2001.

IPCC: Intergovernmental Panel on Climate Change, Fourth Assessment Report-Working I Report: The physical science basis, Cambridge Univ. Press, Cambridge, 2007.

IPCC, Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, <http://www.ipcc.ch/pdf/assessment-report/ar5/wg3/ipcc_wg3_ar5_full.pdf>, 2014.

Jiang, J. H., Berry, R. J., Siesler, H. W., and Ozaki, Y.: Wavelength interval selection in multicomponent spectral analysis by moving window partial least-squares regression with applications to mid-infrared and near-infrared spectroscopic data, Analytical Chemistry, 74, 3555-3565, https://doi.org/10.1021/ac011177u, 2002.

Kosterev, A., Wysocki, G., Bakhirkin, Y., So, S., Lewicki, R., Fraser, M., Tittel, F., and Curl, R. F.: Application of quantum cascade lasers to trace gas analysis, Appl. Phys. B-Lasers Opt., 90, 165-176, https://doi.org/10.1007/s00340-007-2846-9, 2008.

Lacome, N., Levy, A., and Guelachvili, G.: Fourier transform measurement of self-, N2-, and O2-broadening of N2O lines: temperature dependence of linewidths, Appl. Optics, 23, 425-435, https://doi.org/10.1364/AO.23.000425, 1984.

Lam, S. K., Suter, H., Mosier, A. R., and Chen, D.: Using nitrification inhibitors to mitigate agricultural N_2O emission: a double-edged sword?, Global Change Biology, 23, 485-489, https://doi.org/10.1111/gcb.13338, 2017.

Lin, C. H., Grant, R. H., Heber, A. J., and Johnston, C. T.: Application of open-path Fourier transform infrared spectroscopy (OP-FTIR) to measure greenhouse gas concentrations from agricultural fields, Atmos. Meas. Tech., 12, 3403-3415, https://doi.org/10.5194/amt-12-3403-2019, 2019.

Loos, J., Birk, M., and Wagner, G.: Pressure broadening, -shift, speed dependence and line mixing in the v(3) rovibrational band of N_2O, Journal of Quantitative Spectroscopy & Radiative Transfer, 151, 300-309, https://doi.org/10.1016/j.jqsrt.2014.10.008, 2015.

Mosier, A. R., Duxbury, J. M., Freney, J. R., Heinemeyer, O., and Minami, K.: Nitrous oxide emissions from agricultural fields: Assessment, measurement and mitigation, Plant and Soil, 181, 95-108, https://doi.org/10.1007/bf00011296, 1996.

Muller, U., Heise, H. M., Mosebach, H., Gartner, A. G., and Hausler, T.: Improved strategies for quantitative evaluation of atmospheric FTIR spectra obtained in open-path monitoring, Field Anal. Chem. Technol., 3, 141-159, https://doi.org/10.1002/(sici)1520-6521(1999)3:3<141::aid-fact2>3.0.co;2-5, 1999.

Nelson, D. D., Zahniser, M. S., McManus, J. B., Shorter, J. H., Wormhoudt, J. C., and Kolb, C. E.: Recent improvements in atmospheric trace gas monitoring using mid-infrared tunable diode lasers, Proc. SPIE 2834, 148-159, https://doi.org/10.1117/12.255321, 1996.

Paton-Walsh, C., Smith, T. E. L., Young, E. L., Griffith, D. W. T., and Guerette, E. A.: New emission factors for Australian vegetation fires measured using open-path Fourier transform infrared spectroscopy - Part 1: Methods and Australian temperate forest fires, Atmospheric Chemistry and Physics, 14, 11313-11333, https://doi.org/10.5194/acp-14-11313-2014, 2014.

Phillips, F. A., Naylor, T., Forehead, H., Griffith, D. W. T., Kirkwood, J., and Paton-Walsh, C.: Vehicle Ammonia Emissions Measured in An Urban Environment in Sydney, Australia, Using Open Path Fourier Transform Infra-Red Spectroscopy, Atmosphere, 10, https://doi.org/10.3390/atmos10040208, 2019.

Rothman, L. S., Jacquemart, D., Barbe, A., Benner, D. C., Birk, M., Brown, L. R., Carleer, M. R., Chackerian, C., Chance, K., Coudert, L. H., Dana, V., Devi, V. M., Flaud, J. M., Gamache, R. R., Goldman, A., Hartmann, J. M., Jucks, K. W., Maki, A. G., Mandin, J. Y., Massie, S. T., Orphal, J., Perrin, A., Rinsland, C. P., Smith, M. A. H., Tennyson, J., Tolchenov, R. N., Toth, R. A., Vander Auwera, J., Varanasi, P., and Wagner, G.: The HITRAN 2004 molecular spectroscopic database, J. Quant. Spectrosc. Radiat. Transf., 96, 139-204, https://doi.org/10.1016/j.jqsrt.2004.10.008, 2005.

Russwurm, G. M., and Childers, J. W.: FT-IR open-path monitoring guidance document (3rd edition), ManTech Environmental Technology, Inc., Research Triangle Park, NC (United States), 1999.

Russwurm, G. M., and Phillips, B.: Effects of a nonlinear response of the Fourier-transform infrared open-path instrument on the measurements of some atmospheric gases, Appl. Optics, 38, 6398-6407, https://doi.org/10.1364/ao.38.006398, 1999.

Russwurm, G. M.: Long-path open-path Fourier transform infrared monitoring of atmospheric gases: compendium method TO-16, in: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd ed., Center for Environmental Research Information, Office of Research and Development, US Environmental Protection Agency, Cincinnati, OH, EPA/625/R-96/010b, 1999.

Russwurm, G. M. and Childers, J. W.: “Open-path Fourier transform infrared spectroscopy”. In Handbook of Vibrational Spectroscopy Edited by: Chalmers, J. M. and Griffiths, P. R. Vol. 2, 1750–1773. New York: Wiley, 2002.

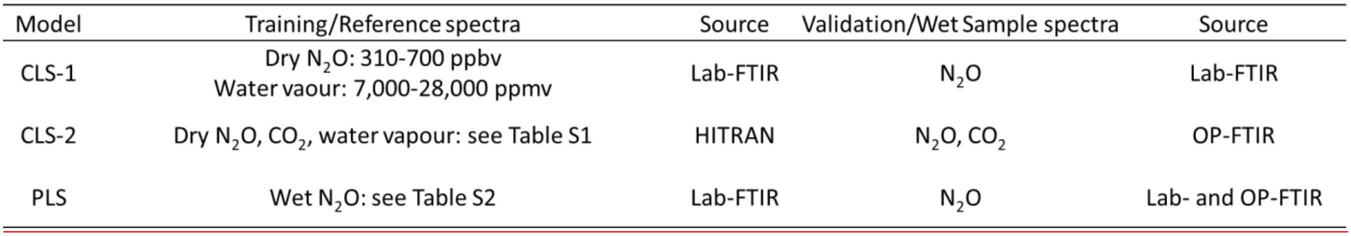
Shao, L., Pollard, M. J., Griffiths, P. R., Westermann, D. T., and Bjorneberg, D. L.: Rejection criteria for open-path Fourier transform infrared spectrometry during continuous atmospheric monitoring, Vib. Spectrosc., 43, 78-85, https://doi.org/10.1016/j.vibspec.2006.06.016, 2007.

Shao, L., Griffiths, P. R., and Leytem, A. B.: Advances in Data Processing for Open-Path Fourier Transform Infrared Spectrometry of Greenhouse Gases, Anal. Chem., 82, 8027-8033, https://doi.org/10.1021/ac101711r, 2010.

Smith, T. E. L., Wooster, M. J., Tattaris, M., and Griffith, D. W. T.: Absolute accuracy and sensitivity analysis of OP-FTIR retrievals of CO_2, CH_4 and CO over concentrations representative of "clean air" and "polluted plumes", Atmos. Meas. Tech., 4, 97-116, https://doi.org/10.5194/amt-4-97-2011, 2011.

Zhu, C., and Griffiths, P. R.: Extending the Range of Beer's Law in FT-IR Spectrometry. Part I: Theoretical Study of Norton-Beer Apodization Functions~~Extending the range of Beer's law in FTIR spectrometry by selection of the apodization functions~~, Appl. Spectrosc. 52, 1403-1408~~Proc. SPIE 2089, 434-435~~, https://doi.org/10.1366/0003702981943022~~10.1117/12.166652~~, ~~1994~~1998.

Table1. Multivariate models (i.e. CLS and PLS) used for N_2O and CO_2 quantification: 1) the CLS-1 model was built by five dry N_2O spectra (310, 400, 500, 600, 700 ppbv) and four water vapour spectra (7 000, 15 000, 22 000, 28 000 ppmv) collected from the lab-FTIR, 2) CLS-2 model was built by twelve dry N_2O, seventeen dry CO_2, and sixteen water vapour spectra generated from the HITRAN database (see Table S1 in the supplement), and 3) the PLS model was built by a total of sixty wet N_2O spectra collected from Lab-FTIR (see Table S2 in the supplement).



Model	Training/Reference spectra	Source	Validation/Wet Sample spectra	Source
CLS-1	Dry N_2O: 310-700 ppbv Water vaour: 7,000-28,000 ppmv	Lab-FTIR	N_2O	Lab-FTIR
CLS-2	Dry N_2O, CO_2, water vapour: see Table S1	HITRAN	N_2O, CO_2	OP-FTIR
PLS	Wet N_2O: see Table S2	Lab-FTIR	N_2O	Lab- and OP-FTIR

~~Table1~~Table2. Spectral windows for quantification of N_2O and CO_2.

Gas	Windows (cm^{-1})	Interferences
N_2O	W_N1: 2170.0-2223.7	H_2O, CO, CO_2
	W_N3: 2188.7-2204.1 + 2215.8-2223.7	H_2O, CO, CO_2
CO_2	W_C2: 2075.5-2084.0	H_2O

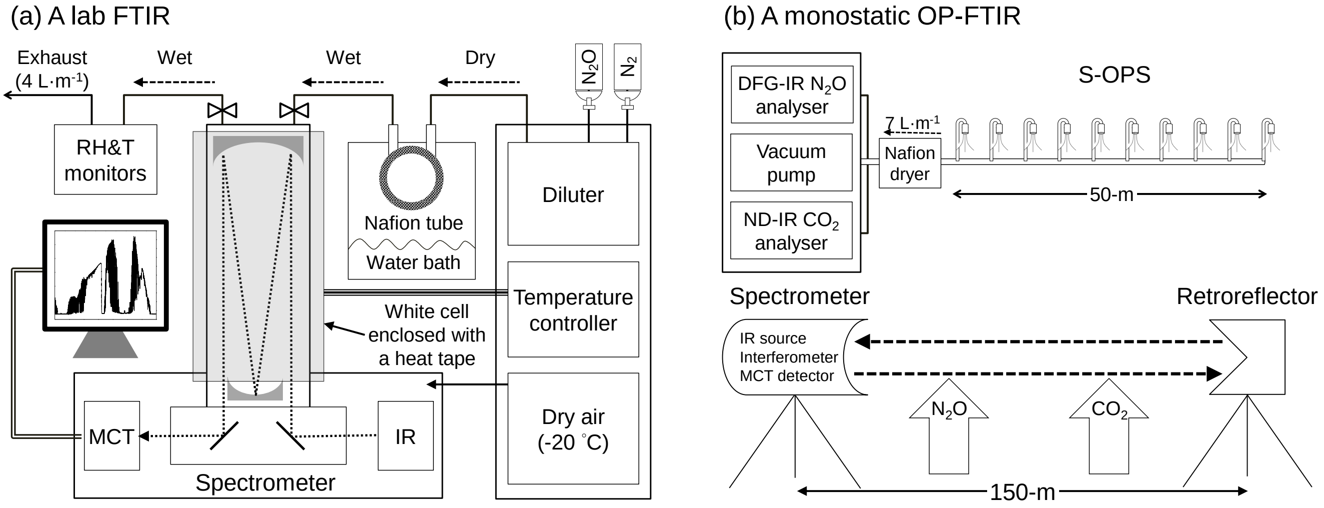


Figure 1. Schematic of the instrumentation used to assess the effects of water vapour and temperature on gas quantification: (a) lab-FTIR with a multi-pass gas cell (optical path length of 33 m); (b) DFG-IR N_2O and ND-IR CO_2 analysers combined with synthetic open path gas sampling system (S-OPS) were used as benchmarks to assess quantification of N_2O and CO_2 from OP-FTIR.

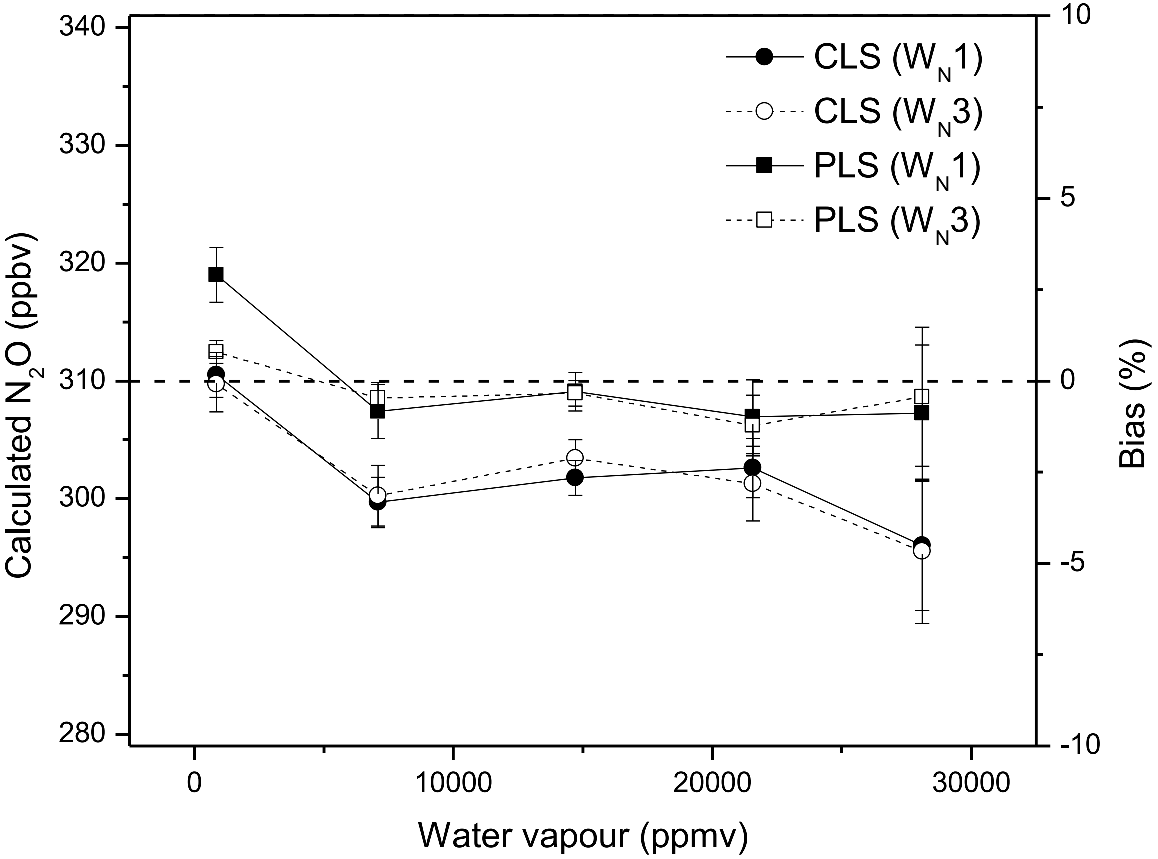


Figure 2. Effects of water vapour on N_2O quantification: the lab-FTIR spectra of dry N_2O and N_2O/water vapour mixtures (310 ppbv N_2O at the relative humidity of 20 %, 40 %, 60 %, and 80 % at 30 °C) were used to calculate N_2O concentrations using CLS and PLS models and two spectral windows (W_N1 and W_N3).

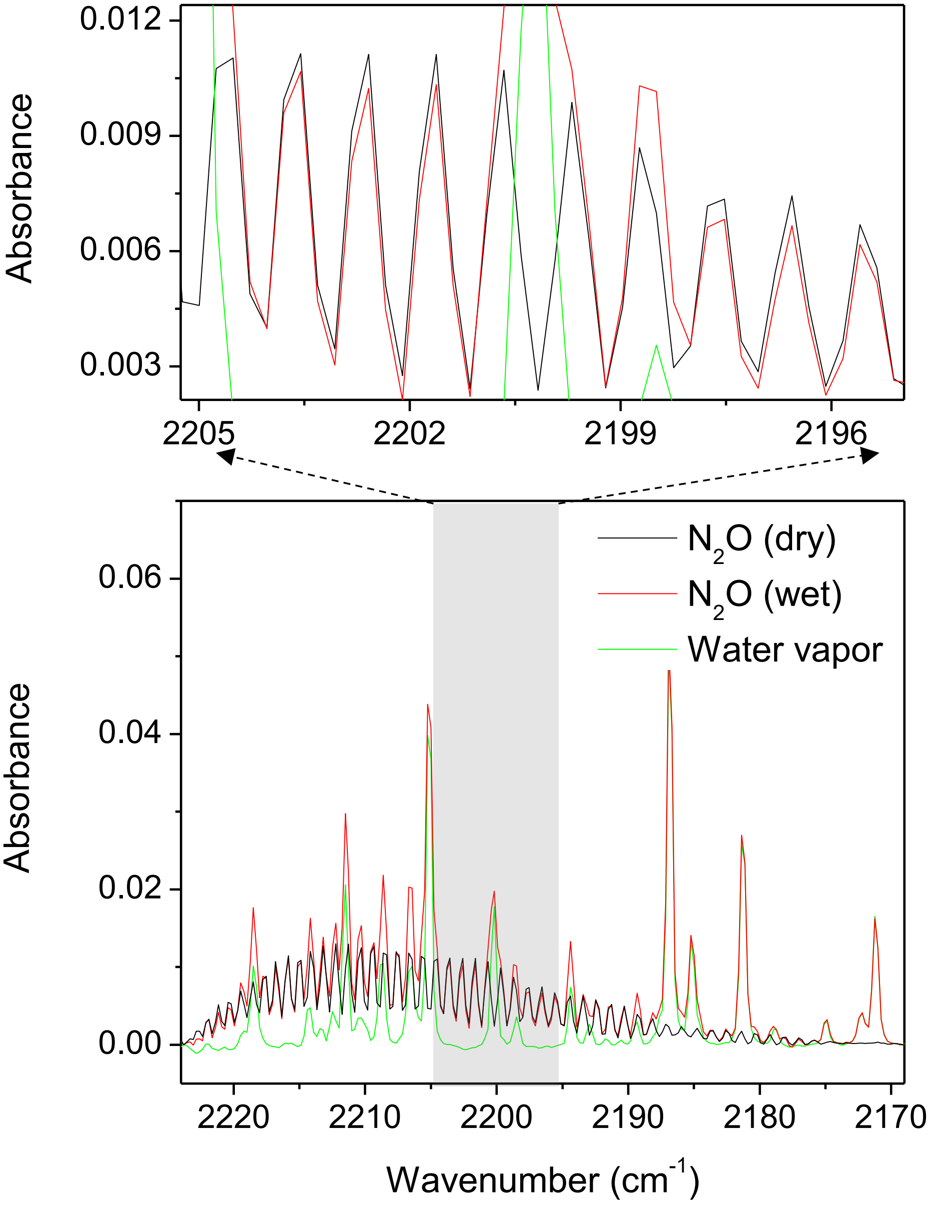


Figure 3. The lab-FTIR spectra of dry N_2O (310 ppbv), wet N_2O (310 ppbv N_2O plus 28 000 ppmv water vapour), and water vapour (28 000 ppmv) were acquired at 30 °C.

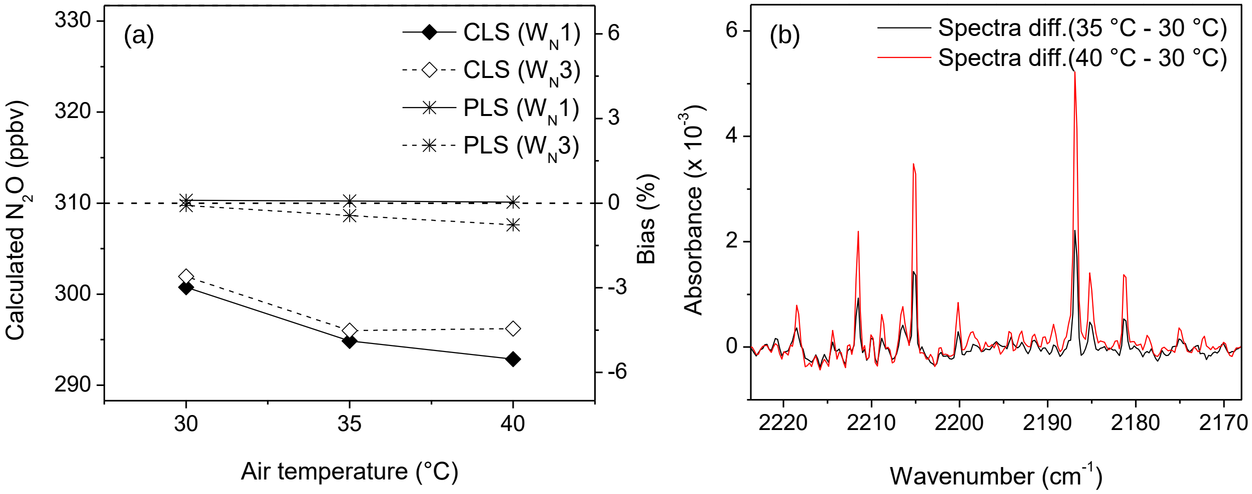


Figure 4. Effects of temperature on N_2O quantification: the lab FTIR spectra containing wet N_2O (310 ppbv N_2O plus 21 500 ppmv water vapour) were acquired at 30 °C, 35 °C, and 40 °C. Temperature affected (a) N_2O concentrations calculated by the CLS and PLS models and two spectral windows (W_N1 and W_N3) and (b) spectral differences in wet N_2O absorbance (310 ppbv N_2O plus 21 500 ppmv water vapour) among different temperature.

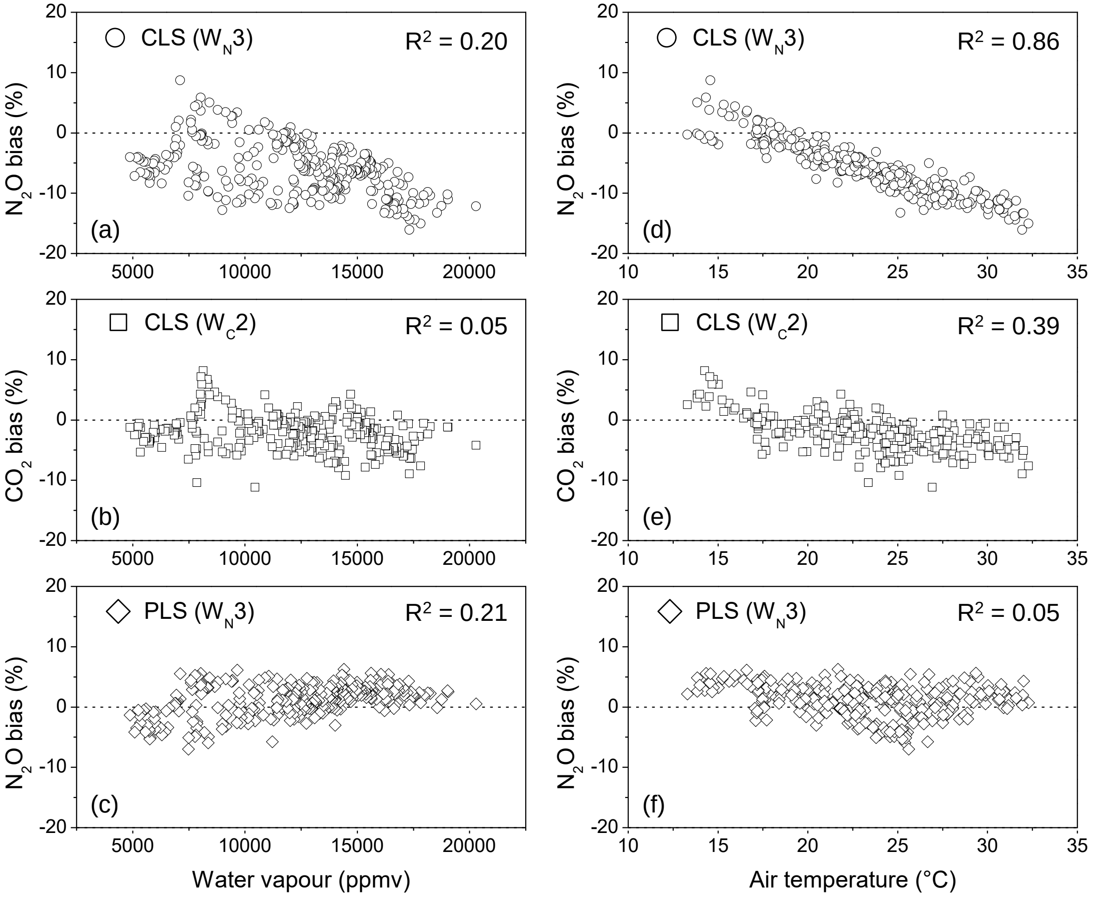


Figure 5. Effects of water vapour and temperature on N_2O and CO_2 concentrations calculated from the OP-FTIR spectra using CLS and PLS models and the optimum windows (W_N3 for N_2O and W_C2 for CO_2) during 9-19 June 2014. Assumed temperature and bias are a linear relationship.

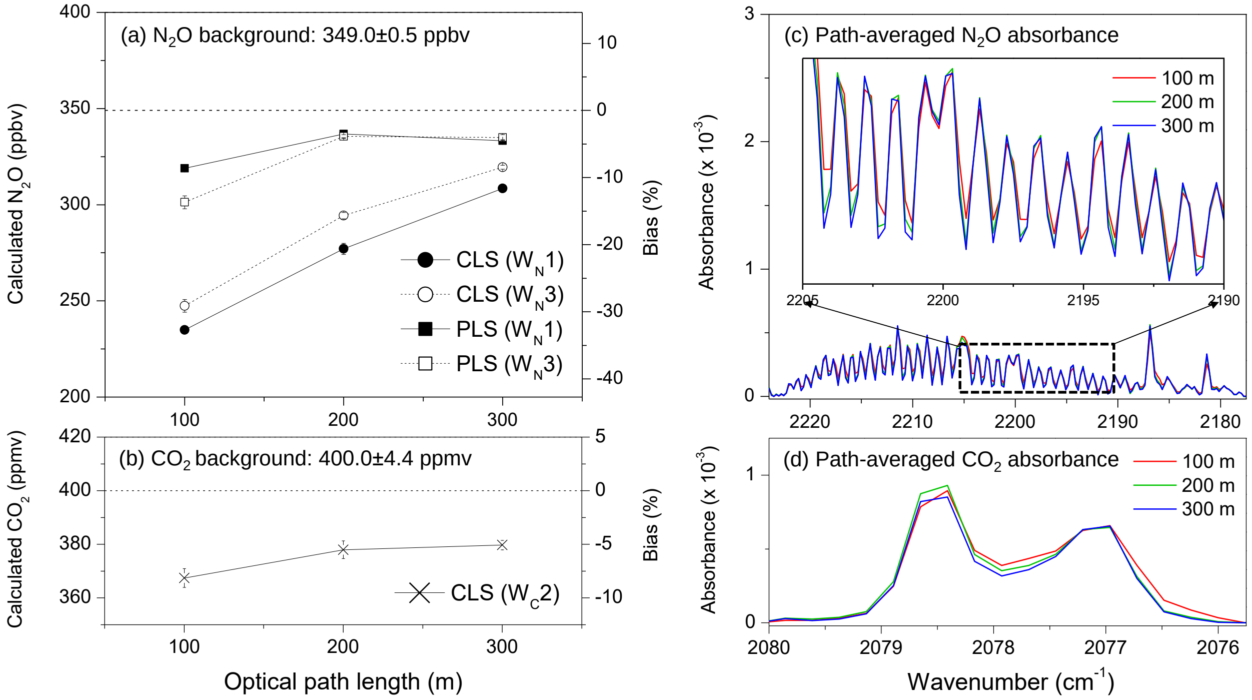


Figure 6. Effects of path lengths on N_2O and CO_2 quantification: OP-FTIR spectra were acquired under backgrounds of N_2O (349.0 ± 0.5 ppbv) and CO_2 (400.0 ± 4.4 ppmv), and relative humidity of 35 % at 25 °C from optical path lengths of 100, 200, and 300 m for quantification of (a) N_2O using CLS and PLS and windows of W_N1 and W_N3, (b) CO_2 using a CLS model and the window of W_C2. The path-averaged absorbance spectra of (c) N_2O and (d) CO_2 showed the inconsistency of absorbance spectra.

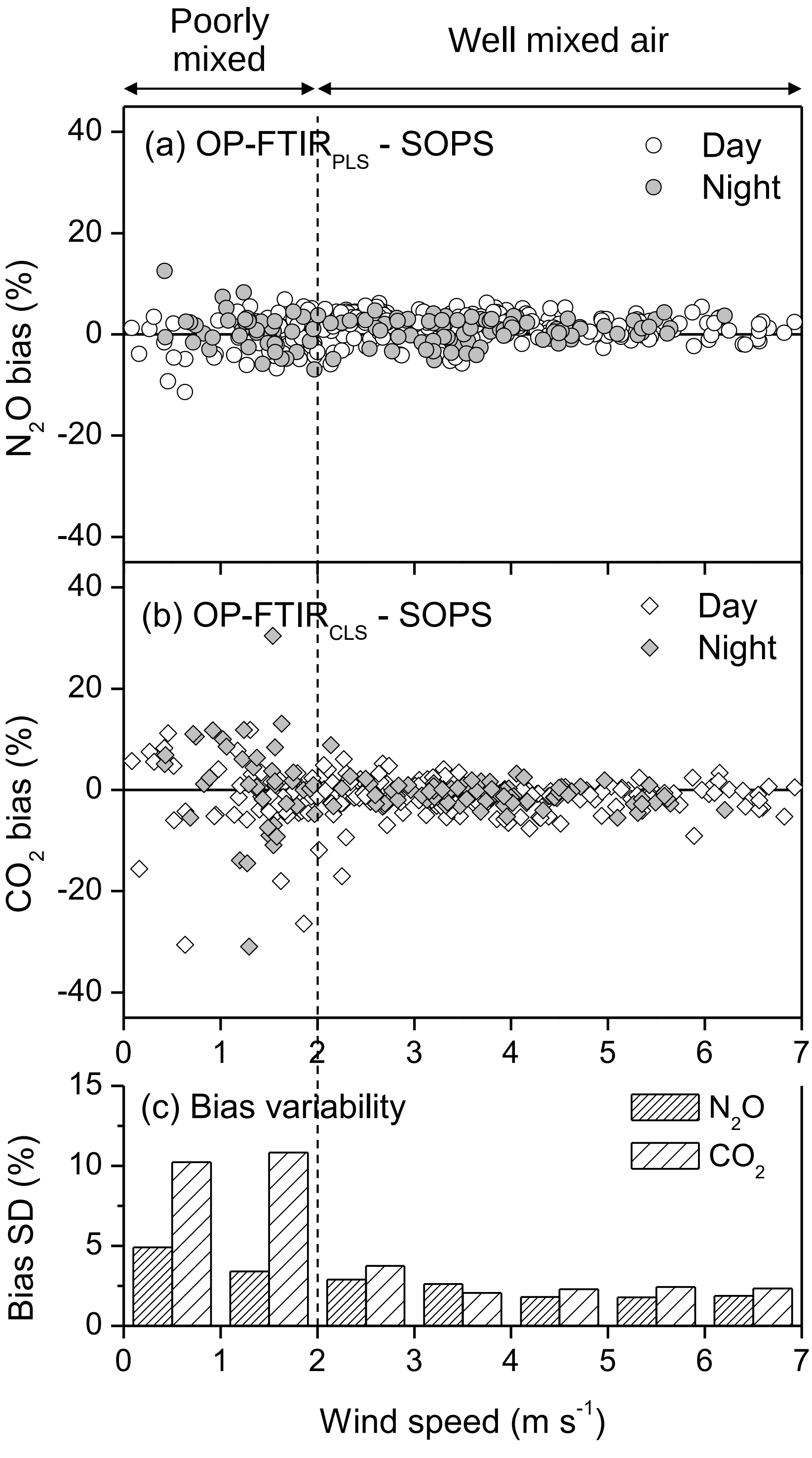


Figure 7. Effects of the wind speed on differences in the path-averaged concentrations between the OP-FTIR and S-OPS: (a) N_2O, (b) CO_2, and (c) variability of biases (Standard deviation, SD).