

# TROPOSPHERIC AND STRATOSPHERIC MEASUREMENTS OF KEY ATMOSPHERIC COMPOUNDS FROM THE GROUND AND SPACE

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## ABSTRACT

Ground-based remote sensing global networks have been actively monitoring, developing instrumentation, and pushing the boundaries of analysis techniques for the last 15 years or more. One such network, the Network for the Detection of Atmospheric Composition Change (NDACC), has deployed spectroscopic UV/Visible, near and mid-IR, microwave and mm-wave instrumentation that can measure a large range of chemical and aerosol species, tackling many questions of current interest to the scientific community. The University of Wollongong, a complimentary site within the NDACC network, operates a high resolution Infrared Fourier Transform Spectrometer and will install a NDSC standard UV/Visible spectrometer in 2007. In combination with established mid-IR retrieval techniques, recent advances in UV/Visible retrieval techniques promises to provide limited vertical information on species like HCHO, SO<sub>2</sub>, NO<sub>2</sub>, and aerosols. Wollongong is also uniquely placed on the Australian coastal fringe where atmospheric column measurements sample marine, sub-tropical forest, and occasional intense forest fire emissions. This dataset will be compared with collocated ENVISAT overpasses looking at a number of atmospheric constituents including both tropospheric and stratospheric species. These measurements will be supported by examining the chemistry and transport of a tracer gas (CO) with model calculations.

## 1. BACKGROUND

### 1.1 Ground-based Measurements

High-resolution solar infrared absorption spectra have been recorded from the campus of the University of Wollongong on the Australian east coast (34.45 °S 150.88 °E, 35m asl), using a Bomem DA8 FTIR spectrometer at 0.004 cm<sup>-1</sup> resolution (250cm optical path difference). These measurements have been made on a routine basis since May 1996 as part of the Network for Detection of Atmospheric and Composition Change (NDACC) [1], (<http://www.ndsc.ncep.noaa.gov/>). Wollongong is one

of 70 worldwide stations originally established to monitor stratospheric chemical and dynamical changes. The network has since expanded its mandate to explore the effects of the stratosphere on the troposphere, and vice versa. A key technique in this network is infrared spectroscopy using Fourier Transform Spectrometers in a remote sensing mode. The instruments passively track the sun, recording the radiation through a column in the atmosphere.

Over 35 gases in the stratosphere and troposphere can be determined including ozone, the dominant chlorine and fluorine reservoirs HCl and ClONO<sub>2</sub>, HF and COF<sub>2</sub>, several CFCs such as CFC-12 (CF<sub>2</sub>Cl<sub>2</sub>) and HCFC-22 (CHFCl<sub>2</sub>), nitrogen oxides (NO, NO<sub>2</sub>, HNO<sub>3</sub> and HO<sub>2</sub>NO<sub>2</sub>), greenhouse gases (H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O), as well as a number of other gases of interest such as CO, HCHO, OCS, HCN, NH<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub>. Spectra are analysed by iterative calculation of the atmospheric transmission spectrum to achieve best fit with the measured spectrum. Atmospheric transmission is calculated layer by layer from a database of spectral line parameters (positions, strengths, widths etc.) and the assumed or measured atmospheric structure (pressure, temperature, trace gas profile shapes).

The algorithm used in the spectroscopic analysis of Wollongong data, SFIT2 (version 3.91), has been developed jointly by several groups within the NDACC (NASA Langley Research Center, University of Denver, NCAR, NIWA Lauder, and the University of Wollongong). SFIT2 is capable of retrieving the vertical profiles of several gases simultaneously from ground-based infrared spectra. The inverse model is based on a semi-empirical application of the optimal estimation method (OEM) [2]. Both the forward and inverse models have been described in some detail previously [3].

### 1.2 Model Studies

The GEOS-Chem model version 7-04-06 (<http://www-as.harvard.edu/chemistry/trop/geos/index.html>), is driven by assimilated meteorological fields from the

Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office (GMAO) with a horizontal resolution of 2° latitude by 2.5° longitude and 30 vertical levels up to 0.01hPa. The model includes 43 transported tracers, more than 80 species and 300 chemical reactions [4] to describe the Ox -NOx -VOC photochemistry. The model's use of heterogeneous reactions on aerosols is described in [5] and [6]. Photolysis frequencies are calculated with the FAST-J algorithm [7], while the aerosol fields are computed online using the Global Ozone Chemistry Aerosol Radiation and Transport (GOCART) model [8]. The inventory of anthropogenic emissions is similar to [9] except for the replacement of the European emissions with Co-operative Programme for monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) emissions and the use of Emission Database for Global Atmospheric Research (EDGAR) global NOx, CO, and SO<sub>2</sub> emissions. Biomass burning emissions are from Global Emissions Fire Database version 2 (GFED2), and biogenic emissions are from the Model of Emissions of Gases and Aerosols from Nature (MEGAN). Transport of O<sub>3</sub> from the stratosphere is parameterized using the Synoz method (synthetic ozone) proposed by [10].

### 1.3 ENVISAT data

The satellite data discussed in this paper are from validation studies using measurements from two instruments on-board ENVISAT, namely, SCIAMACHY [11] an imaging spectrometer that makes limb and nadir observations in the UV through to the near-infrared, and MIPAS [12], a middle infrared Fourier Transform spectrometer measuring the atmospheric emission spectrum in a limb sounding geometry mode. We briefly highlight the stratospheric species that have been validated against ground-based FTIR NDACC measurements, specifically ozone [13], HNO<sub>3</sub> [14, 15], and ClONO<sub>2</sub> [16], and then discuss the tropospheric species CO and CH<sub>4</sub> [17].

## 2. RESULTS AND DISCUSSION

### 2.1 Stratosphere

In general all ground based stations compare very well with stratospheric species from the MIPAS instrument, with biases that are of the same order as the measurement precision. This is particularly surprising for ClONO<sub>2</sub>, a species that is challenging for ground based measurements outside of the polar vortex regions. The reported bias [16] is only 1% between the MIPAS stratospheric column and 8 ground stations

located from high, mid, and tropical latitudes. For MIPAS v4.61 ozone data, the Wollongong stratospheric partial column showed no statistically significant bias [13], although the strict collocation criteria meant that the number of correlative points was only 4 points for the Wollongong location. For HNO<sub>3</sub>, original analysis [14] indicated issues with different HNO<sub>3</sub> line parameters adopted by MIPAS and ground based stations introducing a bias of order 14%. When this is taken into account the agreement is of order 3-5% in the column.

### 2.2 Troposphere

Fig. 1 shows results for Wollongong only, adopted from fig. 7 of [17]. A discussion of the different SCIAMACHY retrieval approaches, labeled MCPI, IMLM, WFMD, and IMAP are described in detail in [17]. These different approaches represent different retrieval algorithms used in the analysis process. The FTIR data, blue crosses, are ground mixing ratios deduced from CO retrieved profiles. The method of analysis is detailed in [18]. All data displays the known seasonal cycle in CO, with a summer maximum. Wollongong, being a coastal city, has a number of heterogeneous sources including marine, anthropogenic, dry inland, as well as seasonal biomass burning. The bias between the FTIR and SCIAMACHY CO data is approximately 25%, the FTIR data being higher. The high bias is noted at other southern hemisphere sites compared with equivalent northern hemisphere sites, and is due to a constant 5 ppbv offset between SCIAMACHY and ground based FTIR. This constant offset becomes noticeable in the cleaner southern hemisphere troposphere.

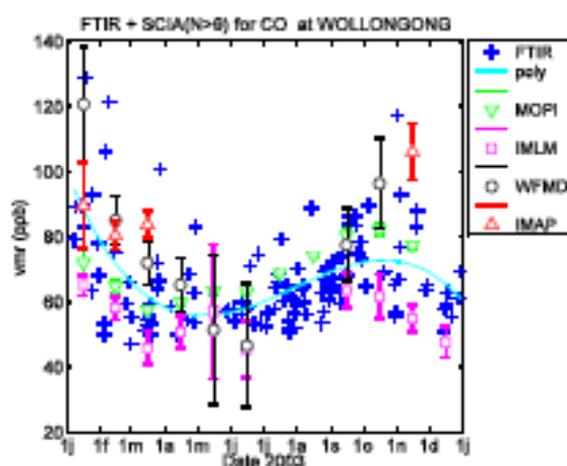


Figure 1. Comparison of derived CO mixing ratios from Wollongong ground based data (blue crosses) and SCIAMACHY data, from Fig. 7 of [16].

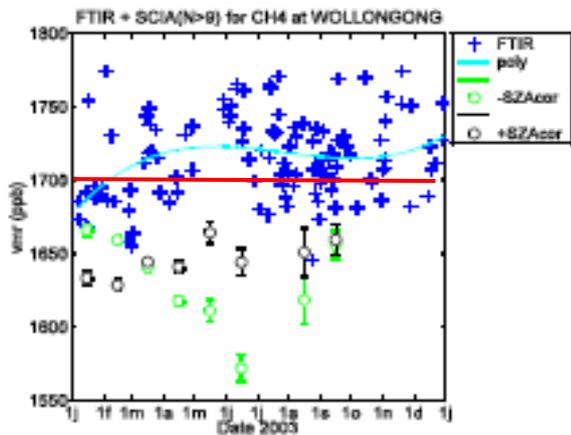


Figure 2. Comparison of derived  $\text{CO}$  mixing ratio from Wollongong ground based data (blue crosses) and SCIAMACHY data, from fig. 11 of reference [16]. The red line indicates the approximate  $\text{CH}_4$  concentration from in-situ data.

Methane, Fig. 2, also from [17] Fig. 11, shows a small bias of approximately -4% between SCIAMACHY and FTIR, compared with a mean bias of -3.3% for all NDACC stations. The global mean methane concentration in 2003 was approximately 1751 ppbv

while the local concentration in Wollongong is about 1700 ppbv and is indicated in Fig. 2 with a solid horizontal red line. The Wollongong FTIR data is only about 0.5% lower than this value.

### 2.3 Measured and modeled CO

One interesting application of ENVISAT data products in the context of Australian climate is biomass burning. During the summer of 2002/2003 for example there were widespread and intense fires in the Australian state of New South Wales, particularly in and around the capital city Canberra in January of 2003. Wollongong is approximately 200km to the NE of Canberra, so a number of these plumes passed over our measurement site and were subsequently sampled by our FTIR system. In Fig. 3 we show contour plots of the Australasian region for a specific fire event on January 26<sup>th</sup> that transported large amounts of biomass burning products across the Tasman Sea to New Zealand. In the top two plots of Fig. 3 (a,b), are total column CO contour plots from SCIAMACHY data (WFMD v06). Measurements within the given grid area (15-55S, and 110-180E) binned over two days were combined. The data was then interpolated with a kriging algorithm onto a 75 by 75 point grid using a spherical semivariogram model. The GEOS-Chem

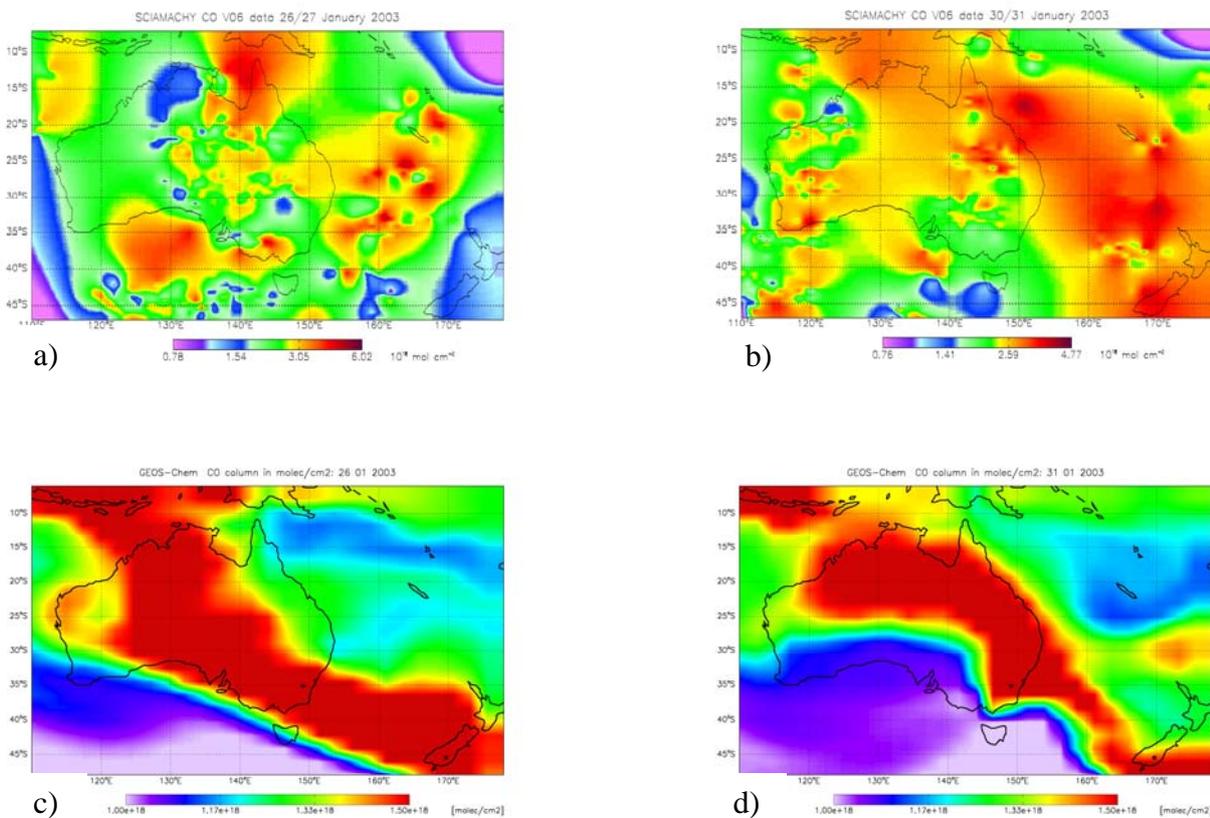


Figure 1. Contour plots of total column CO from SCIAMACHY (Fig. 3a) and GEOS-Chem (Fig. 3b) for the 26<sup>th</sup> January and similarly SCIAMACHY (Fig. 3c) and Goes-Chem (Fig. 3d) for the 31st of January 2003. The SCIAMACHY data is averaged over 2 days to improve statistics.

model is described in section 1.2. Comparing the plots in Fig. 3, i.e., Fig. 3a and 3c for the 26<sup>th</sup> from SCIAMACHY and GEOS-Chem respectively, there appears to be significant differences between the spatial patterns, as well as the absolute amounts. The spatial pattern differences are more than likely due to undersampling in the SCIAMACHY two day averaging (i.e., not enough real measurement points in the interpolation process). Fig. 3b and 3d on the other hand show better agreement in the spatial pattern, but the absolute amounts still disagree (by up to a factor of 3, the models being lower). This difference between global GCM's and measurements has been noted before, mainly in cases where the CO columns are very high [19].

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