MOPITT Validation Using Ground-Based IR Spectroscopy

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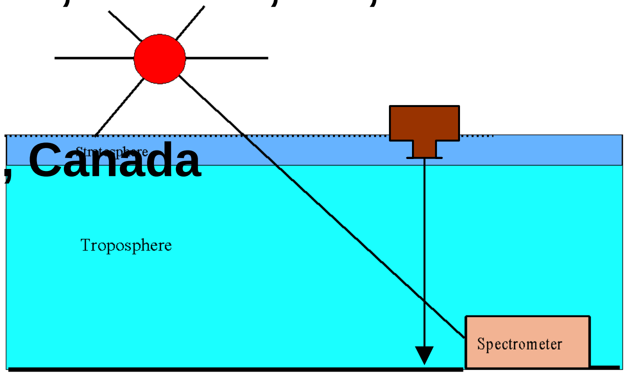


ABSTRACT.

Three sun-viewing grating spectrometers installed in Russia and Argentina are being used for validation of carbon monoxide measurements from the MOPITT instrument on board of the Terra satellite. Considerable efforts to upgrade the spectrometers and to improve the retrieval procedures were necessary. The instruments were compared to FTIR spectrometers in Canada and USA, as well as to direct sampling from an aircraft in Russia. Good agreement in results, obtained between March, 2000 and April 2001 demonstrated the high quality of MOPITT data for the free troposphere. Some updated results of CO long-term monitoring from the Russian station are shown as well.

SPECTRA AND RETRIEVALS.

Infrared spectra of the total atmospheric depth using the sun as a light source are being measured by a grating spectrometer with spectral resolution of around 0.2 cm^{-1}. A new retrieval algorithm was recently developed using non-linear least squares minimization (Fig. 1).

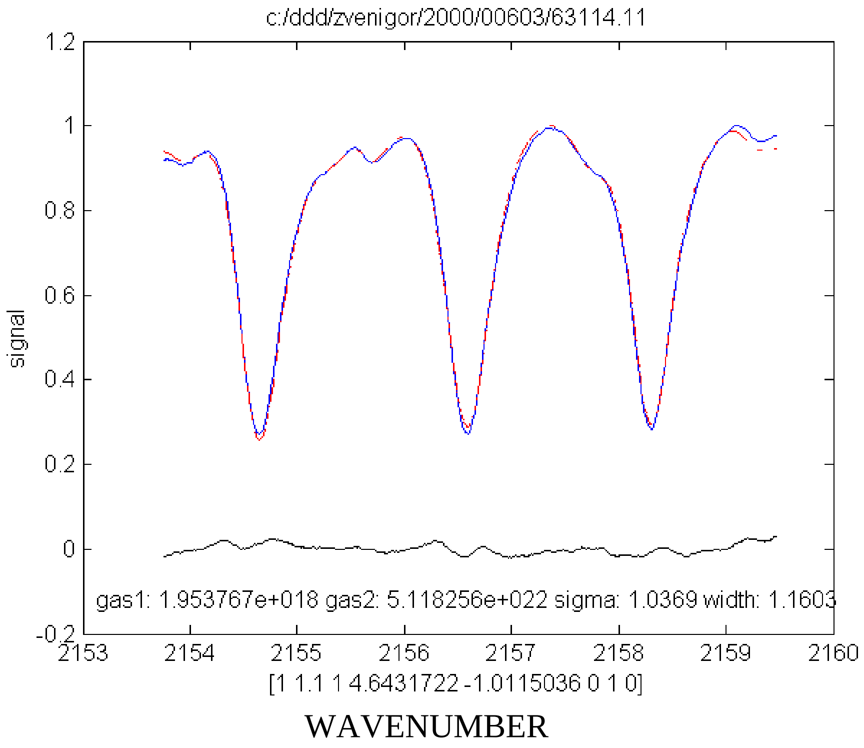


Fig. 1. Spectrum of the total atmosphere, observed in Zvenigorod, June 3, 2000 (blue) and calculated spectrum (red) which was fitted to the observed one by changing 8 parameters (gas 1(CO), gas 2 (H2O), resolution, gain, slope of the gain, 3 parameters of the wavenumber scale). Lower curve is 'Observed minus Calculated'.

ESTIMATES OF THE MOST IMPORTANT ERRORS

a) The uncertainty due to instrumental function

The spectral resolution of the grating spectrometer (known in Russia under the nickname *"Sarcofag"*) is around 0.2 cm^{-1}. This means that it can not measure the actual shape of spectral lines, broadened mainly by molecular collisions in the troposphere. The spectrum is distorted and the function, describing this effect is called the instrumental function (IF). The shape of the IF, included into the procedure of spectrum calculation, is known just approximately, and it changes with time, degree of alignment, etc. A corresponding error may be estimated from side-by-side comparisons against high resolution Fourrier-Transform Infrared interferometers (FTIR) (Fig. 2 & 3). This uncertainty was estimated to be ± 4%.

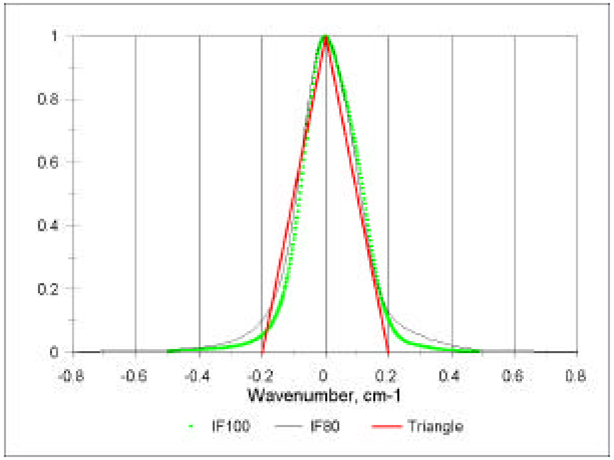
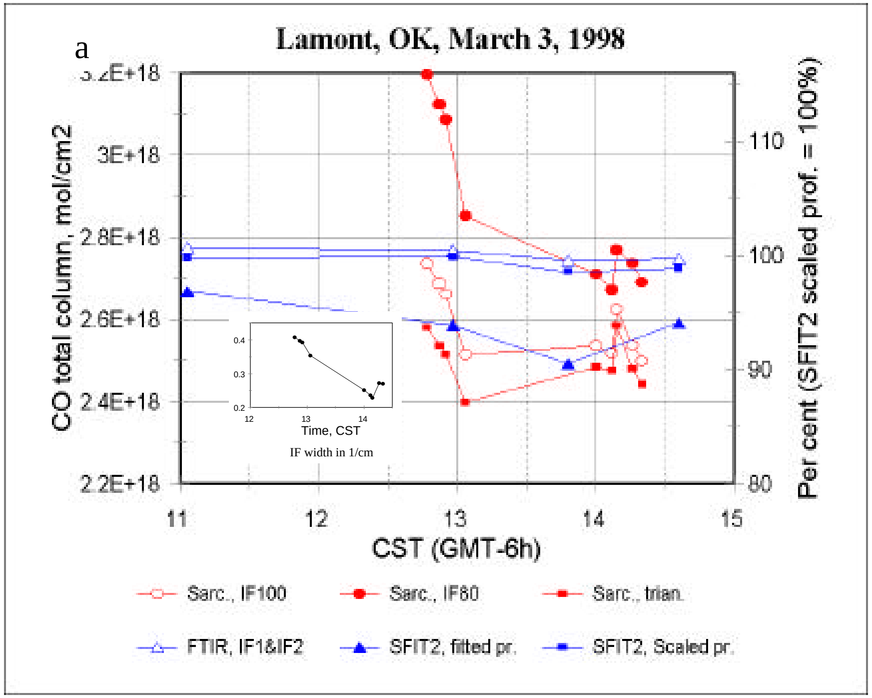


Fig. 2. Instrumental functions of the spectrometer, measured with two geometric slit width 100 µm (green) and 80 µm (black), normalized on unity in the maximum and on 0.2 cm^{-1} in width (note that normal slit width is 100 µm). These shapes, however, should be considered just as possible realizations of the IF; the actual shape depends on many things. Triangle function (red) is the IF for the "ideal" spectrometer.



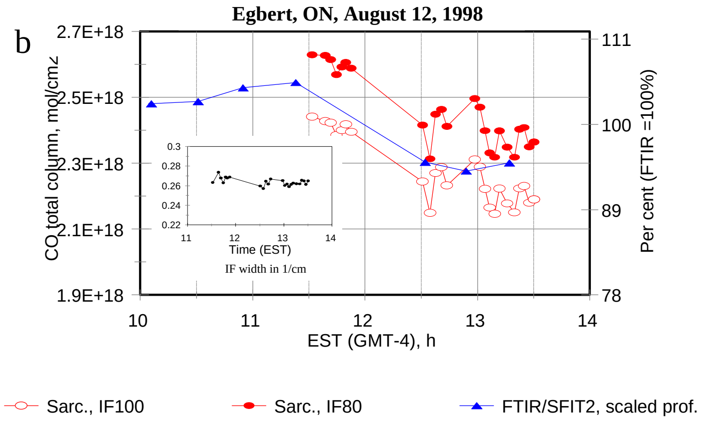


Fig. 3, a, b. Side-by side comparisons between spectrometer Sarcofag (red) and FTIR (blue). CO total columns were retrieved from Sarcofag spectra with three a priori IF, (see Fig. 2) and with scaled a priori standard CO profile (see Fig. 10). FTIR spectra were processed using the same code as one for Sarcofag (open triangles) and SFIT2 code with scaling standard profile (rectangles). The results were similar. Also SFIT2 was applied to fit the CO profile (full triangles), total column was 7% lower (reflects profile dependence, see below). Inserted is the width of IF retrieved from Sarcofag spectra; the instrument was under alignment (focussing) before 13 GMT. The range of retrieved total columns after 13:30 can be considered as uncertainty due to the shape of IF.

a) The uncertainty due to unknown profile of the gas

Strictly speaking, the grating spectrometer (like most of other remote sensors, e.g., MOPITT) does not directly measure the total column number of molecules. Its sensitivity varies to different atmospheric heights and can be described by the averaging kernel. As a result, the retrieved total column may depend on actual vertical distribution of the measured trace gas and its *a priori* (assumed) profile. We used a set of 129 CO profiles, measured in different regions of the world (at Carr, CO, near Tasmania, field campaigns like TROPOZ, etc) to test this dependence (i.e., "profile uncertainty").

The equation, that connects "retrieved" (or "effective") total column Q and real gas profile *q(p)*, where *p* is air pressure, is as follow:

$$\mathrm{Q} = \int \{\mathrm{q_a} + a(p)[q(p) - q_a(p)]\}dp \text{....................} (1)$$

Here *a(p)* is averaging kernel (Fig. 4, 5) and $q_a(p)$ is *a priori* CO profile.

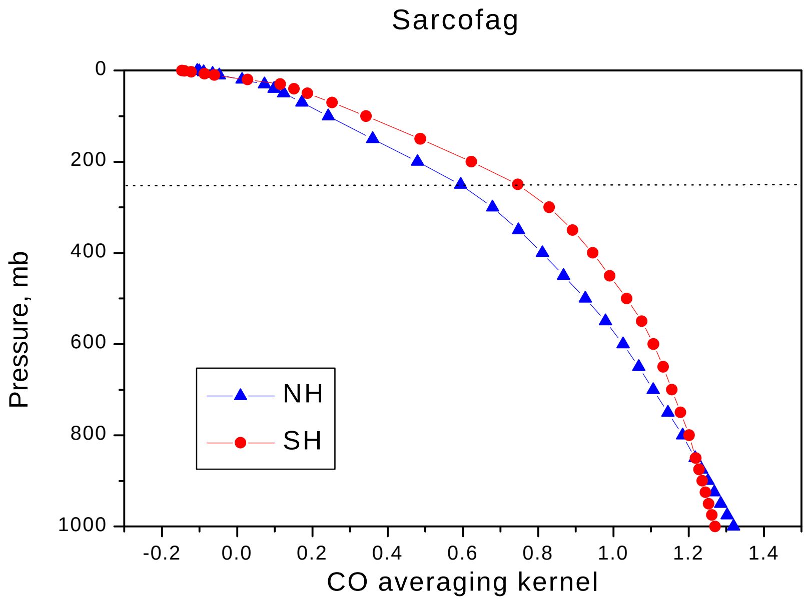


Fig. 4.

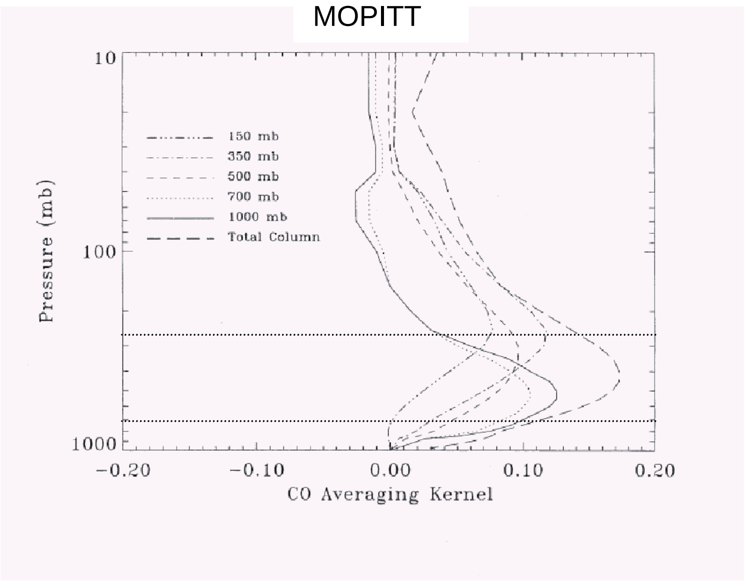


Fig. 5.

CO averaging kernels for the *Sarcofag* spectrometer (Fig. 4) (for *a priori* CO profiles assumed for northern hemisphere (NH) and southern hemisphere (SH) see Fig. 10) and for MOPITT (Fig. 5). Dotted lines indicate altitude regions in the atmosphere used below for averaging retrieved mixing ratios (250 - 1000 mb for *Sarcofag* and 250 - 700 mb for MOPITT).

Results of integration according to formula (1) are in Fig. 6.
STD uncertainty due to the unknown profile is ± 3% for Zvenigorod data.

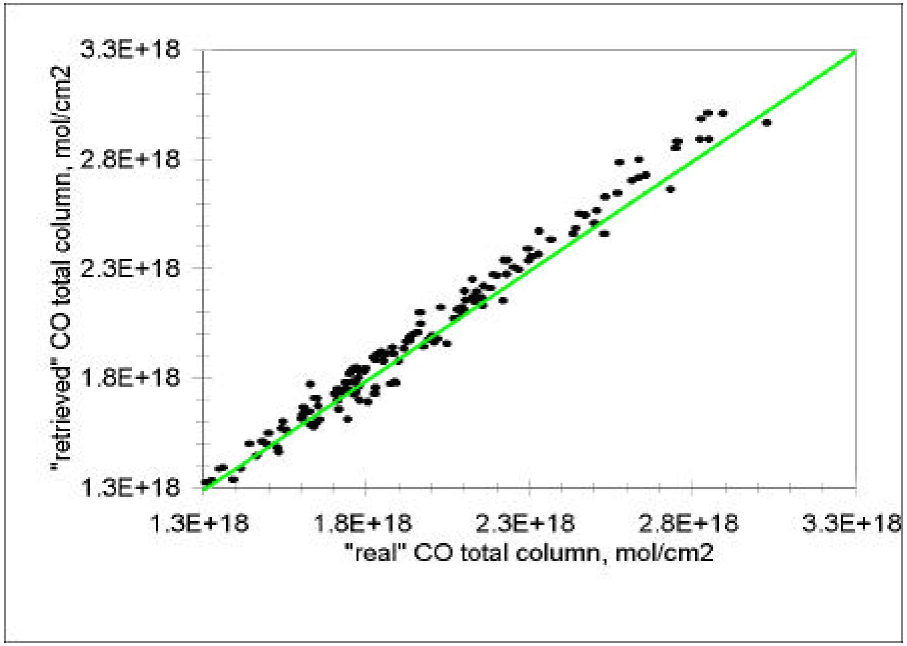
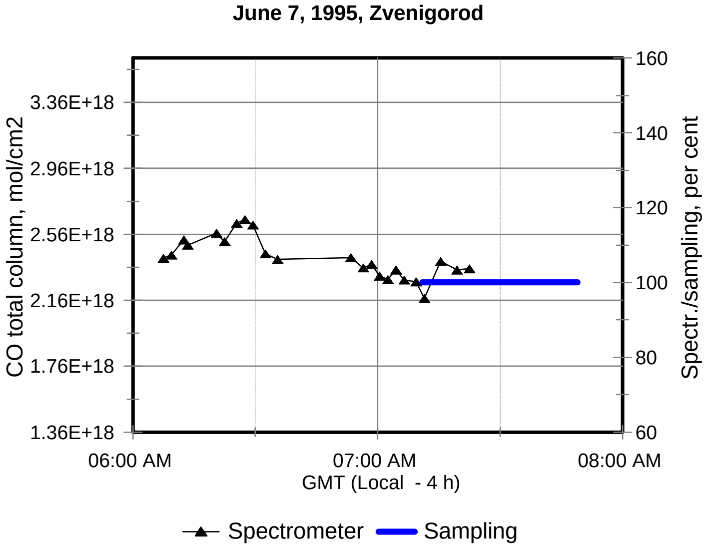


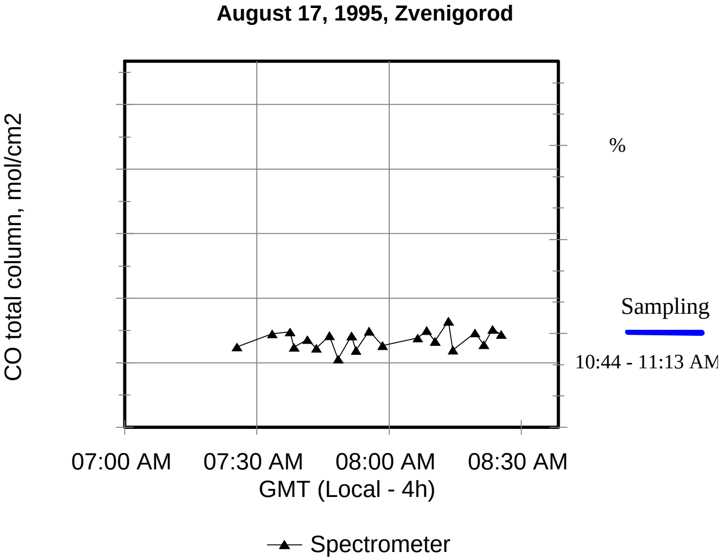
Fig. 6. An exercise to estimate an uncertainty due to profile variations. "Real" total columns are integrated CO profiles measured in various sites of the Northern Hemisphere. "Retrieved" total columns were calculated using the formula (1) and represents the values which would be retrieved from spectra with our standard *a priori* assumed profile (see Fig. 10). Green line is "retrieved" = "real".

The uncertainty of an individual total column CO measurement is estimated to be +/- 6-8%. A very similar uncertainty can be attributed to the estimate of the mean tropospheric mixing ratio (i.e., tropospheric partial CO column divided by the column number of air molecules). Actually, troposphere contains 90-95% of total CO.

COMPARISONS TO DIRECT SAMPLINGS FROM AN AIRCRAFT.

CMDL/NOAA in collaboration with Russians conducted 8 flights between June 1995 and July 1996 in the vicinity of Moscow. Three of these coincided with measurements of CO in Zvenigorod (Fig. 7). The distance between Zvenigorod and the site of profiling was around 100 km. In two cases (95/06/07 and 95/08/17) total columns measured spectroscopically and directly were similar. On March 25, 1996, CO over Zvenigorod was found to be ~15% higher than measured directly at the same time but 100 km far away; however, CO observed by spectrometer dropped to the lower level by 9:30 am, i.e., 1.5 h later. Most probably the aircraft and spectrometer were in different air masses at the moment of sampling.





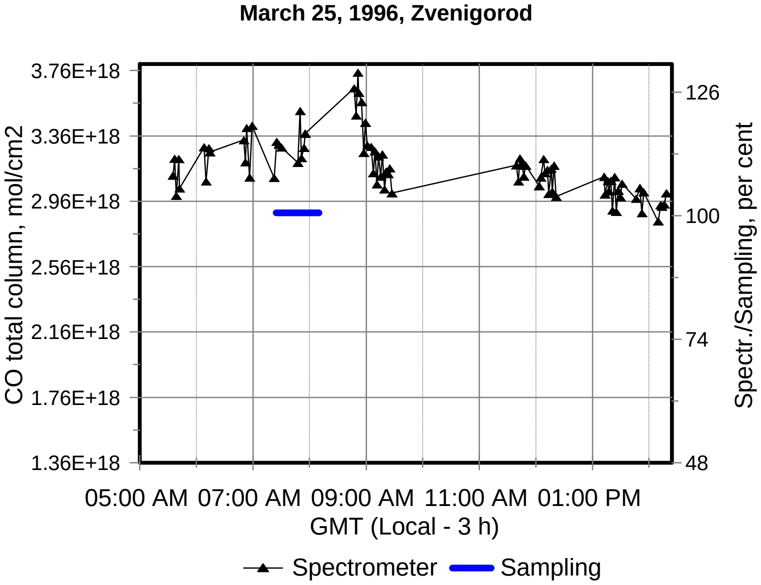


Fig. 7. Comparisons between *Sarcofag* and direct sampling of CO mixing ratio from an aircraft with consequent GC analysis. The value of total column for sampling is obtained by integration over the profile in the sampled vertical range (0.2 - 6 km) and extended for the heights above the ceiling. This profile was used as the *a priori* for spectral retrievals. Horizontal span of the bars corresponds to the actual duration of flights. Note that vertical scales are the same for these 3 plots. Direct sampling was assumed 100% for the right-hand scales.

COMPARISON TO MOPITT MEASUREMENTS.

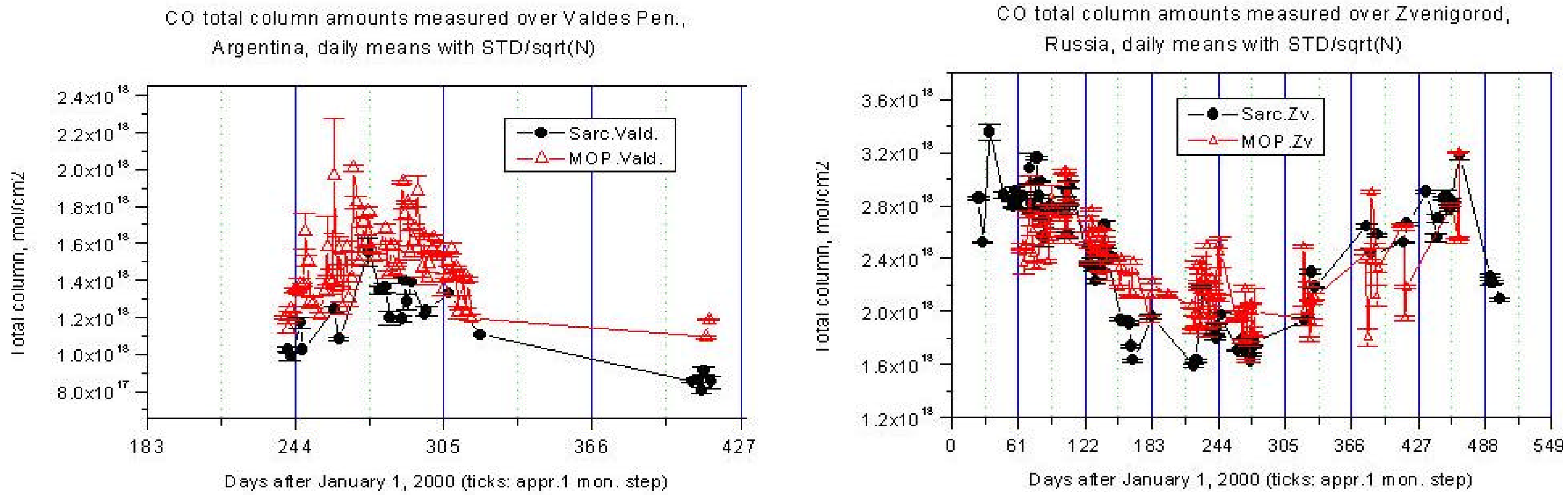
MOPITT supplies the following standard data products: mixing ratios for selected pressure levels (i.e., profiles) and the total columns derived by integration of the profiles.

First we tried to compare total columns (Fig. 8). We found a persistent 20% bias for the Argentine site and wide range of disagreements for the Russian Zvenigorod site (from -20% to +20%). This picture seems to be very difficult to interpret.

As a matter of fact, the averaging kernels of these two instruments are different (Fig. 4, 5). Current version of MOPITT retrievals is based on channels centered at ~4.5 μm and a drop in sensitivity near the surface takes place. As a result, a layer between zero and 2 or 3 km of altitude, which is very important for total column amount, is almost missing. So, Fig.9 presents a comparison of mixing ratios, averaged over altitudes, where averaging kernels of these two instruments are sufficiently high; 250-1000 mb for Sarcofag (entire troposphere) and 250-700 mb for MOPITT (free troposphere). In the SH (left picture) these mixing ratios become closer to one another, but MOPITT is still higher. In the NH summer MOPITT and Sarcofag data are similar, but in March-April a difference between them amounts to 35% (tropospheric mean is higher than free tropospheric mean). Also plotted are mixing ratios retrieved by MOPITT algorithm for the lower level (centered at 850 mb) and available data on CO mixing ratio measured directly near the surface at Tierra-del-Fuego, Argentina, 54º S.

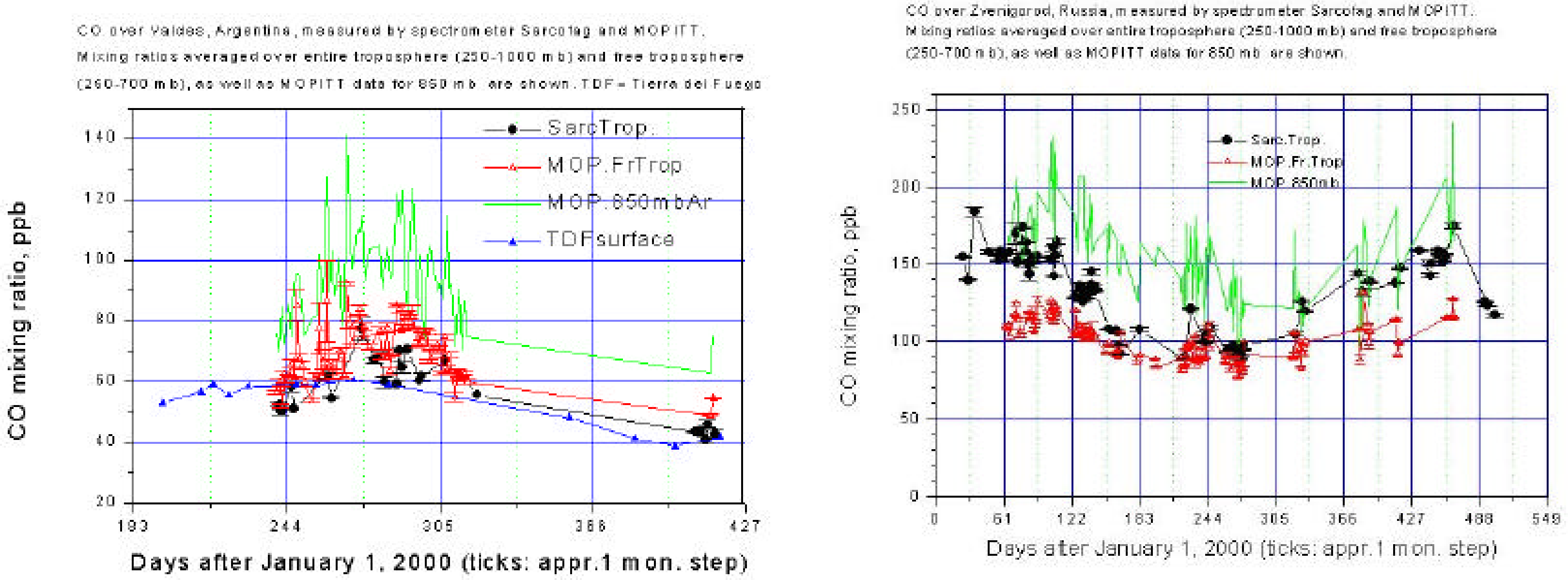
One may assume that MOPITT overestimates CO boundary layer mixing ratio in the NH summer time as well as in SH by 40 - 50 ppb.
This assumption is based on comparison of data for different heights. A look at the available information on CO profiles would be helpful.

Fig. 8. COMPARISON OF CARBON MONOXIDE TOTAL COLUMN AMOUNTS


CO total column amounts measured over Valdes Pen., Argentina, daily means with STD/sqrt(N)

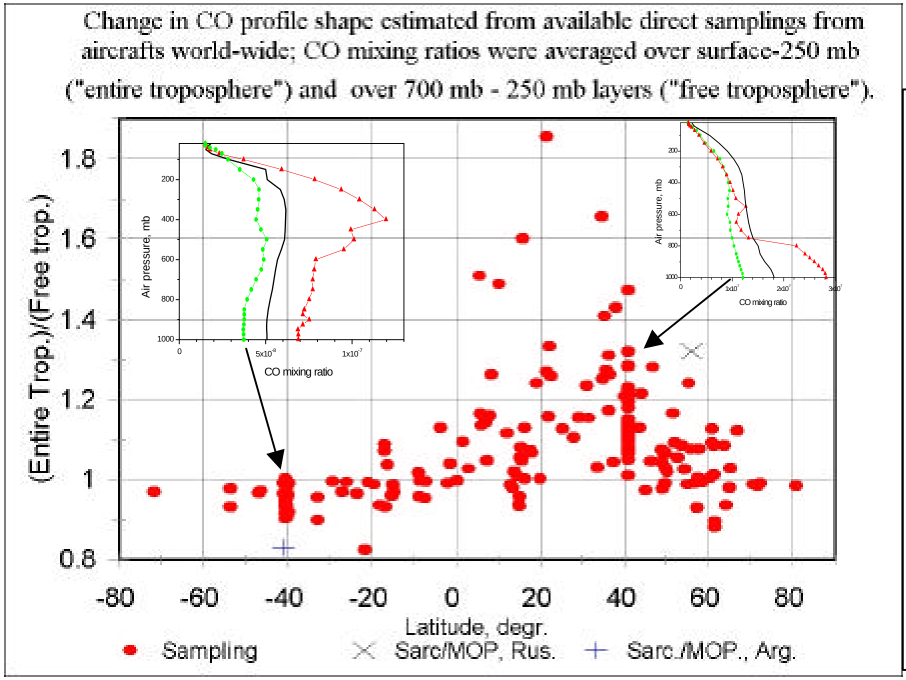
CO total column amounts measured over Zvenigorod, Russia, daily means with STD/sqrt(N)

Fig. 9. COMPARISON OF CARBON MONOXIDE AVERAGE MIXING RATIOS


CO over Valdes, Argentina, measured by spectrometer Sarcofag and MOPITT. Mixing ratios averaged over entire troposphere (250-1000 mb) and free troposphere (250-700 mb), as well as MOPITT data for 850 mb are shown. TDF = Tierra del Fuego

CO over Zvenigorod, Russia, measured by spectrometer Sarcofag and MOPITT. Mixing ratios averaged over entire troposphere (250-1000 mb) and free troposphere (250-700 mb), as well as MOPITT data for 850 mb are shown.

EVOLUTION OF CO PROFILES WITH LATITUDE



Change in CO profile shape estimated from available direct samplings from aircrafts world-wide; CO mixing ratios were averaged over surface-250 mb ("entire troposphere") and over 700 mb - 250 mb layers ("free troposphere").

Fig. 10. CO mixing ratio, measured by *Sarcofag* for the entire troposphere relates to CO mixing ratio measured by MOPITT for the free troposphere as 1.32/1 (Russia) and 0.83/1 (Argentina). One can compare these values (crosses) to available information derived by world-wide direct sampling. Inserted are examples of CO profiles measured over Tasmania (left) and Carr, Colo. (right) together with a priori profiles used for our retrievals (black lines).

According to Fig. 10, the observed relation between mixing ratios measured from the ground and from space (crosses in Fig. 10) seems reasonable.

EVOLUTION OF CO VERTICAL DISTRIBUTION DURING THE YEAR

In 1995 the spectrometer, which is now in Argentina, measured CO spectra in Fairbanks, Alaska, concurrently with direct measurements by D. Jaffe in the surface layer. Also continuos data of CO monitoring in Barrow, Alaska (appr. 700 km to the North), conducted by CMDL were available. More recently these spectra were reprocessed using the current version of retrieval algorithm and newer HITRAN parameters (Fig. 11). We see that in May-April, 1995, CO mixing ratios for the entire troposphere were in the range 140-160 ppb with surface layer values near 180 ppb. Beginning with May the two data sets converge with just one spike of tropospheric average in July.

This seasonal pattern agrees well with that observed in 2000 over Zvenigorod. One may speculate that the boundary layer over the considerable part of NH is polluted by man-made CO during cold part of the year. This pollution starts to grow in September-October, reaches its maximum in March and almost disappears by the end of May. No similar polluted bottom layer presents in the SH mid/high latitudes. On the contrary, the SH boundary layer is relatively clean, a moderate pollution from biomass burning is observed in the free troposphere over Southern Argentina.

CO measured by grating spectrometers over 2 Russian sites between June 1 and October 31, 2000, in comparison to concurrent MOPITT data (mean mixing ratios for altitude ranges specified below).

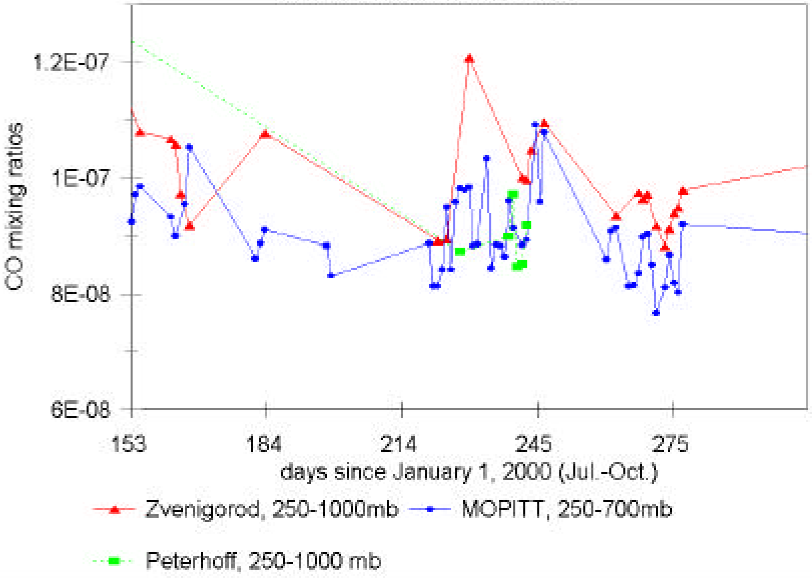
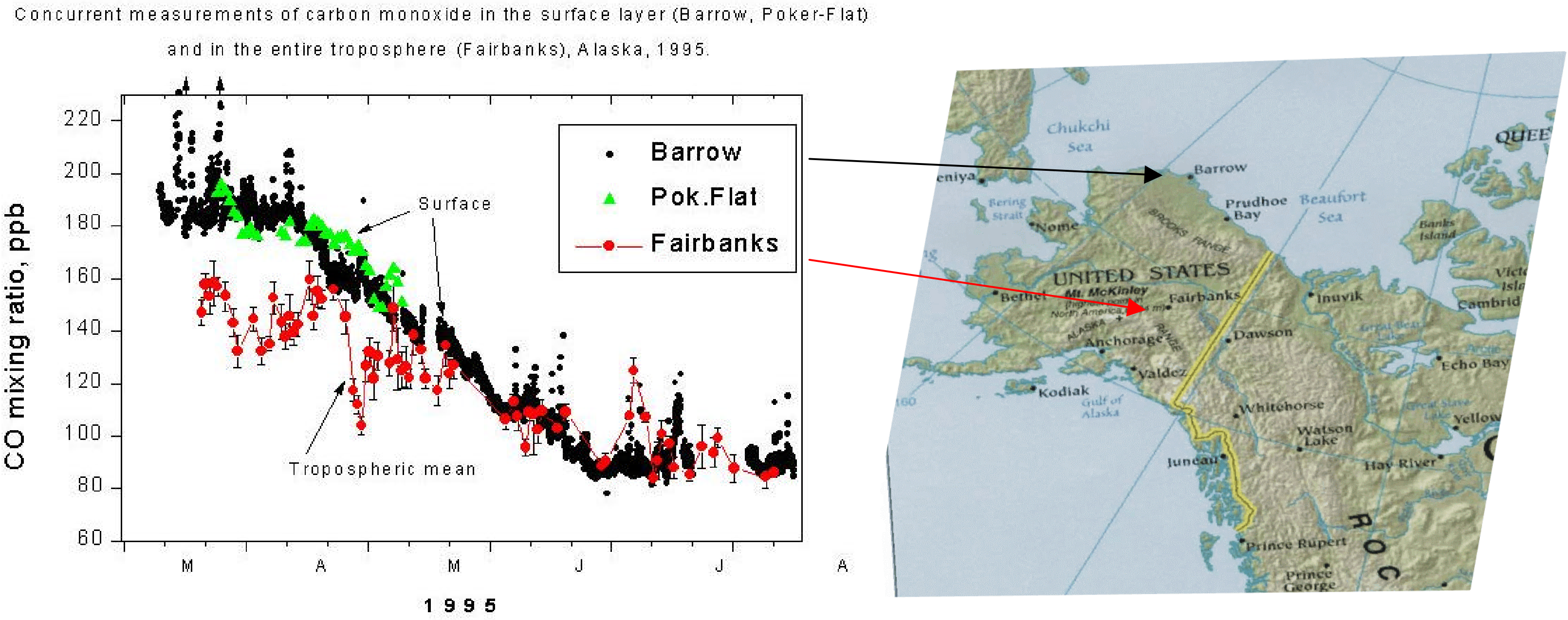


Fig. 12. A good vertical atmospheric mixing during summer time over Russia is similar to that observed in Alaska in 1995. Peterhoff locates 650 km to the North -West from Zvenigorod and 30 km to the West from St.Petersburg.



Concurrent measurements of carbon monoxide in the surface layer (Barrow, Poker-Flat) and in the entire troposphere (Fairbanks), Alaska, 1995.

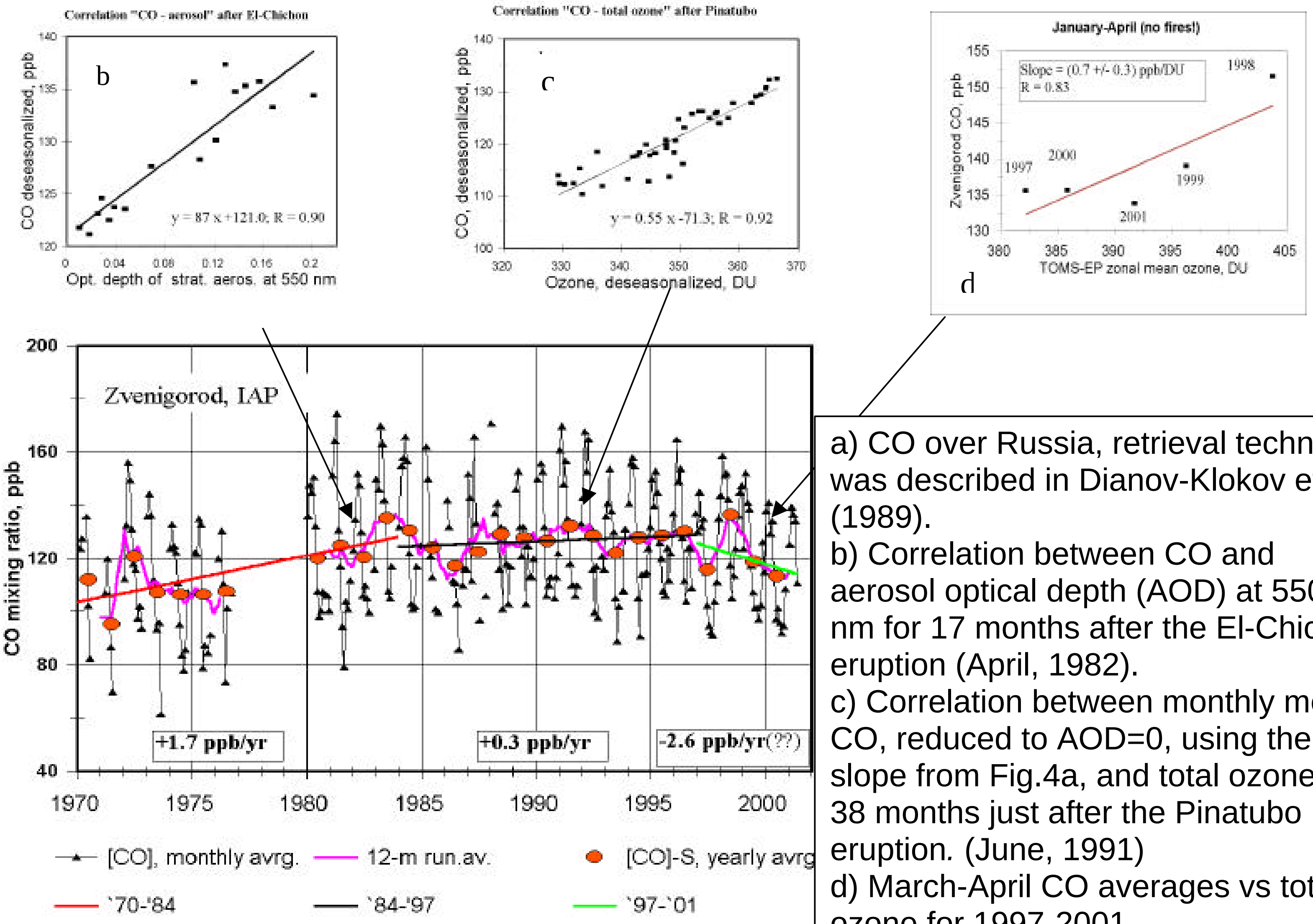
Fig. 11. In 1995 the *Sarcofag* was set up in Fairbanks and measured CO concurrently with in-situ sensors in Poker Flat Range (30 km from Fairbanks) and in Barrow (700 km from Fairbanks). In March-early April tropospheric mixing ratio, measured by the spectrometer, was 140-160 ppb in contrast to 180-200 ppb observed in the surface layer. Between May and August we did not determine any considerable difference between these two kinds of sensors (one possible exclusion was in July).

PRELIMINARY CONCLUSIONS ON VALIDITY OF MOPITT DATA.

Due to a rather low sensitivity of the current version of MOPITT data products to the boundary layer (just the radiation for the long-wave channels centered around 4.5 μm have been used), errors in total column measurements may be as high as ±20%. Free tropospheric mixing ratios, retrieved from MOPITT measurements, agree quite well with independent measurements from the ground both in the SH and in the NH. However, seasonal/latitudinal profile variability should be taken into account for this comparison. Planned inclusion of short-wave channels near 2.3 μm would fix the problem. It seems vitally important for observations of pollution transport, because significant CO emissions happen on the ground and a very long-range advection of pollutants may occur well inside the boundary layer.

A combination of ground-based grating spectrometer data with space-based remote sensing in the middle IR gives an opportunity to determine concentrations of CO in the lower and upper tropospheric layers over the spectrometer location.

UPDATED ZVENIGOROD LONG-TERM SERIES



a) CO over Russia, retrieval technique was described in Dianov-Klokov et al. (1989).
b) Correlation between CO and aerosol optical depth (AOD) at 550 nm for 17 months after the El-Chichon eruption (April, 1982).
c) Correlation between monthly mean CO, reduced to AOD=0, using the slope from Fig.4a, and total ozone for 38 months just after the Pinatubo eruption. (June, 1991)
d) March-April CO averages vs total ozone for 1997-2001.