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

10   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 ℃ using a classical least squares (CLS) model. 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.

15   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. The quantified errors can be used as references for current or future OP-FTIR

20   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

25   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

30   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,

5   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).

10   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

15   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,

20   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,

25   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

30   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

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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
5   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
10 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; 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 (SB) spectrum converted by Fourier transformation, different apodization functions affect spectrum linearity differently.
15 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).

20 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 N_2O. Shao et al. (2007) investigated the effect of wind on spectrometer vibrations and spectra qualities
25 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 SO_2, CO, CO_2, and
30 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 test the quality of OP-FTIR methods for multiple gas quantification due to interferences and the lack of proper measurement benchmarks. Also, the

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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

5 ### 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

10 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

15 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 ℃ dew point) from a zero air generator (model 701H, Teledyne, Thousand Oaks, CA). Gas samples were produced using a diluter (series 4040,

20 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. Humidity and

25 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 ℃).

2.1.2 Data collections and gas quantification

Spectra were collected when the N_2O and water vapour concentrations and temperature of the introduced samples were

30 steady. Concentrations of N_2O and water vapour were calculated from the mixed-gas (wet N_2O) absorbance spectra by CLS

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and PLS models using TQ Analyst software Version 8.0 (Thermo Fisher Scientific, Inc.) A total of 9 single-gas spectra of dry N_2O (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 N_2O. Two windows reported by Lin et al. (2019) were used for N_2O quantification (W_N1: 2170.0-

5   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 N_2O quantification using CLS and PLS was examined by collecting spectra at 30, 35, and 40 ℃.

2.2 Open-path FTIR experiment

10   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

15   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 $g \cdot cm^{-3}$ 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

20   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

25   collected by co-adding 64 IFGs and a resolution of 0.5 cm^{-1}. A zero-filling factor of one, 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

30   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 N_2O, CO_2, and water vapour, were generated at 30 ℃ to calculate N_2O and CO_2 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 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.

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 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

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

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

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 compromised the intensity of N_2O absorbance (P branch). 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.

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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

5   blending with 21 000 ppmv water vapour) were collected at 30 ℃, 35 ℃, and 40 ℃. Reference spectra of dry N_2O, water vapour, and wet N_2O were acquired at 30 ℃ and used to calculate N_2O concentrations from spectra collected at temperatures of 35 ℃ and 40 ℃. 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 ℃. As mentioned, water

10   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 ℃ 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). The increased strength of water vapour led to more interference in spectral analyses and great biases (Fig. 4b). PLS methods showed less sensitivity

15   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 increased N_2O biases using CLS (Fig. 5a). In the lab experiment, the increased water vapour from 5000 to 20 000 ppmv at 30 ℃ only

20   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 negligible correlation ($R^2 = 0.20$ shown in Fig. 5a) between water vapour content and the N_2O bias was because water vapour was confounded by temperature (i.e. temperature ranged from 10 ℃ to 35 ℃ in fields) and became insignificant when the calculated biases were categorized by temperature (i.e. $R^2 = 0.01$ at the interval of 25-30 ℃, data not shown). CO_2

25   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 bias estimations from CLS models (Fig. 5d and 5e). Since the

30   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 N_2O biases ($R^2 = 0.86$) showed

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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 ℃). The excess bias (12.0 % minus 3.0 %)

5 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). 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). The PLS models were less influenced by temperature for N_2O quantification ($R^2 = 0.05$) and provided better accuracy for N_2O estimations

10 (Fig. 5f).

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

15 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. $\frac{Absorbance}{Path\ length(m)}$) 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;

20 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

25 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

30 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).

3.2.3 Wind speed effect

5   Nitrous oxide is predominantly 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 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

10   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 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

15   (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 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

20   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 ℃ 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 ℃ difference introduced 1.9 % (Lab) and 9.1 % (Field) more biases

25   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.

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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

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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

5   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-to-noise ratio (Griffiths and de Haseth, 2007).

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Table1. 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

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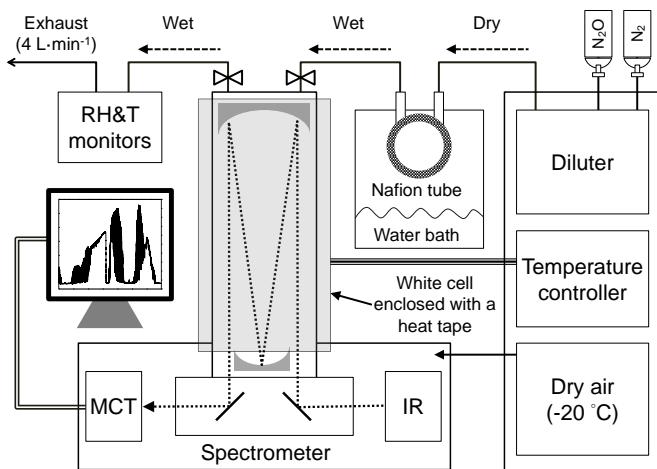
(a) A lab FTIR

(b) A monostatic OP-FTIR
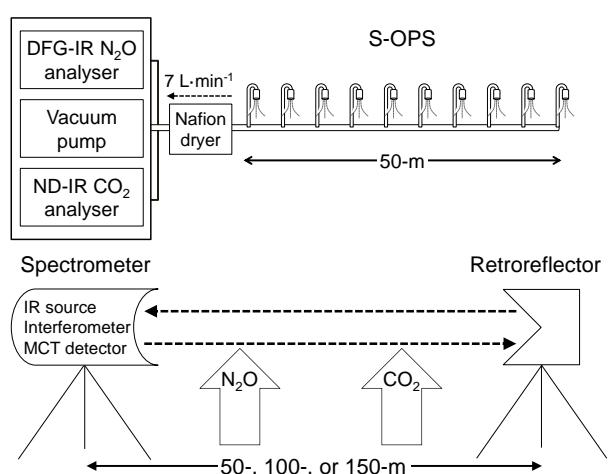
Figure 1. Schematic of the instrumentation used to assess the effects of water vapour and temperature on gas quantification: (a) lab-FTIR with a multi-pass gas cell (optical path length of 33 m); (b) DFG-IR N_2O and ND-IR CO_2 analysers combined with synthetic open path gas sampling system (S-OPS) were used as benchmarks to assess quantification of N_2O and CO_2 from OP-FTIR.
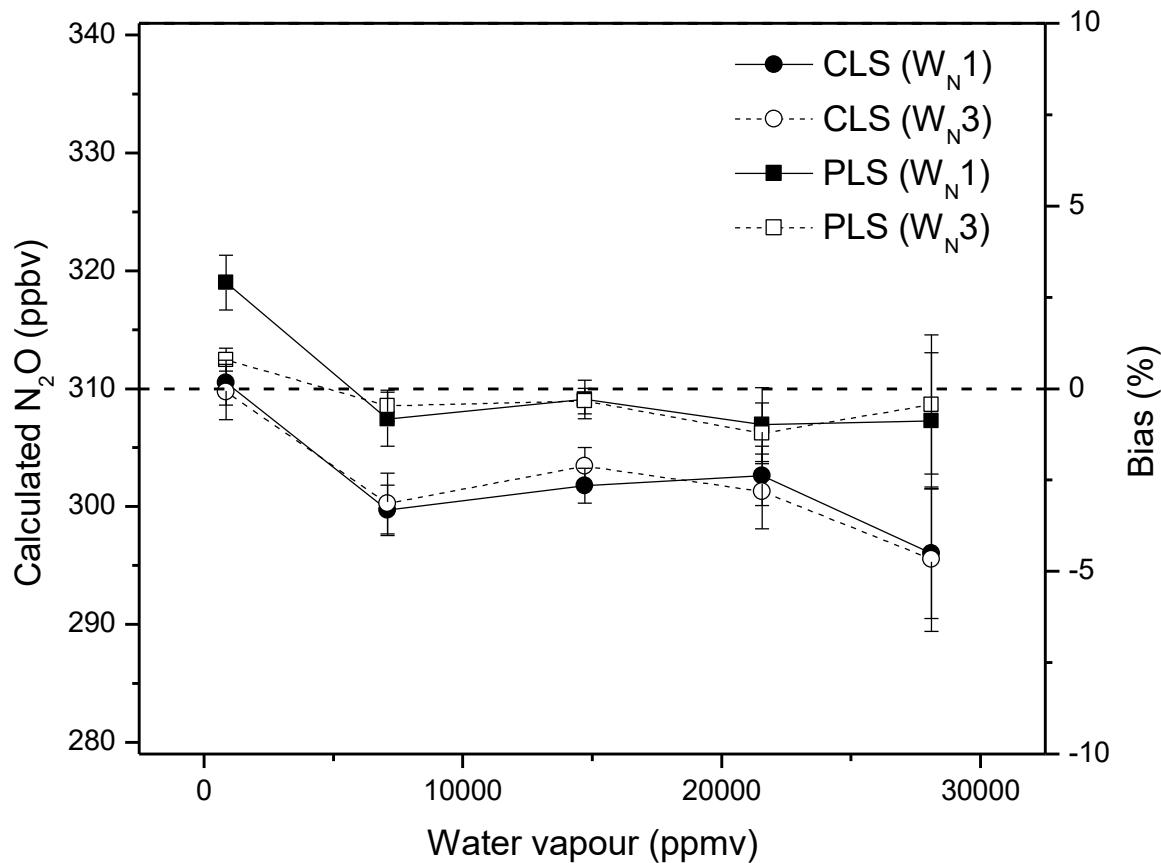
Figure 2. Effects of water vapour on N_2O quantification: the lab-FTIR spectra of dry N_2O and N_2O/water vapour mixtures (310 ppbv N_2O at the relative humidity of 20 %, 40 %, 60 %, and 80 % at 30 ℃) were used to calculate N_2O concentrations using CLS and PLS models and two spectral windows (W_N1 and W_N3).
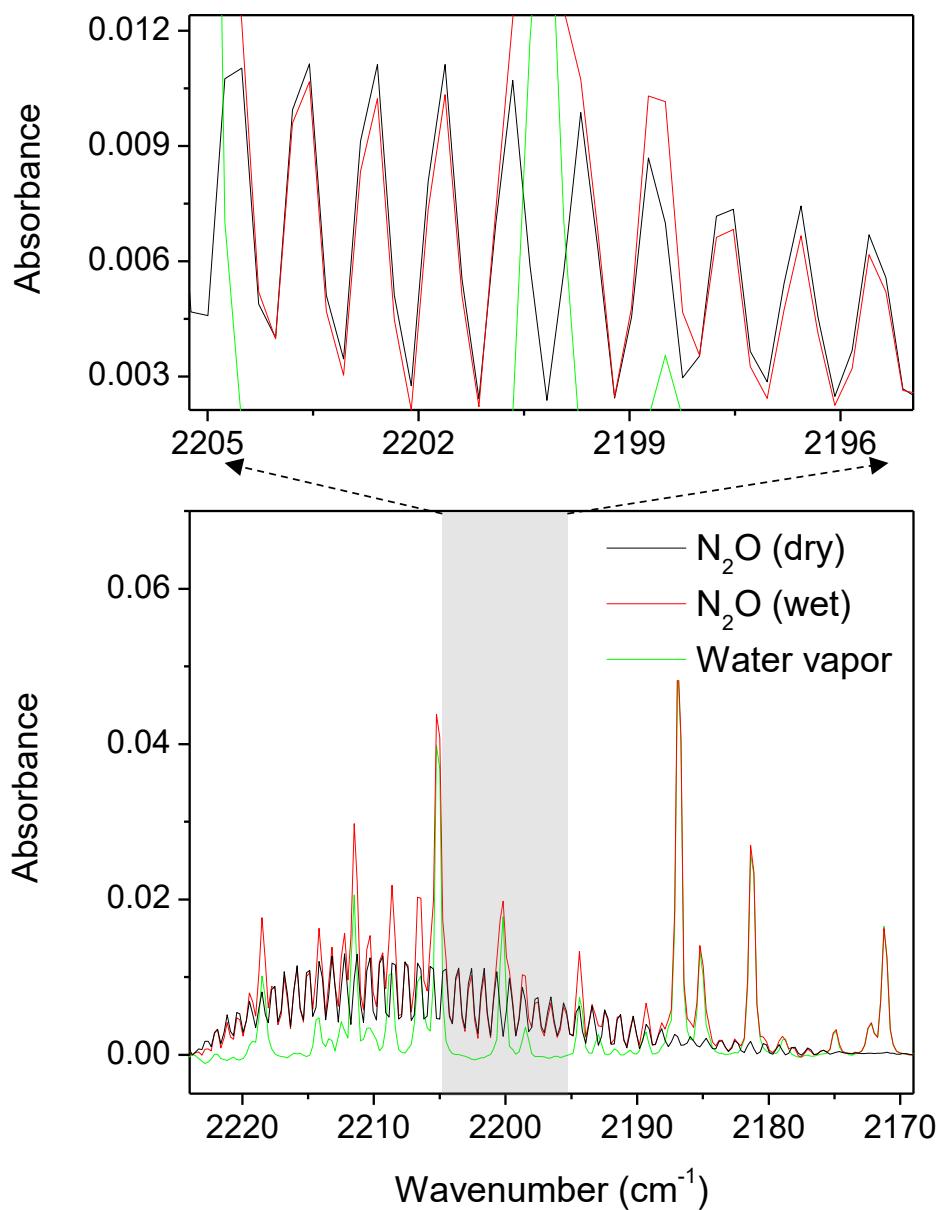
Figure 3. The lab-FTIR spectra of dry N_2O (310 ppbv), wet N_2O (310 ppbv N_2O plus 28 000 ppmv water vapour), and water vapour (28 000 ppmv) were acquired at 30 °C.
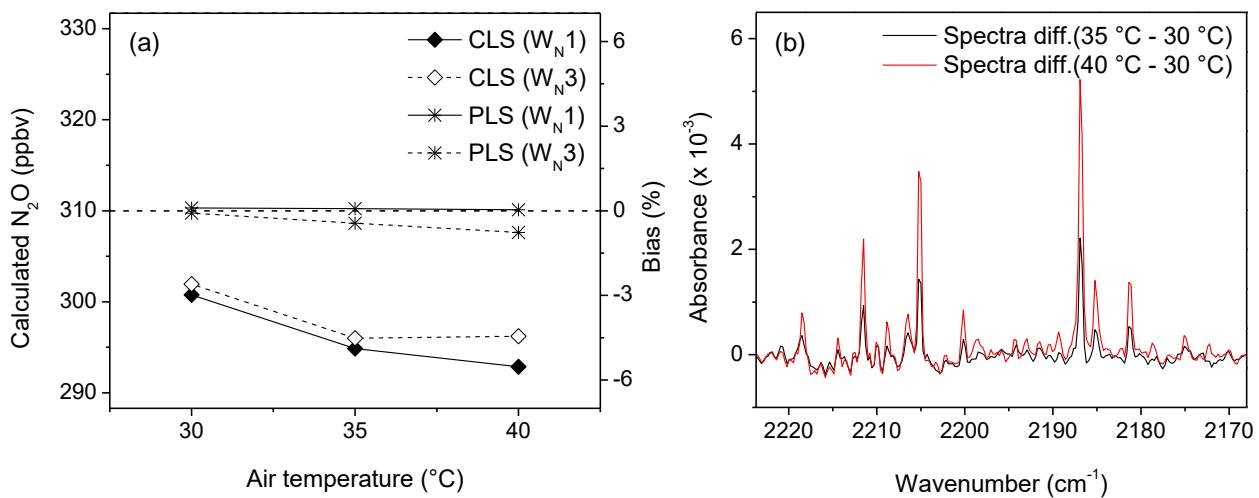
Figure 4. Effects of temperature on N_2O quantification: the lab FTIR spectra containing wet N_2O (310 ppbv N_2O plus 21 500 ppmv water vapour) were acquired at 30 °C, 35 °C, and 40 °C. Temperature affected (a) N_2O concentrations calculated by the CLS and PLS models and two spectral windows (W_N1 and W_N3) and (b) spectral differences in wet N_2O absorbance (310 ppbv N_2O plus 21 500 ppmv water vapour) among different temperature.

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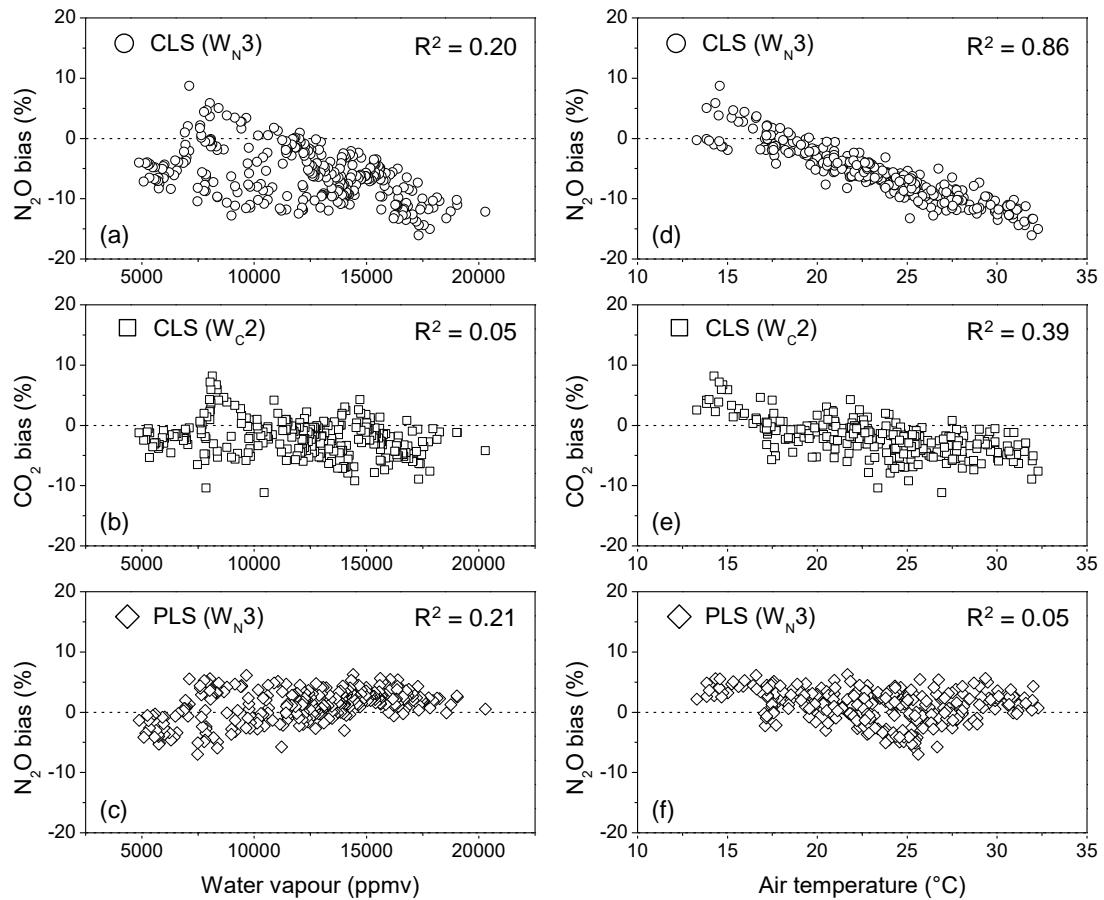
Figure 5. Effects of water vapour and temperature on N_2O and CO_2 concentrations calculated from the OP-FTIR spectra using CLS and PLS models and the optimum windows (W_N3 for N_2O and W_C2 for CO_2) during 9-19 June 2014. Assumed temperature and bias are a linear relationship.

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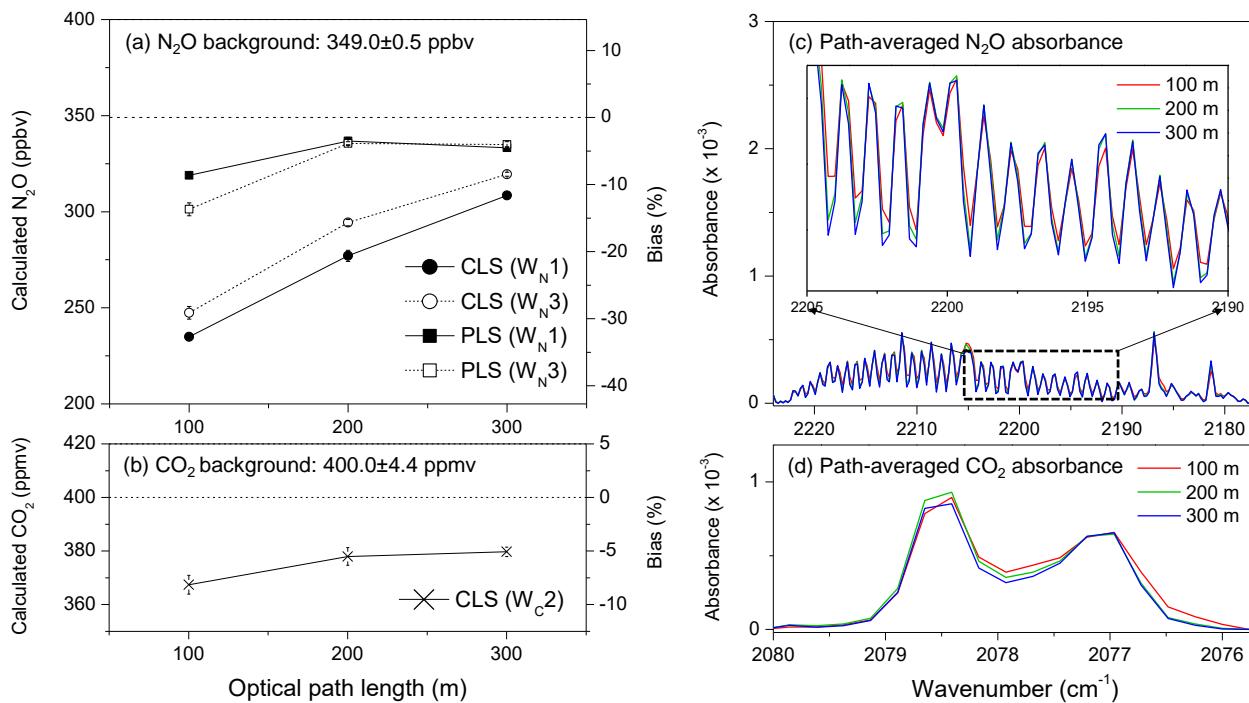
Figure 6. Effects of path lengths on N_2O and CO_2 quantification: OP-FTIR spectra were acquired under backgrounds of N_2O (349.0 ± 0.5 ppbv) and CO_2 (400.0 ± 4.4 ppmv), and relative humidity of 35 % at 25 °C from optical path lengths of 100, 200, and 300 m for quantification of (a) N_2O using CLS and 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.

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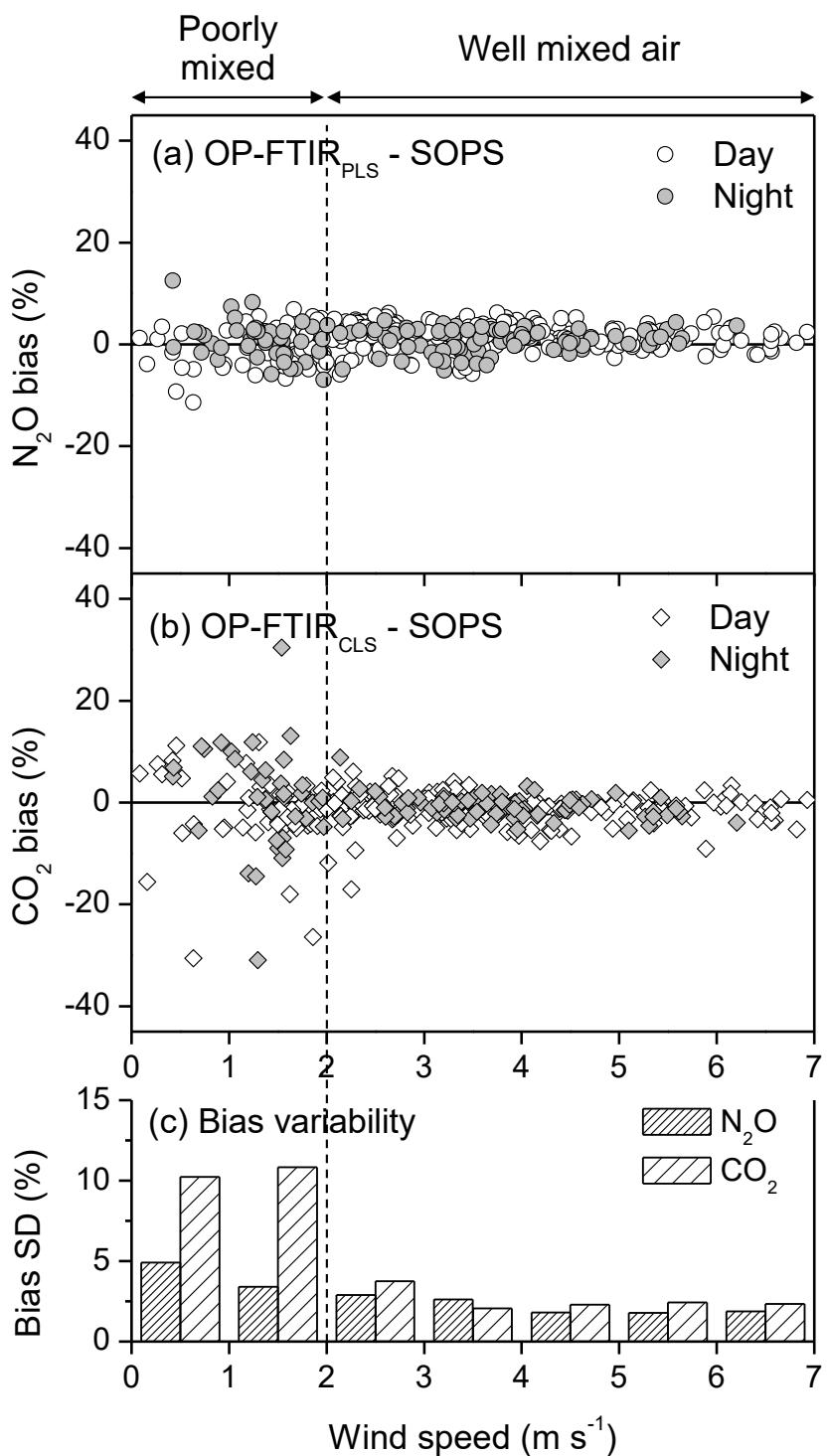
Figure 7. Effects of the wind speed on differences in the path-averaged concentrations between the OP-FTIR and S-OPS: (a) N_2O, (b) CO_2, and (c) variability of biases (Standard deviation, SD).