ATMOSPHERIC CARBON DIOXIDE: RETRIEVAL FROM GROUND-BASED FOURIER TRANSFORM INFRARED SOLAR ABSORPTION MEASUREMENTS AND MODELLING USING A COUPLED GLOBAL-REGIONAL SCALE APPROACH

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By

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“There is nothing like looking, if you want to find something. You certainly usually find something, if you look, but it is not always quite the something you were after.”

- J.R.R. Tolkien
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ABSTRACT

Atmospheric carbon dioxide (CO₂) was retrieved from ground-based solar absorption measurements using Fourier transform infrared (FTIR) spectrometry in three European stations (Biscarrosse, Bremen and Ny-Ålesund). Functioning as an internal standard and a means to determine the dry air mixing ratio, molecular oxygen (O₂) was likewise retrieved. The effects of instrumental parameters such as the resolution, the aperture size and high folding limits were assessed to identify correlated errors in both the CO₂ and the O₂. Changes in the field of view, the maximum optical path difference and the high folding limit seem to change the trace gas column concentrations of O₂ and CO₂ and just partially cancels out in the CO₂/O₂ ratio. Correction factors on the O₂ column to minimize these instrumental effects were determined and applied to the FTS data. These correction factors seem to be more effective in Ny-Ålesund than in Bremen as the degree of these instrumental changes appear to be more subtle in Ny-Ålesund. Additional correction strategies, particularly for the CO₂, are still being examined and investigated. Comparisons of FTIR CO₂ with integrated CO₂ aircraft data were performed in the Biscarrosse station as a means of calibrating the FTIR data. Aside from this, the Stochastic Time Inverted Lagrangian Transport (STILT) model was also used as a “transfer standard” between FTIR column concentrations and measurements made in situ by a co-located tower. STILT and tower data compared reasonably well. However, comparison of STILT with the FTIR showed a large bias. This bias is attributed to the scaling factor used in calibrating the FTIR data with the integrated CO₂ aircraft data. The scaling factor was derived to a large extent from aircraft measurements that sampled within a 50 km distance from the FTS and this introduces spatial heterogeneity in the carbon dioxide volume mixing ratios around the FTIR station. Long-term time series of column averaged carbon dioxide volume mixing ratios for the Bremen and Ny-Ålesund stations were compared to STILT (only the Bremen station) and to CarbonTracker. A “clear sky” bias was pin pointed as models see increased CO₂ during frontal zone conditions – a meteorological condition when FTIRs often cannot measure. The spatial heterogeneity of carbon dioxide around the Bremen station was also assessed by comparing FTIR data with varying resolutions of STILT and it was found that column concentrations are not sensitive to small scale local carbon dioxide emission sources amidst Bremen being situated in an urban setting. The difference in variability between fine to coarse scales are approximately 0.2 ppm.
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1 Introduction

Atmospheric carbon dioxide (CO₂) has been increasing as a result of the burning of fossil fuel and land-use changes such as the conversion of forests into agricultural areas. This is a big concern with respect to the environment and climate change because CO₂ absorbs infrared radiation in the atmosphere. Looking at the composition of air trapped in ice core bubbles from Greenland and Antarctica (Fig. 1.1), it is clear that the current concentrations of greenhouse gases, like carbon dioxide, far exceed pre-industrial values indicating that the increase in the amount of these gases do not come from natural processes (Fig. 1.2) (IPCC, 2007). Also, from the atmospheric carbon dioxide measurements started by Charles David Keeling in 1958 on Mauna Loa in Hawaii (Keeling, 1961) as well as from the correlation of this data with globally averaged temperature records from the National Oceanic and Atmospheric Administration (NOAA) (Fig. 1.3), it is clear that the increase in global temperatures for the past 250 years can be attributed to human activity (Fig. 1.2) and that anthropogenic influence would continue to change the composition of the atmosphere in the next years (McCartney, 1983). Due to man’s insatiable need for energy and industrialization, CO₂, a by-product of fossil fuel combustion and biomass burning (brought about by land use change), has become the most significant anthropogenic greenhouse gas (IPCC, 2005).
Fig. 1.1. 650,000 year ice core data showing the pre- and post-industrial concentrations of nitrous oxide (N\textsubscript{2}O), carbon dioxide (CO\textsubscript{2}), methane (CH\textsubscript{4}) and temperature (proxied by deuterium (\delta D)). The gray bands indicate interglacial warm periods (IPCC, 2007).

Fig. 1.2 Anthropogenic Influence on Atmospheric CO\textsubscript{2} Concentrations (IPCC, 2007).
Fig. 1.3 Carbon dioxide concentrations from ice cores, Mauna Loa and NOAA global temperatures since 1880 (The Woods Hole Research Center: [http://www.whrc.org/](http://www.whrc.org/)).

The combustion of fossil fuels as well as other human activities has perturbed the natural cycle of carbon dioxide, which involves fluxes between the biosphere, the atmosphere and the oceans. However, only 40% of the anthropogenic CO₂ linger in the atmosphere and the rest are taken up by “sink” processes in the oceans (30%) and on land (30%). This implies that the oceans and the terrestrial biosphere play an important role in society since if this was not the case, atmospheric carbon dioxide concentrations would even be higher and global warming would even be a bigger problem. An important question now is where on land are these sinks located. For a long time, computer models have estimated that a large amount of carbon dioxide is emitted from the tropics (+1.8 petagrams of carbon per year [Pg C year⁻¹ = billions of tons of carbon per year or gigaton carbon per year = GtC year⁻¹]) as a result of deforestation, and a large amount is taken up by forests in the northern latitudes (-2.4 Pg C year⁻¹). However, researchers on the ground looking for that carbon have not been able to
find it. This is termed as “the missing carbon sink.” Aircraft measurements flown in locations all over the world have shown that the tropics actually emit lower CO₂ (+0.1 Pg C year⁻¹) and the northern latitude forest take up lesser carbon dioxide (-1.5 Pg C year⁻¹) (Fig. 1.4). This suggests that intact and undisturbed tropical forests are taking up more CO₂ than what was previously estimated and they play a major role in absorbing carbon dioxide. The incorrect estimates of computer models was a result of inaccurately simulating the vertical motion of atmospheric CO₂ allowing too much carbon dioxide toward the ground in the summer, when growing vegetation take it up, not too much CO₂ higher up during winter and assuming that a large amount of carbon dioxide is coming out of the tropics moving through the atmosphere and taken up in other regions causing an overestimation of uptake in the north and an underestimation of uptake in the tropics (Stephens et al., 2007). This has important implications for understanding the processes responsible for this uptake – factors affecting carbon dioxide uptake in the tropics are very much different from mechanisms in the northern latitudes. This would allow us to make better predictions of climate change and evaluate sustainable strategies for mitigating global warming.

![Image of carbon sink](https://i.imgur.com/123456789.png)

**Fig. 1.4. The Missing Carbon Sink.** Intact and undisturbed tropical forests actually take up more atmospheric carbon dioxide than what was previously estimated (http://www.ucar.edu/news/releases/2007/carbonsink.shtml).
Due to this, much attention is being given on the absorption characteristics of CO₂, its contribution to possible climate changes due to its increased concentration in the atmosphere as well as the identification of carbon dioxide sources and sink regions. With regard to identifying CO₂ sources and sinks and understanding the underlying carbon cycle processes, two approaches are currently being used and combined to quantify these mechanisms. These are the bottom-up approach and the top-down approach. The bottom-up approach (Fig. 1.5 (Left Panel)) involves sampling and inventory of biomass and soil carbon throughout land areas, performing process studies as well as ecosystem flux estimation by eddy covariance measurement techniques. Using data obtained from these local processes, such as photosynthesis, respiration, litterfall root dynamics, forest biometry, soil fluxes and canopy phenology, simulation models (bottom-up modelling) extrapolates these parameters to regional or global scales estimating the spatial and temporal variabilities of CO₂ uptake and release over these larger areas. The disadvantage of the bottom-up approach is the representativeness of the local study site to similar broader regions. On the other hand, the top-down approach (Fig. 1.5 (Right Panel)) allows one to infer carbon sources and sinks from patterns in the variations of atmospheric carbon dioxide, taking into consideration transport to estimate fluxes. This method, sometimes referred to as inverse modelling, observes the effect (variations in CO₂) and infers the cause (surface sources and sinks). Depending upon the type of atmospheric observations collected, this can be applied to numerous spatial and temporal scales. The disadvantage of the top-down approach is that it offers very few or no information about the underlying mechanisms behind the carbon cycle processes. Combining these independent approaches implies a multiple-constraint approach (Fig. 1.5 (Lower Panel)) to analyze, assess and interpret consistencies or inconsistencies between the two methods and make improvements where necessary (http://biocycle.atmos.colostate.edu_strategy.htm).
Fig. 1.5. (Left Panel) Bottom-Up Approach. (Right Panel) Top-Down Approach. (Lower Panel) Multiple-constraint approach. Image courtesy of [http://biocycle.atmos.colostate.edu/strategy.htm](http://biocycle.atmos.colostate.edu/strategy.htm)

Currently, global transport models utilize in-situ measurements of carbon dioxide from a global network of surface sites for analyzing, estimating and predicting its concentrations (Tans et al., 1990) as well as determining regional scale exchanges of CO₂ (Rödenbeck, et al. 2006; Peylin, et al. 2005; Peters, et al. 2007). These in-situ surface measurements have the advantage that they are highly accurate. However, they have a limited spatial coverage and an increasing number of measurements are performed within the proximity of local sources and
sinks with networks of tall towers over the continents. The limited spatial coverage and the proximity to local sources and sinks makes model estimates susceptible to transport errors, such as errors in vertical transport processes (moist convection and turbulent mixing in the boundary layer), especially for continental regions (Washenfelder et al. 2006; Gerbig et al. 2007). This, in turn, provides uncertainties in the geographic (spatial) and temporal distributions of CO₂ sources and sinks (Dufour et. al. 2004; Gerbig et al. 2007). The uncertainties imply that difficulties would come about in predicting the response of carbon dioxide due to climate and land-use changes (IPCC, 1995), as well as in projecting the future rate of increase of atmospheric CO₂ (Schimel et al., 2001).

Space-borne or satellite measurements, such as the Orbiting Carbon Observatory (OCO) (whose planned launch is in January 15, 2009) (Crisp et al. 2004), the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) (Burrows et al., 1990) and the Greenhouse Gases Observing Satellite (GOSAT) (planned to be launched in January 21, 2009) nicknamed “Ibuki” (which means “to breathe” or “to puff”) (http://www.jaxa.jp/projects/sat/gosat/index_e.html), may offer the solution to the problem of sparse spatial and temporal distributions of carbon dioxide sources and sinks by providing global column measurements of CO₂ (Rayner and O’Brien, 2001). To supplement and validate the satellite data, ground-based solar absorption spectrometry in the infrared or Fourier transform infrared (FTIR) spectrometry is employed (Warneke et. al. 2005). It measures the same quantity (column concentrations) as the satellite and exhibits less temporal variability as compared to in-situ data while retaining information about the surface fluxes and the diurnal behavior of carbon dioxide. It also complements existing in-situ networks and provides information about CO₂ exchange on regional scales (Washenfelder et al., 2006). The Total Carbon Column Observing Network (TCCON) (Fig. 1.6), which is a system of high-resolution ground-based FTIR spectrometers, provides this capability. Currently composed of stations in the United States of America, Canada, Germany, the Arctic, Australia, New
Zealand and in the island of Tenerife, with upcoming stations in Poland, France and Ascension Island, TCCON measures column densities of greenhouse gases particularly atmospheric carbon dioxide, methane (CH₄), water vapour (H₂O), nitrous oxide (N₂O) and carbon monoxide (CO) along with molecular oxygen (O₂) and hydrogen fluoride (HF) to convert the aforementioned column densities to mean mixing ratios. TCCON aims to use these column observations, in combination with the existing surface measurements, to improve estimates of surface fluxes of greenhouse gases allowing better predictions of future concentrations (http://www.tccon.caltech.edu/). In 2007, Yang et al. showed that total column CO₂ measurements from FTIR instruments and partial column observations of atmospheric carbon dioxide from aircrafts could be utilized to estimate the Northern Hemisphere growing season net flux resulting in the observation that computer models underestimate the net ecosystem exchange (NEE) because of employing a weak vertical mixing scheme (Yang et al., 2007). This demonstrates the importance of column measurements of CO₂ to understanding the different carbon cycle mechanisms and processes envisioned by TCCON. However, not all great ideas are free from problems and challenges. Comparison of molecular oxygen among the different TCCON stations show differences that may be attributed to dissimilar instrumental parameters. Therefore it is essential to investigate the effects of instrumental parameters on retrieved molecular oxygen and carbon dioxide column concentrations. This is discussed in this study.
Fig. 1.6. The Total Carbon Column Observing Network. Image courtesy of http://www.tecon.caltech.edu/site-locations/index.html.

Additionally, in this work, CO₂ column abundances from solar absorption FTIR measurements during the CarboEurope Regional Experiment Strategy (CERES) in Biscarrosse, France are presented as well as a method to calibrate these measurements against aircraft data. To provide as a “transfer standard” between incomparable measurement techniques, such as in-situ tower data and column concentrations from FTIR measurements, the Stochastic Time Inverted Lagrangian Transport (STILT) model (Lin et al., 2003) was utilized.

CO₂ has currently reached a record high amount of 387 parts per million (ppm) according to the latest Mauna Loa record, a value 40% higher since the industrial revolution (IPCC, 2007). Due to this, round the clock analyses are being performed on current satellites that measure carbon dioxide and numerous models dedicated for CO₂ are being constantly developed and improved. However, due to instrumental and computational limitations, these satellites and models have horizontal resolutions ranging from 3 km to 350 km. Because of these differences in horizontal resolutions, determining the carbon dioxide concentration in a particular region or comparison of data on a certain location may produce a misrepresentation of the measurement point (representation error) for satellites or a misrepresentation of the
fluxes (aggregation error) for models. Neglecting these errors may cause an overestimation of the observational constraint \((\text{satellites} - \text{pixels}; \text{models} - \text{grid size})\), which may produce biased results in the dataset (Lin et al. 2004). Quantifying this representation and aggregation errors is therefore necessary before conclusions can be made of the temporal and spatial variations of carbon dioxide. Fourier transform spectrometer (FTS) data as well as STILT model outputs (with horizontal grids varied from 10 km to 320 km) would provide a means of examining this issue over an urban area (Bremen, Germany). The near field around the Bremen FTS is likewise analyzed to assess whether local sources from industries affect the column average volume mixing ratios of carbon dioxide. These data together with retrieved CO₂ column concentrations from the Arctic (Ny-Ålesund, Spitzbergen) are also compared to in situ flask measurements and to the NOAA Earth System Research Laboratory (ESRL) CarbonTracker model (Peters, et al. 2007). A “clear sky” bias was also pinpointed in the study as models see increased CO₂ during frontal zone conditions—a meteorological condition when FTIRs often cannot measure.

1.1 The Chemical Composition of the Atmosphere: Origins and Present Day

The origin of the present chemical composition of the Earth’s atmosphere can be traced back to approximately 3 to 3.8 billion years ago with the rise of oxygen \((\text{O}_2)\) emanating from bacteria that reside in the oceans. \(\text{O}_2\) was then rapidly consumed through oxidation of minerals exposed to the atmosphere or through reactions involving hydrogen \((\text{H}_2)\) and other reduced gases. Since \(\text{H}_2\) gradually escaped from the atmosphere, these minerals in the Earth became more oxidized and oxygen, liberated by photosynthesis, began to accumulate in the atmosphere. Together with this increase in \(\text{O}_2\), came the formation of the ozone \((\text{O}_3)\) layer. As a consequence, the evolution of more complex life on Earth began. This ever growing intricate relationship between life and its surroundings, as well as increasing geological events happening on Earth and the ever constant orbital and planetary cycles and motions, gave rise
to today’s composition of the Earth’s atmosphere. It is primarily composed of nitrogen (N₂), which comprises 78.08% of the atmosphere. Oxygen comes next at 20.95% then argon (Ar) at 0.93%. The rest of the atmosphere is composed of trace gases. Even though these trace gases are negligible in amount, their radiative effect is significant. Since most of these trace gases are infrared active such as water vapour (H₂O), carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and ozone (O₃), they are very effective in trapping radiation emitted by the Earth producing a “greenhouse effect” (these gases are termed as greenhouse gases) that regulates temperatures on Earth and making it conducive for life to exist and flourish. The concentrations of gases in the Earth’s atmosphere are summarized in Table 1.1 (Wallace and Hobbs, 2006).

Table 1.1. Fractional concentrations by volume of gases that make up Earth’s atmosphere.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Fractional Concentration by Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N₂)</td>
<td>78.08%</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>20.95%</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>0.93%</td>
</tr>
<tr>
<td>Water Vapor (H₂O)</td>
<td>0-5%</td>
</tr>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td>380 ppm</td>
</tr>
<tr>
<td>Neon (Ne)</td>
<td>18 ppm</td>
</tr>
<tr>
<td>Helium (He)</td>
<td>5 ppm</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>1.75 ppm</td>
</tr>
<tr>
<td>Krypton (Kr)</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>0.5 ppm</td>
</tr>
<tr>
<td>Nitrous Oxide (N₂O)</td>
<td>0.3 ppm</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>0 – 0.1 ppm</td>
</tr>
</tbody>
</table>

1.2 Vertical Structure of the Atmosphere

The atmosphere can be divided into layers based on turbulent mixing and in terms of temperature characteristics. In terms of turbulent mixing, Earth’s atmosphere is composed of
the homosphere and the heterosphere. The homosphere is a layer of the atmosphere where its composition is more or less uniform (except for water vapour) as described in Table 1.1. Its altitude range begins at the surface of the Earth and reaches up to approximately 100 km and is bounded by a layer where turbulence ceases called the turbopause. The heterosphere, on the other hand, which starts at approximately above 100 km, is a layer of the atmosphere where its chemical composition varies with altitude. This is due to the absence of mixing wherein the density of a gas decreases with altitude at a rate proportional to its molecular weight. Hence, heavier molecules such as nitrogen and oxygen drop off more rapidly than lighter ones like helium, molecular hydrogen and atomic hydrogen (Wallace and Hobbs, 2006).

The homosphere is further divided into layers based on temperature properties. These layers are the troposphere, the stratosphere, the mesosphere and the thermosphere. These are depicted in Fig. 1.7. The troposphere is characterized by decreasing temperatures with height. It comprises approximately 80% of the total mass of the atmosphere and is relatively well-mixed. Nearly most weather phenomena occur in this layer and it ranges from the surface to approximately 12 km in the tropics and approximately 8 km in the polar regions. It is bounded on top by the tropopause. The stratosphere is described as having increasing temperatures with altitude due to the ozone rich content of this layer, which absorbs ultraviolet (UV) radiation from the sun. Because of this, turbulent mixing is inhibited. The stratosphere is extremely dry. This layer of the atmosphere extends up to approximately 50 km and is bounded at this altitude by the stratopause. The mesosphere is characterized by decreasing temperature with height reaching a minimum at the mesopause at an altitude of approximately 85 km. The thermosphere, the top most layer of the atmosphere, is described by increasing temperatures with altitude due to absorption of solar radiation associated with the photodissociation and photoionization of molecular nitrogen and oxygen (Wallace and Hobbs, 2006).
Fig. 1.7. The layers of Earth’s atmosphere based on temperature characteristics are the troposphere, the stratosphere, the mesosphere and the thermosphere. Pressure and density decrease exponentially with altitude (Encyclopedia Britannica, 2007).

Another essential characteristic of the atmosphere is that there is a hydrostatic equilibrium between the pressure gradient and gravity. Due to this, the pressure decreases exponentially with height as

$$ p = p_0 e^{-z/H} $$

(1.1)

where $p$ is the pressure at altitude $z$, $p_0$ is the pressure at a particular reference height (usually at sea level, $z = 0$) and $H$ is termed as the scale height. The scale height is the altitude at which the pressure drops by a factor of $e$ and is given by
\[ H = \frac{R_d T}{g} \]  

(1.2)

where \( R_d \) is the gas constant for dry air (287 J K\(^{-1}\) kg\(^{-1}\)), \( T \) is the mean surface temperature in Kelvin and \( g \) is the surface acceleration due to gravity.

### 1.3 The Carbon Cycle

The carbon cycle is an essential process in examining climatic changes in Earth’s atmosphere since it regulates the concentrations of two important greenhouse gases namely, carbon dioxide (CO\(_2\)) and methane (CH\(_4\)). The important carbon reservoirs (arranged according to increasing capacity) are the atmosphere, the biosphere, the oceans and the Earth’s crust. The higher the capacity of a carbon reserve, the longer is the residence time of carbon in the reserve. The exchange rates of carbon into and out of a reservoir depend on their capacities and residence times. The exchange rate of a large reservoir with a long residence time, such as the Earth’s crust, is orders of magnitude slower than a small reservoir with a short residence time, like the atmosphere. The Earth’s biosphere is intermediate in its exchange rate of carbon between reservoirs. Figure 1.8 provides an overview of processes involved in the carbon cycle. Carbon in the atmosphere, mostly in the form of carbon dioxide, is taken up by the biosphere and the oceans through the process of photosynthesis. Leafy plants and phytoplanktons use the carbon in the atmosphere (CO\(_2\)) and the water (H\(_2\)O) in the soil and oceans to produce sugar (C\(_6\)H\(_{12}\)O\(_6\)) and oxygen (O\(_2\)). This chemical reaction is shown below:

\[ 6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \]  

(1.3)

In the reaction of respiration and decay, carbon is released back into the atmosphere. However, some of the carbon absorbed by the land and marine biosphere gets buried into the Earth’s crust where some of it gets subducted into the Earth’s mantle. Sea floor spreading may then release this subducted carbon from the mantle to the Earth’s crust where it could
then be released to the atmosphere through weathering. Carbon in the Earth’s mantle may also be released directly into the atmosphere through volcanic activity (Wallace and Hobbs, 2006).

Fig. 1.8. The carbon cycle. Shown are the annual fluxes in GtC year$^{-1}$ with the black values indicating the natural fluxes and the red values depicting the anthropogenic fluxes (IPCC, 2007).
2 Fourier Transform Infrared Spectrometry

The humble beginnings of infrared spectrometry commenced with the discovery of infrared radiation by Friedrich Wilhelm Herschel in the year 1800 using a glass prism to divide the light coming from the sun to its component colors. Using blackened bulb thermometers, he observed that temperatures can be measured beyond the red portion of the spectrum. Gratings then replaced these prisms and in the mid 1960’s, Michelson interferometers utilized the Fourier transform concept to produce spectra in the near, mid and far infrared regions. Thus, Fourier transform infrared (FTIR) spectrometry was born.

2.1 The Michelson Interferometer

The heart and soul of FTIR spectrometry is the Michelson interferometer as shown in Fig. 2.1. Collimated radiation emitted from a source (such as a lamp or the sun) is split through the use of a beamsplitter, which ideally reflects 50% of the incoming beam unto a fixed mirror, M1, and transmits the remaining half to a moving mirror, M2. The beams are then recombined and directed unto a detector (used in this study is the Indium Galium Arsenide, InGaAs, near infrared detector) where, depending upon the distance the moving mirror travels, $\Delta x$ (termed as the optical retardation or the optical path difference), constructive and destructive interferences may occur. The resulting signal is called the interferogram.

2.2 Fourier Transformation

The measured interferogram, $I(n\Delta x)$, is discrete in nature as a result of analog to digital conversion at the detector. To obtain the spectra, $S(k\Delta \nu)$ as a function of the wavenumber $\nu$, from the digitized interferogram, as shown in Fig. 2.1, a mathematical operation called the discrete Fourier transform (DFT) is performed. This operation can be expressed as

$$S(k\Delta \nu) = \sum_{n=0}^{N-1} I(n\Delta x) e^{i2\pi nk/N}$$  \hspace{1cm} (2.1)
Fig. 2.1. The Michelson interferometer, the interferogram and the spectra after discrete Fourier transformation.
where \( n \) is the discrete interferogram point, \( N \) is the total number of discrete interferogram points and \( k \) is the discrete spectrum points.

### 2.3 The Instrumental Line Shape Function

Real world applications of FTIR spectrometry entail consideration of limitations in certain instrumental parameters. The properties that are generally taken into account are the *limited optical path difference (apodization)* and the *finite entrance aperture size*. The effect of these two factors are combined into an *instrumental line shape* function, \( ILS(v) \). The observed spectrum is a *convolution* of the true spectrum and the instrumental line shape as shown in Fig. 2.2 (Davis, Abrams and Brault, 2001).

![Graph of True Spectra, ILS (14 mK Resolution), and Observed Spectra](image)

**Fig. 2.2. The Instrumental Line Shape Function.** The observed spectrum is a convolution of the true spectrum and the instrumental line shape function.

### 2.4 Modulation

A monochromatic radiation source would give out a cosine interferogram. Due to the finite entrance aperture size, the interferogram is *modulated* by a *sine* function. Figure 2.3 shows a
100% modulation (ideal instrument), an 80% modulation and a 60% modulation. This property is better characterized for a particular wavenumber, \( v_0 \), by a quantity called the modulation efficiency and is defined as

\[
m(\Delta x, v_0) = \frac{A_{\text{real}}(\Delta x, v_0) / A_{\text{real}}(0, v_0)}{A_{\text{ideal}}(\Delta x, v_0) / A_{\text{ideal}}(0, v_0)}
\]  

(2.2)

where \( A_{\text{real}}(\Delta x, v_0) \) is the amplitude of the interferogram envelope of a real and non-ideal instrument, \( A_{\text{real}}(0, v_0) \) is the amplitude of the interferogram at zero optical path difference and the variables in the denominator are similar quantities but for an ideal instrument. Modulation losses cause a broadening of the instrumental line shape function as shown in Figure 2.3 (Davis, Abrams and Brault, 2001).

### 2.5 Phase

Ideal spectra are real and positive, therefore the phase is zero and the interferogram is symmetric about the zero optical path difference (the centerburst). However, due to experimental, instrumental and computational limitations, this is not always the case. Phase errors may occur due to errors in sampling and apodization, due to dispersive effects producing frequency dependent optical path differences (the zero path difference is not the same for all wavelengths) and due to electronic delays in amplifiers and filters. The phase error is mathematically expressed as

\[
\phi(\Delta x, v_0) = \phi_{\text{real}}(\Delta x, v_0) - \phi_{\text{ideal}}(\Delta x, v_0)
\]  

(2.3)
Fig. 2.3. Modulation. (Top) A monochromatic radiation source modulated by a sinc function. (Bottom) Effect of modulation losses on the instrumental line shape function (Hase et al, 1999).

Figure 2.4 shows the effects of phase errors on the symmetry of the instrumental line shape (Davis, Abrams and Brault, 2001).
Fig. 2.4. Phase errors produce asymmetries in instrumental line shape function (Hase et al., 1999).
3 Retrieval

Quantities measured from remotely sensed platforms (spectral radiance, Doppler shift or refraction) such as from satellite or ground-based data are not necessarily the parameters of interest in atmospheric science (where temperature profiles, vertical distributions or column concentrations of gases are more important). Analysis of the data therefore requires a retrieval or an inversion of the direct measurements in order to derive the desired atmospheric parameters. Retrieval involves solving the inverse of a forward function that relates the measurements, $\bar{y}$, with the quantities or parameters of interest, $\bar{x}$. Here, $\bar{x}$ is termed the state vector which is usually a continuous function of position such as altitude for the vertical profile of a gas. However, in practice, the state vector is discretized into $n$ elements and is given as

$$\bar{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_i \\ \vdots \\ x_n \end{pmatrix} \quad (3.1)$$

On the other hand, $\bar{y}^M$ is called the measurement vector with $m$ elements expressed as

$$\bar{y}^M = \begin{pmatrix} y_1^M \\ y_2^M \\ y_3^M \\ \vdots \\ y_i^M \\ \vdots \\ y_m^M \end{pmatrix} \quad (3.2)$$
Each measurement has an accompanying error and this is represented with a measurement error vector, \( \bar{\mathbf{E}} \) given as

\[
\bar{\mathbf{E}} = \begin{pmatrix}
\mathbf{E}_1 \\
\mathbf{E}_2 \\
\mathbf{E}_3 \\
\vdots \\
\mathbf{E}_i \\
\vdots \\
\mathbf{E}_m
\end{pmatrix}
\] (3.3)

The physical principles relating the measurement, the state and the error vectors is characterized by the forward function expressed as

\[
\bar{\mathbf{y}}^M = f(\bar{x}) + \bar{\mathbf{E}}
\] (3.4)

The actual or true forward function, due to its complexity or intractability, is normally approximated to what is called the forward model (Rodgers, 2000).

### 3.1 The Forward Model for Atmospheric Radiative Transfer

The forward model for the atmosphere is based on radiative transfer theory. It begins with Beer-Lambert’s law, which gives how much incident radiation intensity, \( I_0 \), is decreased as it passes through an absorbing medium. In simplest terms it is expressed as

\[
I(v) = I_0(v) e^{-\int_0^s \sigma(v)n(s')ds'}
\] (3.5)

where \( \sigma(v) \) is the absorption cross-section of the atmospheric specie in the medium \([m^2]\), \( s \) is the radiation path length \([m]\) and \( n(s') \) is the number density of absorbers \([m^{-3}]\). Equation (3.5) is often expressed in terms of transmittance, \( T \), given by

\[
T(v) = \frac{I(v)}{I_0(v)} = e^{-\int_0^s \sigma(v)n(s')ds'}
\] (3.6)
The product $\sigma(v)n(s')$ is called the absorption coefficient, $k(v,s')$. However, in analyzing measured spectra, a discrete, line-by-line, multilayer and multispecies expression for the atmospheric transmittance is employed. It is expressed as

$$T(v_i) = e^{-\sum_{j=0}^{70} \sum_{k}^{K} \sum_{l}^{L} \left\{ c_k w_{0,k,j} \left[ R_{l,k,j} F_{l,k,j} (v_i - v_{k,j}) \right] n_j s_j \right\}} \quad (3.7)$$

where $w_{0,k,j}$ is the a priori volume mixing ratio (VMR) of the $k^{th}$ gas in the $j^{th}$ atmospheric layer (which ranges from 0 to 70 km at 1 km intervals), $c_k$ is a factor multiplied to the a priori volume mixing ratio of the $k^{th}$ gas, $R_{l,k,j}$ and $F_{l,k,j}$ is the absorption strength [cm cm$^{-1}$] and the normalized line shape function [cm], respectively, of the $l^{th}$ line of the $k^{th}$ gas in the $j^{th}$ layer, $v_{k,j}$ is the wavenumber center of the $k^{th}$ gas in the $j^{th}$ layer [cm$^{-1}$], $n_j$ is the number density of absorbers in the $j^{th}$ layer [cm$^{-3}$] and $s_j$ is the effective radiation path length in the $j^{th}$ level [cm]. For each atmospheric layer, pressure and temperature dependent absorption coefficients are calculated for every gas and for every line (Yang, 2007). Pressure and temperature profiles are taken from reanalyzed NCEP/NCAR data (http://www.cdc.noaa.gov/cdc/reanalysis/). Spectral parameters (e.g. absorption strength, line widths, absorption coefficients) were derived from compilations of spectroscopic parameters used for predicting and simulating transmission and emission of radiation in the atmosphere. These are called spectroscopic linelists. The spectroscopic linelist used in this study primarily comes from the Atmospheric Trace Molecule Spectroscopy (ATMOS) linelist (Brown et al., 1996) (wherein the main linelist is an updated version of the 1992 High Resolution Transmission (HITRAN) molecular absorption database (Rothman et al., 1998)) with modifications based on the studies of Newman et al. (2000), Smith and Newnham (2000), Smith et al. (2001) and improvements from Washenfelder and Toon (http://www.gps.caltech.edu/~rebecca/work_archive/) for the discrete lines and absorption
continuum of molecular oxygen ($\text{O}_2$) and modifications based on the studies of Toth et al. (2005) and improvements from Toon (http://mark4sun.jpl.nasa.gov/toon/linelist/) for carbon dioxide. The background solar linelist comes from the work of Wallace and Livingston (1990).

Using the transmittance calculated in (3.7), the forward model is calculated using

$$y^c_i = \left\{ C + S(v_i - v_0) \right\} y_{i,\text{top}} \cdot ILS(v_i, \delta) \otimes T(v_i) \right\} + z_{\text{offset}} \quad (3.8)$$

where $y^c_i$ is an element of the forward model matrix $f(\bar{x})$ which we also denote as $\tilde{y}^c_i$ (referred to as the calculated spectra), $y_{i,\text{top}}$ is the spectra at the top of the atmosphere, $C$ is the continuum level (see Fig. 3.1), $S$ is the continuum tilt (see Fig. 3.1), $\delta$ is the frequency shift, $v_0$ is the frequency at the center of the spectral range being considered (the spectral window), $ILS(v_i, \delta)$ is the instrumental line shape function which is convolved ($\otimes$) with the transmittance $T(v_i)$ and $z_{\text{offset}}$ is the zero level offset of the spectra (Yang, 2007).

![Fig. 3.1 Continuum Level and Continuum Tilt](image)
3.2 Solution to the Atmospheric Inverse Problem

To solve the atmospheric inverse problem, a non-linear least-squares fitting algorithm developed at NASA JPL, called GFIT, is used (Toon et al., 1992). It calculates for the elements of the state vector which are the scale factors for each of the gases in the window, the continuum level, the spectrum tilt, the frequency shift and the zero level offset of the spectra as expressed below

\[
\tilde{x} = \begin{pmatrix}
  c_1 \\
  c_2 \\
  c_3 \\
  \vdots \\
  c_k \\
  C \\
  S \\
  \delta \\
  z_{\text{offset}}
\end{pmatrix} \quad (3.9)
\]

such that the percent root-mean-square (%RMS) fit between the measured spectra, \( \tilde{y}^M \), and the calculated spectra, \( \tilde{y}^C \) are minimized. The %RMS is expressed as

\[
%\text{RMS} = 100 \times \sqrt{\frac{\sum_{i=1}^{m} (y_i^M - y_i^C)^2}{m}} \quad (3.10)
\]

where \( m \) is the number of spectral points. The quantity \( (y_i^M - y_i^C) \) is called the residual and the % residual is simply the residual multiplied by 100. These quantities are depicted in Fig. 3.2.
Fig. 3.2. The measured and calculated transmittance of carbon dioxide in the near-infrared window. Shown also are the %residuals and the %RMS.

3.3 Vertical Column Concentrations

The vertical column concentration is defined as the number of molecules a particular gas has from the surface to the top of the atmosphere per unit area. This is depicted in Figure 3.3.

Once the state vector described in the previous section has been solved, the vertical column concentration of the $k^{th}$ gas can then be calculated by integrating its scaled a priori volume mixing ratio profile, $c_k w_{vk}(p)$, using the expression

$$ column_{gas} = \int_0^p c_k w_{vk}(p) \frac{dp}{m_{dry} g(\varphi, p)} $$

where $p$ is the pressure, $g(\varphi, p)$ is the latitude dependent acceleration due to gravity at a specific pressure level (pressure dependent acceleration due to gravity), $m_{dry}$ is the mean molecular mass of dry air (28.964 kg-kmol$^{-1}$) and $P_s$ is the surface pressure. The unit of the vertical column concentration is [molecules cm$^{-2}$] (Washenfelder et. al, 2006).
Fig. 3.3. The vertical column concentration of carbon dioxide is the amount of carbon dioxide molecules per unit area from the surface to the top of the atmosphere.

### 3.4 Column Average Volume Mixing Ratio

The average concentration of the $k^{th}$ gas in the vertical column can be determined using

$$X_{gas} = \frac{column_{gas}}{total\ dry\ column} \quad (3.12)$$

where the total dry column is expressed as

$$total\ dry\ column = \frac{P_{obs}}{m_{dry} g(\varphi)} - column_{H_2O} \left( \frac{m_{H_2O}}{m_{dry}} \right) \quad (3.13)$$

where $P_{obs}$ is the observed surface pressure, $m_{dry}$ is the mean molecular mass of dry air (28.964 kg-kmol$^{-1}$), $m_{H_2O}$ is the mean molecular mass of water vapour (18.02 kg-kmol$^{-1}$) and $g(\varphi)$ is the latitude dependent surface acceleration due to gravity. The total dry column can also be determined from the retrieved O$_2$ column using the relation (Washenfelder et. al, 2006)

$$total\ dry\ column = \frac{column_{O_2}}{0.2095} \quad (3.14)$$
Using (3.14) minimizes systematic and correlated errors present in both the \( column_{gas} \) and the \textit{total dry column} such as errors present in the pressure and in the instrumental line shape (Yang et al., 2002).
4 The Stochastic Time Inverted Lagrangian Transport (STILT) Model

The Stochastic Time Inverted Lagrangian Transport (STILT) model is a tool designed to obtain surface fluxes from atmospheric concentration data among distributed sources or sinks over land. In other words, STILT links trace gas observations at a measurement location (the receptor) with emissions emanating from the surface. It can be utilized to represent surface flux influences on measurements in the near-field. The near-field indicates approximately 3 day temporal and 100 to 1000 km spatial coverages. It is based on the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model using a similar mean advection scheme but employing a different turbulence module. The analysis framework of STILT is depicted in Fig. 4.1 below (Gerbig et. al, 2003):

![STILT Analysis Framework Diagram]

Fig. 4.1 STILT Analysis Framework
4.1 Meteorological Fields, Multiple Receptor Scheme and Influence Functions

Using winds, surface sensible heat and momentum fluxes as well as computed convective mass fluxes from the European Centre for Medium-Range Weather Forecasts (ECMWF) assimilated meteorological fields, STILT simulates transport through tracking the temporal evolution of particle ensemble (Lin et al., 2003). Being originally designed for comparisons with in situ (single receptor) measurements, STILT was modified for comparisons with column measurements (multiple receptors). The multiple receptor scheme is depicted in Fig. 4.2. Receptor points were placed at equal intervals along the vertical for each altitude range.

Fig. 4.2. Multiple Receptor Scheme

The altitude ranges were set at 1-500 m, 500 – 3000 m, 3 – 6 km, 6 – 11 km and 11 – 18 km. For each the receptor location, $\mathbf{x}_r$, a representative particle was released at a time $t_r$ giving rise to particle densities, $\rho(\mathbf{x}_r,t_r | \mathbf{x},t)$ at $\mathbf{x}$ and time $t$. The influence, $I(\mathbf{x}_r,t_r | \mathbf{x},t)$ [volume$^{-1}$]
1] is then related to the particle density by dividing it with the total number of particles released, \( N_{tot} \). These influences quantitatively relate surface fluxes (sources or sinks), \( S(\bar{x}, t) \) [ppm s\(^{-1}\)], to the concentration, \( C(\bar{x}_r, t_r) \) [ppm], at the measurement location (the receptor) through

\[
C(\bar{x}_r, t_r) = \int_{t_0}^{t} dt \int_{v} d^3x I(\bar{x}_r, t_r | \bar{x}, t) S(\bar{x}, t) + \int_{v} d^3x I(\bar{x}_r, t_r | \bar{x}, t_0) C(\bar{x}, t_0)
\]  
(4.1)

where the second term is the contribution from the initial tracer field, \( C(\bar{x}, t_0) \), brought about by transport (Gerbig et al., 2003).

The surface sources or sinks can be represented as interior (volume) fluxes by diluting the surface flux into an atmospheric column of height \( h \) as given by

\[
S(\bar{x}, t) = \begin{cases} 
\frac{F(x, y, t) m_{air}}{h \rho(x, y, t)} & \text{for } z \leq h \\
0 & \text{for } z > h
\end{cases}
\]  
(4.2)

where \( F(x, y, t) \) is the surface flux in \( \mu\text{mol m}^{-2} \text{ s}^{-1} \), \( \rho(x, y, t) \) is the column averaged density of air and \( m_{air} \) is the molar mass of air. From this, the change in tracer concentration at the receptor can be determined at finite temporal (from \( t_i \) to \( t_i + \Delta \bar{t} \)) and spatial (\( \Delta x \) and \( \Delta y \)) resolutions at surface grid elements \( j \) and \( k \) as

\[
\Delta C_{i,j,k}(\bar{x}_r, t_r) = F(x_j, y_k, t_i) \frac{m_{air}}{h \rho(x_j, y_k, t_i)} \int_{t_i}^{t_i + \Delta \bar{t}} dt \int_{x_j}^{x_j + \Delta x} dx \int_{y_k}^{y_k + \Delta y} dy \int_{0}^{h} dz I(\bar{x}_r, t_r | \bar{x}, t)
\]  
(4.3)

where \( \frac{m_{air}}{h \rho(x_j, y_k, t_i)} \int_{t_i}^{t_i + \Delta \bar{t}} dt \int_{x_j}^{x_j + \Delta x} dx \int_{y_k}^{y_k + \Delta y} dy \int_{0}^{h} dz I(\bar{x}_r, t_r | \bar{x}, t) \) is the “footprint” element, \( f(\bar{x}_r, t_r | x_j, y_k, t_i) \), in units of ppm \( \mu\text{mol}^{-1} \text{ m}^2 \text{ s}^{-1} \). The footprint relates the surface fluxes (in \( \mu\text{mol m}^{-2} \text{ s}^{-1} \)) to changes in concentration at the receptor.

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4.2 Lateral, Initial and Surface Boundary Condition for Tracers

The CO$_2$ concentration output from the model (in ppm) is determined by

\[ CO_2 = CO_{2,\text{background}} + CO_{2,\text{fossil fuel}} + CO_{2,\text{photosynthetic uptake}} + CO_{2,\text{respiration}} \]  \hfill (4.4)

The lateral or initial boundary tracer concentrations, $C(x,t_0)$ or $CO_{2,\text{background}}$, link near-field concentrations with global background concentrations. This is done by coupling the high resolution regional grid of STILT with that of the TM3 global transport model (Gerbig et al., 2003). This is depicted in Fig. 4.3.

$CO_{2,\text{fossil fuel}}$ comes from fossil fuel emissions due to combustion estimated using the recent greenhouse gas emissions inventory from the Institute of Economics and the Rational Use of Energy (IER), University of Stuttgart (http://carboeurope.ier.uni-stuttgart.de/). The Greatly Simplified Biosphere (GSB) model uses the SYNMAP land cover (Jung et al, 2006) and flux data from AMERIFLUX with a correction for the gross ecosystem exchange (GEE) and respiration parameters based on the inversion of data obtained in the CO$_2$ Budget and Rectification Airborne (COBRA) study performed in 2000 (Gerbig et al., 2003) to produce the $CO_{2,\text{photosynthetic uptake}}$, which is the carbon dioxide concentration taken up by the vegetation and the $CO_{2,\text{respiration}}$, which is the amount of CO$_2$ released by plants. Biospheric exchange for the GSB is based on light and temperature responses on 3 vegetation classes namely forests, shrubs and crops (Gerbig et al., 2006).
Fig. 4.3. The STILT-TM3 Coupled System. (Left) Surface influences or footprints are shown for 10-day backtrajectories to illustrate the regional dynamic near-field and fixed far-field resolutions of STILT. The far-field resolution is close to the resolution of TM3. (Right) Scheme of interaction between STILT and TM3 (figure courtesy of Christoph Gerbig).
5 Results and Discussions

In this work, solar absorption spectra in the near infrared were measured in locations outlined in Table 5.1. Due to its proximity to the solar Planck function maxima, the near infrared region provides high signal-to-noise ratio (SNR). Vertical column concentrations of molecular oxygen (O₂) and carbon dioxide (CO₂) were retrieved with windows or spectral ranges given in Table 5.2.

5.1 Retrieval of the O₂ 7885 cm⁻¹ Band as “Internal Standard”

Being well mixed in the atmosphere, having approximately a constant dry air volume mixing ratio (to the degree required) of 0.2095, retrieval of molecular oxygen offers an internal standard that can be utilized to assess the short-term and long-term precision of the FTIR column concentration retrievals (Washenfelder et al., 2006) as well as a means to determine the dry air mixing ratio, avoiding uncertainties from the surface pressure and the water vapor column. Molecular oxygen, O₂, was retrieved in the 7765 – 8005 cm⁻¹ near infrared spectral region centered at 7885 cm⁻¹. The measured and simulated spectra in this wavenumber region together with their corresponding residuals are shown in Fig. 5.1.

The spectrum is composed of O₂ line spectra, a superimposed O₂ continuum and solar lines with water vapor, H₂O, as interfering species. These are shown in Fig. 5.2.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum GDP from 4.5 – 5.5 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median age</td>
<td>Years</td>
<td>0.5 - 1.5</td>
</tr>
<tr>
<td>Percentage of women</td>
<td></td>
<td>0.5 - 2.5</td>
</tr>
<tr>
<td>Percentage of men</td>
<td></td>
<td>0.5 - 2.5</td>
</tr>
<tr>
<td>Percentage of children</td>
<td></td>
<td>0.5 - 2.5</td>
</tr>
<tr>
<td>Length of stay</td>
<td>Days</td>
<td>0.5 - 2.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>Degrees</td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>Humidity</td>
<td></td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>Pressure</td>
<td>MmHg</td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>Precipitation</td>
<td>Mm</td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>Dew point</td>
<td>Degrees</td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>Wind speed</td>
<td>Kmh</td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>Visibility</td>
<td>Meters</td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>Precipitation density (%)</td>
<td></td>
<td>0.5 - 2.0</td>
</tr>
</tbody>
</table>

**Table 3.1:** Instrument Locations and History

<table>
<thead>
<tr>
<th>Location</th>
<th>Instrument Type</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Location 1]</td>
<td>Type</td>
<td>Description</td>
</tr>
<tr>
<td>[Location 2]</td>
<td>Type</td>
<td>Description</td>
</tr>
<tr>
<td>[Location 3]</td>
<td>Type</td>
<td>Description</td>
</tr>
<tr>
<td>[Location 4]</td>
<td>Type</td>
<td>Description</td>
</tr>
<tr>
<td>[Location 5]</td>
<td>Type</td>
<td>Description</td>
</tr>
<tr>
<td>[Location 6]</td>
<td>Type</td>
<td>Description</td>
</tr>
<tr>
<td>[Location 7]</td>
<td>Type</td>
<td>Description</td>
</tr>
<tr>
<td>[Location 8]</td>
<td>Type</td>
<td>Description</td>
</tr>
<tr>
<td>[Location 9]</td>
<td>Type</td>
<td>Description</td>
</tr>
</tbody>
</table>
# Near Infrared Windows

<table>
<thead>
<tr>
<th>Gas</th>
<th>Center Frequency [cm(^{-1})]</th>
<th>Window Width [cm(^{-1})]</th>
<th>Spectral Region [cm(^{-1})]</th>
<th>Interfering Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>7885.00</td>
<td>240.00</td>
<td>7765 – 8005</td>
<td>H(_2)O</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>6220.00</td>
<td>80.00</td>
<td>6180 – 6260</td>
<td>H(_2)O, HDO, CH(_4)</td>
</tr>
<tr>
<td></td>
<td>6339.50</td>
<td>85.00</td>
<td>6297 – 6382</td>
<td>H(_2)O, HDO</td>
</tr>
</tbody>
</table>

![Near Infrared Windows Graph](image)

**Fig. 5.1** Measured and simulated O\(_2\) spectra in the 7765 – 8005 cm\(^{-1}\) spectral region.
Fig. 5.2 O$_2$ Line Spectra, O$_2$ continuum, solar lines and interfering H$_2$O.

The O$_2$ line spectra originate from an electronic transition ($\Sigma^3^g(0,0) - \alpha^1\Delta_g$) responsible for airglow emission. It is a weak magnetic dipole allowed band (Van Vleck, 1934; Jones and Harrison, 1958; McClatchey et al., 1973). The O$_2$ continuum arises from O$_2$-O$_2$ self collision induced absorption (SCIA) and O$_2$-N$_2$ foreign collision induced absorption (FCIA) (Smith et al., 2001). Even though the O$_2$ continuum is fitted, only the line spectra are used to calculate the O$_2$ vertical column concentrations. Separately fitting the O$_2$ continuum “protects” the discrete lines from the effects of continuum curvature.

5.1.1 FTIR Column Observations of Atmospheric Molecular Oxygen

Using column concentrations of atmospheric molecular oxygen as a means to determine the total dry column as shown in Eq. 3.14 and utilizing this quantity to calculate the column average volume mixing ratio of trace gases in the near-infrared as in (3.12), cancels or at least minimizes systematic and correlated errors (such as solar pointing, zero level offset and instrumental lineshape errors) between the trace gas and O$_2$. Aside from this advantage, the O$_2$ 7885 cm$^{-1}$ band is also close to the wavelengths of CO$_2$, CH$_4$ and CO as well as
similar in line strengths with carbon dioxide and methane. Ideally, the dry air column average volume mixing ratio of O$_2$, $XO_2$, should be constant in time (0.2095) as well as in space and independent of the surface pressure or the amount of water vapor. However, this does not seem to be the case. Three problems were identified for the retrieved O$_2$ among four stations of the Total Carbon Column Observing Network (TCCON):

1. $XO_2$ is ~2% larger than the established 0.2095 value as seen in Fig. 5.3. This has been attributed to errors and uncertainties in the O$_2$ line strengths of the spectroscopic linelist.

2. $XO_2$ shows a 1% difference between sites also shown in Fig. 5.3. Differences in instrumentation and instrumental parameters used between these sites could have been the cause. The effect of instrumental parameters are discussed further in Section 5.3.

3. $XO_2$ has an ~0.5% solar zenith angle (i.e. airmass) dependence attributed to linelist line width errors as depicted in Fig. 5.4. A small width error of 1.0% causes an easily detectable 0.4% diurnal artifact.

The question now is, “does it really matter that the dry air column average volume mixing ratio of atmospheric molecular oxygen varies with time?” The answer is both yes and no. No, because as long as the correlated errors affects other column concentrations of trace gases (such as carbon dioxide) equally, there will be no impact on the dry air column average volume mixing ratio of these trace gases. Yes, because it would deprive us of an inter-calibration standard ($XO_2$) (Geoffrey Toon, private communication)
Fig. 5.3 Atmospheric Molecular Oxygen from four Total Carbon Column Observing Network Stations: Parkfalls, Wisconsin, USA; Darwin, Australia; Lauder, New Zealand; and Bremen, Germany (Figure courtesy of Paul Wennberg).

Fig. 5.4 Airmass Dependence of Atmospheric Molecular Oxygen from the Darwin TCCON station for the date of September 15, 2005. Shown on the y-axis is the scale factor multiplied to the a priori O₂ vmr (Figure courtesy of Geoffrey Toon).
5.1.1.1 Mean O₂ Level Comparisons for Single Stations

Column concentrations of atmospheric molecular oxygen was retrieved and investigated for the Ny-Ålesund, Bremen and Biscarrosse stations (station details in Table 5.1) with the column average volume mixing ratio of O₂ calculated using Eq. 3.12. These are shown in Fig. 5.5 along with instrumental parameters that were varied throughout the presented time period which are the field of view (FOV), the maximum optical path difference (maximum OPD) and the high folding limit (HFL) as well as the O₂ continuum level.

In Biscarrosse (120 M), where the FOV, the maximum OPD and the HFL are kept consistent all through out the measurements, the O₂ VMR (~0.218) as well as the O₂ continuum level (~0.1) maintains the same value. In Ny-Ålesund, which uses the 120 HR, the change in the mean O₂ level (from ~0.218 in 2002-2003 to ~0.216 in 2005-2007) could have been brought about by a combination of changes with the field of view (from 4.1 mrad in 2002-2003 to 1.2 mrad in 2005-2007 which resulted in changes to the O₂ continuum level from 0.55 to 0.1), changes to the resolution (from 12.86 cm in 2002-2003 to 30.00 cm in 2005-2007) as well as to changes to the high folding limit (from 31596 cm⁻¹ in 2002-2003 to 15798 cm⁻¹ in 2005-2007). In Bremen, the mean O₂ level, FOV, maximum OPD and HFL changes are outlined in Table 5.3.
Fig. 5.5 The column averaged volume mixing ratio of atmospheric molecular oxygen ($XO_2$), field of view (FOV), maximum optical path difference (maximum OPD), high folding limit (HFL) and $O_2$ continuum level for Biscarrosse, Ny-Alesund and Bremen. The solid lines indicate the mean $O_2$ level. The black and red boxes indicate the $O_2$ level changes for the Bremen data corresponding to changes in the FOV and the maximum OPD. *Note: 2004 Ny-Alesund data was not included due to saturated detectors.
<table>
<thead>
<tr>
<th>Time Period</th>
<th>Instrument</th>
<th>Mean O₂ Level</th>
<th>Field of View [mrad]</th>
<th>Maximum Optical Path Difference [cm]</th>
<th>High Folding Limit [cm⁻¹]</th>
<th>O₂ Continuum Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mid-2003</td>
<td>120 HR</td>
<td>0.2150</td>
<td>1.2</td>
<td>12.86</td>
<td>31596</td>
<td>0.15</td>
</tr>
<tr>
<td>February 2004</td>
<td>120 HR</td>
<td>0.2140</td>
<td>1.9</td>
<td>18.00</td>
<td>31596</td>
<td>0.4</td>
</tr>
<tr>
<td>May 2004</td>
<td>125 HR</td>
<td>0.2125</td>
<td>3.1</td>
<td>18.00</td>
<td>31596</td>
<td>0.45</td>
</tr>
<tr>
<td>July 2004</td>
<td>125 HR</td>
<td>0.2165</td>
<td>4.8</td>
<td>18.00</td>
<td>31596</td>
<td>0.1</td>
</tr>
<tr>
<td>Rest of 2004 and 2005</td>
<td>125 HR</td>
<td>0.2160/0.2135/0.2120</td>
<td>4.1/2.4/1.2</td>
<td>45.00</td>
<td>31596/31596/31596</td>
<td>0.2/0.15/0.1</td>
</tr>
<tr>
<td>2006-2007</td>
<td>125 HR</td>
<td>0.2140</td>
<td>1.2</td>
<td>45.00</td>
<td>15798</td>
<td>0.15</td>
</tr>
</tbody>
</table>

**RECAP:** From the observations from each station:

- increasing the field of view (the aperture size) seem to increase the mean O₂ value
- increasing the maximum optical path difference, hence the resolution, appear to generally decreases the mean O₂ level
- and decreasing the high folding limit looks as if it increases the mean O₂ level

These effects are further discussed in Section 5.3.

### 5.1.1.2 Mean O₂ Level Comparisons Between the Ny-Ålesund, Bremen and Biscarrosse Stations

In comparing the Ny-Ålesund and Bremen stations, we focus on the period of 2006-2007.

During these years, both stations use similar field of views (1.2 mrad) and high folding limits (15798 cm⁻¹). Ny-Ålesund uses the 120 HR instrument measuring at a maximum optical path difference of 30 cm while Bremen utilizes the 125 HR spectrometer at 45 cm maximum OPD. From these instrumental parameters, a 1% difference in the mean O₂ level (0.216 for Ny-Ålesund and 0.214 for Bremen) was observed with the higher resolution (45 cm for Bremen) instrument producing a lower mean O₂ level.
Comparing now Ny-Ålesund and Biscarrosse, we focus ourselves during the year 2005. Both instruments use a 30 cm maximum optical path difference and a high folding limit value of 15798 cm$^{-1}$. Ny-Ålesund uses the 120 HR at 1.2 mrad field of view while Biscarrosse measures with the 120 M at 2.4 mrad FOV. It can be seen that, the difference in field of views produce a 1% dissimilarity between their mean O$_2$ levels (0.218 for Biscarrosse and 0.216 for Ny-Ålesund) with the higher field of view (2.4 mrad for Biscarrosse) instrument producing a higher mean O$_2$ level.

For the Bremen and Biscarrosse stations, we again focus on the 2005 period. As can be seen in Fig. 5.5, all the three parameters being considered, the FOV, the maximum OPD and the HFL are different for the two stations making it difficult to assess the effect that these instrumental settings have. A more comprehensive comparison between the Bremen and Biscarrosse instruments are presented in Section 5.3.

**RECAP:**
- the higher resolution instrument appears to produce a lower mean O$_2$ level
- the higher field of view instrument seems to produce a higher mean O$_2$ level

### 5.1.1.3 Mean O$_2$ Level Comparisons Between the Darwin, Park Falls, Lauder and Bremen Stations

The mean O$_2$ level of the Darwin, Park Falls, Lauder and Bremen TCCON stations as well as their FOVs, maximum OPDs, HFLs, low pass filter cut-off frequencies and scanner velocities are outlined in Table 5.4. The 1% difference between Darwin/Park Falls and Lauder seem to coincide with the 1.2 mrad difference in the field of view. Again, the higher field of view instrument seems to produce a higher mean O$_2$ level. For Bremen, the higher field of view of 2.4 mrad as compared to Lauder (1.2 mrad) would suggest a higher mean O$_2$ level. However, similar mean O$_2$ levels were observed between Lauder and Bremen (0.2135) probably caused by the higher high folding limit (31596 cm$^{-1}$) used in Bremen. When a field of view of 1.2 mrad was used for Bremen, the mean O$_2$ level
correspondingly decreased to 0.2120 for the same 31596 cm\(^{-1}\) high folding limit value. Comparing Lauder and Bremen at the same field of view of 1.2 mrad, the lower high folding limit (15798 cm\(^{-1}\) for Lauder) instrument appear to produce a higher mean O\(_2\) level.

**Table 5.4. Mean O\(_2\) level and instrumental parameters of four TCCON stations for the time period shown in Fig. 5.3.**

<table>
<thead>
<tr>
<th>TCCON Station</th>
<th>Instrument</th>
<th>Mean O(_2) Level</th>
<th>Field of View [mrad]</th>
<th>Maximum Optical Path Difference [cm]</th>
<th>Low Pass Filter [kHz]</th>
<th>Scanner Velocity [kHz]</th>
<th>High Folding Limit [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darwin, Australia</td>
<td>125 HR</td>
<td>0.2145</td>
<td>2.4</td>
<td>45</td>
<td>10</td>
<td>10</td>
<td>15798</td>
</tr>
<tr>
<td>Park Falls, Wisconsin, USA</td>
<td>125 HR</td>
<td>0.2145</td>
<td>2.4</td>
<td>45</td>
<td>7.5</td>
<td>7.5</td>
<td>15798</td>
</tr>
<tr>
<td>Lauder, New Zealand</td>
<td>120 HR</td>
<td>0.2135</td>
<td>1.2</td>
<td>45</td>
<td>12</td>
<td>20</td>
<td>15798</td>
</tr>
<tr>
<td>Bremen, Germany</td>
<td>125 HR</td>
<td>0.2135 0.2120</td>
<td>2.4 1.2</td>
<td>45</td>
<td>20</td>
<td>20</td>
<td>31596</td>
</tr>
</tbody>
</table>

**RECAP:**

- the higher field of view instrument seem to produce a higher mean O\(_2\) level
- the lower high folding limit instrument appear to produce a higher mean O\(_2\) level

The effects mentioned in sections 5.1.1.1, 5.1.1.2 and 5.1.1.3 are summarized in Table 5.5. These effects are further discussed in Section 5.3.
Table 5.5. Summary of FOV, maximum OPD and HFL effects on the Mean O₂ Level

<table>
<thead>
<tr>
<th>Instrumental Parameter</th>
<th>Instrumental Parameter Direction</th>
<th>Effect on the Mean O₂ Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field of View (FOV)</td>
<td>INCREASE</td>
<td>INCREASE</td>
</tr>
<tr>
<td>Maximum Optical Path Difference (maximum OPD)</td>
<td>INCREASE</td>
<td>DECREASE</td>
</tr>
<tr>
<td>High Folding Limit (HFL)</td>
<td>INCREASE</td>
<td>DECREASE</td>
</tr>
</tbody>
</table>

5.1.2 O₂ Scaling

Spectroscopic linelist errors in the O₂ discrete lines cause the mean O₂ level to have an offset with the established 0.2095 volume mixing ratio. Comparing the retrieved O₂ column to 20.95% of the total dry column (eq. (3.13)), derived from the observed surface pressure and dividing or reducing (scaling) the retrieved O₂ column with the slope of a zero-intercept least squares fit to these two data sets, allows one to come up with an O₂ volume mixing ratio that is reasonably close to the established value of 0.2095. The slopes and the scaled O₂ column compared with 20.95% of the total dry column for Biscarrosse, Ny-Ålesund and Bremen are shown in Fig. 5.6. Shown also are the % residuals calculated using

\[
\% residual = 100 \times \frac{\langle column_{O_2} \rangle - 0.2095 \langle total\ dry\ column \rangle}{\langle 0.2095\ total\ dry\ column \rangle}
\]  

(5.1)

where \( \langle 0.2095\ total\ dry\ column \rangle \) is the mean value of 20.95% of the total dry column.
Fig. 5.6 Biscarrosse, Ny-Ålesund and Bremen were reduced by 3.77 ± 0.6%, 2.98 ± 0.9% and 2.25 ± 0.42%, respectively. The uncertainties in the scaling factors were derived from the 90%ile deviations of the % residuals (which means that 90% of the data fall within this range).

It can be noticed in Fig. 5.3 that each site has a different value for its scaling factor. Since the offset is due to errors in the spectroscopic linelist, all the sites should have a common scaling factor since all the data sets have been processed with the same linelist. The reason why each site has a different value for its scaling factor can be traced back to the fact that each site has a different mean O₂ level as a result of using dissimilar instrumental parameters as discussed in Section 5.1.1. As pointed out also in Section 5.1.1, one station can produce differing mean O₂ levels if it keeps changing its instrumental parameters (Ny-Ålesund and Bremen) such as the field of view, the maximum optical path difference and the high folding limit. This could tempt one to use separate scaling factors within a single station – one scaling factor for each time period that the instrumental parameters change. However, as shown in Fig. 5.6, a single scaling factor for each station was used. The reason for this is that the effects of the instrumental parameters in O₂ could also be affecting other trace gases like CO₂ and using a separate O₂ scaling factor within each site would probably
not cancel or minimize systematic and correlated errors common to \(O_2\) and to other trace gases when their column average volume mixing ratios are calculated.

**RECAP:**

- Each site has a different value for its \(O_2\) scaling factor due to dissimilar instrumental parameters

### 5.1.3 Precision of Retrieved \(O_2\) Column Concentrations

The upper limit of the precision of the \(O_2\) volume mixing ratio can be determined using its diurnal (daily) variation given by

\[
X_{O_2,\text{diurnal}} = 100 \times \left( \frac{X_{O_2}}{\langle X_{O_2} \rangle} - 1 \right)
\]

(5.2)

where \(\langle X_{O_2} \rangle\) is the daily mean of \(X_{O_2}\). The \(X_{O_2,\text{diurnal}}\) for Biscarrosse, Ny-Ålesund and Bremen are shown in Fig. 5.7 together with its 90\%ile deviation (which means that 90\% of the data fall within this range) which gives the upper limit of the precision.

![Fig. 5.7 O2 VMR Diurnal Variations for Biscarrosse, Ny-Ålesund and Bremen. Values in parenthesis are the 90\%ile deviations of the O2 volume mixing ratio.](image-url)
The higher diurnal variation of Biscarrosse and Ny-Ålesund can be attributed to their lower recorded intensities as shown by their O\textsubscript{2} continuum levels in Fig. 5.8A. The O\textsubscript{2} continuum level, serving as a proxy for the signal intensity, is shown in Fig. 5.8B to differentiate it from the O\textsubscript{2} continuum. Lower intensities cause the analog-to-digital converter to misrepresent intermediate signal levels. This causes poorer fits as evidence from their higher %RMS values (see Fig. 5.8C) producing more scatter.

Fig. 5.8 A.) O\textsubscript{2} VMR Diurnal Variations as a function of the O\textsubscript{2} continuum level for Biscarrosse, Ny-Ålesund and Bremen; B.) The O\textsubscript{2} continuum level; C.) O\textsubscript{2} %RMS as a function of the The O\textsubscript{2} continuum level.

Spectroscopic problems with the O\textsubscript{2} column concentration retrievals outlined in Section 5.1.1 (nos. 1 and 3), can be identified by looking at systematic residuals present in the spectral fits and by examining if unrealistic behavior exists with the columns or VMRs as a function of time, solar zenith angles, airmass, season, altitude or other bands. Since the linelists mostly use calculated spectral parameters, such as line strengths and widths (except for isolated and reasonably strong lines), empirical fixes, in which one switches from calculated to measured spectral parameters, greatly improve the fits. However, whenever a new linelist is released, it will always be used with the calculated spectral parameters and improvements would have to
be always repeated. A diagram depicting the relationship of the spectroscopic community with the spectrometry community is shown in Fig. 5.9 (Geoffrey Toon, private communication).

Fig. 5.9. Interactions between the spectroscopic community and the spectrometry community (Figure courtesy of Geoffrey Toon).

The reasons for the above mentioned spectroscopic problems are outlined below:

1.) Weak feedback to the spectroscopy community, except during satellite missions (e.g. ATMOS, MIPAS, ACE, OCO, GOSAT, etc.)

2.) Spectroscopists rarely analyze atmospheric spectra

3.) Spectrometrists rarely analyze laboratory spectra

A way out of this problem would be for the spectrometry community to provide annual “wish lists” (stemming from collated examples of spectroscopic inadequacies) to the spectroscopy community. This would also help in minimizing duplication of effort in correcting these problems (Geoffrey Toon, private communication). This is not only applicable to O₂, but with other gases as well.

With regards to the problem of site differences in the retrieved O₂ VMR (Section 5.1.1 no. 2), it has been shown that the mean O₂ level seems to be sensitive to the instrumental parameters used (such as the field of view, the resolution and the high folding limit). In order to reduce these site differences in the mean O₂ level, each station must adopt similar or consistent
instrumental parameters to be used in their measurements. The effects of these mentioned instrumental parameters on the retrievals of trace gases, particularly \( \text{O}_2 \) and \( \text{CO}_2 \), are further discussed in Section 5.3.

**RECAP:**

- empirical fixes, in which one switches from calculated to measured spectral parameters, greatly improve the fits
- the mean \( \text{O}_2 \) level seems to be sensitive to the instrumental parameters used (such as the field of view, the resolution and the high folding limit)
5.2 Retrieval of the CO₂ 6220 cm⁻¹ and 6339 cm⁻¹ Bands

Carbon dioxide was retrieved using two bands or spectral regions. The 6220 cm⁻¹ band, which ranges from 6180 – 6260 cm⁻¹ and centered at 6220 cm⁻¹, and the 6339 cm⁻¹ band, which encompasses the 6297 – 6382 cm⁻¹ region centered at 6339.5 cm⁻¹. The measured and the simulated spectra from the two bands are shown in Fig. 5.10 and in Fig. 5.11.

![Graph of measured and simulated spectra in the 6180 – 6260 cm⁻¹ spectral region.](image)

**Fig. 5.10** Measured and simulated spectra in the 6180 – 6260 cm⁻¹ spectral region.

![Graph of measured and simulated spectra in the 6297 – 6382 cm⁻¹ spectral region.](image)

**Fig. 5.11** Measured and simulated spectra in the 6297 – 6382 cm⁻¹ spectral region.
The 6220 cm\(^{-1}\) band is composed of CO\(_2\) line spectra, weak CH\(_4\) lines, H\(_2\)O, heavy water (HDO) and solar lines while the 6339 cm\(^{-1}\) band has a similar structure with the absence of CH\(_4\) as shown in Fig. 5.12 and Fig. 5.13.

**Fig. 5.12 The 6220 cm\(^{-1}\) band.**

**Fig. 5.13 The 6339 cm\(^{-1}\) band.**
5.2.1 The CO₂ 6220 cm⁻¹ and 6339 cm⁻¹ Column Concentration Ratio
The ratio of the 6220 cm⁻¹ band with the 6339 cm⁻¹ column concentration for Biscarrosse, Ny-Ålesund and Bremen, together with the 6220 cm⁻¹ band continuum level, the 6339 cm⁻¹ band continuum level, the retrieved water vapor column and the unscaled O₂ volume mixing ratio are shown in Fig. 5.14. Shown also is the data when the 120 M instrument was used in Bremen prior to deployment in Biscarrosse.

The ratio of the two CO₂ bands is a good indicator if the carbon dioxide retrievals are influenced by the instrumental parameters used or other factors. Ideally, this ratio should be equal to 1. Two factors seem to affect the ratio of the two CO₂ bands: the CO₂ continuum level (as seen in 2002-2003 Ny-Ålesund data), the water vapor column (as seen for Biscarrosse) and proximity to the coast (as seen for Biscarrosse). However, these effects are still unclear and needs further investigation.
Fig. 5.14 Ratio of the 6220 cm\(^{-1}\) and 6339 cm\(^{-1}\) CO\(_2\) bands together with the 6220 cm\(^{-1}\) band continuum level, the 6339 cm\(^{-1}\) band continuum level, the retrieved water vapor column and the unscaled O\(_2\) volume mixing ratio (XO\(_2\)).
**RECAP:** The unresolved issues regarding the disagreements between the two CO₂ bands occur in:

- Ny-Ålesund from 2002 to 2003. Its probable causes are:
  - Larger fields of view (aperture sizes) during this period (see Fig. 5.5) leading to higher O₂ and CO₂ continuum levels (intensities) probably causing
detector non-linearities
- Biscarrosse in 2005. Its probable causes are:
  - Sensitivity to increased water vapor column for the 120 M
  - Sensitivity of one or both CO₂ bands to sea salt aerosols due to its proximity to the coast

Further investigations are still necessary though as to what exactly causes these disagreements.

### 5.2.2 Precision of Retrieved CO₂ Column Concentrations

The upper limit of the precision of the carbon dioxide retrievals is calculated using the diurnal variation of the column averaged volume mixing ratio of CO₂, \( X_{CO₂} \), using

\[
X_{CO₂,\text{diurnal}} = 100 \times \left( \frac{X_{CO₂}}{\langle X_{CO₂} \rangle} - 1 \right)
\]  

(5.3)

\( X_{CO₂} \) is calculated using (3.12) where in the total dry column can be computed in two ways: using the observed surface pressure given by (3.13) which we will refer to as pressure normalized; or using the retrieved O₂ column (3.14) which we will call as \( O₂ \) normalized. O₂ normalization is said to improve the precision of the CO₂ VMR as it cancels or at least minimizes correlated systematic errors present in both the CO₂ column and in the O₂ column brought about by uncertainties in the instrumental line shape, in the surface pressure and in the solar zenith angle. These systematic errors will be further discussed in Section 5.3. The CO₂ VMRs using the two methods will be further discussed in Section 5.5. The diurnal variations are shown in Fig. 5.15, Fig. 5.16 and Fig. 5.17 for Biscarrosse, Ny-Ålesund and
Bremen, respectively. As can be seen, only the Bremen data showed slight improvement in the upper limit of the precision by normalizing with O2. This can be attributed to the relatively lower continuum levels for Biscarrosse and Ny-Ålesund as depicted in Fig. 5.14 which produces higher RMS.

**Fig. 5.15 Diurnal Variations of the Column Averaged Volume Mixing Ratio of Carbon Dioxide for Biscarrosse, France (indicated in parenthesis is the 90%ile deviation, which means that 90% of the data fall within this range).**

**Fig. 5.16 Diurnal Variations of the Column Averaged Volume Mixing Ratio of Carbon Dioxide for Ny-Ålesund, Spitzbergen (indicated in parenthesis is the 90%ile deviation, which means that 90% of the data fall within this range).**
Fig. 5.17 Diurnal Variations of the Column Averaged Volume Mixing Ratio of Carbon Dioxide for Bremen, Germany (indicated in parenthesis is the 90%ile deviation, which means that 90% of the data fall within this range).

**RECAP:** Improving the precision of trace gas retrievals, be it atmospheric carbon dioxide or molecular oxygen, entails measuring spectra at a high enough intensity (high signal-to-noise ratio (SNR)) keeping in mind not to saturate or operate the detectors in the non-linear regime of the detector response.
5.3 Effects of Instrumental Parameters on \(O_2\) and \(CO_2\) Retrievals

In this section, the effects of the instrumental parameters (the maximum optical path difference, the field of view and the high folding limit) on \(O_2\) and \(CO_2\) retrievals were assessed to see whether these effects cancel or remain in the \(CO_2/O_2\) ratio (see equations 3.12 and 3.14). These investigations are, however, simply starting points or “spring boards.” Hopefully, future researchers can use these investigations to arrive at the exact cause of these effects. A comparison of the 120 M with the 125 HR instrument as well as between two 125 HR instruments will also be discussed in this section.

5.3.1 Effect of the Maximum Optical Path Difference and the Field of View on the Retrieved \(O_2\) Column Concentrations

To assess the effect of the maximum optical path difference and the field of view on the retrieved \(O_2\) column concentrations, the resolution and the aperture size were systematically varied in August 1, 2007 while keeping the signal intensity approximately constant by covering the input solar beam. Shown in Fig. 5.18 are the time series of the volume mixing ratio of molecular oxygen and the maximum optical path difference (maximum \(OPD\)). The maximum \(OPD\) is related to the resolution \(\Delta v\) by

\[
\text{Maximum } OPD = \frac{0.9}{\Delta v}
\]  

(5.4)

Also shown are the time series of the \(O_2\) VMR and the field of view \(\text{FOV}\). The \(\text{FOV}\) is related to the aperture size by

\[
\text{FOV} = \frac{\text{aperture size}}{\text{focal length}}
\]  

(5.5)

Figure 5.19 shows how \(XO_2\) changes as a function of maximum optical path difference (for specific FOVs) as well as how \(XO_2\) changes as a function of field of view (for specific maximum OPDs). The slopes represent how much \(XO_2\) changes in percent per cm and in percent per mrad.
Fig. 5.18 Time series of the O\textsubscript{2} VMR, the maximum OPD and the FOV.

Fig. 5.19 Correlation Plots of the O\textsubscript{2} VMR, the maximum OPD and the FOV. The slopes are in percent per cm and in percent per mrad.

Looking at a retrieved O\textsubscript{2} line spectra as shown in Fig. 5.20, a low maximum optical path difference (low resolution) would have fewer data points to represent the spectral line. This causes a different line depth and line width producing a different factor (VF) to scale the a priori O\textsubscript{2} VMR. The low resolution measurement produces a higher scale factor (1.0261 as
compared to the high resolution measurement (1.0242)) making it have a higher O₂ VMR (see Fig. 5.19).

![Graph](image)

**Fig. 5.20** A Retrieved O₂ Line Spectrum at Different Maximum OPDs. VF is a factor used to scale the a priori O₂ VMR. A larger scale factor has a larger retrieved O₂ VMR.

Examining the depth of the retrieved O₂ continuum for different apertures (different FOVs) as shown in Fig. 5.21 one can notice that the depth of the O₂ continuum gets shallower as the aperture size is increased producing increased factors used to scale the a priori O₂ VMRs. This in turn produces increased retrieved O₂ VMRs.
Fig. 5.21 Retrieved O₂ Continuum for Different FOVs. Values in the parenthesis indicate the factor used to scale the a priori O₂ VMR, minutes from the first measurement (0 minute = 9.7895 UTC), the ambient temperature and the O₂ continuum level (CL). A larger scale factor has a larger retrieved O₂ VMR. A zoomed view is provided on the lower right hand corner. The stars (*) indicate similar temperature and continuum level conditions.

It can also be noticed that the depth of the O₂ continuum also gets shallower for a constant aperture (constant FOV) as shown in Fig. 5.22. However since Fig. 5.21 and Fig. 5.22 use the same 0 minute measurement (9.7895 UTC), decreasing the aperture size from 1.7 mm (70 minutes after 9.7895 UTC in Fig. 5.21) to 0.5 mm (182 minutes after 9.7895 UTC in Fig. 22) also made the O₂ continuum depth deeper (from 0.911 to 0.907) indicating that increasing the aperture size (increasing the FOV) makes the depth of the O₂ continuum shallower producing higher O₂ a priori VMR scale factors thus producing higher retrieved O₂ VMRs. This is further illustrated in Fig. 5.23 and Fig. 5.24.
Fig. 5.22 Retrieved O₂ Continuum for a Constant FOV. Values indicate the factor used to scale the a priori O₂ VMR and the values in parenthesis show the minutes from the first measurement (0 minute = 9.7895 UTC), the ambient temperature and the O₂ continuum level (CL). A larger scale factor has a larger retrieved O₂ VMR. The stars (*) indicate similar temperature and continuum level conditions.

In the upper panel of Fig. 5.23, it is shown that the O₂ continuum depth has a solar zenith angle dependence. In order to isolate the effects coming from the field of view, a parabola was fitted (Fig. 5.23 lower panel) and subtracted from the O₂ continuum depth time series (Fig. 5.24 upper panel). The dependence is clearer particularly when the field of view drops from 3.1 mrad (1.3 mm aperture size) to 1.2 mrad (0.5 mm aperture size) (Fig. 5.24 upper and middle panel). The correlation between the O₂ continuum minus the parabolic fit and the field of view is shown in the lower panel of Fig. 5.24.
Fig. 5.23 (Upper Panel) Solar Zenith Angle Dependence of the O$_2$ Continuum Depth. (Lower Panel) A Parabolic Fit to the O$_2$ Continuum Depth Time Series.

Fig. 5.24 (Upper Panel) O$_2$ Continuum Depth – Parabolic Fit Time Series. (Middle Panel) Field of View Time Series. (Lower Panel) Correlation Plot between the O$_2$ Continuum Depth Minus the Parabolic Fit and the Field of View.

Even though it is only the O$_2$ line spectra that is used to calculate the retrieved O$_2$ column, the O$_2$ continuum seems to also affects the retrieved O$_2$ column.
**RECAP:**

The observations discussed in the previous paragraphs are summarized in Table 5.6.

**Table 5.6. Summary of maximum OPD and FOV effects on the Retrieved O₂**

<table>
<thead>
<tr>
<th>Instrumental Parameter</th>
<th>Instrumental Parameter Direction</th>
<th>Quantity to Look at</th>
<th>Effect on Quantity</th>
<th>Effect on the O₂ a priori VMR scale factor</th>
<th>Effect on the Retrieved O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Optical Path Difference (maximum OPD)</td>
<td>INCREASE</td>
<td>Retrieved O₂ Line Spectra</td>
<td>DECREASE</td>
<td>DECREASE</td>
<td>DECREASE</td>
</tr>
<tr>
<td>Field of View (FOV)</td>
<td>INCREASE</td>
<td>Retrieved O₂ Continuum Minus Parabolic Fit</td>
<td>INCREASE</td>
<td>INCREASE</td>
<td>INCREASE</td>
</tr>
</tbody>
</table>

**5.3.2 Effect of the Maximum Optical Path Difference and the Field of View on the Retrieved CO₂ Column Concentrations**

The effects of the maximum optical path difference and the field of view were likewise assessed from the August 1, 2007 data, this time on the retrieved CO₂ column concentrations, particularly on the pressure and O₂ normalized column average volume mixing ratios of carbon dioxide. Their time series are shown in Fig. 5.25 together with the time series of the maximum optical path difference and the field of view. Shown in Fig. 5.26 are their correlation plots.

CO₂ generally seem to increase with increasing maximum optical path difference with the O₂ normalized volume mixing ratio increasing more as a result of a decreasing O₂ with increasing maximum OPD (Fig. 5.19).
Fig. 5.25 Time series of the CO₂ 6220 cm⁻¹ band VMR, the maximum OPD and the FOV.

Fig. 5.26 Correlation Plots for the CO₂ 6220 cm⁻¹ band VMR, the maximum OPD and the FOV. The slopes are in ppm per cm and in ppm per mrad.

Examining the retrieved CO₂ line spectra in the 6220 cm⁻¹ band, shown in Fig. 5.27, one notices similar characteristics with the O₂ line spectra with the shorter maximum optical path difference (lower resolution measurement) having a shallower line depth and a broader line width (Fig. 5.20). However, for CO₂, the factor used to scale the a priori CO₂ VMR is
lower for the shorter maximum OPD producing lower CO₂ VMRs (Fig. 5.26) (as opposed to what was observed with the O₂ (Fig. 5.19)).

![Graph showing CO₂ Line Spectrum for the 6220 cm⁻¹ Band at Different Maximum OPDs.](image)

**Fig. 5.27** A Retrieved CO₂ Line Spectrum for the 6220 cm⁻¹ Band at Different Maximum OPDs. VF is a factor used to scale the a priori O₂ VMR. A larger scale factor has a larger retrieved CO₂ VMR.

For the case of a changing field of view or aperture size, CO₂ increases as the FOV increases (see Fig 5.25 and Fig. 5.26 (right panel)). Looking at some retrieved carbon dioxide line (Fig. 5.28) and a zoomed view of a portion of the spectra (Fig. 5.29) indicated by the red box in Fig. 28, shows a correlation of the height of the CO₂ line “shoulder” with the aperture size. Similar features are also seen for the other lines in the two CO₂ windows.
Fig. 5.28 Retrieved CO₂ Line Spectra. The red box is zoomed in Fig. 5.29.

Fig. 5.29 The CO₂ line “shoulder” at different field of views.

The CO₂ line “shoulder” is also dependent on the solar zenith angle. In order to isolate the effects from the FOV only, a parabola was fitted and subtracted from the carbon dioxide “shoulder” time series for a particular spectral range (from 6237.5 to 6238.5) as shown in
Fig. 5.30 and Fig. 5.31. As can be seen, the CO₂ line “shoulder” minus the parabolic fit seem to decrease as the field of view increases producing an increase in the factors used to scale the a priori CO₂ volume mixing ratio increasing the retrieved CO₂ VMRs as well.

Fig. 5.30 (Upper Panel) Solar Zenith Angle Dependence of the CO₂ Line “Shoulder”. (Lower Panel) A Parabolic Fit to the CO₂ Line “Shoulder” Time Series.

Fig. 5.31 (Upper Panel) CO₂ Line “Shoulder” – Parabolic Fit Time Series. (Middle Panel) Field of View Time Series. (Lower Panel) Correlation Plot between the CO₂ Line “Shoulder” Minus the Parabolic Fit and the Field of View.
RECAP:

The observations discussed in the previous paragraphs are summarized in Table 5.7.

<table>
<thead>
<tr>
<th>Instrumental Parameter</th>
<th>Instrumental Parameter Direction</th>
<th>Quantity to Look at</th>
<th>Effect on Quantity</th>
<th>Effect on the CO₂ a priori VMR scale factor</th>
<th>Effect on the Retrieved CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Optical Path Difference (maximum OPD)</td>
<td>INCREASE</td>
<td>Retrieved CO₂ Line Spectra</td>
<td>Deepening of the Line Depths / Narrowing of the Line Widths</td>
<td>INCREASE</td>
<td>INCREASE</td>
</tr>
<tr>
<td>Field of View (FOV)</td>
<td>INCREASE</td>
<td>Retrieved CO₂ Line “Shoulder” Minus Parabolic Fit</td>
<td>DECREASE</td>
<td>INCREASE</td>
<td>INCREASE</td>
</tr>
</tbody>
</table>

5.3.3 Instrumental Line Shapes at Different Maximum OPDs and FOVs

The maximum optical path difference and field of view effects on the retrieved and CO₂ column concentrations partially cancel out when normalizing with the retrieved O₂ indicating that the retrievals appear to be affected by an instrumental parameter that is dependent on the maximum OPD (resolution) and the FOV (aperture size) – the instrumental line shape or ILS. As discussed in Section 2.3, the observed spectrum is a convolution of the true spectrum and the instrumental line shape. Therefore changes in the maximum OPD and in the FOV entail changes in the instrumental line shape (Fig. 5.32) and changes to the observed spectra producing an increase or decrease in retrieved trace gas amounts as illustrated in the previous two sections (5.3.1 and 5.3.2) for atmospheric molecular oxygen and carbon dioxide. This is illustrated in Fig. 5.33 when a spectra measured at 22.5 cm maximum optical path difference (blue) was retrieved using an 11.25
cm instrumental line shape (black). The resulting retrieved spectra followed the shape of a spectra that was measured at 11.25 cm maximum OPD (red) but with more data points as a result of the higher resolution when it was measured (22.5 cm maximum OPD). However, looking at the CO$_2$ a priori VMR scale factors indicated in Fig. 5.33 (VF), the 22.5 cm maximum OPD spectra retrieved with the 11.25 cm instrumental line shape had a VF value similar to that of the original 22.5 cm maximum OPD spectra. This is also the case for changing field of view.

Fig. 5.32 Instrumental Line Shapes at Different: (Left Panel) maximum optical path difference and (Right Panel) field of view.
**RECAP:**

- Changes in the ILS can be seen in changes to the retrieved spectral lines
- The factor used to scale the a priori VMR is relatively the same even when the OPD and FOV are changed in the retrieval algorithm
- The factor used to scale the a priori VMR is different when the OPD and FOV are changed in the instrument

**5.3.4 AC and DC Recoding**

A Fourier transform infrared spectrometer can measure interferograms by either using AC or DC recording. Considering a simple interferogram, it can be mathematically expressed as

\[
I(x) = I_0 + I_0 \cos(2\pi nx)
\]

where \( I_0 \) is the amplitude. The first term is the DC component of the interferogram and the second term is the AC component. Interferograms may then be measured by considering only the AC component (this is termed as AC recording) as in Fig. 5.34 or by considering both of the terms (this is termed as DC recoding) as shown in Fig. 5.35.
Fig. 5.34 AC Recording

Fig. 5.35 DC Recording
DC recording enables one to store solar brightness information giving an additional criterion for filtering cloud contaminated spectra as well as reducing the impacts from source brightness fluctuations (Keppel-Alecks et al., 2007).

5.3.5 Sampling

As stated in Section 2.2, the measured interferogram is digital in nature. The *digitation* of the interferogram is in effect a multiplication of the continuous interferogram with a sampling comb function which is simply a comb of delta functions. This is illustrated in Fig. 5.36 for a hypothetical signal.

![Interferogram and Comb Function](image)

Fig. 5.36 (Upper Panel) A Continuous hypothetical interferogram. (Middle Panel) A Comb of delta functions. (Lower Panel) A digitation of the continuous hypothetical interferogram.

Discretization implies the use of the *Nyquist-Shannon sampling theory* which states that one has to sample at least twice the maximum frequency of interest. One-half of the sampling frequency is called the *Nyquist frequency* sometimes termed as the *folding frequency* or the *high folding limit*. Signals higher than the high folding limit are “folded” or “mirrored” and convolved back with signals below the Nyquist frequency and vice versa. To avoid
extraneous signals being folded back to the frequencies of interest, a low pass filter is normally employed which removes signals above a particular cut-off frequency. For Fourier transform spectrometers, the cut-off wavenumber is given by

\[ \sigma_{\text{cut-off}} \left[ \text{cm}^{-1} \right] = \frac{f_{\text{cut-off}} \left[ \text{Hz} \right]}{v_{\text{scanner}} \left[ \text{cm s}^{-1} \right]} \] (5.7)

where \( f_{\text{cut-off}} \) is the low pass filter cut-off frequency and \( v_{\text{scanner}} \) is the scanner velocity.

### 5.3.6 Effect of High Folding Limits

The effect of varying the high folding limit was investigated on September 12, 2008 (using AC recording and a 15798 cm\(^{-1}\) low pass filter cut-off wavenumber (equivalent to a 20 kHz cut-off frequency and a 1.266 cm s\(^{-1}\) scanner velocity) – similar to Bremen 2005 measurements). A comparison of the spectra that uses a 15798.06 cm\(^{-1}\) (used in measurements in Bremen from the beginning of 2006 and onwards) and a 31596.12 cm\(^{-1}\) (used in measurements in Bremen prior to 2006) high folding limit is shown in Fig. 5.37. The inset shows the 10000 – 31596.12 cm\(^{-1}\) region of the 31596.12 cm\(^{-1}\) high folding limit measurement. Intensities from 15798.06 - 31596.12 cm\(^{-1}\) appear to be folded or “mirrored” back to the 0 - 15798.06 cm\(^{-1}\) region of the 15798.06 cm\(^{-1}\) high folding limit spectra as shown in Fig. 5.38 and Fig. 5.39 for the O\(_2\) and CO\(_2\) bands, respectively. The amount of intensity that is folded back and convolved to the 0 - 15798.06 cm\(^{-1}\) region of the 15798.06 cm\(^{-1}\) high folding limit spectra are approximately 0.165% for the O\(_2\) band and 0.05% for the CO\(_2\) band. This corresponds to a 0.25% decrease in the retrieved O\(_2\) volume mixing ratio (Fig. 5.40) and a 0.06% decrease in the retrieved CO\(_2\) pressure normalized VMR (Fig. 5.41) for the 15798.06 cm\(^{-1}\) high folding limit measurement. The 0.25% decrease in the O\(_2\) for a 15798.06 cm\(^{-1}\) high folding limit produces a 0.26% increase in the CO\(_2\) O\(_2\) normalized VMR.
Fig. 5.37 Comparison of a 15798.06 cm\(^{-1}\) and a 31596.12 cm\(^{-1}\) high folding limit spectra. The inset shows the 16000 – 32000 cm\(^{-1}\) region of the 31596.12 cm\(^{-1}\) high folding limit measurement which are folded or “mirrored” back in the 0 – 15798.06 cm\(^{-1}\) region of the 15798.06 cm\(^{-1}\) spectra.

Fig. 5.38 Folded intensities in the O\(_2\) 7885 cm\(^{-1}\) band.
Fig. 5.39 Folded intensities in the CO$_2$ 6220 cm$^{-1}$ band.

Fig. 5.40 Comparison of O$_2$ VMRs for different high folding limits.
Fig. 5.41 Comparison of CO₂ VMRs for different high folding limits.

The intensities above 15798.06 cm⁻¹ come from filter artifacts and/or from the effects of sampling.

**RECAP:**

- Intensities from 15798.06 - 31596.12 cm⁻¹ appear to be folded or “mirrored” back to the 0 - 15798.06 cm⁻¹ region of the 15798.06 cm⁻¹ high folding limit spectra.
- The amount of intensity that is folded back and convolved to the 0 - 15798.06 cm⁻¹ region of the 15798.06 cm⁻¹ high folding limit spectra are approximately 0.165% for the O₂ band and 0.05% for the CO₂ band.
- This corresponds to a 0.25% decrease in the retrieved O₂ volume mixing ratio and a 0.06% decrease in the retrieved CO₂ pressure normalized VMR for the 15798.06 cm⁻¹ high folding limit measurement.

**5.3.6.1 Filter Artifacts**

On December 5, 2008, the source of the extraneous signals above 15798.06 cm⁻¹ (see Fig. 5.37) were investigated. Using a near infrared lamp, a 2 mm aperture size, a 1 cm⁻¹
resolution, DC recording and a 31596.12 cm\(^{-1}\) high folding limit, the cut-off wavenumber of the low pass filter was varied (by varying the low pass filter cut-off frequency and the scanner velocity) and the presence and strength of the these extraneous signals were observed. These are shown in figures 5.42, 5.43, 5.44 and 5.45. One can observe that as the cut-off wavenumber is increased, the strength of the extraneous signals seem to become weaker and more noise is seen eventually making these extraneous signals appear to be buried in the noise.

![5 kHz Low Pass Filter Cut-off Frequency](image)

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Scanner Velocity (cm s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>15798</td>
<td>0.316 (5 kHz)</td>
</tr>
<tr>
<td>10532</td>
<td>0.475 (7.5 kHz)</td>
</tr>
<tr>
<td>7899</td>
<td>0.633 (10 kHz)</td>
</tr>
<tr>
<td>3950</td>
<td>1.266 (20 kHz)</td>
</tr>
</tbody>
</table>

Fig. 5.42 Extraneous Signals above 15798.06 cm\(^{-1}\) at 5 kHz Low Pass Filter Cut-off Frequency at Different Scanner Velocities
### 10 kHz Low Pass Filter Cut-off Frequency

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Scanner Velocity (cm s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31596 cm⁻¹</td>
<td>0.316 cm s⁻¹ (5 kHz)</td>
</tr>
<tr>
<td>21064 cm⁻¹</td>
<td>0.475 cm s⁻¹ (7.5 kHz)</td>
</tr>
<tr>
<td>15798 cm⁻¹</td>
<td>0.633 cm s⁻¹ (10 kHz)</td>
</tr>
<tr>
<td>7899 cm⁻¹</td>
<td>1.266 cm s⁻¹ (20 kHz)</td>
</tr>
</tbody>
</table>

**Fig. 5.43** Extraneous Signals above 15798.06 cm⁻¹ at 10 kHz Low Pass Filter Cut-off Frequency at Different Scanner Velocities

### 20 kHz Low Pass Filter Cut-off Frequency

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Scanner Velocity (cm s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>63192 cm⁻¹</td>
<td>0.316 cm s⁻¹ (5 kHz)</td>
</tr>
<tr>
<td>42128 cm⁻¹</td>
<td>0.475 cm s⁻¹ (7.5 kHz)</td>
</tr>
<tr>
<td>31596 cm⁻¹</td>
<td>0.633 cm s⁻¹ (10 kHz)</td>
</tr>
<tr>
<td>15798 cm⁻¹</td>
<td>1.266 cm s⁻¹ (20 kHz)</td>
</tr>
</tbody>
</table>

**Fig. 5.44** Extraneous Signals above 15798.06 cm⁻¹ at 20 kHz Low Pass Filter Cut-off Frequency at Different Scanner Velocities
Fig. 5.45 Extraneous Signals above 15798.06 cm⁻¹ at Open (40 kHz) Low Pass Filter Cut-off Frequency at Different Scanner Velocities

The same low pass filter and scanner velocity settings were repeated this time with an optical filter that cuts off frequencies at 15500 cm⁻¹. The 15500 cm⁻¹ optical filter seem to have no effect indicating that these extraneous signals above 15798.06 cm⁻¹ could have come from artifacts from the electronic low pass filter.

The structure of these extraneous signals appears to have stem from a folding (with diminished intensities) of the main spectra at 15798.06 cm⁻¹ and a double folding of the main spectra at 7899.03 cm⁻¹ and at 15798.06 cm⁻¹ as shown in Fig. 5.46.
Fig 5.46. Structure of the Extraneous Signals above 15798.06 cm⁻¹

The double folding is suspected to come from sampling effects (Axel Keens, private communication) discussed in the next section. However, further investigation is needed.

RECAP:

- As the cut-off wavenumber is increased, the strength of the extraneous signals seem to become weaker and more noise is seen eventually making these extraneous signals appear to be buried in the noise.
• The 15500 cm\(^{-1}\) optical filter seem to have no effect indicating that these extraneous signals above 15798.06 cm\(^{-1}\) could have come from artifacts from the electronic low pass filter.

• The structure of these extraneous signals appears to have stem from a folding (with diminished intensities) of the main spectra at 15798.06 cm\(^{-1}\) and a double folding of the main spectra at 7899.03 cm\(^{-1}\) and at 15798.06 cm\(^{-1}\).

### 5.3.6.2 Sampling Effects

A Fourier transform interferometer performs data sampling through the use of a Helium Neon (HeNe) laser typically with a wavelength of 633 nm (equivalent to 15798.06 cm\(^{-1}\)). Sampling is done on every zero-crossings (for a 15798.06 cm\(^{-1}\) high folding limit) of the HeNe laser as shown in Fig. 5.47. However, it may occur that the HeNe laser would have a zero-offset (due to amplifier electronics) generating unequal sampling lengths (Axel Keens, private communication) as depicted in Fig. 5.48. This however has been remedied with new amplifier circuit boards.

![Fig. 5.47 Sampling at an Ideal HeNe Laser Signal Zero-Crossing. The circles indicate sampling points.](image1)

![Fig. 5.48 Sampling at a Non-Ideal HeNe Laser Signal Zero-Crossing. Zero-offsets may occur for the He Ne laser. The circles indicate sampling points.](image2)
5.3.7 Instrument Intercomparisons

Intercomparisons between the main Bremen instrument and FTS containers that was deployed to Biscarrosse, France for the 2005 CarboEurope Integrated Project and another one that will be sent to Bialystok, Poland were performed in March 2005 and in May to October 2008, respectively. The instrument that was used in Biscarrosse was a Bruker 120 M and the one that will be used in Bialystok is a Bruker 125 HR.

5.3.7.1 120 M vs. 125 HR

In March 10, 14, 21, 24 and 31, 2005, measurements from the Bruker 120 M FTS situated on the ground were compared to a Bruker 125 HR instrument. Both instruments were located at 53° 06’ 13.32” N latitude and at 8° 50’ 58.26” E longitude. An altitude difference of 25.4 m exists between the two instruments. Among the intercomparison dates, March 14, 2005 makes use of the most consistent instrumental parameters. It is also a day with the most optimal cloud cover and weather conditions. Focusing on the O₂ VMR for this date, as shown in Fig. 5.49, the ratio between the 120 M and the 125 HR is approximately 7.5 per mil. The difference comes from different modulation efficiencies and phase errors of the two instruments as depicted in Fig. 5.50. The modulation efficiencies and phase errors were derived from instrumental line shape retrievals from hydrogen bromide (HBr) cell measurements using LINEFIT (Hase et al., 1999). Details on the instrumental line shape retrievals for the Biscarrosse 120 M and the Bremen 125 HR are discussed in Al-Hazaimay (2008). As can be seen in Fig. 5.50, the 120 M has a higher modulation loss and phase error than the 125 HR.

Shown in Fig. 5.51 are the O₂ normalized and pressure normalized CO₂ column averaged volume mixing ratios for the 6220 cm⁻¹ and the 6339 cm⁻¹ bands during the March 14, 2005 intercomparison date. The O₂ normalized CO₂ VMRs agree more since taking the CO₂/O₂ ratio eliminates or at least minimizes instrumental differences between the two instruments.
Fig. 5.49 O₂ VMRs Between the 120 M and 125 HR Intercomparison on March 14, 2005. Upper panel shows the XO₂ ratio - 1 between the two instruments.

Fig. 5.50 Modulation Efficiency (upper panel) and Phase Error (lower panel) of the Bruker 120 M and 125 HR FTS (Figure courtesy of Sadam Al-Hazaimay).
Fig. 5.51 CO₂ 6220 cm⁻¹ Band VMRs and Differences During the 120 M and 125 HR Intercomparison on March 14, 2005. (Left Panels) O₂ Normalized and (Right Panels) Pressure Normalized.

5.3.7.2 Comparison Between Two 125 HR Instruments

An intercomparison of two 125 HR instruments were likewise performed from May to October 2008 between the permanent 125 HR Bremen FTS (which we will call as the radom) and the mobile 125 HR instrument that will be deployed to Bialystok, Poland (which we will denote as IUP002). Shown in Fig. 5.52 is the O₂ volume mixing ratios of the two instruments during the intercomparison period. The dissimilarities between the two instruments are caused by differences in modulation efficiencies and phase errors as shown in Fig. 5.53. The radom XO₂ is generally lower than the IUP002. On May 21, 2008, the detectors of the two instruments were exchanged making the IUP002 have a lower XO₂. This means that aside from effects from the modulation efficiencies and phase errors, the differences in the XO₂ seem to be also affected by the detectors. The detectors in the two instruments have different resistor and capacitor values. On July 24, 2008, the detectors were again exchanged at particular hours, AC and DC measurement modes were compared and the analog-to-digital converter (ADC) counts, hence, the
continuum levels, were systematically varied. The effect of the ADC counts (continuum levels) is also depicted in Fig. 5.8.

Fig. 5.52 O₂ VMRs During the Radom and IUP002 Intercomparison. Upper panel shows the XO₂ ratio - 1 between the two instruments.
Fig. 5.53 Modulation Efficiency (upper panel) and Phase Error (lower panel) of the Radom and the IUP002 (Figure courtesy of Sadam Al-Hazaimay).

Looking at Fig. 5.54, the O$_2$ normalized CO$_2$ VMRs agree more than the pressure normalized CO$_2$ VMRs (Fig. 5.55) since taking the CO$_2$/O$_2$ ratio eliminates or at least minimizes instrumental and pressure differences between the two instruments.
Fig. 5.54 O$_2$ Normalized CO$_2$ Column Averaged VMR in the 6220 cm$^{-1}$ Band During the Radom and IUP002 Intercomparison
Optical realignments were done with the two instruments and on September 27, 2008 a comparison was again performed. The results are shown in figures 5.56, 5.57 and 5.58. The differences in the O\textsubscript{2} between the two instruments have been significantly reduced (compared with Fig. 5.52) as a result of the optical realignments. For the CO\textsubscript{2}, the differences are of the same order as with figures 5.54 and 5.55, with the O\textsubscript{2} normalized CO\textsubscript{2} volume mixing ratios agreeing more as compared with the pressure normalized carbon dioxide VMRs.
Fig. 5.56 O₂ VMRs During the Radom and IUP002 Intercomparison on September 27, 2008. Upper panel shows the XO₂ ratio - 1 between the two instruments.

Fig. 5.57 O₂ Normalized CO₂ Column Averaged VMR in the 6220 cm⁻¹ Band During the Radom and IUP002 Intercomparison on September 27, 2008
Fig. 5.58 Pressure Normalized CO$_2$ Column Averaged VMR in the 6220 cm$^{-1}$ Band During the Radom and IUP002 Intercomparison on September 27, 2008
5.4 A Framework for Comparing Remotely Sensed and In-Situ CO2 Concentrations (Biscarrosse, France)

Fourier transform infrared (FTIR) spectroscopy measurements were performed during the CarboEurope Regional Experiment Strategy (CERES) from May to June 2005. CERES aims to come up with a comprehensive database of atmospheric CO2 concentrations, fluxes, as well as meteorological parameters at the regional scale. An overview of the experiment is given in Dolman et al (2006). The experiment area is a 250 km x 150 km region located Southwest of France bounded to the west by the Atlantic ocean with a shoreline almost rectilinear along a north-northeast orientation. The Les Landes forest dominates the western half of the domain with 80% incorporated in the regional experiment area. It is mainly composed of maritime pines containing clearings of different sizes composed of agricultural land, mainly crop, and also grassland and pasture. Historically, a plantation forest was originally planted in the area to drain the marshlands. Now, the region is managed as a commercial forest with regular harvests and crop rotations (Dolman et al., 2006).

During the measurement campaign, carbon dioxide was analyzed in the near infrared region of the electromagnetic spectrum (1.597 – 1.618 µm or 6180 – 6260 cm⁻¹ band centered at 1.607 µm or 6220 cm⁻¹). The Fourier transform spectrometer (FTS) was stationed in Biscarrosse, France at 44°22’40” N latitude, 1°13’52” W longitude and 67.6 m (above sea level) altitude. A total of 4908 spectra were analyzed during the CarboEurope regional experiment encompassing measurements from 8 May 2005 to 26 June 2005. The Bruker 120 M (Mobile) Fourier transform spectrometer was utilized during the campaign. A maximum optical path difference of 30 cm was employed and a resolution of 0.03 cm⁻¹ was used. The 120 M has a focal length of 220 mm and an aperture size of 0.5 mm was used during the dates mentioned. This produces a field of view of 2.3 mrad. Forward and backward scans were taken totaling an average acquisition time of 24.0 s for each spectrum.
Beside the FTS station is a tower instrumented by the Laboratoire des Sciences du Climat et de l’Environment (LSCE). It houses a continuous in-situ monitoring station called CARIBOU, which includes a LICOR analyzer that measures CO₂ concentrations with a ± 0.5 ppm precision. The tower is located at a latitude of 44°22’40.6” N, a longitude of 1°13’52.5” W with the inlet at 114.71 m (above sea level). It also houses a pressure sensor located at 106.81 m (above sea level) (Galdemard et al., 2006). Several aircraft measurements were also performed during the regional experiment. Among them is the METAIR Dimona (Dimona), a touring motor glider (TMG), in which CO₂ is measured onboard using a combination of a fast, open path LICOR 7500, a slower, more precise closed path LICOR 6262 (Neininger et al., 2001), and flask samples that are analyzed for CO₂ in the laboratory at the Max Planck Institute for Biogeochemistry (MPI-BGC) in Jena, Germany with an accuracy of 0.1 ppm. The overall precision of the combined CO₂ dataset (the fast open path LICOR 7500, the slower closed path LICOR 6262 and the flask samples) at 1 Hz is 0.5 ppm.

5.4.1 Calibrations of CO₂ Retrievals Using Aircraft-Model-Balloon Data Fusion

The accuracy of the CO₂ retrievals was determined by comparing the FTS CO₂ VMRs with integrated aircraft carbon dioxide volume mixing ratios. Of the mentioned measurement dates, simultaneous Dimona and FTS measurements were available during five days, May 25, May 26, May 27, June 6 and June 14. During these days, only those data from the aircraft that fell within a 50 km distance from the FTS station were selected. From this, seven instances were identified. These instances are shown in Fig. 5.59 together with the FTS location and its pointing directions as well as the flight paths and the maximum altitude of the MetAir Dimona.
Fig. 5.59 Spatial and Temporal Coverage. Shown are the instance dates and times, the FTS location and its pointing directions as well as the flight paths and the maximum altitude of the MetAir Dimona.

The Dimona reached a maximum altitude of approximately 3 km during the CarboEurope experiment. It was thus necessary to append CO₂ profiles above the aircraft ceiling. For the free troposphere portion of the profile, data were taken from the TM3 global transport model, which was coupled to surface fluxes from fossil fuel emissions as well as to the BIOME-BGC model to include biospheric exchange (Heimann and Körner, 2003). For the stratospheric part of the profile, in-situ balloon data from the Observations of the Middle Stratosphere (OMS) experiment performed in Fort Sumner, New Mexico (35°N, 104°W) on 17 September 2004 were utilized. Since the balloon measurements were not performed during the same period as CERES, the balloon profile was corrected for age using the annual increase rate of CO₂. Since also the balloon measurements were not done in Biscarrosse, France, a coordinate transformation is necessary. Measurements of potential temperature during the balloon flight were used. Potential temperature is approximately a conserved quantity in the stratosphere.
The potential temperature was then converted to altitude using the equation formulated by Knox (Knox, 1998)

\[
z = \frac{\ln\left(\frac{\theta}{350}\right)}{0.045} + 13
\]  

(5.8)

where \( \theta \) is the potential temperature in Kelvin and \( z \) is the altitude in km. It was then converted back to pressure using NCEP altitude-pressure-temperature profiles for Biscarrosse, France during the specific aircraft overpass dates and the CO\(_2\) concentration values were then interpolated. A \( \pm 0.75 \) ppm uncertainty was assigned based on the precision of the balloon data and from the 0.5 year uncertainty in the mean age of the air in the stratosphere. A 0.5 year uncertainty in the stratosphere translates into approximately 0.75 ppm uncertainty in the carbon dioxide concentration when one considers the 1.4 ppm year\(^{-1}\) annual increase rate of CO\(_2\). The CO\(_2\) concentrations for the aircraft have an uncertainty of \( \pm 0.5 \) ppm. For the model, a pressure dependent uncertainty in the CO\(_2\) profile was assigned ranging from \( \pm 0.5 \) ppm at the aircraft ceiling increasing to a maximum of \( \pm 0.75 \) ppm at the tropopause.

To compare the combined (aircraft, model and balloon) carbon dioxide concentrations with the FTS data, it is necessary to consider the different characteristics of the observing systems. Derived quantities, such as total columns, may then be compared properly among different measurement platforms. In this case, the combined (aircraft, model and balloon) data is said to be “simulated” by the FTS retrievals by using the FTS a priori CO\(_2\) VMR and by weighting the combined (aircraft, model and balloon) CO\(_2\) concentrations with the FTS column averaging kernels (Rodgers et al., 2003). This procedure is summarized in the following equation:

\[
CO_{2,simulated} = CO_{2,a\ priori} + A(CO_{2,\text{aircraft+MODEL+balloon}} - CO_{2,a\ priori})
\]  

(5.9)

where \( CO_{2,a\ priori} \) is the a priori CO\(_2\) profile used in the retrieval, \( A \) is the column averaging kernel (shown in Fig. 5.60 (left) for instance 7) and \( CO_{2,\text{aircraft+MODEL+balloon}} \) is the aircraft data.
appended with the model and balloon data. The “simulated” CO₂ profile for instance 7, as shown in Fig. 5.60 (right), was then additionally weighted with a pressure dependent gravitational acceleration and integrated with respect to pressure using a trapezoidal numerical integration. The result was then divided by the mean molecular mass of dry air to determine the column CO₂. The column averaged volume mixing ratio is then determined by dividing the column CO₂ by the dry pressure column. A similar procedure was performed for the carbon dioxide column uncertainties with an additional error propagation done on the uncertainties in the profile. The uncertainties in each pressure level were squared, integrated with respect to the square of the pressure and the square root of the integrated value was calculated.

Fig. 5.60 CO₂ Profile for Instance 7 (14 June 2005; 10:00 – 15:00 UTC). (Left) The a priori and the column averaging kernel used in the FTS retrieval was applied to the combined (aircraft, model and balloon) data to make a comparison with the CO₂ concentrations retrieved from the Fourier transform spectrometer using Eq. (5.9). (Right) “Simulated” CO₂ profile. CO₂ concentration data for the aircraft have an uncertainty of ± 0.5 ppm. Above the aircraft ceiling, the modeled CO₂ data was assigned to have a pressure dependent uncertainty varying from ± 0.5 ppm to ± 0.75 ppm. The uncertainty in the balloon data was estimated to have a ± 0.75 ppm based upon the variability of the measured CO₂ data and the uncertainty in the mean age of the air in the stratosphere.
Figure 5.61 shows the comparison of the averaged (retrieval error weighted) FTS CO₂ VMR (20.95% of the CO₂/O₂ column ratio) for the aforementioned instances to the integrated (combined “simulated” aircraft, model and balloon) CO₂ VMRs. CO₂ columns were reduced by 1.07% wherein the scaling factor was determined from the slope of a zero-intercept linear fit. The correlation coefficient is 0.67 and the residuals approximately vary between ±1 ppm. Two instances, 4 and 6, deviated more that expected from the one-to-one line due to differences in the surface influence regions between the FTS and the Dimona (see Section 5.4.3).

Fig. 5.61 FTS and Integrated (Combined “Simulated” Aircraft, Model and Balloon) CO₂ VMR Comparison. CO₂ columns were reduced by 1.07% determined from the slope of a zero intercept linear fit. The correlation coefficient is 0.67 and the residuals approximately vary between ±1 ppm.
5.4.2 The STILT Model: A “Transfer Standard” for Comparing In-Situ and Remotely Sensed CO₂ Measurements

The Stochastic Time Inverted Lagrangian Transport (STILT) model was used for comparison of carbon dioxide concentration time series from the Biscarrosse tower data using a single receptor placed at the same latitude and longitude as the tower with an above ground level height of 47 m. Tower and STILT data simultaneous to the FTS measurements were compared and shown in Fig. 5.62 (upper panel). Aside from this, days prior to the period with enhanced biospheric activity due to changes in phenology (prior to June 16, 2005) were considered. The tower measurements were also compared with the Weather Research and Forecasting - Vegetation Photosynthesis and Respiration Model (WRF-VPRM) modeling system as shown in Fig. 5.62 (lower panel). WRF-VPRM is a coupled modeling system designed to simulate high-resolution atmospheric CO₂ concentration fields. Here, WRF is the mesoscale meteorological model and it is coupled to the diagnostic biospheric model VPRM. VPRM produces biospheric CO₂ fluxes and passes these to WRF, which performs atmospheric CO₂ tracer transport simulation. The modeling system also takes into account anthropogenic CO₂ fluxes. The comprehensive description of the modeling system and setup can be found in Ahmadov et al., 2007. Statistics for the comparisons are shown in Table 5.8. A more detailed analysis of the comparison of WRF-VPRM and the Biscarrosse tower is currently being prepared by Ahmadov et al.
Fig 5.62 STILT – WRF-VPRM – Biscarrosse Tower Comparisons. The statistics were calculated for times simultaneous to the FTS measurements and days prior to the period with enhanced biospheric activity due to changes in phenology (prior to June 16, 2005) since the greatly simplified biosphere (GSB) used in STILT simulate phenological changes with less certainty.

Table 5.8. Standard Deviation and Mean Differences Between Datasets. All values indicate tower, STILT and WRF-VPRM times during the FTIR measurements prior to June 16, 2005 and afternoon values indicate values of the datasets during the FTIR measurements from 3 PM to 8 PM local time also prior to June 16, 2005. The effective biases shown are the difference between the STILT-tower and STILT-FTIR comparisons as well as the difference between the WRF-VPRM-tower and the WRF-VPRM-FTIR comparisons.

<table>
<thead>
<tr>
<th>Dataset</th>
<th>All Values (Prior to June 16, 2005)</th>
<th>Afternoon Values (Prior to June 16, 2005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STILT-tower</td>
<td>4.53</td>
<td>-0.62</td>
</tr>
<tr>
<td>WRF-VPRM-tower</td>
<td>3.25</td>
<td>-0.50</td>
</tr>
<tr>
<td>STILT-FTIR</td>
<td>0.99</td>
<td>1.88</td>
</tr>
<tr>
<td>WRF-VPRM-FTIR</td>
<td>0.97</td>
<td>1.68</td>
</tr>
</tbody>
</table>
The STILT model was then extended for comparison to vertical column concentrations of CO₂ using multiple receptors along the column (see Fig. 4.2). Similar to what was done with the aircraft profiles, OMS in-situ balloon data, corrected for age and transformed in coordinates, were appended above the STILT model. The modeled carbon dioxide profile is shown in Fig. 5.63 for instance 7 compared to the Dimona-TM3-OMS CO₂ profile. The FTS retrieval a priori CO₂ and its averaging kernel were also applied (Eq. 5.9) to the STILT modeled CO₂ profiles before integrating the column. The column averaged VMRs of carbon dioxide from the STILT model and the FTIR data were then compared. The column averaged CO₂ volume mixing ratio retrieved from the FTIR data were also compared with WRF-VPRM similarly “simulated” with the FTS a priori CO₂ VMR and with the FTS column averaging kernel. The comparisons are shown in Fig. 5.64 and the pertinent statistics are summarized in Table 5.8. Additionally, taking only afternoon values (3 PM to 8 PM local time), the standard deviation of the differences and the mean differences were calculated among the datasets. The effective bias, which is in effect the difference between the FTIR data and the tower data, was then computed as the difference between the model-tower and the model-FTIR mean differences. These are also noted in Table 5.8.

![Graph showing CO₂ profiles](image)

**Fig. 5.63. Dimona-TM3-OMS and STILT Carbon Dioxide Profiles for Instance 7.**
Fig. 5.64. STILT, WRF-VPRM and FTIR Comparisons. The statistics were also calculated prior to June 16, 2005. Afternoon values are also shown.

5.4.3 Discussion

Surface influence functions, or footprints, which quantify the contribution of surface fluxes to the concentration of the aircraft measurement as well as of the FTIR column, can be used to assess potential reasons for disagreement between the two types of measurements. The time integrated footprints shown in Fig. 5.65a have been determined using STILT. They show that the surface influences for instances 4 and 6 have a significant difference for the FTS and for the Dimona aircraft. For instance 4, where the CO₂ column averaged VMR of the FTS is lower compared to the Dimona (see Fig. 5.61, instance 4), the FTS footprint has a discontinuity in the area of northern Spain. Surface fluxes in this region would therefore not affect the FTS measurements as it does for the Dimona producing the mentioned difference. This discontinuity can be attributed to particles rising above the surface hence producing no surface influence at that region. Aside from this, the aircraft is also more confined in a smaller region for this instance compared with the other instances (see Fig. 5.59, instance 4). This gives it a rather limited sampling area, in which other processes can influence the aircraft
data as compared to the FTIR. For instance 6, the FTS column averaged VMR is higher than the Dimona (see Fig. 5.61, instance 6). The footprints of the Dimona show more influences on land than the FTS (see Fig. 5.65b), consistent with the flight track covering more vegetated areas (see Fig. 5.59, instance 6). Given that the land region at that time of the year is a much stronger sink for CO₂ as compared to the ocean due to the active land biosphere, explains the lower CO₂ observed by the aircraft (see Fig. 5.67).

Fig. 5.65a Footprints for Instances 1 to 7. Instances 4 and 6 footprints have a significant difference between the FTS and the Dimona explaining their larger than expected deviation from the one-to-one line.
Fig. 5.65b FTS and Aircraft Footprints for Instances 6. The FTS has surface influence regions mostly coming from the ocean while the aircraft sees a portion of its footprints inland.

In Fig. 5.66, decomposition of the STILT modeled CO₂ concentrations for the different altitude ranges is shown. The lower altitude ranges (1-500 m and 500-3000 m), show significant influence of the biosphere in the CO₂ concentrations. These altitude ranges, which are well within the planetary boundary layer where significant turbulence is experienced (hence more vertical mixing), get more contributions from vegetation photosynthetic uptake and respiration. Higher up, from 3 km to 18 km, the carbon dioxide is dominated mostly by the background values with little variability due to vegetation.
**Fig. 5.66 Decomposition of the STILT modeled CO2 by Altitude Range.** The CO2 multiple receiver signal is decomposed into the different altitude ranges of 1 – 500 m, 500 – 3000 m, 3 – 6 km, 6 – 11 km and 11 – 18 km. The lower altitude ranges (1-500 m and 500-3000 m), show significant influence of the biosphere in the CO2 concentrations.

Decomposition of the STILT modeled carbon dioxide concentrations by altitude range and sources / sinks is shown in Fig. 5.67 for instances 2, 3 and 6 at the location of the FTS. Instances 2 and 3 get more biospheric influences because their footprints are inland while instance 6 receives less influence from the biosphere, since its footprint originate mostly from the ocean (see Fig. 5.65a) producing a higher CO2 value detected by the FTS than the aircraft (see Fig. 5.61) (sampling over vegetation (see Fig. 5.59)).
detected by the T6s than the tropical (subtropical) magnification.

The other hand, T6s receive less influence from the atmosphere. Since the tropical atmosphere is more sensitive to variations in temperature, instance 6 (b) lower panel at the T6s location. Instance 7 and 3 get more atmosphere influence because their technologies are urban. Instance 4, instance 5, and instance 6 have different CO2 levels due to the different technologies and climates.
Referring to Fig. 5.59, one can see that there are instances (instances 4 and 6) where the Dimona was taking samples in locations where the FTS was not pointing. One might say that this could be a potential source of disagreement between the FTIR spectrometer and the aircraft. However, looking at the FTS slant and vertical column averaged VMRs in Fig. 5.68, it becomes clear that taking slant or vertical column averaged VMRs does not matter even under these conditions of highly variable CO₂ mixing ratios over a continental area. This was also verified with the WRF-VPRM also shown in Fig. 5.68.

![Figure 5.68](image)

**Fig. 5.68 2.75-Minute Averaged Slant and Vertical Columns from the FTS and the WRF-VPRM Model**

The comparison between the carbon dioxide column averaged VMRs measured with the FTIR spectrometer and the integrated (combined “simulated” aircraft, model and balloon) CO₂ concentrations can be considered to be in agreement with each other since the error bars fall within the one-to-one line (see Fig. 5.61). The most significant source of error for the FTS CO₂ column averaged volume mixing ratio is the precision of the instrument (120 M) used in the CarboEurope experiment. For the integrated carbon dioxide VMR, the most significant
source of uncertainty is the spatial heterogeneity of CO₂ measured by the aircraft in the planetary boundary layer (see Fig. 5.60, right panel). The spatial heterogeneity is a result of taking aircraft data within a 50 km distance around the FTS station. Flying closer to the FTS station can therefore improve FTS validations with aircrafts. Note that the aircraft trajectory was also constrained by other objectives during the experiment such as characterizing the CO₂ distribution within the whole domain (Dolman et al., 2006).

After validating the FTS carbon dioxide column averaged VMRs with the integrated (combined “simulated” aircraft, model and balloon) CO₂ data, a meaningful next step would be to compare FTS measurements with in-situ tower data. The problem of directly comparing in-situ and remotely sensed data is that the quantities are different in nature to start with. One needs a tool to mediate between the two measuring techniques to assess whether the in-situ and FTS data are consistent. The STILT model provides this tool. WRF-VPRM is also used for additional verification. Pertinent statistics were calculated for days with FTS measurements and days prior to the period with enhanced biospheric activity due to changes in phenology (prior to June 16, 2005) since the greatly simplified biosphere (GSB) used in STILT simulate phenological changes with less certainty. Additional statistics were calculated using only afternoon values for the carbon dioxide concentrations of the datasets. Using only afternoon values reduces the uncertainties between the flux-concentration relationships due to a deeper boundary layer during these times compared to morning and night time hours. Models better represent deeper boundary layers than shallower ones due to limitations in its vertical resolution. Therefore, comparisons between modeled and measured data would be more substantial when only afternoon data are considered. For the tower comparisons, the statistics reveal that the models have difficulties capturing the variability in the in-situ data as evidence of approximately 3 – 4.5 ppm standard deviation of the differences. The mean differences or biases, however, show smaller values (~ 0.5 – 0.7 ppm).
The differences in using STILT and using WRF-VPRM for the tower comparisons come from
the dissimilar transport simulation and biosphere models that are employed.

For the FTIR comparisons, the models experience lesser difficulties in simulating the
variability in the column (standard deviation of the differences ~ 1 ppm). This is expected
since the column is less sensitive to local and to synoptic changes in CO₂ concentrations.
However, for the mean differences or biases between the FTIR data and the models, the
values are larger (~ 2 ppm) than with the tower. The differences between the model-tower
and the model-FTIR were then used to calculate an effective bias of approximately -2.5 ppm
between the FTIR and the tower. This bias comes from the scaling factor used in calibrating
the FTIR data with the integrated (combined “simulated” aircraft, model and balloon) CO₂
data. The uncertainty in the applied scaling factor for the FTS columns results from spatial
heterogeneity in the aircraft data used to scale the CO₂ columns (not evident in the modeled
profile in Fig. 5.63). Additional information on this spatial heterogeneity will be available
from the simulation of CO₂ along the flight track.
5.5 Column Concentrations of Atmospheric Carbon Dioxide over Bremen and Ny-Ålesund

Near-infrared spectra have been acquired using a Bruker 125 HR (High Resolution) and a Bruker 120 HR Fourier transform infrared (FTIR) spectrometer. The FTIRs are located on the rooftop of the Institute of Environmental Physics of the University of Bremen in Bremen, Germany and at the Alfred Wegener Institut Polaire Français Arctic Research Base in Ny-Ålesund, Spitzbergen with coordinates and instrumental parameters outlined in Table 5.1. Carbon dioxide column concentrations were retrieved using the GFIT nonlinear least squares spectral fitting algorithm (version 2.40.2) developed by NASA/JPL (Toon et al.,1992). Vertical column concentrations of molecular oxygen (O2) and carbon dioxide (CO2) were retrieved with windows or spectral ranges given in Table 5.2. Spectra were screened based on cloud cover observations resulting in a total of 4055 and 7280 spectra being analyzed for Bremen and Ny-Ålesund, respectively.

The CO2 retrievals were then compared with models (STILT and CarbonTracker) as well as with in situ flask measurements from NOAA.

5.5.1 Bremen, Germany

STILT model outputs were produced for Bremen, Germany and compared with the CO2 retrievals along with an additional model comparison with CarbonTracker. The CO2 retrievals were also compared with NOAA in situ flask data from Macehead, Ireland.

5.5.1.1 Enhanced Vegetation Index – Weighted STILT-GSB

Model outputs from STILT were initially used with the Greatly Simplified Biosphere (GSB) model as depicted in Fig. 4.1 and discussed in section 4. Since GSB assumes constant light use efficiency in photosynthesis the photosynthetic uptake term in Eq. 4.4 has to be corrected by multiplying this term with the Enhanced Vegetation Index (EVI) obtained from the Moderate Resolution Imaging Spectroradiometer (MODIS) / Terra vegetation indices (http://igskmncw001.cr.usgs.gov/modis/mod13a3v5.asp) (for the domain shown in Fig. 4.3
left panel). A vegetation index is a quantity utilized to determine biomass or vegetative vigor. The simplest type of vegetation index is obtained from the ratio of the near infrared reflectance and the red reflectance. During spring and summer this ratio will be high due to the abundance of healthy living vegetation since there is an inverse relationship between vegetation brightness in the infrared and red regions of the spectrum (http://rangeview.arizona.edu/Glossary/veg_index.html). The correction is performed by first normalizing the vegetation indices like so

\[ EVI_{\text{norm}} = \frac{EVI - EVI_{\text{min}}}{EVI_{\text{max}} - EVI_{\text{min}}} \]  

(5.10)

where \( EVI_{\text{norm}} \) is the normalized vegetation index, \( EVI \) is the biweekly (every two weeks) vegetation index for an entire year, \( EVI_{\text{min}} \) is the minimum vegetation index for a year and \( EVI_{\text{max}} \) is the maximum vegetation index for a year. As discussed in section 4, GSB uses 3 vegetation classes namely forest, shrub and crop. A weighted average of \( EVI_{\text{norm}} \) was then calculated with respect to the vegetation fraction (computed based on SYNMAP (Jung et al, 2006)) of forest, shrub and crop over the mentioned domain producing \( EVI_{\text{norm}} (\text{forest}) \), \( EVI_{\text{norm}} (\text{shrub}) \) and \( EVI_{\text{norm}} (\text{crop}) \). The photosynthetic term in Eq. 4.4 was then modified to

\[ CO_{2,\text{photosynthetic uptake}} = CO_{2,\text{photosynthetic uptake (forest)}}EVI_{\text{norm}} (\text{forest}) + CO_{2,\text{photosynthetic uptake (shrub)}}EVI_{\text{norm}} (\text{shrub}) + CO_{2,\text{photosynthetic uptake (crop)}}EVI_{\text{norm}} (\text{crop}) \]  

(5.11)

The original STILT-GSB and the EVI-weighted STILT-GSB CO\(_2\) column average model results and their difference are shown in Fig. 5.69. An approximate 4 ppm difference is observed during spring and mid-summer.
Fig. 5.69 STILT-GSB and EVI-Weighted STILT-GSB Model Outputs

5.5.1.2 2003 - 2007 Time Series

The 6-hour means of the pressure and O₂ normalized column averaged volume mixing ratios of atmospheric carbon dioxide for the mean of the two CO₂ bands are shown in Fig. 5.70 together with the 6-hour averaged column integrated EVI–weighted STILT-GSB multiple receptor 3-hour model outputs, column integrated multiple level CarbonTracker 6-Hour model outputs (Peters et. al, 2007) and NOAA surface flask data from Macehead, Ireland (Carbon Cycle Greenhouse Gases Group (CCGG), (2003)).

As stated in Section 5, in the period prior to 2006, numerous instrumental parameters were varied for the FTS during this time (maximum OPD, FOV and high folding limit). Using the FTS O₂ column data in 2006 onwards (a period with consistent instrumental parameters) as reference, correction factors on every possible combination of maximum OPD, FOV and HFL were determined and applied to the FTS data by taking the ratio of the average O₂ column at a particular maximum OPD, FOV and HFL combination to the mean O₂ column data from 2006 onwards. The correction factors for O₂ are outlined in Table 5.9.
To minimize the bias between the FTS and the models, the FTS data was reduced by the slope (1.0108) of a zero-intercept least-squares linear fit obtained by comparing the FTS data (125 HR data) with STILT model outputs. The bias in the FTS is due to uncertainties in CO₂ line strengths and/or pressure broadening coefficients (Yang, 2007). However, care has to be taken when scaling the FTS data to models. Three aspects of models can be pointed out:

1. models (e.g. CarbonTracker, TM3-analyzed fields) use surface data (e.g. tall towers, flasks) to match observations
2. models have an issue with vertical mixing (Stephens et al., 2007; Gerbig et al., 2007)
3. models fit planetary boundary layer CO₂ but vertical mixing bias may lead to biases in the column

Since STILT uses TM3-analyzed fields, scaling the FTS data with the model may include these vertical mixing biases as well. It is therefore essential that dedicated aircraft validations for the FTS be performed. Once aircraft validations are carried out, the FTS can then be used to evaluate the vertical transport in models (Yang et al., 2007). However, due to the lack of aircraft validation in Bremen (as well as in Ny-Ålesund), the FTS data was scaled to the model. The correlation coefficients among the datasets are shown in Table 5.10.
Fig. 5.70 (Upper Panel) CO₂ Column Averaged Volume Mixing Ratios over Bremen, Germany (FTS CO₂ column data (average of the two CO₂ bands) were reduced by 1.08%). The black line indicates the seasonal cycle (calculated from moving averages of the STILT dataset). The black dotted line indicate the transition from 120 HR to 125 HR. (Lower Panel) Monthly Standard Deviation to Represent CO₂ Seasonal Variabilities.

Table. 5.9. Bremen O₂ Column Correction Factors. O₂ columns at particular maximum OPD, FOV and HFL combinations were divided by the following correction factors with the mean O₂ column of 2006 onwards (4.59075 x 10²⁴ molecules cm⁻²) as reference.

<table>
<thead>
<tr>
<th>FOV [mrad]</th>
<th>Maximum OPD [cm]</th>
<th>High Folding Limit [cm⁻¹]</th>
<th>Correction Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>12.86</td>
<td>31596.12</td>
<td>1.0039</td>
</tr>
<tr>
<td>1.2</td>
<td>45</td>
<td>31596.12</td>
<td>1.0081</td>
</tr>
<tr>
<td>1.9</td>
<td>45</td>
<td>31596.12</td>
<td>1.0055</td>
</tr>
<tr>
<td>2.4</td>
<td>30</td>
<td>31596.12</td>
<td>0.9878</td>
</tr>
<tr>
<td>2.4</td>
<td>45</td>
<td>31596.12</td>
<td>0.9964</td>
</tr>
<tr>
<td>2.8</td>
<td>12.86</td>
<td>31596.12</td>
<td>1.0086</td>
</tr>
<tr>
<td>2.8</td>
<td>45</td>
<td>31596.12</td>
<td>0.9978</td>
</tr>
<tr>
<td>3.1</td>
<td>22.5</td>
<td>31596.12</td>
<td>1.0019</td>
</tr>
<tr>
<td>3.1</td>
<td>45</td>
<td>31596.12</td>
<td>0.9988</td>
</tr>
<tr>
<td>3.6</td>
<td>30</td>
<td>31596.12</td>
<td>0.9946</td>
</tr>
<tr>
<td>4.1</td>
<td>18</td>
<td>31596.12</td>
<td>0.9817</td>
</tr>
<tr>
<td>4.1</td>
<td>45</td>
<td>31596.12</td>
<td>1.0016</td>
</tr>
<tr>
<td>4.8</td>
<td>11.25</td>
<td>31596.12</td>
<td>0.9828</td>
</tr>
<tr>
<td>4.8</td>
<td>18</td>
<td>31596.12</td>
<td>1.0060</td>
</tr>
</tbody>
</table>
Table. 5.10. Correlation Coefficients of comparisons of the FTS Bremen data with STILT, CarbonTracker and Mazehead carbon dioxide concentrations

<table>
<thead>
<tr>
<th>Dataset</th>
<th>FTS XCO₂ (Pressure Normalized)</th>
<th>FTS XCO₂ (O₂ Normalized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STILT</td>
<td>0.9243</td>
<td>0.8953</td>
</tr>
<tr>
<td>CarbonTracker</td>
<td>0.9026</td>
<td>0.8752</td>
</tr>
<tr>
<td>NOAA In Situ Surface Flask</td>
<td>0.7221</td>
<td>0.6875</td>
</tr>
</tbody>
</table>

Due to the large degree of changes in the FOV and the maximum OPD (Table 5.9), correcting only for the O₂ column still retain the discrepancies between the FTS CO₂ and the models (unlike in Ny-Ålesund - this is discussed later in the Section 5.5.2) prior to 2006. Further investigations of correction strategies have to be also performed on CO₂. Effects of other instrumental parameters have to be also further examined.

From Fig. 5.70 (upper panel), a steep decrease can be observed during mid-March to July with a minimum in July. This period is the growing season when the vegetation takes up more CO₂ in the atmosphere due to increased photosynthesis. Variabilites of approximately 2 ppm can also be observed (see Fig. 5.70 (lower panel) during this period due to deep planetary boundary layer mixing and strong convection. On the other hand, a slow increase in atmospheric CO₂ column concentrations can be observed from August to mid-March reaching a maximum in March. Vegetation growth is inhibited during this time increasing soil respiration. Lower variabilities of approximately 0.5 ppm can also be seen. This is brought about by a shallow mixing layer and weak convection during these months.

5.5.1.3 2005 and 2006 Time Series

The XCO₂ anomalies (XCO₂ minus the seasonal cycle) for 2005 and 2006 are shown in figures 5.71 and 5.72, respectively. To see the small scale variations clearer, the 2005 data were rescaled this time by 1.0176 instead of 1.0108. The “spikes” in XCO₂ and in the XCO₂ anomalies in the models are often associated with frontal zones (which are on a scale that can be resolved by the model) allowing boundary layer CO₂ to be pushed along the front (the CO₂
may be both of European origin, with a possible contribution of long-range transport) (Sander Houweling, private communication). This is depicted in Fig. 5.73. These meteorological conditions are often associated with bad weather or “FTIR-unfriendly” conditions. However, as seen in figures 5.71 and 5.72, there are instances that there have been FTIR measurements during these conditions. This also shows that “clear sky” measurement selection introduces a real CO₂ measurement bias (Corbin et al., in preparation). The same applies to satellite data such as to SCIAMACHY (Schneising et al., 2008) (see Fig. 5.74), OCO and GOSAT. Making sure that the model used to interpret the measurements has a fair representation of these variations is one way to mitigate this “clear sky” bias (Sander Houweling, private communication).

![Graph](image)

**Fig. 5.71 2005 XCO₂ and XCO₂ Anomalies.** To see the variations clearer, the 2005 FTS data (CO₂ column (average of the two CO₂ bands ) ) were reduced by 1.76% instead of 1.08%.
Fig. 5.72 2006 XCO₂ and XCO₂ Anomalies. The 2006 FTS data uses the original scaling factor of 1.0108.

Fig. 5.73 CO₂ In a Frontal Zone
Fig. 5.74. Monthly Averages of CO₂ Column Averaged Volume Mixing Ratios from the FTS, SCIAMACHY and CarbonTracker over Bremen, Germany (Figure from Schneising et al., 2008). Boxed data indicate relatively higher than seasonal average CO₂ FTS and SCIAMACHY VMRs.

5.5.1.4 Clear Day Time Series

Figure 5.75 shows unaveraged clear day carbon dioxide column concentrations over Bremen, Germany in March (maximum) and in July (minimum). In March, column concentrations approximately vary 2 ppm during the day while in July XCO₂ varies approximately 4 ppm indicating the deep planetary boundary layer mixing and strong convection during CO₂ minimum and the shallow mixing layer and weak convection during CO₂ maximum.
Fig. 5.75 Clear Day XCO₂ Variations. The FTS data uses the 1.0108 scaling factor.

5.5.1.5 Spatial Heterogeneity of Atmospheric Carbon Dioxide

The spatial heterogeneity of atmospheric carbon dioxide was then assessed by running the STILT model with varying horizontal resolutions (which we will denote by the aggregation) outlined in Table 5.11. Shown also are the horizontal resolutions of CarbonTracker (Peters et al., 2007), SCIAMACHY (Schneising et al., 2008) and OCO (Crisp et al. 2004). A moving standard deviation was then calculated between the different resolution runs with the highest resolution as reference. A similar procedure was then performed this time with the FTIR data as reference.
Table 5.11. Horizontal resolutions of STILT (and its aggregation), CarbonTracker, SCIAMACHY and OCO

<table>
<thead>
<tr>
<th>Dataset</th>
<th>Longitudinal Resolution</th>
<th>Latitudinal Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>aggregation = 1</td>
<td>0.125</td>
<td>0.083</td>
</tr>
<tr>
<td>STILT</td>
<td>aggregation = 4</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>aggregation = 16</td>
<td>4</td>
</tr>
<tr>
<td>SCIAMACHY</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>OCO</td>
<td>0.0167</td>
<td>0.025</td>
</tr>
<tr>
<td>CarbonTracker</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure 5.76 shows the 6-month moving standard deviation of differences among the datasets with the highest STILT resolution (aggregation = 1) as reference. Shown in figures 5.77 – 5.78 are the same quantities using the FTS measurements as reference.

Fig. 5.76 6-month moving standard deviation of the difference among the different aggregations of the STILT model as well as CarbonTracker with the highest resolution (aggregation = 1) as reference.
Fig. 5.77 6-month moving standard deviation of the difference among the different aggregations of the STILT model as well as CarbonTracker with the FTS pressure normalized CO$_2$ VMR as reference. The larger values in 2003 and 2004 uses the 120 HR.

Fig. 5.78 6-month moving standard deviation of the difference among the different aggregations of the STILT model as well as CarbonTracker with the FTS O$_2$ normalized CO$_2$ VMR as reference. The larger values in 2003 and 2004 uses the 120 HR.

Fossil fuel contributions in the column are approximately 2.207 ppm. Since most of the variability would come from fossil fuels, the moving standard deviations of the differences should be around this value. As can be seen, the moving standard deviation of the differences
is approximately 2 ppm (Fig. 5.77 and Fig. 5.78). It can also be seen that the differences in the variations between fine and coarse resolution model data with the FTS are approximately 0.2 ppm (Fig. 5.77 and Fig. 5.78) indicating that measurements of column concentrations in Bremen, Germany are not sensitive to small scale local carbon dioxide emission sources amidst being situated in an urban setting.

5.5.2 Ny-Ålesund, Spitzbergen

A similar analysis was performed for Ny-Ålesund, Spitzbergen. Due to the limitation in the STILT domain, only the CarbonTracker (Peters et. al, 2007) model was compared to the CO₂ retrievals. Additionally a comparison with NOAA surface flask data from Zeppelin, Spitzbergen (Carbon Cycle Greenhouse Gases Group (CCGG), (2003)) are presented. These are shown in Fig. 5.79. The O₂ column was corrected for FOV, maximum OPD and HFL combinations using the correction factors outlined in Table 5.12. The FTS data was then scaled with respect to the CarbonTracker model outputs using the slope (1.0116) of a zero-intercept least squares linear fit through the dataset. As can be seen in Table 5.12, the changes in FOV are not as large as in Bremen and the maximum OPD is kept constant during these field of view changes. These FOV and maximum OPD combinations seem to affect the CO₂ only slightly, thus, correcting only the O₂ column produce smaller dissimilarities with the modeled CO₂ variations. Shown in Table 5.13 are the correlation coefficients among the datasets.

In Ny-Ålesund, the decrease in CO₂ starts in April while the increase begins in August. Seasonal variabilities of 2 ppm can be observed in the summer and 0.5 ppm during the winter.
Fig. 5.79 (Upper Panel) CO₂ Column Averaged Volume Mixing Ratios over Ny-Ålesund, Spitzbergen (FTS data were reduced by 1.16%). The black line indicates the seasonal cycle (calculated from moving averages of the CarbonTracker dataset). (Lower Panel) Monthly Standard Deviation to Represent CO₂ Seasonal Variabilities.

Table. 5.12. Ny-Ålesund O₂ Column Correction Factors. O₂ columns at particular maximum OPD, FOV and HFL combinations were divided by the following correction factors with the mean O₂ column of 2005-2006 (a period of consistent instrumental parameters) (4.60522 x 10^{24} molecules cm^{-2}) as reference.

<table>
<thead>
<tr>
<th>FOV [mrad]</th>
<th>Maximum OPD [cm]</th>
<th>High Folding Limit [cm^{-1}]</th>
<th>Correction Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6</td>
<td>12.86</td>
<td>31596.12</td>
<td>1.0284</td>
</tr>
<tr>
<td>4.1</td>
<td>12.86</td>
<td>31596.12</td>
<td>0.9989</td>
</tr>
<tr>
<td>4.8</td>
<td>12.86</td>
<td>31596.12</td>
<td>1.0279</td>
</tr>
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</table>

Table. 5.13. Correlation Coefficients of comparisons of the FTS Ny-Ålesund data with CarbonTracker and Zeppelin carbon dioxide concentrations

<table>
<thead>
<tr>
<th>Data Set</th>
<th>FTS XCO₂ (Pressure Normalized)</th>
<th>FTS XCO₂ (O₂ Normalized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CarbonTracker</td>
<td>0.9740</td>
<td>0.9763</td>
</tr>
<tr>
<td>NOAA Surface Flasks (Zeppelin, Spitzbergen)</td>
<td>0.9628</td>
<td>0.9740</td>
</tr>
</tbody>
</table>

Shown in figures 5.80 – 5.83 are the XCO₂ anomalies.
Fig. 5.80 2002 XCO₂ and XCO₂ Anomalies

Fig. 5.81 2003 XCO₂ and XCO₂ Anomalies
Fig. 5.82 2005 XCO₂ and XCO₂ Anomalies

Fig. 5.83 2006 XCO₂ and XCO₂ Anomalies

As can be seen, the model seems to have some difficulty capturing the small scale variations of carbon dioxide. This can be due to several factors:

1.) the large diurnal variations of carbon dioxide in Ny-Ålesund (see Fig. 5.16) as a result of smaller measured intensities (continuum levels) at this site (see Fig. 5.5)

2.) lack of vegetation in Ny-Ålesund (that models may have over estimated) as shown in a clear day variation of XCO₂ in Fig. 5.84
Fig. 5.84 Clear Day XCO$_2$ Variations.
6. Summary, Conclusion and Outlook

Atmospheric carbon dioxide (CO$_2$) was retrieved from ground-based solar absorption measurements using Fourier transform infrared (FTIR) spectrometry in stations in Biscarrosse, France, in Bremen, Germany and in Ny-Ålesund, Spitzbergen. Molecular oxygen (O$_2$) was also retrieved to function as an internal standard that can be used to assess the short-term and the long-term precision of the FTIR column concentrations as well as to determine the dry air mixing ratio, such that uncertainties in the surface pressure and the water vapor column are avoided.

The effects of several instrumental parameters were also initially assessed in the study to investigate which errors are correlated to both the CO$_2$ and the O$_2$. Changes in the field of view, the maximum optical path difference and the high folding limit seem to change the trace gas column concentrations of O$_2$ and CO$_2$ and just partially cancels out in the CO$_2$/O$_2$ ratio. Correction factors on the O$_2$ column to minimize these instrumental effects were determined and applied to the FTS data. These correction factors seem to be more effective in Ny-Ålesund than in Bremen as the degree of these instrumental changes appear to be more subtle in Ny-Ålesund. Additional correction strategies, particularly for the CO$_2$, are still being examined and investigated.

Different instruments were also compared. A Bruker 120 M (Mobile) FTIR was compared to a Bruker 125 HR (High Resolution) Fourier transform spectrometer (FTS) as well as to another 125 HR at different altitude locations. In the intercomparisons, the CO$_2$/O$_2$ ratios agree considerably well with slight differences coming from the difference in modulation efficiencies and phase errors. Optical realignments of the instruments greatly reduce the difference between the O$_2$ and CO$_2$ VMRs.
CO₂ measurements during the CarboEurope Regional Experiment Strategy (CERES) from May to June 2005 in Biscarrosse, France allowed calibrations with in situ aircraft data from the METAIR Dimona. The Dimona, being a touring motor glider, had a maximum altitude of approximately 3 km. Data above this ceiling was therefore necessary to be appended to come up with a CO₂ profile that can then be integrated to produce a column concentration. These appended data were taken from the TM3 model for the free troposphere portion of the profile and from Observations of the Middle Stratosphere balloon measurements for the stratosphere. Footprints or surface influences computed using the Stochastic Time Inverted Lagrangian Transport (STILT) model were used to explain the differences in the aircraft and the Fourier transform spectrometer data. Oceanic influence regions produce higher CO₂ concentrations than inland vegetative areas during the growing season due to photosynthetic uptake.

Comparison of single receptor STILT model outputs with a tower beside the FTS show a small bias, but large variabilities in their differences. However, comparison of multiple receptor STILT data with the FTS show a large bias, but with small variabilities in their differences. This bias is attributed to the scaling factor used in calibrating the FTIR data with the integrated (combined “simulated” aircraft, model and balloon) CO₂ data. The scaling factor was derived to a large extent from aircraft measurements that sampled within a 50 km distance from the FTS and this introduces spatial heterogeneity in the carbon dioxide volume mixing ratios around the FTS. Since identical model parameters were used for land-atmosphere fluxes when STILT was compared with in-situ tower data (single receptor) and with column measurements from the FTS (multiple receptors), STILT can be used as a “transfer standard”. Using STILT for comparing remotely sensed CO₂ data with tower measurements of carbon dioxide and quantifying this comparison by means of the effective bias, provided a framework that allowed validating the FTIR retrievals versus measurements made in-situ. Since these in-situ measurements are done frequently and at high accuracy on
the global calibration scale, linking this scale with FTIR retrievals ultimately provides a calibration scale for remote sensing.

Long term trends of CO₂ were analyzed for the Bremen, Germany and for the Ny-Ålesund, Spitzbergen FTIR instruments whose biases from the simulations were reduced by comparing them to the STILT and the CarbonTracker models, respectively. Care has to be taken though when scaling the FTS data to the models as vertical mixing biases are still an issue for models. FTS aircraft validations are therefore necessary. Once this is performed, the vertical transport in models can be evaluated using the calibrated FTS data. However, due to the lack of aircraft validation in Bremen and Ny-Ålesund, the FTS data were scaled to the models.

Comparisons of CO₂ anomalies between the FTS data and the models show more reasonable agreement in Bremen than in Ny-Ålesund. The reasons for which come from the larger diurnal variations in Ny-Ålesund as a result of smaller measured intensities and the lack of vegetation in Ny-Ålesund that the model may have over estimated. With the better agreement of the models in Bremen to the measurements, a “clear sky” bias was pin pointed as models see increased CO₂ during frontal zone conditions – a meteorological condition when FTIRs often cannot measure.

The spatial heterogeneity of carbon dioxide was also assessed for Bremen by varying the horizontal resolutions of the STILT model from a fine to a coarse scale. The model outputs from these resolutions were then compared to STILT results with the highest resolution as well as to the FTS data. From the standard deviation of differences among these datasets, column concentrations are not sensitive to small scale local carbon dioxide emission sources amidst Bremen being situated in an urban setting. The difference in variability between fine to coarse scales are approximately 0.2 ppm.
In the course of this work, much has been done to understand all the processes involved in the instrumentation and in the physical interpretations of the data to the best of one’s ability. However, the intrinsic nature of research is that the more one understands, one realizes that there are more concepts out there that have to be understood. In this research, certain aspects were found out that needs further investigation. These are:

- Discrepancies with the two CO₂ bands
- Instrumental effects
- Aircraft validations
- “Clear sky” bias

It is the hope of every researcher that their studies would be “picked up” by other researchers to correct, improve or strengthen the results that were found.
7. References


Hase, F., Blumenstock, T., Paton-Walsh, Clare (1999), Analysis of the instrumental line shape of high-resolution Fourier IR spectrometers with gas cell measurements and new retrieval software. Applied Optics, 38 (15).


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