Interactive comment on "Formaldehyde total column densities over Mexico City: comparison between MAX-DOAS and solar absorption FTIR measurements"

Answers to Anonymous Referee #1

We thank Referee #1 for providing insightful comments and suggestions.

All changes made in the manuscript, following Referee 1 comments and suggestions, can be easily identified in color **blue**. NOTE: changes in color **green** represent changes made following comments and suggestions made by both Referees.

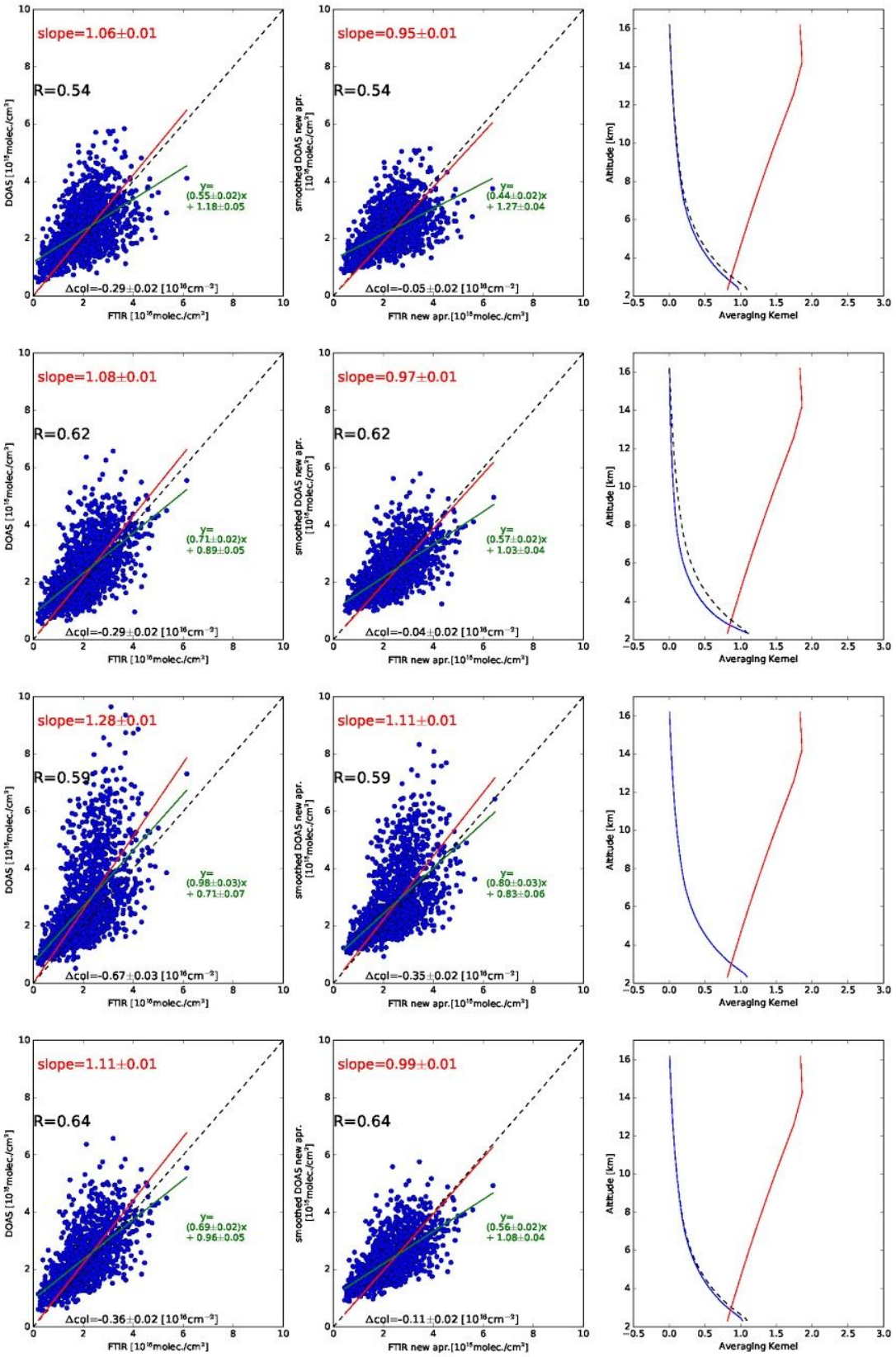
General comments

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?
ANSWER: Following both Referees suggestions, the comparison between FTIR and DOAS V1 during the morning and FTIR and DOAS V2 during the afternoon was conducted. The results, presented in Figure 5 (fourth row) reveal a better agreement between the two measurement techniques. The text of the caption of Figure 5 as well as the text of section 3.3.1 was modified accordingly.

The new caption reads as follows:

"Figure 5. Comparison between FTIR and MAX-DOAS measurements conducted at the UNAM measurement site. The first and second row panels correspond to the VCDs retrieved from MAX-DOAS measurements conducted towards the eastern (V1) and western (V2) measurement sides, respectively. For the third row panel, corresponding to the V3 data product, the VCDs are retrieved including both measurement sides. The fourth row panel corresponds to the comparison between FTIR and MAX-DOAS V1 during the morning and FTIR and MAX-DOAS V2 during the afternoon. The linear regression when forced to zero (red) and not constrained (green) is presented. Black lines represent the 1:1 relation. The left column shows the direct correlation between coincident pairs, whereas the middle column compares the retrieved FTIR VCDs with those calculated from the smoothed MAX-DOAS profiles using the averaging kernel from the FTIR (see text). The right column shows the total column averaging kernel of the FTIR (red lines) and MAX-DOAS (blue lines) retrievals. The dashed black lines on the first, second and fourth row represent the Averaging Kernel of V3."

The relevant text that was modified in section 3.3.1 can be identified in color green.



Modified Figure 5

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).
ANSWER: This fact was stated in the abstract.

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).
ANSWER: We thank the Referee for this interesting suggestion, it was added in the Discussion and Conclusions section, as future work.

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.
ANSWER: As suggested by both Referees, the dataset of Altzomoni was discussed in more detail in the manuscript and put in context with other high altitude sites worldwide and previous work.

The following text was added: “HCHO VCDs measured at Altzomoni are in the same order of magnitude as HCHO VCDs reported by Vigouroux et al. (2018) for several "clean" sites stations belonging to the NDACC network, such as Zugspitze, other mountain site (however at a latitude of 47° and an altitude of 3 km) as well as for Mauna Loa, at a latitude of 20° and an altitude of 3.4 km.” … “Vigouroux et al. (2018) report the same behavior (a maximum in the late afternoon between 16 and 18 local time) for other stations of the NDACC network: Bremen, Paris, Toronto and Lauder. Further analysis should be conducted regarding the diurnal HCHO cycle at Altzomoni, however the detected maximum at late afternoon could be attributed to upslope transport or to secondary HCHO production that has reached a maximum at a certain hour of the day.”

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.
ANSWER: The text was modified with the objective to clarify the idea. The following text replaced the original one: “The temporal change in the vertical distribution of this pollutant, guided by the evolution of the mixing layer height, affects the comparison of the two retrievals with different sensitivities (total column averaging kernels).“

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

P4, L27: How long does it take to perform 1 scan (i.e., 90, 0, 2, 6, 13, 23, 36, 50, 65,82)?
ANSWER: With this setup, a complete scan takes about 7 min. This text was added to the manuscript.

P4, L31: In addition to the mentioned filters, is any sort of cloud filter applied to the DOAS data?
ANSWER: At the moment there is no cloud filter applied to the DOAS data, however, in this comparison exercise and since the DOAS data was compared to FTIR data, a cloud filter was inherently applied since the FTIR data was measured under no cloudy conditions. The application of a cloud filter to the DOAS data is work in progress.

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.
ANSWER: The following text was added in section 2.2: “For the retrieved HCHO MAX-DOAS VCDs, the calculated noise error of the mean column is 5.8% while the systematic error due to uncertainty in the spectroscopy is 2.2%.”

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).
ANSWER: The fitting settings used were following recommendations sent by Gaia Pinardi in November 2017 in the framework of the NIDFORVal project (S5P NItrogen Dioxide and FORmaldehyde VALidation). BrO and O_3 cross sections are included in the fitting. Two references, that refer to these settings, were added: Hendrick et al. 2016 and Pinardi 2017 (personal communication). A polynomial order 5 was used along with an offset order 1 (linear offset) (Hendrick et al., 2016; Pinardi, 2017). This text was added to the manuscript -in green since both Referees suggested this information should be added-.

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).
ANSWER: As suggested by the reviewer, this section was placed after presenting the results of FTIR and MAX-DOAS observations.

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?
ANSWER: V3 was chosen because it has more information content than V1 and V2. The time series of V1 and V2 were included in the figure, as suggested by the reviewer. The MAX-DOAS dataset was updated to include data up to May 2020. The text in the manuscript and caption of Figure 2 (now Figure 1 due to the order change suggested by the reviewer in the previous point) was updated accordingly.

The following text was added in the manuscript, at the end of section 2.2 and just before section 3:

"Three different versions of HCHO VCDs were retrieved using the MMF code: **V1** retrieved VCDs from MAX-DOAS measurements conducted towards the east (telescope's azimuth angle of 85° with respect to the north), **V2** retrieved VCDs from MAX-DOAS measurements conducted towards the west (telescope's azimuth angle of 265° with respect to the north) and **V3** retrieved VCDs from MAX-DOAS measurements conducted towards both sides of the scanning plane. To simplify terminology, for the remainder of the manuscript version **V1** will be referred as "east", version **V2** will be referred as "west" and version **V3** will be referred as "both".

For **V1**, **V2** and **V3** the same *a priori* is used both for the trace gas and for the aerosol. For **V3**, the "scan" is simply treated as consisting of two different azimuth directions. The **V1**, **V2** and **V3** retrievals are performed independent of each other and differ in the definition of a "scan", where **V3** contains all pointing directions from **V1** and **V2** together. A single vertical profile is retrieved in both directions for **V3**, so assuming horizontal homogeneity. This assumption clearly is not fulfilled, however, it is also not fulfilled in a single viewing direction since the effective light path is around 5-20 km. As pointed out in the manuscript, the advantage of using both directions is a higher information content, the disadvantage is a more rigorous break down of the homogeneity assumption."

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)
ANSWER: The following text was added to the caption of Figure 1 now (before Figure 2) due to the change order suggested by the Reviewer: "The altitude ranges covered by each instrument are FTIR UNAM VCDs 2-16 km, FTIR Altzomoni VCDs 4-16 km and MAX-DOAS UNAM VCDs 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).
ANSWER: A maximum observed later in the afternoon at Altzomoni could be an indication of upslope. The results were further addressed throughout the manuscript, especially in section 3.4. The text "as long as there is no upslope transport" was added.

P7, L6: "...in general larger than...". How much larger? Please, quantify.
ANSWER: The quantities were provided, the following text was added: "0 to 38% for V1, 15 to 47% for V2 and 29 to 61% for V3".

P7, L13: "...VCDs are larger than...". How much larger? Please, quantify.
ANSWER: The quantities were provided, the following text was added: "2 to 35% for V1, 17 to 51% for V2 and 23 to 75% for V3".

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?)
ANSWER: Following both Referees suggestions, the comparison between FTIR and DOAS V1 during the morning and FTIR and DOAS V2 during the afternoon was conducted. The results, presented in Figure 5 (fourth line) reveal a better agreement between the two measurement techniques. The text of the caption of Figure 5 as well as the text of section 3.3.1 was modified accordingly.

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.
ANSWER: The average degrees of freedom for V1, V2 and V3 as well as for both FTIR sites were added, the text was modified as follows "… less than two degrees of freedom (average values being 0.692 for V1, 0.782 for V2 and 0.970 for V3) and do not represent the true atmospheric profile, while the average FTIR degrees of freedom is 1.0 for the UNAM site and 1.1 for the Altzomoni site."

P10, Fig. 5: how is the vertical grid of the FTIR inversion compared to the one used for the MAXDOAS inversion?
ANSWER: This information was added to Figure 6, as a complement (Figure 6b) of the figure already presented.

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 (?).
ANSWER: as suggested by the Referee, the phrase "(if one assumes horizontal homogeneity)" was added after the word profile.
We would like to refer to the Referee to the paragraphs in color green where we provide an answer to comment "P6, L14", where we give estimates of the effective distance and point out that horizontal homogeneity is already not fulfilled for V1 and V2.

P13, L19: please provide a DOAS dSCD error estimation.
ANSWER: For the lower elevation angles (where the HCHO signal is higher), the DOAS dSCD error is typically 15%.

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 (?)
ANSWER: The formulation "taking into account" was replaced by "assuming".

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 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.
ANSWER: These details were included in the methodology as well. In order to provide as many details as possible, we thought it would be a good idea to also include them in the abstract.

P1, L 10: "could demonstrate"
ANSWER: The change was made.

Probably more accurate would be "suggests" or "indicates"
ANSWER: The change was made.

P1, L 12: "Apart from the reported..."
In addition to the reported...
ANSWER: The change was made.

P2, L 12: "... satellites, aircraft, vehicles or ground based"
Balloons as well
ANSWER: Balloons was added to the text.

P2, L 20: Since CINDI is mentioned, probably the authors should also mention the more CINDI2 campaign (Kreher et al., 2020)
ANSWER: As suggested by the Referee, the CINDI-2 campaign was included as well.

P2, L26: LP in LP-DOAS was not introduced before (i.e., long-path DOAS)
ANSWER: Long Path was defined, as suggested by the Referee.

P2, L24-28: FTIR vs MAXDOAs literature. The authors may want to consider including Franco et al., AMT, 2015;
ANSWER: The Franco et al. (2015) reference was added, as suggested by both Reviewers.

P2, L30: "Another study by Garcia et al. ....dominate the HCHO concentration at the surface". The authors may want to split that long sentence.
ANSWER: The long sentence was splitted as suggested by the Referee.

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)?
ANSWER: We believe both, the following text was added after unprecedented comparison "(in terms of length and location)"

P3, L7: "to characterize the difference" in?
ANSWER: "in both measurement techniques" was added.

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.
ANSWER: As suggested by the Referee, the sections where each of the specific topics mentioned in the paragraph were addressed, were added to the text.

P3, L15: "One" of the sites "is..."
ANSWER: The change was made, as suggested by the Reviewer.

P3, L17: "The other" site "is the Altzomoni..."
ANSWER: The change was made, as suggested by the Reviewer.

P3, L21: At Altzomoni, please specify that the FTIR is part of NDACC. Note that NDACC also comprises DOAS instruments.
ANSWER: The clarification was made in the text.

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.
ANSWER: The spectral range where O_4 is retrieved was included, the following text was added "in the 336 to 390 nm wavelength range,"

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.
ANSWER: The size letter of the two sites in the map was enlarged and the region comprising the MCMA was indicated (in white).

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

ANSWER: Yes, they are monthly average data. The clarification was made in the text.

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.
ANSWER: It refers to both FTIR and MAX-DOAS. The black values were plotted to show the average of month and standard error based on monthly means. For the sake of clarity, and since the results of MAX-DOAS V1 and MAX-DOAS V2 were added to the figure, as suggested by Referee 2, the black lines were removed from the figure.

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.
ANSWER: Yes, trace means line. In all the document the word trace was changed for line.

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

P15, L25: "i" stands for?
ANSWER: "*i*" is the index for the hours for which there exist coincident measurements. This information was added to the text.

P15, Eq 8: Equation incomplete:
ANSWER: It was most probably not appropriate using the "...", we have removed them and write explicitly in the line before what we assume:
"… So the average of ΔcolDOAS and ΔcolFTIR are zero. In addition we assume that the errors epsilon_FTIR(i), epsilon_DOAS(i) are independent and in average zero, we assume also that they are independent with respect to AK_DOAS(i), AK_FTIR(i), Xtrue(i), so that we can simplify the calculation of equation (7) to equation (8)."

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.
ANSWER: This very long sentence was split.

P17, L21: Given all the assumptions needed, more than "to demonstrate", probably it would be better "to support"
ANSWER: The change was made, according to the Referee suggestion.

P17, L21-24: The paragraph is a bit confusing. The authors may want to clarify what they mean.
ANSWER: The paragraph was reformulated and hopefully it is now more comprehensible: "The individual plots in Figure 10, showing the correlations and their slopes for each hour, allow us to support the fact that instead of simply cross validating the FTIR and MAX-DOAS retrievals, it is possible to assume that the mixing layer height dominates the variability and that such simplification is valid on a certain hour. The validation is therefore given by the fact that a plausible variability for each hour explains the slope and correlation for different hours, rather than that the slope and the correlation is close to 1.0."

P18, L20: “...depending on atmospheric conditions ...” and the wavelength.
ANSWER: The change was made, according to the Referee suggestion.

P19, L28-36: This paragraph presenting the megacity of Mexico might fit better in the introduction (Sect. 1).
ANSWER: The paragraph was moved to the introduction, as suggested by the Referee.