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Abstract
Solar absorption measurements using Fourier transform infrared (FTIR) spectrometry carry information about the atmospheric abundances of many constituents, including non-CO_2 greenhouse gases. Such observations have regularly been made for many years as a contribution to the Network for the Detection of Stratospheric Change (NDSC). They are the only ground-based remote sensing observations available nowadays that carry information about a number of greenhouse gases in the free troposphere. This work focuses on the discussion of the information content of FTIR long-term monitoring data of some direct and indirect greenhouse gases (CH_4, N_2O, O_3 and CO and C_2H_6, respectively), at six NDSC stations in Western Europe. This European FTIR network covers the polar to subtropical regions. At several stations of the network, the observations span more than a decade. Existing spectral time series have been reanalyzed according to a common optimized retrieval strategy, in order to derive distinct tropospheric and stratospheric abundances for the above-mentioned target gases. A bootstrap resampling method has been implemented to evaluate trends of the tropospheric burdens of the target gases, including their uncertainties. In parallel, simulations of the target time series are being made with the Oslo CTM2 model: comparisons between the model results and the observations provide valuable information to improve the model and, in particular, to optimize emission estimates that are used as inputs to the model simulations. The work is being performed within the EC project UFTIR. The paper focuses on N_2O for which the first trend results have been obtained.

Keywords: *FTIR remote sensing, tropospheric trends, chemistry-transport modelling*

1. Introduction

Climatic changes caused by increases in the amounts of radiatively active gases are among the most important global environmental problems we are confronted with nowadays. The gas with the largest contribution to the radiative forcing (about 50%) due to its increases since preindustrial times is CO_2, but one cannot neglect the contributions from methane (CH_4) and ozone (O_3), about 17 and 16%, respectively, as well as that from nitrous oxide (N_2O), about 3%. Note that the actual values of the percentage contributions to the radiative forcing are quite uncertain, because of strong non-linearities in the coupled climate-chemistry system. Indirect greenhouse gas effects must also be accounted for. For example, the indirect contribution of an increase in CH_4, through the additional O_3 it produces, is as important as its direct effect. In this sense, carbon monoxide (CO) and ethane (C_2H_6) are indirect greenhouse gases, because they contribute to the production of tropospheric ozone. Furthermore, they play a central role in tropospheric chemistry through their reactions with the hydroxyl radical (OH) (Brasseur et al. 1999).

There is great interest in obtaining a better estimate of the actual trends in the concentrations and emissions (sources and sinks) of the above-mentioned gases, in the context of the Kyoto Protocol and regulations concerning air quality. The progressive modification and fertilization of the terrestrial biosphere are believed to be the main cause of the rise in N_2O. CH_4 is produced by biospheric processes, including wetlands, biomass burning, as well as leakages from gas-distribution systems. CO is released at the surface by incomplete combustion associated with biomass and fossil fuel burning (industries, car traffic, etc.); it is also produced by oxidation of methane and other hydrocarbons. The major anthropogenic sources of non-methane hydrocarbons, including ethane (C_2H_6), are fossil-fuel combustion, natural-gas emissions, and industrial processing of chemicals and waste; biomass burning is another important source in non-industrialized regions. Tropospheric ozone increases result from complex photochemical processes involving industrial and biogenic emissions of nitrogen oxides, hydrocarbons, and certain other organic compounds.

In this paper, we describe work that is ongoing in the frame of the EC project UFTIR (http://www.nilu.no/uftir), and we indicate how the results of the project will be useful for supporting greenhouse-related policies (e.g. regulations of emissions). UFTIR is about the exploitation of existing and new observations from ground-based Fourier transform infrared (FTIR) spectrometers and focuses on several target gases, O_3, CO, N_2O, CH_4, C_2H_6, and HCFC-22; however, the last of these is not discussed in this paper. First, we discuss the information content of the FTIR long-term monitoring data for these target species. We show that it is possible to derive distinct time series of tropospheric and stratospheric abundances. As such, the FTIR observations are complementary to existing surface observations: they provide information about the total abundance and distribution of the trace gases in the atmosphere, which is important because the amount of radiative forcing caused by concentration changes depends on the altitudes where the changes occur. They are also indispensable for the validation of correlative remote sensing data from space looking down into the troposphere, especially since there are no alternative long-term data available concerning the abundances of greenhouse gases in the free troposphere. These will help model developers verify and improve the emissions and the tropospheric chemistry scheme used in their CTM models of the troposphere. Major problems associated with current tropospheric chemistry schemes are connected to hydrocarbon chemistry and transport processes on small spatial scales not resolved by the models. Observations of hydrocarbons such as CH_4 and C_2H_6, but also CO, which has strong links to hydrocarbon chemistry, will

help verify the models in this respect. Ground-based observations of the long-lived species N_2O help improving emissions in the models even if the chemistry scheme may be less accurate, since N_2O does not take an active part in tropospheric chemistry. This argument is partly true for CO as well, albeit on smaller spatial scales since CO has a shorter lifetime. In practice, models are so far off observations that missing chemistry or inaccurate reaction rates cannot explain the discrepancy. In such cases, errors in the emission fields or non-resolved transport processes have to be considered. Here, point measurements of chemical key components are of great value. In this paper, we will discuss some improvements of the model that have been guided by comparisons of model results with network FTIR data. Comparisons are shown explicitly for N_2O.

It is shown also that the bootstrap resampling method—which is explained in the paper—is an appropriate statistical technique by which to evaluate long-term trends of this kind of atmospheric data sets. First results for the trends of the N_2O abundance in the free troposphere over Europe are given as a demonstration.

In Sections 2, 3, and 4, we describe the observations, the model used for simulating the observed time series, and the trend analysis method, respectively. Section 5 provides a demonstration of the methodology using example results for N_2O over Europe. Conclusions are drawn in Section 6, and the perspectives for further work are indicated.

2. Observations from the UFTIR network

The UFTIR network consists of high spectral-resolution FTIR spectrometers located at six sites in Europe, spanning the latitude range from 28°N to 79°N (see Figure 1). For many years, the instruments have taken regular solar-absorption measurements from which total column abundances for a large number of atmospheric gases have been derived. These data
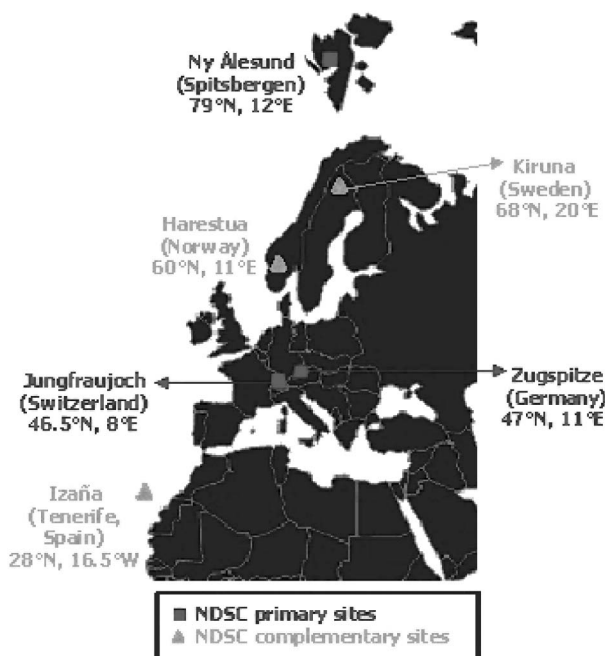

Figure 1. UFTIR sites.

are contributing to the database of the Network for the Detection of Stratospheric Change (NDSC; http://www.ndsc.ncep.noaa.gov/).

In the framework of the UFTIR project, a special effort has been dedicated to the re-analysis of time series of spectral data at each site, for the derivation of vertical profiles of the above-mentioned tropospheric target gases (O_3, CO, N_2O, CH_4, and C_2H_6), for the period 1990–2004. The derivation of vertical profiles, albeit at a low vertical resolution, is called inversion. This is possible because the target absorption line shapes depend on the vertical pressure conditions met at the various absorption heights. The inversion algorithms used are SFIT2 and PROFITT (Hase et al. 2004): both are based on an empirical implementation of the Optimal Estimation Method (Rodgers 2000) and have been shown to provide compatible results. Part of the UFTIR effort has been to harmonize the inversion parameters among the partners, especially to make a common, best choice of the microwindows in which the inversion is carried out. This optimal inversion strategy has been described in De Mazière et al. (2004). It has been guided by the following criteria: maximal information content, minimal interferences from other than the target species, and smallest uncertainties in the spectroscopic parameters involved.

The existing spectral time series at each UFTIR location have been re-analysed according to the common retrieval strategy and will be available from the respective PIs via the UFTIR Web pages. Some of the revised time series of vertical profile data of the target species go back to the early 1990s, like those at Ny Alesund and at Jungfraujoch, but a common time period covered by almost all (except Izana and Kiruna) is the period 1995 to the end of 2004; therefore, the focus for comparisons between stations will be on this period. The information content in the vertical profile results varies with species and, to a lesser extent, with location. It goes from about one for a species like C_2H_6 to about five for O_3. Five (one) indicates that five (one) independent elements of information are resolved in the vertical profile data; in other words, the information retrieved from the spectral data is limited to five partial column amounts or to the total column amount, respectively. In any case, it has been demonstrated that it is possible to distinguish the tropospheric column from the stratospheric or total column amount, except in the case of C_2H_6 for which the total column amount is approximately equal to the tropospheric column amount. In the remainder of this paper, we will therefore focus on partial tropospheric column burdens for the target species.

3. Oslo CTM model

The Oslo CTM2 is a global-scale 3-D chemical transport/tracer model (CTM). The model uses pre-calculated transport and physical data (e.g. wind velocities, cloud fraction and cloud liquid water content, 3-D rainfall, convective fluxes, and surface fields) which are generated by running the IFS model (Integrated Forecast System, ECMWF) for selected years. Model studies are currently being done with horizontal resolutions T21 ($5.6° \times 5.6°$), T42 ($2.8° \times 2.8°$) and T63 ($1.9° \times 1.9°$). The model includes 40 levels from the surface up to 10 hPa. The Oslo CTM2 is also set up to run with meteorological fields from ECMWF ERA-40 (ECMWF Re-Analysis project 1957–2002, providing a comprehensive set of global analyses of the state of the atmosphere from mid-1957 to 2001; http://badc.nerc.ac.uk/data/ecmwf-e40/e40_background.html). In the latter case, the model domain extends up to 0.1 hPa and includes 60 layers. Meteorological fields for the time period 1990–2001 are available. Both vertical grids have a resolution of 0.5–1.0 km in the free troposphere up to the tropopause, and slightly more than 1 km in the lowermost part of the stratosphere.

The chemical scheme includes calculations of both stratospheric and tropospheric chemical processes, in particular ozone production and loss in the upper troposphere/lower stratosphere (UT/LS), and tropospheric oxidation including chemical processes involving NO_x, CO, CH_4, and non-methane hydrocarbon reactions. Furthermore, the calculations of photo-dissociation rates are done online.

Distributions of surface emissions and their evolution in the $1990-2000$ period have been integrated in the model. Anthropogenic emissions are based on the EDGAR3 inventories, and biomass burning emissions are estimated from CO_2 climatological emissions and fire counts from the ATSR satellite. Natural emissions are taken from the GEIA inventories (http://arch.rivm.nl/env/int/coredata/edgar/ and http://geiacenter.org/).

4. Trend-analysis method

A statistical trend-analysis tool has been developed to analyse the atmospheric profile data provided by the observation teams. The objective of this tool is to assess whether there are any statistically significant long-term trends in the various datasets, and to determine the statistical uncertainty in these trends. The trend-analysis tool enables the confidence limits for the trends to be determined without requiring assumptions about the distributions of the measurement uncertainties.

Simple regression analysis (straight-line fitting) is often not appropriate because it smooths much of the fine structure (and therefore information) in the raw data and reduces a large number of data points to a single value. The possibilities for a sound statistical analysis are then limited by the small size of the remaining sample. Most importantly, the simple regression analysis does not provide realistic confidence intervals without making additional assumptions (such as normal distribution of data), which may not be justified for these atmospheric datasets.

One of the other requirements for the statistical trend model is that it should model the atmospheric data to account for the inherent statistical variability in the data set. This includes taking into account the intra-annual cycles in the data that are present for many of the species in addition to any underlying trends. In addition, since the analysis needs to combine the data from the different sites, it should be suitable for comparing data from many sites in order to assess overall trend behaviour.

One statistical technique that has been identified as being more suitable for this type of analysis is bootstrap resampling; this method has been used to analyse the UFTIR data. In this technique, a model function F is fitted to the data such that the values for year i are M_{ij}:

$$M_{ij} = F(t_{ij}, a, b_j), \tag{1}$$

where t_{ij} is the time at which the measurement (or sample) M_{ij} was obtained, a is the underlying trend parameter, b_j is the intra-annual variability function, and j indicates the fraction of the year. The intra-annual function is determined by fitting a low-order Fourier series to the annual distribution. This function reduces the impact of sparse data and enables regular gaps in the data series, such as those during the winter months at high-latitude sites, to be easily accommodated. Having performed an initial fit, a set of residuals can then be determined by comparing the fit results with the measured values V_{ij}:

$$R_{ij} + V_{ij} - M_{ij}. \tag{2}$$

A new set of simulated data, V_{ij}^+, is then created by adding a random sample from the residual data set, R, to each of the fit (or model) values:

$$V_{ij}^+ = M_{ij} + R. \tag{3}$$

A new set of values for a and b_j can now be calculated using the original model. By repeating this a large number of times, an approximation of the statistical distributions of a and b_j can be built up, and hence an estimate of the associated confidence limits can be determined without making any assumptions about the statistical distribution of the residuals. This can therefore be applied generally to results for different species and sites.

It is worth noting that the actual implementation of the method takes into account explicitly the intra-annual variability, without making any a priori assumption about it, but that the inter-annual variability is taken up in the uncertainty on the trend results. The statistical question posed on the data is whether there is an annual trend in them, and then to quantify this trend and associated uncertainties. The inter-annual variability shows up as noise in the fitting process and will therefore feed into the uncertainties through the resampling process.

5. Example results

We haven chosen results obtained for N_2O to demonstrate the methodology explained in the previous sections.

5.1. Information content of ground-based FTIR data for N_2O

Nitrous oxide can be observed in two spectral ranges, namely around $4\,\mu m$ and $8.5\,\mu m$. Optimization of the inversions has led to the identification of the best retrieval strategy: this involves making the spectral inversion in four microwindows around $4\,\mu m$ simultaneously, which are (in cm^{-1}) $[2481.30 - 2482.60]$, $[2526.40 - 2528.20]$, $[2537.85 - 2538.80]$, and $[2540.10 - 2540.70]$. The species that, next to N_2O, are absorbing significantly in these windows are H_2O/HDO, CO_2, O_3, and CH_4. The combination of strong and weak absorption provides information about the vertical distribution of N_2O from the lower troposphere to the stratosphere: one can retrieve four to five independent elements of information about the vertical distribution. Figure 2 shows the time series of N_2O abundances above the Jungfraujoch station, from 1995 to 2004. Quasi-independent layers for determining partial column amounts have been identified in the troposphere (from the station altitude at $3.58 - 8.2\,km$), in the upper troposphere/lowest stratosphere (UT/LS, $8.2 - 15.4\,km$) and in the lower to mid-stratosphere ($15.4 - 21.4\,km$). It is interesting to see that advanced retrievals of FTIR observations provide distinct information in the troposphere and above. For example, the seasonal variation of the N_2O abundance shows a maximum in mid-winter in the troposphere but a maximum by the end of summer in the UT/LS. One can also observe that the impact of dynamics on the total column abundance of N_2O (outlier red points) is situated essentially in the UT/LS layer. Apparently, linear rising trends are observed in all layers. It is evident that these data are complementary to the data obtained in situ at the surface.

5.2. How has the Oslo CTM2 model been improved, based on comparisons with FTIR data?

One of the main purposes of the models is to make predictions of future trends or calculate trends for the past when observations were not available. The model can also be
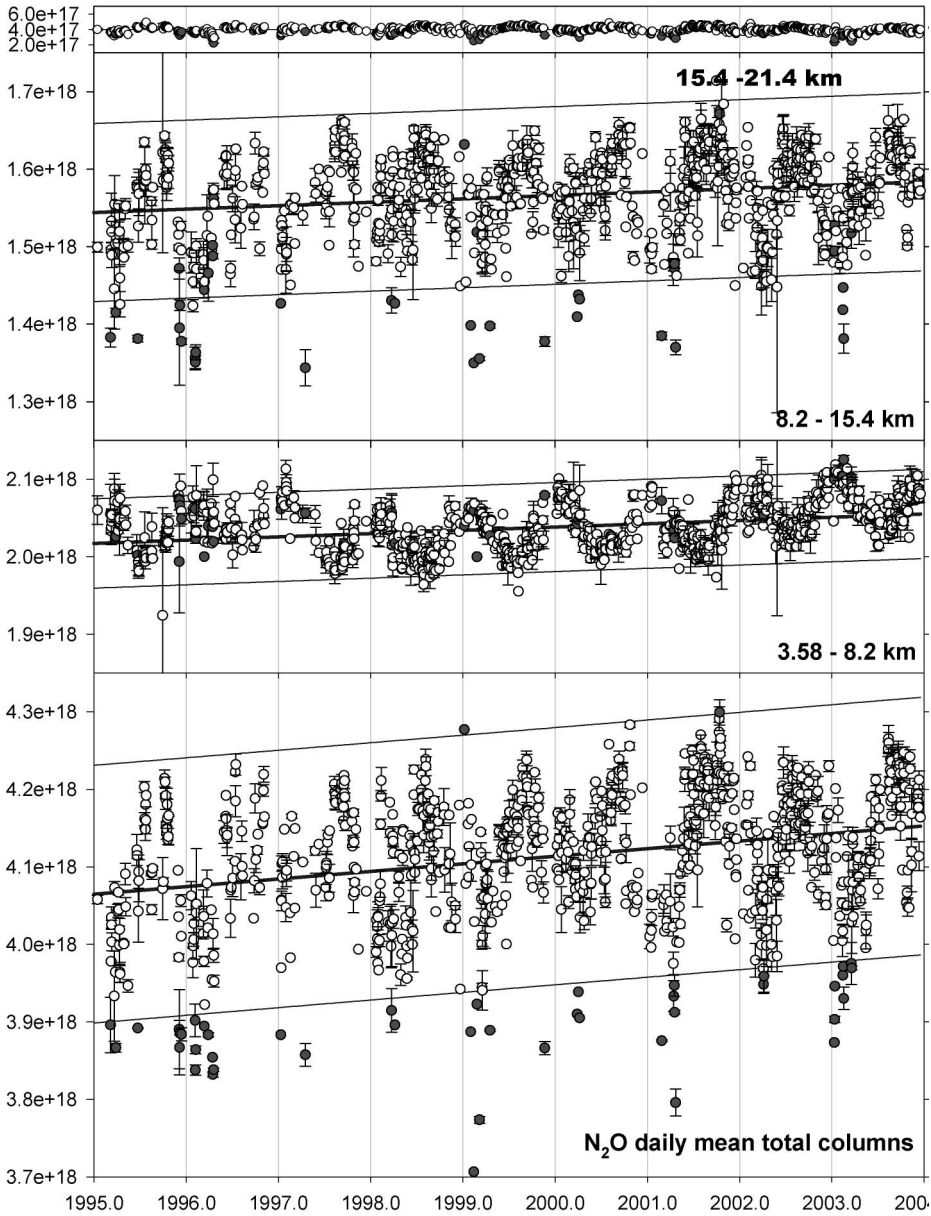
Figure 2. Time series of N_2O above Jungfraujoch (3.58 km asl), from 1995 to 2004, retrieved from ground-based FTIR observations at the station. From bottom to top: total column amounts, partial column amounts between 3.58 and 8.2 km, between 8.2 and 15.4 km, and between 15.4 and 21.4 km, respectively.

used to support the interpretation of observed trends at various stations. Before doing so, one has to test if the model can reproduce trends over a period that has been observed. This has been the purpose of part of the work reported here, and as such is very important.

Oslo CTM2 model runs have been performed in T21 horizontal resolution using IFS (ECMWF) meteorology for 1997 and 2000 as well as for 1990–2000 using ERA-40

(ECMWF) meteorology. Both types of runs have been made to evaluate the ERA-40 data that had not been used sufficiently before and that we want to use to simulate long-term trends.

It was known from previous work (TRADEOFF project 2002) that the model systematically overestimated total ozone columns; this was again confirmed in the comparisons with UFTIR data. The implementation in the model of a new package for Polar Stratospheric Cloud (PSC) formation and heterogeneous chemistry has resulted in better agreement between model and observational data. It has also been observed that the agreement has become better using IFS than ERA-40 meteorology: ERA-40 seems to include a Brewer–Dobson circulation that is too fast, leading to a residual overestimation of the ozone amounts by the model.

Comparisons between model results and observations for ethane abundances have shown rather large (30–40%) discrepancies: since ethane has a lifetime of 92 days, and since we are looking at small spatial scales for the comparisons, such a discrepancy must be due mainly to errors in emission estimates or a resolution that is too low. In the stratosphere, another reason may be the absence of a detailed hydrocarbon chemistry scheme. Both aspects are being investigated.

Figure 3 shows an intercomparison between model results and observational data for the tropospheric (0–7 km layer) abundance of N_2O at Harestua. The FTIR averaging kernel, describing the smoothing effect of the FTIR retrieval on the true partial column, has not yet been applied to the model data, but this does not impact the observed overestimation of N_2O by the model that amounts to about 30%. Such a discrepancy has been observed at the other stations as well. Since N_2O is not chemically active in the troposphere—therefore
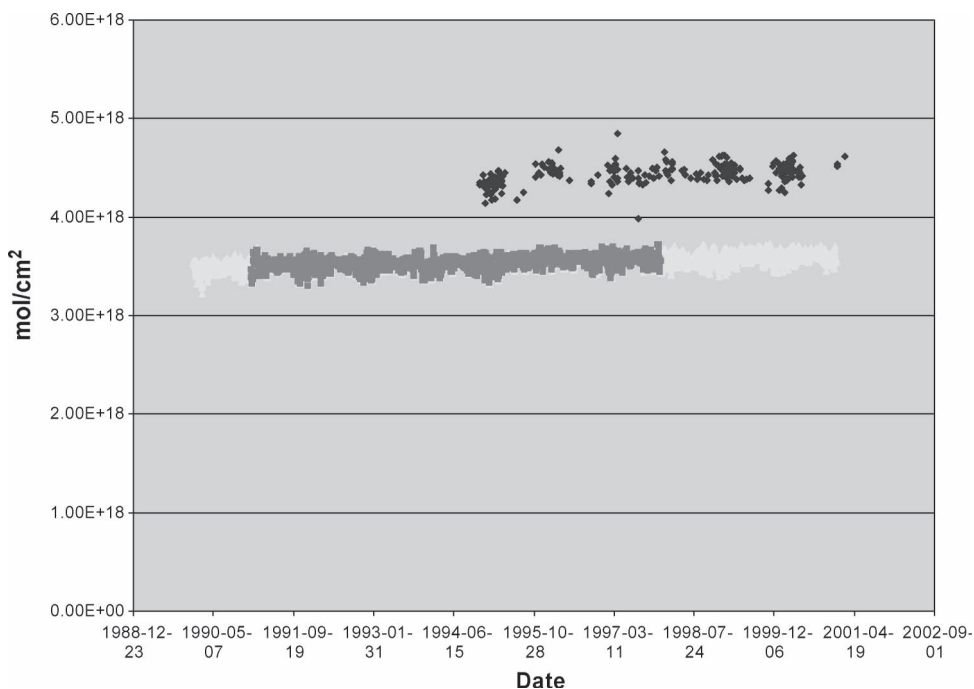

Figure 3. Modelled and observed time series of tropospheric (0–7 km altitude) N_2O above Harestua. Dark blue diamonds represent the FTIR data; yellow and magenta squares represent the model results, for the old and new PSC-chemistry schemes, respectively (see text).

there is no tropospheric chemistry for N_2O in the model—the observed discrepancy must originate in an incorrect estimation of the emissions of N_2O. Up to now, the model has assumed the WMO recommended global emission value. The comparisons between the UFTIR data and the model results illustrated in Figure 3 have identified the need for using more detailed emission inventories for N_2O in the model instead of the WMO recommended value.

5.3. *Quantitative trend estimates*

The analysis and interpretation of the trends in the UFTIR datasets are under way. The following discussion gives an example of the results that are being produced—in this case, the preliminary trend analysis of the nitrous oxide profile data—to demonstrate the approach.

The left-hand plot of Figure 4 shows the trend in the vertical profile of nitrous oxide from Kiruna, one of the UFTIR sites, in terms of the annual change in mixing ratio. The right-hand plot shows the same data in terms of the percentage change relative to the average mixing ratio value in 2000. In both cases, the blue line shows the trend in the complete profile with the dotted line showing the uncertainty, while the red points show the trend in a series of sub-columns in the profile. The number and altitude boundaries of these sub-columns have been selected based upon the typical averaging kernels and degrees of freedom of the retrieved profile time series. In the example case, there are five sub-columns with boundaries at 0.4, 6, 16, 22, 32, and 40 km, respectively.

Similar analyses have been performed for the profile measurements from the different sites. The results for the tropospheric trends in nitrous oxide for the UFTIR network, taken to be the trends in the lowest sub-columns, are given in Table I. This shows similar trends for all of the sites, with a possible correlation with site latitude. The interpretation hereof and the trend analyses for the other species are being undertaken in conjunction with the 3D atmospheric model analyses.
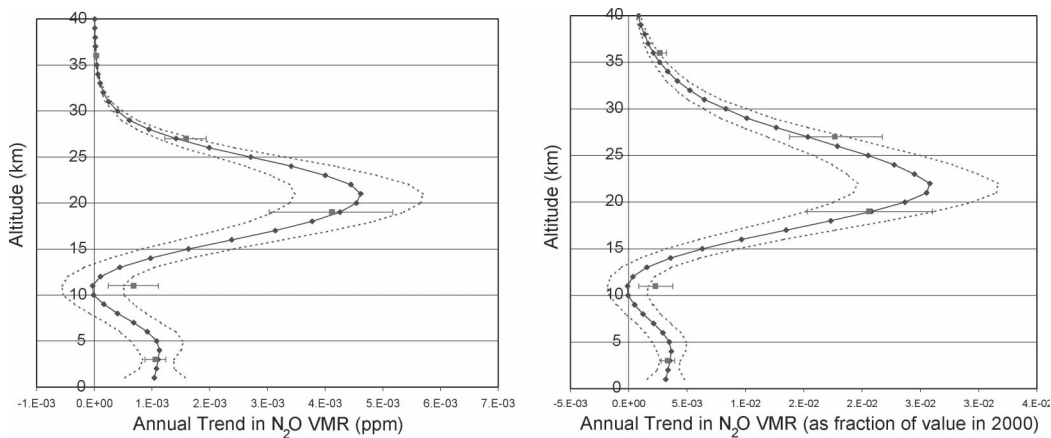

Figure 4. Vertical profile trend of nitrous oxide at Kiruna. Left-hand side: absolute annual trend in volume mixing ratio units; right-hand side: fractional annual trend relative to the average profile in 2000. Blue symbols and line: full profile trend; red squares: trend in partial columns (or sub-columns), the symbol being located at the center altitude of the partial column. The dashed blue lines and red error bars indicate the uncertainties on the profile and partial column trend values, respectively.

Table I. Preliminary results for tropospheric trends in nitrous oxide.

Site	Latitude	Period of trend determination	Annual trend in N_2O tropospheric mixing ratio (percentage of 2000 value)
Ny Alesund	79°N	1995–2004	0.45 ($\pm$0.20)
Kiruna	68°N	1996–2004	0.34 ($\pm$0.06)
Harestua	60°N	1995–2004	0.38 ($\pm$0.06)
Zugspitze	47°N	1995–2004	0.27 ($\pm$0.03)
Jungfraujoch	47°N	1995–2004	0.27 ($\pm$0.06)
Izana	28°N	1999–2004	0.17 ($\pm$0.05)

6. Conclusions and perspectives

It has been argued that remote sensing ground-based FTIR measurements provide valuable information about the free-tropospheric abundances of a number of key greenhouse gases and related species. At many sites over the world, such measurements have started in the 1980s or early 1990s, thus providing trend estimates that complement those derived from in situ surface measurements. The FTIR ground-based measurements are also extremely useful for the validation of data from new tropospheric satellite sounders, and for supporting the development and improvement of tropospheric chemistry-transport models.

The above-stated value of tropospheric column data retrieved from ground-based FTIR observations has been demonstrated using the results obtained in the frame of the EC project UFTIR, for the example case of nitrous oxide (N_2O).

The implementation of an optimal retrieval strategy has enabled the determination of the N_2O partial column abundances in at least four independent layers, from the surface to the stratosphere. Free tropospheric abundances and their associated trends can therefore be distinguished from total column amounts (and trends) and, when available from complementary local in situ measurements, from surface data and trends.

The Oslo CTM2 is a global-scale 3-D chemical transport/tracer model that will be used to predict and calculate trends. Before doing so, one should verify whether it is capable of reproducing actually observed trends. The FTIR tropospheric data obtained in UFTIR have done a good job in identifying problems in the chemistry schemes included in the model, as well as in identifying errors in emission estimates. In particular, the WMO recommended value for the N_2O emissions has turned out to be inappropriate.

A statistically sound trend-analysis method, the so-called bootstrap resampling method, has been implemented and applied to the observational data sets. The major advantages of the method are that it does not assume any a priori statistical distribution of the data and that the result includes the uncertainty associated with the estimated trend value. The results for the trends in the tropospheric mixing ratio of N_2O above Europe over the period 1995–2004 (with an exception for Izana where the period is limited to 1999–2004) indicate a rising annual trend of 0.17–0.45% of the 2000 value, when going from South (Izana, 28°N) to North (Ny Alesund, 79°N). The uncertainty on the trend value is of the order of 0.05% (except for Ny Alesund, where it amounts to 0.20%).

Work is ongoing to improve the partial column definition for trend determination in a more consistent way throughout the UFTIR network, and to extend the analysis to the other target

species. The same trend-analysis method will also be applied to the model data, taking into account the characteristics of the observations as to their information content, to support the interpretation of the observed trends.

Acknowledgements

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