Authors' Response to Anonymous Referee #1

We thank the reviewers for their comments and the time they invested in this thoughtful review. We also appreciate them noting the quality of the literature survey and the innovative approach used to estimate in situ NO_2 vertical columns. We have addressed in detail the reviewers' comments below.

Scientific Significance: Comment 1/1

In the view of this referee, the conclusions presented in Section 4 are not really substantial in the sense that they do not provide new insights in terms of scientific knowledge or major methodological advances with respect to any of the measurement techniques being used.

Authors' Response to Scientific Significance: Comment 1/1

We respectfully disagree with the reviewer's assertion that, "The conclusions presented in Section 4 are not really substantial in the sense that they do not provide new insights in terms of scientific knowledge or major methodological advances with respect to any of the measurement techniques being used." While some past studies have compared in situ and satellite derived columns, satellite and MAX-DOAS derived columns, or in-situ and MAX-DOAS derived columns, no previous study has compared all three in an urban setting. In this way, the study is novel and it has helped to elucidate the similarity and difference between what is measured using these methods.

We have provided a useful advance to the comparison methodology by proposing a simple method to estimate NO_2 columns based on measurements with a 2.3 km horizontal resolution. While our approach is not without inherent assumptions and limitations, it has demonstrated that NO_2 is not well-mixed within the first 500 m of the troposphere, which suggests that previous vertical columns derived assuming a well-mixed boundary layer likely overestimated its contribution to the tropospheric NO_2 VCD. The result of this useful advance has been added to the paper's discussion and conclusion.

The methodology used in this paper to derive NO_2 columns using in situ measurements also provides an alternative to using a model-derived profile. The authors have revised the introduction of the paper to note that few models can derive a NO_2 vertical profile with a horizontal resolution less than 5 km on a local scale. Furthermore, the use of a local-scale CTM requires a well-characterized emissions inventory (Bechle et al., 2013; Simpson et al., 2012), which currently does not exist for Toronto.

Finally, we have provided some new insight into how the magnitude of the difference between in situ and remotely-sensed VCDs can be interpreted in terms of the horizontal spatial heterogeneity of a region.

Scientific Quality: Comment 1/2

With respect to the question if the methods applied are valid, I think it is quite striking that few, or no arguments are given in support of the central assumption for the tropospheric NO_2 column derived from the in-situ monitors, namely that it is reasonable to expect a vertical NO_2 profile which can be described by an exponentially decreasing function (characterized by a certain scale height and an integrated column amount of NO_2), which can be properly constrained by measurements at two fixed altitudes. In my view, this assumption is of such importance for this manuscript that it should at least be accompanied by an elaborate discussion on the validity. For such a discussion, please use the following questions as a guideline:

Authors' Response to Scientific Quality: Comment 1/2

The authors agree, and have added more discussion as outlined on a point by point basis below. In general, the authors feel that the proposed method was the best way to estimate the in situ VCD by incorporating all the available information. While others have estimated VCDs for NO_2 using ground based measurements only, and by assuming a well mixed layer, we found that this approach contradicted the available measurements at 0.5 km above ground level.

Referee Guideline [A]

Please describe why the authors choose an exponential profile shape. The atmospheric pressure profile may show an exponential decrease with altitude, and so may well-mixed long lived species, but why would this be expected for a photochemically active species like NO_2? The exponential profile shape may be similar to the 'average' NO_2 profile, averaged over many days/weeks/months, but this does not necessarily imply that this assumption is reasonable for individual cases. In fact, it is probably more likely that realistic profiles show a sharp decrease at some altitude. This sharp decrease may be very low in the morning.

Authors' Response to Referee Guideline [A]

The authors have incorporated the following discussion into Section 2.2 of the revised manuscript:

"The assumption of a vertically decaying NO_2 profile was founded on the following criteria: NO_2 originates at ground level, and undergoes photochemical conversion and dilution primarily through a first order elimination process. A similar vertically decaying NO_2 profile shape has been observed by Isaac et al., 1998 during summertime aircraft measurements conducted over Egbert, Ontario between the elevations of 600 to 2,900 m (approximately 80 km N of Toronto). These measurements demonstrated that the NO_2 concentration decreases with height by following a profile similar to the water vapour concentration, and has been predominantly associated with the dilution of ground-level emissions. There are limited studies available for evaluation that have derived NO_2 VCDs from in-situ data without assuming a well-mixed NO_2 vertical profile in the boundary layer. Previous research conducted by Schaub et al., (2006) demonstrated that in situ measurements from ground level up to 3.6 km generally obeyed a hyperbolic profile shape. This shape was applied to extract a NO_2 VCD assuming the NO_2 mixing ratio was 0.02 ppb at 8 km. Overall, the application of Eq. (2) in this paper aligns with the available research that does not rely on a CTM."

Regarding the reviewer's comment, "In fact, it is probably more likely that realistic profiles show a sharp decrease at some altitude. This sharp decrease may be very low in the morning", the authors have included seasonally averaged diurnal profiles of the ratio of the NO_2 concentration at CN and DT. Please see Figure 4 (c) and (d), which demonstrate that the average $[NO_2]_{CN}/[NO_2]_{DT} > 0.40 \pm 0.02$ during Dec. – Mar at 7:00 EST (n = 219) and $> 0.34 \pm 0.02$ during May to Aug (n =198) for the days meeting all criteria in Table 3 of the paper. Therefore, at 0.5 km above ground-level, over 30% of the NO_2 concentration detected near ground-level is present.

Referee Guideline [B]

[B] Is the result that most characteristic heights reported in Fig. 2 correspond roughly to the altitude above the surface of the upper in-situ monitor really plausible? Would higher characteristic heights have been found if the upper monitor would have been twice as high above the surface? Why (not)?

Authors' Response to Referee Guideline [B]

The heights in Fig. 2 are well above the height of the upper in situ monitor in most months. Please see Figures 4 (c) and (d), which demonstrate that the average NO_2 characteristic height varies diurnally and on a seasonal basis. Thus, we do not believe that a different height would have been obtained if the upper monitor had been twice as high; although, we cannot prove this.

Referee Guideline [C]

[C] Can the authors convincingly show that the reported characteristic heights and tropospheric columns would be substantially different and less plausible if instead of the actual observations of the upper monitor, a single climatological background value would have been used? Or to put it different: can the authors provide argumentation which convinces the reader that the relative contribution of the upper monitor to the retrieved vertical columns and characteristic heights is substantial?

Authors' Response to Referee Guideline [C]

Please see Figures 4 (c) and (d), which illustrate that $[NO_2]_{CN}/[NO_2]_{DT}$ is greater than 0.3 during 7:00 – 17:00 EST. Using Figure 4 (c) as an example, $[NO_2]_{CN}/[NO_2]_{DT}$ is an average of 0.39 ± 0.02 during the hours of 7:00 – 10:00 EST, and reaches an average of 0.47 ± 0.01 during the hours of 11:00 – 17:00. Therefore, the relative contribution of the upper monitor to the retrieved vertical columns and characteristic heights is substantial.

Referee Guideline [D]

[D] Is criterion 6 (Table 3) in an indirect sense not merely a way to 'ignore' cases that do not correspond to the exponential profile shape? (See also p. 835, l. 16-19). This question is especially important in the case of relatively high (summer noon) atmospheric mixing layers (>0.45km)? Is it not the selection method itself that causes the characteristic heights reported for the summer months to be on the low side, rather than the hypothesis mentioned in the manuscript that the higher photochemical conversion rate in summer leads to lower profiles and lower columns? Although this effect will certainly play a role, the argument would be stronger if it was supported by estimates of the typical vertical velocity in a convective boundary layer, combined with estimates of the NO_2 lifetime in this season.

Authors' Response to Referee Guideline [D]

The filtering process used to remove hours that were strongly influenced by horizontal NO_2 gradients and did not follow a vertically decaying profile recognized that NO_x consists predominantly of NO upon being emitted from a combustion process, and that $[NO]/[NO_2]$ decreases with altitude due to the oxidation of NO. Days with a greater $[NO]/[NO_2]$ at CN than at DT were excluded, since this discrepancy was potentially due to the influence of rapidly rising ground-level vehicular emissions at the CN site on some days. As shown in Table 1 of the paper, the CN site experienced 24-hour average weekday vehicle counts that were over 5 times greater than the DT site. Alternatively, stack emissions from nearby sources may have impacted the CN measurements, resulting in a higher $[NO]/[NO_2]$ than at ground level. The application of criteria 5 and 6 in Table 3 eliminated (31%) of the data (364 of the 1181 days) that could not be represented by an exponential profile, but still provided a reasonable representation of a vertically decaying NO_2 gradient.

As suggested by the reviewer, the authors have included Figures showing a frequency histogram of NO_2 volume mixing ratios for the low and the high in-situ monitor, both with and without applying the selection criteria and a frequency histogram for the ratio of the two, both with and without applying the selection criteria. Please see Figure 2 (c), which shows the frequency distribution of the $[NO_2]_{CN}$ / $[NO_2]_{DT}$ volume mixing ratio (corrected for NOz interference) before and after applying selection criteria 6 – 7 in Table 3. Overall, $[NO_2]_{CN}$ / $[NO_2]_{DT}$ is between 0.15 and 0.75 for the majority (83%) of the 1181 days considered (Table 3: criteria 1 - 4), and for all data meeting criteria 1 – 7 in Table 3. The application of criteria 6 – 7 excludes all data (4% of the 1181 days) with $[NO_2]_{DT}$ / $[NO_2]_{CN} < 0.15$ and all data (13% of the 1181 days) with $[NO_2]_{CN}$ / $[NO_2]_{DT} > 0.75$. Furthermore, the median $[NO_2]_{CN}$ / $[NO_2]_{DT}$ for Table 3: criteria 1 – 4 is 0.47 and the median for Table 3: criteria 1 – 7 is 0.43. These results demonstrate that the application of selection criteria 1 – 7 in Table 3 maintained a reasonable representation of $[NO_2]_{DT}$ / $[NO_2]_{CN}$ obtained from the original sample size of 1181 days. Therefore, the application of criterion 6 did not selectively bias the mixing heights in the summer, resulting in lower values.

Referee Guideline [E]

How different would Fig.2 be if only characteristic heights between (for example) 12AM and 2PM local time are considered. This is around the overpass time of OMI, and in addition around the time when the mixing layer is expected to be on its highest.

Authors' Response to Referee Guideline [E]

Figure 2 of the AMTD paper only considers characteristic heights averaged between 12:00 – 14:00 EST as stated in the caption.

Referee Guideline [F]

[F] Would the authors adopt the same approach for other gases, such as ozone? (if so, then see [*] below; if not, then please argue why this approach can be used for NO2 and not for ozone)

Authors' Response to Referee Guideline [F]

We would not recommend this approach for ozone or other regional pollutants such as fine PM. The two major assumptions underlying this approach are: (1) the majority of NO_2 originates at ground level and (2) NO_2 is being eliminated through a first order process as it travels vertically away from the ground. These assumptions would not be valid for ozone. The authors have added the following comments corresponding to Figures 4 (a) and (b), which are to be included in the final paper.

"Figure 4 (a) provides the diurnal variation of the NO_2 concentration measured at DT and CN during the fall and winter months of December – March (average temperature = -0.6 ± 0.2°C), while Fig. 4 (b) shows this diurnal variation during the spring and summer months of May – August (average temperature = 21.1 ± 0.2°C). In both figures, the NO_2 concentration at DT exhibits a peak during the morning hours that corresponds to the evolution of the rush-hour traffic period from 7:00 – 9:00 EST, and decreases during the afternoon. The afternoon decrease is attributed to the increase in planetary boundary layer height, and the increased photolysis rate of NO_2 to produce O_3. The average O_3 concentration (not shown) also reached a maximum during the afternoon hours. The average O_3 concentration at DT during 13:00 – 15:00 EST in December – March was 27.9 ±1.2 ppb, while in May – August it was 41.7 ± 1.8 ppb. These hours generally corresponded to when the NO_2 concentration at DT reached a minimum.

The NO_2 concentration at CN in Fig. 4 (a) and (b) follows a similar profile as the NO_2 concentration at DT. In both figures, the morning rush hour peak is not as pronounced as at DT, likely due to the vertical dilution and photochemical conversion of NO_2 to O_3 with increasing altitude. The NO_2 concentration at CN also reaches a minimum during the afternoon when the O_3 concentration at CN reaches a maximum. The average O_3 concentration at CN during 13:00 – 15:00 EST in December – March was 33.2 ±1.1 ppb (19% greater than at DT), while in May – August it was 47.8 ± 4.7 ppb (15% greater than at DT). The NO_2 concentration at CN was an average of 27 ± 8% (2.4 ± 0.2 ppb) lower in the morning, and 52 ± 2% (4.0 ± 0.1 ppb) lower in the afternoon/evening during the warmer months than during the colder months."

Referee Guideline [G]

How should, with this approach, uncertainty estimates be derived for the characteristic height and tropospheric column? Please comment.

Authors' Response to Referee Guideline [G]

The precision of the in situ columns and heights for a given day could be estimated from multiple measurements of NO_2 at the ground and tower levels. Unfortunately, only hourly averaged values were publically available for use. Thus, the precision might be estimated using the standard deviation over three hours. Estimation of the accuracy is more difficult as this is likely determined by the limitations of the assumed exponential profile.

The authors have added the following discussion to the paper regarding the uncertainty of the in situ NO_2 VCD.

"The uncertainty of the in situ NO_2 VCD was estimated using the fraction of the NO_2 VCD that exceeded 2 km, which for this study was recognized as an average maximum boundary layer height under turbulent mixing conditions based on previous measurements conducted in Southwestern Ontario (Halla et al., 2011). The rationale for this uncertainty estimate is that the NO_2 concentration

may have not decayed at a consistent rate within and above the boundary layer. Overall, the fraction of the NO_2 VCD contained above 2 km ranged from 0% to 22%, with a median of 3%."

Referee Guideline [H]

What is the correlation between the tropospheric column and the characteristic height, and how is this correlation interpreted?

Authors' Response to Referee Guideline [H]

The authors have added the following discussion to the paper regarding the relationship between the NO_2 VCD and characteristic height.

"The NO_2 VCD in Eq. (1) is linearly dependent on H_{NO2} in Eq. (2). Since $z >> H_{NO2}$, the term $[1-exp(-z/H_{NO2})]$ in Eq. (1) equals 1 at the tropopause, so that Eq. (1) can be simplified to: $NO_2\ VCD_{in-situ} = H_{NO2}[NO_2]_{10m}$.

Linear regression of the tropospheric $NO_2\ VCD_{in-situ}$ versus H_{NO2} yields a slope of $[NO_2]_{10m}$.

$$NO_2\ VCD_{in-situ} = H_{NO_2}[NO_2]_{10m}\left[1 - \exp(-z/H_{NO_2})\right]. \quad (1)$$

$$H_{NO2} = 1/\left(\frac{1}{z}\ln\frac{[NO_2]_{10m}}{[NO_2]_{445m}}\right). \quad (2)"$$

Referee Guideline [I]

Do the retrieved characteristic heights show a diurnal cycle? This diurnal cycles is to be expected to show at least some similarity to the typical diurnal increase of the boundary layer height between the morning and the first half of the afternoon.

Authors' Response to Referee Guideline [I]

The authors have prepared Figures 4 (c) and (d) for inclusion in the revised manuscript. The following discussion points for these figures have also been included. It should be noted that the method proposed for estimating the VCD and characteristic height is likely not applicable overnight or in the early morning hours when the boundary layer is well mixed and little photochemical elimination is occurring.

"Figure 4 (c) shows the diurnal variation of the NO_2 characteristic height, and $[NO_2]_{CN}/[NO_2]_{DT}$ during the fall and winter months of December – March (average temperature = -0.6 ± 0.2°C), while Fig. 4 (d) shows this diurnal variation during the spring and summer months of May – August (average temperature = 21.1 ± 0.2°C). Both H_{NO2} and $[NO_2]_{CN}/[NO_2]_{DT}$ follow a similar profile since $[NO_2]_{CN}/[NO_2]_{DT}$ was used to derive H_{NO2}. As shown in Eq. (2), an increase in $[NO_2]_{CN}/[NO_2]_{DT}$ results in an increased H_{NO2}.

The NO_2 characteristic height during the months of December – March exhibited a diurnal trend that is similar to the evolution of the atmospheric mixing height, which increases during the morning hours and peaks in the afternoon (Jacob, 1999). The NO_2 characteristic height (and $[NO_2]_{CN}/[NO_2]_{DT}$) is an

average of 0.5 ± 0.3 km (0.39 ± 0.02) during the hours of 7:00 – 10:00 EST, and reaches an average of 0.65 ± 0.01 km (0.47 ± 0.01) during the hours of 11:00 – 17:00.
During the months of May – August, a statistically significant difference for both the hourly averaged H_{NO2} and $[NO_2]_{CN}/[NO_2]_{DT}$ was not witnessed between the hours of 8:00 to 19:00 EST. The average characteristic height during these hours was 0.56 ± 0.01km: 14% lower than the average maximum characteristic height in December – March, while the average $[NO_2]_{CN}/[NO_2]_{DT}$ during these hours was 0.41 ± 0.01: 13% lower than the average maximum ratio in December – March. These results demonstrate that the vertical distribution of NO_2 within 0.5 km during the spring – summer does not follow the typical diurnal profile of the convective boundary layer, which is generally higher during warmer months than colder months.

Previous research using radiosonde measurements has demonstrated that the atmospheric mixing height in southern Ontario (43.682^{o}N, 79.612^{o}W) is an average of 1.5 km during the summer. An increased mixing height during the summer is directly related to the increase in solar radiation and surface heat flux (Ning et al., 1986). The NO_2 characteristic heights shown in Fig. 4 (d) are over 60% lower than these radiosonde measurements of atmospheric mixing height, which suggest they cannot be considered representative of the diurnal evolution of the atmospheric boundary layer height. Overall, Fig. 4 (d) shows that assuming a well-mixed NO_2 concentration within the planetary boundary layer will lead to an over-estimate of the NO_2 VCD."

Scientific Quality: Comment 2/2

The retrieval of tropospheric NO_2 columns from the differential slant NO_2 columns measured with MAX-DOAS is based on geometrically determined air mass factors. This approach is defensible for high elevations (<20 degrees) where it can give a reasonable first order estimate, but questionable for an elevation of 10 degrees, which is also used. The authors do not explicitly mention if they use both elevations to derive the vertical NO_2 column from the MAX-DOAS observations, or if they use the 10 degrees observation only for the selection criterion mentioned on p.839 l.15. Also this selection criterion, which leads to the rejection of two thirds of all MAX-DOAS observations is questionable. In a region not far away from sources (i.e. a region where horizontal gradients can be expected) the differences between the differential slant column at 10 degrees and 20 degrees (or 30 degrees) does not necessarily follow the 'rule of thumb' that the differential slant column at 10 degrees is within 15% of the differential slant column at 20(30) degrees. Furthermore, the horizontal gradients do not only lead to observations of different air masses, but also to changes in time, even if the elevation remains unchanged. Are these changes within 15%?

Authors' Response to Scientific Quality: Comment 2/2

The authors have stated on line 26 of page 839 in the AMTD paper,

"*The NO_2 differential AMF ($\Delta AMF = \Delta SCD/VCD$) was calculated as shown in Eq. (7), and verified by using the criteria NO_2 $VCD_{10°} = VCD_{20°(or\ 30°)}$ ± 15% (Halla et al. 2011; Brinksma et al., 2008) to ensure tropospheric photon scattering occurred above the NO_2 column."*

The authors have added the following text in Section 2.3 of the revised manuscript:

"Thus, 56 hours (33%) of MAX-DOAS NO_2 ΔSCDs (measured at 20° or 30°) were converted to geometric VCDs during 7:00 -16:00 EST for 15 days during the spring, summer, and winter collectively. Of these 56 measurements, 34 were conducted at 10° and 20°, and agreed within ± 15%,

so the 20° VCD was reported; 12 were conducted at 10° and 30°, and agreed within ± 15%, so the 30° VCD was reported; 10 measurements were conducted at 20° and 30°, and agreed within ± 15%, so the 30° VCD was reported. Therefore, these measurements represent the upper limit of the geometric VCD."

As stated in lines 19 – 25 of the AMTD discussion paper, the geometric VCD agreement criteria was verified by Halla et al. (2011), who demonstrated that when the geometric NO_2 $VCD_{10°} = VCD_{30°} \pm$ 15%, the geometric VCD underestimated the NO_2 VCD retrieved using radiative transfer modeling by 8 – 12%. Based on previous studies, the authors also have estimated the uncertainty of the geometric AMF to be ≤ 15%. Please see lines 25 – 29 on page 840, and lines 1 – 5 on page 841 of the AMTD paper.

While the authors agree that the selection criteria used to apply the geometric AMF is conservative, currently MAX-DOAS radiative transfer modelling parameterizes NO_2 assuming that its horizontal distribution is heterogeneous. Therefore, at this point, based on the available methodology, the authors cannot validate that using an agreement criterion such that NO_2 $VCD_{10°} = VCD_{20°(\text{or } 30°)} \geq 15\%$ would be a correct assumption.

Presentation Quality

The use of the English language is very good, and also the manuscript is well-structured. I think the manuscript could be improved by adding a few more figures, or by describing the content of the figures suggested below in the text.

Authors' Response to Presentation Quality

The authors thank the reviewers for their positive comments regarding the structure of the manuscript. The authors have added / described the content of the figures suggested by the reviewer. The new figures and descriptions are provided below

Suggested Figure (A)

(A) one Figure showing a map with the city of Toronto, the location of the various measurement sites and (if possible), one example of a small and one of large OMI pixel.

Authors' Response to Suggested Figure (A)

The authors have included the following figure in the revised manuscript:

Figure 1. Location of DT and CN monitoring sites characterized in Table 1. Location of MAX-DOAS instrument during campaigns in Table 2: 1 = Wallberg Building, 2 = Centre Island, and 3 = McLennan Physics Building. The 4 points surrounding the MAX-DOAS and in situ measurement locations refer to the corners of a 13 km x 24 km OMI pixel with its area centered on DT.

The authors have added the following clarifying points in Section 2.1 of the revised manuscript:

"An example OMI pixel from May 27, 2008 with its centre located at DT is also shown in Figure 1. The in-situ and MAX DOAS measurement sites are well-contained within this pixel. Approximately 60% of the pixel area overlaps mainland Toronto, while the remaining 40% is over Lake Ontario."

Suggested Figure (B)

(B) one Figure showing a frequency histograms of tropospheric columns measured with the ground-based/MAXDOAS/OMI instruments.

Authors' Response to Suggested Figure (B)

The authors have added the following information in Section 2.2 of the revised manuscript:

"The minimum, median, and maximum average NO_2 VCD during 12:00 – 14:00 EST was 1.57 x 10^{15} molec/cm^2, 1.58 x 10^{16} molec/cm^2, and 1.18 x 10^{17} molec/cm^2, respectively. 60% of data exhibited a NO_2 VCD between 1.00 – 2.00 x 10^{16} molec/cm^2."

The authors have added the following information in Section 2.3 of the revised manuscript:

"56 hours (33%) of MAX-DOAS NO_2 ΔSCDs (measured at 20° or 30°) were converted to geometric VCDs during 7:00 -16:00 EST for 15 days during the spring, summer, and winter collectively. Using this method, the minimum, median, and maximum NO_2 VCD was 1.53x 10^{15} molec/cm^2, 1.56 x 10^{16} molec/cm^2, and 5.96 x 10^{16} molec/cm^2, during 7:00 -16:00 EST respectively. 20% of data exhibited a NO_2 VCD below 5.00 x10^{15} molec/cm^2, and 70% of data exhibited a NO_2 VCD between 1.00 – 2.00 x 10^{16} molec/cm^2."

The authors have added the following information in Section 2.4 of the revised manuscript:

"The minimum, median, and maximum values for the 56 days OMI v 2.0 data that obeyed all criteria in Table 4 (Table 5 in the AMTD paper) *was 3.00 x 10^{14} molec/cm^2, 6.95 x 10^{15} molec/cm^2, and 2.21 x 10^{16} molec/cm^2, respectively. 72% of data exhibited a NO_2 VCD below 1.00 x10^{16} molec/cm^2."*

Suggested Figure (C)

(C) one Figure showing a frequency histogram of NO_2 volume mixing ratios for the low and the high in-situ monitor, both with and without applying the selection criteria (left panel) and a frequency histogram for the ratio of the two, both with and without applying the selection criteria (right panel).

Authors' Response to Suggested Figure (C)

The authors have included the following figure in the revised manuscript:

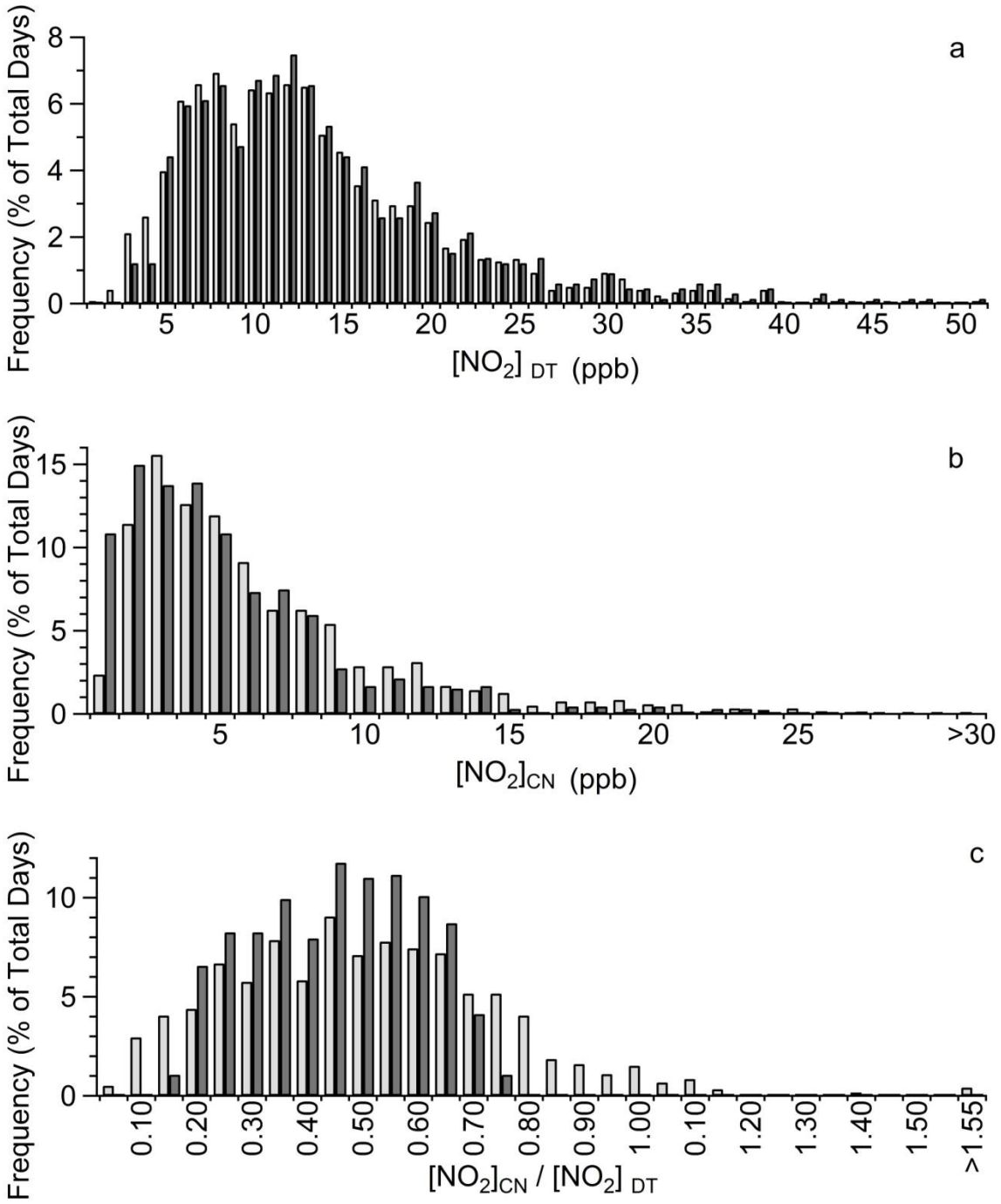

Figure 2. (a) Frequency distribution of NO_2 DT volume mixing ratio during OMI overpass time. Light grey bars refer to data meeting criteria 1 – 4 in Table 3 (Total Days = 1181) and dark grey bars refer to data meeting all criteria in Table 3 (Total Days = 654). (b) Same as (a), but for NO_2 CN. (c) Same as (a), but for ratio of $[NO_2]_{CN}$ to $[NO_2]_{DT}$.

The authors have added the following discussion points to strengthen the methodology applied in Section 2.2 of the revised manuscript:

"Figure 2 (a) and (b) provide the frequency distribution of the NO_2 volume mixing ratio (corrected for NOz interference - see Sect. 3.1 for results) at the DT and CN sites before and after applying selection criteria 6 – 7 in Table 3. At both measurement sites, the NO_2 volume mixing ratio retains a similar frequency distribution before and after applying these criteria. The NO_2 volume mixing ratio at DT is below 12 ppb for 54% of the 1181 days considered (Table 3: criteria 1 - 4), and for 51% of the 654 days meeting criteria 1 – 7 in Table 3. Therefore, the use of these criteria to remove hours strongly impacted by horizontal NO_2 gradients, along with those that did not follow a vertically decaying profile, did not bias the magnitude nor the frequency distribution of the NO_2 concentration at DT and CN.

Figure 2 (c) shows the frequency distribution of the $[NO_2]_{CN} / [NO_2]_{DT}$ volume mixing ratio (corrected for NOz interference) before and after applying selection criteria 6 – 7 in Table 3. Overall, $[NO_2]_{CN} / [NO_2]_{DT}$ is between 0.15 and 0.75 for the majority (83%) of the 1181 days considered (Table 3: criteria 1 - 4), and for all data meeting criteria 1 – 7 in Table 3. The application of criteria 6 – 7 excludes all data (4% of the 1181 days) with $[NO_2]_{DT} / [NO_2]_{CN} < 0.15$ and all data (13% of the 1181 days) with $[NO_2]_{CN} / [NO_2]_{DT} > 0.75$. Furthermore, the median $[NO_2]_{CN} / [NO_2]_{DT}$ for Table 3: criteria 1 – 4 is 0.47 and the median for Table 3: criteria 1 – 7 is 0.43. These results demonstrate that the application of selection criteria 1 – 7 in Table 3 maintained a reasonable representation of $[NO_2]_{DT} / [NO_2]_{CN}$ obtained from the original sample size of 1181 days."

Suggested Figure (D)

(D) one Figure showing frequency histogram of the characteristic heights.

Authors' Response to Suggested Figure (D)

The authors have provided the following information in Section 2.3 of the revised manuscript regarding the frequency distribution of the characteristic heights.

"After applying the criteria in Table 3, the median H_{NO2} during 12:00 – 14:00 EST was 0.56 km, and 58% of data had a NO_2 characteristic height that was within 0.33 to 0.63 km."

Suggested Figure (E)

(E) one Figure showing the monthly averaged NO_2 volume mixing ratio (similar to Figures 2 and 3) for both stations (both with and without applying the selection criteria).

Authors' Response to Suggested Figure (E)

The authors have included the following figure in the revised manuscript:

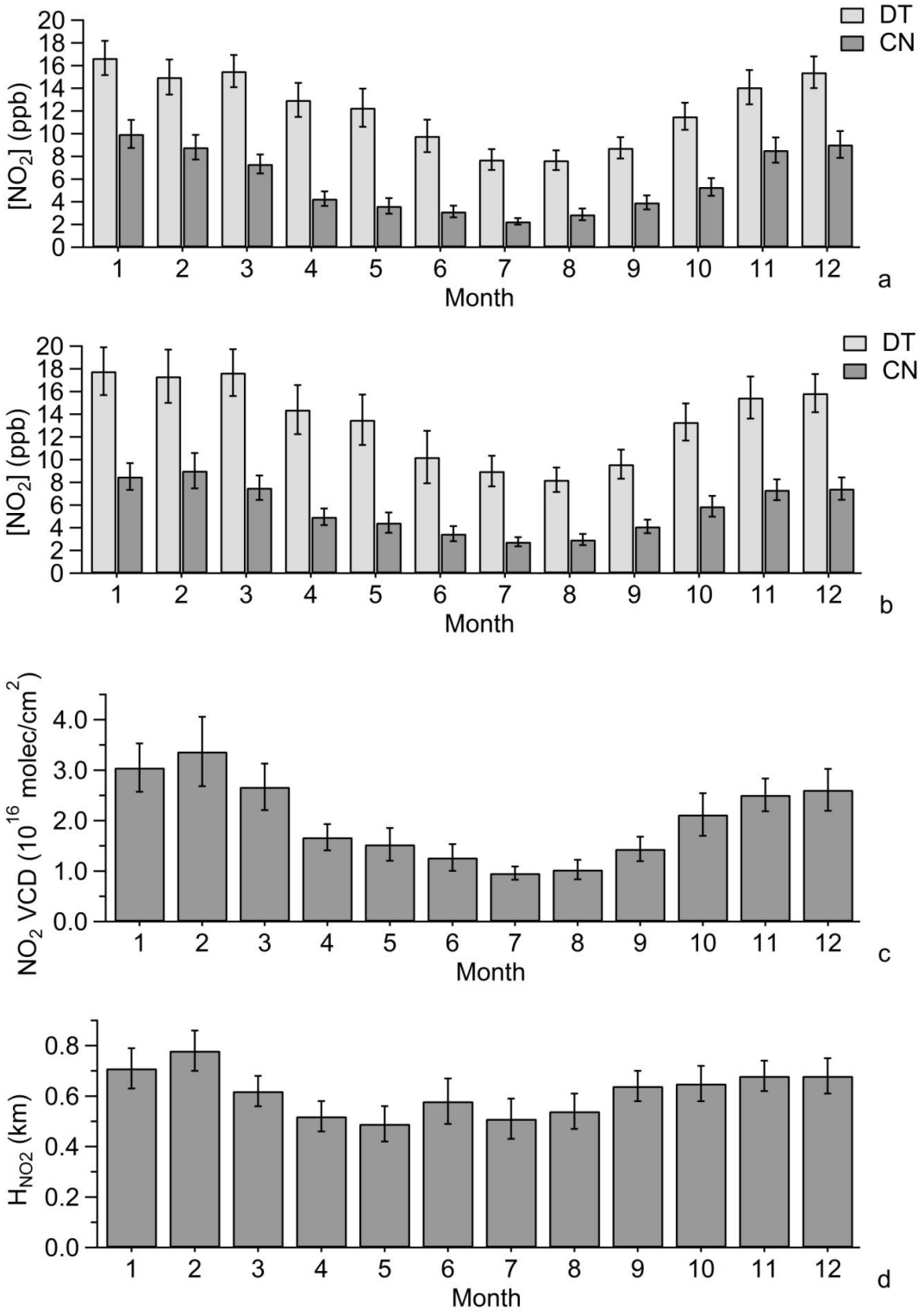

Figure 3 (a) Monthly averaged in situ NO_2 concentration at DT and CN during 12:00 – 14:00 EST for data meeting criteria 1 – 4 in Table 3 (n = 1181) and (b) for data meeting all criteria in Table 3 (n =654). (c) Same as (b), but for in situ NO_2 VCD. (d) Same as (b), but for in situ NO_2 characteristic height.

The authors have added the following discussion points in Section 3.2 of the revised manuscript to strengthen the methodology applied in Section 2.2 of the revised manuscript:

"The seasonal variation of the in situ NO_2 concentration at DT and CN is shown in Fig. 3 (a) for data meeting criteria 1 – 4 in Table 3 and in Fig. 3 (b) for data meeting all criteria in Table 3. The difference between the monthly averaged NO_2 concentrations shown in Fig 3. (a) versus (b) was not statistically significant (p-value = 0.05). These results demonstrate that the monthly averaged NO_2 concentration at CN and DT determined by applying selection criteria 6 – 7 in Table 3 provided a sufficient representation of the concentrations determined using the original sample size of 1181 days."

Figure 3 (c) and (d) were labelled as Fig. 1 and 2, respectively in the AMTD paper, and discussed in detail in Section 3.2. This discussion has been maintained in the revised manuscript.

Suggested Figure (F)

(F) one Figure showing for at least two example days the diurnal evolution of all relevant parameters: NO_2 volume mixing ratio of both in-situ monitors, the characteristic height and the vertical column. If possible, then select one day which shows a typical winter time behaviour, and one day with a typical summer time behaviour. Does the retrieval give a consistent picture which can be understood in terms of NO_2 production at the surface, vertical transport and photo-dissociation?

Authors' Response to Suggested Figure (F)

The authors have included the following figure in the revised manuscript:

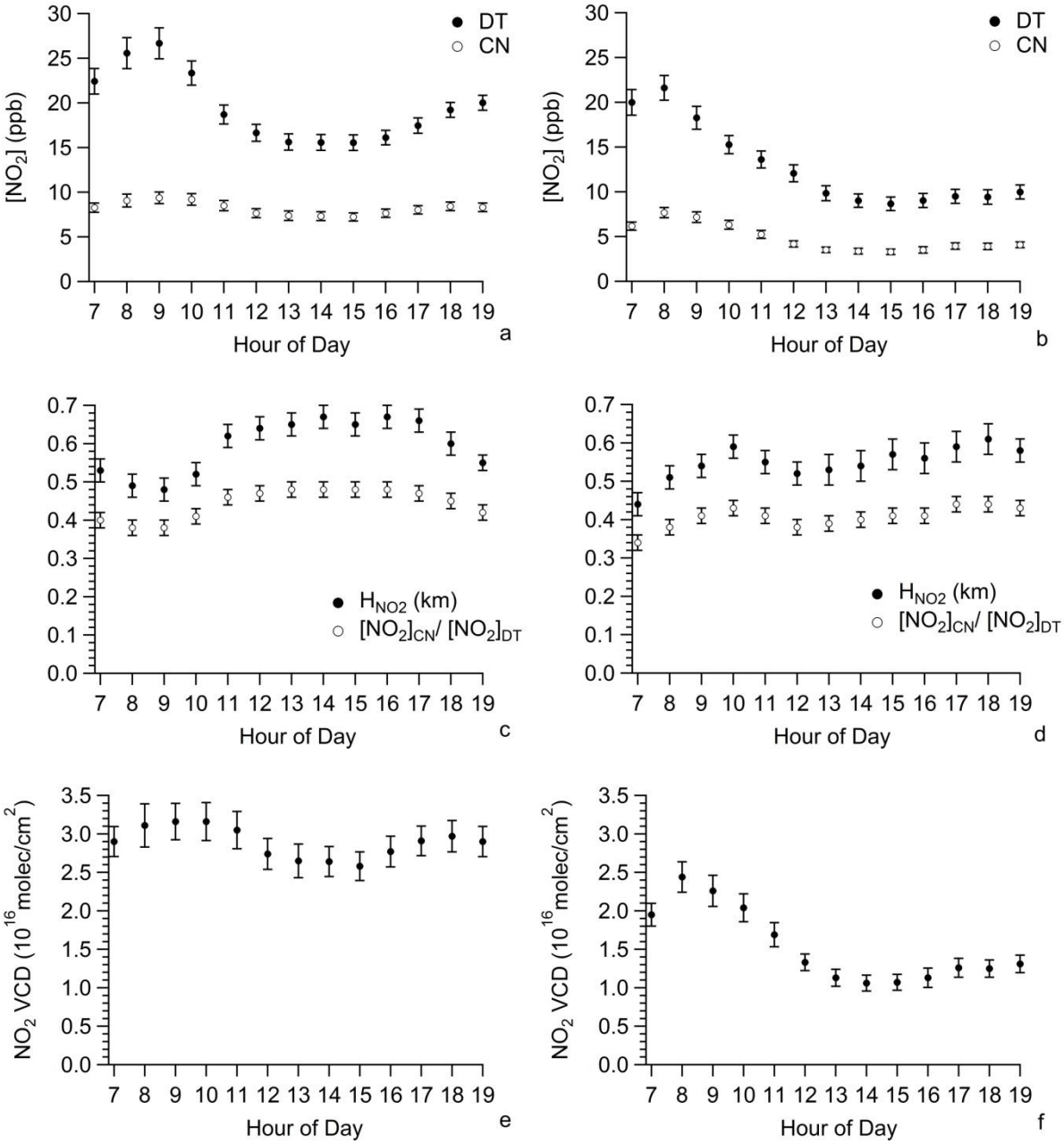

Figure 4 (a) Diurnal profile of $[NO_2]$ at DT and CN during Dec. – Mar. and (b) during May – Aug. (c) Diurnal profile of H_{NO2} and $[NO_2]_{CN}/[NO_2]_{DT}$ during Dec. – Mar. and (d) during May – Aug. (e) Diurnal profile of NO_2 VCD during Dec. – Mar. and (f) during May – Aug.

The authors have added the following discussion points in Section 3.2 of the revised manuscript to strengthen the methodology applied in Section 2.2 of the revised manuscript:

"Figure 4 (a) provides the diurnal variation of the NO_2 concentration measured at DT and CN during the fall and winter months of December – March (average temperature = -0.6 ± 0.2°C), while Fig. 4 (b) shows this diurnal variation during the spring and summer months of May – August (average temperature = 21.1 ± 0.2°C). In both figures, the NO_2 concentration at DT exhibits a peak during the morning hours that corresponds to the evolution of the rush-hour traffic period from 7:00 – 9:00 EST, and decreases during the afternoon. The afternoon decrease is attributed to the increase in planetary

boundary layer height, and the increased photolysis rate of NO_2 to produce O_3. The average O_3 concentration (not shown) also reached a maximum during the afternoon hours. The average O_3 concentration at DT during 13:00 – 15:00 EST in December – March was 27.9 ±1.2 ppb, while in May – August it was 41.7 ± 1.8 ppb. These hours generally corresponded to when the NO_2 concentration at DT reached a minimum.

During December – March at 17:00 EST, the NO_2 concentration at DT began to increase in conjunction with the evening rush hour period, and decreasing planetary boundary layer height. During May – August, the NO_2 concentration remained relatively constant from 13:00 – 19:00 EST, as the higher boundary layer height during warmer months likely resulted in the turbulent mixing, and in turn, dilution of emissions during the evening rush hour period. The NO_2 concentration at DT was an average of 25 ± 1% (5.6 ± 1 ppb) lower in the morning, and 52 ± 2% (4.0 ± 0.2 ppb) lower in the afternoon/evening during the warmer months than during the colder months.

The NO_2 concentration at CN in Fig. 4 (a) and (b) follows a similar profile as the NO_2 concentration at DT. In both figures, the morning rush hour peak is not as pronounced as at DT, likely due to the vertical dilution and photochemical conversion of NO_2 to O_3 with increasing altitude. The NO_2 concentration at CN also reaches a minimum during the afternoon when the O_3 concentration at CN reaches a maximum. The average O_3 concentration at CN during 13:00 – 15:00 EST in December – March was 33.2 ±1.1 ppb (19% greater than at DT), while in May – August it was 47.8 ± 4.7 ppb (15% greater than at DT). The NO_2 concentration at CN was an average of 27 ± 8% (2.4 ± 0.2 ppb) lower in the morning, and 52 ± 2% (4.0 ± 0.1 ppb) lower in the afternoon/evening during the warmer months than during the colder months.

Figure 4 (c) shows the diurnal variation of the NO_2 characteristic height, and $[NO_2]_{CN}/[NO_2]_{DT}$ during the months of December – March, while Fig. 4 (d) shows this diurnal variation during May – August. Both H_{NO2} and $[NO_2]_{CN}/[NO_2]_{DT}$ follow a similar profile since $[NO_2]_{CN}/[NO_2]_{DT}$ was used to derive H_{NO2}. As shown in Eq. (2), an increase in $[NO_2]_{CN}/[NO_2]_{DT}$ results in an increased H_{NO2}.

The NO_2 characteristic height during the months of December – March exhibited a diurnal trend that is similar to the evolution of the atmospheric mixing height, which increases during the morning hours and peaks in the afternoon (Jacob, 1999). The NO_2 characteristic height (and $[NO_2]_{CN}/[NO_2]_{DT}$) is an average of 0.5 ± 0.3 km (0.39 ± 0.02) during the hours of 7:00 – 10:00 EST, and reaches an average of 0.65 ± 0.01 km (0.47 ± 0.01) during the hours of 11:00 – 17:00.

During the months of May – August, a statistically significant difference for both the hourly averaged H_{NO2} and $[NO_2]_{CN}/[NO_2]_{DT}$ was not witnessed between the hours of 8:00 to 19:00 EST. The average characteristic height during these hours was 0.56 ± 0.01km – 14% lower than the average maximum characteristic height in December – March, while the average $[NO_2]_{CN}/[NO_2]_{DT}$ during these hours was 0.41 ± 0.01 – 13% lower than the average maximum ratio in December – March. These results demonstrate that the vertical distribution of NO_2 within 0.5 km during the spring – summer does not follow the typical diurnal profile of the convective boundary layer, which is typically higher during warmer months than colder months.

Previous research using radiosonde measurements has demonstrated that the atmospheric mixing height in southern Ontario (43.682^{o}N, 79.612^{o}W) is an average of 1.5 km during the summer. An increased mixing height during the summer is directly related to the increase in solar radiation and surface heat flux (Ning et al., 1986). The NO_2 characteristic heights shown in Fig. 4 (d) are over 60% lower than these radiosonde measurements of atmospheric mixing height, which suggest they cannot be considered representative of the diurnal evolution of the atmospheric boundary layer height. Overall,

Fig. 4 (d) shows that assuming a well-mixed NO_2 concentration within the planetary boundary layer will lead to an over-estimate of the NO_2 VCD.

Figure 4 (e) provides the diurnal variation of the in situ NO_2 VCD during the months of December – March, while Fig. 4 (f) shows this diurnal variation during May – August. The diurnal profile shown in both figures closely replicate the diurnal profile of the NO_2 concentration at DT (R = 0.87 and R = 0.93, respectively). During the afternoon/evening hours, the NO_2 VCD is at least 2 times greater during December – March versus during May – August. This is due to both the increased concentration of NO_2 DT and the increased $[NO_2]_{CN}/[NO_2]_{DT}$ during the colder months."

Suggested Figure (G)

(F) one Figure showing a scatter-plot of tropospheric NO_2 column versus characteristic height.

Authors' Response to Suggested Figure (G)

Please see the Authors' Response to Referee Guideline [H] for clarification.

References for Authors Response to Anonymous Referee #1

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