Anonymous Referee #1:

We thank the reviewer for his useful and constructive remarks. As described below, we have modified the manuscript as suggested and clarified the text where necessary. We hope that the revised manuscript has improved in respect to the original paper. Please find a rebuttal against each point below.

1)

The paper introduces a new method to retrieve the trop. NO2 column based on the ZS DOAS measurements. The performance of the method is validated by comparisons between the trop. NO2 VCDs obtained from the other techniques (e,g., MAX-DOAS, SAOZ, DS-DOAS) and those from this new method. The paper is well structured and carries informative contents to many scientists in the similar fields. However, some important revisions need to be conducted in the paper before being published in AMTD. Comments: 1.Please address the merits of utilizing ZS-DOAS for measurements of NO2 VCD, compared to the other measurement and retrieval methods such as DSDOAS, PANDORA, MAX-DOAS in INTRODUCTION.

The merits and added-value of tropospheric NO_2 retrieval from ZS-DOAS were already briefly discussed in the introduction (P939 L7) and in the conclusion (P965 L28). Based on your remark, this has been further extended to clarify the added-value of the ZS-DOAS approach in relation to the MAX-DOAS technique. For more details, please see also our answer to remark 2.

In the revised manuscript, this remark is addressed in section 1 (Introduction) as follows (P3 L27):

…The sensitivity of MAX-DOAS observations to the lower troposphere is larger when compared to ZS-DOAS observations and therefore it is generally considered as a more suitable technique for tropospheric NO_2 retrieval. However, the major merit of the ZS-DOAS approach in comparison to MAX-DOAS relates to the fact that a large number of historical stations, e.g. within NDACC (Network for the Detection of Atmospheric Composition Change), are equipped with instruments that only perform zenith observations. For these stations, the proposed algorithm offers possibilities for tropospheric trace gas retrieval, in addition to the more common stratospheric monitoring. Furthermore, applied to historical decadal time series of observations (as available at some stations of the NDACC), the proposed algorithm would enable to document the long-term variability of tropospheric NO_2 in addition to stratospheric NO_2. On the other hand, the independent tropospheric NO_2 estimates, retrieved by the presented ZS-DOAS algorithm, provide a way to validate MAX-DOAS retrievals at sites equipped with MAX-DOAS instruments….

2)

Given that MAX-DOAS and ZS-DOAS are both ground based techniques and they eventually aims to provide the true quantities (trop. NO2 VCD in this present study), I think the agreements are poor between the data obtained from MAX-DOAS and ZSDOAS in Fig. 7 (b). If the comparisons were made between ZS-DOAS data and the satellite data, the agreements such as R=0.9 and slope=1.0 (slope is very good though) are good enough. I am aware of that MAX-DOAS, which is known to be one of the most sensitive ground based instruments to trop. NO2, also has errors. However, the agreements shown in Fig. 7 (b) are thought to be poor so that I doubt the necessity of the ZS-DOAS for retrieval of trop. NO2 VCDs. Authors need to provide the quantitative reasons that explains the agreements shown in Fig. 7.

We wouldn't immediately qualify a correlation of 0.91 as poor, but we understand your point. Indeed the sensitivity of the MAX-DOAS approach to the lower troposphere is larger when compared to the ZS-DOAS and therefore it is generally considered as a more suitable technique for tropospheric NO_2 retrieval. The major merit of the ZS-DOAS approach in comparison to MAX-DOAS (which has become a mature technique for tropospheric trace gas retrieval), relates to the fact that a large number of historical stations (e.g. within NDACC) are equipped with instruments that only perform zenith observations. For these stations, the proposed algorithm offers possibilities for tropospheric trace gas retrieval, in addition to the more common stratospheric monitoring. Furthermore, applied to historical decadal time series of observations (as available at some stations of the NDACC), the proposed algorithm would enable to document the long-term variability of tropospheric NO_2 in addition to stratospheric NO_2, which is something that we will further investigate in future studies. At sites equipped with MAXDOAS instruments, independent tropospheric NO_2 estimates can be obtained by application of our approach (hence providing a way to compare with and validate MAXDOAS retrievals).

The tropospheric NO_2 retrieval algorithms applied to ZS-DOAS and MAX-DOAS observations are different in concept, so their error budget is different and they also feature different sensitivities to the vertical distribution of NO_2. In our study the overall uncertainty on retrieved tropospheric vertical column densities (TVCDS) has been estimated to 28% on average for TVCDS > $5x10^{15}$ molec/cm^2 and of the order of $1x10^{15}$ molec/cm^2 for smaller TVCDS. On the other hand, the uncertainty on MAXDOAS NO_2 retrievals has been estimated in a recent study by Hendrick et al. (2014) to be comprised between 12 and 30%, a significant part of this error being systematic in nature. Therefore the scatter in the correlation plots of Fig. 7 can certainly be explained to a large extent by combined uncertainties on the different retrieval algorithms.

In Piters et al. (2012), a first comparison of TVCDs retrieved from MAX-DOAS, ZS-DOAS and DS-DOAS was done by the Laboratory for Atmospheric Research, Washington State University (WSU) reporting that the three types of measurements agree on average within 30%. Vlemmix et al. (2011) compared partial tropospheric NO_2 columns from MAX-DOAS with columns derived from a NO_2 lidar finding a correlation of 0.78.

Finally differences between ZS-DOAS and MAXDOAS tropospheric NO_2 columns can also be explained by the fact that different air masses are sampled in both cases due to the different viewing geometries of the multi-axis and zenith-sky approach. This can lead to increased uncertainties especially if the horizontal distribution of NO_2 is inhomogeneous and in the presence of scattered clouds, as to be expected in a site like Cabauw.

We have modified different paragraphs of Section 4.4 (discussion of the correlative comparison) in order to take into account your remarks (P19 L8):

…To reduce the effect of temporal variability in the tropospheric signals in combination with different measurement sampling, and in order to intercompare the different datasets in a meaningful way, the retrievals are averaged in 30 min bins. An overall good agreement can be observed between ZS-DOAS, SAOZ, MAX-DOAS and DS-DOAS during the CINDI campaign, demonstrating the robustness and reliability of the presented approach.

Fig. 7 shows the scatterplot and linear regression analysis of the binned and averaged NO_2 TVCDs, retrieved for the whole time series from (a) ZS-DOAS versus SAOZ, and (b) ZS-DOAS versus MAX-DOAS, respectively. For both comparisons a correlation coefficient higher than 0.9 can be observed. The linear regression analysis shows slopes within 18% of unity and intercepts close to zero. In case of small NO_2 TVCD retrievals, we see a positive bias for the SAOZ with respect to ZS-DOAS retrievals, while the bias gets negative at higher TVCD values. The tropospheric NO_2 retrieval algorithms applied

are different in concept, so their error budget is different and they also feature different sensitivities to the vertical distribution of NO_2. In this study the overall uncertainty on retrieved tropospheric vertical column densities (TVCDS) has been estimated to 28% on average for TVCDS > $5x10^{15}$ molec/cm^2 and of the order of $1x10^{15}$ molec/cm^2 for smaller TVCDS. On the other hand, the uncertainty on MAX-DOAS NO_2 retrievals has been estimated in a recent study by Hendrick et al. (2014) to be comprised between 12 and 30%, a significant part of this error being systematic in nature. Therefore the scatter can be explained to a large extent by combined uncertainties on the different retrieval algorithms. According to Roscoe et al. (2010), a part of the scatter can also be attributed to the combination of the temporal variability in the tropospheric signals and different measurement sampling, as averaging the retrievals in 30 min bins reduces, but does not eliminate this effect.

In Fig. 8 the NO_2 TVCD daily mean time series, retrieved from (a) ZS-DOAS and SAOZ, and (b) ZS-DOAS and MAX-DOAS, respectively, are compared. A very good consistency can be observed between the ZS-DOAS and SAOZ NO_2 TVCD retrievals, for both low and high TVCD values. The MAX-DOAS retrievals show similar day-to-day variations with respect to the ZS-DOAS and SAOZ retrievals. However, a positive bias of about 18% on average can be observed for MAX-DOAS retrievals.

The same feature can be seen in Fig. 9, showing the retrieved NO_2 TVCD diurnal cycle of two subsequent days in the dataset, i.e. July 3, 2009 (day 184; see Fig. 9.a) and July 4, 2009 (day 185; see Fig. 9.b). For most retrievals, MAX-DOAS data shows a positive offset while DS-DOAS and SAOZ retrievals are very close to each other. Different air masses were sampled in both cases due to the different viewing geometries of the multi-axis and zenith-sky approach. This can lead to increased uncertainties especially if the horizontal distribution of NO_2 is inhomogeneous and in the presence of scattered clouds, as to be expected in a site like Cabauw. It should also be noted that MAX-DOAS has a higher sensitivity to NO_2 present close to the ground than the other techniques…

3)

The similar in-depth explanations need to be given to Fig 7 (a), as well.

First of all, the ZS-SAOZ and MAX-DOAS instrument have different characteristics and performances, thus leading to slight differences in sensitivity and observations. For the instrumental characteristics of the SAOZ instrument we can refer to Pommereau and Goutail (1998). Also the ZS-DOAS retrieval algorithms applied by CNRS-LATMOS and BIRA-IASB differ in the different steps (i.e. spectral fit analysis, determination of the RSCD and SVCD, and AMF calculations), having an impact on the retrievals and error budget. Unfortunately the CNRS-LATMOS retrieval algorithm is not discussed thoroughly in Dieudonné et al. (2013) or any other formal publication.

The reader should also be aware that differences in the comparison can be explained by the temporal variability in the tropospheric signals at the site in combination with different measurement sampling. The frequency of ZS observations for the SAOZ instrument (each two minutes) is about 10 times higher than for the MAX-DOAS instrument (a ZS observation each 20 minutes). Averaging the retrievals in 30 min bins reduces but does not eliminate this effect, with the result that a significant part of the scatter can probably be explained by the temporal variability and different measurement sampling, also confirmed in Roscoe et al. (2010).

References

Dieudonné, E., Ravetta, F., Pelon, J., Goutail, F., Pommereau, J. P.: Linking NO_2 surface concentration and integrated content in the urban developed atmospheric boundary layer, Geophys. Res. Lett., 40, 1247–1251, doi:10.1002/grl.50242, 2013.

Goutail, F., Pommereau, J.-P., and Sarkissian, A.: Total nitrogen dioxide at the Arctic Polar Circle since 1990, Geophys. Res. Lett., 21, 1371–740, 1994.

Hendrick, F., Müller, J.-F., Clémer, K., Wang, P., De Mazière, M., Fayt, C., Gielen, C., Hermans, C., Ma, J. Z., Pinardi, G., Stavrakou, T., Vlemmix, T., and Van Roozendael, M.: Four years of ground-based MAX-DOAS observations of HONO and NO_2 in the Beijing area, Atmos. Chem. Phys., 14, 765–781, doi:10.5194/acp-14-765-2014, 2014.

Piters, A. J. M., Boersma, K. F., Kroon, M., Hains, J. C., Van Roozendael, M., Wittrock, F., Abuhassan, N., Adams, C., Akrami, M., Allaart, M. A. F., Apituley, A., Beirle, S., Bergwerff, J. B., Berkhout, A. J. C., Brunner, D., Cede, A., Chong, J., Clemer, K., Fayt, C., Frieß, U., Gast, L. F. L., Gil-Ojeda, M., Goutail, F., Graves, R., Griesfeller, A., Großmann, K., Hemerijckx, G., Hendrick, F., Henzing, B., Herman, J., Hermans, C., Hoexum, M., van der Hoff, G. R., Irie, H., Johnston, P. V., Kanaya, Y., Kim, Y. J., Klein Baltink, H., Kreher, K., de Leeuw, G., Leigh, R., Merlaud, A., Moerman, M. M., Monks, P. S., Mount, G. H., Navarro-Comas, M., Oetjen, H., Pazmino, A., Perez-Camacho, M., Peters, E., du Piesanie, A., Pinardi, G., Puentedura, O., Richter, A., Roscoe, H. K., Schönhardt, A., Schwarzenbach, B., Shaiganfar, R., Sluis, W., Spinei, E., Stolk, A. P., Strong, K., Swart, D. P. J., Takashima, H., Vlemmix, T., Vrekoussis, M., Wagner, T., Whyte, C., Wilson, K. M., Yela, M., Yilmaz, S., Zieger, P., and Zhou, Y.: The Cabauw Intercomparison campaign for Nitrogen Dioxide measuring Instruments (CINDI): design, execution, and early results, Atmos. Meas. Tech., 5, 457–485, doi:10.5194/amt-5-457-2012, 2012.

Roscoe, H. K., Van Roozendael, M., Fayt, C., du Piesanie, A., Abuhassan, N., Adams, C., Akrami, M., Cede, A., Chong, J., Clémer, K., Frieß, U., Gil Ojeda, M., Goutail, F., Graves, R., Griesfeller, A., Grossmann, K., Hemerijckx, G., Hendrick, F., Herman, J., Hermans, C., Irie, H., Johnston, P. V., Kanaya, Y., Kreher, K., Leigh, R., Merlaud, A., Mount, G. H., Navarro, M., Oetjen, H., Pazmino, A., Perez-Camacho, M., Peters, E., Pinardi, G., Puentedura, O., Richter, A., Schönhardt, A., Shaiganfar, R., Spinei, E., Strong, K., Takashima, H., Vlemmix, T., Vrekoussis, M., Wagner, T., Wittrock, F., Yela, M., Yilmaz, S., Boersma, F., Hains, J., Kroon, M., Piters, A., and Kim, Y. J.: Intercomparison of slant column measurements of NO_2 and O_4 by MAX-DOAS and zenith-sky UV and visible spectrometers, Atmos. Meas. Tech., 3, 1629–1646, doi:10.5194/amt-3-1629-2010, 2010.

Vlemmix, T., Piters, A. J. M., Berkhout, A. J. C., Gast, L. F. L., Wang, P., and Levelt, P. F.: Ability of the MAX-DOAS method to derive profile information for NO_2: can the boundary layer and free troposphere be separated, Atmos. Meas. Tech., 4, 2659–2684, doi:10.5194/amt-4-2659-2011, 2011.