

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 will be 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 , $n = 1, 2, \dots, m$), 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} . I think that it would be clearer to express ZFF as two instead of one.

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 N₂O estimations quoted in the abstract reconcile with those from the companion paper (-4.9% for N₂O 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.

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Response:

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 N₂O bias of -4.9 ± 3.1 % was calculated from ninety spectra which contained similar N₂O 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.

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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?

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Response:

The spectra containing single gas species (e.g. N₂O or water vapour only) were used to build CLS models, and the spectra containing mixed-gas species (e.g. N₂O 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 N₂O 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 N₂O spectra and sixteen water vapor spectra generated from HITRAN database at 30 °C (see the table S1 in the supplement published by Lin et al. 2019). The PLS model was created using a total of sixty mixed-gas spectra (N₂O mixed with water vapour) collected from the lab-FTIR spectrometer at 30 °C (see the table S1 in the supplement published by Lin et al. 2019). Validation/sample spectra of the wet N₂O were both collected from the lab- and OP-FTIR spectrometers to evaluate model performances. The CLS-1 and PLS were used

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to calculate N₂O concentrations from the validation spectra (wet N₂O) collected from the lab-FTIR; the CLS-2 and PLS were used to calculate N₂O 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 N₂O and water vapour (310 ppbv N₂O 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 N₂O biases within the water vapour range of 5,000-20,000 ppmv (Fig.2 in the manuscript).

Model	Training/Reference spectra	Validation/Sample spectra
CLS-1	Lab-FTIR: N ₂ O spectra: 310, 400, 500, 600, and 700 ppbv H ₂ O spectra: 7K, 15K, 22K, and 28K ppmv	Lab-FTIR: Wet N ₂ O spectra
CLS-2	HITRAN database: (see Table S1 published by Lin et al, 2019)	OP-FTIR: Wet N ₂ O spectra
PLS	Lab-FTIR: A total of sixty wet N ₂ O spectra (see Table S2 published by Lin et al, 2019)	Lab- and OP-FTIR: Wet N ₂ O spectra

Fig. 1. The information of quantitative models (CLS and PLS), training and validation spectra.

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 $< 2 \text{ m s}^{-1}$) also led to uncertainties in delta concentration, so that the concentrations collected under low wind condition ($< 2 \text{ m s}^{-1}$) 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; however, we had a difficulty to generate the mixed-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, LICOR Inc., Lincoln, NE) provided high precision for N_2O ($< 0.15 \text{ ppbv}$, 1σ) and CO_2 ($< 1.0 \text{ ppmv}$, 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 N_2O P-branch. How does it “compromise” the intensity of the N_2O 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:

5 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).

- 10 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, $R^2=0.20$ (weak) with water and $R^2=0.86$ (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:

15 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).

- 20 12. In explaining the excess bias in field values of N_2O interferences by CO and CO_2 are invoked as ‘‘presumable’’. Can one not look at the spectral fit residuals to see if CO and CO_2 interferences are being captured correctly?

Response:

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

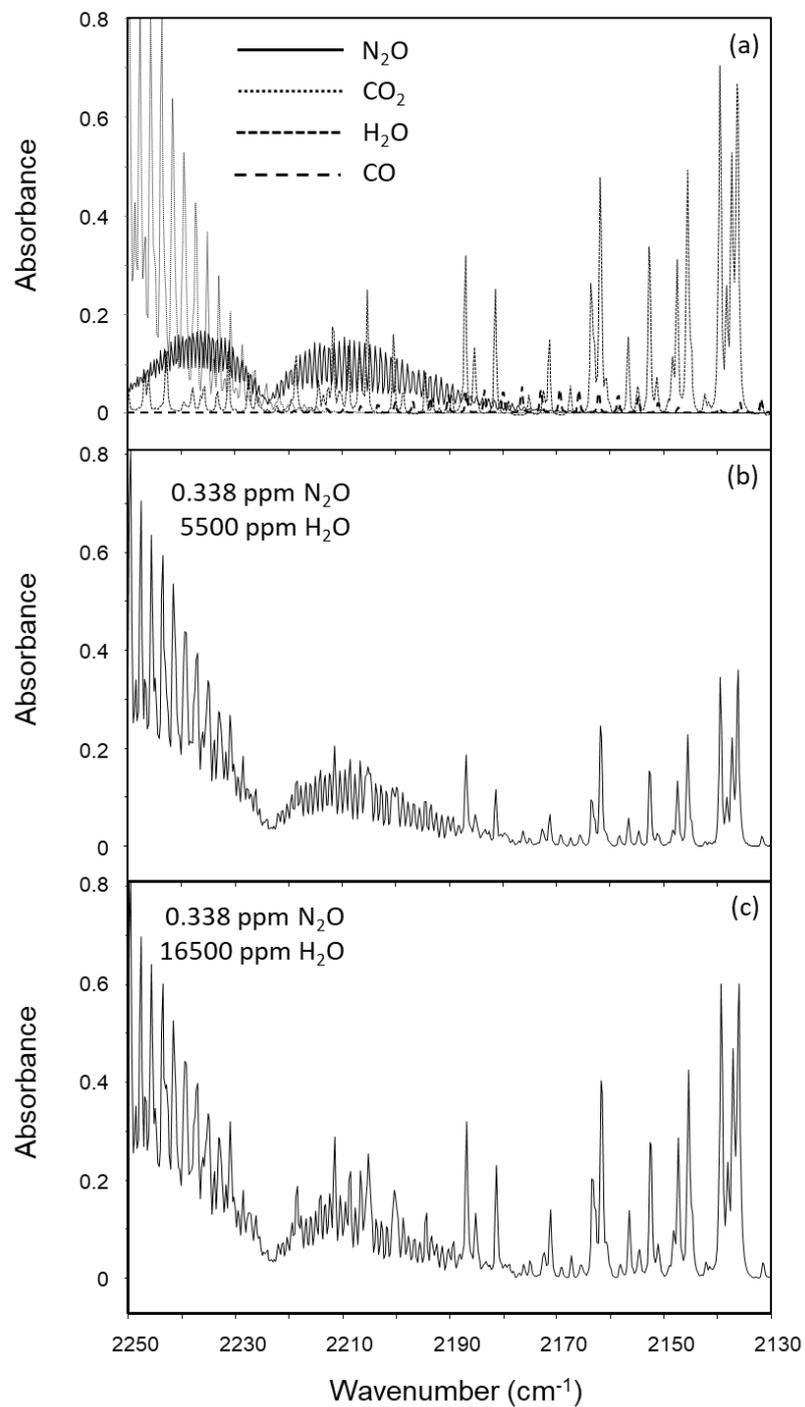


Fig.2 – Comparisons between the HITRAN and the OP-FTIR absorption spectra: (a) HITRAN N_2O , CO_2 , CO , and water vapour, and OP-FTIR spectra of 0.338 ppm N_2O in (b) low humidity, and (c) high humidity conditions.

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?

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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 N₂O at 2170-2224 cm⁻¹, the less complicated features of CO₂ absorption make CO₂ quantification less sensitive to a short path length than N₂O quantification using CLS model (Figure-6 in manuscript). CO₂ 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 CO₂ absorption spectra acquired from a short path. The ‘stronger’ absorption signal from a short path was attributed to a strong water vapour signal.

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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.

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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, CO₂ can be produced from both soil and canopy respirations, and plant uptake via photosynthesis. N₂O was predominately produced from soil nitrification and denitrification. The CO₂ 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, CO₂ concentrations in the air tended to have higher variabilities than N₂O 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 CO₂ 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.

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Sources of error in open-path FTIR measurements of N₂O and CO₂ 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 (N₂O) and carbon dioxide (CO₂) concentrations derived from OP-FTIR spectra. The presence of water vapour resulted in underestimating N₂O in both lab (−3 %) and field (−12 %) experiments at 30 °C using a classical least squares (CLS) model. Differences in temperature between the sample and reference spectra also underestimated N₂O 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. N₂O and CO₂ concentrations were underestimated by 30 % and 7.5 %, respectively, at the optical path of 100 m using CLS models). For N₂O 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 N₂O and CO₂. The quantified errors can be used as references for current or future OP-FTIR users.

20 1 Introduction

Agriculture substantially contributes greenhouse gases (GHGs), mostly N₂O and CH₄, 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 CO₂ 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. NH₃) emitted from agricultural fields (Childers et al., 2001a and 2001b; Bjerneberg 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 ($400\text{-}4000\text{ cm}^{-1}$) (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 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 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-beam-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, Alternatively, 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).

For OP-FTIR measurements, many 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 N₂O. 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 on trace gas absorption intensity and bandwidth have been 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 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 SO₂, CO, CO₂, and CH₄ quantification, but not for N₂O.

To the best of our knowledge, there has never been a study of exploring the influence of changing temperature and path length on N₂O quantification under interferences of water vapour in spectra. It is challenging to test the quality of OP-FTIR methods for multiple gas quantification 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 N₂O and CO₂ 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 N₂O quantification from spectra. An FTIR spectrometer equipped with a variable-path length gas cell was used to acquire reference spectra of N₂O, water vapour, and N₂O plus water vapour mixtures (i.e. wet N₂O) 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 N₂ 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 N₂O was diluted with ultra-pure N₂ 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 N₂O gas samples were produced by passing dry N₂O from the diluter through Nafion tube with a constant flow rate (4 L·min⁻¹). Gas samples were continuously introduced into the White cell. 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, N₂O (dry and wet) was diluted from 30.0 ppmv (N₂O in N₂) 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 N₂O and water vapour concentrations and temperature of the introduced samples were steady. Concentrations of N₂O and water vapour were calculated from the mixed-gas (wet N₂O) absorbance spectra by CLS and PLS models using TQ Analyst software Version 8.0 (Thermo Fisher Scientific, Inc.) A total of 9 single-gas spectra of dry N₂O (310.0-700.0 ppbv) and water vapour (7000-28 000 ppmv) were used to build CLS models. A total of 60 mixed-gas spectra were used to build PLS models. Spectral windows (Table 1) and linear baseline correction were applied in CLS and PLS models to calculate N₂O. Two windows reported by Lin et al. (2019) were used for N₂O quantification (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). The influence of air temperature on N₂O quantification using CLS and PLS was examined by collecting spectra at 30, 35, and 40 °C.

5 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 N₂O and CO₂ 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~~two, triangular apodization, and Mertz phase correction 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 spectra were generated from the HITRAN database (Rothman et al., 2005) and used to create CLS models. Identical parameters, including resolution, apodization, zero-filling factor, were used to acquire both reference and field spectra. The HITRAN reference spectra, including N₂O, CO₂, and water vapour, were generated at 30 °C to calculate N₂O and CO₂

concentrations from field spectra using optimum windows (W_{N3} for N_2O and W_{C2} for CO_2 shown in Table 1) published by Lin et al. (2019). 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.

10 Ambient temperature and relative humidity in the field were measured using an HMP45C probe (Vaisala Oyj, Helsinki, Finland) 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 15 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, so the path-averaged concentrations measured from the S-OPS were used as benchmarks to examine the accuracy and the sensitivity of OP-FTIR on gas quantification.

2.2.3 Path lengths experiment

20 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), 25 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 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 30 the true gas concentrations (x_t) of either the introduced gas (Lab) or the S-OPS measurements (Field), following Eq. (1):

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

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 N₂O 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 N₂O concentrations.

3.1 Lab FTIR experiment

3.1.1 Water vapour effect

Water vapour interfered with spectral windows and resulted in underestimations of N₂O concentrations using CLS models; increased water vapour increased the bias (Fig. 2). The PLS model provided more accurate predictions for N₂O 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 N₂O (Fig. 3) showed that the interference of water vapour compromised the intensity of the N₂O P-branch absorbance (Fig. 3P-branch). The reduced N₂O absorbance in wet samples resulted in underestimations of N₂O concentrations using CLS models created based on references of dry N₂O samples and water vapour. PLS models, created by wet N₂O references, showed improved accuracy in wet samples but overestimated N₂O in dry samples (Fig. 2). It is still unclear how water vapour interfered with gas quantification. The N₂O 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 N₂O 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.

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 N₂O quantification is shown in Fig. 4a. Spectra of wet N₂O (310 ppbv N₂O blending with 21 000 ppmv water vapour) were collected at 30 °C, 35 °C, and 40 °C. Reference spectra of dry N₂O, water

vapour, and wet N₂O were acquired at 30 °C and used to calculate N₂O concentrations from spectra collected at temperatures of 35 °C and 40 °C. The difference in temperature led to biases in N₂O calculations (Fig. 4a). Smith et al. (2011) calculated concentrations of CO₂, CH₄, 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 N₂O 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 N₂O 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 N₂O 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). PLS methods showed less sensitivity to temperature (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 the increased water vapour showed the increased N₂O 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 N₂O 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 negligible correlation (~~R² = 0.20 shown in Fig. 5a~~) between water vapour content and the N₂O bias (R² = 0.20 shown in Fig. 5a) was because water vapour was confounded by temperature (i.e. temperature ranged from 10 °C to 35 °C in fields) and became insignificant when the calculated biases were categorized by temperature (~~i.e.e.g.~~ R² = 0.01 at the interval of 25-30 °C, data not shown). CO₂ measured by CLS was less sensitive to changing water vapour content (R² = 0.05) than N₂O (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, N₂O biases became consistent but slightly increased with increasing water vapour (Fig. 5c).

3.2.2 Temperature effect

Increased air temperature increased both N₂O and CO₂ ~~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 strong correlation of air temperature to N₂O biases (R² = 0.86) showed the N₂O quantification was more sensitive to temperature effects than CO₂ (R² = 0.39). The lab experiment (Fig. 4) showed that CLS underestimated N₂O by 3.0 % in wet air for samples with a low delta-temperature. N₂O 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 %) ~~presumably~~ resulted from interferences from CO and CO₂ 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 CO₂ values were less influenced by temperature ($R^2 = 0.39$) than N₂O (Fig. 5e), attributed to the reduced complexity of CO₂ 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). The PLS models were less influenced by temperature for N₂O quantification ($R^2 = 0.05$) and provided better accuracy for N₂O estimations (Fig. 5f).

3.2.3 Path length effect

OP-FTIR spectra containing N₂O concentrations of 349.0 ± 0.5 ppbv and CO₂ concentrations of 400.0 ± 4.4 ppmv were collected from optical lengths of 100, 200, and 300 m. As path lengths decreased, both N₂O and CO₂ concentrations were underestimated (Fig. 6a and 6b). For N₂O, 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 N₂O and CO₂ (i.e. $\frac{\text{Absorbance}}{\text{Path length(m)}}$) did not conform to the Beer-Lambert law even though background concentrations of N₂O and CO₂ 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 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).

Presumably, this short-path-derived bias (Fig. 6a and 6b) 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, N₂O quantification was more sensitive to path lengths than CO₂. With increasing optical path lengths from 100 m to 300 m, the accuracy of N₂O calculated from CLS models increased by approximately 20.0 % (N₂O biases reduced from -30.0 % to -10.0 % shown in Fig. 6a). For CO₂, the accuracy only increased 2.5 % (CO₂ 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. N₂O absorption features in 2170.0-2224.0 cm⁻¹ were more complicated than CO₂ in 2075.0-2085.0 cm⁻¹; furthermore, more interfering gases (CO, CO₂, and water vapour in 2170.0-2224.0 cm⁻¹) interfered with N₂O 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 N₂O biases and showed less sensitivity to path length than CLS (Fig. 6a).

3.2.3 Wind speed effect

Nitrous oxide is predominately produced via soil microbial activities (nitrification and denitrification) and CO₂ 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 N₂O and CO₂ from soil and/or canopy result in inhomogeneous gas concentrations 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 N₂O and CO₂ concentrations between the S-OPS and OP-FTIR was used to calculate quantification bias (Fig. 7). Variabilities of N₂O and CO₂ biases were small but increased when the wind speed was less than 2 m s⁻¹ (Fig. 7c and Table S1 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, CO₂ bias showed higher variability than N₂O presumably due to a greater environmental variation in CO₂ concentrations than N₂O (Lin et al., 2019). Low wind conditions likely occurred during the night period. For instance, 22.0 % (57 out of 259) of the collected data (30-min-averaged N₂O) 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 N₂O and CO₂ quantified by CLS and PLS models. Water vapour in spectra underestimated N₂O concentrations by 3.0 % (lab experiment) and 12.0 % (field experiment) at 30 °C using CLS models. PLS models improved the accuracy of N₂O 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 N₂O, 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. CO₂ quantification using CLS model was less influenced by environmental variables than N₂O 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.

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 ($< 0.5 \text{ cm}^{-1}$) 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 singlesignal-to-noise ratio (Griffiths and de Haseth, 2007).

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

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Table1. Spectral windows for quantification of N₂O and CO₂.

Gas	Windows (cm ⁻¹)	Interferences
N ₂ O	W _N 1: 2170.0-2223.7	H ₂ O, CO, CO ₂
	W _N 3: 2188.7-2204.1 + 2215.8-2223.7	H ₂ O, CO, CO ₂
CO ₂	W _C 2: 2075.5-2084.0	H ₂ O

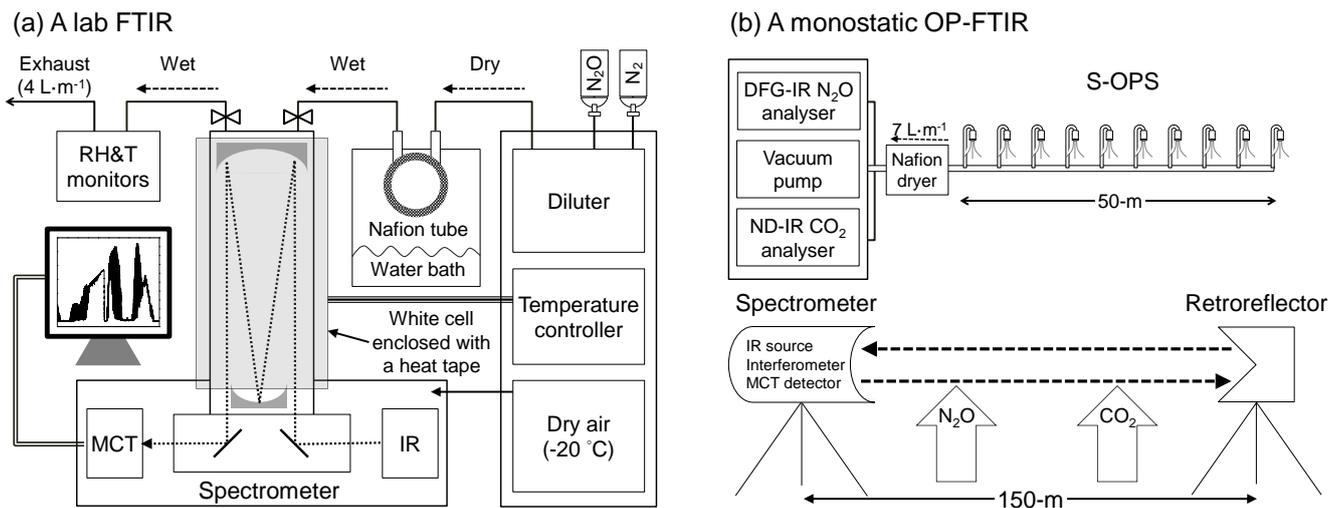


Figure 1. Schematic of the instrumentation used to assess the effects of water vapour and temperature on gas quantification: (a) lab-FTIR with a multi-pass gas cell (optical path length of 33 m); (b) DFG-IR N₂O and ND-IR CO₂ analysers combined with synthetic open path gas sampling system (S-OPS) were used as benchmarks to assess quantification of N₂O and CO₂ from OP-FTIR.

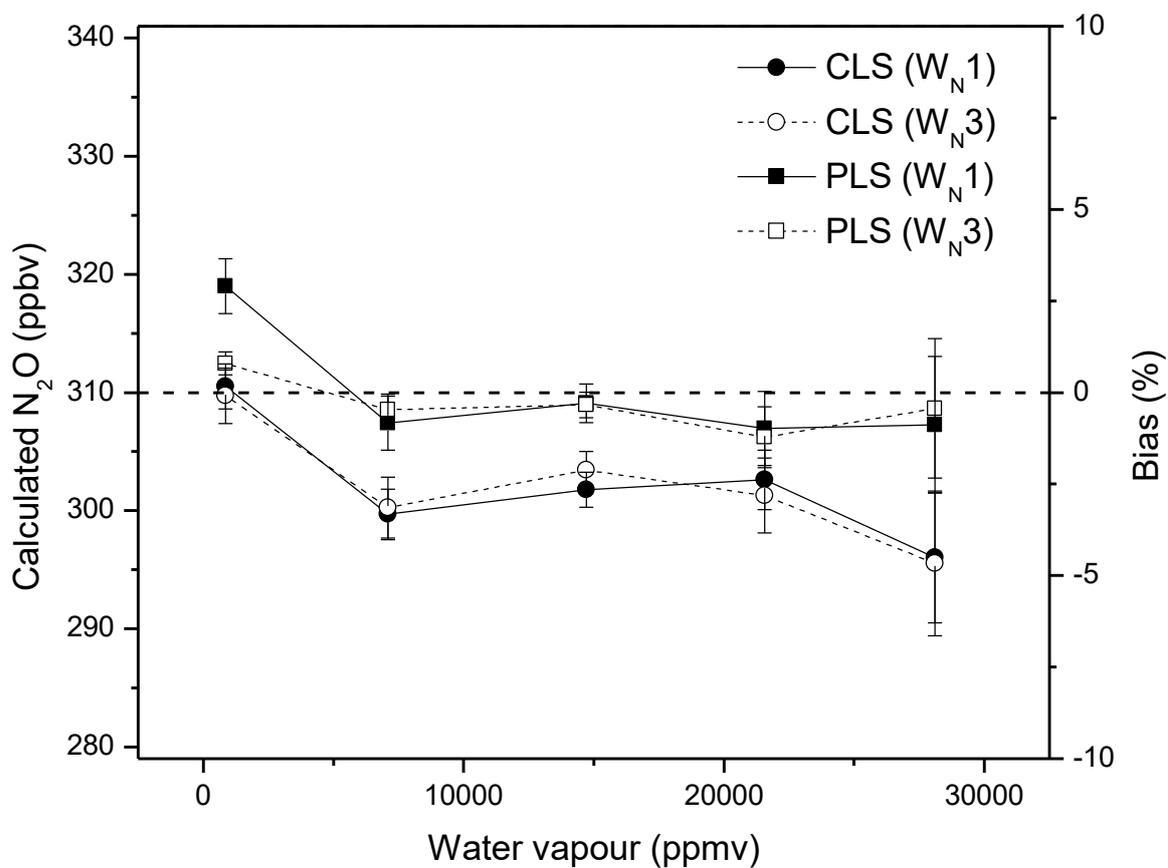


Figure 2. Effects of water vapour on N₂O quantification: the lab-FTIR spectra of dry N₂O and N₂O/water vapour mixtures (310 ppbv N₂O at the relative humidity of 20 %, 40 %, 60 %, and 80 % at 30 °C) were used to calculate N₂O concentrations using CLS and PLS models and two spectral windows (W_{N1} and W_{N3}).

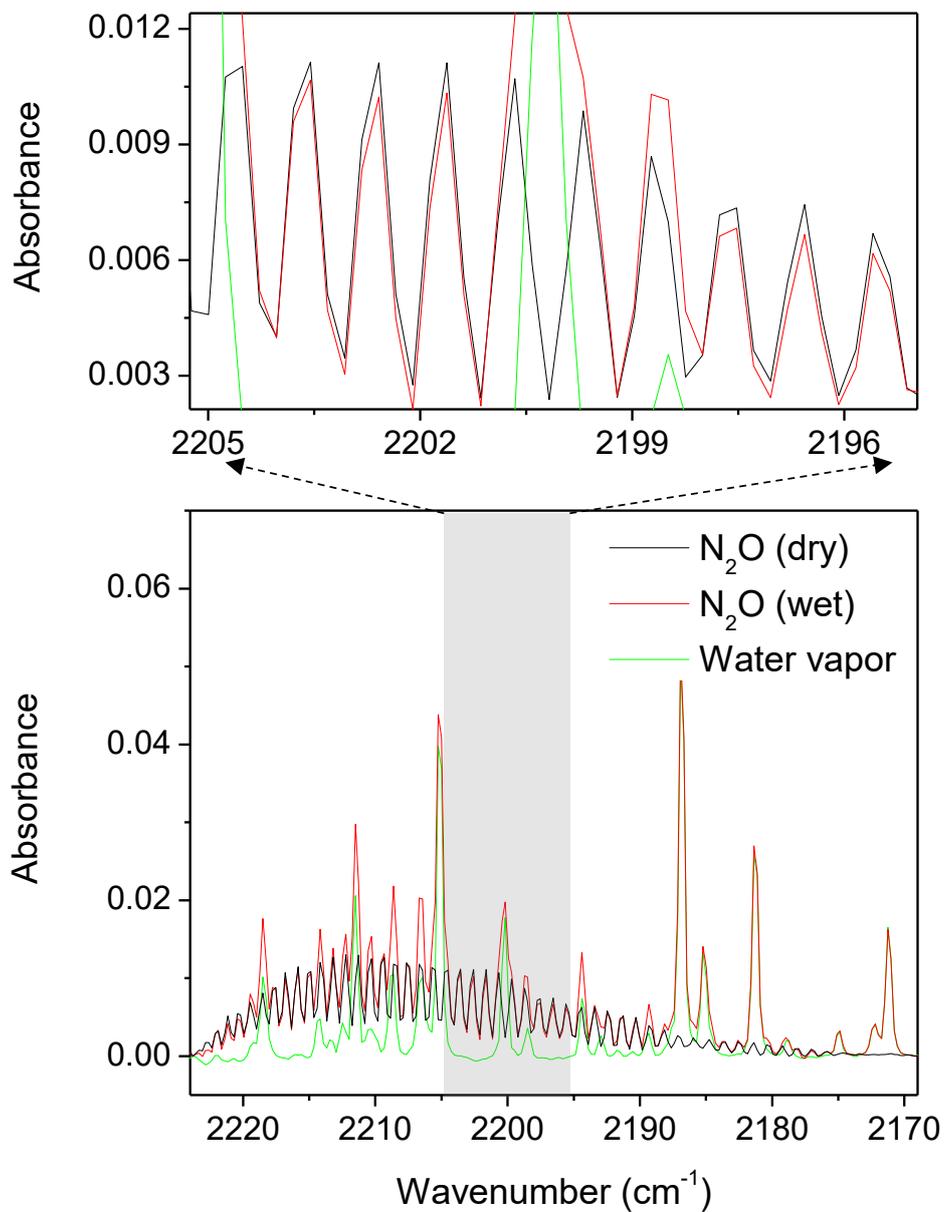


Figure 3. The lab-FTIR spectra of dry N₂O (310 ppbv), wet N₂O (310 ppbv N₂O plus 28 000 ppmv water vapour), and water vapour (28 000 ppmv) were acquired at 30 °C.

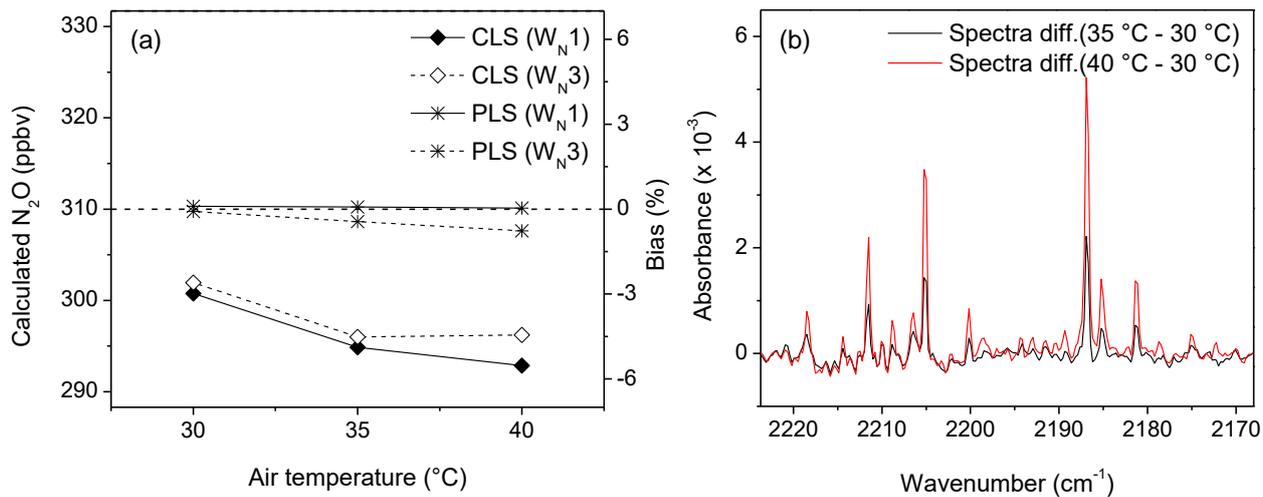


Figure 4. Effects of temperature on N_2O quantification: the lab FTIR spectra containing wet N_2O (310 ppbv N_2O plus 21 500 ppmv water vapour) were acquired at 30 $^{\circ}C$, 35 $^{\circ}C$, and 40 $^{\circ}C$. Temperature affected (a) N_2O concentrations calculated by the CLS and PLS models and two 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.

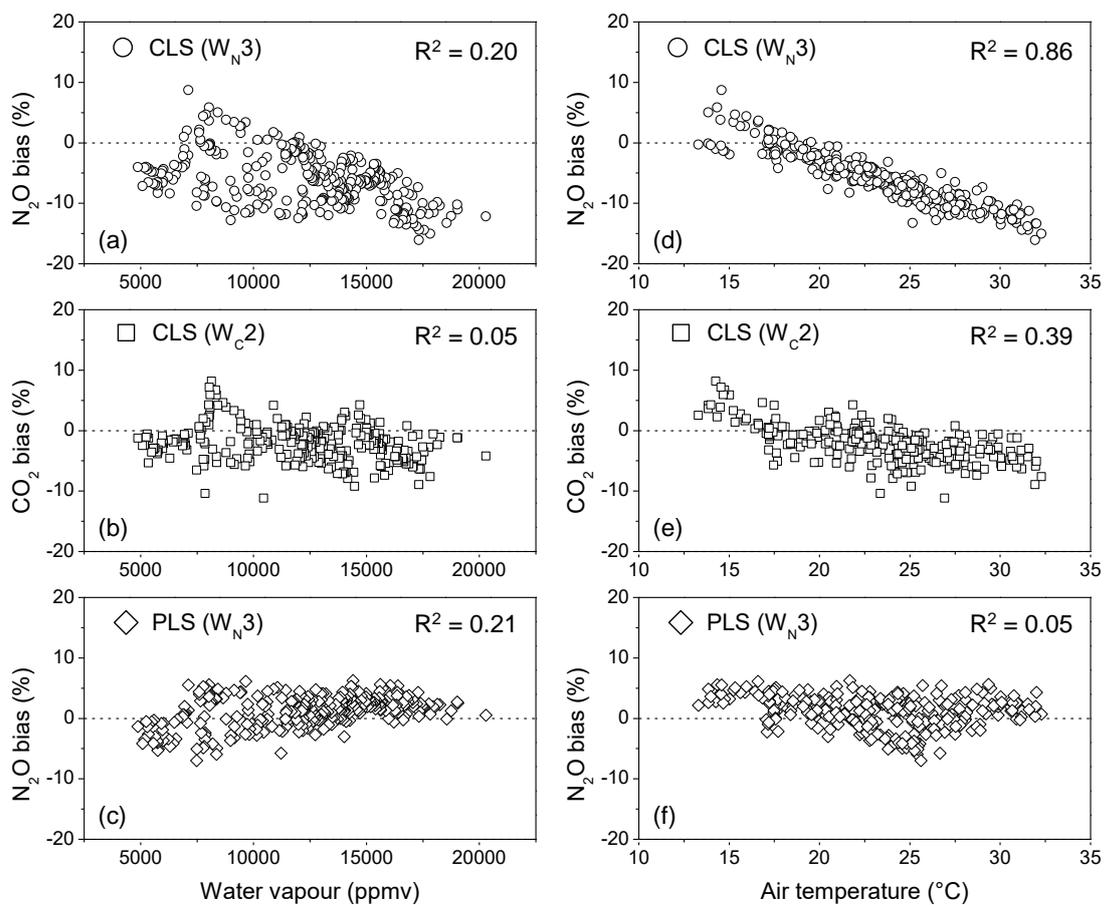


Figure 5. Effects of water vapour and temperature on N_2O and CO_2 concentrations calculated from the OP-FTIR spectra using CLS and PLS models and the optimum windows (W_{N3} for N_2O and W_{C2} for CO_2) during 9-19 June 2014. Assumed temperature and bias are a linear relationship.

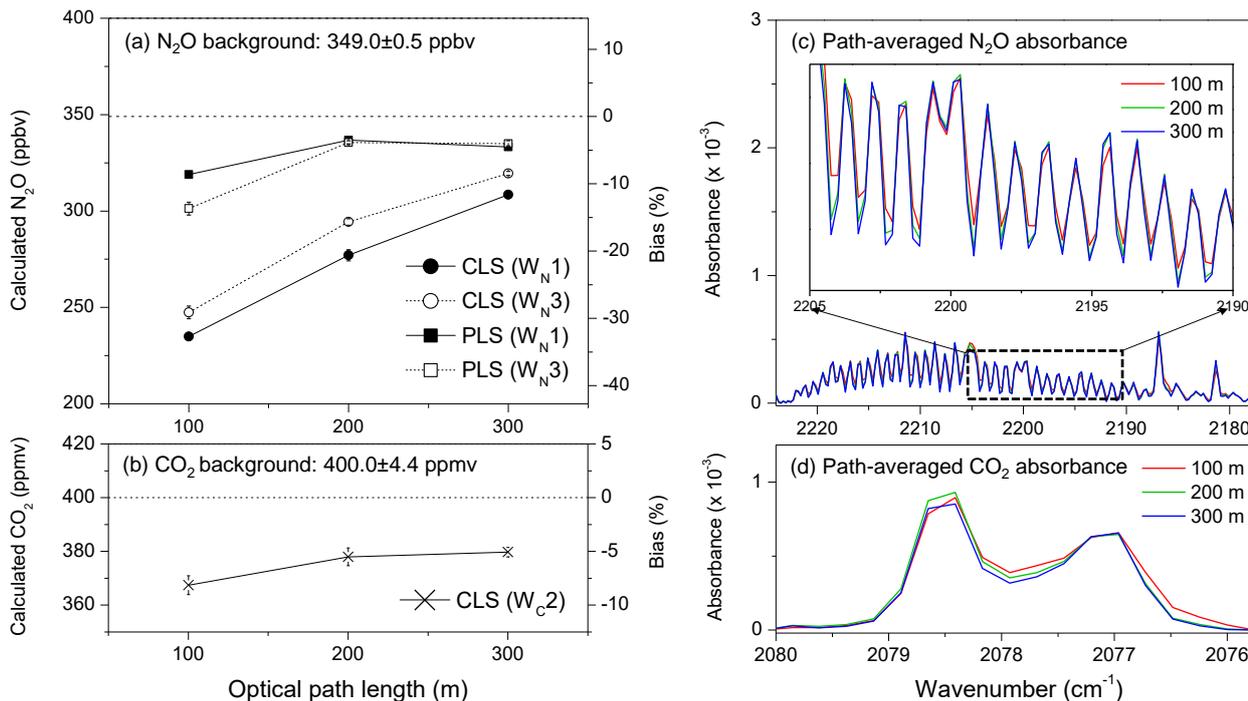


Figure 6. Effects of path lengths on N₂O and CO₂ quantification: OP-FTIR spectra were acquired under backgrounds of N₂O (349.0 ± 0.5 ppbv) and CO₂ (400.0 ± 4.4 ppmv), and relative humidity of 35 % at 25 °C from optical path lengths of 100, 200, and 300 m for quantification of (a) N₂O using CLS and PLS and windows of W_N1 and W_N3, (b) CO₂ using a CLS model and the window of W_C2. The path-averaged absorbance spectra of (c) N₂O and (d) CO₂ showed the inconsistency of absorbance spectra.

5

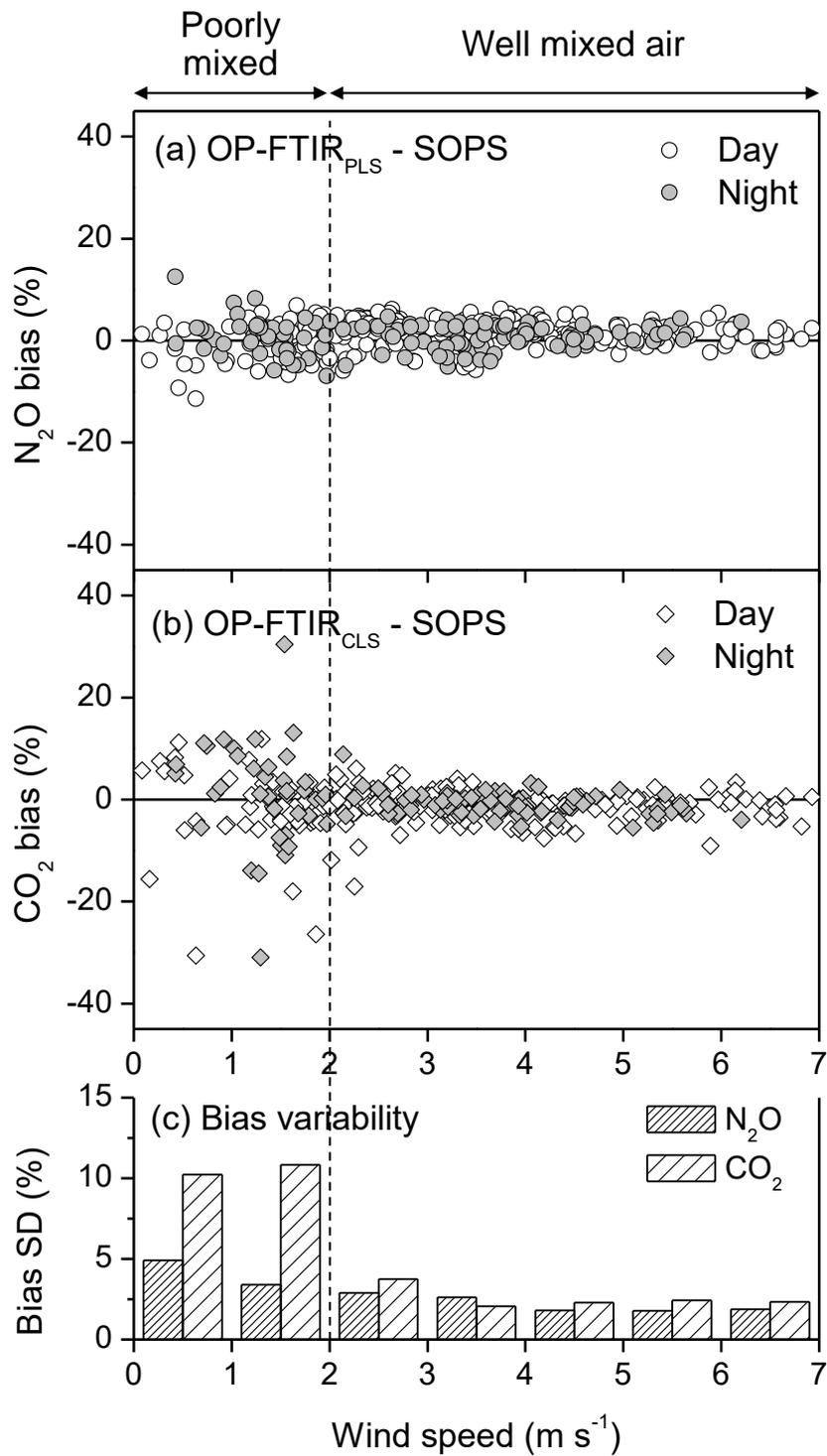


Figure 7. Effects of the wind speed on differences in the path-averaged concentrations between the OP-FTIR and S-OPS: (a) N_2O , (b) CO_2 , and (c) variability of biases (Standard deviation, SD).