

Interactive comment on “Application of Open Path Fourier Transform Infrared Spectroscopy (OP-FTIR) to Measure Greenhouse Gas Concentrations from Agricultural Soils” by C.-H. Lin et al.

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Dear referees, we truly appreciated that your valuable comments that help us clarify some concepts in this manuscript. My responses to your questions are as follows,

1. Title: "...GHG concentrations from agricultural soils" - you measure GHG concentrations in ambient air above ground surface - these concentrations can stem from emissions from the soil (including roots and microorganisms) or from the above ground vegetation. You do not measure fluxes - so be careful within your introduction - to

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estimate fluxes the concentration is only one of the variables needed!!!

Response: I would modify this title to 'Application of Open Path Fourier Transform Infrared Spectroscopy (OP-FTIR) to Measure Greenhouse Gas Concentrations at a Maize Cropping System'

2. Page 2, line 10 ff: The authors mention chamber measurements as the most common way to investigate emissions from soils. In the same time they point out the relatively small footprint as the main limit of this method. However, I would like to introduce in this context the opportunity to measure GHG fluxes on larger scale using the Eddy Covariance flux measurements. This method is also an established method nowadays and a common micro-meteorological technique with an increased footprint to determine emissions for instance of CO₂, CH₄ and water from soils and vegetation. (e.g., Baldocchi, D. (2003): Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future. <https://doi.org/10.1046/j.1365-2486.2003.00629.x>). Concerning to comment No. 1 - all methods are based on the measurement of the concentrations of GHGs and have their own processes to obtain emission rates.

Response: It is a good idea to point out the eddy covariance and its advantage (e.g., larger footprint) for gas flux measurements. I would briefly introduce this method into the context before I submit the final version. Chamber measurements are the most common method for soil gas emission measurements because this method also provides numbers of strengths. One of the advantages is that chamber is sensitive enough to make comparisons of gas emissions in different treatments (e.g., field and N management practices in small plots (< 3 ha)), which is challenging to the eddy covariance. The OP-FTIR combined with inversion dispersion techniques (e.g., backward Lagrangian stochastic dispersion model) is capable of measuring gas emissions frequently and with a field-scale footprint (1-3 ha), that can both compensate the limitations of chamber measurements and measure gas emissions from different treatment plots. That is the reason why we did not introduce the eddy covariance in the first

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place.

3. General comment: Time series on GHG concentrations at S-OPS including measured ambient air conditions (to have an idea about the variability of wind speed, direction, air temp, etc.) would be helpful.

Response: I would like to add the information of the environmental variables in supplementary materials, but probably not in the main manuscript in order to simply figure 7 in this paper. Please see supplementary figure 1.

4. Page 4, line 24: How often did you acquire single beam spectra (how many spectra did you measure during the operational period - also to make the number of 877 valid OP-FTIR spectra more valuable)?

Response: Gas sample were continuously collected from the S-OPS, and the collected gas samples were measured for N₂O concentrations every ten seconds using the difference frequency generation (DFG) mid-IR laser-based N₂O/H₂O analyzer (IRIS 4600). Then, the measured N₂O concentrations were averaged every thirty minutes to represent the 'actual' ambient N₂O concentrations at the 30-min interval. The 30-min averaged N₂O was used to benchmark the concentrations derived from the OP-FTIR spectrum. A single beam spectrum was collected every minute based on 64 sample scans. Within a 30-min interval, two to three single beam spectra were collected and measured N₂O concentrations. These two-three 'one-minute' N₂O concentrations were also averaged to calculate 30-min N₂O, compared with the SOPS-measured concentrations. An example was shown in supplementary table 1. The whole OP-FTIR spectra used in this study should be 793 spectra.

5. Page 5, line 17: What do you mean here: "we selected ninety spectra containing 338 ppbv N₂O and ninety-three spectra containing 400 ppmv CO₂?" These spectra do contain the same concentration like the measurements at the S-OPS? Is the impact of IR absorbance due to water vapor within this spectra not so significant (my interpretation of figure 2d)? (In Figure 2 the readers find the histograms of 418 half-hour

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average-intervals? In Fig.2a the light grey line is located at x = 340 ppb and not at x = 338 ppb, by the way ...).

Response: That is correct. Concentrations of N₂O (338 ppbv) and CO₂ (400 ppmv) were measured by the S-OPS. The OP-FTIR and S-OPS were deployed at the same path and used to collect OP-FTIR spectra and measure N₂O/CO₂ concentrations, respectively. Ninety spectra containing 338 ppbv N₂O (measured by the S-OPS) and ninety-three spectra containing 400 ppmv CO₂ (also measured by the S-OPS) were used to test the performances of quantification methods, including least square models, SB backgrounds usages, and spectral windows. 'Is the impact of IR absorbance due to water vapor within this spectra not so significant?': Water vapor content was measured from 0.4 to 2.0 %, and ambient temperature was measured from 10 to 35 °C from June 9-20th 2014. One of the objectives of this study is to investigate the sensitivity of the OP-FTIR to ambient water vapor and temperature. Since spectra containing consistent concentrations of N₂O and CO₂ but the varied water vapor content and temperature, the variations in the FTIR-calculated concentrations (Fig.5 and 6) resulted from the confounding effects of ambient water vapor interferences and temperature. I will modify the position of the light grey line from 340 ppbv to 338 ppbv before the submission.

6. Page 6, line 23: I see the potential and limitation of the here discussed methods to obtain a target gas free background spectrum. In my opinion, using one background spectrum per day for the zap-bkg determination is to less due to the extensive impact of changing environmental conditions on the measured IR spectra (which is surely occurring during the day in ambient air conditions like air humidity, pressure variability,).

Response: Ideally, the zap-bkg spectrum needed to be created from each sample single beam spectrum to obtain absorbance. In this study, however, we only created one zap-bkg spectrum for each day. This idea was inspired by the methodology of the zero-path single beam spectrum used for absorbance spectra conversion. For

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continuous gas measurements, zero-path single beam spectrum was usually acquired once per day and used to convert sample single beam spectra to absorbance. Also, it is time-consuming to create the zap-bkg spectrum for each single beam spectrum for continuous gas measurements. Yes, I would agree that this is the potential limitation of using the zap-bkg method and suggest that the future OP-FTIR users can test the effect of multiple zap-bkg on gas quantification before continuous gas measurements.

7. Page 6, line 30: what is meant with: all data points are stored as one data file? You calculated from each SB spectra the synthetic background and store this in the same manner like the original data spectra and use these files for the calculation of abs-spectra? How many data points are used to determine the smooth background spectra function (which order of polynom).

Response: The idea of the synthetic SB background is to select multiple points from the sampled SB spectrum and these selected points were used to fit the curvature of the SB spectrum using the polynomial function. The positions (or wavenumbers) of these selected points are important and need to be consistent for every sample SB spectrum. For instance, the positions must not be selected within the absorbance features. These data points were selected from a quality SB spectrum acquired from each day, and the positions of these data points were stored in one file (a data-point file is a feature provided by the IMACC software). A data-point file was applied in sample SB spectra to make sure the points applied in every sample SB spectrum have consistent positions. Six points within 2050-2500 cm⁻¹ were selected from the SB spectrum to smooth the SB background spectrum using polynomial function (six orders) (Figure 3b in the paper) for N₂O and CO₂ quantification.

8. Page 8, line 27: humidity Response: Yes, I will change to the humidity.

9. Page 9 / 10: Figure 5 and 6 imply, that the authors did not show all the results. To evaluate the presented methods in order to agree with the proposed "optimal approaches", a comparison of all concentration estimations (CLS, PLS, used spectral

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windows and background spectra) should be shown (or at least mentioned for instance as a table). Otherwise, the assessment is very hard for the reader... (For instance in chapter 3.3 the PLS for CO₂ is missing.)

Response: Yes, that would be helpful for readers to follow the approaches, including CLS, PLS, SB backgrounds, and spectral windows, by using tables. We did not analyze CO₂ concentrations using the PLS model because we are limited to acquire the wet CO₂ reference spectra (CO₂/H₂O mixed spectra). Therefore, the 'optimal approach' might imply that the CLS model is better than the PLS model for CO₂ quantification and mislead readers. I think that would be a good idea to make a short statement that CO₂ was only determined by the CLS model but different processes (e.g., SB background spectra, spectral windows).

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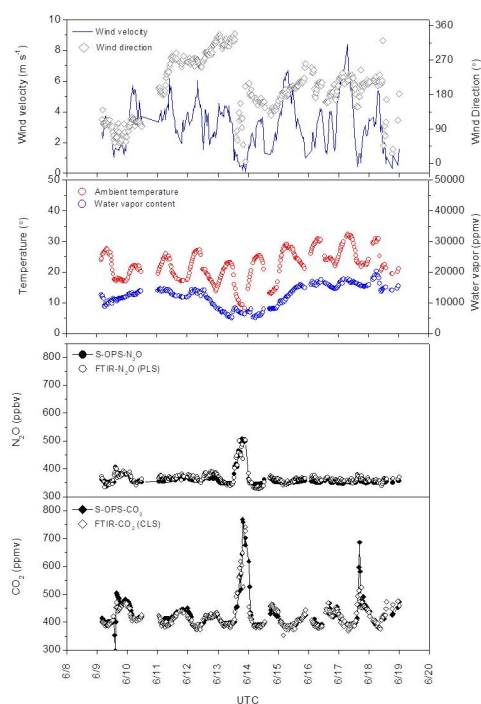


Fig. 1. Supplementary figure 1: Measurements of N₂O/CO₂ concentrations (S-OPS and OP-FTIR), ambient wind speed and direction, temperature, and humidity from June 9th to 20th 2014

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An example of the timing for measuring N₂O concentrations using the S-OPS (SOPS-N₂O) and for acquiring the OP-FTIR single beam (SB) spectra (e.g., FTIR-N₂O) on June 9th, 2014. The measurement period was from June 9-20th 2014, and the total 793 SB spectra were collected by the OP-FTIR.

Time of SOPS-N ₂ O (UTC)	Time of FTIR-N ₂ O (UTC)	Time of SOPS-N ₂ O (UTC)	Time of FTIR-N ₂ O (UTC)
06/09/2014 16:00	06/09/2014 15:37	06/09/2014 22:00	06/09/2014 21:33
	06/09/2014 15:39		06/09/2014 21:58
06/09/2014 16:30	06/09/2014 16:02		06/09/2014 21:59
	06/09/2014 16:03	06/09/2014 22:30	06/09/2014 22:22
	06/09/2014 16:28		06/09/2014 22:24
06/09/2014 17:00	06/09/2014 16:53	06/09/2014 23:00	06/09/2014 22:49
	06/09/2014 16:55	06/09/2014 23:30	06/09/2014 23:13
06/09/2014 17:30	06/09/2014 17:18		06/09/2014 23:15
	06/09/2014 17:19	06/10/2014 00:00	06/09/2014 23:40
06/09/2014 18:00	06/09/2014 17:44	06/10/2014 00:30	06/10/2014 00:05
06/09/2014 18:30	06/09/2014 18:09		06/10/2014 00:29
	06/09/2014 18:10	06/10/2014 01:00	06/10/2014 00:31
06/09/2014 19:00	06/09/2014 18:35		06/10/2014 00:56
06/09/2014 19:30	06/09/2014 19:00	06/10/2014 01:30	06/10/2014 01:20
	06/09/2014 19:01	06/10/2014 02:00	06/10/2014 01:45
	06/09/2014 19:25		06/10/2014 01:47
	06/09/2014 19:26	06/10/2014 02:30	06/10/2014 02:12
06/09/2014 20:00	06/09/2014 19:51	06/10/2014 03:00	06/10/2014 02:36
06/09/2014 20:30	06/09/2014 20:16		06/10/2014 02:38
	06/09/2014 20:17	06/10/2014 03:30	06/10/2014 03:01
06/09/2014 21:00	06/09/2014 20:42		06/10/2014 03:03
06/09/2014 21:30	06/09/2014 21:07		06/10/2014 03:28
	06/09/2014 21:08	06/10/2014 04:00	06/10/2014 03:53

Fig. 2. Supplementary table 1

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