DEVELOPMENT OF A BROMINE OXIDE PRODUCT FROM GOME

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ABSTRACT

Bromine monoxide (BrO) is an atmospheric constituent playing an important role in the chemistry of both the stratosphere and the troposphere. Recent studies have demonstrated that BrO total columns can be retrieved on a global scale by analysis of backscattered solar spectra measured by the Global Ozone Monitoring Experiment (GOME), aboard the ERS-2 satellite since April 1995. The data analysis of this minor atmospheric trace gas however presents significant difficulties, so that the achievable precision of GOME BrO measurements still remains to be firmly established. The aim of the project described in this paper is to progress in the development of a state-of-the-art GOME BrO operational retrieval algorithm, carefully tested for stability and efficiency, and thoroughly evaluated. The project started in November 1998. First results presented here show the current status of the IASB-BIRA GOME BrO spectral fitting algorithm, results of initial sensitivity tests, and results of an intercomparison exercise involving GOME data evaluated by four different groups and BrO vertical profiles measured by the SAOZ-balloon instrument.

1. INTRODUCTION

GOME [Ref. 1] is a spectrometer which observes solar radiation back scattered from the atmosphere in a spectral region extending from the ultraviolet to the near-infrared with a moderately high resolution (0.2-0.4 nm). The instrument, aboard the ESA/ERS-2 satellite, flies in a sun-synchronous orbit at an altitude of 780 km with a local crossing time at the equator of approximately 10h30. Global coverage is achieved in about 3 days at the Equator and less than one day polewards of 70° latitude. The analysis of measured nadir radiances by the technique of differential absorption (DOAS) [Ref. 2] allows the retrieval of the vertical column abundance of ozone and nitrogen dioxide, as well as several other atmospheric trace gases [Ref. 1].

GOME operational data products are generated at the German Remote Sensing Data Centre of the DLR (DLR-DFD), these comprise Level-1 (earthshine radiance and solar irradiance spectra) and Level-2 (O_3 and NO_2 total columns, plus fractional cloud cover) products. Among the additional research products that can be obtained through the exploitation of the full spectral information available from GOME, BrO has received much attention in the last few years. Scientific studies have established [Ref. 3] and subsequently demonstrated [Ref. 4] the capability of GOME to measure BrO globally. The GOME observations have also been analysed to identify and characterise the sources of tropospheric BrO in polar spring [Ref. 5, 6].

As a result of these activities, much progress has been made in several aspects of the data processing so that the development of an operational BrO product from GOME can now be envisaged. Here we present the status of a project recently started at IASB-BIRA which aims at the development of a prototype operational retrieval algorithm, with capabilities for state-of-the-art retrieval of GOME BrO slant and vertical columns by the differential absorption technique (DOAS). The performances of the algorithm will be tested and verified by comparison with existing alternative algorithms developed by other groups, and comparisons with correlative ground-based data will be used for further validation of the results.

In section 2, the spectral analysis package currently developed at IASB-BIRA for both ground-based and GOME applications is presented. Its application to the analysis of GOME spectral data is then illustrated in section 3 with the presentation of first results on sensitivity tests and retrieval comparisons carried out so-far.

2. THE IASB-BIRA SPECTRAL INVERSION ALGORITHM

IASB-BIRA has been involved in ground-based UV-visible spectroscopic measurements of stratospheric trace species since early nineties. These activities have led to the development of a software package called Windoas, written in C language for Windows 95/NT. This software includes many refinements for DOAS analysis of atmospheric spectra in the spectral range from 300 to 700 nm, associated with a powerfull and convenient user interface (allowing for full menu-driven configuration of analysis parameters). It has been validated on several occasions in the past through participations to international intercomparison exercises, e.g. organised in the context of the Network for the Detection of Stratospheric Changes NDSC [Ref. 7, 18].

Windoas is currently used by six different European groups for the analysis of various kind of ground-based and balloon experiments. Within the present project, it is being adapted and further optimized for treatment of GOME spectral data. The analysis method implemented is the well-known differential absorption technique [Ref. 2], where characteristic absorption features of molecular constituents of interest are used to derive their atmospheric abundance. The method consists in fitting, using non-linear least-squares routines, the (GOME) atmospheric and solar reference spectra to a set of molecular absorption cross-sections measured in the laboratory. Despite the apparent simplicity of the technique, obtaining precise results requires advanced algorithms with capabilities for additional instrument characterisation and treatment of fine atmospheric effects.

The IASB-BIRA DOAS analysis software currently implements the following main features:

- Two fitting modes: standard DOAS (optical thickness) and intensity fitting.
- Accurate wavelength calibration including slit width determination by non-linear least-squares (NLLS) fitting to a Fraunhofer reference spectrum.
- Extended shift and stretch possibilities.
- Correction for wavelength dependent air mass factors (modified DOAS approach).
- Correction for the so-called I_0-effect [Ref. 9].
- Correction for GOME undersampling effects [Ref. 10]
- Ring cross-sections calculation [Ref. 11]

In its current state of optimisation, the algorithm allows the analysis of a complete GOME BrO orbit to be completed in approximately 2 minutes when running in standard DOAS mode and 4 minutes in Intensity fitting mode (tests made with a Pentium 400 Mhz running under Windows 95).

3. FIRST RESULTS

3.1 Precise wavelength alignment of GOME spectra

GOME irradiance spectra are re-calibrated in wavelength using a NLLS fitting method similar to the one originally described in Caspar and Chance [Ref. 8] where portions of the measured GOME spectra are adjusted to a Fraunhofer reference spectrum [Ref. 11, 12] degraded to the GOME spectral resolution. The procedure allows a determination of both the wavelength registration and the width of the (Gaussian) slit function with an accuracy in the range of respectively 0.003 nm and 0.01 nm, as estimated from the dispersion of the shift and width values retrieved in successive micro-windows (see Fig. 1). The algorithm is fast (GOME channel 2 analysed in less than 4 sec on a Pentium 400 Mhz) and includes a correction for residual O_3 absorption features present in the Fraunhofer reference.

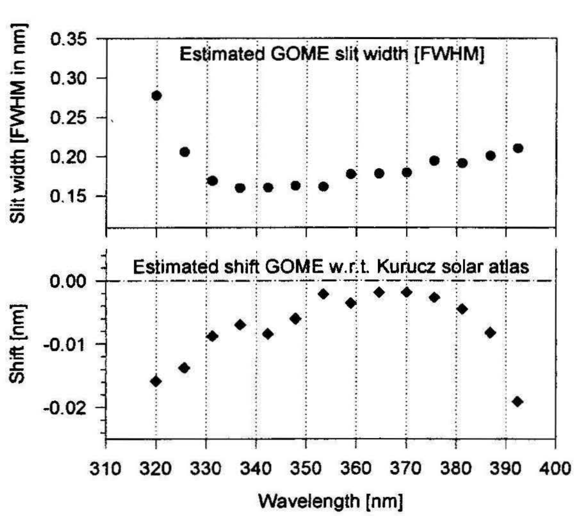

Figure 1. Shift and slit width parameters derived from non-linear least-squares fitting between a GOME solar irradiance and the high-resolution Kurucz atlas (see text).

3.2 BrO fitting

BrO fitting routines currently include the wavelength calibration procedure described above and use reference spectra for BrO, O_3, NO_2, OClO, O_4 and the Ring effect. The temperature dependence of the O_3 absorption cross-sections is accounted for by fitting two cross-sections. I_0-corrections are applied to NO_2 and O_3 reference spectra. The BrO absorption cross-section used is from Wahner (228 K). It is corrected for the stated shift of −0.17 nm in its wavelength calibration [Ref. 13]. Ring spectra are generated by rotational Raman scattering calculation [Ref. 11] using a GOME solar irradiance as the source spectrum.

Typical results of GOME BrO spectral evaluations are shown in Fig. 2. The upper plot illustrates one of the major difficulties encountered in the spectral evaluation, i.e. the large systematic residual features one obtains due to interpolation errors when shifting the undersampled GOME radiances. One possible way to overcome this problem is to apply low-pass filters to the spectra [Ref. 14]. An alternative approach is to try and model the effect [Ref. 10]. Current undersampling correction algorithms however are still imperfect, leaving systematic residual structures that can be (empirically) eliminated by fitting an additional cross-section generated by averaging residuals over one orbit (lower plot). Work is underway within the present project to try and improve this part of the data processing.

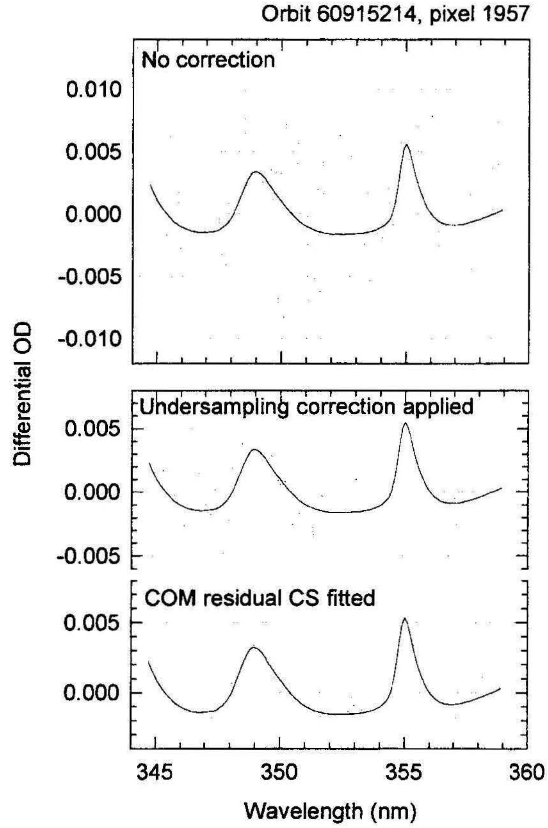

Figure 2. Results of the BrO spectral evaluation in three different analysis configurations. The solid and dotted lines show respectively the calculated and measured differential optical densities (OD).

3.3 Preliminary sensitivity tests

The flexibility of the Windoas programme makes it particularly well suited to investigate the sensitivity of the retrieval to different possible choices when setting up analysis parameters. Fig. 3 displays the results of a series of preliminary sensitivity tests recently performed. The aim is to try and define confidence limits for the retrieved slant column amounts. Test results presented here have been obtained for three pixels of the GOME orbit 60915214. They show the observed changes in BrO slant column amounts when using different Ring effect spectra, applying or not an undersampling correction, fitting spectra in DOAS or intensity fitting modes, re-calibrating or not the GOME wavelength scale, slightly changing the fitting interval, etc. Main findings coming up from this preliminary exercise can be summarized as follows:

- the difference between DOAS and intensity fitting results is small;
- the use of an offset parameter (constant term added to the radiance – to account e.g. for possible errors in the dark current correction) can have a relatively large impact on the retrieved BrO;
- there are differences in behavior when comparing different GOME pixels;
- the low-pass triangle filtering (used as an alternative to the undersampling correction) seems to lower the retrieved BrO amounts.

3.4 Comparisons GOME/ SAOZ-BrO balloon data

Knowledge about the vertical distribution of BrO is important for the determination of the so-called air mass factors (AMFs) needed to convert slant columns into vertical columns. Its is also important to investigate whether BrO total columns determined from GOME are consistent with integrated stratospheric profiles of BrO which can be measured using balloon instruments.

The SAOZ-BrO balloon instrument is a light UV-visible spectrometer developed at CNRS Service d'Aéronomie for the measurement, by solar occultation, of the vertical distribution of stratospheric O_3, NO_2 and OClO from small balloon gondolas (5000-10000 m^3) [Ref. 15]. Adaptations to the original design have allowed the detection of BrO in early 1997 [Ref. 16] and, since then, eight successful SAOZ-BrO flights have been performed in various atmospheric conditions: summer and winter high latitudes, mid-latitudes and tropics (Brazil). Recently the evaluation of all flight data

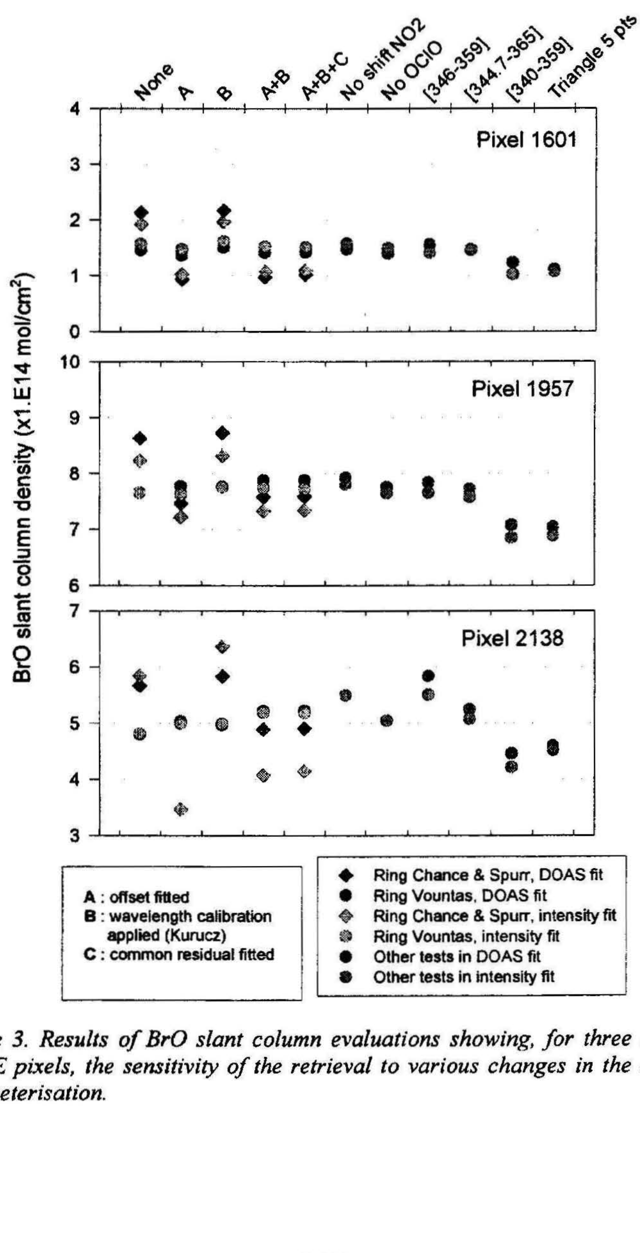

Figure 3. Results of BrO slant column evaluations showing, for three selected GOME pixels, the sensitivity of the retrieval to various changes in the analysis parameterisation.

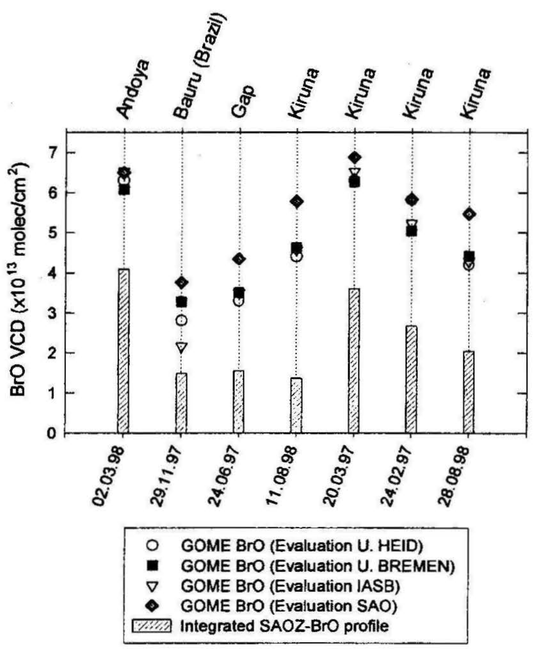

Figure 4. Comparison between BrO VCDs measured by GOME and integrated stratospheric profiles measured by the SAOZ-BrO balloon instrument.

has been revised in collaboration with IASB-BIRA.

In this work we have compared seven (out of the eight available) SAOZ-BrO profiles to BrO vertical column densities (VCDs) derived from GOME observations at coincident ground-pixels. The evaluation of GOME data has been performed by four independent groups (IASB, Uni. Bremen, Uni. Heidelberg and SAO). Fig. 4 displays the results of the comparison.

The determination of integrated column densities from SAOZ-balloon measurements requires assumptions about the BrO concentration at altitudes not sampled by the technique. For atmospheric levels above the balloon float altitude (30 km) a constant volume mixing ratio (vmr) of 14 pptv has been assumed while the BrO vmr was set to zero at altitudes lower than 10 km. The estimated uncertainty on BrO concentrations derived in the altitude region 10-35 km translates to an uncertainty on the VCD in the range 2.5-5.0 E12 molec/cm^2.

Although the error budget of GOME BrO evaluations is still difficult to establish (possible unknown sources of systematic error cannot be confidently ruled out), the dispersion of the results obtained by the different groups provides a good hint as to one can consider as reasonable confidence limits. When comparing GOME evaluations (symbols) we see a reasonably good consistency although differences as large as 1E13 molec/cm^2 can still be obtained. SAO evaluations in particular seem to be positively offset compared to IASB-BIRA and other ones. These differences mainly originate in the spectral analysis (BrO AMFs used by each group were found to agree within a few percents). Analysis parameters used by each group are currently explored in order to try and understand the discrepancies. Note that the larger dispersion in Bauru evaluations are largely due to the Southern Atlantic anomaly in the earth magnetic field which locally degrades the performance of the satellite instrument.

Despite the uncertainties on both GOME and SAOZ evaluations reported here, the comparison of Fig. 4 displays two striking features:

(1) there is a rather good (and encouraging) correlation between GOME and SAOZ BrO observations

(2) GOME VCDs appear to be systematically larger than stratospheric columns derived from balloon data.

Although measurement errors cannot be ruled out, these observations suggest that significant BrO amounts might be present at altitudes below the region where the balloon instrument is measuring, as suggested already by K. Pfeilsticker and co-workers [Ref. 17]. A BrO mixing ratio in the range 1-2 pptv below 10 km altitude would be sufficient to reconcile the observations.

4. CONCLUSION

Activities recently started at IASB-BIRA in view of the development of a prototype algorithm for operational GOME BrO retrieval have been described. The project includes algorithmic developments (optimisation of GOME BrO fitting and AMFs calculations) as well as validation tasks. It is supported by ESA/ESRIN and conducted in collaboration with other groups actively involved in GOME BrO retrieval activities.

The current preliminary version of the IASB-BIRA GOME BrO algorithm is shown to provide results consistent with those of other groups. Its large flexibility makes it ideal to investigate the sensitivity of the retrieval to a large variety of changes in the analysis configuration.

The comparison between GOME BrO VCDs evaluated at ground-pixels in coincidence with the location of seven flights of the SAOZ-BrO balloon instrument shows that both sets of measurements are nicely correlated. There is, however, a systematic offset between GOME and balloon data, GOME BrO VCDs derived from GOME being larger by 2-3 E13 molec/cm^2. Although better characterisation of the measurement errors is required before drawing definitive conclusions, this result suggests that significant amounts of BrO (in the range 1-2 pptv) could be present at tropospheric altitudes.

5. ACKNOWLEDGEMENTS

ERS-2 GOME operational level-1 products have been processed at DFD/DLR on behalf of ESA. The reported activities are funded by the ESA/ESRIN contract no. 13153/98/I-DC. We greatly acknowledge Dr. Claus Zehner for his support to the project and Dr. M. Vountas for providing Ring cross-sections data sets.

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