Validation of MOPITT carbon monoxide and methane measurements using remote sensing by IR solar spectroscopy of moderate resolution combined with in-situ measurements.

(A progress report on NASA-approved validation project)
June 1999

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INTRODUCTION

The aim of the project is to validate the measurements of a gas-correlation space-based spectrometer MOPITT, which is a part of the EOS/Terra spacecraft, using spectroscopy of moderate resolution. The focus is on routinely operating Russian spectrometers. One of the spectrometers is now in Canada; it has been upgraded and compared with other instruments. Its measurements will constitute a valuable complement to the measurements of the existing FTIR/NDSC network (cf. projects, supervised by Dr. N. Pougatchev and Dr. F.Murcray). It is funded by Canadian and Russian funding agencies. This is a report for the period between January 1998 and May 1999.

Because of a delay in the Terra launch a real validation of MOPITT is still on schedule. However, during the period between the start of this project and the present time, important preparatory work has been done. This work included upgrading the instrument itself, improving retrieval procedures and comparisons with other instruments. Also a joint Russian-Canadian analysis of available spectroscopic information on CO over Russia during last 27 years has been performed.

UPGRADING THE SPECTROMETER

The spectrometer (aka *Sarcophagus*) was designed and manufactured at the Institute of Atmospheric Physics, Moscow in the early 1970s. However, its elegant optical design and durability allows continued use. Its drive mechanics required upgrading. It was performed at the UofT electronic workshop (PERC). Its scanning drive was replaced by a modern precise stepping motor, compatible with LabView software. The data acquisition block was also upgraded: now both scanning control and data recording are managed by LabView software. The very significant efforts of Mr. Eamonn McKernan (UofT), Mr. Paul Ruppert and Mr. Peter Hurley (both of PERC/UofT) are highly acknowledged.

CHARACTERISATIONS OF THE SPECTROMETER IN A LAB

The performance of the spectrometer was studied using a method proposed by Dr. Boyd Tolton. A sealed cell containing some amount of CO, which is approximately equal to the total amount of this gas in the atmosphere, was used for this purpose. A transmission spectrum of this cell at the wavelengths of the CO fundamental band was measured using the spectrometer. Then the spectrum of the same cell was obtained using the laser spectrometer of very high resolution (0.00006 cm-1). After that both spectra were fitted by a calculated spectrum with number of CO molecules as a fitting parameter. There were two goals of this experiment: (i) a standard cell can be used for a comparison of spectrometers to one another; (ii) narrow lines of the CO spectrum can be used to determine the shape of the instrumental function.

IMPROVEMENTS IN RETRIEVAL TECHNIQUES

The most reliable and convenient approach for retrieving information from spectra of the total atmospheric column is multi-parameter fitting using the minimum variance between a calculated and a measured spectrum as a criterion of proximity. There is a code, named SFIT and designed by Dr. C. Rinsland (NASA), which has been in use for many years to analyze FTIR spectra. However, this program can not be used for spectra of grating spectrometers directly. A new code was developed by Mr. McKernan. It was based on MATLAB software, GENASIS line-by-line code and common HITRAN-96 line parameters compilation. The technique was compared to the traditional equivalent width procedure (see below for examples of retrievals)

FIELD COMPARISONS TO OTHER INSTRUMENTS

Field comparisons are a key component of the project. We should be confident in the data being obtained by our own instrument before validating data from space. There are two groups of foreign techniques: (i) air sampling at different altitudes and consequent gas-chromatographic analysis; (ii) ground-based spectrometers of high resolution (FTIRs). Comparisons to both groups are necessary. Consistency with FTIRs ensures a comparability of our moderate resolution spectrometers' data to the data of NDSC; a consistency with the most precise presently GC techniques allows us to interpret the satellite data in absolute units of atmospheric mixing ratios of trace gases.

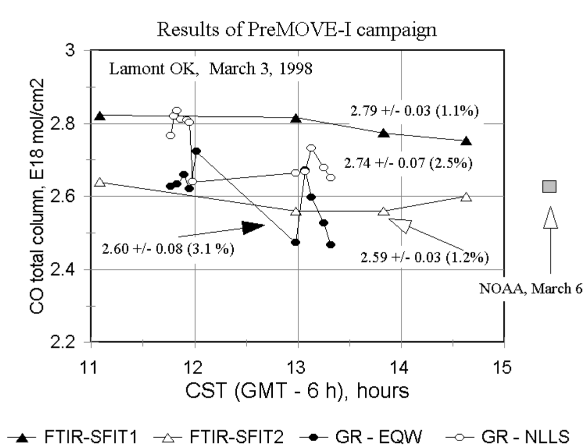
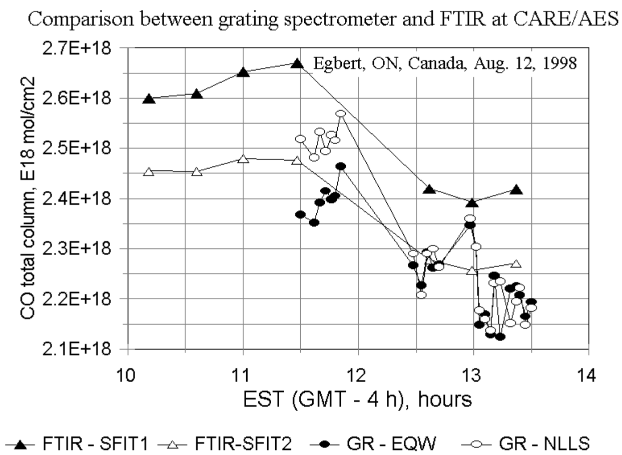


Figure 1 Spectroscopic measurements of CO total column amount using FTIR and grating spectrometer. Retrieval procedures were SFIT1 and SFIT2 (both proposed by Curtis Rinsland, LaRC/NASA), equivalent width (EQW) and non-linear least square technique (by Eamonn McKernan). FTIR measurements were performed by Thomas Steven (DU), SFIT2 retrievals

were made by Nicholas Jones (NIWA, New Zealand). REFMOD-95 initial profile was used for all the retrievals.

In 1998 two comparisons have been done. The first one was performed at the ARM CART site in Lamont, Oklahoma in early March 1998. Our instrument was installed side-by-side SORTI (Solar Radiance Transmission Interferometer) which is actually a Bruker FTIR (120M) and used in its low-resolution mode (0.025 cm-1). This resolution was 8 times better than ours. Weather conditions and malfunctioning of SORTI permitted just one day of concurrent measurements (March 3, 1998). We compared these data to flask samples collected on March 6, 1999 by CMDL/NOAA (Paul Novelli) over the site at heights between 0 and 8 km.



The second comparison was done in the summer of 1998 at the Center for Atmospheric Research Experiments (CARE), in Egbert, Ontario, Canada.

Figure 2. Results of CO spectroscopic measurements in Egbert, Ontario. Symbols are the same with Fig. 1. No air sampling was available.

The grating spectrometer was compared to a BOMEM FTIR (resolution 0.004 cm-1) operated by Hans Fast and Richard Mittermeier (AES Canada) (Fig 2). There were three days of measurements in Egbert. The results of other days were similar to those on August 12. Two sets of spectra were recorded by FTIRs (triangles) and *Sarcophagus* (grating spectrometer, circles) concurrently. SFIT1 determines the total column by a simple scaling of the *a priori* profile, meanwhile the SFIT2 modifies the apriori profile layer by layer. Both algorithms for the *Sarcophagus* spectra used the same procedure as SFIT1. The *a priori* profile was assumed to be 110 ppb between the surface and 5 km, 100 ppb between 5 km and 10km. Lower values (down to 20 ppb) were assumed for the stratosphere. The shift in FTIR data, processed by these two techniques, reflects the different nature of the techniques and illustrate an influence of the shape of the a priori profile on the retrieved total column. For the two given cases caracterized by the mixing ratios diminishing with height an error due to the wrong a priori profile was 6-7%. The systematic difference between SFIT1/FTIR and the *Sarcophagus* results was 4-6%.

The measurements revealed that FTIR has instrumental noise around 1% comparing to appr. 2%-scatter of the data, obtained by the *Sarcophagus*. Preliminarily we attribute this difference to the less precise drive mechanism of the latter rather than to lower spectral resolution. We plan to conduct one field campaign more and after that final conclusions on the consistency between spectroscopic and in-situ GC techniques could be performed. The results of comparisons were published in a paper by Wang et al. (1999)

ANALYSIS OF AVAILABLE CO DATA

CO and CH4 measurements have been underway near Moscow since 1971. They started when calculations were performed using shifting rulers. At that time a manual procedure was proposed for spectra processing. This technique dealt with spectra recorded by a chart recorder. Just recently the Moscow team began computer recording of spectra. However, this historical set of data is very valuable. Its main advantage is in its consistency. Another feature is that the spectroscopic technique provides data for the whole atmosphere (in this case mostly for the troposphere) in contrast to air sampling in the surface layer.

Russian measurements were reported to the International Conference on Atmospheric Carbon Monoxide and its Environmental Effects in Portland, Oregon, in December 1997 (L. N. Yurganov E. I. Grechko and A. V. Dzhola, . Zvenigorod Carbon Monoxide Total Column Time Series: 27 Years of Measurements). It was decided to publish the papers, presented to the Conference, in a special issue of the *Chemosphere* journal. Now this issue is in press.

The main conclusions of the paper follow.

1. A surprisingly close correlation between Zvenigorod data total column data set and free tropospheric *in situ* measurements at Niwot Ridge, Colorado, was found. CO mixing ratios over Russia had a positive trend for the period between 1971 and 1983. However, the CO data taken after 1983 do not show any long-term increase. This is in contradiction with a CO decline reported for the marine boundary layer.
2. We have found positive correlations between measured CO mixing ratio in the entire troposphere and total ozone: a slope of the regression line is 0.53 ppb CO / Dobson Unit of O_3. This correlation probably reflects the dependence of CO sink, i.e., OH concentration, on the intensity of UV radiation. It is known that the total column amount of ozone is diminishing in mid latitudes of the Northern Hemisphere. Ozone diminished with time with a rate of – 1.28 +/- 0.15 DU /year.

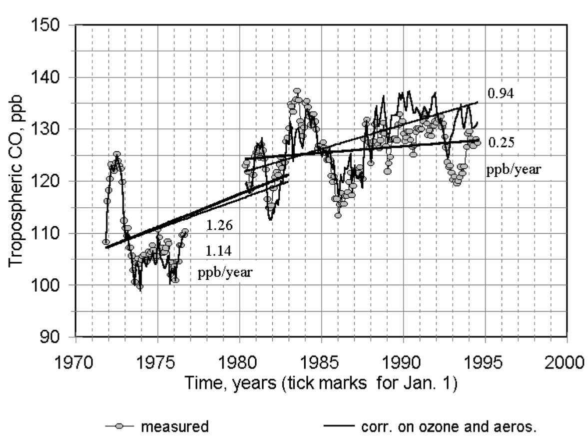


Figure 3. Smoothed and deseasonalized CO tropospheric mixing ratios, measured by a spectrometer of moderate resolution in Zvenigorod near Moscow (circles); the trend after 1983 is small (0.25 ppb/y). The values, corrected for ozone and aerosol influence have a positive trend 0.94 ppb/y, which is close to that before the start of ozone depletion (i.e., 1970 - 1983).

3. Actually measured CO mixing ratios in Zvenigorod have been corrected for unstable ozone after 1983 and this corrected CO had a slope 0.94 ppb/year, which is close to the “normal” CO incline (Fig. 3).
4. Therefore, the instability in total ozone and associated changes in UV radiation can explain the measured changes of CO in the troposphere of the Northern Hemisphere.
5. This last conclusion is important in assessments of a long-term trend in tropospheric hydroxyl, which is a sink for numerous atmospheric trace gases, including “greenhouse” gases. In particular, the current deceleration of methane increase seems to be a result of ozone depletion.

PLANNED ACTIVITIES

1) July 1999. PreMOVE-II experiment in Colorado (Canadian participation is funded by CSA and NSERC). It is planned to compare at least 3 techniques: FTIR (F. Murcray, DU), grating spectrometer (UofT) and airborne sampling with GC analysis (P. Novelli, NOAA).
2) August 1999. The Sarcophagus spectrometer is planned to be moved to Argentina and deployed at Valdes Peninsula National Park (application for International Opportunity Fund is submitted to NSERC by Dr. Tolton).
3) September 1999. Dr. L.Yurganov plans to travel to Russia for inspection of measurement facilities (an application for travel funds has been submitted to NATO Science Programme).
4) Exchange of researchers between Russia and Canada is planned during 1999-2000 as a part of the NATO Collaboration Linkage Grant (a proposal has been submitted by Dr. B. Tolton).
5) November 1999 – January 2000. The first validation campaign MOVE-I. We plan to record spectra from the ground at 3 or 4 sites (2 or 3 sites in Russia and 1 site in Argentina). Analysis of spectra will be performed in Toronto. Results will be submitted to NCAR for a comparison with MOPITT measurements.
6) We plan to attend several scientific meetings during 1999 (Gordon Research Conference in June 1999, OSA Meeting in June 1999, SPIE Meeting in July 1999, NCGG-2 Meeting in September 1999, IGAC Meeting in September 1999).

PUBLISHED PAPERS

J.Wang et al. The pre-launch MOPITT validation exercise (Pre-MOVE). 1999. *The Earth Observer*, 11, No 1, 5-9.

Yurganov L.N., E.I. Grechko, and A.V. Dzhola, 1999, Zvenigorod Carbon Monoxide Total Column Time Series: 27 years of Measurements. *Chemosphere*, in press.