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Atmospheric Measurement Techniques
Discussions

Interactive comment on "Sources of error in open-path FTIR measurements of N_2O and CO_2 emitted from agricultural fields" *by* Cheng-Hsien Lin et al.

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The authors appreciate all comments from reviews to improve this paper. Beside more details and deeper discussions that need be incorporated in the modified manuscript, the point-to-point responses are as follows: 1. 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 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.

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±0.3âĂĽppbv) 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. biasâĂĽ=1.4±2.3âĂĽ%). 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.

2. 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?

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 Fig.1) 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 the HITRAN database at 30 °C (see 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 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 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 (Fig.1). Since these quantitative models are temperature-specific (i.e. 30 °C), the temperature variation between reference and the validation/sample spectra leads to biased in gas quantification. For instance, the OP-FTIR validation spectra were collected at 10-35 °C in field experiments (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).

3. 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 a 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 minutes. Since ambient temperature and humidity presumably remained stationary within thirty minutes, the effect of temperature and humidity variation on the delta concentration can be negligible. The path length set-up and wind condition, however, significantly influence the calculation of delta concentrations and fluxes. For instance, a set-up of the short path length (e.g. physical length = 50 m) resulted in greater underestimations than a long path length (e.g. physical length = 100 m or 150 m). Difference path length set-ups (i.e. short and long) likely distorted the actuality of the delta concentration and led to biases in flux estimations. Thus, the criterion for path length is to make sure the same path length used in the measurement system, either short (i.e. physical length less than 100 m) or long (i.e. physical length greater than 100 m) path lengths. The poor-mixed air (wind speed < 2 m s-1) also led to uncertainties in delta concentration, so that the concentrations collected under low wind conditions (< 2 m s-1) were excluded. 2) Ambient variables likely interfere with the quantification of gas concentrations from the OP-FTIR spectra, resulting in an 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 was used to collect the spectra which both contained N2O, water vapour, and temperature. 3) The third-degree polynomials were used for the NLLS regression applied in the 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 N2O analyzer (IRIS 4600, Thermo Fisher Scientific Inc., Waltham, MA) and CO2 analyzer (LI20 840, LI-COR Inc., Lincoln, NE) provided high precision for N2O (< 0.15 ppbv, 1σ) and CO2 (< 1.0 ppmv, 1σ) concentration measurements and calibrated using the certified standard gas every four hour to ensure the stability of analyzers as well as the accuracy for gas measurements.

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

Response: The N2O (310 ppbv) spectra were acquired in both dry and wet (28,000 ppmv water vapour content) conditions. Ideally, the N2O absorbance/intensity should be identical because of the same concentrations (310 ppbv). The intensity of the N2O P-branch in the wet N2O spectra (red solid line) was observed to be lower than the dry N2O spectra (black solid line) (Figure 3 in the manuscript). To resolve the strong overlap of water vapour in N2O 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 N2O measurements.

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

Response: Yes, the increased intensity of water vapour with increasing temperature was observed in Figure 4b. It is difficult to avoid the water vapour interference, but this interference could be mitigated via window selection (e.g. WN1 vs. WN3 in CLS models shown in Figure 4a in the manuscript).

6. Are water vapour and temperature really confounding variables (P8L21) or are their

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

Response: Temperature is considered as a confounding variable influencing both humidity and quantitative bias. The higher temperature tends to have higher water vapour content in the air. In this study, the increased temperature increased biases (R2 = 0.86), and the spurious correlation between water vapour content and bias (R2 = 0.20) likely resulted from temperature effect (i.e. the confounder).

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

Response: N2O concentrations were calculated from the analytical window of 2224-2170 cm-1 which includes the information of N2O, water vapour, CO, and CO2 (Fig.2).

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

Response: The non-linear relationships between the path length and absorbance respond to different spectral resolution and analyte species (Russwurm and Phillips, 1999: Effects of the 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-species 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.

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

Response: 1) Since quantitative bias was calculated by comparing the path-averaged concentrations between the S-OPS and OP-FTIR, the spatial distribution of gas concentrations in the atmosphere substantially influence the bias calculation. For instance, CO2 can be produced from both soil and canopy respiration, 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 respiration or photosynthesis leads 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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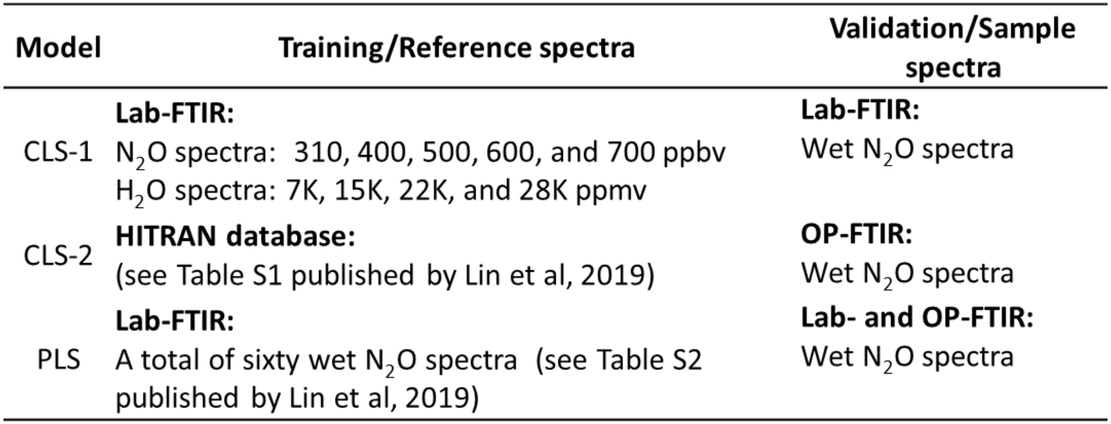

Model	Training/Reference spectra	Validation/Sample spectra
CLS-1	**Lab-FTIR:** N_2O spectra: 310, 400, 500, 600, and 700 ppbv H_2O spectra: 7K, 15K, 22K, and 28K ppmv	**Lab-FTIR:** Wet N_2O spectra
CLS-2	**HITRAN database:** (see Table S1 published by Lin et al, 2019)	**OP-FTIR:** Wet N_2O spectra
PLS	**Lab-FTIR:** A total of sixty wet N_2O spectra (see Table S2 published by Lin et al, 2019)	**Lab- and OP-FTIR:** Wet N_2O spectra

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

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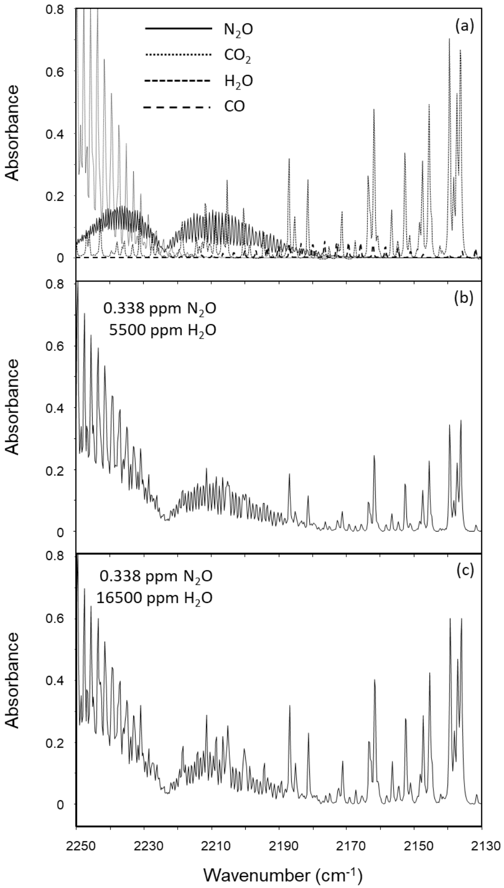

Fig. 2. Comparisons between the HITRAN and the OP-FTIR absorption spectra: (a) HITRAN N2O, CO2, CO, and water vapour, and OP-FTIR spectra of 0.338 ppm N2O in (b) low humidity, and (c) high humidity conditions

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