

Interactive comment on “MAX-DOAS detection of glyoxal during ICARTT 2004” by R. Sinreich et al.

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Interactive comment on “MAX-DOAS detection of glyoxal during ICARTT 2004” by R. Sinreich et al. T. Kurosu (Referee) tkurosu@cfa.harvard.edu Received and published: 10 November 2006 — Overview — Sinreich et al. report ground- and ship-based MAX-DOAS measurements of glyoxal (CHOCHO) during the ICARTT 2004 campaign (July/August 2004). In this, the first of two papers, the authors focus on the instrumentation and the CHOCHO measurements (the companion paper, not part of this review, supposedly deals with the chemistry).

With the advent of recent satellite-based detection, glyoxal has gained importance as a tool for air quality monitoring. Sinreich et al. expand the still sparse reports on ground-based detection of this molecule, hence the paper is relevant for atmospheric chemistry. The manuscript is well organized and clearly written: The instrumentation is introduced in detail and measurements as well as the retrieval approach are described concisely, so the reader obtains a through idea of the work that has been done. The

measurement approach (DOAS) is sound and well proven.

There is little to criticize. Aside from the treatment of O4 absorption, where I suggest to switch to a different set of absorption cross sections due to the problems associated with the Greenblatt measurements, most of my comments are technical and/or editorial.

The only addition I would like to see are the average values for the diurnal variations of the retrieved quantities CHOCHO and NO2 (alternatively, the CHOCHO-to-NO2 ratio) for the whole measurement campaign. This will give a better estimate of the CHOCHO-to-NO2 ratios than one single day for each site, particularly for the measurements obtained from the RV Ron Brown.

I recommend that the paper be accepted with minor modifications as outlined below.

Author reply: We want to thank Thomas Kurosu for the positive assessment and the helpful comments. We mostly followed them (and explained the reasons in cases we did not follow them), as outlined in detail below.

———— General Comments —————

No general comments. See Specific Comments below.

———— Specific Comments —————

(1) Greenblatt O4 cross sections There are several issues with the Greenblatt cross section. In particular, there appears to be a wavelength shift in the UV, and there are also questions regarding the absolute calibration of the cross sections. In this study, the O4 is retrieved in the UV (338-364nm) and the appropriate correction is then made in the VIS (420-460nm) where CHOCHO is being retrieved. The general approach is sound, of course, but the Greenblatt cross sections are an unfortunate choice. I suggest to change this to the BIRA-IASB cross sections measured by Hermans, available at www.oma.be/BIRA-IASB/Scientific/Topics/Lower/LabBase/Laboratory.html This might reduce the fitting uncertainties for CHOCHO by improving the correction for O4.

However, the effect is likely to be small, and for the purpose of this manuscript I don't see the need to redo the analysis prior to publication.

Author reply: In order to avoid a potential wavelength shift, already in our original version, we had used a corrected version of the Greenblatt O4 cross section modified by Andreas Richter with an improved wavelength calibration. We apologize that we did not reference this already in the ACPD version. Furthermore, in the process of finding the best retrieval for CHOCHO, the O4 cross section of Greenblatt et al. was replaced by the one of Hermans et al. in a sensitivity study and we could not find any significant discrepancies in the fit quality. In the absolute calibration of the O4 cross section there are still large uncertainties between the different publications (especially also in the temperature dependence). Therefore, in our opinion we cannot derive a decision for a particular O4 cross section, and also not against Greenblatt et al.. One specific advantage of the Greenblatt et al. cross section is that it features a high signal-to-noise ratio and does not show spectral artifacts e.g. caused by Fourier transformation.

(2) Optical Density (Section 4) The definition of Optical Density is: "Absorbance of an optical element for a given wavelength per unit distance [cm^{-1}]." On the other hand, the product of mixing height [m] and aerosol extinction coefficient [m^{-1}] is dimensionless. So this AOD should really be optical thickness, not density.

Author reply: In our opinion the optical density is dimensionless (see e.g. Platt (1994)). Therefore, we would like to keep the expression "density". See also "The degree of opacity of a translucent medium expressed by $\log I_0/I$, where I_0 is the intensity of the incident ray, and I is the intensity of the transmitted ray. Abbreviated OD. " (<http://www.answers.com/topic/optical-density>).

(3) AMF Page 9462 Line 20: Stating that the AMF represents the "light path extension" of the SCD vs. the VCD is somewhat misleading: A "scattering" AMF is often smaller than the geometric AMF due to reduced sensitivity in the near-surface part of the atmosphere (more of an issue in the UV than in the VIS). "light path difference between

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SCD and VCD" may be a better way to formulate this.

Author reply: We altered the sentence as suggested.

(4) CHOCHO-to-NO₂ ratio The case of high CHOCHO-to-NO₂ ratios observed on the RV Ron Brown on 17 July is intriguing, but I would be interested to see the average values for this ratio at both sites (possibly limited to sunny days, if need be). Earlier in the manuscript it was pointed out during the discussion of the retrieved NO₂ (Figure 2e) that, in the afternoon of 17 July, the Ron Brown changed course, possibly entering a cleaner air mass. If that was indeed the case, then the original NO₂ loading assumed in the discussion on NO₂ removal from air masses that have been impacted by major urban areas (end of Section 5) may be an overestimate.

In addition to the one day shown for each measurement site, a plot with the average diurnal variation of the CHOCHO-to-NO₂ ratio for the whole measurement campaign (or at least for several days) should be provided for both sites. This average will give a much better idea on the relationship of CHOCHO-to-NO₂ ratios at the two measurement sites.

The Conclusion provides some numbers on the average for the maxima of the CHOCHO-to-NO₂ ratios at both sites, but it isn't clear how exactly they were computed (all observations? a subset?). A plot with the average diurnal variation for each site would be more instructive.

Author reply: While in principle we could agree with this suggestion, in this paper we focus on the methodological aspects of the CHOCHO retrieval. The interpretation of this data will be subject of a companion paper, which we do not like to anticipate here. Additional data would inevitably lead to a further discussion with a more meteorological and chemical focus, which is beyond the scope of this paper. Furthermore, we have chosen two very clear days. Adding cloudy days or showing an average might give systematical distortion. Concerning "the cleaner air mass" we made a small mistake. Actually the air mass seems not be cleaner but with less aerosol load while the

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trace gas concentrations are still enhanced. We changed this in the manuscript. The discussion on the NO₂ removal at the end of section 5 actually refers to the peaks of the CHOCHO-to-NO₂ ratio and we added in the manuscript “Ēratio of the CHOCHO-to-NO₂ peaks”. Thus, the changed air in the late afternoon does not affect the rough estimate for the midday. In order to clarify that the numbers in the conclusion refer to the chosen days we added “... on the chosen day”.

(5) References References should be limited to publicly available, peer-reviewed publications. Conference presentations, manuscripts under review, and Ph.D. or Masters/Diploma do not belong in the Reference section. The following following references must be deleted: * Brobrowski 2005 (Ph.D. thesis) * Bussemer 1993 (Diploma thesis) * Friesz 2001 (Ph.D. thesis) * Garcia 2005 (ACPD! If this paper has been accepted, state so) * Heintz 1996 (Ph.D. thesis) * Kurosu 2005 (Conference presentation; reference as "private communication" and/or place in footnote as "presentation at 2005 AGU Fall Meeting") * Kraus 2001 (ditto) * Sinreich 2004 (ditto) * vFriedeburg 1996 (Ph.D. thesis) The following references are questionable: * Beirle 2006 (conference proceedings, not peer-reviewed) * Fayt 2001 (Users Manual; at a minimum list availability if no other reference is available)

Author reply: We deleted Bobrowski (2005), Bussemer (1993) and vFriedeburg (2003). As suggested from the second referee Folkard Wittrock, for Frieß (2001) we added the internet link which enables the access to any time. We replaced Garcia (2005) by the reference of ACP We deleted Heintz (1996) and replaced it with Solomon et al. (1989), Heintz et al. (JGR) (1996) and Wagner et al. (2000). Since Kurosu (2005), Kraus (2001) and Sinreich (2004) are presentations we do not think that they should be referenced as “private communication”. We would like to keep these references also because footnotes should be avoided according to the submission rules of ACP. The same is valid for Beirle (2006). We also would like to keep Fayt (2001), because WinDOAS has been a very common and good retrieval program for many years, which Caroline Fayt and Michel v. Roozendael made available to interested users at no charge.

———— Editorial Comments ———— (1) Time: Either use "5:15PM" or "05:15h" but not "05:15 p.m." This occurs at various places in the manuscript.

Author reply: We changed all times to the X:XXPM format.

(2) "unequivocally": Substitute "unambiguously" for at least some of the "unequivocal" detections.

Author reply: We replaced one of the three "unequivocal" with "unambiguous".

(3) "convoluted": Change "convoluted by/with" to "convolved with" throughout. (4) Detailed comments Page 9461 Line 09: "(a Xe-arc light source)" Page 9461 Line 14/15: "In this study we present the first observation ..." Page 9461 Line 20: "by applying Lambert-Beer's law" Page 9461 Line 23: "The DOAS technique has been used in the detection of a large variety of trace gases, including ..." Page 9462 Line 15: "concentration along the light path" Page 9462/9463: "at the Massachusetts Institute of Technology (MIT) in Cambridge, MA, and in the Harvard Forest ..., and at Brookhaven ..." Page 9463 Line 20: delete "at the same time" Page 9464 Line 09: "The spectra were recorded ..." Page 9464 Line 12: delete "already" Page 9464 Line 14/15: "covered the wavelength range of 325-460 nm ..." Page 9465 Line 12: "Rayleigh and aerosol scattering" Page 9465 Line 13: "calculated from the respective FRS for each sequence" Page 9465 Line 15: "was allowed to shift against" Page 9465 Line 16: "convolved with the instrument slit function" Page 9466 Line 08: "above average" Page 9466 Line 22: "in the fit" Page 9467 Line 02: "Several sensitivity studies ..." [i.e., delete "Furthermore"] Page 9467 Line 12: "a slightly hazy but sunny day" Page 9467 Line 13: "without a NO2 cell" Page 9467 Line 12: "a slightly hazy but sunny day" Page 9467 Line 17/18: "the inversion procedure Sinreich et al. (2005) employed" Page 9469 Line 10: "over altitude" Page 9469 Line 15: "appear to be dominated by" Page 9471 Line 01: "For a rough estimate"

Author reply: Thank you very much for these corrections! We changed them all as suggested.

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