Atmospheric
Measurement
Techniques

Discussions

Interactive comment on "Sources of error in open-path FTIR measurements of N₂O and CO₂ emitted from agricultural fields" by Cheng-Hsien Lin et al.

The authors describe a study of error sources in a set of innovative measurements of N2O and CO2 emitted from agricultural fields by OP-FTIR and in situ methods (described earlier in a companion paper). The field setup includes in situ measurements from a linear array (50 m long) to characterize the concentration of target gases (N2O and CO2) along an open path of 50 to 150 m. The in situ gas analyzer measurements then serve as a benchmark for quantifying OP-FTIR errors.

The authors consider errors in concentrations derived from FTIR absorption spectra of target gases due to interfering water vapour, atmospheric temperature, open path length as well as the chemometric models used (CLS vs. PLS for N2O, CLS only

for CO2). They also investigate the effects of spectral window width. Finally, they recommend that their quantified error results "be used as references for current or future OP-FTIR users."

General Comments:

The paper is well written and presented, but the description of methodology (the CLS and PLS approach in particular) reads tersely (also in the companion paper and its supplementary material) to someone who uses NLLS for spectral analysis. Furthermore, the discussion of results could drill deeper in places, as outlined below.

The underestimations of N2O referred to in the abstract (from -3% to -30%) were based on concentrations obtained using the CLS model, which assumes a linear relationship between absorbance and target gas concentration. Given the known issues with CLS analysis (e.g., Smith et al., 2011) and the parallel use of the NLLS approach within the OP-FTIR user community, the applicability of these values as references for current or future OP-FTIR users must be qualified accordingly.

P3L17 This is the only spot where NLLS spectral analysis is acknowledged. Four relevant papers are cited but advantages over CLS and PLS are not discussed, even though it takes a lot of work (as outlined in the present paper) to generate the reference libraries central to the CLS and PLS approach. The NLLS approach in the cited works avoids this step entirely by relying on calculated spectra at the correct pressure, temperature and water vapour, and based on spectral parameters from HITRAN. And, as stated by the authors, it overcomes nonlinearity between absorbance and concentration and improves accuracy. What advantage does CLS and PLS offer over NLLS as implemented in the works cited here?

How do the N2O estimations quoted in the abstract reconcile with those from the companion paper (-4.9% for N2O with CLS over 5000-20000 ppmv water from from 10-35C). In general, if there was a 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.

Given the innovative field setup where OP-FTIR measurements were made alongside simultaneous gas analyzer measurements drawing air along a linear array, this paper is uniquely positioned to evaluate biases in CLS, PLS and NLLS approaches. This non-trivial effort would greatly increase the relevance of this work to the broadest OP-FTIR community.

Specific Comments:

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?

Section 2.2.2: I would like to see the 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?

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.

"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?

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.

P9L4: 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?

P9L23: 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?

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.

Technical Correction:

P3L14 single-bean -> single-beam