

Review of

Intercomparing CO₂ amounts from dispersion modeling, 1.6 μm differential absorption lidar and open path FTIR at a natural CO₂ release at Caldara di Manziana, Italy

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1. General Remarks

In the presented manuscript, the authors attempt to compare three different techniques for deriving column-averaged CO₂ concentrations along a given line-of-sight in the diffuse CO₂ degassing Caldara di Manziana in Central Italy. The most established technique that the authors apply is CO₂ detection by active Open Path Fourier Transform Infrared (OP-FTIR) Spectroscopy along a fixed light path. In addition to this, a novel Differential Absorption Lidar (DIAL) specifically designed for measuring CO₂ is used. This instrument is still under development, and the comparison with the FTIR is used to verify its functionality. In a third approach, the authors also perform micro-scale meteorological dispersion modeling using a combination of the DISGAS code and the DWM wind model. The model is used to simulate the CO₂ concentration in the air above the degassing features in three dimensions. Then, the concentration map is sampled along the approximate measurement line-of-sight of the instruments.

The study is of considerable interest to the volcanology community because it discusses two rather new techniques for quantitative determination of CO₂ concentrations and fluxes: the DIAL and the dispersion modelling. In principle, the combination of the two approaches might in the future be used to determine the CO₂ flux emitted from a diffuse degassing region, an application that I believe the authors fail to mention but should be touched upon, as it lends additional importance to their study.

Unfortunately, there are a number of unresolved issues with the experimental setup and the author's interpretation of the data. One stems from the fact that the light paths along which the two open-path measurements were performed were not the same. Given the strong vertical non-linear gradient of CO₂ concentration expected in the area, this mismatch causes problems. It is also unclear whether modelling the CO₂ concentration at a single height above ground (0.5 m) is sufficient to assess the situation in the pit crater. The presented modelling study requires quite a number of assumptions, many of which are not mentioned in the manuscript. And while the model time resolution of two minutes is significantly lower than that of the measurements, it did not become clear to me how this can cause the systematic bias toward lower values that the authors argue for. Finally, the authors state that the datasets recorded by the FTIR and the DIAL are consistent and see this is a successful validation test of the DIAL. I am not convinced of this. The DIAL does appear to be calibrated such that its average measured concentration is about the same as that of the FTIR, but it fails to pick up any fluctuations at all during the measurement period. This is worrisome and to me indicates it may not be working properly. I feel that these issues, which are described in more detail below, all need to be addressed before the manuscript should be considered for publication in Atmospheric Measurement Techniques.

2. Specific Comments

2.1 *Difference in light paths*

One problem arises from the different light paths chosen for the two open-path instruments. Though the paths are close to one another, the fact that the FTIR path runs at a constant 0.5 m above the ground while the DIAL path starts 1 m above the ground and ends at the ground itself is unfortunate. The first meter of air above the ground in regions of diffuse CO₂ degassing such as Caldara di Manziana is characterized by a very strong vertical gradient in the CO₂ concentration. The CO₂ mixing ratio can approach 100% a few mm above the ground (or water) surface, decrease rapidly and reach practically background concentrations at 1 meter. Since this gradient is caused by diffusion of CO₂ into the background atmosphere, it is not expected to be constant, but rather exponential in first order approximation. Therefore, an instrument aimed at the ground will be extremely sensitive to degassing occurring near the point where the light path touches the ground. At the same time, the sensitivity to degassing occurring at the instrument's location 1 m off the ground is negligible in comparison.

Given the different optical paths of the two instruments, it is unclear to me whether one should even expect consistent CO₂ column amounts. It probably depends upon the spatial distribution of degassing sources along the light path. If a single significant source (in this case perhaps the water pool) were located in the center of the light path where both instruments' views are approximately at the same height above the ground, then yes, a consistent measurement would be expected. However, if the main source is towards one end of the path or the other (as appears to be the case in your experiment), I would expect a significantly higher value for the instrument with the lower path at that location (in your case the DIAL). Given the spatial inhomogeneity of diffuse emissions in the crater, I expect this will be hard to work out. However, I believe that some sort of treatment of this issue is needed because if one simply assumes a spatially homogeneous soil emission along the path and an exponential decay of CO₂ concentration with height above ground, the CO₂ values obtained along the two different light paths would not be expected to be the same.

2.2. Assessing the importance of a vertical CO₂ gradient

One very simple approach to assessing the magnitude of the vertical CO₂ gradient and its importance for the study is to look at measured concentrations as a function of height. The authors mention that at least one such measurement was performed above the water pool (page 4332, line 15). Please show the results of this measurement in the manuscript. What was the range of heights that were included? How did the CO₂ concentration vary with height? Were any other such measurements performed in the area? Perhaps some general assumptions about vertical gradients could be gleaned from these?

Another approach to evaluating the importance of the vertical gradient in CO₂ concentration might be to look at the model predictions for change in concentration with height above the ground. Unfortunately,

though the authors state that a three-dimensional CO₂ map is produced by the model, no vertically-resolved modelling results are given or discussed. Somewhere, rather late in the manuscript, the author mention that the vertical resolution of the model is 0.5 m. My feeling is that this may not be enough. The authors are encouraged to, if possible, increase the vertical grid resolution in the lower-most meters above the ground to try to capture the vertical concentration gradient. At least this way the importance of the effect could be assessed. In principle, the DIAL light path might even be sampled out of the vertically resolved model data if multiple heights were available along the path.

2.3. Assumptions made for the modeling study

It appears to me that the expected accuracy of the dispersion modeling is likely very dependent on the accuracy of the initialization of the model. It seems that quite a few assumptions must go into the initialization, a number of which are not currently mentioned in the manuscript. Parameters that are mentioned include the topography and soil flux (from the accumulation chamber survey). Also, the authors mention that the wind speed and direction are given by a meteorology station located within the model domain. However, this meteorology station only measures wind speed and direction (averaged over 2 minutes) at a single point in space. How is the rest of the model domain initialized? Surely not all points are initialized with the same values, or are they? Also, what about the influence of ground temperature? I can imagine that the temperature of the soil (and/or water) could significantly influence air flow at the small scales that are considered here. What other assumptions are made in the model study? Which effects are omitted and why?

2.4. Dealing with different time resolutions of the individual techniques

Clearly, the different techniques compared in this study operate at different time resolutions. The DIAL obtains a measurement every couple of seconds, the FTIR takes a few tens of seconds and the model only gets a result every 2 minutes because this is the time resolution of the meteorology station used to initialize it. This difference in time resolution is mentioned frequently throughout the manuscript and in places is called upon to explain differences in the results (e.g. page 4336 line 20). After reading the manuscript, it is not clear to me how this difference in sampling rate can cause significant differences in measurement/model results. If a range of wind speeds or wind directions are encountered during the 2 minutes integration time, wouldn't the model results still approximately correspond to the measurement results averaged over 2 minutes? Could you please explain this in more detail?

2.5. How consistent are the measurements really?

Another issue that I feel is not adequately addressed in the manuscript is the question of how well the results really compare to one another. For an paper titled 'intercomparsion', I find it odd that there is not a single figure plotting the results of one technique against those of another. Figure 4 is all the

reader has to go on, but the time series plots leave something to be desired. And even though the residual (difference between FTIR and DIAL) is mentioned somewhere but it's not plotted.

In my opinion, there are some major issues with the comparison between FTIR and DIAL that are more or less glossed over by the authors. They state that the measured values tend to agree quite well when averaged over many tens of minutes or when looking only at long term trends. This may be true, but it's not that convincing of an argument because it could depend on some sort of absolute gain that is set by the user. Where any measurements performed outside the crater area? Were these used to in some way calibrate the DIAL? Since two different laser sources are used for the two different wavelengths (ON and OFF), don't you need to somehow normalize the relative signals from the two? In other words, you don't know the expected intensity ratio for the two wavelengths for a given a CO₂ column. There must be some sort of calibration, and this is what is responsible for setting the long-term average value. How was this calibration performed for your measurements?

Comparing shorter-term trends (within the instruments' time resolution) seems more interesting to me. And here there appear to be some pretty serious discrepancies. For example, on 15 October between 16:45 and 16:50, the FTIR measured a column amount between 600 and 800 ppmm above background while the DIAL showed no increase whatsoever above the average value of 400 ppmm. This appears to be true in several other time periods as well. Could you please include a figure plotting the DIAL measurements (perhaps smoothed to the time resolution of the FTIR) vs the FTIR measurements? Can you fit a straight line through those? What is the confidence of that fit? Is the correlation statistically relevant?

Now of course one can argue that a correlation isn't necessarily expected due to the difference in light paths (see comments above). However, the DIAL doesn't seem to show any change at all above the measurement noise during the measurements on October 15. This is surprising and to me indicates something probably isn't working properly. Given that the DIAL is aimed at the ground, it would expect it to be even more susceptible to variations in the gas flux (the 'pulsing' that you mention). And the time resolution should be even better than that of the FTIR. So can you explain why you see practically no variations on timescales of around 5 minutes while the FTIR clearly sees these in the latter part of the measurement on October 15?

The bottom line is that the data seems to show that the chosen calibration of the DIAL gives similar mean CO₂ columns as the FTIR. However, it also seems to show that it is incapable of measuring the variations on the order of 400 ppmm that the FTIR sees. This is worrisome.

3. Minor comments and corrections

First of all, the manuscript would benefit a lot from English language proof reading. Parts of it are difficult to comprehend due to convoluted sentence structure and awkward vocabulary. It is beyond the scope of this review to correct all language related issues.

P4328

L10 – The instrument “is undergoing” validation studies. They are going on right now.

L15 – What are “Volcanic CO₂ amounts”? please be more specific.

L17 – I fail to see how you would use a dispersion model to simulate CO₂ concentrations in a well-mixed background atmosphere. I don’t think you would need a model for that, would you?

L21 – Non steady? I assume you mean variable in time?

L26 – “The FTIR used HERE is a MIDAC...”

P4329

L10 – “An interferogram is produced, which is...”

L11 – “BY fitting ...”

L12 - “path-averaged”

L16 – “Many volcanoes exhibit quiescent degassing...”

L19 – “Even IN good visibility,...”

L28 – Corresponding to what? How about “slightly different wavelengths”

P4330

L20 – Here you talk about the normalization with the transmitted laser intensity. Later, you state that this was not done. If it’s not done, you don’t need to mention it here. Or say that it’s normally done, but couldn’t be done in this experiment.

L25 – I did not understand the scheme used to mitigate the scintillation noise. Please explain it more clearly or just give a reference.

P4331

L9 – “crossing each other IN HORIZONRAL DIRECTION at the IR source.”

L10 “disperses INTO THE ATMOSPHERE”.

P4333

L14 – Instead of just giving the mean residual, showing it in a plot would be nice.

L15 – I think the main issue here is the height of the light path above the vent, not so much the FOV. See comments above.

L25 – Here and throughout the manuscript, all measurements are given in ppm ABOVE THE BACKGROUND. This seems like a strange unit to work in. Both measurement techniques should measure the actual number of molecules in the light path, regardless of the background concentration. It is probably more of an issue related to the modelling approach – here perhaps you assume the background to be 0 and just work in ppm above background. But that’s more of a technical issue, and to me it’s quite counterintuitive to work in ppm above background. I would strongly recommend switching all values to absolute ppm.

P 4334

L2 – “data variability CAUSED BY atmospheric...”

L3 – “turbulence or water droplets emitted from the vent”

L5 – “it showed that, using the current...”

L11 – “the DIAL is currently being modified to allow for simultaneous sensing of the ON and OFF band signals.”

L14 – I disagree with this statement. The DIAL has not yet been turned on at the beginning, and the FTIR is significantly lower (on average) than the model.

L15 – you state that measured CO₂ concentrations decrease during the first 15 minutes of the measurement, just like the model. But the measurements decrease much less than the model predicts! The model predicts a decrease to 20% of the initial value! Please be more quantitative! Also, it is unclear if the DIAL has a decrease at all.

L22 – It is unclear to me why the 3m accuracy of the spatial location of the instruments is important if the model has a 10m spatial resolution. I assume the effect of this should be small...

P4335

L27 – “... associated with October 16, where the atmospheric conditions...”

P4336

L3 – You mean 800 ppm above background! That’s about 1200 ppm.

L3 – “However, the mean modeled mixing ratio of 480 ppm was still significantly higher than the measured value of 200ppm...”

P4337

L7 – “1. Discrete absorption measurement with DIAL”

L8 – “2. Evaluation of absorption spectra...”

L14 – “... is currently being implemented...”

P4342 – You might indicate the size of the modelling domain in figure 1.

P4345 – The y axis label is misleading, as this is mixing ratio above background, not concentration. As mentioned before, I recommend switching all labels to absolute CO₂ mixing ratio by adding the background value to all numbers.