February 1, 2013

For our manuscript in ACPD we received three comments. Two from anonymous referees #1 and #2 and one contributed comment from Rainer Volkamer and Roman Sinreich. We thank all contributors for their thoughtful and intensive comments which we will answer in the following. Since the main objection was raised by Volkamer and Sinreich: "... there is a strong indication that there is a measurement artifact in the CHOCHO data reported by Li et al." we will answer this point first.

Contributed comment by Volkamer and Sinreich

The comment by Volkamer and Sinreich was triggered by the high CHOCHO/HCHO ratios (R_{GF}) reported in our study (average R_{GF}=0.135). This value is three to four times higher than observations in Mexico City. In their comment the authors compare their unpublished measurements which were done at the same location with our results. Their average R_{GF} is 0.032 which is substantially lower than our value. Also Referee #1 raised a question about the high R_{GF} values. In addition, Volkamer and Sinreich claim that the smaller wavelength range which we used for our evaluation (smaller compared to their instrument) could cause part of this difference.

In order to investigate a possible measurement artifact we performed a number of investigation on our evaluation procedures going beyond the issue of the wavelength range which was highlighted by Volkamer and Sinreich.

- Wavelength range: Volkamer and Sinreich (VS) assumed that the different wavelength range of our instrument compared to their instrument caused the difference between their and our glyoxal values. The wavelength range used by VS for glyoxal and NO_2 evaluation covers the most prominent absorption line of glyoxal at 455 nm. In our work, we used the wavelength range of 416–441 nm. To assess this point we performed a number of tests on the basis of data which we recorded in Jülich using an instrument which covers the same range as the VS instrument. We found that the different spectral range cannot account for larger differences as outlined in the VS comment (see Fig. A5 for details).
- Effect of the Ring spectrum: The ring spectrum is included in the DOAS fit in order to correct for the ring effect (Platt et al., 1997). The ring spectrum can be calculated either from the locally measured Fraunhofer spectrum (FRS) or from the high resolution FRS (HR FRS) convoluted by the instrument slit function. In our work, we used the first method for the ring spectrum calculation. Here, we checked the DOAS fit results of NO_2 and glyoxal using the ring spectrum calculated by the other method. For the entire data set obtained during the campaign, we found that the fit residual is lower

when using the ring spectrum calculated from the locally measured FRS, especially during noontime. On average, the difference of the retrieved NO_2 and glyoxal DSCDs by using the two different ring spectrum is less than 1% and 8%, respectively.

- Effect of the spectral resolution of the reference spectra: Since NO_2 is always the strongest absorber in the wavelength range for the NO_2 and glyoxal evaluation, a small misalignment of the NO_2 absorption spectrum can result in a big error of the retrieved glyoxal DSCD. The good alignment of the reference spectra largely depends on the quality of the wavelength calibration and on how well the spectral resolution (i.e. the instrument slit function) is determined. For data used in the paper, it was based on wavelength calibration performed by DOASIS software. In the first step, we convoluted the high resolution Fraunhofer spectrum (HR FRS) in the wavelength range of our instrument. It was done by using a preliminary wavelength calibration and convolution kernel of Hg line at 334 nm. Then, we fitted the convoluted HR FRS to the measured FRS in the entire wavelength range of the instrument (i.e. 290 – 445 nm). A wavelength shift and squeeze factor were derived from the fit. By applying the shift and squeeze factor to the preliminary wavelength calibration, the final wavelength calibration can be obtained. However, now we noticed that this wavelength calibration can be problematic, considering the wavelength calibration factor and the spectral resolution of the instrument are not constant over the entire spectral range. We accessed this effect by the WinDOAS software. In WinDOAS, the entire spectral range is divided into several sub-windows, and a wavelength calibration factor and a parameter defining the convolution kernel are used for each sub-window. By fitting the convoluted HR FRS to the measured FRS at each sub-window, the wavelength calibration factor and the convolution kernel parameter can be retrieved, which are then used for adjusting the preliminary wavelength calibration. Fig. A1 shows the difference between the DOASIS wavelength calibration and the WinDOAS wavelength calibration. A wavelength dependent difference of 0 – 0.3 nm was found for the wavelength range of 320 – 445 nm. In Fig. A2, it is clear that the spectral resolution is changing over the wavelength as derived from WinDOAS analysis. In order to prove the WinDOAS wavelength calibration can better represent the instrument properties, we compared the NO_2 reference cross section with our measured NO_2 absorption spectrum. The NO_2 absorption spectrum was measured during the campaign by putting a 1 cm long NO_2 cuvette in front of the telescope of the MiniMaxDOAS instrument. We found that the NO_2 reference cross section created from the WinDOAS wavelength calibration and convolution kernels better matches the measured NO_2 absorption spectrum (Fig. A3). Using the wavelength calibration and wavelength dependent convolution kernel derived from WinDOAS, we created a new set of reference cross sections from the high

> resolution reference cross sections. New DOAS fit were then performed for the whole campaign data set. Compared to the DSCDs values described in the paper, the newly derived DSCDs of NO_2, HCHO, and CHOCHO are on average 33%, 32%, and 86% lower. Since the O_4 reference cross section has similar resolution as our instrument, no convolution was performed. The difference between the old and new O_4 DSCDs is less than 3%. Given the big changes of trance gases DSCDs can have direct effect on the trace gas vertical profile retrieval, we performed new vertical profile retrievals for NO_2, HCHO, and CHOCHO.

Using the new data set, we re-run all the analysis described in the paper. We found that the NO_2 mixing ratios derived by MAX-DOAS agree with the in-situ measurements. The new average CHOCHO/HCHO ratio of 0.062 is much lower than before (i.e. 0.135), but it is still higher than the values which are thought to be representing regions influenced by anthropogenic emissions. However, the measured NO_2 VCDs turned to be much lower than the NO_2 VCDs observed by OMI. The diurnal variations of the newly retrieved HCHO and CHOCHO concentrations are less prominent than in the old results.

VS described that the VOCs composition in Guangzhou (c.f. Chan et al. (2006)) is similar to that in Mexico City. However, during the PRIDE-PRD2006 campaign, our VOC measurements at the supersite in downtown Guangzhou and at the Back Garden site showed different results from those described by VS (Table 1). This indicates the production of HCHO and CHOCHO in our study can be different from that in Mexico City.

Referee #1: General comments

C1: Can the assumption of box shape profiles affect the degree of agreement in the vertical column densities derived from the geometric and RTM approaches? If assuming different shapes, the agreement is perturbed significantly?
A1: As we described in the text, the trace gas retrieval was first done using three parameters to define the trace gas vertical distribution, i.e. VCD, F, and H. The retrieved VCDs are in good agreement with box shape profile retrieval and the VCDs derived from the geometric method. For regions like PRD which are characterized by strong emissions and high photochemical activity, trace gases like NO_2, HCHO, and CHOCHO are concentrated in the layer close to the ground. The geometric method assumes that the last scattering event of photons registered by the MAX-DOAS happens above the trace gas layer, which is valid under PRD like conditions. On the other hand, any change of VCD will have the same effect on the RTM simulated DSCDs at all elevation angles. For a certain trace gas, we found that its retrieved VCD is not sensitive to the shape of its vertical profile. Therefore, we think that the agreement between geometric VCDs and RTM VCDs will not be

perturbed significantly as long as the assumed profile shape is appropriate.

C2: Do the differences in the NO_2 VCD derived from the two approaches depend systematically on the aerosol abundance? This information, defining the conditions where the simple geometric approach is valid, would be useful when the MAX-DOAS analysis methodology is chosen.
A2: Since the differences between NO_2 VCD$_{geo}$ and NO_2 VCD$_{rtm}$ are small, we are not able to determine a robust relationship between ΔVCD (= VCD$_{geo}$ - VCD$_{rtm}$) and other measured parameters (e.g. aerosol abundance). During the 9 clear sky days during the PRD2006 campaign, the aerosol optical depth (AOD) measured by MAX-DOAS ranged from 0.15 to 4.81 with average value of 1.56 ± 0.97 (Li et al., 2010). High AODs were usually observed in morning hours (6:00 – 09:00). During the same period, NO_2 concentrations were also highest and the height of both aerosol and NO_2 layers were low. Under thess conditions, the assumption that the last scattering event of photons happens above the NO_2 layer can be valid, and therefore the simple geometric method is applicable. When restrain the data to morning hours, the agreement between NO_2 VCD$_{geo}$ and NO_2 VCD$_{rtm}$ (B_0 = 1.04 ± 0.22, r^2 = 0.96, N = 25) is almost the same as that shown in Fig. S2 in the paper ($B_0 = 1.06 \pm 0.15$, $r^2 = 0.95$, $N = 109$).

C3: Can the nighttime chemistry of HCHO and CHOCHO result in unique behaviors of the CHOCHO/HCHO ratio at this location? Even with this nighttime source, can the CHOCHO/HCHO ratios during this field campaign be compared systematically with those in the past studies?
A3: The detailed analysis of the nighttime chemistry of HCHO and CHOCHO needs photochemical modeling taking simultaneously measured OH, NO, NO_2, O_3, CO, NMHCS, etc. into account, which is what we have been working on in the past weeks. The behaviors of R_{GF} in PRD is not unique. Actually, besides the papers by DiGangi et al. (2012) and by MacDonald et al. (2012) which were published on ACPD several days later than our paper, there are limited studies reporting the diurnal variations of the R_{GF}. While the R_{GF} reported by DiGangi et al. (2012) for a rural site is systematically lower than that we observed in PRD, values of R_{GF} obtained by MacDonald et al. (2012) in a tropical rain forest are higher with our observation results. Both studies illustrate the influence of VOCs compositions on the behaviors of the CHOCHO/HCHO ratio. DiGangi et al. (2012) identified a prominent increase of R_{GF} when the detected air plume includes elevated anthropogenic VOCs. R_{GF} observed by DiGangi et al. (2012) and MacDonald et al. (2012) show similar diurnal variation pattern as in our study. However, the effect of nighttime OH on the production of HCHO and CHOCHO was not reported in their papers. We think the nighttime chemistry initiated by OH can result in different diurnal variation of HCHO and CHOCHO in PRD than in other areas. However, more work is needed to investigate how the nighttime chemistry influence the R_{GF}.

C4: In my opinion the HCHO diurnal variation pattern with daytime decrease is unique. Can the authors find past studies suggesting similar diurnal patterns and increase discussion more on this point?
A4: After the new data evaluation, we found the HCHO diurnal variation shown by the new data was not as prominent as was shown by the old data. The HCHO concentrations during early morning hours were only slightly higher than in the afternoon. The cause of the temporal behavior of HCHO at BG site is going to be discussed in a separate paper, which is focusing on the model study of HCHO and CHOCHO during the PRD2006 campaign.

Referee #1: Technical and specific points

With respect to the technical comments 1 – 4, 6, 11 – 14, 20, 21, 24, and 28 the text has been changed in the revised version. For all other comments see below.

C5: Page 3989, line 9. "Box" air mass factor is a more correct term than simple air mass factor?
A5: In our opinion, the "box" air mass factor is more referring to the condition that the vertical extension of the atmosphere is divided into several layers / boxes, in which the trace gas concentration is assumed to be constant. This is usually the treatment of the atmosphere in many radiative transfer models, e.g. McArtim. The path enhancement in each box is called "box air mass factor" (Wagner et al., 2007). In Page 3989, Lines 6 – 9, we intend to provide the universal definition of the air mass factor considering the photon path in the whole atmosphere. Therefore, we used air mass factors instead of box air mass factors.

C7: Page 3989, line 28. The assumption of the constant number density results in mixing ratios at a high altitude (e.g., 3 km) higher than those at the ground level.
A7: Yes, this is the case if the height of the trace gas mixing layer is high (i.e. above 3 km). As illustrated in Fig. 4 in the paper, trace gases are concentrated in the layer lower than 2 km in most of the time, the change of the factor that convert number density to mixing ratio is around 12%, i.e. the mixing ratio at 2 km is 12% higher than at ground.

C8: Page 3991, line 11. The authors fix F = 1: is this applied only for the gases (i.e., NO_2, HCHO, and CHOCHO)? Is the previous detailed description of the profiles (i.e., page 3990, equations (2)-(4)) still necessary for describing aerosol profiles used in this study?
A8: The aerosol profiles are taken from the previous study on the aerosol measurement from the same instrument (Li et al., 2010). The aerosol profile was defined similar to Eqs. (2) and (3). As described in the paper, the fixing F = 1 was decided based on the finding that the trace gases are mostly concentrated in the layer near the ground (i.e. F>0.95 when F is not fixed). In this case, setting F as a free parameter in the retrieval only leads to the increased uncertainty of the retrieval

results. However, for aerosols, their retrieved profiles suggest that part of the AOD exits above the mixing layer and thus the box shape profile (i.e. fixing F = 1) is not advised.

C9: Page 3991, line 20 and Figure 2. How is the NO_2 information used in the further HCHO and CHOCHO analysis?
A9: The DSCD calculation of HCHO and CHOCHO by the RTM (McArtim) also needs the information of absorbers like NO_2 and O_3 which also absorbs light at the same wavelength range. While O_3 as minor influence on the DSCD simulation, the influence of NO_2 can be up to few percent (see Table 3 in the revised paper). Therefore, during the retrieval of HCHO and CHOCHO, the NO_2 profile derived from the MAX-DOAS NO_2 measurement is used as input of McArtim. We add sentences about the use of the NO_2 information in the HCHO and CHOCHO analysis in the revised paper.

C10: Page 3992, lines 7-8. The increase of AOD results in a decrease of modeled DSCDs in Table 3, however, the values of the sensitivities are always positive.
A10: The signs are added in Table 3 in the revised paper.

C15: Pages 3998-3999, comparison to CMAQ. More discussion should be made about the degrees of agreement between the observed and modeled NO_X and O_3 concentrations etc. at the same/different locations during the same period, to confirm the authors conclusion that the NO_X emission rates need to be reduced in the model.
A15: We agree with the referee that the robust conclusion that the NO_X emission rates need to be reduced in the model can only be made once taken more locations into consideration. We compared the measured and CMAQ simulated NO_2 concentrations during the same period at other two sites in PRD, i.e. TianHu (23.65°N, 113.62°E) and WanQingSha (23.71°N, 113.55°E), which were in the similar pollution conditions as the BG site in this study. The simulated NO_2 concentrations for these two sites are also higher than the observations. However, as discussed in the paper, the overestimation of NO_2 concentrations by CMAQ can be caused either by meteorological conditions or by emissions. In this study, we only would like to demonstrate that the MAX-DOAS NO_2 measurements can help us to identify the possible problems in the CMAQ simulation. The confirmation of the cause of these problems certainly needs more work on the model run and comparison with various measurements, which are beyond the scope of this study.

C16: Page 4000, lines 8-10. Is the primary emission of HCHO from local sources important, as well as nighttime production, to explain the high concentrations in the morning?
A16: The primary emission of HCHO can be one source of HCHO at BG site during nighttime, which can lead to the high HCHO concentrations in the morning. We modified Lines 8 – 10 in Page 4000 accordingly in the revised paper. However,

only using the observation data, we are not able to determine the contribution of the primary emission to the ambient HCHO during daytime. As described in A3, the sources of HCHO have been investigated by a 0-D photochemical model and will be discussed in details in the upcoming manuscript.

C17: Page 4000, line 16. It is not fair to define the NO_2 lifetime against its photolysis, because the photolysis gives NO that easily reproduces NO_2 via its reactions with O3 and peroxy radicals.
A17: The referee is right. The lifetime of NO_X is the relevant quantity. Under the conditions here it is mainly defined by the OH+NO_2 reaction. The lifetime of NO_X is about 30 min, still less than the values for HCHO and CHOCHO. We changed the text accordingly. We also included the aerosol layer height from Li et al. (2010) in Figure 6 of the revised version on request of Referee #2. Since the lifetime of the aerosol is much longer (days) it is consistent with the observation an even higher value of H for the aerosol retrieval.

C18: Page 4000, line 25. The authors should give references suggesting that HCHO is produced before CHOCHO. Do the authors mainly think about isoprene oxidation? How high were the isoprene concentrations?
A18: References have been added in the revised paper. We also considered the oxidation of aromatics and other NMHCs. However, at BG site, increase of isoprene concentrations to 1 –3 ppb in the afternoon was often observed, and the production of HCHO and CHOCHO in this time period is dominated by isoprene degradation (which will be discussed in details in the upcoming manuscript with regard to the modeling of HCHO and CHOCHO at BG site). A detailed analysis of the photochemistry is also given by Lu et al. (2012) and Lou et al. (2010).

C19: From last line of page 4001 to line 7 of page 4002. Are Giesta, Sao Paulo, and Mexico City raised as exceptions for the generally accepted tendency that the CHOCHO/HCHO ratio is high in the rural environment and low under urban conditions? The logic is not very clear here.
A19: Giesta, Sao Paulo, and Mexico City were considered as examples for the highly variable CHOCHO/HCHO ratio. The text is updated.

C22: Page 4003, at the end of section 4.2. Can the authors discuss potential impact of the nighttime production of CHOCHO and HCHO?
A22: As described before, the discussions on the nighttime production of HCHO and CHOCHO will be part of the upcoming paper focusing on the modeling of HCHO and CHOCHO.

C23: Page 4003, line 18. How high were the AOD values during the nine days under investigation?
A23: In the 9 clear sky days during the PRD2006 campaign, the aerosol optical depth (AOD) measured by MAX-DOAS ranged from 0.15 to 4.81 with average

value of 1.56 ± 0.97 (Li et al., 2010). Information on AOD values is added in the revised paper.

C25: Table 3. How does the O3 concentration affect the HCHO and CHOCHO retrievals?
A23: After checking Table 3 we found that the information on "NO_2 ($\leq$1 km)" and "O_3 ($\leq$1 km)" were misplaced for the rows HCHO and CHOCHO. Therefore, we carefully re-checked the table and the results of the sensitivity studies. Table 3 in the revised paper illustrates that the influence of O_3 on the HCHO and CHOCHO retrieval is small and can be neglect.

C26: Table 4. Are all of the listed mixing ratios observed in the midday periods?
A26: The listed mixing ratios do not refer to the data in the midday periods but are the campaign average values. We have made this point clear in the revised paper.

C27: Figure 9. If the regression lines are not forced to pass the origin, significant y intercepts could occur?
A27: When we perform a linear regression without forcing the line passing the origin, the the slope changes to (0.65 ± 0.06) with an intercept of (0.51 ± 0.53) ppb (Fig. A4).

Referee #2: General comments

C1: The model predicts higher NO_2 than observed and the authors interpret this as too large NO_X sources. They also report unusually high OH levels. Are these high OH levels prescribed / reproduced by the model? If not, could the model have a too long lifetime for NO_2 which would then lead to too large NO_2 values at the right emission strength??
A1: The noontime OH concentrations in the CMAQ model at ground level are between $1 \times 10^7 \mathrm{cm}^{-3}$ and $2 \times 10^7 \mathrm{cm}^{-3}$ which is similar to the measured OH concentrations of $1.4 \times 10^7 \mathrm{cm}^{-3}$ on average for the days considered here.

C2: The measurements nicely illustrate that CHOCHO is mixed to higher altitudes than HCHO. The authors explain this by the fact that CHOCHO is produced at a later stage of the VOC oxidation chain when the boundary layer has grown. However, I do not really see why this should lead to more CHOCHO at higher altitudes as we can assume that the boundary layer is relatively well mixed in the afternoon and similar vertical distributions can be expected for all species in the BL with no pronounced surface source. If the precursors of CHOCHO are in the free troposphere, then the HCHO produced from them should also be above the BL for which there seems to be indication on some but not all days. I would therefore argue that the observations are indicative of VOCs above the BL and that the assumption of a box profile for these species is not fully appropriate. Alternatively, NO_2 and HCHO must have continuous surface based sources that explain why they are not well mixed in the BL.

A2: The difference in the mixing heights of different trace gases has also been observed by Wagner et al. (2011) in summer time in Po Valley. They found the mixing heights of HCHO are higher than that of NO_2, which has been validated by aircraft measurements. Our study and Wagner et al. (2011) show that even in the summer when the radiation is strong and the vertical mixing is effective, the height of a well mixed layer for different trace gases can be different. The vertical distribution of HCHO and CHOCHO is determined by their production and destruction processes. Although the lifetime of HCHO and CHOCHO were comparable as we described in the paper, the production pathways of HCHO and CHOCHO can be different. First, compared to CHOCHO, HCHO has possibly primary sources. Therefore, we agree with the referee that a continuous surface source of HCHO can result in the detected HCHO layer much lower than the CHOCHO layer. However, at BG site, except the occasional combustion events happening during night, there was no evidence that the direct emission of HCHO was occurring during daytime. Second, our recent model studies suggest that the degradation of isoprene was the major pathway producing HCHO and CHOCHO in the afternoon at BG site; its contribution to the HCHO and CHOCHO production was around 50%. While the other half of HCHO production was caused by the oxidation of alkenes, degradation of aromatics accounted for the other half of CHOCHO production. With regard to the isoprene oxidation, we found from our model study that most HCHO was formed as the first generation product whereas CHOCHO was mostly produced in the third and forth generation of the isoprene oxidation. At BG site, the noontime OH concentration of $1.5 \times 10^7\,\mathrm{cm}^{-3}$ resulted in a lifetime of isoprene of around 10 min which is shorter than the typical time needed for an effective mixing in the boundary layer (i.e. $\approx$15 min c.f. Stull (1988)). So, when isoprene is being degraded along its way being mixed to higher altitudes, it is likely that the HCHO production happens at lower altitudes than the CHOCHO production. Moreover, due to the faster reaction rate with OH, the lifetimes of isoprene and alkenes are shorter than those of aromatics, which can result in different vertical distribution between different NMHCs. According to the CMAQ model simulation, aromatics were mixed to higher altitudes (up to 4 km) than isoprene and alkenes at BG site, especially around noon (Fig. A8). Since aromatics is the other major precursor of CHOCHO besides isoprene, production of CHOCHO at higher altitudes can be expected. The text describing the cause of the different H between HCHO and CHOCHO is updated in the revised paper.

C3: I'd suggest to add the aerosol mixing heights from Li et al., 2010 to Fig. 6. This would make it obvious that only CHOCHO follows the evolution of the aerosol mixing heights. This could indicate that the source of CHOCHO and aerosols is the same while NO_2 and HCHO are from other sources.
A3: The aerosol mixing heights are included in Fig. 6 in the revised paper, and more discussions with regarding to the different mixing heights between aerosol, NO_2, HCHO, and CHOCHO are added (c.f. response to Referee #1, A15).

C4: Why are figures 9 and 10 shown as log-log display? Was the linear fit performed in log-space or on the original data? What is the reason for forcing the regression lines through 0? These choices have a large impact on the results and need to be well justified or changed.
A4: The log-log display is just for better view of the inter-comparison results since the range of NO_2 concentrations is relatively large. The linear fit was preformed on the original data. When we compared the MAX-DOAS observed NO_2 concentrations with in-situ / OMI data, we were thinking about if the ratio of the two data sets is different from 1. Therefore, we chose the regression forcing through origin. Figs. A4 and A9 shows the regression results by without forcing the regression line through origin. The regression considers the errors in both coordinates. Significant intercept are identified in both regressions. Though the slopes changed a lot compared to the regression forcing through origin, the conclusion that the OMI NO_2 VCDs do not agree with the MAX-DOAS observations and the NO_2 concentrations measured by MAX-DOAS agree with the in-situ measurements is still valid if taking the intercept of the regression into account.

C5: I'm not at all convinced by the "good" agreement between ground-based and OMI NO_2 columns, in particular for the case including all data. OMI results are more or less constant for ground-based measurements covering more than one order of magnitude! The argument that OMI misses the NO_2 because of clouds is also not convincing first, the authors explain that over their site, it was cloud free so OMI should have seen the NO_2. Second, the TEMIS product has a cloud correction scheme that should compensate for such effects. I believe that this points needs more discussion and a linear display of the results would help.
A5: After we updated the data in the paper, we found the statement "the good agreement between ground-based and OMI NO_2 VCDs" is no longer valid. The OMI NO_2 columns were higher than the MAX-DOAS observations during the nine cloud-free days (i.e. dots in Fig. 9). In cloudy conditions (i.e. triangles in Fig. 9a), the NO_2 VCDs derived from OMI observations are lower than those from the MAX-DOAS measurements. In the paper, our argument of OMI misses the NO_2 because of clouds is made only for the cloudy conditions (i.e. cloud fraction > 0.5). The cloud fraction data used in this paper was indeed derived from OMI measurements.

C6: Some discussion at the beginning of the paper is concerned with details of the profile retrieval and how it was set-up. However, at a later point it is explained that in fact not the more complex 3 parameter model is used but rather a simple box layer model as already applied in previous studies. I do not see why a complicated method is introduced only to be abandoned and suggest to limit the description to the method actually employed.
A6: In this study, we would like to provide a MAX-DOAS profile retrieval method that can be used in more general conditions. Therefore, we described the profile definition and the retrieval method in details. Although in the end we only used a

profile shape defined by 2 instead of 3 parameters, the idea was came up by first running the 3-parameter model. Without the retrieval results from the 3-parameter model, we could not know that the trace gases were mostly concentrated in the layer near ground and thus fix F = 1 in order to reduce the unnecessary uncertainties of the profile retrieval.

C7: Why was a log scale used for Fig. 11? I think a linear scale would be more appropriate (and more clearly show the large variation of R_{GF} for the columns which is quite an interesting result.
A7: Fig. A10 in this document shows the diurnal variation of R_{GF} with Y-axis in linear scale. However, in our opinion the message of Fig. 11 is more clearly seen in log-scale since it provides ratio information.

Referee #2: Technical and specific comments

The text has been changed in the revised version following the technical comments. For all other comments see below.

C: P3986, line5: what is large photochemical turnover? Why do high HCHO concentrations indicate large turnover couldn't they just indicate high VOC levels?
A: The photochemical turnover describes how fast the trace gases in the atmosphere being oxidized by OH radicals. It depends on the OH concentration and the OH reactivity of trace gases like CO, NO_2, and VOCs. Since HCHO is mainly produced through the OH oxidation of various VOCs, higher HCHO concentration can be expected at higher OH and higher VOC levels. Therefore, we think it is better to relate the HCHO concentration to the photochemical turnover than to VOC levels only (cf. Lou et al., 2010).

C: P3991, line 20: Was NO_2 from the first retrieval in fact used in the HCHO and CHOCHO analysis or is NO_2 included as an interfering species?
A: The DSCD calculation of HCHO and CHOCHO by McArtim also needs the information of absorbers like NO_2 and O_3 which also absorb light in this wavelength range. While O_3 has minor influence on the DSCD simulation, the influence of NO_2 can be in the order of several percent (see Table 3 in the revised paper). Therefore, during the retrieval of HCHO and CHOCHO, the NO_2 profile derived from the MAX-DOAS NO_2 measurement was used as input of McArtim. In the revised version we add how the NO_2 information was used in the HCHO and CHOCHO analysis.

C: P3992, line 9: This section is confusing is this about SSA and AOD measured by MAXDOAS? If not, what is the relevance of the data here?
A: According to Table 3, SSA and AOD have influences on the trace gas DSCDs calculation and thus the profile retrieval. Therefore, the uncertainties of the measured SSA and AOD are needed to estimate the error of the trace gas profile re-

trieval.

C: P3996, line 25: neither in Celarier et al., nor in Chen et al., any comparisons between MAX-DOAS and in-situ are reported.
A: The citation of Celarier et al. is removed. Chen et al. compared the NO_2 concentrations derived from zenith-sky DOAS measurements with in-situ data. The measurement principle of the zenith-sky DOAS and MAX-DOAS are very similar. In the revised version we make a clear statement that Chen et al. refers to zenith-sky DOAS measurements.

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Table 1: Mean Mixing Ratios, m in ppb, of the 10 Most Abundant NMHCs in Guangzhou and Backgarden during the PRD2006 campaign, and those measured by Chan et al. (2006) in different areas in Guangdong province. Also listed in the table are the corresponding rate constants of NMHCs reacting with OH radicals at 298 K (unit: 10^{12} cm^{3}molecule^{-1}s^{-1}).

	Guangzhou	m	k_{OH}	Backgarden	m	k_{OH}	Guangdong[a]	m	k_{OH}
1	Propane	11.	1.10	Ethene	3.0	8.52	Toluene	13.5	5.63
2	Ethyne	9.7	0.78	Toluene	2.8	5.63	Ethyne	6.0	0.78
3	Toluene	7.8	5.63	Propane	2.3	1.10	Ethene	5.1	8.52
4	Ethene	5.4	8.52	Ethyne	1.7	0.78	Propane	3.7	1.10
5	n-Butane	4.7	2.36	Benzene	1.6	1.22	m-Xylene	3.6	19.0
6	Ethane	3.7	0.25	Ethane	1.5	0.25	Benzene	2.8	1.22
7	i-Butane	3.5	2.12	Propylene	1.2	26.3	n-Butane	2.6	2.36
8	Benzene	3.1	1.22	n-Butane	1.2	2.36	Ethane	2.3	0.25
9	i-Pentane	2.9	3.60	Isoprene	0.9	101.	i-Pentane	2.2	3.60
10	m,p-Xylene	1.9	19.0	n-Hexane	0.8	5.20	Ethylbenzene	2.0	7.00

[a] Chan et al. (2006)

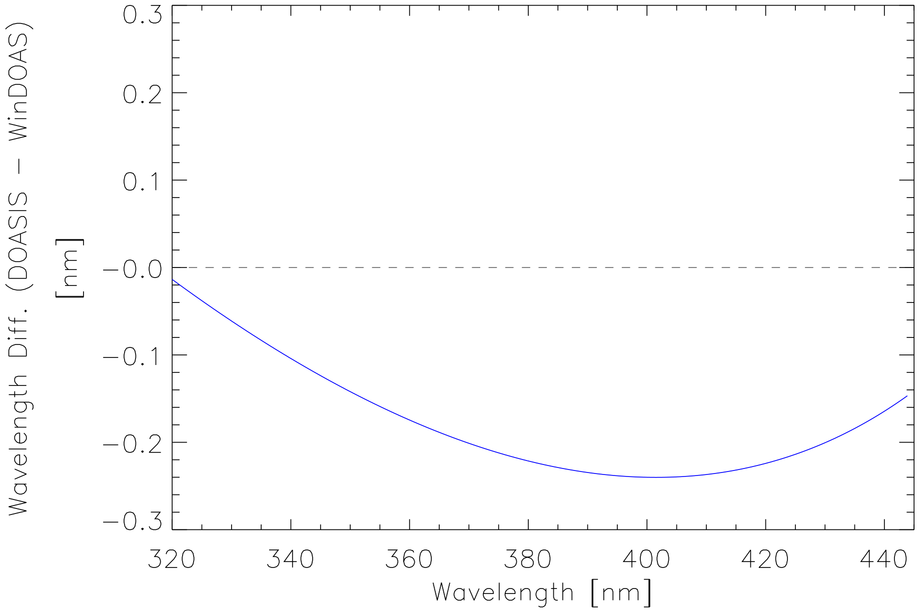

Figure A1: Difference of the wavelength between derived from DOASIS and WinDOAS for the detector of the MiniMaxDOAS instrument.

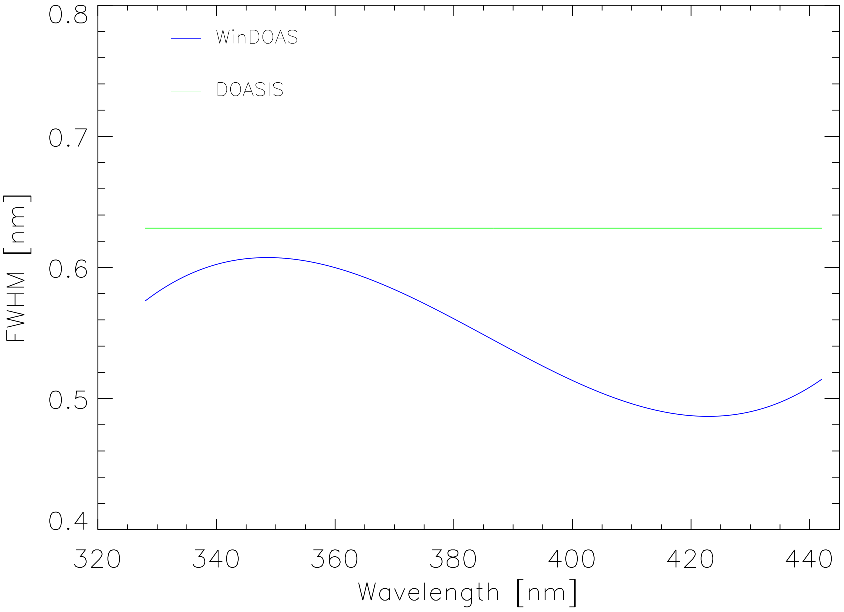

Figure A2: Spectral resolution used in DOASIS analysis and calculated from the wavelength calibration by WinDOAS.

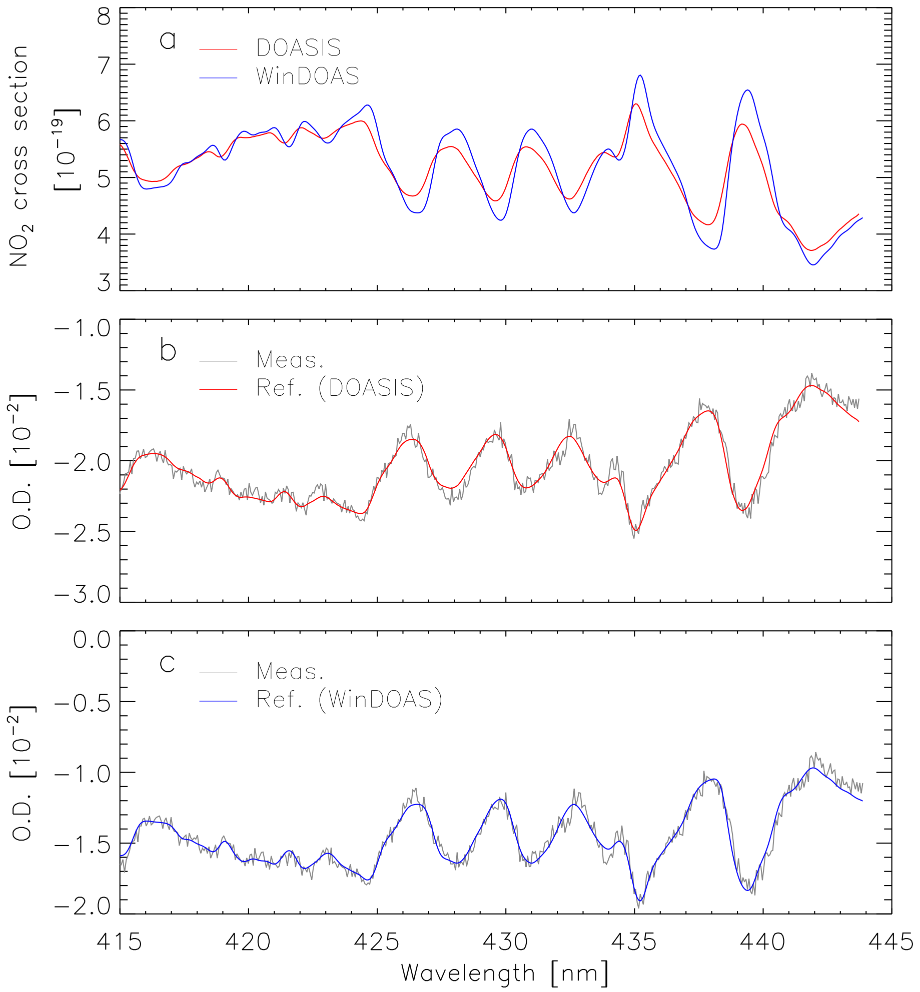

Figure A3: Comparison between the fit of the measured NO_2 cuvette spectrum in 416 – 442 nm using two different NO_2 cross sections. a. NO_2 reference cross sections created by DOASIS (red) and WinDOAS (blue), based on the high resolution reference cross section Voigt et al. (2002). b and c are the fit results. The grey lines represent the measured NO_2 spectrum, while the red and blue lines are the fitted NO_2 cross sections. It is clear that the NO_2 cross section generated from the wavelength dependent convolution kernel (WinDOAS) has higher resolution than the one from using Hg line at 334 nm as convolution kernel (DOASIS), and can better represent the measured NO_2 spectrum.

Figure A4: Intercomparison of NO_2 mixing ratios measured by MAX-DOAS and in-situ chemiluminescence technique during the PRIDE-PRD2006 campaign. Data displayed here are obtained in the 9 cloud-free days.

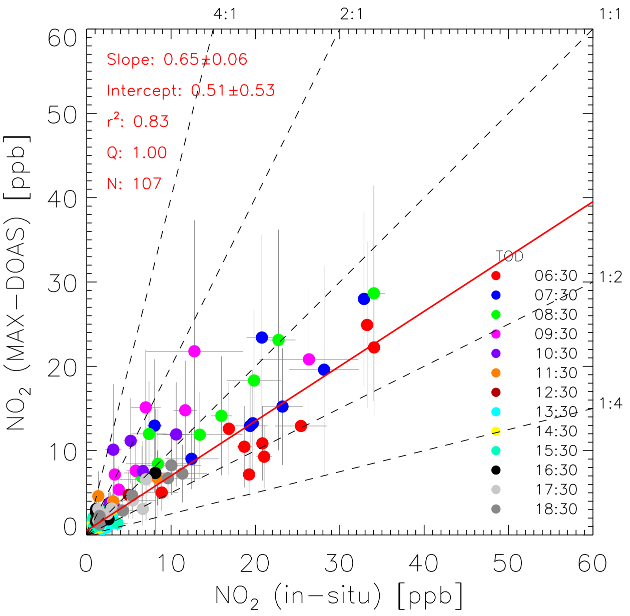

Figure A5: Results of the sensitivity study on the selection of wavelength interval for the DOAS fit of CHOCHO. The sensitivity study is based on the Mini-MAX-DOAS instrument we are currently operating at Jülich. This instrument covers the wavelength range from 320 nm to 458 nm, which is similar to the instrument R.V̇olkamer used during the PRD2006 campaign. The procedure of the sensitivity study is as following. 1. Choose one measured Fraunhofer spectrum (FRS) as the reference spectrum (i.e. I0). The chosen FRS was recorded on 2011-06-13 10:53 at Jülich. 2. Add absorptions from NO_2 (2 ppb), HCHO (1 ppb), CHOCHO (100 ppt), O_4 (2.7×10^{37} cm^{-3}), O_3 (10 ppb), H_2O (7×10^{17} cm^{-3} corresponding to 70% RH at 27 degree Celsius), and BrO (1 ppt) on a 10 km light path and a Ring with 0.001 O.D. to I0, generating absorption spectrum Ia. 3. Fit Ia to I0 using the DOAS fit in different wavelength intervals. For CHOCHO retrieval, the fitting species are NO_2, CHOCHO, H_2O, O_3, O_4, ring, 3rd order polynomial, and 2nd order offset (i.e. the same as we applied for the PRD2006 data). 4. Compare the fit result of the target species with the predefined concentration / absorption in different wavelength range of the DOAS fit. For NO_2, CHOCHO, and H_2O, the corresponding absorption should be 5×10^{16}, 2.5×10^{15}, and 7×10^{23}, respectively. The pink and red “X” in the figure refers to the wavelength interval used in our study (i.e. 416 – 441 nm) and in Rainer Volkamer’s work (i.e. 420 – 460 nm), respectively. Note that the prominent CHOCHO absorption locates at around 455 nm. As shown in the figure, in the wavelength interval of 416 – 441 nm in which the prominent CHOCHO absorption is not included, the retrieved CHOCHO concentration is almost as the expected value. Although for some wavelength intervals, the retrieved CHOCHO concentration is either higher or lower than the expected value, the difference is within 20%. For NO_2, the retrieved absorption is always in line with the expectation. For H_2O, the 416 – 441 nm fitting range is just at the edge of making significant overestimation.

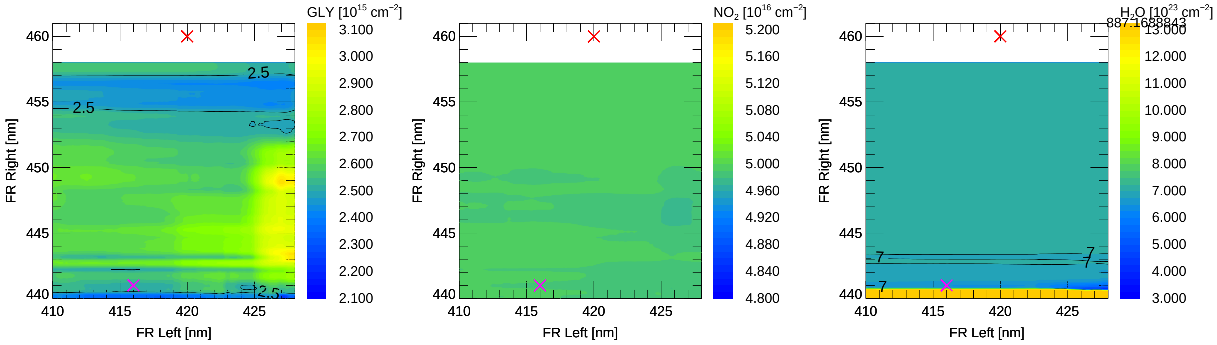

Figure A6: Relationship between CHOCHO DSCDs and HCHO DSCDs obtained at 3° elevation angle during the 9 cloud free days during the PRIDE-PRD2006 campaign. The solid line refers to the linear regression by forcing the linear regression line through origin. The dashed line refers to the least normal linear regression using bootstrap estimates for the errors of the parameters.

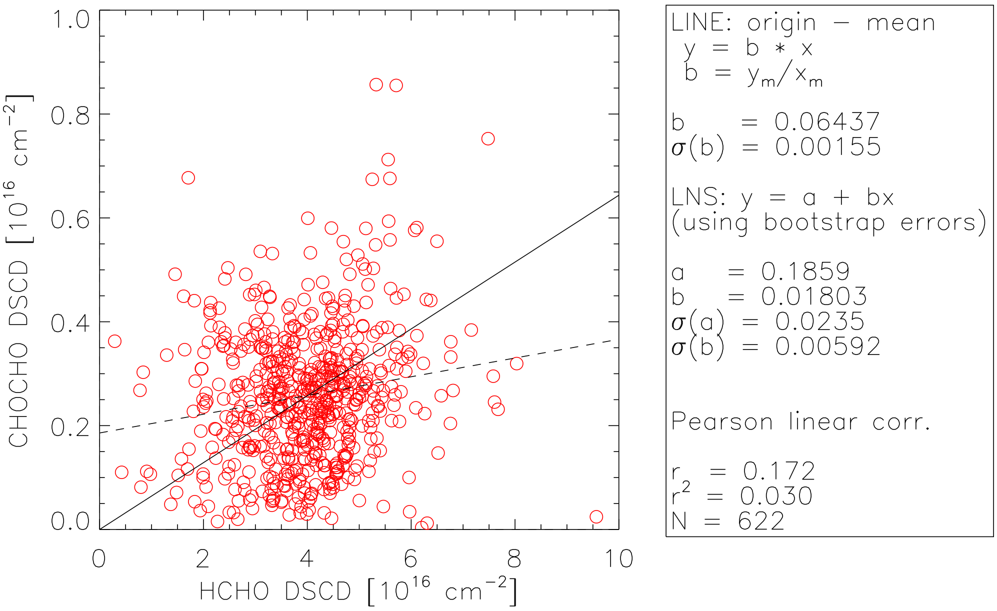

Figure A7: Time series of OH concentrations measured by LIF (black dots), and simulated by the CMAQ model in the 9 cloud-free days during the PRIDE-PRD2006 campaign. The “ground” (red “+”), “1 km” (blue triangle), and “3 km” (orange triangle) represent the average OH concentrations calculated by the CMAQ model in the layer of 0 – 18 m, 0 – 1 km, and 0 – 3 km, respectively.

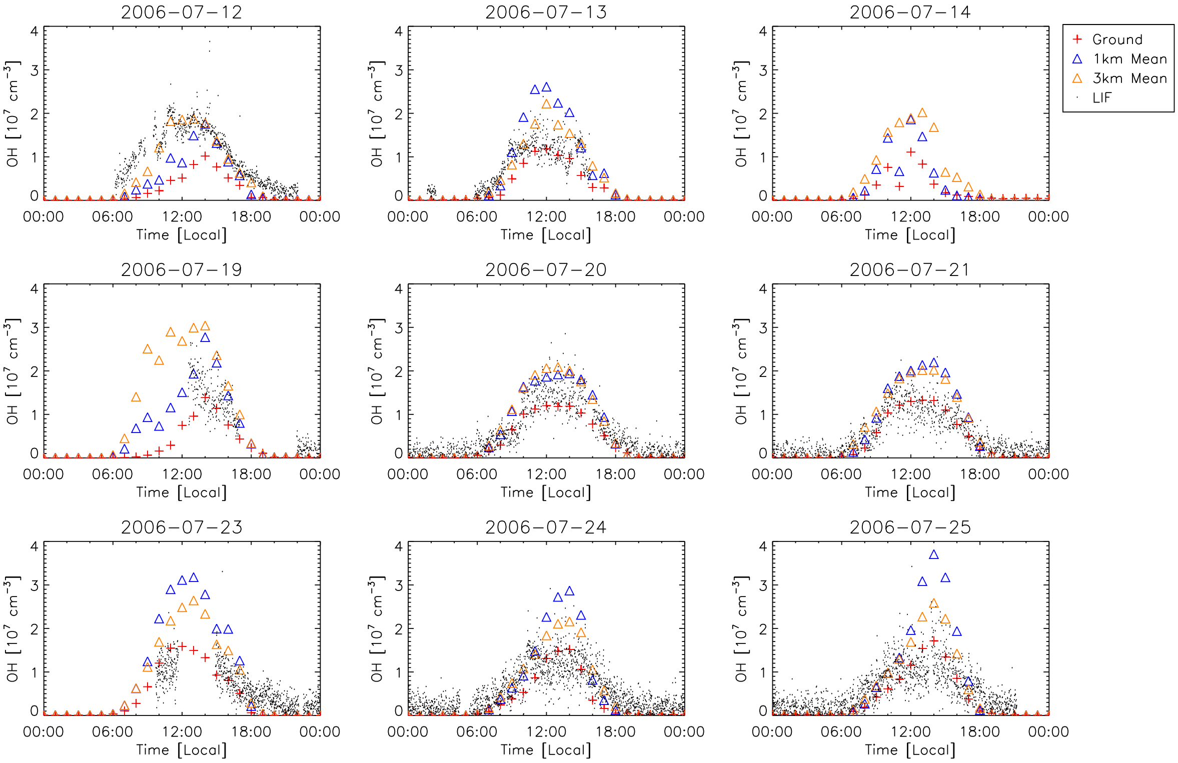

Figure A8: Vertical profiles of aromatics (black), alkenes (red), and isoprene (green) generated by CMAQ model for 20-JUL-2006 at BG site.

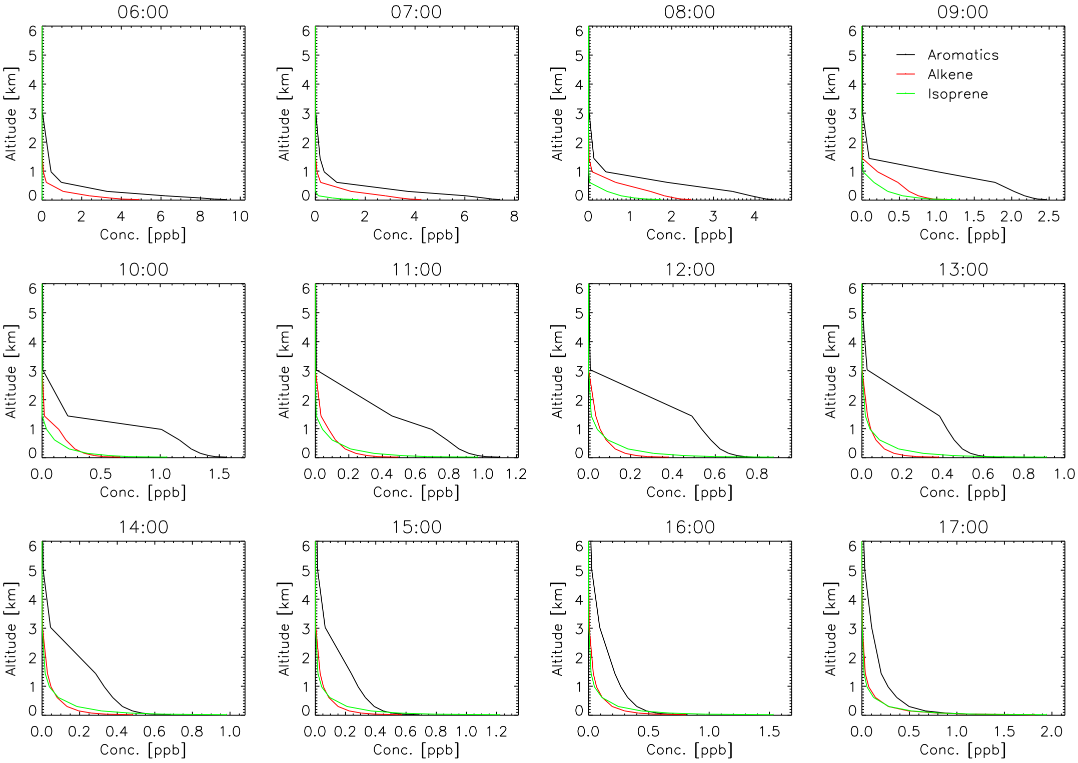

Figure A9: Intercomparison of tropospheric NO_2 VCDs derived from MAX-DOAS and OMI observations during the PRIDE-PRD2006 campaign. The X-axis in (a) and (b) corresponds to the NO_2 VCDs derived from the geometric approach and the NO_2 vertical distribution retrieval, respectively. The dots represent data obtained in the 9 cloud-free days. The regression and correlation results for all data (i.e. dots and triangles) and dots only are shown in grey and red texts, respectively.

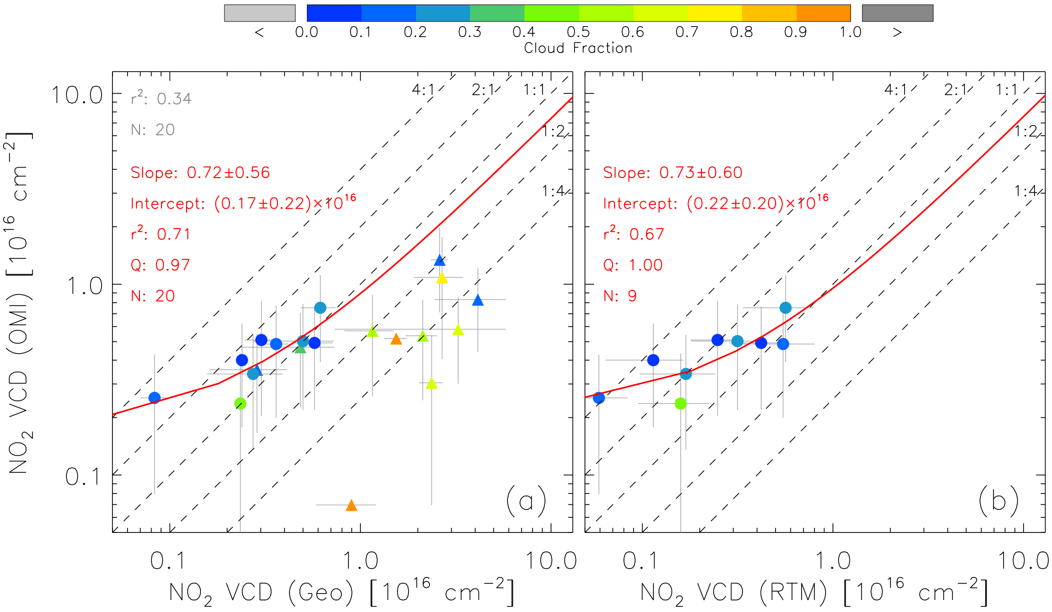

Figure A10: Diurnal variation of CHOCHO/HCHO ratio (R_{GF}) in the 9 cloud-free days during the PRIDE-PRD2006 campaign. The dots are values calculated from individually measured m_0 (Pannel a) and VCD$_{rtm}$ (Pannel b). Solid lines refer to the average values of the individual points.