Bremen, 31.01.2017

Dear Hal Maring,

you kindly accepted the editorship of our manuscript "Investigating differences in DOAS retrieval codes using MAD-CAT campaign data" and we would like to take the opportunity to thank you for the consideration of your work.

We individually answered point-by-point to all comments and questions of Referee #1 and Referee #2. We revised the original manuscript according to their suggestions and provided also additional information the referees asked for.

In addition to changes motivated by the reviewers, during the interactive discussion phase two participating institutes (INTA and NIWA) found a fault in their retrieval code - which is also a benefit of the present study - and repeated their data analysis. The new results are included in addition to the original ones in the revised manuscript as INTA2 and NIWA2 and a lot of differences, which could not be attributed to any of the performed sensitivity test before, disappeared. We feel that this is actually a highlight demonstrating the improvement achieved in the context of this study, and therefore included it in the revised manuscript.

Below, you find again the answers to the referees that we also uploaded to the AMT web page. We also provide here a version of the revised manuscript in which changes in comparison to the initial version are marked color-coded.

We hope that with the submission of the author's comments and the revision of the manuscript, our article will be accepted for publication in AMT.

Yours sincerely,

Enno Peters

List of Attachments

- Author comments to Referee #1
- Author comments to Referee #2
- Revised manuscript
- Revised manuscript with color-coded changes

Point-by-point answers to Anonymous Reviewer #1

Note: Reviewers comments are printed in black, author's replies in blue (and italic).

General Evaluation

Peters et al. present a comparison study on NO2 slant column retrievals from a range of different DOAS

retrieval codes on the same set of MAX-DOAS observations acquired during the 2013 MAD-CAT campaign. Results of NO2 columns and RMS values from the retrieval codes, which are run with a basic set of harmonized settings for molecular absorption cross-sections and closure polynomials, are compared and a range of possible sources for their differences is investigated. Based on this study, a short list of recommendations is given as general guidance for DOAS retrievals to obtain high confidence/low RMS retrievals.

The paper is solidly written, and there is little to criticize in methodology and overall quality of presentation. My main criticism is that, at 27 journal pages, the manuscript is overly long for a study that concludes with five basic recommendations. The paper provides excellent insight into the workings of DOAS retrievals, and as such is valuable for both data providers and data users, but this reviewer strongly suggests that the discussion be tightened and the main part of the message conveyed more concisely.

We would like to thank the reviewer for these general encouraging comments and evaluation. We also fully agree with the main criticism concerning the length of the study and tried to shorten it following the suggestions provided by the reviewer (see below).

The meat of the paper is straight forward and relatively simple:

- 1. A set of MAX-DOAS observation from MAD-CAT was selected for a retrieval algorithm comparison.
- 2. A common set of basic spectral fitting settings was prescribed with which to run the retrieval codes.
- 3. Differences in NO2 slant columns and RMS were found, relative to a reference retrieval.
- The reference retrieval code was run with modified settings for five essential code elements

 radiance reference spectrum, slit function, offset correction, IO correction, matrix inversion

 to investigate their effect on the retrievals and to possibly explain the differences in the results.
- 5. The modified retrieval runs lead to the final recommendations, while the attempt to attribute differences between the codes to the investigated five sources is only moderately successful.

Please note, INTA and NIWA found a fault in their retrieval code (which is a benefit of the present study) and repeated their data analysis, after the paper was published in AMT discussions. The new results are included in the revised manuscript as INTA2 and NIWA2 and a lot of differences, which could not be attributed to any of the performed tests before, disappeared. With this, almost all observed differences between groups could now be attributed to the performed tests (or attributed to faults in retrieval codes which are now corrected).

The majority of the "take home messages" comes from Bullet 4 above, but the attribution of those effects in the actual differences observed between the results from the various retrieval codes remains qualitative at best. With this in mind, any figures and discussions relating primarily to relationships between the results from different codes - in particular figures 4 and 6 and their discussion - are non-essential and should be marked for removal.

The attribution is much more successful in the revised manuscript after faults in retrieval codes have been corrected (see above), which is good for the "detection rate" but also good for participating groups. We agree that the paper needs to be shortened, but in our opinion the statistics reflected in figure 4 (and 6) are essential as they document quantitatively the agreement between retrieval codes that can be expected – without them the manuscript would be purely qualitative. Therefore, we decided to skip figure 6 (with corresponding text) to tighten the manuscript, but to leave figure 4 demonstrating statistics and the quantitative agreement between groups. The basic results of figure 6 as well as results of different fit settings (which were not included as figures in the manuscript at all) are then summarized in Table 3 (which needs at least one figure to be understandable for the reader).

Below are some more specific comments. Very few of these are copy-editorial, since the level of presentation of this paper is very high.

Recommendation

The manuscript is acceptable for publication, but should undergo some tightening and add a few clarifications. Since there are no basic problems with methodology or presentation, a second round of review is not necessary.

Specific Comments

Retrieval Uncertainties

While the paper compares NO2 slant columns and retrieval RMS, no NO2 slant column uncertainties are

shown. Purely spectral minimization-based uncertainties are a combination of RMS and fitting covariances, and thus provide important information on the quality of the retrieved slant columns beyond the RMS.

This is in general true. However, slant column errors are calculated from RMS, SCs, and covariance of the (pseudo-inverted) DOAS matrix. For this exercise, the DOAS matrix is (ideally) the same for all groups, as fit settings were prescribed and the same cross sections were used distributed to all groups (see above). Thus, an investigation of the fit errors would provide very little new insight beyond the comparison performed for SCs and RMS.

Nevertheless, an important aspect is how large slant column disagreements between groups are in comparison to slant column errors. This is mentioned in Sect 3.1 (stating in summary that NO_2 slant column differences between groups were found to be up to 2-3 times larger than typical slant column errors). We agree that this is a remarkable finding, and put it also in the conclusions of the revised manuscript.

Reference Cross-Section Wavelength Scale

Three (admittedly very basic) questions regarding wavelength registration:

1. Does the IUPB MAX-DOAS instrument measure in vacuum or air?

It measures in air.

2. Which wavelength registration (vacuum or air) was used for the retrievals? *Wavelength in air.*

3. Was it assured that all molecular and solar reference spectra were on the same type of wavelength registration as the MAX-DOAS spectra?

All cross sections were converted to wavelength in air (unless they were already given in wavelength in air) before they were distributed to participating groups. It was prescribed to use the provided cross sections as summarized in Tab. 1. (However, even a potential error in the wavelength-conversion would affect all groups in the same way and should therefore have no influence on the objective of this study).

Slit Function

The measured slit function as shown in Figure 8 is slightly asymmetric. Yet, no attempts are reported of

having fit an asymmetric Gaussian to the measurement for use in the retrievals. At least part of the comparison exercise utilized pre-convolved molecular absorption cross-sections, so this should have

been an easy case to include. It is not very surprising that results from original and re-centered original slit function are virtually identical: the asymmetry should mainly manifest as a spectral shift, which is taken care of by the shift parameter during the retrieval process.

Regarding the differences introduced by removing the offset of 0.001: was the resulting slit function renormalized to the same area as the one with the offset?

Yes, the slit function was of course re-normalized after an offset was subtracted. However, there seems to be a small misunderstanding as the value of 0.001 is not the subtracted offset (first column of Table 5) but the cut-off value (tests summarized in third column of Table 5) for the discrete convolution.

The reviewer is right, different centered slit functions should result in a shift of cross sections. However, in the DOAS test fits performed in this section, no shift between cross sections and optical depth was allowed (but the shift between I and I0 will partly compensate for it). We included this statement and generally rephrased the whole section in order to increase readability and clarity.

Asymmetric slit function test: It is correct that some retrieval codes offer the possibility to fit more sophisticated line shape parameters taking into account potential asymmetry (as seen here) much better. The detailed use of the slit function was not included in the prescribed fit settings as being implemented differently in different retrieval codes. The tests performed here demonstrate in summary two extreme scenarios which characterize the maximum difference resulting from the slit function treatment, namely (1) using the (asymmetric) slit function as it is, or (2) fitting basic line parameters. The use of an asymmetric fitted slit function would clearly lead to a result in between these scenarios, but would not help a lot for the attribution of differences between groups to their sources as the exact implementations could not be reproduced here. We included this explicitly in the revised manuscript.

Section 4 "Understanding differences between retrieval codes"

Ultimately, this is the most important section of the manuscript since it systematically investigates the effect of different fit settings on the retrieved slant columns and the resulting RMS. It is also here that the five recommendations in the Summary are derived. In principle, this exercise is independent of the MAD-CAT comparison. While the differences in results from the various retrieval codes are a good motivation to perform these tests, they are valuable in their own right, and more emphasis should be placed on this. By referring to this part of the study as "differences between retrieval codes", this reviewer believes that the importance of these tests is somewhat muddled and degraded. The reader would benefit from a clear statement of the type "differences between the harmonized MAD-CAT retrieval results prompted the team to systematically investigate effects of the non-harmonized aspects of the retrievals, with the aim to derive a key set of Best Practices recommendations". Since quantitative attribution of "what part of the differences originates from which non-harmonized retrieval setting" turns out to be unfeasible/unsuccessful, more emphasis should be placed on the derived recommendations for DOAS retrievals.

We thank the reviewer for this good suggestion and changed section 4, now called "Sensitivity studies of non-harmonized retrieval aspects" accordingly. Similar changes have been made in the conclusions, the introduction, and the abstract as well. However, we think the MAD-CAT intercomparison results are more than a good motivation leading to these tests because (as mentioned above) after finding and eliminating additional faults in retrieval codes (unfortunately after publication in AMT discussions), almost all systematical differences between groups could now be attributed to sources found in section 4.

Editorial Comments

Line 122: suggest to reword as "real data without cross-instrumental bias", to avoid confusion with measurements free of instrumental bias.

We rephrased this as: "The work reported here overcomes limitations from previous studies by using real measurements originating from a single instrument. This facilitates the study of the agreement

between different retrieval codes on real data without instrumental biases between results from different groups."

Figure 1 caption: suggest to include "(90° = Zenith)" for the benefit of readers less familiar with MAX-DOAS observation methodology.

Thanks, we changed that figure accordingly.

Figure 2: Use a different color for the fitted spectrum. Green and Blue are hard to distinguish. *We changed the blue dashed line to red and increased the linewidth.*

Figure 2: What is the definition of "differential cross section", and is it optical "density", "depth", or "thickness"? None of these quantities would be expected have negative values, thus there has to be a reference point.

The differential cross section is the absolute cross section minus a (fitted) polynomial. We clarified this in the revised manuscript. The optical density shown here is the differential optical density (same definition as above), which is also explicitly mentioned in the revised manuscript. In general, optical "thickness", "depth" and "density" are often mixed-up in the literature. Within this manuscript, we tried to use only "optical depth" (i.e. avoid thickness) and used "optical density" when referring to one specific trace gas only (while "depth" is used for the total absorption effects of all trace gases, i.e. the measured quantity In(I/I0)).

Line 138: "However, these are normally the ones of interest". *Changed.*

Line 171: "*r*, the root mean square (RMS) of the fit residual, is an important quantity used within this study to identify and evaluate differences between the DOAS retrieval codes." *No, r is not the root mean square of the fit residual, but it is the fit residual itself (as denoted in the corresponding equation and explained in the text). So the text was correct (remains unchanged).*

Line 229: either "groups participating in MAD-CAT" or "participating MAD-CAT groups". *Thanks, changed to "groups participating in MAD-CAT".*

Line 305: delete "one" after "WCRS". *Thanks, we deleted "one".*

Point-by-point answers to Anonymous Reviewer #2

Note: Reviewers comments are printed in black, author's replies in blue (and italic).

General Evaluation:

The paper by Peters et al. investigates differences in NO2 DOAS retrieval due to differences in different DOAS retrieval codes. A same set of MAX-DOAS observations and DOAS retrieval settings were provided to various groups using different DOAS retrieval codes to retrieve NO2 differential slant column densities (dSCD). Resulting NO2 dSCD and RMS were then compared and a range of possible sources for their differences were investigated. In the end, the authors provide a list of 5 recommendations aimed at improving the NO2 DOAS retrievals. These recommendations are fairly straight forward and largely constitute best practices that are already followed to improve DOAS retrievals. Overall, the paper is very nicely written but way too long. I suggest the authors make changes to shorten the length of the paper.

Recommendation:

The paper fits the scope of AMT journal as it documents differences is DOAS retrieval codes and hence the paper is acceptable for publication in AMT with modifications to (i) make the differences between the codes more explicit and (ii) shorten the manuscript.

We like to thank the reviewer for the generally encouraging comments. We also share the opinion that the manuscript should be shortened. We did this following the specific reviewer's suggestions as described below.

Specific Comments:

There are two parts to the paper and they could very easily be two separate papers. The first part focuses on the intercomparison of NO2 from different retrieval codes. While in the surface it seems like a nice and interesting idea to compare different DOAS retrieval codes, it becomes very clear after section 3.1 (Part 1) that differences due to retrieval codes are very small compared to differences due to instrumental design (see Roscoe et al, 2010). The second part investigates the potential sources of these differences. However it appears like a sensitivity study to determine best features to have in a retrieval code. The authors performed the sensitivity tests first, and then compared the results from the sensitivity tests to the results from various groups. Based on the results the authors went back to the groups to verify their findings. There is disconnect between section 3 and 4 as there is lack of basis for the tests being performed. I suggest the authors include an overview table (using the survey data) which highlights the differences between different retrieval codes.

We changed the motivation for Part2 to make a stronger connection and better explanation for Part 2 following from Part1 (we did this already in response to comments of Anonymous Reviewer #1).

It is not true that we performed the sensitivity tests first. The intercomparison between groups was performed first, then a survey to identify possible reasons for observed differences, and then the sensitivity studies in order to evaluate the effect of each of the potential reasons. We state this more clearly in the revised manuscript.

It is true that differences are smaller than observed in Roscoe et al. 2010 and we agree that instrumental differences are supposed to be larger. However, we cannot strictly conclude that remaining differences come from instrumental design alone. For example, during CINDI (Roscoe et al, 2010), the instruments did not point at exactly the same time into the same direction (and also in real measurements all kinds of misalignments are potentially present). In this aspect, the recent CINDI-2 campaign is interesting because instruments followed a strict measurement protocol, i.e. coinciding measurements are assured. However, there are no CINDI-2 results published yet.

In order to meet the reviewer's comments, we changed and shortened Sect. 2.4. In particular, instead of the list of participating groups we now introduce each retrieval code and emphasize important differences (we also tried to put all content into a table, as suggested by the reviewer, but it turned out that the table format is not suited). We did not include an additional table for the survey as this

would again increase the length of the manuscript while providing little new insight. We therefore directly mention the result of the survey leading to the 5 systematic differences which are then subject of the performed sensitivity tests.

The amount of details for different retrieval codes are not comparable. Some codes are described in details while others (e.g. IUPHD) barely include a sentence.

This whole section has been changed in the revised manuscript (see above). Explanations of retrieval codes still differ a bit in length, but sufficient references are always included.

The authors make 5 recommendations to improve fit quality and harmonization between MAX-DOAS retrievals. Is there one/many DOAS retrieval code which already have these features? If so please include this/these codes as the current state of the art. This would be especially useful for new users. *Of course some of the retrieval codes allow all recommended options, e.g. NLIN (obviously, as it was used for performing the sensitivity tests) or QDOAS in its latest version (which features the use of an interpolated reference spectrum). However, it is a bit delicate to nominate one or a subset of participating retrieval codes as the current state of the art. It is also not the objective of this work to recommend any retrieval for new users (also, some of them are in-house software and not even publicly available). Moreover, while some of the recommended best practices are intrinsic features of the code (e.g. numerical computation) others are normally options for the user (e.g. choice of background spectrum). The given recommendations are therefore valuable for both, users (best practices independent from specific code) as well as designers (intrinsic features) that either programmed the participating codes (some faults have already been found and corrected within this study) or intend to design an own retrieval in the future.*

Why does the reference after the scan (T6 settings) results in larger differences? Is it simply due to the time difference between 2 degree EA and reference spectra? What is the time difference between the two spectra? Also do you see similar behavior between references taken before the scan and spectra further away? For example between refA and spectra EANA, or refA and spectra EA2B in the following scan sequence (refA,EA2A, ..., EANA, refB, EA2B,..., EANB, refC, ...).

Please notice that this question affects fit TR6 in Fig. 7, which is in the revised manuscript Fig. 6 as one of the previous plots have been removed in order to shorten the manuscript (following a suggestion from Reviewer #1).

In the reference fit used for differences plotted here the I_0 spectrum is the zenith spectrum before and after the scan interpolated to the measurement time. As the vertical scanning sequence starts from low to high elevations, the one before is closer to the measurement time (additional comment: tests TR4 and TR5 are therefore almost identical) than the one after the scan. So the reviewer is correct. Unfortunately, all options for the sequential reference that are currently implemented in our retrieval code are shown in Fig. 6 and at the moment no option is possible to test the referee's question. Nevertheless, it is very likely that references further away but before the scan would result again in larger differences.

There is no specific need to include all the QDOAS results in the paper. I suggest the authors consolidate the QDOAS results. This could be done by either presenting select QDOAS results or grouping all QDOAS results together for clarity (e.g. similar symbol in figure 3 or one side of the plot in figure 4). It would help compare and contrast the results between QDOAS and other codes.

We partly agree and followed the referee's suggestion indicating all QDOAS groups by the same symbol in Fig. 3 and 5 (formally Fig. 6) for clarity and better comparison to non-QDOAS groups. We also indicated QDOAS groups in Fig. 4 for the same reason.

However, we do not think that consolidating all QDOAS results is a good option because groups using QDOAS show clearly different results and no systematic similar pattern, which is an interesting finding that is explicitly mentioned in the conclusion section and has some impact for other studies: The amount of prescribed fit settings in this study is comparable to intercomparison campaigns like CINDI

or CINDI-2. Consequently, groups participating those campaigns will provide intrinsic (and nonsystematic) differences in their results due to small differences in non-harmonized (detailed) settings (even if using the same retrieval code), which have to be expected in the same range as observed here. We point this out more clearly in the revised manuscript. Finally, the QDOAS versions used here are different.

Line 790: "differences of up to 8% have to be expected" – Does this also hold true for other elevation angles where dSCDs are smaller? To some extent quoting 8% as expected uncertainty is somewhat misleading knowing that the particular spectrum was affected by direct sunlight and such a scenario is not common in MAX-DOAS measurements. I suggest the authors make this distinction clear in the manuscript in order to avoid misuse of 8% as inherent uncertainty in DOAS retrievals.

The value of 8% does not correspond to the first data point in Fig. 3 (although this holds true as well) but to the sequential references seen in Fig. 5 where disagreements of 8% are frequently obtained. We stated this more clearly in the revised manuscript.

In general, the value of 8% is representative for small elevations as Figure 1 (below) shows. Fig. 5 (formally Fig. 6) in the paper has been reproduced here, but this time for 8° elevation instead of 2°. Although absolute differences between groups appear to be a bit smaller in 8° than in 2°, relative differences are even a bit larger because slant columns are smaller (but nevertheless, 8% appears to be reasonable even for 8° elevation measurements shown here).



Figure 1: NO₂ differences between groups for 8° elevation angle.

Investigating differences in DOAS retrieval codes using MAD-CAT campaign data

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Abstract. The Differential Optical Absorption Spectroscopy (DOAS) method is a well-known remote sensing technique that is nowadays widely used for measurements of atmospheric trace gases, creating the need for harmonization and characterization efforts. In this study, an intercomparison exercise of DOAS retrieval codes from 17 international groups is presented focusing on NO₂ slant columns. The study is based on data collected by one instrument during the Multi-Axis DOAS Comparison campaign for Aerosols and Trace gases (MAD-CAT) in Mainz, Germany, in summer 2013. As data from the same instrument is used by all groups, the results are free of biases due to instrumental differences, which is in contrast to previous intercomparison exercises.

While in general an excellent correlation of NO_2 slant columns between groups of > 99.98% (noon reference fits), and > 99.2% (sequential reference fits) for all elevation angles is found, differences between individual retrievals are as large as 8% for NO_2 slant columns and 100% for RMS residuals in small elevation angles above the horizon.

Comprehensive sensitivity studies revealed that absolute slant column differences result predominantly from the choice of the reference spectrum while relative differences originate from the numerical approach for solving the DOAS equation as well as the treatment of the slit function. Furthermore, differences in the implementation of the intensity offset correction was found to produce disagreements for measurements close to sunrise (8-10% for NO₂, 80% for RMS residual). The largest effect of $\approx 8\%$ difference in NO₂ was found to arise from the reference treatment, in particular for fits using a sequential reference. In terms of RMS fit residual, the reference treatment has only a minor impact. In contrast, the wavelength calibration as well as the intensity offset correction were found to have the largest impact (up to 80%) on RMS residual while having only a minor impact on retrieved NO₂ slant columns.

1 Introduction

In this study, the consistency of Differential Optical Absorption Spectroscopy (DOAS) retrievals of tropospheric nitrogen dioxide (NO₂) from ground-based scattered light observations is evaluated. NO₂ is released into the atmosphere predominantly in the form of NO as a result of combustion processes at high temperatures. Through reaction of NO with ozone (O₃), NO₂ is rapidly produced and (during the day) back-converted into NO by photolysis. Therefore, nitrogen oxides are often discussed in terms of NOx (NO + NO₂ = NOx). NO₂ is a key species in the formation of tropospheric ozone and a prominent pollutant in the troposphere, causing (together with aerosols) the typical brownish colour of polluted air. In addition, it is harmful for lung tissue and a powerful oxidant. In the lower troposphere, the lifetime of NO₂ is short (several hours) due to reaction with OH and photo-dissociation, and thus it is found mostly close to its sources, making it a good tracer of local pollution. Both anthropogenic sources such as burning of fossil fuel in industry, power generation, and traffic as well as biogenic sources including bush and forest fires contribute to the tropospheric NOx loading. In addition, NO₂ is released from soil microbial processes and lightning events (Lee et al., 1997). As a result, high NO₂ amounts are mostly observed above industrialized and urban areas, traffic routes and over bush fires.

Using its characteristic absorption bands in the UV and visible spectral range, NO2 has been successfully measured for many years using the DOAS technique (Brewer, 1973; Noxon, 1975; Platt, 1994) both from the ground and from space (e.g. Richter et al., 2005; Beirle et al., 2011). In addition, airborne and car-based measurements (e.g. Schönhardt et al., 2015; Shaiganfar et al., 2011), have been performed to close the gap between ground-based observations providing continuous temporal, but poor spatial resolution and satellite measurements which offer global observations, but only up to one measurement per day above each location. Using ground-based multi-axis (MAX)-DOAS measurements at different elevation angles, a more accurate vertical column (VC) can be retrieved with information on the vertical distribution of NO_2 and other trace gases in the troposphere (e.g. Hönninger et al., 2004; Wittrock, 2006; Frieß et al., 2011; Wagner et al., 2011).

As result of the viewing geometry, ground-based MAX-DOAS observations are most sensitive to the lowest layers of the troposphere. Here they provide high sensitivity and low relative measurement errors. Averaging over longer integration times can further reduce statistical noise. Another advantage is that MAX-DOAS stations can be operated automatically and usually require little maintenance. MAX-DOAS measurements were therefore performed in remote regions for the investigation of background concentrations and in many locations for the validation of satellite observations (e.g. Takashima et al., 2012; Peters et al., 2012).

There currently exists a variety of different instruments and retrieval codes designed to perform and analyse MAX-DOAS measurements. While the basic approaches are similar, differences exist which can potentially lead to inconsistencies in measurements from different instruments and retrievals. As this is an important limitation for the use of MAX-DOAS measurements in a global observing system, the Network for the Detection of Atmospheric Composition Change NDACC (formerly known as NDSC) has organised several intercomparison campaigns aimed at comparing instruments, retrievals, and uncertainties of a wide range of DOAS instruments. The first of these campaigns were focused entirely on zenith-sky observations for stratospheric absorbers (Hofmann et al., 1995; Vaughan et al., 1997; Roscoe et al., 1999) but later also included other viewing directions (Vandaele et al., 2005). The Cabauw Intercomparison of Nitrogen Dioxide Measuring Instruments (CINDI) campaign in 2009 in Cabauw, the Netherlands



Figure 1. NO_2 slant columns and fit residual root mean square (RMS) obtained from the IUPB retrieval code for the intercomparison day used in this study. Different elevation angles are color-coded. The fit settings correspond to v1 settings as described in Sect. 2.4 (Tab. 1).



Figure 2. (a) Example of the fitted NO₂ differential optical density in 2° elevation angle at 14:40 UT corresponding to a slant column of \approx 7E16 molec/cm² (compare Fig. 1). The solid line is the NO₂ differential optical density (= differential cross section, i.e. the cross section after subtraction of a fitted polynomial, multiplied by the retrieved slant column) and the dashed line is the solid line plus the fit residual. The NO₂ differential optical density is much larger than the residual, which is explicitly shown in (b).

was the first to also have a focus on MAX-DOAS observations of tropospheric species (Roscoe et al., 2010; Piters et al., 2012; Pinardi et al., 2013) and has recently been followed by the CINDI-2 campaign performed in 2016, also in Cabauw. However, these intercomparison exercises concentrated mostly on results originating from different retrieval codes and instruments, and separation of instrument and retrieval effects was not easily possible. In some cases, synthetic spectra were used to intercompare retrieval algorithms, and while such tests can highlight differences between retrieval approaches, they give no insight into the way different

retrieval codes deal with instrumental effects such as intensity offsets, resolution changes or spectral drifts.

The present study was performed in the framework of the European FP7 project QA4ECV (Quality Assurance for Essential Climate Variables) which aims at providing quality assurance for satellite derived ECVs such as NO₂, HCHO and CO by characterizing the uncertainty budgets through uncertainty analysis and error propagation but also by validation with external data sets. In this context, ground-based MAX-DOAS measurements can play an important role, and harmonisation of the retrieval approaches and quality assur-

ance for the reference measurements are needed. The results of the analysis performed in the QA4ECV project are expected to contribute to the harmonisation of data from MAX-DOAS instruments, in particular for the ongoing integration of such measurements in the NDACC network.

The work reported here overcomes limitations from previous studies by using real measurements originating from a single instrument. This facilitates the study of the agreement between different retrieval codes on real data without instrumental biases between results from different groups. The intercomparison was performed on spectra recorded by the University of Bremen (IUPB) instrument during the Multi-Axis DOAS Comparison campaign for Aerosols and Trace gases (MAD-CAT) carried out in Mainz, Germany, in summer 2013 (http://joseba.mpch-mainz.mpg.de/mad cat. htm). Data was distributed to 17 international groups working on ground-based DOAS applications. Each group analysed these spectra using their own DOAS retrieval code but prescribed fit settings for fitting window, cross-sections, polynomial and offset correction. Resulting slant columns from all groups were then compared to IUPB results chosen as the arbitrary reference, evaluating the level of agreement and systematic differences and investigating their algorithmic origins. With this set-up, nearly all sources of disagreement were removed, and only those differences between retrieval codes were investigated which are not usually reported.

This intercomparison exercise concentrates on one day (18 June 2013) during the MAD-CAT campaign having the best weather and viewing conditions. As an example, Fig. 1 shows NO₂ slant columns (left) and fit RMS residual (right) retrieved with the IUPB software. It is nicely seen that NO₂ slant columns measured at different elevation angles are separated as a result of differences in the light path. It should be mentioned that NO₂ slant columns are relatively large as a result of anthropogenic pollution at the densely populated and industrialized measurement location and thus the findings of this study correspond to polluted urban environments. However, these are normally the ones of interest for NO₂ observations. Fig. 1 also shows that the RMS of the fit residuals (in the following simply denoted as RMS) separates with elevation angles as well. In addition, the shape of the RMS in small elevation angles is very similar to that of NO₂ slant columns, indicating that predominantly NO₂ related effects such as the wavelength dependence of the NO2 AMF (which was not included in the fit shown here) limit the fit quality (note, this study aims not at finding best NO₂ fit settings but studying disagreements originating from different retrieval codes). This is supported by the observation that the shape of NO₂ slant columns is not seen in the RMS for larger elevation angles as effects related to the NO₂ absorption are smaller and other effects limiting the fit quality dominate. In addition, the RMS is very large in the early morning for small elevations, which is discussed in detail later and results from pointing towards sunrise. However, in general NO₂ is retrieved very accurately as Fig. 2 demonstrates, showing the NO_2 optical density and fit residual for a measurement in 2° elevation angle (this is a typical example fit).

The manuscript is structured in the following way: Sect. 2 provides details about the MAD-CAT campaign, measurements, the NO₂ intercomparison exercise as well as participating retrieval codes. Intercomparison results between groups are presented in Sect. 3. Sensitivity studies of non-harmonized retrieval aspects attempting to reproduce observed differences between groups and evaluating the impact on NO₂ slant columns and DOAS fit quality are performed in Sect. 4. The manuscript ends with conclusions and recommendations for better harmonization of ground-based MAX-DOAS measurements.

2 Measurements

2.1 DOAS technique

The DOAS technique is based on Lambert-Beer's law which describes the attenuation of light passing through a medium. Here, it is applied to measurements of scattered sunlight. The spectral attenuation caused by scattering is smooth in wavelength (e.g., λ^{-4} -dependence for Rayleigh scattering) while molecular absorption often has structured spectra. In DOAS, the total spectral attenuation is therefore split into a high-frequency part consisting of the (high-frequency components of) trace gas absorptions and a low-frequency part accounting for elastic scattering which is described by a loworder polynomial also compensating for intensity changes, e.g. caused by clouds. In addition, the effect of inelastic scattering, which is predominantly due to Rotational-Raman-Scattering known as the Ring effect (Shefov, 1959; Grainger and Ring, 1962) is accounted for by a pseudo cross section (e.g. Vountas et al., 1998). Similarly, intensity offsets mostly resulting from stray light within the spectrometer are accounted for by pseudo cross sections σ_{off} (see Sect. 4.3 for more details). In total, the optical depth τ is approximated by

$$\tau = \ln\left(\frac{I_0}{I}\right) = \sum_i \sigma_i \cdot SC_i + \sigma_{\text{Ring}} \cdot SC_{\text{Ring}} + \sigma_{\text{off}} \cdot SC_{\text{off}} + \sum_p a_p \lambda^p + r$$
(1)

where the first sum is over all *i* absorbers having cross section σ_i , the polynomial degree is *p*, and the residual term *r* contains the remaining (uncompensated) optical depth. An important quantity used within this study to identify and evaluate differences between DOAS retrieval codes is the root mean square of the fit residual *r* (for simplicity denoted as RMS in the context of this study), which is a measure of the fit quality. In Eq. 1, known as the *DOAS equation*, all quantities with the exception of a_p depend on wavelength λ . For tropospheric absorbers, the spectrum *I* is normally taken

at small elevation angles above the horizon where the tropospheric light path is large. The reference spectrum I_0 is normally a zenith spectrum either at small solar zenith angle (SZA), which is in the following called a noon reference fit, or close in time to the measured spectrum I, in the following called a sequential reference fit.

The DOAS equation is usually an over-determined problem (τ is measured at more wavelengths λ than unknowns exist in Eq. 1) and solved by means of a least-squares fit (see also Sect. 4.5), i.e. minimizing the residual term. The resulting fit factors are the polynomial coefficients a_p and the so-called slant columns SC_i , which are the quantities of interest. The slant column is the integrated concentration ρ_i of absorber *i* along the effective light path *s* (for simplicity we use the SC also for the fit coefficients of the Ring and offset spectra):

$$SC_i = \int \rho_i ds \tag{2}$$

Note that this is a simplification as normally an ensemble of different light paths contribute to the measurement. In extreme cases, the absorption optical depth can become a non-linear function of the trace gas concentration. However, this is usually only of importance for satellite limb measurements and is discussed in detail for example in (Pukite and Wagner, 2016). A comprehensive discussion of the DOAS technique can be found for example in (Hönninger et al., 2004; Platt and Stutz, 2008).

2.2 The MAD-CAT campaign

The Multi-Axis DOAS Comparison campaign for Aerosols and Trace gases (MAD-CAT) was carried out in Mainz, Germany, in summer 2013. During the intensive phase of the campaign (7 June to 6 July 2013), 11 groups deployed MAX-DOAS instruments on the roof of the MAX-Planck Institute for Chemistry at the Mainz University campus. Being located in the densely populated Rhine-Main region, the observations are dominated by anthropogenic pollution, predominantly by NO₂ (in the visible). The main azimuthal viewing direction was 51° (from north), pointing roughly in the direction of the city of Frankfurt \approx 30 km away. Series of vertical scans comprising elevation angles of 0° , 1° , 2° , 3° , 4° , 5° , 6° , 8° , 10° , and 30° were performed. In each direction, single measurements of varying exposure time depending on illumination were integrated for 20 s (for the IUPB instrument, other instruments used different integration times). Between vertical scans, multiple zenith measurements were performed (see Fig. 1 for an example of resulting NO₂ slant columns). Detailed information about MAD-CAT can be also found at http://joseba.mpch-mainz.mpg.de/mad_cat.htm and the first campaign data focusing on range-resolved distributions of NO2 measured at different wavelengths was published by Ortega et al. (2015). Furthermore, Lampel et al. (2015) demonstrated the presence of vibrational Raman scattering on N₂ molecules in spectra measured during MAD-CAT. In addition, publications based on MAD-CAT data are in preparation focusing on HCHO (Pinardi, 2017), HONO (Wang et al., 2016) and CHOCHO (Ortega et al., 2017).

2.3 The IUPB MAX-DOAS instrument

The IUPB MAX-DOAS instrument deployed in Mainz during the MAD-CAT campaign is a two-channel CCDspectrometer system measuring in the UV and visible, respectively. Within this exercise, only data from the visible spectrometer are used as NO₂ is best retrieved in this spectral range. The spectrometer is an ANDOR Shamrock 303i covering a spectral range from 399-536 nm at a resolution of ≈ 0.7 nm. The spectrometer was actively temperature stabilized to 35°C. Spectra were recorded with a CCD of the ANDOR iDUS 420 type having 1024x255 pixels (26x26 μ m each) leading to a spectral sampling of 7-8 pixels/nm.

Light was collected by a telescope unit mounted on a commercial ENEO VPT-501 pan-tilt head allowing pointing in any viewing direction. Photons entering the telescope through a fused silica window were focused by a lens on an optical fiber bundle. The instrument's field-of-view (FOV) was $\approx 1.2^{\circ}$. The Y-shaped optical fiber bundle (length 20 m) connecting the telescope to both spectrometers consists of 2x38 = 76 single fibres minimising polarization effects. A video camera inside the telescope housing takes snap shots for every recorded spectrum for scene documentation and a mercury-cadmium (HgCd) line lamp allows wavelength calibration measurements. Dark current and slit function measurements are performed every night. The same instrumental set up has been used in previous campaigns, e.g. CINDI and TransBrom (Roscoe et al., 2010; Peters et al., 2012).

2.4 Intercomparison exercise

Spectra recorded by the IUPB MAX-DOAS instrument on 18 June 2013 during MAD-CAT were distributed to partners. It is worth mentioning that this intercomparison exercise was not restricted to groups participating in MAD-CAT, as common observations were provided. 18 June 2013 was selected as having good viewing and weather conditions. However, temperature stabilization of the IUPB spectrometer was problematic due to unusually hot weather which due to a lack of air conditioning on that day led to overheating of the instrument. As a result, spectral stability was not as good as usual, providing the opportunity to investigate how different retrieval codes deal with potential spectral shifts during the day. The provided data comprised observations at several elevation angles in the main azimuthal viewing direction of 51° (see Fig. 1 for an example). In addition, common trace gas cross sections as well as DOAS fit settings were distributed as summarized in Tab.1, which are the common fit settings as agreed on during the MAD-CAT campaign. All groups then performed DOAS fits using these prescribed settings on

Fit	Reference	Window	Cross sections	Intensity offset	Polynomial	
v1	noon	425-490	1,2,4,5,6,7	Constant (0th order)	5 (6 coefs)	
v1a	sequential	425-490	1,2,4,5,6,7	Constant (0th order)	5 (6 coefs)	
v2	noon	411-445	1,3,4,5,6,7	Constant (0th order)	4 (5 coefs)	
v2a	sequential	411-445	1,3,4,5,6,7	Constant (0th order)	4 (5 coefs)	
Cross sections:						
1	NO ₂ at 298K (Vandaele et al., 1996), I_0 -correction using 1E17 molec/cm ²					
2	NO ₂ at 220K orthogonalized to 298K within 425-490 nm					
3	NO2 at 220K orthogonalized to 298K within 411-445 nm					
4	O ₃ at 223K (Bogumil et al., 2003)					
5	O ₄ Hermans et al., unpublished, http://spectrolab.aeronomie.be/o2.htm					

H₂O, HITEMP (Rothman et al., 2010)

Ring, NDSC2003 (Chance and Spurr, 1997)

Table 1. Summary of fit settings used for the NO₂ intercomparison. These fit settings were agreed on during the MAD-CAT campaign and can be found also at http://joseba.mpch-mainz.mpg.de/mad_analysis.htm.

IUPB spectra using their own retrieval software. The influence of different retrievals was then analyzed, focusing on the impact on NO_2 columns. A brief description of retrieval codes is given in the following. Participating groups (with abbreviations used within this study) and retrieval codes they

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2.4.1 NLIN

used are summarized in Tab. 2.

NLIN (Richter, 1997) was originally developed at IUPB for the analysis of ground-based measurements but over time extended and also used for airborne and satellite data sets. The DOAS matrix is inverted using a singular value decomposition (SVD) which is comprised in an iterative nonlinear fit for calibration of the wavelength axis using a Marquardt-Levenberg fit.

2.4.2 QDOAS

QDOAS (Dankaert et al., 2013) is the multi-platform (Windows, Unix/Linux and Mac) successor of WinDOAS. A coupled linear/non-linear least squares (NLLS) algorithm (Marquardt-Levenberg fitting and SVD decomposition) is used to solve the DOAS equation including a wavelength calibration module. During this operation, the slit function can be characterized in addition to the wavelength registration of the measured spectra. QDOAS is widely used within the DOAS community and has been applied in different versions for the present exercise: AUTH (version 2.109.3), JAMSTEC (version 2.109), University of Toronto (version 2.109), CSIC (QDOAS windows 2.110.1 beta 20151123), BIRA (version 2.110.1), USTC (version 2.109.4), UNAM (version 2.109.3), NUST (version 2.111), CU Boulder (version 2.110). These various versions do not differ in the core-implementation of the DOAS analysis, but can feature slightly different capabilities in terms of data handling or specific retrieval functionalities (see http://uv-vis.aeronomie.be/ software/QDOAS/LastChanges.php).

2.4.3 LANA

LANA is a two-step iterative algorithm developed at INTA and used since 1994. In the first step, cross sections and spectra are positioned and in the second step the linear equations system is solved using a Gauss-Jordan procedure. For this exercise, the intensity offset correction was based on the reference spectrum I_0 .

2.4.4 MDOAS

MDOAS is a Matlab DOAS code developed at MPIC, but calibration and convolution have been performed in WinDOAS. For sequential reference fits, two versions MPIC_MDa and MPIC_MDb are included in this exercise, which used a different treatment of the Ring spectrum.

2.4.5 KMDOAS

KMDOAS was recently (2013-2014) developed at KNMI and verified using QDOAS. It is written in Python using standard modules (matplotlib, numpy, scipy, pandas).

2.4.6 DOASIS

DOASIS has been used by IUPHD in its version 3.2.4595.39926. A detailed explanation can be found in (Kraus, 2006). In the version submitted here, an additional shift of cross sections w.r.t. the optical depth was allowed and a saturation correction was implemented.

2.4.7 STRATO

The *NIWA-Strato* package was originally (1980s) used for processing zenith DOAS spectra, but extended as needed to

Table 2. Summary of participating institutes (with abbreviation) and retrieval codes used by each group.

Abbr.	Retrieval(s)	Institute	
IUPB	NLIN	Institute for Environmental Physics, University of Bremen, Germany	
AUTH	QDOAS	Aristotle University of Thessaloniki, Greece	
BIRA	QDOAS	Belgian Institute for Space Aeronomy, Brussels, Belgium	
JAMSTEC	QDOAS	Japan Agency for Marine-Earth Science and Technology, Japan	
Toronto	QDOAS	Department of Physics, University of Toronto, Ontario, Canada	
IUPHD	DOASIS	Institute of Environmental Physics, University of Heidelberg, Germany	
Boulder	QDOAS	University of Colorado, Boulder, USA	
KNMI	KMDOAS	Royal Netherlands Meteorological Institute, De Bilt, The Netherlands	
INTA	LANA	National Institute for Aerospace technology, Madrid, Spain	
MPIC	MDOAS,	Max Planck Institute for Chemistry, Mainz, Germany	
	WinDOAS		
CSIC	QDOAS	Department of Atmospheric Chemistry and Climate,	
		Institute of Physical Chemistry Rocasolano, CSIC, Madrid, Spain	
NIWA	STRATO	National Institute of Water and Atmospheric Research, Lauder, New Zealand	
IAP	RS.DOAS	A. M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences, Moscow, Russia	
BSU	WinDOAS	Belarusian State University, Minsk, Belarus	
USTC	QDOAS	University of Science and Technology, Hefei, China	
UNAM	QDOAS	National Autonomous University of Mexico, Mexico	
NUST	QDOAS	Institute of environmental sciences and engineering (IESE),	
		National University of Sciences and Technology, Islamabad, Pakistan	

handle MAX-DOAS measurements. The fitting code uses least squares or optional SVD fitting inside iterations applying shift, stretch and (optional) offset, for minimum residual. In contrast to other groups, an internal equidistant wavelength grid is applied using the average interpixel spacing.

2.4.8 RS.DOAS

RS.DOAS (Ivanov et al., 2012; Borovski et al., 2014; Postylyakov et al., 2014; Postylyakov and Borovski, 2016) was developed by IAP. The DOAS inversion is performed by LU decomposition. The wavelength calibration uses several subwindows, and for each of them a non-linear shift and stretch fit including all trace gases (resulting from the linear DOAS fit) is applied. From a set of shifts obtained for the subwindows a 2nd-order polynomial approximation of the shift dependency on pixel number is constructed. For convolution of cross-sections the QDOAS software (offline version 2.0 at 5 March 2012) was used.

2.4.9 WinDOAS

WinDOAS (Fayt and Van Roozendael, 2001) is the precursor of QDOAS. It has been used by BSU as well as MPIC for this intercomparison exercise (the MPIC submission is denoted as MPIC_WD, the reference has been selected by hand), but only for noon reference fits.

3 Intercomparison results

3.1 Noon reference, 425-490 nm fit window (v1 fit parameters)

Differences between groups for the 425-490 nm fit using a noon reference (v1 fit settings, see Tab. 1) are shown in Fig. 3 for individual measurements at an elevation angle of 2° . Small elevation angles above the horizon are associated with long tropospheric light paths and therefore important for the detection of tropospheric absorbers. Differences shown in Fig. 3 are relative to IUPB results. For the objective of identifying retrieval-code specific effects, the use of a single retrieval code as a reference seems advantageous in comparison to using the mean of all retrieval codes which would average over all retrieval-specific features. Note that this does not exclude IUPB from the intercomparison as problems of the IUPB retrieval would be easily detected as leading to the same systematic patterns in all lines shown in Fig.3.

Absolute differences (institute-IUPB) and relative differences (absolute difference/IUPB) of NO₂ slant columns and fit RMS are shown in Fig. 3a-d. In general, NO₂ slant column differences are in the range of $\pm 2-3 \cdot 10^{15}$ molec/cm² or < 2%. This is about a factor of 2-3 larger than NO₂ slant column errors, which are typically < $1 \cdot 10^{15}$ molec/cm², resp. < 0.6% for 2° elevation. A clearly enhanced disagreement is observed for the first data point in the INTA time-series as well as for MPIC_WD. The latter could be linked to the reference spectrum, which is in this case not the one having smallest sun zenith angle (SZA) while the outlier in the INTA timeseries was identified to arise from different implementa-



Figure 3. Results from v1 fit settings in 2° elevation angle as a function of time. (a, b) Absolute NO₂ slant column and RMS differences, (c, d) relative NO₂ slant column and RMS differences, (e) NO₂ slant columns, (f) RMS, (g, h) fitted spectral shift (h is a zoom-in of g without INTA and KNMI lines, but including the reanalyzed INTA2 and NIWA2 lines). (a-d) are differences w.r.t. IUPB, (e-h) are absolute results and IUPB is explicitly shown in black. Triangular markers indicate groups using QDOAS, circular markers indicate groups using independent software, and diamonds indicate groups that corrected faults in their code during the course of this study and submitted a re-analyzed data set.



Figure 4. Linear regression results (slope, intercept, correlation) for different elevation angles (w.r.t. IUPB) for fit settings v1 (noon reference). Groups using QDOAS (in different versions) are indicated by a star (*).

tions of the intensity offset correction (see Sect. 4.3). Note that these NO_2 differences for individual measurements are much smaller than the variability (diurnal cycle) of NO_2 and thus almost invisible in Fig. 3e where no differences but absolute NO_2 slant columns from each groups (including IUPB in black) are plotted.

Interestingly, many groups show a smooth behavior (constant offset) in absolute NO_2 differences (Fig. 3a), which is mostly an effect of the choice of the reference (see Sect. 4.1) while relative differences (Fig. 3c) reflect the shape of NO_2 slant columns in Fig. 3e (smaller slant columns lead to larger relative differences and vice versa). However, some groups show a smooth line not for absolute, but for relative differences. Thus, two types of disagreements are observed, 1) constant in absolute, and 2) constant in relative differences. These two types are linked to differences in retrieval codes, which is investigated in detail in Sect. 4. Absolute RMS differences (w.r.t. IUPB) in Fig. 3b show the same shape as NO₂ slant columns. This is because at small elevations the RMS itself reflects the shape of the NO₂, which was already demonstrated and discussed in Fig. 1. A better measure for the identification of differences between retrieval codes is thus the relative RMS disagreement shown in Fig. 3d. Interestingly, the first data point for INTA showing a large disagreement with IUPB and other groups in NO₂ slant columns is prominent in absolute RMS differences as well, but not in relative RMS differences. The reason is that the RMS in the morning is very large (Fig. 3f, compare also to Fig. 1) and thus decreases the relative difference. Remarkably, relative RMS differences are found up to 80-100%, which is substantially more than NO₂ slant column differences (only a few percent).

The IUPB spectra provided were wavelength precalibrated using nightly HgCd line lamp measurements as explained in Sect. 2.3. However, the DOAS fit quality can be improved (RMS reduced) by applying a post-calibration. In addition, the nighttime calibration can change during the day as a result of temperature drifts. This is accounted for by DOAS retrieval codes in terms of a nonlinear shift fit (for a more detailed discussion see Sect. 4.6). Figs. 3g and h (being a zoom-in of g) show the reported shift resulting from the wavelength calibration in participating retrieval codes. Note, absolute values for the shift are shown here and the IUPB result is explicitly included. For an ideal spectrometer without drifts, only a very small shift would be expected caused by a non-commutivity of convolution and DOAS polynomial, which is known as the *tilt effect* and typically in the order of less than 1-2pm, depending on the instrument resolution (Sioris et al., 2003; Lampel et al., 2017). The shift retrieved here is larger than that and driven by overheating of the system on this day. In general, timeseries of shifts shown in Fig. 3g and h agree well in shape. A small offset is observed for NIWA, who successfully found and corrected a fault in their retrieval code (related to the intensity offset calculation) in the course of this exercise. The DOAS fit was then repeated using the corrected retrieval code and the result called NIWA2 is included in Fig. 3. Apparently, NIWA2 shows much better comparison to other groups (most obvious in the fitted spectral shift) and performs better as the RMS in Fig. 3d is much smaller than before. Similarly, INTA fixed a problem in their retrieval code related to the wavelength calibration. The reanalyzed INTA data are denoted as INTA2 in Fig. 3. The INTA2 shift is comparable to other groups, while large disagreements were seen before, and the RMS is largely reduced in comparison to the first INTA submission. Notably, almost no differences between INTA and INTA2 are observed in terms of NO2 slant columns, in particular the first data point is still outlying. This indicates (1) that the wavelength calibration has a large impact on the fit RMS but only a minor impact on the NO_2 slant columns, and (2) that the disagreement of the first data point is not related to the wavelength calibration. Despite INTA and NIWA, only KNMI is fitting a rather different shift (and provides the shift only in 0.01 nm resolution which leads to the displayed discrete steps). This is caused by different definitions of the shift (see Sect. 4.6): KNMI is fitting the shift of the optical depth relative to the cross sections while the other groups are fitting the shift of I relative to the reference spectrum I_0 . As a result, the shift of KNMI and other groups cannot be expected to match.

The agreement between groups including also other elevation angles has been quantified by linear regression analyses to correlation plots (of each group relative to IUPB results, not shown). Resulting slopes, offsets, and correlation coefficients are summarized in Fig. 4, color-coded for different elevation angles. As expected, the correlation coefficient is > 99.98% with the only exception of the INTA (and INTA2) 2° elevation which is predominantly caused by the outlier already seen in Fig. 3. The slope ranges between 0.985 and

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1.01, the offset between -4 to $2.5 \cdot 10^{15}$ molec/cm². Apart from USTC and INTA, no large separation of slope and offset with elevation angle is observed. An important observation is that groups using the same retrieval code (QDOAS) do not necessarily show the same systematic behavior in Fig. 4, implying that the influence of remaining fit parameters different from the harmonized general settings in Tab. 1 is still larger than the effect of the specific retrieval software used. For example, the best agreement in terms of slope, offset and correlation coefficient is found between IUPB, AUTH, IAP, and CU Boulder, which are all using different retrieval codes.

3.2 Other fit parameters

The agreement between groups was investigated in the same way when using a sequential reference (denoted as v1a fit setting, see Tab. 1) instead of a noon reference spectrum (v1 fit). A sequential reference is often preferred if tropospheric absorbers are of interest as stratospheric effects are removed to a large extent.

Fig. 5 is similar to Fig. 3, but some groups are missing here (e.g. IAP) as they only provided noon reference fits. The range of disagreements for individual NO2 slant columns is up to $\approx 8\%$ and therefore larger than NO₂ disagreements using a noon reference (v1 fit). In addition, neither absolute nor relative differences between groups are smooth (Fig. 5 a and c). The reason is that in contrast to the noon reference, a different (zenith) I_0 spectrum is used for every scan and thus the impact of details of the implementation of the reference changes from scan to scan. Different implementations of the reference spectrum are further investigated in Sect. 4.1 and were found to be the major reason for NO2 disagreements between groups. The outlier (first data point) seen for v1 (noon) fit settings is present for v1a as well but it is not prominent here as fluctuations for the above mentioned reason are of same magnitude.

In terms of RMS, differences between groups are comparable to v1 results and as large as $\approx 80\%$.

Compared to the noon reference fit, correlations from linear regressions (not shown) are smaller, especially for 30° elevation angle, mainly resulting from the larger disagreements as explained above (but also partly expected as slant columns are smaller using a sequential reference). Correlations are still > 99.2% for 30° elevation and even > 99.8% for smaller elevations.

In addition to the 425-490 nm fit (v1 and v1a), a smaller fit window used within the MAD-CAT campaign was intercompared (v2 and v2a using a spectral range of 411-445 nm, see Tab. 1). Results of these fits are not explicitly shown as mainly confirming observations and findings above. Typical correlation coefficients (as well as offsets and slopes) are summarized in Tab. 3 for all performed fits. A very small tendency of better agreement between groups if using the larger fit window is seen. Although this should not be overinterpreted, it could be caused by more information being



Figure 5. Results from v1a fit settings (sequential reference spectrum) on 2° elevation angle data as a function of time. (a and b) Absolute NO₂ slant column and RMS differences, (c and d) relative NO₂ slant column and RMS differences. All differences are relative to IUPB. Triangular markers indicate groups using QDOAS, circular markers indicate groups using independent software, and diamonds indicate groups that corrected faults in their code during the course of this study and submitted a re-analyzed data set.

Table 3. Correlations, slopes and offsets from linear regressions on NO_2 slant columns between each group and IUPB (neglecting the INTA 2° outlier).

Fit	Correlation (%)	Slope	Offset (1E15 molec/cm ²)
v1	>99.98	0.985 to 1.01	-4 to 3
vla	>99.2	0.96 to 1.01	-1.5 to 1
v2	>99.94	0.985 to 1.005	-4 to 3
v2a	>99.2	0.96 to 1.01	-2 to 1

present in the large fit window and therefore more accurate results (less statistical fluctuations).

4 Sensitivity studies of non-harmonized retrieval aspects

The observed differences between the harmonized MAD-CAT retrieval results prompted the team to systematically investigate effects of the non-harmonized aspects of the retrievals, with the aim to derive a key set of Best Practices recommendations. A survey suggested five potential sources of differences in the DOAS fit results: 1) the selection/calculation of the reference spectrum, predominantly for sequential reference fits, 2) treatment of the slit function, 3) the intensity offset correction, 4) differences in the numerical calculation of the DOAS fit (linear fit), 5) differences in the wavelength calibration (non-linear fit). In the following, tests using the same retrieval code (IUPB) have been performed to characterize the impact of each of the above mentioned systematic differences.

4.1 Effect of the reference spectrum

In the IUPB spectra provided to intercomparison partners, two different zenith spectra at the same smallest SZA were reported, which is of course non-physical. Actually, the second zenith spectrum is the one having the smallest SZA, but for rounding reasons (the SZA was a 4-digits number in the input data provided), both spectra had the same SZA. Consequently, for the noon reference fits v1 and v2 within this intercomparison exercise, four options exist: 1) taking the first zenith spectrum of smallest SZA, 2) taking the second one, 3) taking the first for a.m. and the second for p.m. (i.e. always taking the closest in time), and 4) taking the average of both spectra. Similarly, different options exist for calculating

Table 4. Tests performed to study the influence of different refere	ence spectra
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Test	Reference (fit setting)	Remarks
TR0	noon (v1)	first spectrum of smallest SZA
TR1	noon (v1)	second spectrum of smallest SZA
TR2	noon (v1)	first for a.m., second for p.m.
TR3	noon (v1)	average of both
TR4	sequential (v1a)	closest zenith in time
TR5	sequential (v1a)	closest before the scan
TR6	sequential (v1a)	closest after the scan
TR7	sequential (v1a)	average of before and after
TR8	sequential (v1a)	interpolation of before and after to time of measurement



Figure 6. Different test results (see Tab. 4) in 2° elevation angle as a function of time. Top: Absolute NO₂ SC differences, Middle: Relative SC differences, Bottom: Relative RMS differences. Left is for noon reference (differences are w.r.t. IUPB v1 fit results), right is for sequential references (differences are w.r.t. IUPB v1a fit results).

the sequential references for fits v1a and v2a: 1) always taking the zenith spectrum closest in time, 2) always taking the last zenith spectrum before the actual measurement, 3) always taking the next zenith spectrum after the measurement,

4) taking the average of the two (before and after), and 5) interpolating the two zenith spectra to the time of the actual measurement.

All different options for noon and sequential reference fits were evaluated using the IUPB retrieval code NLIN (Tab. 4). Fig. 6 shows the resulting absolute and relative slant column differences (top and middle) as well as relative RMS differences (bottom) for noon reference (left) and sequential reference (right) w.r.t. v1, resp. v1a fit results.

Taking another noon reference spectrum results in a constant offset in absolute NO2 differences (Fig. 6, top left). Test TR0 (using the first spectrum) yields the same results as the IUPB v1 fit from Sect. 3, which uses the first zenith spectrum as well. In contrast, using the second zenith spectrum as a reference (TR1) results in a constant offset of 1.5E15 molec/cm² (0.5-2.5% in relative differences, depending on the actual NO2 slant column), because the second zenith spectrum had apparently a smaller NO₂ content. The change of the NO₂ content could be related to changes of the atmospheric NO₂ amount or the atmospheric light path. In terms of RMS, TR1 is up to 3% larger (Fig. 6, bottom left). The main reason for this is probably the larger NO2 slant columns as associated effects like the wavelengthdependence of the NO₂ slant column (Pukite et al., 2010) were not compensated in this intercomparison exercise as discussed in Sect. 1.

Test TR2 yields results which are identical to TR0 am and TR1 pm values. This is not seen for any groups in Fig. 3 above, i.e. this option is apparently not present in any retrieval code. Not surprisingly, TR3 (averaging both zenith spectra) yields results which are between TR0 and TR2.

In contrast to noon reference tests, sequential references show no smooth behavior, neither for absolute, nor for relative differences (Fig. 6, right). The reason is that for each vertical scanning sequence (from which only the 2° elevation is shown here and in Fig. 3) another reference spectrum is used and consequently reference-related differences between groups are also changing from scan to scan. Note that almost no difference can be seen in Fig. 6 between TR4 and TR5 as the 2° elevation angle is shown here and consequently the closest zenith measurement in time is normally the one before the scan as IUPB measurements proceed from low to large elevations. TR8 (interpolation to the measurement time) resembles the sequential reference treatment normally implemented in the IUPB code, and thus the TR8 line is zero. For TR6 and TR7, absolute and relative differences (up to 8%) are remarkably similar to observed differences between groups using v1a fit settings, both in shape and in absolute values (compare to Fig. 5).

To conclude, the exact treatment of reference spectra is the major reason for observed NO_2 discrepancies between groups in Sect. 3, causing differences of up to 8%. Unfortunately, no clear recommendation can be derived from relative RMS differences in Fig. 6 (bottom right) as all lines scatter around zero. However, the relative difference in RMS can



Figure 7. Examples of different slit function treatments. Blue: Measured slit function (from HgCd line at ≈ 480 nm). Red: Fitting a Gaussian shape with $\mu = 0$. Light green: Akima interpolation of the red line to a finer 0.01 nm grid. Dark green: Interpolating first (linearly) to 0.01 nm and fitting a Gaussian shape afterwards.

be as large as 6% and in general, using a single zenith reference spectrum before or after the scan tends to produce larger RMS. However, while the reference treatment explains the majority of NO₂ disagreements, it cannot explain the large RMS differences (up to 100%) between groups.

4.2 Slit function treatment

The slit function distributed to intercomparison participants originated from HgCd line lamp measurements made in the night before 18 June 2013. It was pre-processed in terms of subtraction of the (also measured) dark signal, centered, and provided on an equidistant 0.1 nm grid.

While some groups used this slit function as is, other retrieval codes include a further *online* processing of the slit function, e.g. by fitting line parameters. In order to evaluate resulting differences, trace gas cross sections have been convolved off-line (before the fit) using different treatments of the slit function as summarized in Tab. 5. Again, the IUPB retrieval code NLIN has been used then performing the DOAS fit.

Examples of different treatments of the slit function are shown in Fig. 7. The original slit function is displayed in blue. If fitting a Gaussian shape to it, the maximum is not exactly centered around zero, pressumably caused by a small asymmetry. The slit function after fitting a Gaussian shape

Test	sub. offset	geom. centering	cutoff value	fit line parameters
TS0	no	yes	0.0	no
TS1	no	no	0.001	no
TS2	yes	no	0.001	no
TS3	no	yes	0.001	no
TS4	yes	yes	0.001	no
TS5	no	no	0.0	no
TS6	no	no	0.001	Gaussian
TS7	no	no	0.001	Gaussian ($\mu = 0$)
TS8	no	no	0.001	Gaussian ($\mu = 0$) fitted on 0.01 nm grid
TS9	no	no	0.0	Gaussian
TS10	no	no	0.0	Gaussian ($\mu = 0$)
TS11	no	no	0.0	Gaussian ($\mu = 0$) fitted on 0.01 nm grid

Table 5. Different treatments of the slit function.

and forcing centering (i.e. $\mu = 0$) is shown in red (as used in TS7 and TS10). Furthermore, performing a discrete convolution of cross sections requires the same wavelength sampling, i.e. the slit function has to be interpolated to the cross section grid, which was 0.01 nm. Here, an Akima interpolation has been applied (green line). However, if the original slit function is first linearly interpolated to the required 0.01 nm grid and then a Gaussian shape is fitted, a slightly different result is obtained, shown in dark green (as used in TS8 and TS11). Note that often not a discrete convolution but a (faster) convolution using Fourier transformation is implemented in DOAS retrieval codes (see below).

Fig. 8 shows resulting absolute and relative differences in NO_2 slant columns (top and middle) as well as relative differences of the fit RMS (bottom) w.r.t. the IUPB v1 fit (without I0-correction as this was not applied to the slit function test fits). The reference IUPB v1 fit uses an online convolution of cross sections using FFT and a further geometrical centering of the slit function is applied.

No difference between the reference fit, TS0 and TS5 is observed, neither for NO_2 nor for the RMS. In TS0, the same slit function treatment is applied as in the reference fit, but using discrete convolution instead of FFT, meaning that no difference arises due to the method of convolution. In addition, TS5 and TS0 are identical tests except for TS0 applying an explicit geometrical centering (i.e. centering the area) of the slit function. As this has no visible effect on NO_2 slant columns and RMS, the centering during pre-processing was already sufficient (or the nonlinear shift fit was compensating for small deficits in the slit function centering).

The largest impact on NO₂ (up to -1.3%) is seen for TS2 and TS4 which both subtract the smallest value from the slit function (i.e. forcing the slit function to be zero for the smallest value measured). This is usually not performed in DOAS fits and only advisable if instrumental stray light is a large problem or if the dark signal drifts which is normally not the case in state-of-the-art CCD detectors that are cooled and temperature-stabilised using Peltier elements. In contrast, the largest effect in terms of RMS (up to 6.5%) occurs not for TS2 and TS4, but for all tests using a fitted Gaussian. Interestingly, the Gaussian tests (TS6-TS11) show almost no difference among them in terms of RMS in the morning, but split up towards the evening. This might have to do with decreasing NO₂ slant columns in the afternoon or changes of the slit function during the day. In terms of NO₂, all tests using Gaussian slit functions yield smaller NO₂ slant columns of 0.2-0.7\%.

In addition to the basic Gaussian line parameters fitted here, some retrieval codes offer the possibility to fit more sophisticated line shape parameters taking into account potential asymmetry much better (the slit function in Fig. 7 shows indeed slight asymmetry). However, the exact implementations differ and were therefore not reproduced in the tests performed here, which can therefore be regarded as two extreme scenarios, namely (1) using the (original, slightly asymmetric) slit function as it is, or (2) fitting basic line parameters (a more sophisticated fit taking into account the slit function's slight asymmetry would clearly lead to a result in between these scenarios).

An important finding is that all performed tests lead to constant offsets in relative (and not absolute) NO_2 differences. In addition, all tests yield larger RMS than the reference fit using the measured slit function.

4.3 Intensity offset correction

Photons may hit the CCD detector at locations not corresponding to their wavelength (e.g. through scattering on mirrors, surfaces etc. inside the spectrometer) which produces an intensity offset, also called stray light. In addition, other effects such as changes in the dark current can lead to intensity offsets and the vibrational Raman scattering (VRS) is known to produce spectral effects that are very similar to intensity offsets (Peters et al., 2014; Lampel et al., 2015). In the DOAS fit, usually pseudo cross sections are included in order to compensate for intensity offsets. If the measured



Figure 8. NO₂ slant columns and RMS differences w.r.t IUPB v1 fit results in 2° elevation angle for different treatments of the slit function.

spectrum I is superimposed by a constant intensity C (which is the most simple assumption), the optical depth reads

$$-\tau = \ln\left(\frac{I+C}{I_0}\right) = \ln\left(\frac{I}{I_0}\right) + \ln\left(1+\frac{C}{I}\right)$$
$$\approx \ln\left(\frac{I}{I_0}\right) + \frac{C}{I}$$
(3)

with the Taylor expansion $\ln(1+x) \approx x$. Thus, in first approximation the intensity offset causes an additive term of optical depth that is proportional to 1/I, which is often used as a pseudo absorber (and showing large similarities to the Ring cross section as this compensates a filling-in of Fraunhofer lines).

However, often more sophisticated approaches are used. For example, the IUPB retrieval code NLIN allows either the simple implementation of $\sigma_{\rm off}=1/I$ or

$$\sigma_{\rm off} = \ln\left(\frac{I + C \cdot I_{\rm max}}{I}\right) \tag{4}$$

omitting the Taylor expansion in Eq. 3 and superimposing I by a certain constant C of the maximum intensity within the fit interval. In addition, sometimes also higher correction terms are used assuming that not only a constant superimposes the spectrum, but also a contribution changing with wavelength (in which case often λ/I is included in the DOAS fit). Furthermore, sometimes the offset is not included in the linear DOAS fit, but fitted nonlinearly (this is not included in tests performed here).

Different implementations summarized in Tab. 6 were tested in order to evaluate the influence of the intensity offset correction. Fig. 9 shows resulting absolute and relative differences of NO_2 slant columns and RMS values. Again, the reference for these differences is the IUPB v1 (noon) fit.

No difference in NO₂ or RMS is seen between TI0 and the v1 fit as both fits use the same simple approach of $\sigma_{\text{off}} = 1/I$. In contrast, TI1 uses $1/I_0$. In terms of NO₂ differences, the TI1 line follows slightly the shape of total fit RMS and NO₂ slant columns (compare to Fig. 3). Interestingly, while the

disagreement of TI1 w.r.t the reference fit is on average $\approx 2\%$ for NO₂, the first data point is clearly off by almost 10% for NO_2 and 60% for RMS. This agrees perfectly with the observed outlier in the INTA analysis (compare to Fig. 3), i.e. the reason for this disagreement could be identified as a different offset implementation (which has been verified by INTA). The SZA and the sun azimuth angle (SAA) of this measurement are $\approx 90^{\circ}$ and 58° (from north), respectively, while the instrument's elevation angle is 2° and the azimuthal viewing direction 51° , i.e. the instrument was pointing close to the rising sun. Enhanced stray light in the spectrometer (caused by the large contribution of photons at longer wavelengths while observing the red sky during sunrise) seems plausible and using 1/I is a better choice for compensation. It was verified (not shown) that the fit coefficient of the offset (also called the offset slant column) is particularly large not only in this but also in adjacent measurements and a color index indicated that these spectra are indeed more reddish. However, these measurements could also be affected by direct sunlight in the instrument, which is known to increase RMS (e.g. due to polarization issues). Fig. 3f demonstrates that the respective measurement is affected by a very large RMS (potentially caused by a combination of direct light and stray light).

TI2 and TI3 are more sophisticated approaches (Eq. 4) based on either I or I_0 . However, the resulting lines follow largely TI0 and TI1 (simple approaches). Unexpectedly, both TI2 and TI3 lead to larger RMS values for the sunrise measurement in the morning where the simple approach performs better.

The total effect of using an intensity offset compensation is evaluated by TI4 which includes no offset correction. The resulting effect on NO₂ is almost the same as TI1 and TI3 (based on I₀) leading to the clear recommendation of using an offset compensation based on *I* instead of I_0 , which is supported by largely increased RMS values of TI4 (Fig. 9 bottom).

An intensity offset correction of first order (i.e. a term varying linearly with λ in addition to a constant term) was tested in TI5, which is in practice often used not only for intensity offsets but also for compensation of the wavelengthdependence of the Ring slant column. The resulting NO₂ differences w.r.t. the reference fit (or TL0) are small with the exception of the first data point that is slightly off. In terms of RMS, TI5 leads to improvements of $\approx 20\%$ in the morning. Interestingly, the TI5 RMS line shows some similarities to the IUPHD-IUPB line in Fig. 3d. However, no first order offset was included in the IUPHD fit, i.e. the offset implementation is not causing the observed similar shape in the morning (and the reason remains unclear). This is supported by increasing IUPHD RMS values in the evening in Fig. 3d, which are not present in TI5.

Fit TI6 includes again only a 0th order intensity offset, but a pseudo cross section accounting for the wavelengthdependence of the Ring slant column was added (the Ring

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Table 6. Tests performed for different implementations of the intensity offset correction (and I_0 correction). A 0th order offset correction means applying a constant term only, a first order correction means applying a constant and slope term.

Test	Offset order	Offset approach	I ₀ -correction
TI0	Oth	1/I	yes
TI1	0th	$1/I_0$	yes
TI2	0th	Eq. 4 using I	yes
TI3	0th	Eq. 4 using I_0	yes
TI4	None	No offset correction	yes
TI5	1st	$1/I, \lambda/I$	yes
TI6	Oth	1/I, additionally Ring $\cdot\lambda$	yes
TI7	0th	1/I (simple approach)	no

cross section was multiplied by λ and orthogonalized against the original cross section). The resulting RMS is indeed almost identical to TI5 (using a first order intensity offset) while the NO₂ is identical to TI0, i.e. the outlying first data point which is still partially present in TI5 disappeared in TI6. Thus, using a pseudo-cross section for compensation of the Ring wavelength-dependence seems preferable compared to using a first order intensity offset correction.

4.4 I₀-correction

In addition to the intensity offset tests, the effect of inclusion of an I_0 -correction was evaluated in TI7 (which is identical to TI0 except for the I_0 -correction, see Tab. 6). The respective line is shown in addition to the intensity offset investigations in Fig. 9. The I_0 -effect adresses the problem that the limited instrument's resolution can cause an incomplete removal of Fraunhofer structures in the vicinity of strong narrow-banded absorption bands (Johnston, 1996; Wagner et al., 2001; Aliwell et al., 2002).

Only a very small constant offset in relative NO₂ slant column differences is obtained in TI7 ($\approx 0.25\%$, which is almost invisible in Fig. 9, middle). In terms of RMS, exclusion of the I_0 -correction leads up to 20% increased RMS, which is comparable to different treatments of the intensity offset correction. Thus, inclusion of an I_0 -correction is recommended in polluted environments such as the MAD-CAT site. It should be noted that the first data point is not an outlier in TI7, i.e. it is not sensitive to the I_0 -correction.

4.5 Numerical methods (linear DOAS inversion)

The DOAS equation (Eq. 1) is a linear inverse problem

$$\mathbf{A} \mathbf{x} = \mathbf{b} \tag{5}$$

with the vector \mathbf{x} (size n) containing the n trace gas slant columns and polynomial coefficients of interest, the vector $\mathbf{b} = \ln(\frac{I_0}{I})$ (size m) containing the measured optical depths at m wavelengths, and the $m \times n$ DOAS matrix \mathbf{A} with



Figure 9. Absolute (top) and relative (middle) NO₂ slant column differences, and relative RMS differences (bottom) w.r.t. IUPB v1 fit results in 2° elevation angle resulting from different implementations of the intensity offset correction (and I₀ correction).

Table 7. Different methods tested for solving the linear DOAS equation A x = b.

Test	Retrieval code	Spectral grid	Method	Remarks
Reference TL0 TL1 TL2	NLIN Python Python Python	$\begin{matrix} I_0 \\ I_0 \\ I_0 \end{matrix}$	Pseudo-inverse of \mathbf{A} using SVD Pseudo-inverse of \mathbf{A} using SVD Solving quadratic $\mathbf{A}^{T}\mathbf{A}\mathbf{x} = \mathbf{A}^{T}\mathbf{b}$ using LU decomposition Invert $\mathbf{A}^{T}\mathbf{A}$ using LU decomp.	following Press (1989)
TL3 TL4	Python Python	0.01 nm 0.01 nm	same as TL0	linear interpolation to 0.01 nm cubic spline interpolation to 0.01 nm

columns consisting of absorption cross sections and polynomial terms (1, λ , λ^2 , etc.) for the m wavelengths.

Different numerical methods exist to solve Eq. 5 for x. As A is non-square, no inverse exist. However, most re-



Figure 10. Absolute (top) and relative (middle) NO₂ slant column differences, and relative RMS differences (bottom) w.r.t. IUPB v1 results (only linear fit) in 2° elevation angle resulting from different numerical methods solving the linear DOAS equation.

trieval codes calculate a pseudo-inverse A^{-1} (almost) fulfilling $A^{-1}A = I$ (identity matrix) using a singular value decomposition (SVD) and obtain the slant columns of interest by $\mathbf{x} = A^{-1}$ b. This method is frequently recommended for solving overdetermined linear inverse problems in terms of least squares (see e.g. Press, 1989).

However, after multiplying Eq. 5 with A^{T} , the matrix $A^{T}A$ is quadratic and can be decomposed into an upper and a lower triangular matrix, L and U. The linear inverse problem

$$\mathbf{A}^{\mathbf{T}}\mathbf{A}\mathbf{x} = \mathbf{L}\mathbf{U}\mathbf{x} = \mathbf{A}^{\mathbf{T}}\mathbf{b}$$
(6)

can be solved then by forward substitution obtaining y from $\mathbf{L} \mathbf{y} = \mathbf{A}^{T} \mathbf{b}$ and backward substitution obtaining x from $\mathbf{U} \mathbf{x} = \mathbf{y}$.

Furthermore, $\mathbf{A}^{T}\mathbf{A}$ can also be directly inverted, normally by LU decomposition as well. The vector of slant columns is then obtained by $\mathbf{x} = (\mathbf{A}^{T}\mathbf{A})^{-1} \mathbf{A}^{T} \mathbf{b}$. As the inversion takes normally much more computational steps, this method is known to be subject to roundoff errors, and therefore not recommended (Press, 1989).

The influence of these different numerical methods on resulting slant columns could not be easily tested with the IUPB retrieval code and was thus evaluated in a Python script solving the DOAS equation using the same input (spectra, cross sections). Python (which is a well-established programming language in scientific computing) provides numerous different routines within its *numpy* and *scipy* packages (based on different subroutines from the *LAPACK* package, *http://www.netlib.org/lapack/*) that were tested for solving the DOAS equation. All performed tests are summarized in Tab. 7. Again, differences of NO₂ slant columns and fit RMS have been calculated with respect to the IUPB v1 fit results (i.e. using NLIN). In order to restrict differences to the influence of numerical approaches only, the same slit function treatment as the IUPB retrieval code NLIN was applied in

the Python script and the same (noon) reference spectrum was used. In addition, no further wavelength calibration, i.e. no nonlinear shift and squeeze fit was performed (neither in the Python script nor in the NLIN reference fit used here) and no I_0 -correction was included. The test results are shown in Fig. 10, again for the 2° elevation angle.

Results of test TL0 appear to be identical to the reference fit of the IUPB retrieval code, both using a SVD for inversion of the DOAS matrix. However, very small differences exist between TL0 and the reference fits (too small to be seen on the scale of Fig. 10), which are < 0.006% for NO₂ slant columns and < 0.07% for RMS. These tiny disagreements can be attributed to numerical differences in programming languages.

TL1 and TL2 yield identical NO₂ slant columns (both are using an LU decomposition) which differ from SVD results by up to 0.7%. However, the RMS from TL2 was found to be an order of magnitude larger compared to the other tests and is therefore not shown in Fig. 10 (bottom). This is most likely due to problems mentioned above, i.e. this finding is in agreement with common recommendations in textbooks. Interestingly, both TL1 (and TL2) NO₂ and RMS lines (which are differences w.r.t. IUPB) are similar in shape to the total fit RMS (compare to Fig. 3f). Thus, when the RMS increases, SVD inversion and LU decomposition lead to larger disagreements, both in RMS and NO₂. As the SVD yields smaller RMS values, it seems to be preferable, although the obtained improvement is only about 2.5%.

Numerical differences may be obtained when performing the linear DOAS fit (Eq. 5) on another wavelength grid. Changes of the grid potentially arise from the wavelength calibration. Some retrieval codes (e.g. NIWA) also use an internal, equidistant wavelength grid. To test the effect of changes in the wavelength grid, the TLO fit was repeated on an equidistant 0.01 nm grid (i.e. I, I_0 , and cross sections were interpolated to 0.01 nm before solving Eq. 5). TL3 and TL4 are identical to TL0, but a linear interpolation was applied in TL3, while TL4 uses a cubic spline interpolation to 0.01 nm. Apparently, this results in a constant offset in relative NO_2 differences, which is seen most clearly in the TL3 line in Fig. 10 (middle). The resulting constant shift is $\approx 0.4\%$ for TL3, but only $\approx 0.02\%$ for TL4 meaning that the type of interpolation to the equidistant grid is of importance and the spline interpolation (not surprisingly) seems to resemble the spectrum better than a linear interpolation. However, using different wavelength grids might for example explain some of the observed differences between IUPB and NIWA, which were found to be constant in relative differences as well. In terms of RMS, the computation on an equidistant 0.01 nm grid using linear interpolation behaves on average even a bit better (up to 1%). However, no recommendation can be drawn from this as discussed above.

4.6 Nonlinear wavelength calibration

As mentioned in Sect. 2.3, the spectra provided from the IUPB instrument were pre-calibrated using nightly HgCd line lamp measurements, which provide accuracies better than 0.1 nm. However, usually a post-calibration is included in DOAS retrieval codes in order to increase the fit quality (reducing RMS). This wavelength calibration is implemented in different ways in participating retrieval codes. Most groups calibrate the reference spectrum I_0 to a high resolution Fraunhofer atlas, apply the resulting calibration to all measured spectra, and allow in addition a shift and squeeze between I and I_0 in order to compensate spectral shifts of the spectrometer during the day, e.g. caused by temperature changes (KNMI uses a slightly different definition of the shift as discussed below). This nonlinear shift and squeeze fit of the wavelength axis is mostly implemented in an iterative scheme together with the linear DOAS fit on $\ln(I_0/I)$. However, codes differ for example in whether trace gases are included in the shift and squeeze fit of I_0 to the high resolution Fraunhofer atlas. Sometimes also a higher order calibration is allowed or several sub-windows are used in order to characterize differently different parts of the spectra.

Tab. 8 summarizes tests performed to investigate the impact of different wavelength calibration approaches using the IUPB retrieval code NLIN. In addition, some tests were performed with the Python script form Sect. 4.5 which has therefore been extended to perform the nonlinear shift fit as not all tests could be easily implemented in the comprehensive NLIN software. Note, in contrast to the shift, the squeeze has been excluded from the intercomparison as it was found to be always 1.0 for measurements shown here. Also QDOASspecific implementations were not tested here.

Fig. 11 shows the resulting impact on NO₂ and RMS as well as the fitted shift between I and I_0 (not present in all tests). NO₂ and RMS are again differences relative to the IUPB v1 fit results (without I_0 -correction as this was not implemented in the Python routine). As in Fig. 3, the shift in Fig. 11d is no difference, and for comparison the shift from the reference fit is shown explicitly in black. The (fixed) shift retrieved from the nonlinear fit of I_0 to the Fraunhofer atlas is -0.035 nm. This is roughly a factor of 10 larger than the fitted shift between I and I_0 shown in Fig. 11d. It is interesting to note that the shift is not zero around noon (time of the reference spectrum), indicating correlations between shift fit and other effects (predominantly intensity offset correction) and also indicating the presence of the tilt effect (Lampel et al., 2017).

The most extreme test is TW0 which excludes both the calibration of I_0 to the Fraunhofer atlas as well as the shift between I and I_0 . When omitting both calibration steps, the RMS is largely enhanced by up to 80% peaking in the morning and decreasing towards noon with a second smaller maximum around 12 UT. Interestingly, a very similar shape is seen in the RMS differences of KNMI, NUST, UNAM,

Table 8. Different wavelength calibration approaches evaluated.

Test	Retrieval code code	Shift I_0 to Fraunhofer atlas	Shift I to I_0	Remarks
Reference	NLIN_D	yes	yes	Alternating scheme, v1 fit settings
TW0	NLIN_D	no	no	Linear DOAS fit only
TW1	NLIN <u></u> D	no	yes	
TW2	NLIN_D	yes	no	
TW3	Python	yes	yes	same a TW0
TW4	Python	yes	yes	same a TW3, but linear interpolation
TW5	Python	yes	yes	same a TW3, all trace gases included in Fraunhofer I_0 fit



Figure 11. Absolute (a) and relative (b) NO₂ slant columns differences, and relative RMS differences (c) in 2° elevation angle resulting from different wavelength calibration approaches (Tab. 8). Corresponding shifts between *I* and *I*₀ resulting from nonlinear fits are shown in (d).

USTC and INTA (but not in INTA2 correcting a fault in the wavelength registration module) in Fig. 3d. Although all of these groups are performing a wavelength calibration, TW0 indicates that differences in the calibration procedure are causing most of the disagreements between groups in terms of RMS. This is in contrast to NO_2 where changes of only 0.4% are obtained from TW0.

TW1 still excludes the absolute calibration to the Fraunhofer atlas, but includes the shift fit between I and I_0 . As seen before, the impact on NO₂ is very small ($\approx 0.4\%$), but absolute NO₂ differences of TW1 reflect the shape of total RMS and NO₂ slant columns (compare to Fig. 3), i.e. the relative differences are smooth in shape. The RMS is similar in shape as TW0, but the morning maximum is slightly later at 7 UT, the noon maximum around 11 UT and a small maxi-

mum in the evening occurs at 18 UT. This shape is similar to the relative RMS of NUST, UNAM, and NIWA in Fig. 3, but absolute numbers are different. However, this behaviour indicates that differences in the fitted Fraunhofer shift are partially responsible for observed differences between these and other groups. Interestingly, the fitted shift between I and I_0 of TW1 in Fig. 11d is very similar to corresponding values of the reference fit, which is because the missing Fraunhofer shift is a different effect than the shift between I and I_0 .

In contrast to TW1, TW2 includes the Fraunhofer shift fit, but excludes the shift between I and I_0 . As this is the larger effect (-0.035 nm compared to only \approx 0.004 nm), the RMS is much smaller than in TW1 with a single maximum (up to 50%) in the early morning at 6 UT. The RMS timeseries shape is similar to the KNMI line in Fig. 3. The reason is a

different definition of the shift in the KNMI retrieval: While in most retrievals I is shifted relative to I_0 , KNMI calculates the optical depth $\tau = \ln(I_0/I)$ without any shifts but allows then a shift of all cross sections relative to τ . This is in first order compensating the effect of the Fraunhofer shift but neglecting potential shifts between I and I_0 (in this case Fraunhofer lines would not cancel out completely in the optical depth τ). As a result, the KNMI approach is similar (but not identical) to TW2. The fit quality following the KNMI approach is expected to be better using a sequential reference as the temperature drift of the spectrometer is much smaller then. It has to be mentioned that the change of NO₂ in TW2 is small (0.3%) compared to the change in fit RMS (50%).

TW3 uses the same wavelength calibration treatment as the IUPB reference fit, but is performed in another programming code (Python) evaluating how much difference is caused by use of another programming code and numerical issues. The fitted shift is mostly identical to the reference fit except for the early morning and late evening when also the NO₂ shows very slight differences. The largest disagreement of NO₂ is 0.2% for the first measurement of the day that was affected by large stray light effects (and potentially direct light) and thus most likely indicating cross-correlations between shift fit and intensity offset correction. The resulting RMS is almost identical to the reference fit (Fig. 11c).

TW4 is the same as TW3 but the spline interpolation (calculating I at spectral points of I_0 during the nonlinear shift fit) is replaced by a simple linear interpolation. The fitted shift is changed slightly and NO₂ differences are of almost the same order than when not performing any shift fit at all demonstrating that the shift fit has a negligible impact on NO₂. In contrast, it has a large impact on RMS, where the marginally different methods between TW3 and TW4 produce the same RMS while the effect of excluding the shift completely leads to largely enhanced RMS.

In the Fraunhofer calibration of the reference fit using NLIN (nonlinear shift fit of I_0) as well as in TW3 all trace gas absorptions are omitted, i.e. an iterative scheme between shift fit and DOAS fit comprising only a polynomial of order 4 is applied. In contrast, all trace gas absorptions are included in the Fraunhofer calibration in TW5. As a result, the RMS of the DOAS fit between Fraunhofer spectrum and I_0 is reduced by a factor of 2 and the nonlinearly fitted shift is -0.031 nm instead of -0.035 nm in the reference fit. However, this has only a marginal influence on NO₂, RMS and fitted shift between I and I_0 in Fig. 11 and consequently explains none of the observed differences between groups.

Notably, all shifts (even TW1) in Fig. 11d show the same general shape that is also retrieved by most groups in Fig. 3. Only shifts of KNMI clearly differ, for the reasons mentioned above. RMS shapes in Fig. 11c suggest that differences in the wavelength calibration are the major reason of observed RMS disagreements between groups in Fig. 3.

5 Summary and conclusions

An intercomparison of DOAS retrieval codes using measured spectra from the same instrument during the MAD-CAT campaign and harmonized fit settings was performed. Excellent agreement was found between different DOAS fit algorithms from 17 international groups. In some of the retrieval codes, faults were identified and corrected in the course of the study leading to even better agreements. For noon reference fits, the correlation in terms of NO₂ slant columns was found to be larger (> 99.98%) than for sequential references (> 99.2%), which is caused by different implementations of the sequential reference.

Despite of the excellent overall correlation, for individual measurements in low elevations differences of up to 8% in resulting NO₂ slant columns were observed, which is up to 2-3 times larger than corresponding typical NO₂ slant column errors. In terms of fit RMS, large differences of up to $\approx 100\%$ were found.

Interestingly, groups using the same retrieval code (QDOAS groups) do not always produce results showing the same systematic behavior, which is the result of different options - other than the harmonization settings agreed on - users select. This has some impact for the interpretation of other studies as the extent of prescribed fit settings in this study is comparable to intercomparison campaigns like CINDI or CINDI-2. Consequently, groups participating in those campaigns will provide intrinsic differences in their results due to non-harmonized (detailed) settings even if using the same retrieval code, which have to be expected in the same range as observed here.

Comprehensive sensitivity studies systematically investigating effects of the non-harmonized retrieval aspects were performed in order to (1) attribute observed differences between groups to certain sources, and (2) evaluate the impact of each of these sources on NO₂ slant columns and fit RMS. For this purpose, five reasons were identified in a survey of participating retrieval codes. Typical impacts on NO₂ slant columns and RMS are summarized in Tab. 9.

In general, the wavelength calibration and the intensity offset correction were found to produce the majority of observed RMS differences, but have a negligible impact on NO₂ slant columns (< 0.4%, resp. < 2% except for the first measurement of the day affected by stray light and possibly direct light in the telescope). In contrast, the reference selection explains the majority of observed NO₂ slant column differences between groups while having a minor impact on the RMS. Thus, if harmonization of NO₂ slant columns is of interest, the reference treatment needs to be harmonized (otherwise in small elevation angles differences of up to 8% - and even more for larger elevation angles due to decreasing absolute slant columns - have to be expected predominantly in the case of using a sequential reference) while for RMS reduction/harmonization, the offset intensity correction and the wavelength calibration need to be harmonized.

Reason for disagreement	ΔNO_2 (%)	ΔRMS (%)	Remarks
Reference treatment (noon)	2.5	3	Produces constant absolute NO ₂ SC offsets.
Reference treatment (seq.)	8	6	
Slit function treatment	1.3	6.5	Produces constant relative NO ₂ SC offsets.
Intensity offset correction	2 (typically)	20 (typically)	
	10 (outlier)	60 (outlier)	
I ₀ correction	0.25	20	Produces constant relative NO ₂ SC offsets.
Numerical methods	0.3 (0.7)	2.5	Produces constant relative NO ₂ SC offsets.
(for linear DOAS fit)			Disagreements increase with RMS.
Wavelength calibration (nonlinear shift fit)	0.4	up to 80	

Table 9. Summary of performed sensitivity tests and associated impacts on NO₂ slant columns and RMS.

In terms of NO₂, two types of disagreements have been observed, which are (1) constant in absolute, or (2) constant in relative differences. The latter was found to arise from the numerical approach used for solving the DOAS equation as well as the treatment of the slit function while the choice of the reference spectrum causes absolute differences.

Best practices aiming at improvement of the fit quality and harmonization between MAX-DOAS retrievals derived from this study are:

- Reference treatment: Using averaged or interpolated sequential reference spectra matches the atmospheric conditions at the measurement time better and was found to produce slightly smaller RMS.
- 2) Slit function: Using a measured slit function performed better than fitting line parameters in the data set used here. However, slit function measurements then have to be performed regularly (e.g., daily to monitor possible instrument changes).
- 3) Intensity offset: An approach based on I instead of I_0 is recommended. Surprisingly, the simple approach performs better for measurements pointing close to sunrise but this could be just a coincidence in this data set. Inclusion of an additional Ring spectrum multiplied by wavelength is preferred over adding a linear term to the offset as this mostly compensates the wavelength-dependence of the Ring slant column.
- Numerical approaches: Using an SVD is most stable and produces slightly smaller RMS than LU decomposition.
- 5) Wavelength calibration: Although HgCd line lamp calibration measurements lead to absolute accuracies (in this case) of ≈ 0.03 nm, a Fraunhofer shift fit reduces the RMS by up to 40-50%. For the I_0 fit w.r.t. the Fraunhofer spectrum, inclusion of all trace gases showed no advantage over inclusion of a polynomial only. Temperature instabilities of the spectrometer produced shifts of I relative to I_0 changing over the day. Compensation

of this effect within DOAS retrieval codes further improves the RMS by up to 40-50% when using a noon reference spectrum.

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Investigating differences in DOAS retrieval codes using MAD-CAT campaign data

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Abstract. The Differential Optical Absorption Spectroscopy (DOAS) method is a well-known remote sensing technique that is nowadays widely used for measurements of atmospheric trace gases, creating the need for harmonization and characterization efforts. In this study, an intercomparison exercise of DOAS retrieval codes from 17 international groups is presented focusing on NO_2 slant columns. The study is based on data collected by one instrument during the Multi-Axis DOAS Comparison campaign for Aerosols and Trace gases (MAD-CAT) in Mainz, Germany, in summer 2013. As data from the same instrument is used by all groups, the results are free of biases due to instrumental differences, which is in contrast to previous intercomparison exercises.

While in general an excellent correlation of NO₂ slant columns between groups of > 99.98% (noon reference fits), and 5 > 99.2% (sequential reference fits) for all elevation angles is found, differences between individual retrievals are as large as 8% for NO₂ slant columns and 100% for RMS residuals in small elevation angles above the horizon.

Two kinds of disagreements were identified: (1) Absolute Comprehensive sensitivity studies revealed that absolute slant column differences were found to result predominantly from the choice of the reference spectrum . (2) Relative differences were found to while relative differences originate from the numerical approach for solving the DOAS equation as well as

- 10 the treatment of the slit function. Differences in the implementations Furthermore, differences in the implementation of the intensity offset correction lead to disagreements for retrievals was found to produce disagreements for measurements close to sunrise (8-10% for NO₂, 80% for RMS residual). Apart from this, the The largest effect of \approx 8% difference in NO₂ was found to arise from the reference treatment, in particular for fits using a sequential reference. In terms of RMS fit residual, the reference treatment has only a minor impact. In contrast, the wavelength calibration as well as the intensity offset correction
- 15 were found to have the largest impact (up to 80%) on RMS residual while having only a minor impact on retrieved NO₂ slant columns.

1 Introduction

In this study, the consistency of Differential Optical Absorption Spectroscopy (DOAS) retrievals of tropospheric nitrogen dioxide (NO_2) from ground-based scattered light observations is evaluated. NO_2 is released into the atmosphere predominantly

- in the form of NO as a result of combustion processes at high temperatures. Through reaction of NO with ozone (O_3) , NO₂ is rapidly produced and (during the day) back-converted into NO by photolysis. Therefore, nitrogen oxides are often discussed in terms of NOx (NO + NO₂ = NOx). NO₂ is a key species in the formation of tropospheric ozone and a prominent pollutant in the troposphere, causing (together with aerosols) the typical brownish colour of polluted air. In addition, it is harmful for lung tissue and a powerful oxidant. In the lower troposphere, the lifetime of NO₂ is short (several hours) due to reaction with
- OH and photo-dissociation, and thus it is found mostly close to its sources, making it a good tracer of local pollution. Both anthropogenic sources such as burning of fossil fuel in industry, power generation, and traffic as well as biogenic sources including bush and forest fires contribute to the tropospheric NOx loading. In addition, NO₂ is released from soil microbial processes and lightning events (Lee et al., 1997). As a result, high NO₂ amounts are mostly observed above industrialized and urban areas, traffic routes and over bush fires.

30 Using its characteristic absorption bands in the UV and visible spectral range, NO₂ has been successfully measured for many years using the DOAS technique (Brewer, 1973; Noxon, 1975; Platt, 1994) both from the ground and from space (e.g. Richter et al., 2005; Beirle et al., 2011). In addition, airborne and car-based measurements (e.g. Schönhardt et al., 2015; Shaiganfar et al., 2011), have been performed to close the gap between ground-based observations providing continuous temporal, but poor spatial resolution and satellite measurements which offer global observations, but only up to one measurement per day above each location. Using ground-based multi-axis (MAX)-DOAS measurements at different elevation angles, a more accurate vertical column (VC) can be retrieved with information on the vertical distribution of NO₂ and other trace gases in the troposphere (e.g. Hönninger et al., 2004; Wittrock, 2006; Frieß et al., 2011; Wagner et al., 2011).

- As result of the viewing geometry, ground-based MAX-DOAS observations are most sensitive to the lowest layers of the troposphere. Here they provide high sensitivity and low relative measurement errors. Averaging over longer integration times can further reduce statistical noise. Another advantage is that MAX-DOAS stations can be operated automatically and usually require little maintenance. MAX-DOAS measurements were therefore performed in remote regions for the investigation of background concentrations and in many locations for the validation of satellite observations (e.g. Takashima et al., 2012;
- 10 Peters et al., 2012).

There currently exists a variety of different instruments and retrieval codes designed to perform and analyse MAX-DOAS measurements. While the basic approaches are similar, differences exist which can potentially lead to inconsistencies in measurements from different instruments and retrievals. As this is an important limitation for the use of MAX-DOAS measurements in a global observing system, the Network for the Detection of Atmospheric Composition Change NDACC (formerly known

15 as NDSC) has organised several intercomparison campaigns aimed at comparing instruments, retrievals, and uncertainties of a wide range of DOAS instruments. The first of these campaigns were focused entirely on zenith-sky observations for stratospheric absorbers (Hofmann et al., 1995; Vaughan et al., 1997; Roscoe et al., 1999) but later also included other viewing directions (Vandaele et al., 2005). The Cabauw Intercomparison of Nitrogen Dioxide Measuring Instruments (CINDI) cam-



Figure 1. NO_2 slant columns and fit residual root mean square (RMS) obtained from the IUPB retrieval code for the intercomparison day used in this study. Different elevation angles are color-coded. The fit settings correspond to v1 settings as described in Sect. 2.4 (Tab. 1).


Figure 2. (a) Example of the fitted NO₂ <u>differential</u> optical density in 2° elevation angle at 14:40 UT corresponding to a slant column of \approx 7E16 molec/cm² (compare Fig. 1). The solid line is the NO₂ <u>differential</u> optical density (= differential cross section, i.e. the cross section after subtraction of a fitted polynomial, multiplied by the retrieved slant column) and the dashed line is the solid line plus the fit residual. The NO₂ <u>differential</u> optical density is much larger than the residual, which is explicitly shown in (b).

paign in 2009 in Cabauw, the Netherlands was the first to also have a focus on MAX-DOAS observations of tropospheric species (Roscoe et al., 2010; Piters et al., 2012; Pinardi et al., 2013) and has recently been followed by the CINDI-2 campaign performed in 2016, also in Cabauw. However, these intercomparison exercises concentrated mostly on results originating from different retrieval codes and instruments, and separation of instrument and retrieval effects was not easily possible. In some

5 cases, synthetic spectra were used to intercompare retrieval algorithms, and while such tests can highlight differences between retrieval approaches, they give no insight into the way different retrieval codes deal with instrumental effects such as intensity offsets, resolution changes or spectral drifts.

The present study was performed in the framework of the European FP7 project QA4ECV (Quality Assurance for Essential Climate Variables) which aims at providing quality assurance for satellite derived ECVs such as NO₂, HCHO and CO by

- 10 characterizing the uncertainty budgets through uncertainty analysis and error propagation but also by validation with external data sets. In this context, ground-based MAX-DOAS measurements can play an important role, and harmonisation of the retrieval approaches and quality assurance for the reference measurements are needed. The results of the analysis performed in the QA4ECV project are expected to contribute to the harmonisation of data from MAX-DOAS instruments, in particular for the ongoing integration of such measurements in the NDACC network.
- 15 The work reported here overcomes limitations from previous studies by using real measurements originating from a single instrument, facilitating. This facilitates the study of the agreement between different retrieval codes on real data without

instrumental biasbiases between results from different groups. The intercomparison was performed on spectra recorded by the University of Bremen (IUPB) instrument during the Multi-Axis DOAS Comparison campaign for Aerosols and Trace gases (MAD-CAT) carried out in Mainz, Germany, in summer 2013 (http://joseba.mpch-mainz.mpg.de/mad_cat.htm). Data was distributed to 17 international groups working on ground-based DOAS applications. Each group analysed these spectra using

- 5 their own DOAS retrieval code but prescribed fit settings for fitting window, cross-sections, polynomial and offset correction. Resulting slant columns from all groups were then compared to IUPB results chosen as the arbitrary reference, evaluating the level of agreement and systematic differences and investigating their algorithmic origins. With this set-up, nearly all sources of disagreement were removed, and only those differences between retrieval codes were investigated which are not usually reported.
- 10 This intercomparison exercise concentrates on one day (18 June 2013) during the MAD-CAT campaign having the best weather and viewing conditions. As an example, Fig. 1 shows NO₂ slant columns (left) and fit RMS residual (right) retrieved with the IUPB software. It is nicely seen that NO₂ slant columns measured at different elevation angles are separated as a result of differences in the light path. It should be mentioned that NO₂ slant columns are relatively large as a result of anthropogenic pollution at the densely populated and industrialized measurement location and thus the findings of this study correspond to
- 15 polluted urban environments. However, these are normally the ones of interest for NO₂ observations. Fig. 1 also shows that the RMS of the fit residuals (in the following simply denoted as RMS) separates with elevation angles as well. In addition, the shape of the RMS in small elevation angles is very similar to that of NO₂ slant columns, indicating that predominantly NO₂ related effects such as the wavelength dependence of the NO₂ AMF (which was not included in the fit shown here) limit the fit quality (note, this study aims not at finding best NO₂ fit settings but studying disagreements originating from different retrieval
- codes). This is supported by the observation that the shape of NO_2 slant columns is not seen in the RMS for larger elevation angles as effects related to the NO_2 absorption are smaller and other effects limiting the fit quality dominate. In addition, the RMS is very large in the early morning for small elevations, which is discussed in detail later and results from pointing towards sunrise. However, in general NO_2 is retrieved very accurately as Fig. 2 demonstrates, showing the NO_2 optical density and fit residual for a measurement in 2° elevation angle (this is a typical example fit).
- The manuscript is structured in the following way: Sect. 2 provides details about the MAD-CAT campaign, the measurements, and measurements, the NO₂ intercomparison exercise as well as participating retrieval codes. The comparison between results from the different groups is Intercomparison results between groups are presented in Sect. 3. Sect. 4 attempts Sensitivity studies of non-harmonized retrieval aspects attempting to reproduce observed differences between groups using the IUPB retrieval code with different settings in order to identify and quantify sources of disagreements and evaluating the impact on
- 30 NO₂ slant columns and DOAS fit quality are performed in Sect. 4. The manuscript ends with a summary conclusions and recommendations for better harmonization of ground-based MAX-DOAS measurements.

2 Measurements

2.1 DOAS technique

The DOAS technique is based on Lambert-Beer's law which describes the attenuation of light passing through a medium. Here, it is applied to measurements of scattered sunlight. The spectral attenuation caused by scattering is smooth in wavelength (e.g.,

- 5 λ^{-4} -dependence for Rayleigh scattering) while molecular absorption often has structured spectra. In DOAS, the total spectral attenuation is therefore split into a high-frequency part consisting of the (high-frequency components of) trace gas absorptions and a low-frequency part accounting for elastic scattering which is described by a low-order polynomial also compensating for intensity changes, e.g. caused by clouds. In addition, the effect of inelastic scattering, which is predominantly due to Rotational-Raman-Scattering known as the Ring effect (Shefov, 1959; Grainger and Ring, 1962) is accounted for by a pseudo
- 10 cross section (e.g. Vountas et al., 1998). Similarly, intensity offsets mostly resulting from stray light within the spectrometer are accounted for by pseudo cross sections σ_{off} (see Sect. 4.3 for more details). In total, the optical depth τ is approximated by

$$\tau = \ln\left(\frac{I_0}{I}\right) = \sum_i \sigma_i \cdot SC_i + \sigma_{\text{Ring}} \cdot SC_{\text{Ring}} + \sigma_{\text{off}} \cdot SC_{\text{off}} + \sum_p a_p \lambda^p + r \tag{1}$$

where the first sum is over all *i* absorbers having cross section σ_i, the polynomial degree is *p*, and the residual term *r* contains the remaining (uncompensated) optical depth. An important quantity used within this study to identify and evaluate differences
between DOAS retrieval codes is the root mean square of the fit residual *r* (for simplicity denoted as RMS in the context of this study), which is a measure of the fit quality. In Eq. 1, known as the *DOAS equation*, all quantities with the exception of *a_p* depend on wavelength λ. For tropospheric absorbers, the spectrum *I* is normally taken at small elevation angles above the horizon where the tropospheric light path is large. The reference spectrum *I*₀ is normally a zenith spectrum either at small solar zenith angle (SZA), which is in the following called a noon reference fit, or close in time to the measured spectrum *I*, in the

20 following called a sequential reference fit.

25

The DOAS equation is usually an over-determined problem (τ is measured at more wavelengths λ than unknowns exist in Eq. 1) and solved by means of a least-squares fit (see also Sect. 4.5), i.e. minimizing the residual term. The resulting fit factors are the polynomial coefficients a_p and the so-called slant columns SC_i , which are the quantities of interest. The slant column is the integrated concentration ρ_i of absorber *i* along the effective light path *s* (for simplicity we use the SC also for the fit coefficients of the Ring and offset spectra):

$$SC_i = \int \rho_i ds \tag{2}$$

Note that this is a simplification as normally an ensemble of different light paths contribute to the measurement. In extreme cases, the absorption optical depth can become a non-linear function of the trace gas concentration. However, this is usually only of importance for satellite limb measurements and is discussed in detail for example in (Pukite and Wagner, 2016).

A comprehensive discussion of the DOAS technique can be found for example in (Hönninger et al., 2004; Platt and Stutz, 2008).

2.2 The MAD-CAT campaign

The Multi-Axis DOAS Comparison campaign for Aerosols and Trace gases (MAD-CAT) was carried out in Mainz, Germany, in summer 2013. During the intensive phase of the campaign (7 June to 6 July 2013), 11 groups deployed MAX-DOAS instruments on the roof of the MAX-Planck Institute for Chemistry at the Mainz University campus. Being located in the

- 5 densely populated Rhine-Main region, the observations are dominated by anthropogenic pollution, predominantly by NO₂ (in the visible). The main azimuthal viewing direction was 51° (from north), pointing roughly in the direction of the city of Frankfurt \approx 30 km away. Series of vertical scans comprising elevation angles of 0°, 1°, 2°, 3°, 4°, 5°, 6°, 8°, 10°, and 30° were performed. In each direction, single measurements (of varying exposure time depending on illumination)-were integrated for 20 s (for the IUPB instrument, other instruments used different integration times). Between vertical scans,
- 10 multiple zenith measurements were performed (see Fig. 1 for an example of resulting NO₂ slant columns). Detailed information about MAD-CAT can be also found at http://joseba.mpch-mainz.mpg.de/mad_cat.htm and the first campaign data focusing on range-resolved distributions of NO₂ measured at different wavelengths was published by Ortega et al. (2015). Furthermore, Lampel et al. (2015) demonstrated the presence of vibrational Raman scattering on N₂ molecules in spectra measured during MAD-CAT. In addition, publications based on MAD-CAT data are in preparation focusing on HCHO (Pinardi, 2017), HONO
- 15 (Wang et al., 2016) and CHOCHO (Ortega et al., 2017).

2.3 The IUPB MAX-DOAS instrument

The IUPB MAX-DOAS instrument deployed in Mainz during the MAD-CAT campaign is a two-channel CCD-spectrometer system measuring in the UV and visible, respectively. Within this exercise, only data from the visible spectrometer are used as NO₂ is best retrieved in this spectral range. The spectrometer is an ANDOR Shamrock 303i covering a spectral range from

20 399-536 nm at a resolution of \approx 0.7 nm. The spectrometer was actively temperature stabilized to 35°C. Spectra were recorded with a CCD of the ANDOR iDUS 420 type having 1024x255 pixels (26x26 μ m each) leading to a spectral sampling of 7-8 pixels/nm.

Light was collected by a telescope unit mounted on a commercial ENEO VPT-501 pan-tilt head allowing pointing in any viewing direction. Photons entering the telescope through a fused silica window were focused by a lens on an optical fiber bundle. The instrument's field-of-view (FOV) was ≈ 1.2°. The Y-shaped optical fiber bundle (length 20 m) connecting the telescope to both spectrometers consists of 2x38 = 76 single fibres minimising polarization effects. A video camera inside the telescope housing takes snap shots for every recorded spectrum for scene documentation and a mercury-cadmium (HgCd) line lamp allows wavelength calibration measurements. Dark current and slit function measurements are performed every night. The same instrumental set up has been used in previous campaigns, e.g. CINDI and TransBrom (Roscoe et al., 2010; Peters et al., 2012).

Table 1. Summary of fit settings used for the NO₂ intercomparison. These fit settings were agreed on during the MAD-CAT campaign and can be found also at http://joseba.mpch-mainz.mpg.de/mad_analysis.htm.

Fit	Reference	Window	Cross sections	Intensity offset	Polynomial
v1	noon	425-490	1,2,4,5,6,7	Constant (0th order)	5 (6 coefs)
v1a	sequential	425-490	1,2,4,5,6,7	Constant (0th order)	5 (6 coefs)
v2	noon	411-445	1,3,4,5,6,7	Constant (0th order)	4 (5 coefs)
v2a	sequential	411-445	1,3,4,5,6,7	Constant (0th order)	4 (5 coefs)

Cross sections:

- 1 NO₂ at 298K (Vandaele et al., 1996), I_0 -correction using 1E17 molec/cm²
- 2 NO₂ at 220K orthogonalized to 298K within 425-490 nm
- 3 NO₂ at 220K orthogonalized to 298K within 411-445 nm
- 4 O₃ at 223K (Bogumil et al., 2003)

5 O₄ Hermans et al., unpublished, http://spectrolab.aeronomie.be/o2.htm

- 6 H_2O , HITEMP (Rothman et al., 2010)
- 7 Ring, NDSC2003 (Chance and Spurr, 1997)

2.4 Intercomparison exercise

Spectra recorded by the IUPB MAX-DOAS instrument on 18 June 2013 during MAD-CAT were distributed to partners. It is worth mentioning that this intercomparison exercise was not restricted to groups participating in MAD-CAT, as common observations were provided. 18 June 2013 was selected as having good viewing and weather conditions. However, temperature

- 5 stabilization of the IUPB spectrometer was problematic due to unusually hot weather which due to a lack of air conditioning on that day led to overheating of the instrument. As a result, spectral stability was not as good as usual, providing the opportunity to investigate how different retrieval codes deal with potential spectral shifts during the day. The provided data comprised observations at several elevation angles in the main azimuthal viewing direction of 51° (see Fig. 1 for an example). In addition, common trace gas cross sections as well as DOAS fit settings were distributed as summarized in Tab.1, which are the common fit
- 10 settings as agreed on during the MAD-CAT campaign. Note again, the objective of the present study is not finding optimal NO₂ fit settings but identifying disagreements between retrieval codes. All groups then performed DOAS fits using these harmonized prescribed settings on IUPB spectra using their own retrieval software. The influence of different retrieval codes was then analysed retrievals was then analyzed, focusing on the impact on NO₂ columns. In the following, aA brief description of retrieval codes used by the different groups is given in the following. Participating groups /institutes and corresponding
- 15 (with abbreviations used within this study) and retrieval codes they used are summarized in Tab. 2.

Table 2. List Summary of participating institutes	(with abbreviations abbreviation) and retrieval codes used	within this study by each group
	`	

Abbr.	Retrieval(s)	Institute
IUPB	NLIN	Institute for Environmental Physics, University of Bremen, Germany
AUTH	QDOAS	Aristotle University of Thessaloniki, Greece
BIRA	QDOAS	Belgian Institute for Space Aeronomy, Brussels, Belgium
JAMSTEC	QDOAS	Japan Agency for Marine-Earth Science and Technology, Japan
Toronto	QDOAS	Department of Physics, University of Toronto, Ontario, Canada
IUPHD	DOASIS	Institute of Environmental Physics, University of Heidelberg, Germany
Boulder	QDOAS	University of Colorado, Boulder, USA
KNMI	KMDOAS	Royal Netherlands Meteorological Institute, De Bilt, The Netherlands
INTA	LANA	National Institute for Aerospace technology, Madrid, Spain
MPIC	MDOAS,	Max Planck Institute for Chemistry, Mainz, Germany
	WinDOAS	
CSIC	QDOAS	Department of Atmospheric Chemistry and Climate,
		Institute of Physical Chemistry Rocasolano, CSIC, Madrid, Spain
NIWA	STRATO	National Institute of Water and Atmospheric Research, Lauder, New Zealand
IAP	RS.DOAS	A. M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences, Moscow, Russia
BSU	WinDOAS	Belarusian State University, Minsk, Belarus
USTC	QDOAS	University of Science and Technology, Hefei, China
UNAM	QDOAS	National Autonomous University of Mexico, Mexico
NUST	QDOAS	Institute of environmental sciences and engineering (IESE),
		National University of Sciences and Technology, Islamabad, Pakistan

2.4.1 HUPB

The IUPB retrieval code NLIN (Richter, 1997) is an in-house software originally developed for the analysis of ground-based measurements but over time extended and also used for airborne and satellite data sets. The DOAS matrix is inverted using a singular value decomposition (SVD, see Sect. 4.5) which is comprised in an iterative nonlinear fit for calibration of the

5

wavelength axis using a Marquardt-Levenberg fit (see Sect. 4.6). Comparisons with other retrieval codes have repeatedly demonstrated excellent agreement.

2.4.2 QDOAS users

The QDOAS software (Dankaert et al., 2013) is the multi-platform (Windows, Unix/Linux and Mac) successor of the WinDOAS
software (Fayt and Van Roozendael, 2001) developed since the 1990s at BIRA for the analysis of DOAS applications. QDOAS

uses a coupled linear/non-linear least squares (NLLS) algorithm (Marquardt-Levenberg fitting and SVD decomposition) to solve the DOAS equation and includes a wavelength calibration module where measured intensities are fitted to a high resolution reference solar spectrum. During this operation, the slit function can be characterized in addition to the wavelength registration of the measured spectra.

- 5 QDOAS is under constant evolution to match the needs of developing ground-based, aircraft and satellite applications. It is widely used within the DOAS community (more than 130 institutes in 42 countries) and has been applied in different versions for the present exercise: AUTH (version 2.109.3), JAMSTEC (version 2.109), University of Toronto (version 2.109), CSIC (QDOAS windows 2.110.1 beta 20151123), BIRA (version 2.110.1), USTC (version 2.109.4), UNAM (version 2.109.3), NUST (version 2.111), CU Boulder (version 2.110). These various versions do not differ in the core-implementation of the
- 10 DOAS analysis, but can feature slightly different capabilities in terms of data handling or specific retrieval functionalities (see http://uv-vis.aeronomie.be/software/QDOAS/LastChanges.php).

2.4.3 **HNTA**

The INTA retrieval software is named LANA (actual version number: v7.0.0). LANA has been developed at INTA and used
 since 1994. It is a two-step iterative algorithm. In the first step, cross section and spectra are positioned and in the second step
 the linear equations system is solved using a Gauss-Jordan procedure. INTA DOAS instruments using LANA software have
 participated for example at the CINDI campaign in 2009 (Roscoe et al., 2010).

2.4.4 MPIC

- 20 MPIC uses different retrieval codes and procedures, which are included in this intercomparison. In MPIC_WD, the WinDOAS software has been used. This analysis was performed for noon reference fits only and the reference has been selected manually. Another analysis referred to as MPIC_MD has been performed using the retrieval code MDOAS written in Matlab (but calibration and convolution have been performed in WinDOAS). For sequential reference fits, two versions MPIC_MDa and MPIC_MDb exist, which used a different treatment of the Ring spectrum.
- 25

2.4.5 KNMI

The KNMI retrieval code KMDOAS was developed in 2013-2014 at KNMI (by A. Piters) and verified using QDOAS. It is written in Python using standard modules (matplotlib, numpy, scipy, pandas).

2.4.6 HUPHD

IUPHD is using the DOASIS software in its version 3.2.4595.39926 (Kraus, 2006).

2.4.7 NIWA

5 The NIWA-Strato package of programs roots in the first DOAS days (1980s). It was originally used for processing zenith DOAS spectra, but extended as needed to handle MAX-DOAS measurements. The fitting code uses least squares or optional SVD fitting inside iterations applying shift, stretch and (optional) offset, for minimum residual. An internal equidistant wavelength grid is applied using the average interpixel spacing.

10 2.4.8 HAP

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The IAP group uses an own-developed software RS.DOAS for both, wavelength calibration procedure and slant column retrieval. The IAP algorithm was described in (Ivanov et al., 2012) and the more recent version in (Borovski et al., 2014) (in application to formaldehyde retrieval). Most recent developments of the IAP algorithms were described in (Postylyakov et al., 2014) and (Postylyakov and Borovski, 2016). For convolution of cross-sections the QDOAS software (offline version 2.0 at 5 March 2012) is used.

In the IAP algorithm the wavelength calibration of the reference spectrum (WCRS) procedure is iterative. The WCRS algorithm uses several subwindows, and for each of them a non-linear shift and stretch fit including all trace gases (resulting from the linear DOAS fit) is applied. From a set of shifts obtained for the subwindows a 2nd-order polynomial approximation of the shift dependency on pixel number is constructed. The WCRS is corrected using values of this polynomial. The corrected

20 calibration is used as input for the next iteration. This process is repeated until corrections of wavelength calibration become less than 0.001 nm.

The IAP algorithm of the spectra analysis for obtaining SC is similar to WCRS one, but an intensity offset is added to the non-linear terms of the DOAS retrieval procedure and one window is used. Each analyzed spectrum is interpolated to the calibrated grid of the reference spectrum using the 3rd order Lagrange polynomial (Postylyakov and Borovski, 2016).

25 The subroutine of LU decomposition is used for matrix inversions in the algorithm (ALGLIB software, Sergey Bochkanov, www.alglib.net).

2.4.9 BSU

BSU has used WinDOAS (v.2.1, 2001) for this intercomparison exercise.

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2.4.10 Boulder

CU-Boulder used QDOAS v2.110 for wavelength calibration, convolution of trace gas cross sections, and slant column retrieval. The primary zenith DOAS reference was calibrated iteratively against a Kurucz spectrum fitting Ring, O_3 , and NO_2 in several subwindows with the fitted shift of the subwindows used to generate a 3rd order polynomial of shift across

5 the detector. For changing reference analyses the secondary zenith references were calibrated (using the primary reference calibration a priori), but the procedure was run only once. The reference used for changing reference analyses was the zenith immediately following the elevation angle scan analyzed. High resolution cross-sections were convolved online following each calibration, and all cross-sections and the reference were allowed to shift and stretch (1st order) relative to the spectrum.

10 2.4.1 NLIN

NLIN (Richter, 1997) was originally developed at IUPB for the analysis of ground-based measurements but over time extended and also used for airborne and satellite data sets. The DOAS matrix is inverted using a singular value decomposition (SVD) which is comprised in an iterative nonlinear fit for calibration of the wavelength axis using a Marquardt-Levenberg fit.

15 2.4.2 QDOAS

QDOAS (Dankaert et al., 2013) is the multi-platform (Windows, Unix/Linux and Mac) successor of WinDOAS. A coupled linear/non-linear least squares (NLLS) algorithm (Marquardt-Levenberg fitting and SVD decomposition) is used to solve the DOAS equation including a wavelength calibration module. During this operation, the slit function can be characterized in addition to the wavelength registration of the measured spectra. QDOAS is widely used within the DOAS community and has

- 20 been applied in different versions for the present exercise: AUTH (version 2.109.3), JAMSTEC (version 2.109), University of Toronto (version 2.109), CSIC (QDOAS windows 2.110.1 beta 20151123), BIRA (version 2.110.1), USTC (version 2.109.4), UNAM (version 2.109.3), NUST (version 2.111), CU Boulder (version 2.110). These various versions do not differ in the core-implementation of the DOAS analysis, but can feature slightly different capabilities in terms of data handling or specific retrieval functionalities (see http://uv-vis.aeronomie.be/software/QDOAS/LastChanges.php).
- 25

2.4.3 LANA

LANA is a two-step iterative algorithm developed at INTA and used since 1994. In the first step, cross sections and spectra are positioned and in the second step the linear equations system is solved using a Gauss-Jordan procedure. For this exercise, the intensity offset correction was based on the reference spectrum I_0 .

30

2.4.4 MDOAS

MDOAS is a Matlab DOAS code developed at MPIC, but calibration and convolution have been performed in WinDOAS. For sequential reference fits, two versions MPIC_MDa and MPIC_MDb are included in this exercise, which used a different treatment of the Ring spectrum.

5

2.4.5 KMDOAS

KMDOAS was recently (2013-2014) developed at KNMI and verified using QDOAS. It is written in Python using standard modules (matplotlib, numpy, scipy, pandas).

10 2.4.6 DOASIS

DOASIS has been used by IUPHD in its version 3.2.4595.39926. A detailed explanation can be found in (Kraus, 2006). In the version submitted here, an additional shift of cross sections w.r.t. the optical depth was allowed and a saturation correction was implemented.

15 2.4.7 STRATO

The *NIWA-Strato* package was originally (1980s) used for processing zenith DOAS spectra, but extended as needed to handle MAX-DOAS measurements. The fitting code uses least squares or optional SVD fitting inside iterations applying shift, stretch and (optional) offset, for minimum residual. In contrast to other groups, an internal equidistant wavelength grid is applied using the average interpixel spacing.

20

2.4.8 **RS.DOAS**

RS.DOAS (Ivanov et al., 2012; Borovski et al., 2014; Postylyakov et al., 2014; Postylyakov and Borovski, 2016) was developed by IAP. The DOAS inversion is performed by LU decomposition. The wavelength calibration uses several subwindows, and for each of them a non-linear shift and stretch fit including all trace gases (resulting from the linear DOAS fit) is applied. From

25 a set of shifts obtained for the subwindows a 2nd-order polynomial approximation of the shift dependency on pixel number is constructed. For convolution of cross-sections the QDOAS software (offline version 2.0 at 5 March 2012) was used.

2.4.9 WinDOAS

WinDOAS (Fayt and Van Roozendael, 2001) is the precursor of QDOAS. It has been used by BSU as well as MPIC for this intercomparison exercise (the MPIC submission is denoted as MPIC_WD, the reference has been selected by hand), but only for noon reference fits.

5 3 Intercomparison results

3.1 Noon reference, 425-490 nm fit window (v1 fit parameters)

Differences between groups for the 425-490 nm fit using a noon reference (v1 fit settings, see Tab. 1) are shown in Fig. 3 for individual measurements at an elevation angle of 2° . Small elevation angles above the horizon are associated with long tropospheric light paths and therefore important for the detection of tropospheric absorbers. Differences shown in Fig. 3 are

- 10 relative to IUPB results. For the objective of identifying retrieval-code specific effects, the use of a single retrieval code as a reference seems advantageous in comparison to using the mean of all retrieval codes which would average over all retrieval-specific features. Note that this does not exclude IUPB from the intercomparison as problems of the IUPB retrieval would be easily detected as leading to the same systematic patterns in all lines shown in Fig.3.
- Absolute differences (institute-IUPB) and relative differences (absolute difference/IUPB) of NO₂ slant columns and fit RMS 15 are shown in Fig. 3a-d. In general, NO₂ slant column differences are in the range of $\pm 2 - 3 \cdot 10^{15}$ molec/cm² or < 2%. This is about a factor of 2-3 larger than NO₂ slant column errors, which are typically < $1 \cdot 10^{15}$ molec/cm², resp. < 0.6% for 2° elevation. A clearly enhanced disagreement is observed for the first data point in the INTA time-series as well as for MPIC_WD. The latter could be linked to the reference spectrum, which is in this case not the one having smallest sun zenith angle (SZA) while the outlier in the INTA timeseries was identified to arise from different implementations of the intensity offset correction
- 20 (see Sect. 4.3). Note that these NO_2 differences for individual measurements are much smaller than the variability (diurnal cycle) of NO_2 and thus almost invisible in Fig. 3e where no differences but absolute NO_2 slant columns from each groups (including IUPB in black) are plotted.

Interestingly, most many groups show a smooth behavior (constant offset) in absolute NO₂ differences (Fig. 3a), which is mostly an effect of the choice of the reference (see Sect. 4.1) while relative differences (Fig. 3c) reflect the shape of NO₂

25 slant columns in Fig. 3e (smaller slant columns lead to larger relative differences and vice versa). However, some groups show a smooth line not for absolute, but for relative differences, e. g. NIWA... Thus, two types of disagreements are observed, 1) constant in absolute, and 2) constant in relative differences. These two types are linked to differences in retrieval codes, which is investigated in detail in Sect. 4.

Absolute RMS differences (w.r.t. IUPB) in Fig. 3b show the same shape as NO₂ slant columns. This is because at small

30 elevations the RMS itself reflects the shape of the NO₂, which was already demonstrated and discussed in Fig. 1. A better measure for the identification of differences between retrieval codes is thus the relative RMS disagreement shown in Fig. 3d. Interestingly, the first data point for INTA showing a large disagreement with IUPB and other groups in NO₂ slant columns is



Figure 3. Results from v1 fit settings in 2° elevation angle as a function of time. (a, b) Absolute NO₂ slant column and RMS differences, (c, d) relative NO₂ slant column and RMS differences, (e) NO₂ slant columns, (f) RMS, (g, h) fitted spectral shift (h is a zoom-in of g without INTA and KNMI lines, but including the reanalyzed INTA2 and NIWA2 lines). (a-d) are differences w.r.t. IUPB, (e-h) are absolute results and IUPB is explicitly shown in black. Triangular markers indicate groups using QDOAS, circular markers indicate groups using independent software, and diamonds indicate groups that corrected faults in their code during the course of this study and submitted a re-analyzed data set.



Figure 4. Linear regression results (slope, intercept, correlation) for different elevation angles (w.r.t. IUPB) for fit settings v1 (noon reference). Groups using QDOAS (in different versions) are indicated by a star (*).

prominent in absolute RMS differences as well, but not in relative RMS differences. The reason is that the RMS in the morning is very large (Fig. 3f, compare also to Fig. 1) and thus decreases the relative difference. Remarkably, relative RMS differences are found up to 80-100%, which is substantially more than NO₂ slant column differences (only a few percent). In addition, some clusters can be seen in Fig. 3d: A group of smallest RMS comprising e.g. IUPB, BIRA, CU Boulder, AUTH, IAP, and

5 a group of slightly enhanced RMS (≈ 20%) comprising e.g., MPICWD, NIWA, BSU. In the group of largest RMS (up to 80-100%), only UNAM and NUST show similar features, while the timeseries of INTA and USTC is different. The IUPB spectra provided were wavelength pre-calibrated using nightly HgCd line lamp measurements as explained in Sect. 2.3. However, the DOAS fit quality can be improved (RMS reduced) by applying a post-calibration. In addition, the nighttime calibration can change during the day as a result of temperature drifts. This is accounted for by DOAS retrieval codes in terms of a nonlinear shift fit (for a more detailed discussion see Sect. 4.6). Figs. 3g and h (being a zoom-in of g)

- 5 show the reported shift resulting from the wavelength calibration in participating retrieval codes. Note, absolute values for the shift are shown here and the IUPB result is explicitly included. For an ideal spectrometer without drifts, only a very small shift would be expected caused by a non-commutivity of convolution and DOAS polynomial, which is known as the *tilt effect* and typically in the order of less than 1-2pm, depending on the instrument resolution (Sioris et al., 2003; Lampel et al., 2017). The shift retrieved here is larger than that and driven by overheating of the system on this day. Timeseries-In general, timeseries
- 10 of shifts shown in Fig. 3g and h agree well in shape. A small offset is observed for NIWA, which could be caused by NIWA not centering the slit function accurately in the making of their cross sections, but this does not affect their results. Also, who successfully found and corrected a fault in their retrieval code (related to the intensity offset calculationwas previously implemented in a different way in the NIWA retrieval and changed for this exercise meet the common fit settings, but this new code had a fault which was discovered after data submission and successfully corrected () in the corrected results are not
- 15 shown here) . In contrast, as shown course of this exercise. The DOAS fit was then repeated using the corrected retrieval code and the result called NIWA2 is included in Fig. 3. Apparently, NIWA2 shows much better comparison to other groups (most obvious in the fitted spectral shift) and performs better as the RMS in Fig. 3d is much smaller than before. Similarly, INTA fixed a problem in their retrieval code related to the wavelength calibration. The reanalyzed INTA data are denoted as INTA2 in Fig. 3g, The INTA2 shift is comparable to other groups, while large disagreements were seen before, and the RMS is largely
- 20 reduced in comparison to the first INTA submission. Notably, almost no differences between INTA and INTA2 are observed in terms of NO₂ slant columns, in particular the first data point is still outlying. This indicates (1) that the wavelength calibration has a large impact on the fit RMS but only a minor impact on the NO₂ slant columns, and (2) that the disagreement of the first data point is not related to the wavelength calibration. Despite INTA and NIWA, only KNMI is fitting a rather different shift (and provides the shift only in 0.01 nm resolution which leads to the displayed discrete steps). This is caused by different
- 25 definitions of the shift (see Sect. 4.6): KNMI is fitting the shift of the optical depth relative to the cross sections while the other groups are fitting the shift of I relative to the reference spectrum I_0 . As a result, the shift of KNMI and other groups cannot be expected to match. Apart from KNMI, only INTA is retrieving clearly different shifts. The effect of the wavelength calibration is investigated in more detail in Sect. 4.6.

To further quantify the The agreement between groups and include including also other elevation angles , correlation plots

- 30 were calculated for each group w.r.t. IUPB NO₂ slant columns (has been quantified by linear regression analyses to correlation plots (of each group relative to IUPB results, not shown)and a linear regression was performed for each plot providing a slope, offset, and the correlation coefficient. The results Resulting slopes, offsets, and correlation coefficients are summarized in Fig. 4, color-coded for different elevation angles. As expected, the correlation coefficient is > 99.98% with the only exception of the INTA (and INTA2) 2° elevation which is predominantly caused by the outlier already seen in Fig. 3. The slope ranges
- between $\frac{0.995}{0.985}$ and 1.01, the offset between -4 to $2.5 \cdot 10^{15}$ molec/cm². Apart from USTC and INTA, no large separation



Figure 5. Results from v1a fit settings (sequential reference spectrum) on 2° elevation angle data as a function of time. (a and b) Absolute NO₂ slant column and RMS differences, (c and d) relative NO₂ slant column and RMS differences. All differences are relative to IUPB. Triangular markers indicate groups using QDOAS, circular markers indicate groups using independent software, and diamonds indicate groups that corrected faults in their code during the course of this study and submitted a re-analyzed data set..

of slope and offset with elevation angle is observed. An important observation is that groups using the same retrieval code (QDOAS) do not necessarily show the same systematic behavior in Fig. 4, implying that the influence of remaining fit parameters different from the harmonized general settings in Tab. 1 is still larger than the effect of the specific retrieval software used. In generalFor example, the best agreement in terms of regression line slope, offset and correlation coefficient is found between IUPB, AUTH, IAP, and CU Boulder, which are all using different retrieval codes.

3.2 Other fit parameters

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Linear regression results (slope, intercept, correlation) for different elevation angles (w.r.t. IUPB) for fit settings v1a (sequential reference).

The agreement between groups was quantified investigated in the same way when using a sequential reference (see Sect. 2.1 denoted

10 <u>as v1a fit setting, see Tab. 1</u>) instead of a noon reference spectrum , which (v1 fit). A sequential reference is often preferred if tropospheric absorbers are of interest as stratospheric effects are removed to a large extent.

Table 3. Ranges of correlationsCorrelations, slopes and offsets from linear regressions on NO₂ slant column correlation plots columns between each group and IUPB (see also Figs. 4 and ??neglecting the INTA 2° outlier).

Fit	Correlation (%)	Slope Slope	$\frac{\text{Offset}}{\text{Offset (1-10^{15} (1E15 \text{ molec/cm}^2))}}$
v1	>99.98 (without outlier)	0.985 to 1.01	-4 to 3
v1a	>99.2	0.96 to 1.01	-1.5 to 1
v2	>99.94 (without outlier)	0.985 to 1.005	-4 to 3
v2a	>99.2	0.96 to 1.01	-2 to 1

FigsFig. 5 and ?? are similar to Figsis similar to Fig. 3and 4 but using a sequential reference, denoted as v1a fit settings instead of v1 (see Tab. 1). Note that, but some groups are missing here (e.g. IAP) as they only provided noon reference fits. The range of disagreements for individual NO₂ slant columns is up to 8% and therefore larger than NO₂ disagreements using a noon reference (v1 fit). In addition, neither absolute nor relative differences between groups are smooth (Fig. 5 a and c). This is

- 5 because The reason is that in contrast to the noon reference, a different (zenith) I_0 spectrum is used for every scan and thus the impact of details of the implementation of the reference changes from scan to scan. Different implementations of the reference spectrum are further investigated in Sect. 4.1 and were found to be the major reason for NO₂ disagreements between groups. The outlier (first data point) seen for v1 (noon) fit settings is present for v1a as well but it is not prominent here as fluctuations for the above mentioned reason are of same magnitude.
- 10 In terms of RMS, differences between groups are comparable to v1 results and as large as 80%.

Compared to the noon reference fit(Fig. 4), correlations from linear regressions in Fig. ?? (not shown) are smaller, especially for the 30° elevation . This results angle, mainly resulting from the larger disagreements as explained above , but is (but also partly expected as slant columns are smaller using a sequential reference). Correlations are still > 99.2% for 30° elevation and even > 99.8% for smaller elevations. The intercept is mostly below $\pm 1E15$ molec/cm² and therefore smaller than in the v1 fit.

- 15 In contrast, the slope of regression lines ranges between 0.96 and 1.01 and is therefore more variable than in v1. Furthermore, in contrast to v1 where no systematic pattern was observed, all groups using QDOAS (with the exception of USTC) show the same pattern in terms of slope (largest for 2°, smallest for 30°) and even a comparable range, while groups using independent software (INTA, MPICMD, KNMI, IUPBHD, NIWA) do not show this systematic pattern. The reason is that until version v.2.111 only one possibility for the sequential reference was implemented in QDOAS (the closest spectrum after the scan,
- 20 with v.2.111 other options have been included). Consequently, the sequential reference selection is applied in the same way in all QDOAS data sets shown here. This is consistent with findings of Fig. 5 where the exact implementation of the sequential reference was already found to dominate NO₂ differences between groups.

In addition to the 425-490 nm fit (v1 and v1a), a smaller fit window used within the MAD-CAT campaign was intercompared (v2 and v2a using a spectral range of 411-445 nm, see Tab. 1). However, results of fit settings v2 and v2a Results of these fits

25 are not explicitly shown as providing no new insights but mainly confirming observations and findings above. Typical values

Table 4. Tests performed to study the influence of different reference spectra.

Test	Reference (fit setting)	Remarks
TR0	noon (v1)	first spectrum of smallest SZA
TR1	noon (v1)	second spectrum of smallest SZA
TR2	noon (v1)	first for a.m., second for p.m.
TR3	noon (v1)	average of both
TR4	sequential (v1a)	closest zenith in time
TR5	sequential (v1a)	closest before the scan
TR6	sequential (v1a)	closest after the scan
TR7	sequential (v1a)	average of before and after
TR8	sequential (v1a)	interpolation of before and after to time of measurement

of statistics (from linear regressionscorrelation coefficients (as well as offsets and slopes) are summarized in Tab. 3 for all performed fit settingsfits. A very small tendency of better agreement between groups if using the larger fit window is seen. Although this should not be over-interpreted, it could be caused by more information being present in the large fit window and therefore more accurate results (less statistical fluctuations).

5 4 Understanding differences between Sensitivity studies of non-harmonized retrieval eodesaspects

Questionnaires sent to every group The observed differences between the harmonized MAD-CAT retrieval results prompted the team to systematically investigate effects of the non-harmonized aspects of the retrievals, with the aim to derive a key set of Best Practices recommendations. A survey suggested five potential sources of differences in the DOAS fit results: 1) the selection/calculation of the reference spectrum, predominantly for sequential reference fits, 2) treatment of the slit function,

10 3) the intensity offset correction, 4) differences in the numerical calculation of the DOAS fit (linear fit), 5) differences in the wavelength calibration (non-linear fit). In the following, tests using the same retrieval code (IUPB) have been performed to characterize the impact of each of the above mentioned systematic differences.

4.1 Effect of the reference spectrum

In the IUPB spectra provided to intercomparison partners, two different zenith spectra at the same smallest SZA were reported, which is of course non-physical. Actually, the second zenith spectrum is the one having the smallest SZA, but for rounding reasons (the SZA was a 4-digits number in the spectra file input provided), both spectra had the same SZA. Consequently, for the noon reference fits v1 and v2 within this intercomparison exercise, four options exist: 1) taking the first zenith spectrum of smallest SZA, 2) taking the second one, 3) taking the first for a.m. and the second for p.m. (i.e. always taking the closest in time), and 4) taking the average of both spectra. Similarly, different options exist for calculating the sequential references



Figure 6. Different test results (see Tab. 4) in 2° elevation angle as a function of time. Top: Absolute NO₂ SC differences, Middle: Relative SC differences, Bottom: Relative RMS differences. Left is for noon reference (differences are w.r.t. IUPB v1 fit results), right is for sequential references (differences are w.r.t. IUPB v1a fit results).

for fits v1a and v2a: 1) always taking the zenith spectrum closest in time, 2) always taking the last zenith spectrum before the actual measurement, 3) always taking the next zenith spectrum after the measurement, 4) taking the average of the two (before and after), and 5) interpolating the two zenith spectra to the time of the actual measurement.

All different options for noon and sequential reference fits were evaluated using the IUPB retrieval code NLIN (Tab. 4).
5 Fig. 6 shows the resulting absolute and relative slant column differences (top and middle) as well as relative RMS differences (bottom) for noon reference (left) and sequential reference (right) w.r.t. v1, resp. v1a fit results.

Taking another noon reference spectrum results in a constant offset in absolute NO₂ differences (Fig. 6, top left). Test TRO (using the first spectrum) yields the same results as the IUPB v1 fit from Sect. 3, because there which uses the first zenith

spectrum was used as a reference as as well. In contrast, using the second zenith spectrum as a reference (TR1) results in a constant offset of 1.5E15 molec/cm² (0.5-2.5% in relative differences, depending on the actual NO₂ slant column), because the second zenith spectrum had apparently a smaller NO₂ content. The change of the NO₂ content could be related to changes of the atmospheric NO₂ amount or the atmospheric light path. In terms of RMS, TR1 is up to 3% larger (Fig. 6, bottom left).

5 The main reason for this is probably the larger NO_2 slant columns as associated effects like the wavelength-dependence of the NO_2 slant column (Pukite et al., 2010) were not compensated in this intercomparison exercise as discussed in Sect. 1.

Test TR2 yields results which are identical to TR0 am a.m. and TR1 pm p.m. values. This is not seen for any groups in Fig. 3 above, i.e. this option is apparently not present in any retrieval code. Not surprisingly, TR3 (averaging both zenith spectra) yields results which are between TR0 and TR2.

- 10 In contrast to noon reference tests, sequential references show no smooth behavior, neither for absolute, nor for relative differences (Fig. 6, right). The reason is that for each vertical scanning sequence (from which only the 2° elevation is shown here and in Fig. 3) another reference spectrum is used and consequently reference-related differences between groups are also changing from scan to scan. Note that almost no difference can be seen in Fig. 6 between TR4 and TR5 as the 2° elevation angle is shown here and consequently the closest zenith measurement in time is normally the one before the scan as IUPB
- 15 measurements proceed from low to large elevations. TR8 (interpolation to the measurement time) resembles the sequential reference treatment normally implemented in the IUPB code, and thus the TR8 line is zero. For TR6 and TR7, absolute and relative differences (up to 8%) are remarkably similar to observed differences between groups using v1a fit settings, both in shape and in absolute values (compare to Fig. 5).
- To conclude, the exact treatment of reference spectra is the major reason for observed NO_2 discrepancies between groups in 20 Sect. 3, causing differences of up to 8%. Unfortunately, no clear recommendation can be derived from relative RMS differences in Fig. 6 (bottom right) as all lines scatter around zero. However, the relative difference in RMS can be as large as 6% and in general, using a single zenith reference spectrum before or after the scan tends to produce larger RMS. However, while the reference treatment explains the majority of NO_2 disagreements, it cannot explain the large RMS differences (up to 100%) between groups.

25 4.2 Slit function treatment

The slit function distributed to intercomparison participants originated from HgCd line lamp measurements made in the night before 18 June 2013. It was pre-processed in terms of subtraction of the (also measured) dark signal, centered, and provided on an equidistant 0.1 nm grid.

While some groups /retrieval codes used this slit function as is, other retrieval codes include a further *online* processing of
the slit function, e.g. by fitting line parameters. In order to quantify the effects of this processing on the resulting slant columns,
evaluate resulting differences, trace gas cross sections have been convolved off-line (before the fit) using different treatments of the slit function as summarized in Tab. 5. Then, again, Again, the IUPB retrieval code NLIN has been used to calculate NO₂ slant columns then performing the DOAS fit.

Test	sub. offset	geom. centering	cutoff value	fit line parameters
TS0	no	yes	0.0	no
TS1	no	no	0.001	no
TS2	yes	no	0.001	no
TS3	no	yes	0.001	no
TS4	yes	yes	0.001	no
TS5	no	no	0.0	no
TS6	no	no	0.001	Gaussian
TS7	no	no	0.001	Gaussian ($\mu = 0$)
TS8	no	no	0.001	Gaussian ($\mu = 0$) fitted on 0.01 nm grid
TS9	no	no	0.0	Gaussian
TS10	no	no	0.0	Gaussian ($\mu = 0$)
TS11	no	no	0.0	Gaussian ($\mu = 0$) fitted on 0.01 nm grid



Figure 7. Examples of different slit function treatments. Blue: Measured slit function (from HgCd line at \approx 480 nm). Red: Fitting a Gaussian shape to slit function with $\mu = 0$. Light green: Akima interpolation of the red line to a finer 0.01 nm grid. Dark green: Interpolating first (linearly) to 0.01 nm and fitting a Gaussian shape afterwards.



Figure 8. NO₂ slant columns and RMS differences w.r.t IUPB v1 fit results in 2° elevation angle for different treatments of the slit function.

Examples of different treatments of the slit function are shown in Fig. 7. The original slit function is displayed in blue. If fitting a Gaussian shape to it, the maximum is not exactly centered around zero, pressumably caused by a small asymmetry. The slit function after fitting a Gaussian shape and forcing centering (i.e. $\mu = 0$) is shown in red (as used in TS7 and TS10). Furthermore, performing a discrete convolution of cross sections requires the same wavelength sampling, i.e. the slit function has to be interpolated to the cross section grid, which was 0.01 nm. Here, an Akima interpolation has been applied (green

line). However, if the original slit function is first linearly interpolated to the required 0.01 nm grid and then a Gaussian shape

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is fitted, a slightly different result is obtained, shown in dark green (as used in TS8 and TS11). Note that often not a discrete convolution but a (faster) convolution using Fourier transformation is implemented in DOAS retrieval codes (see below).

Fig. 8 shows the resulting absolute and relative differences in NO₂ slant columns (top and middle) as well as relative differences of the fit RMS (bottom) w.r.t. the IUPB v1 fit (without I0-correction as this was not applied to the slit function test

5 fits). The reference IUPB v1 fit uses an online convolution of cross sections using FFT and a further geometrical centering of the slit function is applied.

No difference between the reference fitand, TS0 and TS5 results (black and magenta lines) is observed, neither for NO_2 nor for the RMS. In TS0, the same slit function treatment is applied as in the reference fit, but using discrete convolution instead of FFT. Consequently, meaning that no difference arises due to the method of convolution. In addition, TS5 and TS0 are

- 10 identical tests except for TS0 applying an explicit geometrical centering (i.e. centering the area) of the slit function(overcoming potential small deficits in centering during the pre-processing). As this has no visible effect on NO₂ slant columns and RMS, the centering during pre-processing was already sufficient and the fact that the maximum is not exactly located at zero when fitting a Gaussian shape must be caused by the shape of the original line(or the nonlinear shift fit was compensating for small deficits in the slit function centering).
- The largest impact on NO₂ in Fig. 8 (up to 1.3%smaller NO₂ slant columns-1.3%) is seen for TS2 and TS4 which both subtract the smallest value from the slit function (i.e. forcing the slit function to be zero for the smallest value measured). This is usually not performed in DOAS fits and only advisable if instrumental stray light is a large problem or if the dark signal drifts which is normally not the case in state-of-the-art CCD detectors that are cooled and temperature-stabilised using Peltier elements.
- In contrast, the largest effect in terms of RMS (up to 6.5% larger RMS, Fig. 8 bottom) occurs not for TS2 and TS4, but for all tests using a fitted Gaussianinstead of the original slit function. Interestingly, the Gaussian tests (TS6-TS11) show almost no difference among them in terms of RMS in the morning, but split up towards the evening. This might have to do with decreasing NO₂ slant columns in the afternoon or changes of the slit function during the day. In terms of NO₂, all tests using Gaussian slit functions yield smaller NO₂ slant columns of 0.2-0.7%.
- In addition to the basic Gaussian line parameters fitted here, some retrieval codes offer the possibility to fit more sophisticated line shape parameters taking into account potential asymmetry much better (the slit function in Fig. 7 shows indeed slight asymmetry). However, the exact implementations differ and were therefore not reproduced in the tests performed here, which can therefore be regarded as two extreme scenarios, namely (1) using the (original, slightly asymmetric) slit function as it is, or (2) fitting basic line parameters (a more sophisticated fit taking into account the slit function's slight asymmetry would clearly
- 30 lead to a result in between these scenarios).

An important finding is that all tests of different slit function treatments performed tests lead to constant offsets (smooth lines) in relative differences in relative (and not in absolutedifferences) absolute) NO₂ differences. In addition, all tests yield larger RMS than the reference fit , i.e. using the measured slit function yields the lowest residuals.

Table 6. Tests performed for different implementations of the intensity offset correction (and I_0 correction). A <u>Oth order offset correction</u> means applying a constant term only, a first order correction means applying a constant and slope term.

Test	Offset order	Offset approach	I ₀ -correction
TI0	0th (constant)	1/I (simple approach)	yes
TI1	0th (constant)	1/I ₀ (simple approach)	yes
TI2	0th (constant)	Eq. 4 using I (more sophisticated)	yes
TI3	0th (constant)	Eq. 4 using I_0 (more sophisticated)	yes
TI4	None	No offset correction	yes
TI5	1st (constant + slope)	$1/I$, λ/I (simple approach)	yes
TI6	0th (constant)	1/I, additionally Ring- λ	yes
TI7	0th (constant)	1/I (simple approach)	no

4.3 Intensity offset correction

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Photons may hit the CCD detector at locations not corresponding to their wavelength (e.g. through scattering on mirrors, surfaces etc. inside the spectrometer) which produces an intensity offset, also called stray light. In addition, other effects such as changes in the dark current can lead to intensity offsets and the vibrational Raman scattering (VRS) is known to produce spectral effects that are very similar to intensity offsets (Peters et al., 2014; Lampel et al., 2015). In the DOAS fit, usually pseudo cross sections are included in order to compensate for intensity offsets. If the measured spectrum I is superimposed by

 $-\tau = \ln\left(\frac{I+C}{I_0}\right) = \ln\left(\frac{I}{I_0}\right) + \ln\left(1+\frac{C}{I}\right) \approx \ln\left(\frac{I}{I_0}\right) + \frac{C}{I}$ (3)

a constant intensity C (which is the most simple assumption), the optical depth reads

with the Taylor expansion ln(1+x) ≈ x. Thus, in first approximation the intensity offset causes an additive term of optical
depth that is proportional to 1/I, which is often used as a pseudo absorber (and showing large similarities to the Ring cross section as this compensates a filling-in of Fraunhofer lines).

However, often more sophisticated approaches are used. For example, the IUPB retrieval code NLIN allows either the simple implementation of $\sigma_{\text{off}} = 1/I$ or

$$\sigma_{\rm off} = \ln\left(\frac{I + C \cdot I_{\rm max}}{I}\right) \tag{4}$$

15 omitting the Taylor expansion in Eq. 3 and superimposing I by a certain constant C of the maximum intensity within the fit interval. In addition, sometimes also higher correction terms are used assuming that not only a constant superimposes the spectrum, but also a contribution changing with wavelength (in which case often λ/I is included in addition to the simple approach $\frac{1}{I}$ in the the DOAS fit). Furthermore, sometimes the offset is not included in the linear DOAS fit, but fitted nonlinearly (this is not included in tests performed here).



Figure 9. Absolute (top) and relative (middle) NO₂ slant column differences, and relative RMS differences (bottom) w.r.t. IUPB v1 fit results in 2° elevation angle resulting from different implementations of the intensity offset correction (and I₀ correction).

Different implementations summarized in Tab. 6 were tested in order to evaluate the influence of the intensity offset correction. Fig. 9 shows resulting absolute and relative differences of NO_2 slant columns and RMS values. Again, the reference for these differences is the IUPB v1 (noon) fit.

No difference in NO₂ or RMS is seen between TI0 and the v1 fit as both fits use the same simple approach of $\sigma_{\text{off}} = 1/I$. 5 In contrast, TI1 uses $1/I_0$. In terms of NO₂ differences, the TI1 line follows slightly the shape of total fit RMS and NO₂ slant columns (compare to Fig. 3). Interestingly, while the disagreement of TI1 w.r.t the reference fit is on average $\approx 2\%$ for NO₂, the first data point is clearly off by almost 10% for NO₂ and 60% for RMS. This agrees perfectly with the observed outlier in the INTA analysis (compare to Fig. 3), i.e. the reason for this disagreement could be identified as a different offset implementation (which has been verified by INTA). The SZA and the sun azimuth angle (SAA) of this measurement are $\approx 90^{\circ}$ and 58° (from north), respectively, while the instrument's elevation angle is 2° and the azimuthal viewing direction 51°, i.e. the

- 5 instrument was pointing close to the rising sun. Enhanced stray light in the spectrometer (caused by the large contribution of photons at longer wavelengths while observing the red sky during sunrise) seems plausible and using 1/I is a better choice for compensation. It was verified (not shown) that the fit coefficient of the offset (also called the *offset slant column*) is particularly large not only in this but also in adjacent measurements and a color index indicated that these spectra are indeed more reddish. However, these measurements could also be affected by direct sunlight in the instrument, which is known to increase RMS (e.g.
- 10 due to polarization issues). Fig. 3f demonstrates that the respective measurement is affected by a very large RMS (potentially caused by a combination of direct light and stray light).

TI2 and TI3 are more sophisticated approaches (Eq. 4) based on either I or I_0 . However, the resulting lines follow largely TI0 and TI1 (simple approaches). Unexpectedly, both TI2 and TI3 lead to larger RMS values for the sunrise measurement in the morning where the simple approach performs better.

The total effect of using an intensity offset compensation is evaluated by TI4 which includes no offset correction. The resulting effect on NO₂ is almost the same as TI1 and TI3 (based on I_0) leading to the clear recommendation of using an offset compensation based on *I* instead of I_0 , which is supported by largely increased RMS values of TI4 (Fig. 9 bottom).

An intensity offset correction of first order (i.e. a term varying linearly with λ in addition to a constant term) was tested in TI5, which is in practice often used not only for intensity offsets but also for compensation of the wavelength-dependence of

- 20 the Ring slant column. The resulting NO₂ differences w.r.t. the reference fit (or TL0) are small with the exception of the first data point that is slightly off. In terms of RMS, TI5 leads to improvements of $\approx 20\%$ in the morning. Interestingly, the TI5 RMS line shows some similarities to the IUPHD-IUPB line in Fig. 3d. However, no first order offset was included in the IUPHD fit, i.e. the offset implementation is not causing the observed similar shape in the morning (and the reason remains unclear). This is supported by increasing IUPHD RMS values in the evening in Fig. 3d, which are not present in TI5.
- Fit TI6 includes again only a 0th order intensity offset, but a pseudo cross section accounting for the wavelength-dependence of the Ring slant column was added (the Ring cross section was multiplied by λ and orthogonalized against the original cross section). The resulting RMS is indeed almost identical to TI5 (using a first order intensity offset) while the NO₂ is identical to TI0, i.e. the outlying first data point which is still partially present in TI5 disappeared in TI6. Thus, using a pseudo-cross section for compensation of the Ring wavelength-dependence seems preferable compared to using a first order intensity offset 30 correction.

4.4 I₀-correction

In addition to the intensity offset tests, the effect of inclusion of an I_0 -correction was evaluated in TI7 (which is identical to TI0 except for the I_0 -correction, see Tab. 6). The respective line is shown in addition to the intensity offset investigations in Fig. 9.

Table 7. Different methods	tested for solving the linear l	DOAS equation $\mathbf{A} \mathbf{x} = \mathbf{b}$
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Test	Retrieval code	Spectral grid	Method	Remarks
Reference	NLIN	I ₀	Pseudo-inverse of \mathbf{A} using SVD	following Press (1989)
TL0	Python	I_0	Pseudo-inverse of \mathbf{A} using SVD	different numpy and scipy-
implementations tested TL1	Python	I_0	Solving quadratic $\mathbf{A}^{T}\mathbf{A} \mathbf{x} = \mathbf{A}^{T} \mathbf{b}$	different numpy and scipy-
			using LU decomposition	implementations tested
TL2	Python	I_0	Invert $\mathbf{A}^{T}\mathbf{A}$ using LU decomp.	
			and multiply with $\mathbf{A^T}$ b	
TL3	Python	0.01 nm	same as TL0	linear interpolation
				to 0.01 nm
TL4	Python	0.01 nm	same as TL0	cubic spline interpolation
				to 0.01 nm

The I_0 -effect adresses the problem that the limited instrument? 's resolution can cause an incomplete removal of Fraunhofer structures in the vicinity of strong narrow-banded absorption bands (Johnston, 1996; Wagner et al., 2001; Aliwell et al., 2002).

Only a very small constant offset in relative NO₂ slant column differences is obtained in TI7 ($\approx 0.25\%$, which is almost invisible in Fig. 9, middle). In terms of RMS, exclusion of the I_0 -correction leads up to 20% increased RMS, which is compa-

5 rable to different treatments of the intensity offset correction. Thus, inclusion of an I_0 -correction is recommended in polluted environments such as the MAD-CAT site. It should be noted that the first data point is not an outlier in TI7, i.e. it is not sensitive to the I_0 -correction.

4.5 Numerical methods (linear DOAS inversion)

The DOAS equation (Eq. 1) is a linear inverse problem

10
$$\mathbf{A} \mathbf{x} = \mathbf{b}$$

(5)

with the vector \mathbf{x} (size *n*) containing the *n* trace gas slant columns and polynomial coefficients of interest, the vector $\mathbf{b} = \ln(\frac{I_0}{I})$ (size m) containing the measured optical depths at *m* wavelengths, and the $m \times n$ DOAS matrix **A** with columns consisting of absorption cross sections and polynomial terms (1, λ , λ^2 , etc.) for the *m* wavelengths.

Different numerical methods exist to solve Eq. 5 for x. As A is non-square, no inverse exist. However, most retrieval codes
15 calculate a pseudo-inverse A⁻¹ (almost) fulfilling A⁻¹A = I (identity matrix) using a singular value decomposition (SVD) and obtain the slant columns of interest by x = A⁻¹ b. This method is frequently recommended for solving overdetermined linear inverse problems in terms of least squares (see e.g. Press, 1989).



Figure 10. Absolute (top) and relative (middle) NO₂ slant column differences, and relative RMS differences (bottom) w.r.t. IUPB v1 results (only linear fit) in 2° elevation angle resulting from different numerical methods solving the linear DOAS equation.

However, after multiplying Eq. 5 with \mathbf{A}^{T} , the matrix $\mathbf{A}^{T}\mathbf{A}$ is quadratic and can be decomposed into an upper and a lower triangular matrix, \mathbf{L} and \mathbf{U} . The linear inverse problem

$$\mathbf{A}^{\mathrm{T}}\mathbf{A}\,\mathbf{x} = \mathbf{L}\mathbf{U}\,\mathbf{x} = \mathbf{A}^{\mathrm{T}}\,\mathbf{b} \tag{6}$$

can be solved then by forward substitution obtaining \mathbf{y} from $\mathbf{L} \mathbf{y} = \mathbf{A}^{T} \mathbf{b}$ and backward substitution obtaining \mathbf{x} from $\mathbf{U} \mathbf{x} = \mathbf{5}$ y.

Furthermore, $\mathbf{A}^{T}\mathbf{A}$ can also be directly inverted, normally by LU decomposition as well. The vector of slant columns is then obtained by $\mathbf{x} = (\mathbf{A}^{T}\mathbf{A})^{-1} \mathbf{A}^{T} \mathbf{b}$. As the inversion takes normally much more computational steps, this method is known to be subject to roundoff errors, and therefore not recommended (Press, 1989).

- The influence of these different numerical methods on resulting slant columns could not be easily tested with the IUPB re-5 trieval code and was thus evaluated in a Python script solving the DOAS equation using the same input (spectra, cross sections). 9 Python (which is a well-established programming language in scientific computing) provides numerous different routines 9 within its *numpy* and *scipy* packages (based on different subroutines from the *LAPACK* package, *http://www.netlib.org/lapack/*) 9 that were tested for solving the DOAS equation. All performed tests are summarized in Tab. 7. Again, differences of NO₂ slant 9 columns and fit RMS have been calculated with respect to the IUPB v1 fit results (i.e. using NLIN). In order to restrict dif-
- 10 ferences to the influence of numerical approaches only, the same slit function treatment as the IUPB retrieval code NLIN was applied in the Python script and the same (noon) reference spectrum was used. In addition, no further wavelength calibration, i.e. no nonlinear shift and squeeze fit was performed (neither in the Python script nor in the NLIN reference fit used here) and no I_0 -correction was included. The test results are shown in Fig. 10, again for the 2° elevation angle.

Results of test TL0 appear to be identical to the reference fit of the IUPB retrieval code, both using a SVD for inversion of the DOAS matrix. However, very small differences exist between TL0 and the reference fits (too small to be seen on the scale of Fig. 10), which are < 0.006% for NO₂ slant columns and < 0.07% for RMS. These tiny disagreements can be attributed to numerical differences in programming languages.

TL1 and TL2 yield identical NO₂ slant columns (both are using an LU decomposition) which differ from SVD results by up to 0.7%. However, the RMS from TL2 was found to be an order of magnitude larger compared to the other tests and is
therefore not shown in Fig. 10 (bottom). This is most likely due to problems mentioned above, i.e. this finding is in agreement with common recommendations in textbooks. Interestingly, both TL1 (and TL2) NO₂ and RMS lines (which are differences w.r.t. IUPB) are similar in shape to the total fit RMS (compare to Fig. 3f). Thus, when the RMS increases, SVD inversion and LU decomposition lead to larger disagreements, both in RMS and NO₂. As the SVD yields smaller RMS values, it seems to be preferable, although the obtained improvement is only about 2.5%.

Numerical differences may be obtained when performing the linear DOAS fit (Eq. 5) on another wavelength grid. Changes of the grid potentially arise from the wavelength calibration. Some retrieval codes (e.g. NIWA) also use an internal, equidistant wavelength grid. To test the effect of changes in the wavelength grid, the TL0 fit was repeated on an equidistant 0.01 nm grid (i.e. *I*, *I*₀, and cross sections were interpolated to 0.01 nm before solving Eq. 5). TL3 and TL4 are identical to TL0, but a linear interpolation was applied in TL3, while TL4 uses a cubic spline interpolation to 0.01 nm. Apparently, this results in a constant offset in relative NO₂ differences, which is seen most clearly in the TL3 line in Fig. 10 (middle). The resulting constant shift is ≈ 0.4% for TL3, but only ≈ 0.02% for TL4 meaning that the type of interpolation to the equidistant grid is of importance and the spline interpolation (not surprisingly) seems to resemble the spectrum better than a linear interpolation. However, using different wavelength grids might for example explain some of the observed differences between IUPB and NIWA, which were

found to be constant in relative differences as well(see Fig. 3e)... In terms of RMS, the computation on an equidistant 0.01 nm

Test	Retrieval code code	Shift I_0 to Fraunhofer atlas	Shift I to I_0	Remarks
Reference	NLIN <u></u> D	yes	yes	Alternating scheme, v1 fit settings
TW0	NLIN <u></u> D	no	no	Linear DOAS fit only
TW1	NLIN_D	no	yes	
TW2	NLIN_D	yes	no	
TW3	Python	yes	yes	same a TW0
TW4	Python	yes	yes	same a TW3, but linear interpolation
TW5	Python	yes	yes	same a TW3, all trace gases
				included in Fraunhofer I_0 fit

Table 8. Different wavelength calibration approaches evaluated.

grid using linear interpolation behaves on average even a bit better (up to 1%). However, no recommendation can be drawn from this as discussed above.

4.6 Nonlinear wavelength calibration

As mentioned in Sect. 2.3, the spectra provided from the IUPB instrument were pre-calibrated using nightly HgCd line lamp

- 5 measurements, which provide accuracies better than 0.1 nm. However, usually a post-calibration is included in DOAS retrieval codes in order to increase the fit quality (reducing RMS). This wavelength calibration is implemented in different ways in participating retrieval codes. Most groups calibrate the reference spectrum I_0 to a high resolution Fraunhofer atlas, apply the resulting calibration to all measured spectra, and allow in addition a shift and squeeze between I and I_0 in order to compensate spectral shifts of the spectrometer during the day, e.g. caused by temperature changes - Note, (KNMI uses a slightly different
- 10 definition of the shift as discussed below). This nonlinear shift and squeeze fit of the wavelength axis is mostly implemented in an iterative scheme together with the linear DOAS fit on $\ln(I_0/I)$. However, codes differ for example in whether trace gases are included in the shift and squeeze fit of I_0 to the high resolution Fraunhofer atlas. Sometimes also a higher order calibration is allowed or several sub-windows are used in order to characterize differently different parts of the spectra.
- Tab. 8 summarizes tests performed to investigate the impact of different wavelength calibration approaches using the IUPB
 retrieval code NLIN. In addition, some tests were performed with the Python script form Sect. 4.5 which has therefore been extended to perform the nonlinear shift fit as not all tests could be easily implemented in the comprehensive NLIN software. Note, in contrast to the shift, the squeeze has been excluded from the intercomparison as it was found to be always 1.0 for measurements shown here. Also QDOAS-specific implementations were not tested here.

Fig. 11 shows the resulting impact on NO₂ and RMS as well as the fitted shift between I and I_0 (not present in all tests). 20 NO₂ and RMS are again differences relative to the IUPB v1 fit results (without I_0 -correction as this was not implemented in the Python routine). As in Fig. 3, the shift in Fig. 11d is no difference, and for comparison the shift from the reference fit is



Figure 11. Absolute (a) and relative (b) NO₂ slant columns differences, and relative RMS differences (c) in 2° elevation angle resulting from different wavelength calibration approaches (Tab. 8). Corresponding shifts between I and I_0 resulting from nonlinear fits are shown in (d).

shown explicitly in black. The (fixed) shift retrieved from the nonlinear fit of I_0 to the Fraunhofer atlas is -0.035 nm. This is roughly a factor of 10 larger than the fitted shift between I and I_0 shown in Fig. 11d. It is interesting to note that the shift is not zero around noon (time of the reference spectrum), indicating correlations between shift fit and other effects (predominantly intensity offset correction) and also indicating the presence of the tilt effect (Lampel et al., 2017).

5

The most extreme test is TW0 which excludes both the calibration of I_0 to the Fraunhofer atlas as well as the shift between I and I_0 . When omitting both calibration steps, the RMS is largely enhanced by up to 80% peaking in the morning and decreasing towards noon with a second smaller maximum around 12 UT. Interestingly, a very similar shape is seen in the RMS differences of INTA, KNMI, NUST, UNAM, and USTC in USTC and INTA (but not in INTA2 correcting a fault in the wavelength registration module) in Fig. 3d. Although all of these groups are performing a wavelength calibration, TWO

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indicates that differences in the calibration procedure are causing most of the disagreements between groups in terms of RMS. This is in contrast to NO_2 where changes of only 0.4% are obtained from TW0.

TW1 still excludes the absolute calibration to the Fraunhofer atlas, but includes the shift fit between I and I_0 . As seen before, the impact on NO₂ is very small ($\approx 0.4\%$), but absolute NO₂ differences of TW1 reflect the shape of total RMS and NO₂ slant columns (compare to Fig. 3), i.e. the relative differences are smooth in shape. The RMS is similar in shape as TWO,

15 but the morning maximum is slightly later at 7 UT, the noon maximum around 11 UT and a small maximum in the evening occurs at 18 UT. This shape is similar to the relative RMS of NUST, UNAM, and NIWA in Fig. 3, but absolute numbers are different. However, this behaviour indicates that differences in the fitted Fraunhofer shift are partially responsible for observed differences between these and other groups. Interestingly, the fitted shift between I and I_0 of TW1 in Fig. 11d is very similar to corresponding values of the reference fit, which is because the missing Fraunhofer shift is a different effect than the shift between I and I_0 .

- 5 In contrast to TW1, TW2 includes the Fraunhofer shift fit, but excludes the shift between I and I_0 . As this is the larger effect (-0.035 nm compared to only \approx 0.004 nm), the RMS is much smaller than in TW1 with a single maximum (up to 50%) in the early morning at 6 UT. The RMS timeseries shape is similar to the KNMI line in Fig. 3. The reason is a different definition of the shift in the KNMI retrieval: While in most retrievals I is shifted relative to I_0 , KNMI calculates the optical depth $\tau = \ln(I_0/I)$ without any shifts but allows then a shift of all cross sections relative to τ . This is in first order compensating the
- 10 effect of the Fraunhofer shift but neglecting potential shifts between I and I_0 (in this case Fraunhofer lines would not cancel out completely in the optical depth τ). As a result, the KNMI approach is similar (but not identical) to TW2. The fit quality following the KNMI approach is expected to be better using a sequential reference as the temperature drift of the spectrometer is much smaller then. This matches perfectly with observations in Figs. 4 and ?? showing a better agreement between KNMI and IUPB when using a sequential reference. However, it It has to be mentioned that the change of NO₂ in TW2 is small (0.3%)
- 15 compared to the change in fit RMS (50%).

20

TW3 uses the same wavelength calibration treatment as the IUPB reference fit, but is performed in another programming code (Python) evaluating how much difference is caused by use of another programming code and numerical issues. The fitted shift is mostly identical to the reference fit except for the early morning and late evening when also the NO₂ shows very slight differences. The largest disagreement of NO₂ is 0.2% for the first measurement of the day that was affected by large stray light effects (and potentially direct light) and thus most likely indicating cross-correlations between shift fit and intensity offset correction. The resulting RMS is almost identical to the reference fit (Fig. 11c).

TW4 is the same as TW3 but the spline interpolation (calculating I at spectral points of I_0 during the nonlinear shift fit) is replaced by a simple linear interpolation. The fitted shift is changed slightly and NO₂ differences are up to 0.1% which is of of almost the same order than when not performing any shift fit at all demonstrating that the shift fit has a negligible impact on

25 NO₂. In contrast, it has a large impact on RMS, where the marginally different methods between TW3 and TW4 produce the same RMS while the effect of excluding the shift completely leads to largely enhanced RMS.

In the Fraunhofer calibration of the reference fit using NLIN (nonlinear shift fit of I_0) as well as in TW3 all trace gas absorptions are omitted, i.e. an iterative scheme between shift fit and DOAS fit comprising only a polynomial of order 4 is applied. In contrast, all trace gas absorptions are included in the Fraunhofer calibration in TW5. As a result, the RMS of the

30 DOAS fit between Fraunhofer spectrum and I_0 is reduced by a factor of 2 and the nonlinearly fitted shift is -0.031 nm instead of -0.035 nm in the reference fit. However, this has only a marginal influence on NO₂, RMS and fitted shift between I and I_0 in Fig. 11 and consequently explains none of the observed differences between groups.

It is important that Notably, all shifts (even TW1) in Fig. 11d show the same general shape that is also retrieved by most groups in Fig. 3. Only shifts of INTA and KNMI could not be reproduced by any of the performed tests (but because of the

35 different definition, the KNMI shift is not expected to match with other groups results). However, KNMI clearly differ, for the

Table 9. Summary of performed sensitivity tests (differences in retrieval codes) and associated impacts on NO₂ slant columns and RMS.

Reason for disagreement	$\Delta \mathrm{NO}_2$ (%)	Δ RMS (%)	Remarks
Reference treatment (noon)	2.5	3	Produces constant absolute NO ₂ SC offsets.
Reference treatment (seq.)	8	6	
Slit function treatment	1.3	6.5	Produces constant relative NO ₂ SC offsets.
Intensity offset correction	2 (typically)	20 (typically)	
	10 (outlier)	60 (outlier)	
I ₀ correction	0.25	20	Produces constant relative NO ₂ SC offsets.
Numerical methods	0.3 (0.7)	2.5	Produces constant relative NO ₂ SC offsets.
(for linear DOAS fit)			Disagreements increase with RMS.
Wavelength calibration	0.4	up to 80	
(nonlinear shift fit)			

reasons mentioned above. RMS shapes in Fig. 11c suggest that differences in the wavelength calibration are the major reason of observed RMS disagreements between groups in Fig. 3.

5 Summary and conclusions

An intercomparison of DOAS retrieval codes using measured spectra from the same instrument during the MAD-CAT cam-5 paign and harmonized fit settings was performed. Excellent agreement was found between different DOAS fit algorithms from 17 international groups. In some of the retrieval codes, faults were identified and corrected in the course of the study leading to even better agreements. For noon reference fits, the correlation in terms of NO₂ slant columns was found to be larger (> 99.98%) than for sequential references (> 99.2%), which is caused by different implementations of the sequential reference. For individual measurements ,

10 Despite of the excellent overall correlation, for individual measurements in low elevations differences of up to 8% in resulting NO₂ slant columns (which is substantially larger than were observed, which is up to 2-3 times larger than corresponding typical NO₂ slant column fit errors), and up to errors. In terms of fit RMS, large differences of up to ≈100% for the fit RMS were observedwere found.

Interestingly, groups using the same retrieval code (QDOAS groups) do not always produce results showing the same system-

- 15 atic behavior- except QDOAS users when performing sequential reference fits (which is because the selection of the sequential reference was implemented in a fixed way in those QDOAS versions). This is the, which is the result of different options other than the harmonization settings agreed on users select. A survey of participating DOAS retrieval codes revealed five potential reasons causing differences in fit results, which were investigated in more detail. Typical impacts This has some impact for the interpretation of other studies as the extent of prescribed fit settings in this study is comparable to intercomparison campaigns.
- 20 like CINDI or CINDI-2. Consequently, groups participating in those campaigns will provide intrinsic differences in their results

due to non-harmonized (detailed) settings even if using the same retrieval code, which have to be expected in the same range as observed here.

Comprehensive sensitivity studies systematically investigating effects of the non-harmonized retrieval aspects were performed in order to (1) attribute observed differences between groups to certain sources, and (2) evaluate the impact of each of these

5 sources on NO₂ slant columns and RMS arising from these different implementations/options in DOAS retrieval codes fit RMS.
 For this purpose, five reasons were identified in a survey of participating retrieval codes. Typical impacts on NO₂ slant columns and RMS are summarized in Tab. 9.

In general, the wavelength calibration and the intensity offset correction were found to produce the majority of observed RMS differences, but have a negligible impact on NO₂ slant columns (< 0.4%, resp. < 2% except for the first measurement of

- 10 the day affected by stray light and possibly direct light in the telescope). In contrast, the reference selection explains the majority of observed NO₂ slant column differences between groups while having a minor impact on the RMS. Thus, if harmonization of NO₂ slant columns is of interest, the reference treatment needs to be harmonized (otherwise in small elevation angles differences of up to 8% - and even more for larger elevation angles due to decreasing absolute slant columns - have to be expected predominantly in the case of using a sequential reference) while for RMS reduction/harmonization, the offset intensity
- 15 correction and the wavelength calibration need to be harmonized.

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In terms of NO_2 , two types of disagreements between groups have been observed, which are (1) constant in absolute, or (2) constant in relative differences. The latter was found to arise from the numerical approach used for solving the DOAS equation as well as the treatment of the slit function while the choice of the reference spectrum causes absolute differences.

Recommendations Best practices aiming at improvement of the fit quality and harmonization between MAX-DOAS retrievals derived from this study are:

- Reference treatment: Using averaged or interpolated sequential reference spectra matches the atmospheric conditions at the measurement time better and was found to produce slightly smaller RMS(6%).
- Slit function: Using a measured slit function performed better than fitting line parameters in the data set used here. However, slit function measurements then have to be performed regularly (e.g., daily to monitor possible instrument changes).
- 3) Intensity offset: An approach based on I instead of I_0 is recommended. Surprisingly, the simple approach performs better for measurements pointing close to sunrise but this could be just a coincidence in this data set. Inclusion of an additional Ring spectrum multiplied by wavelength is preferred over adding a linear term to the offset as this mostly compensates the wavelength-dependence of the Ring slant column.
- 4) Numerical approaches: Using an SVD is most stable and produces slightly smaller RMS than LU decomposition.
 - 5) Wavelength calibration: Although HgCd line lamp calibration measurements lead to absolute accuracies (in this case) of ≈ 0.03 nm, a Fraunhofer shift fit reduces the RMS by up to 40-50%. For the I_0 fit w.r.t. the Fraunhofer spectrum, inclusion of all trace gases showed no advantage over inclusion of a polynomial only. Temperature instabilities of the

spectrometer produced shifts of I relative to I_0 changing over the day. Compensation of this effect within DOAS retrieval codes further improves the RMS by up to 40-50% when using a noon reference spectrum.

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