Response to Reviewer #1, Interactive comment on "Aircraft measurements of bromine monoxide, iodine monoxide, and glyoxal profiles in the tropics: comparison with ship-based and in situ measurements" by R. Volkamer et al. – posted on the AMTD website on 25 Feb 2015.

We thank the reviewer for the evaluation of our paper, the valuable suggestions and the references. The reviewer comments are copied below in bold, followed by our detailed response that is typed in blue color below. Text that was added to the manuscript is typed in green font.

The manuscript entitled 'Aircraft measurements of bromine monoxide, iodine monoxide, and glyoxal profiles in the tropics: comparison with ship-based and in situ measurements' describes the validation of trace gas vertical profiles from MAX-DOAS with independent observations during two flights as part of the TORERO campaign. Vertical profiles of aerosols, water vapour, glyoxal, NO2, BrO and IO are compared to ship-borne MAX-DOAS measurements, in situ water vapour and aerosol size distribution observations, as well as profiles from a chemistry-transport model. The inversion of tropospheric trace gas and aerosol profiles from ground-based, shipborne and air-borne MAX-DOAS measurements is a strongly emerging field and a validation of this measurement technique is crucial for an assessment of their overall quality. Therefore, the topic of the manuscript fits well within the scope of AMT. The level of agreement of the AMAX-DOAS measurements with independent observations and model results presented by Volkamer et al. is very impressive. However, I feel that the manuscript requires some modification prior to a publication in AMT.

As detailed below, many open questions remain regarding the methodology for the retrieval of vertical profiles. Furthermore, a comparison of the results obtained within this study with validation results from previous airborne campaigns, which would allow for an assessment of the capabilities of MAX-DOAS compared to other measurement techniques, is missing.

We respond to retrieval questions in detail below. In the revised manuscript we have added discussion and references to previous aircraft campaigns that had compared RAQMS with NO2 measurements during TRACEP (Pierce et al., 2003), and the Collins paper suggested by the reviewer. There are very few measurements of IO, BrO and glyoxal on aircraft, and discussion in sections 4.1.2, 4.1.3, and 4.4.2 cites the few available papers to place AMAX-DOAS into context to other techniques.

I suggest to modify the title of the manuscript. Currently only measurements of BrO, IO and glyoxal profiles are mentioned in the title, but also results for NO2, H2O and aerosols are presented.

We have added 'NO2, H2O, O2-O2 and aerosol extinction' to the title

Specific comments:

In contrast to other MAX-DOAS retrieval algorithms (e.g., Friess et al., 2006; Clemer et al., 2010), the method described here relies on absolute SCDs instead of differential dSCDs. I have to admit that I have difficulties to understand this approach and its implications. Inverse methods should be based on a forward model that accurately describes the measurement process. In case of MAX-DOAS, the primary quantity derived from a spectral analysis is the dSCD, and this is thus the quantity that should be modelled by the retrieval algorithm. An explanation why absolute instead of differential SCDs serve as input for the retrieval is missing. What is the benefit of this approach?

The benefit from knowledge about SCDref depends on the implementation of the MAX-DOAS technique. For AMAX-DOAS the benefit is minimal, since the value of SCDref is systematically minimized by the choice of reference geometry in this work, and comparable to the dSCD fit error. We have added a new Table 3 as requested by reviewer #2. However, for SMAX-DOAS the value of knowing SCDref (constrained here from AMAX-DOAS above the ship) is significant.

Generally speaking, a more direct comparison with a forward model becomes possible if SCDref is known. This is achieved if the spectral analysis has access to a reference geometry that does not contain any absorber (SCDref = zero). This ideal scenario is rarely achieved; but it can be approximated for AMAX-DOAS. However, knowledge about SCDref requires independent information. To our knowledge, RF17 is the first case study where SCDref is known from AMAX-DOAS profiles above the ship, and the benefits of knowledge about SCDref have been assessed for the SMAX-DOAS (Section 3.4). Based on the significant sensitivity of SMAX-DOAS to SCDref we have decided to provide a consistent notation for both AMAX- and SMAX-DOAS retrievals (Sect. 2.7, Eq. 1).

In the revised manuscript we have added in Section 2.7.:

“Knowledge of SCD_{REF} facilitates a more direct comparison with RTM, but requires independent information.”

and

“The effect of uncertain SCD_{REF} is largest for SMAX-DOAS profiles, and plays a negligible role for measurements near instrument altitude; this is assessed in form of a sensitivity study in Sect. 3.4 “Sensitivity of MAX-DOAS profiles to SCD_{REF}”.”

An important implication of the use of absolute instead of differential SCDs is the necessity to accurately derive the reference amount SCDref. Little information is provided on how exactly the values for SCDref were derived. What do you mean with ‘The SCDref was determined explicitly through RTM calculations’ (638.11)? Why is SCDref not determined (explicitly or implicitly) by the retrieval algorithm? From a perspective of information theory, I doubt that the information content of the retrieved atmospheric state can be improved if SCDref is estimated externally from the measurements themselves.

We agree partially. In our opinion the value of SCD_{REF} is by definition not accessible implicitly to the retrieval algorithm without leveraging external information. For example, we use AMAX-profiles above the ship to constrain calculations of SCD_{REF} for SMAX-DOAS; and we use the RAQMS model atmosphere combined with in-situ measurements on the aircraft to calculate SCD_{REF} for AMAX-DOAS. This is described in more detail in Section 2.7.

“SCD_{REF} values for NO_2, H_2O and O_4 were estimated from RTM initialized for the reference geometry using RAQMS NO_2, in situ measurements of temperature/pressure and VCSEL-H_2O at aircraft altitude, and RAQMS profiles at higher altitudes. For BrO, NO_2 and H_2O the values of SCD_{REF} correspond to tropospheric SCDs for the preferred reference geometry (Table 2). For IO SCD_{REF} was estimated from sensitivity studies to assure accurate correction of the stratosphere (Supplement text). For glyoxal, no significant glyoxal was detected when comparing the EA+10 reference from RF17 with the EA0 reference from 14.5 km (RF12), which further supports that SCD_{REF} is essentially zero.”

If SCD_{REF} values are smaller than the fit error, as is the case of AMAX-DOAS (see Sect. 2.7, and the new Table 3), then knowledge about SCD_{REF} will be of negligible benefit -- this is comforting to know. For SMAX-DOAS, the retrieved atmospheric state more closely resembles the ‘true state’ if SCD_{REF} is constrained based on the AMAX-DOAS profiles. This is transparent from the manuscript Table 5 (previously Table 4), and Section 3.4 (no changes).

For the same reasons, I have difficulties to understand the discussion in Section 3.4 on the impact of SCDref on the retrieved profiles. If, as the authors state, the retrieval of profiles for the SMAX measurements uses dSCDs as measurement vector, then the forward model needs to simulate dSCD = SCD – SCDref , i.e. the difference between the SCD simulated for the measurement geometry and the SCD simulated for the reference geometry. This is not equal to the assumption SCDref = 0. The

retrieval algorithm should determine SCDref implicitly and there is no need to prescribe SCDref externally.

We respectfully disagree with 'This is not equal to the assumption SCDref = 0', as the following example makes transparent. The example considers two spectra recorded close in time at EA = 3 and 90 degrees (zenith). The latter is used as a reference to evaluate the low EA spectrum.

For the SCDs we have:

$SCD_{90} = SCD_{REF}$

$dSCD_3 = SCD_3 – SCD_{90} = SCD_3 – SCD_{REF} \Rightarrow SCD_3 = dSCD_3 + SCD_{REF}$

Assuming SCD_{REF} = zero is identical to using dSCDs instead of SCDs for the inversion.

See our above response. Determining SCD_{REF} requires knowledge of the full vertical trace gas profile through the complete atmosphere. SMAX-DOAS dSCD measurements typically do not contain sufficient information to properly constrain SCD_{REF} implicitly, as we believe the reviewer agrees. Optimizing SMAX-DOAS measurement strategies and retrievals to determine SCD_{REF} implicitly from the retrieval (with help from external information) is a very interesting research questions that has been noted in Section 3.4, but is beyond the scope of this paper.

Based on radiative transfer calculations and speculations on the vertical distribution of trace gases and aerosols, Section 2.5 contains an extensive discussion on the choice of the reference spectrum. Why has this complicated approach been chosen, if there is a much simpler method to determine the spectrum with the smallest SCD, namely to analyse the dataset using an arbitrary reference spectrum, and to choose the spectrum with the smallest dSCD (plus other criteria, such as the intensity level) as reference in a final analysis run?

We believe the reviewer is referring to Section 2.6, as Section 2.5 is about in-situ CE-DOAS.

The approach described by the reviewer was the starting point of our analysis. However, relying on the spectrum with the smallest dSCD holds potential for altitude dependent bias, e.g., from spectral cross-correlation of Raman scattering, aerosols, altitude dependent influences of water leaving radiance, or cross-correlations of trace-gases with different vertical profiles in the retrieval, etc. For example, it is not obvious that the minimum BrO dSCD would arise for limb and zenith spectra recorded in the MBL (compare Fig. 5b). To our knowledge there is no previous documentation of (the absence of) altitude dependent bias in the literature.

Section 2.6 serves the purpose to make our approach transparent, document it, and introduce the reference geometries used to assess altitude dependent bias in Section 3.2.

I suppose AMAX-DOAS measurements during ascend and/or descend were used for the retrieval, but this information is not provided explicitly. How many measurements were usually performed per altitude unit?

In the revised manuscript we have added a typical number of measurements per layer in Sect. 2.7.

"There is at least one, and up to three independent measurements within each layer to constrain the inversion."

The agreement between the aerosol extinction profile retrieved from AMAX-DOAS O_4 and modelled based on measured aerosol size distribution and Mie calculations is very impressive. In particular, it seems to be possible to accurately determine the aerosol extinction in the upper troposphere, where Rayleigh extinction is about an order of magnitude higher. It would be important to discuss how the results of TORERO compare to closure studies from other airborne campaigns (e.g., Collins et al., In

situ aerosol-size distributions and clear-column radiative closure during ACE-2, Tellus B, , 52, 498-525, 2000), and what has been done to achieve this high level of agreement between in situ and remote sensing aerosol measurements. A description of the measurement principle of the UHSAS (is it measuring dried aerosol or at ambient humidity, which particle size range is it covering), and its uncertainties is missing.

We appreciate the positive feedback, and the reference. In the revised manuscript we have expanded Section 2.2 with a brief description of the UHSAS, and added reference to (Cai et al., 2008), where the instrument operation and performance is described in more detail. The UHSAS measurement uncertainty has been added in Section 2.2 as well, and the shading range in Figure 3 has been increased accordingly to include these uncertainties.

"The UHSAS measures the concentration of particles from 0.06 to 1.0 μm diameter, resolved in 99 size bins, by the technique of laser light scattering. The wing-mounted probe operates in the free stream. A diffusing inlet with a 10:1 deceleration ratio for isokinetic matching of flow serves for sample intake. At typical GV Mach numbers ranging 0.4 to 0.8 this slowing produces from 8 to 30 K heating. The evaporation of water and other volatile compounds from the particles is minimized by fast delivery to the detection chamber, but some degree of loss prior to detection cannot be ruled out. The UHSAS is designed to have a nearly linear response with log of particle diameter, and to minimize sizing sensitivity to variations in particle refractive index, over its size range. The uncertainties in sizing and concentration are 10% and 5%, respectively. A detailed description of the instrument and its performance is given by Cai et al. (2008)."

We have also added discussion of Collins et al., 2000 in Section 3:

"The results from our radiation closure study are consistent with a previous aircraft study that integrated extinction from in-situ size distributions and compared it with a sun-photometer at 525 nm, where differences of up to 41% were observed at low aerosol loadings in the upper FT (Collins et al., 2000). The good agreement we find in the above correlation of extinction is the result of considerable averaging. Figure 3 shows. oscillations in the boundary layer and lower FT that seem to be affected by the sampling problem in comparing in-situ and column observations that probe different air masses. However, our results agree quite favorably in the upper FT, even at very low aerosol extinction values."

The agreement of NO2 and H2O profiles from AMAX-DOAS with model simulations and in situ measurements is better than anything I've seen before (see, e.g., Brunner et al., An evaluation of the performance of chemistry transport models by comparison with research aircraft observations. Part 2: Detailed comparison with two selected campaigns, ACP, 2003). In particular, most CTMs strongly overestimate NOx in the tropical troposphere. I would therefore appreciate if more details on the chemical and dynamical scheme of the RAQMS model could be provided and if the results obtained during TORERO would be compared to previously published comparisons between airborne trace gas measurements and model simulations.

We appreciate the positive feedback, and have added the following text to Section 4.2:

"The good agreement between the modeled and observed NO2 profiles demonstrates that the RAQMS family approach for total odd nitrogen (NOy), combined with NMHC chemistry appropriate for large-scale applications, is able to accurately represent photochemically active NOy species such as NO2 in the relatively pristine conditions sampled during TORERO. "

We have further added more description and references about the RAQMS model in Section 2.8:

“RAQMS chemistry includes Ox-HOx-NOx-ClOx-BrOx cycles governing the formation and destruction of odd oxygen, tropospheric NOx-HOx reactions, oxidation of CH_4 and CO following Pierce et al., (2003, 2007) with inclusion of non-methane hydrocarbon (NMHC) chemistry following Zaveri and Peters, (1999). The RAQMS online chemistry module is originally based on the LaRC Interactive Modeling Project for Atmospheric Chemistry and Transport (IMPACT) model (Eckman et al., 1995) and uses a family approach to predict total odd oxygen, total odd nitrogen, and total inorganic chlorine and bromine. HOx is assumed to be in photochemical equilibrium. Species such as NO, which is not explicitly transported, are solved by partitioning total odd nitrogen assuming photochemical equilibrium. The family approach allows for longer chemical time steps and minimizes the computational cost of the RAQMS chemistry. This is particularly important since RAQMS is used to provide real-time global chemical and aerosol analyses and forecasts. The RAQMS aerosol prediction uses online aerosol modules from GOCART (Chin et al., 2002, 2003) as discussed in Verma et al., (2009). RAQMS chemical analyses include assimilation of cloud cleared total column ozone from the Ozone Monitoring Instrument (OMI), and stratospheric ozone profiles from the Microwave Limb Sounder (MLS) on the NASA Aura satellite. RAQMS aerosol analyses include assimilation of aerosol optical depth from the Moderate Resolution Imaging Spectroradiometer (MODIS) on the NASA Terra and Aqua Satellites. ”

References

Cai, Y., Montague, D., Mooiweer-Bryan, W., and Deshler, T.: Performance characteristics of the ultra high sensitivity aerosol spectrometer for particles between 55 and 800 nm: Laboratory and field studies, *Journal of Aerosol Science*, 39, 759-769, 2008.

Chin, M., et al.: Tropospheric aerosol optical thickness from the GOCART model and comparisons with satellite and sunphotometer measurements, J. Atmos. Sci., 59, 461–483, doi:10.1175/1520 0469, 2002.

Chin, M., et al.: A global aerosol model forecast for the ACE-Asia field experiment, J. Geophys. Res., 108(D23), 8654, doi:10.1029/2003JD003642, 2003.

Collins, D.R., Jonsson, H.H., Seinfeld, J. H., Flagan, R. C., Gasso, S., Hegg, D. A., Russell, P. B., Schmid, B., Livingston, J. M., Ostrom, E.O., Noone, K. J., Russell, L. M., and Putaud, J. P.: In situ aerosol-size distributions and clear-column radiative closure during ACE-2, Tellus B, , 52, 498-525, 2000.

Eckman, R. S., Grose, W. L., Turner, R. E., Blackshear, W. T., Russell III, J. M., Froidevaux, L., Waters, J. W., Kumer, J. B., and Roche, A. E., Stratospheric trace constituents simulated by a three-dimensional general circulation model: Comparison with UARS data, J. Geophys. Res., 100, 13,951–13,966, 1995.

Pierce, R. B., et al.: Regional Air Quality Modeling System (RAQMS) predictions of the tropospheric ozone budget over east Asia, J. Geophys. Res., 108(D21), 8825, doi:10.1029/2002JD003176, 2003.

Pierce, R. B., et al.: Chemical data assimilation estimates of continental U. S. ozone and nitrogen budgets during the Intercontinental Chemical Transport Experiment–North America, J. Geophys. Res., 112, D12S21, doi:10.1029/2006JD007722, 2007.

Verma, S., et al.: Ozone production in boreal fire smoke plumes using observations from the Tropospheric Emission Spectrometer and the Ozone Monitoring Instrument, J. Geophys. Res., 114, D02303, doi:10.1029/2008JD010108, 2009.

Zaveri, R. A., and Peters, L. K.: A new lumped structure photochemical mechanism for large-scale applications, J. Geophys. Res., 104, 30,387–30,415, doi:10.1029/1999JD900876, 1999.