

# ***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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Received and published: 15 January 2019

Thank you for your comments and suggestions. Our responses to the "Several issues should be addressed" were as follows:

1. In section 2.3, the authors stated that “we selected ninety spectra containing  $338 \pm 0.5$  ppbv N<sub>2</sub>O and ninety-three spectra containing  $400 \pm 5$  ppmv CO<sub>2</sub> which were measured from the S-OPS. These group of spectra covered broad ranges of water vapour content and air temperature. N<sub>2</sub>O and CO<sub>2</sub> concentrations were calculated

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from these selected spectra using different quantitative methods.” What is the exact meaning of “ninety spectra containing  $338 \pm 0.5$  ppbv N<sub>2</sub>O”? The purpose of the selection seems to be “avoid non-linear response of absorbance to the wide range of gas concentrations”, then how could “ $338 \pm 0.5$  ppbv N<sub>2</sub>O” serve this purpose?

Response: 1) The atmospheric N<sub>2</sub>O concentrations were simultaneously measured from the S-OPS and OP-FTIR along the same path. The S-OPS-measured N<sub>2</sub>O was used as a benchmark to examine the performance of the OP-FTIR quantitative methods. Thus, each spectrum was corresponding to a particular N<sub>2</sub>O concentration measured from the S-OPS. These quantitative methods were tested using the selected ninety OP-FTIR spectra where the S-OPS-measured N<sub>2</sub>O concentrations ranged from 337.4 – 338.5 ppbv. Likewise, ninety-three spectra where the CO<sub>2</sub> concentrations ranged from 405.4 – 394.9 ppmv were selected. The statistics of N<sub>2</sub>O and CO<sub>2</sub> concentrations were shown in the following table 1. 2) A broad range of the path-integrated concentration tends to result in a non-linear response of absorbance to concentration. The selected spectra contained particular N<sub>2</sub>O/CO<sub>2</sub> concentrations but various water vapor contents and temperature. The non-linear response of absorbance to the changed water vapor content cannot be solved, but the effect of the changed N<sub>2</sub>O/CO<sub>2</sub> on the non-linearity of absorbance can be minimized by constraining gas concentrations.

2. In section 2.4, the authors stated that "Each sampled spectrum was acquired by coadding 64 single-sided interferograms (IFGs) at a nominal resolution of 0.5 cm<sup>-1</sup>, which accounted for 32,000 data points were collected with the interval of 0.241 wavenumbers between data points, ..." For interferograms, the unit of the interval of data points is cm, not wavenumber.

Response: This sentence might be confused. It means that a resolution of 0.5 cm<sup>-1</sup> accounting for a data point every 0.241 wavenumbers was used for acquiring SB spectra (400 – 4000 cm<sup>-1</sup>), and approximate 32,000 data points were in the interferogram.

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3. In section 2.4, the authors employed some criteria to remove low-quality IFGs, which includes those of very intense centerburst. It is true that intense-centerburst IFGs result in severe non-linear response of MCT detectors. However, such IFGs have high signal-to-noise ratio, and would be valid once the non-linear detector response is corrected. The authors might be interested in correcting method (L. Shao, P.R. Griffiths, Anal. Chem., 2008, 80(13), 5219).

Response: The maximum A/DC capacity in this study was approximately 2.49 Volts. The optical path length of the OP-FTIR was 300 meters. The maximum or minimum value of the IFG centerburst in this study located between 0.61-1.14 volts, which prevented the MCT detector from saturation as well as avoided the non-linear response of the detector.

4. In section 2.5.1, the authors stated using “a high-order fitting function” as the synthetic background. It is better to be specific about the function, is it a quadratic, cubic polynomial, or something else?

Response: Numerous data points were selected from the field SB spectrum. A polynomial function was used to fit the field spectrum to synthesize the SB background without features of gas absorption.

5. In section 2.5.2, some useful information about PLS models is not provided, such as the number of calibration spectra (to build the model), the concentration range that the model covers, the number of factors for the model.

Response: Sixty mixed-gas (i.e., N<sub>2</sub>O + water vapor) spectra were collected from the lab-based FTIR joined with the multi-pass gas cell (the optical path length of 33 meters). Concentrations of N<sub>2</sub>O and water vapor ranged from 0.3 - 0.7 ppmv and 7000 – 30,000 ppmv, respectively. More details of the calibration spectra were shown in the following Table 2.

6. In section 2.6, it is better to be specific about the statistical tests, are they t-test or

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paired t-test?

Response: For N<sub>2</sub>O analysis, twelve quantitative models that were used to calculate N<sub>2</sub>O concentration from ninety OP-FTIR spectra were examined to optimize the combinations of SB backgrounds (i.e., zap- and syn-bkg), multivariate models (i.e., CLS and PLS), and analytical windows (i.e., WN1-WN4). In order to compare the means of the twelve populations, the Fisher's Least significant difference (LSD) was used for multiple comparisons ( $\alpha = 0.05$ ). Likewise, the LSD was also used to compare six population means for the CO<sub>2</sub> analysis.

7. In section 3.2, the authors present the result of CLS (zap-bkg) and CLS (syn-bkg), and the result of PLS (syn-bkg). Why is the result of PLS (zap-bkg) absent? It seems that the authors did not apply PLS to estimate the concentrations of CO<sub>2</sub>, as they did in case of N<sub>2</sub>O. The reason should be explained.

Response: 1) The syn-bkg is one of the recommended methods for converting the SB to absorbance spectra, but the zap-bkg was the new proposed method. Thus, the syn-bkg was used to examine the feasibility as well as the performance of the zap-bkg. The identical field SB spectra, analytical windows, and CLS model were used to calculate gas concentrations from the zap- and syn-bkg converted absorbance spectra. For both N<sub>2</sub>O and CO<sub>2</sub> analyses, the zap-bkg method led to higher biases in concentration calculations than the syn-bkg using CLS models. In section 3.2, the zap-bkg resulted in great underestimations (i.e., Bias > 9%) for N<sub>2</sub>O quantification and the syn-bkg improved the quantitative accuracy. Applying the PLS to quantify gas concentration from the zap-bkg converted spectra unlikely improve the quantitative accuracy. For simplification, we did not report the results of the integrated uses of the zap-bkg and PLS model. 2) Compared with N<sub>2</sub>O analysis, the integration of the syn-bkg and CLS model provided decent predictions for CO<sub>2</sub> concentrations, which was presumably due to the simplicity of the CO<sub>2</sub> absorption feature at 2170-2085 cm<sup>-1</sup>. This combination, however, did not provide the same accuracy for N<sub>2</sub>O predictions. Therefore, we only applied the PLS model for N<sub>2</sub>O predictions, and this model did

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improve its accuracy.

8. Fig.7(b) is strange. As stated in the Fig.7(b),  $\text{bias} = \text{FTIR} - \text{S-OPS}$ . According to this formula, the bias between 11/6/2014 and 12/6/2014 is negative, since the FTIR concentrations are clearly lower than S-OPS. But in the figure the corresponding bias is positive.

Response: The Y-axis of bias (%) is reverse, so the biases should be negative. Also, the updated Fig.7 and the explanation for updating Fig7(b) were described in the author comment (AC1).

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Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2018-373, 2018.

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| Gases                   | Statistics of the S-OPS measured concentrations |     |       |        |       |    |
|-------------------------|---|-----|-------|--------|-------|----|
|                         | Mean  | SD  | Max   | Median | Min   | n  |
| N <sub>2</sub> O (ppbv) | 337.9   | 0.3 | 338.5 | 337.9  | 337.4 | 90 |
| CO <sub>2</sub> (ppmv)  | 399.8   | 3.0 | 405.4 | 398.9  | 394.9 | 93 |

**Fig. 1.** Table 1. The S-OPS measured concentrations of N<sub>2</sub>O/CO<sub>2</sub> used for OP-FTIR quantitative method evaluations.

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(a) N<sub>2</sub>O/water vapor concentrations

| Spectra# | N <sub>2</sub> O<br>(ppm) | N <sub>2</sub> O<br>(ppm*m) | Water vapor<br>(ppm) | Water vapor<br>(ppm*m) | Spectra# | N <sub>2</sub> O<br>(ppm) | N <sub>2</sub> O<br>(ppm*m) | Water vapor<br>(ppm) | Water vapor<br>(ppm*m) |
|----------|---------------------------|-----------------------------|----------------------|------------------------|----------|---------------------------|-----------------------------|----------------------|------------------------|
| 1        | 0.31                      | 10.23                       | 7330.60              | 241909.89              | 31       | 0.31                      | 10.23                       | 20720.00             | 683760.00              |
| 2        | 0.31                      | 10.23                       | 7334.38              | 242034.64              | 32       | 0.31                      | 10.23                       | 20720.00             | 683760.00              |
| 3        | 0.31                      | 10.23                       | 7344.42              | 242365.75              | 33       | 0.31                      | 10.23                       | 20720.00             | 683760.00              |
| 4        | 0.40                      | 13.20                       | 7345.97              | 242417.03              | 34       | 0.40                      | 13.20                       | 21166.00             | 698478.00              |
| 5        | 0.40                      | 13.20                       | 7335.69              | 242077.81              | 35       | 0.40                      | 13.20                       | 21166.00             | 698478.00              |
| 6        | 0.40                      | 13.20                       | 7384.26              | 243680.45              | 36       | 0.40                      | 13.20                       | 21166.00             | 698478.00              |
| 7        | 0.50                      | 16.50                       | 7425.25              | 245033.38              | 37       | 0.50                      | 16.50                       | 21352.00             | 704616.00              |
| 8        | 0.50                      | 16.50                       | 7435.31              | 245365.38              | 38       | 0.50                      | 16.50                       | 21352.00             | 704616.00              |
| 9        | 0.50                      | 16.50                       | 7428.77              | 245149.42              | 39       | 0.50                      | 16.50                       | 21352.00             | 704616.00              |
| 10       | 0.60                      | 19.80                       | 7472.43              | 246590.20              | 40       | 0.60                      | 19.80                       | 22409.00             | 739497.00              |
| 11       | 0.60                      | 19.80                       | 7561.33              | 249524.05              | 41       | 0.60                      | 19.80                       | 22409.00             | 739497.00              |
| 12       | 0.60                      | 19.80                       | 7561.16              | 249518.13              | 42       | 0.60                      | 19.80                       | 22409.00             | 739497.00              |
| 13       | 0.70                      | 23.10                       | 7428.18              | 245129.78              | 43       | 0.70                      | 23.10                       | 25814.00             | 851862.00              |
| 14       | 0.70                      | 23.10                       | 7387.42              | 243784.78              | 44       | 0.70                      | 23.10                       | 25814.00             | 851862.00              |
| 15       | 0.70                      | 23.10                       | 7359.32              | 242857.45              | 45       | 0.70                      | 23.10                       | 25814.00             | 851862.00              |
| 16       | 0.31                      | 10.23                       | 15367.62             | 507131.41              | 46       | 0.31                      | 10.23                       | 26786.16             | 883943.19              |
| 17       | 0.31                      | 10.23                       | 15372.82             | 507303.06              | 47       | 0.31                      | 10.23                       | 26584.12             | 877275.94              |
| 18       | 0.31                      | 10.23                       | 15360.80             | 506906.44              | 48       | 0.31                      | 10.23                       | 26597.24             | 877708.81              |
| 19       | 0.40                      | 13.20                       | 15595.24             | 514643.03              | 49       | 0.40                      | 13.20                       | 30446.93             | 1004748.69             |
| 20       | 0.40                      | 13.20                       | 15704.48             | 518247.72              | 50       | 0.40                      | 13.20                       | 30738.75             | 1014378.88             |
| 21       | 0.40                      | 13.20                       | 15708.70             | 518387.22              | 51       | 0.40                      | 13.20                       | 30386.46             | 1002753.19             |
| 22       | 0.50                      | 16.50                       | 15521.94             | 512224.06              | 52       | 0.50                      | 16.50                       | 29310.16             | 967235.44              |
| 23       | 0.50                      | 16.50                       | 15678.90             | 517403.75              | 53       | 0.50                      | 16.50                       | 28955.07             | 955517.25              |
| 24       | 0.50                      | 16.50                       | 15771.27             | 520452.06              | 54       | 0.50                      | 16.50                       | 28851.81             | 952109.88              |
| 25       | 0.60                      | 19.80                       | 15766.92             | 520308.47              | 55       | 0.60                      | 19.80                       | 28499.03             | 940467.94              |
| 26       | 0.60                      | 19.80                       | 15707.03             | 518332.09              | 56       | 0.60                      | 19.80                       | 28247.49             | 932167.31              |
| 27       | 0.60                      | 19.80                       | 15859.43             | 523361.28              | 57       | 0.60                      | 19.80                       | 27876.50             | 919924.50              |
| 28       | 0.70                      | 23.10                       | 16033.97             | 529121.00              | 58       | 0.70                      | 23.10                       | 28584.89             | 943301.38              |
| 29       | 0.70                      | 23.10                       | 15967.60             | 526930.88              | 59       | 0.70                      | 23.10                       | 29724.95             | 980923.31              |
| 30       | 0.70                      | 23.10                       | 15887.32             | 524281.53              | 60       | 0.70                      | 23.10                       | 29897.34             | 986612.19              |

(b) The number of factors in PLS models

| Analytical window (cm <sup>-1</sup> )               | No. of factors in PLS |             |
|---|-----------------------|-------------|
|   | N <sub>2</sub> O      | water vapor |
| W <sub>N</sub> 1: 2170.0 - 2223.7                   | 3                     | 5           |
| W <sub>N</sub> 2: 2188.5 - 2223.7                   | 4                     | 4           |
| W <sub>N</sub> 3: 2188.5 - 2204.1 + 2215.8 - 2223.7 | 4                     | 4           |
| W <sub>N</sub> 4: 2188.5 - 2204.1                   | 5                     | 4           |

**Fig. 2.** Table 2. Sixty mixed-gases calibration spectra were used to build PLS models for N<sub>2</sub>O quantification: (a) concentrations of N<sub>2</sub>O and water vapor, and (b) the number of factors used in PLS models.