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Atmospheric Measurement Techniques Discussions

Interactive comment on "Formaldehyde total column densities over Mexico City: comparison between MAX-DOAS and solar absorption FTIR measurements" *by* Claudia Rivera Cárdenas et al.

Anonymous Referee #1

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Review of Rivera et al. (2020): Formaldehyde total column densities over Mexico City: comparison between MAX-DOAS and solar absorption FTIR measurements

The manuscript presents 6 years of formaldehyde vertical columns VCD measured from Mexico using two different techniques: FTIR and MAXDOAS. The MAXDOAS dataset comprises 3 different type of observation geometries depending on the azimuth of the instrument (V1: East, V2: West and V3: mixed V1 and V2). The comparison of the results obtained with the different techniques shows that, in general, the total columns retrieved with the DOAS instrument are higher than those from the FTIR VCD (V1: 5% higher than FTIR, V2: 9% higher and V3: 28% higher than FTIR). The authors

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conclude that the differences relay on the different sensitivity of each technique and also on the horizontal distribution of HCHO in the troposphere.

In general, the discussions are mainly focused on the comparison of V3 with FTIR, and the internal consistency between the V1, V2, and V3 data. Moreover, supported by satellite HCHO VCD, through these data the authors point out the horizontal heterogeneity of the HCHO distribution in Mexico City. This confirms, once more, the relevance of ground-based observations for satellite validation and it also emphasizes that, for satellite validations, scientists should bear in mind not only the different sensitivities of the different techniques and observation geometries, but also the effect of horizontal inhomogeneity in the distribution of trace gases.

In addition to the urban HCHO VCD data, the authors also present HCHO VCD data observed with a FTIR located in the high-altitude site of Altzomoni.

The manuscript is well presented and the methodology is well described. Moreover, the MAXDOAS and FTIR data of Mexico City and the FTIR data of Altzomoni presented in the manuscript (6 years) are quite unique and may serve for future publications on more detailed chemical/transport processes in such megacity.

Overall, publication is recommended after addressing the following comments.

————————General Comments————————-

Beyond Sect. 3.3.1, Sect. 3.3.2 and Sec. 3.3.3, one simplistic view of investigating the gathered data would be that, since FTIR performs direct Sun observations and DOAS V1 sense air masses towards the East, and DOAS V2 towards the West, the FTIR observations could be split between morning and afternoon observations in order to compare to V1 and V2 DOAS data, respectively. For instance, once smoothed by the averaging kernel, have the authors compared the FTIR morning data to morning V1 DOAS, and FTIR afternoon data to afternoon V2 DOAS? Would that compare better (or worse) to the FTIR am/pm data than V3? Also, although it is mentioned throughout

the manuscript, it is relevant that the authors state “up front” that, due to the different sensitivities of the techniques, the FTIR and the MAXDOAS information do not refer exactly to the same altitudes of the atmosphere (e.g., averaging kernel in Fig. 5). More than comparing one data set to the other, it might be more useful to use (and present) both data sets as complementary to each other. Also, the inhomogeneity of HCHO in Mexico City could be investigated even further by using the lowest elevation angles of the MAXDOAS data (i.e., near-surface HCHO) at the different azimuth angles (although that might result in another paper by itself).

Also, in addition to the urban data, this work presents HCHO observations form the high-altitude site of Altzomoni (FTIR). Given the sparse number of measurements of HCHO performed from high-altitude locations, the manuscript would probably benefit if the authors could dig a bit further on these data set since, in fact, these data are merely presented in one small paragraph in the manuscript (Sec. 3.4.), but not really discussed (e.g., how do the HCHO VCD in clean and in urban scenario compare or the reasons behind the daily and seasonal evolution shown in Fig. 11), or put in context (even if briefly) with HCHO observations from other high altitude sites worldwide.

————Specific Comments————

P1, L11-12: “A time-dependent comparison revealed that the vertical distribution of this pollutant, guided by the evolution of the mixing layer height, can play an important role in how the results are affected.”

Do the authors mean that the vertical distribution of HCHO can play an important role in how the results are affected? i.e., are the results affected by the distribution of HCHO? Please, clarify.

P1, L21: HCHO is mainly (not “also”) formed from the oxidation of CH4 and NMVOCs. This is particularly relevant for the Altzomoni data presented.

P4, L27: How long does it take to perform 1 scan (i.e., 90, 0, 2, 6, 13, 23, 36, 50, 65,

82)?

P4, L31: In addition to the mentioned filters, is any sort of cloud filter applied to the DOAS data?

Please, similarly to the error estimation offered for FTIR observations (P4, L 14), provide an error estimation of the MAXDOAS data presented in the manuscript.

P5, L2: 324.6-359 nm is chosen for the HCHO spectral DOAS analysis. Why that particular range instead of the one suggested by e.g. Pinardi et al (2013)? Given the chosen spectral range, the possible spectral interference of BrO and/or O3 should be addressed (maybe a test with chosen days?) not only for the city data but also for the high-altitude observations. Also, what polynomial did the authors use for the HCHO DOAS retrieval? Note the impact of the polynomial mentioned by Pinardi et al. (2013).

P6, Sec. 3.1: Since Section 2 addressed FTIR and MAXDOAS observations„ and Section 3 is entitled as "Results", probably Sect. 3.1 would make more sense after presenting the results of FTIR and MAXDOAS observations (Sect. 3.2).

P6, L14: why is V3 chosen (and not V1 and/or V2)? Since V1 and V2 are referred throughout the manuscript, the authors may want to include the time series of not only the V3 VCD in a figure (Fig. 2), but also of V1 and V2. Also, how is V3 retrieved? i.e., do the authors averaged the dSCDs observed at V1 and V2, and then invert V3 VCD from that averaged V1+V2 dSCD?

P7, figure 2: Based on the averaging kernels shown later in Fig. 5, it would be helpful to remind the reader the altitude ranges covered by each instrument (e.g., FTIR UNAM VCD 2-16 km; FTIR UNAM VCD 4-16 km; MAXDOAS UNAM VCD 2-5 km)

P7, L4: ". . .and thus probes cleaner atmospheric columns" as long as there is no upslope transport (is there at Altzomoni?). Also, how do these VCD at Altzomoni compare to HCHO observations at other high altitude research sites? As mentioned in the general comments, authors are kindly advised to address further the results of Altzomoni

data throughout the manuscript since those data are relevant by themselves (note the very scarce HCHO observations from high-altitude sites).

P7, L6: "...in general larger than...". How much larger? Please, quantify.

P7, L13: "...VCDs are larger than...". How much larger? Please, quantify.

P9, Sect. 3.1.1: See general comments (i.e., are the FTIR morning data comparable to morning V1 DOAS, and FTIR afternoon data comparable to afternoon V2 DOAS?)

P9, L24: Please, specify (i.e., quantity) the (average) degrees of freedom (DOF) of the retrieved VCD for each technique (not only MAXDOAS but also FTIR). As for the DOAS V1, V2, V3 measurements, do they have similar degrees of freedom? Figure 8 shows they are not the same, please provide an average DOF for V1, for V2 and for V3 or the time series.

P10, Fig. 5: how is the vertical grid of the FTIR inversion compared to the one used for the MAXDOAS inversion?

P13, L8-9: "the retrieved profile using both sides of the measurement plane is to our current knowledge the best estimation for the HCHO profile" if one assumes horizontal homogeneity (?).

P13, L19: please provide a DOAS dSCD error estimation.

P15, L21: "...both instruments are measuring coincidently the same atmospheric state" Would that be true given Fig. 1? Probably only if V3 is used as measuring vector (?)

————Technical Corrections———

P1, L 3-6: For the MAX-DOAS measurements, the software QDOAS was used to calculate differential Slant Column Densities (dSCDs) from the measured spectra and subsequently the Mexican MAX-DOAS Fit retrieval 5 code (MMF) to convert from dSCDs to Vertical Column Densities (VCDs). The direct-solar absorption spectra measured

with FTIR were analyzed using the PROFFIT retrieval code These sort of details would be better if included later in the text (Sec. 2.1, 2.2), not in the abstract.

P1, L 10: “could demonstrate”

Probably more accurate would be “suggests” or “indicates”

P1, L 12: “Apart from the reported. . .”

In addition to the reported. . .

P2, L 12: “. . . satellites, aircraft, vehicles or ground based”

Balloons as well

P2, L 20: Since CINDI is mentioned, probably the authors should also mention the more CINDI2 campaign (Kreher et al., 2020)

P2, L26: LP in LP-DOAS was not introduced before (i.e., long-path DOAS)

P2, L24-28: FTIR vs MAXDOAs literature. The authors may want to consider including Franco et al., AMT, 2015;

P2, L30: “Another study by Garcia et al. ....dominate the HCHO concentration at the surface”. The authors may want to split that long sentence.

P3, L5: In which sense is the work presented an “unprecedented comparison”? Is it due to the length of the study (i.e., 6 years)? Is it due to the location of the study (i.e., Mexico)?

P3, L7: “to characterize the difference” in?

P3, L5-12: To ease the reader, the authors may want to specify in which section will be addressed each of the topics mentioned in this paragraph.

P3, L15: “One” of the sites “is. . .”

P3, L17: “The other” site “is the Altzomoni. . .”

P3, L21: At Altzomoni, please specify that the FTIR is part of NDACC. Note that NDACC also comprises DOAS instruments.

P5, L4: Even if it is mentioned by Friedrich et al., to ease the reader the authors may want to include at least the spectral range where O4 is retrieved.

P6, Fig. 1: Please, enlarge the size letter of the two sites in the map, they are hard to see. Also, a circle indicating the region that comprises MCMA would be helpful for the reader.

P7, L11: "the seasonal HCHO VCDs" Are those the monthly average data?

P7, L12: The meaning of the black line is not clear. Also, does it relate to FTIR or to MAXDOAS? Note that in Fig. 4 the black data are very hard to distinguish.

P13, L13: What do the authors mean with "the calculation of the red trace"? Do they mean "line"? Note that the equations in page 13 refer to matrices and the word "trace" might be misleading. If refer to line, authors are advised also to change it in the caption of figure 9.

P14, Fig. 9: A horizontal line at VCD difference = 0 might help the reader to understand that figure.

P15, L25: "i" stands for?

P15, Eq 8: Equation incomplete

P17, L15-18: "The slope is given by the averaging kernels of the two instruments and the shape of the variable profile v, and for the simple assumption described above, that the only Eigenvector is constant in the mixing layer but 0 above it, the slope is the fraction of the mean averaging kernel elements in the mixing layer (MAXDOAS/FTIR)."

The authors may want to split this very long sentence.

P17, L21: Given all the assumptions needed, more than "to demonstrate", probably it

would be better “to support”

P17, L21-24: The paragraph is a bit confusing. The authors may want to clarify what they mean.

P18, L20: “. . .depending on atmospheric conditions . . .” and the wavelength.

P19, L28-36: This paragraph presenting the megacity of Mexico might fit better in the introduction (Sect. 1).

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