Ground-based Remote Sensing of Carbon Dioxide, Carbon Monoxide and Methane on Ascension Island Using Fourier Transform Infrared Spectroscopy
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Abstract

In May, 2012, a remote sensing observatory for performing ground-based total column measurements was established on the remote island Ascension Island (7.93°S, 14.39°W) in the South Atlantic Ocean. Measurements are conducted in the framework of the Total Carbon Column Observing Network (TCCON) which is a global network measuring greenhouse gases (GHGs) such as CO₂ and CH₄ and other gases. TCCON data are heavily used for validating space-borne observations of the same gases. The location on Ascension Island was chosen to provide TCCON measurements from an undersampled region of the world, the tropics, that are a key region in carbon cycle research at the same time. Solar absorption spectra in the near-infrared region were measured with a high-resolution Fourier transform spectrometer. From those spectra, column-averaged dry-air mole fractions (denoted as $X_{\text{gas}}$) of CO₂, CH₄ and CO were retrieved. The time series of $X_{\text{CO₂}}$, $X_{\text{CH₄}}$ and $X_{\text{CO}}$ now comprise more than five years. Aircraft profiles of CO₂, CH₄ and CO were used for calibrating the measurements. Due to the successful calibration, the station gained status as full TCCON station in May 2017.

A detailed analysis of the time series of $X_{\text{CO₂}}$ shows that it is influenced by fluxes from both hemispheres. By comparing $X_{\text{CO₂}}$ measurements with in situ measurements performed at the surface, a slightly larger seasonal cycle for $X_{\text{CO₂}}$ was found. This indicates that most of the variability seen in CO₂ on Ascension is due to long-range transport of emissions from the continents. A comparison between $X_{\text{CO₂}}$ from TCCON and space-borne observations from the Orbiting Carbon Observatory-2 (OCO-2) highlights the importance of the TCCON station on Ascension Island for validating observations from OCO-2 performed in ocean glint mode. Furthermore, it is shown that the method for collocating space-borne observations from OCO-2 with ground-based observations by TCCON can be improved by considering the local flux variability of CO₂. This is an important finding for future satellite validation studies.

The time series of $X_{\text{CH₄}}$ is shown and a comparison to in situ data is performed. Additionally, the time series of tropospheric partial column of CH₄ was retrieved by using
N$_2$O as a proxy for the stratospheric partial column. A surprisingly high difference of up to approx. 50 ppb can be measured between lower CH$_4$ values at the surface and higher values in the tropospheric partial column. This positive gradient with altitude can be attributed to transport from the continents and the trade wind inversion occurring around Ascension Island.

The time series of $X_{\text{CO}}$ allows the detection of the two different biomass burning seasons of the African continent. Additionally, higher $X_{\text{CO}}$ values in the second half of 2015 can be related to stronger, El Niño-induced fires in Indonesia. For attributing the different source regions, tagged tracer simulations were performed for CO$_2$ by using emissions of the Global Fire Assimilation System in an atmospheric transport model. The results support the hypothesis that the time series of $X_{\text{CO}}$ on Ascension Island is mainly influenced biomass burning signals from Southern Africa. To a minor extent, also the influences from Northern Africa, tropical Asia and tropical America are visible.

Total column measurements on Ascension Island complement surface measurements performed by NOAA. Observations of both measurement approaches are crucial for improving inverse modeling of GHG emissions in this region. Only together they provide a complete picture of the vertical distribution of GHGs in the atmosphere. Especially for CH$_4$, this is critical as the CH$_4$ concentration has an unusual positive gradient with altitude due to the trade wind inversion. Altogether, time series of $X_{\text{CO}_2}$, $X_{\text{CH}_4}$ and $X_{\text{CO}}$ from Ascension provide valuable input, both for validating satellite data as well as for gaining deeper insight into the tropical carbon cycle.
Publications

Articles in Peer-reviewed Journals


**Presentations at Conferences**

Niebling, S. G.* et al.: A mobile FTIR system for ground-based total column measurements of greenhouse gases, DPG Frühjahrstagung, Berlin, Germany, 2012; *poster.*

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Niebling, S. G.* et al.: Comparisons of ground-based total column CO$_2$ measurements and global transport simulations, TCCON Meeting, Abashiri, Japan, 2013; *poster.*

Niebling, S. G.* et al.: A method to account for the temperature sensitivity of TCCON total column measurements, EGU General Assembly, Vienna, Austria, 2014; *poster.*

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Arnold, S. G. et al.: Validation of the Ascension Island TCCON site with data from ATom-1, TCCON Meeting, Paris, France, 2017; *poster.*
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Chapter 1

Introduction and Motivation

Life on our planet as we know it is only possible due to Earth’s atmosphere, the about 100 km thick layer surrounding the Earth and protecting us by absorbing ultraviolet solar radiation. The atmosphere also contains oxygen which most creatures need to survive, and it is responsible for an average surface temperature of 14°C by retaining some of the energy coming from the Sun. Without this protecting layer, the average temperature on the Earth’s surface would be about -18°C. In Earth’s history, the composition of the atmosphere experienced significant changes. Currently, dry air contains 78.09% nitrogen (N₂), 20.95% oxygen (O₂) and 0.93% argon (Ar) (Roedel and Wagner, 2011). Additionally, trace gases are abundant in only small amounts. Even though their concentrations often account only in the range of some parts per million (ppm), parts per billion (ppb) or even parts per trillion (ppt), those trace gases heavily influence our climate and chemical processes in the atmosphere.

In former times, solely natural processes such as volcanic eruptions, transitions between glacial and interglacial periods and photochemical processes determined changes regarding the concentrations of trace gases in the atmosphere. With the start of the so-called industrialization, mankind also began to act on the composition of the atmosphere by emitting trace gases and aerosols e.g. through burning of fossil fuels. While the pre-industrial concentrations of carbon dioxide (CO₂), a major greenhouse gas (GHG), ranged between 180 ppm in glacial and 300 ppm in interglacial periods for the last 800.000 years (IPCC, 2013), we faced an increase of 45% in the global mean CO₂ concentration between 1750 (278 ppm, IPCC (2013)) and 2016 (402.8 ± 0.1 ppm, Le Quéré et al. (2018)). Concentrations of other GHGs like methane (CH₄) and nitrous oxide (N₂O) sharply increased as well. The rising concentrations of GHGs lead to an additional warming of the atmosphere. This process is known as anthropogenic (human-caused) climate change.
1.1 The Global Carbon Cycle

As two of the major GHGs, CO$_2$ and CH$_4$, contain carbon, the rising concentrations of GHGs also lead to a perturbation of the natural carbon cycle. The Earth system has four main reservoirs or pools that contain carbon: the atmosphere, the oceans, the lithosphere and the terrestrial biosphere. Carbon is moved from one reservoir to another by different biological, physical and chemical processes on very different time and spatial scales. Figure 1.1 shows a schematic overview of the carbon cycle and illustrates in a simple way how the natural cycle is disturbed by anthropogenic influences, see red arrows indicating the anthropogenic carbon fluxes in the figure. These perturbations can lead to feedback mechanism in the Earth system, which further alter the carbon cycle. Investigating and understanding the carbon cycle is therefore essential to predict and mitigate current and future climate change. In the next three paragraphs, the three carbon-containing gases (CO$_2$, CH$_4$, CO), on which this thesis is focused, are briefly presented.

**Atmospheric carbon dioxide**

CO$_2$ is released to the atmosphere mainly through combustion of fossil fuels, cement production, deforestation, biomass burning, and biotic respiration. It is mainly removed from the atmosphere again by inorganic ocean uptake and photosynthesis (Le Quéré et al., 2015). Due to removal processes happening on different time scales, no single atmospheric lifetime can be defined. The IPCC (2013) states that about 15 to 40% of CO$_2$ emitted until the end of this century will stay in the atmosphere for more than 1000 years. The annual growth rate of CO$_2$ is slightly different from year to year due to changes in the land and ocean sinks, the El Niño Southern Oscillation, varying fossil fuel emissions, volcanic eruptions, and changes in land use (Le Quéré et al., 2009). On average, it is approx. 2 ppm per year (Francey et al., 2010).

**Atmospheric methane**

CH$_4$ is the second most important GHG (after CO$_2$). Natural sources of CH$_4$ include the production by anaerobic microorganisms in wetlands, emissions by termites, guts of ruminants, rice paddies, wildfires and some geological sources. Anthropogenic CH$_4$ sources are emissions from the gas and oil industry, agriculture such as rice cultivation and husbandry of ruminants, coal mining, landfills and anthropogenic fires (Kirschke et al., 2013). The major sink of CH$_4$, which is responsible for around 90% of the removal of CH$_4$ from the atmosphere, is oxidation by hydroxyl (OH) radicals (Kirschke et al., 2013). Besides, minor sinks are uptake of CH$_4$ by soils, stratospheric loss through reactions with chlorine radicals and atomic oxygen radicals and oxidation by chlorine radicals in the marine boundary layer (Kirschke et al., 2013). According to the IPCC (2013), the average atmospheric lifetime of CH$_4$ is 12.4 years. Altogether, the atmospheric mixing ratio is 2.5 times larger than in 1750,
Figure 1.1: An overview of the global carbon cycle with the numbers representing the different reservoir mass in PgC (1 PgC = 1 Petagram carbon = $10^{15}$ grams carbon) and annual carbon exchange fluxes in PgC yr$^{-1}$. Reservoir mass and natural fluxes of the pre-industrial times (before 1750) are indicated by black numbers and arrows, anthropogenic fluxes are indicated by red arrows and numbers. Red numbers in the reservoirs indicate how much anthropogenic carbon has been added to (positive sign) or removed from (negative sign) the reservoir since 1750. Figure taken from IPCC (2013).

It reached 1810 ppb in 2012 (Saunois et al., 2016). However, the growth rate of CH$_4$ is much more variable than that of CO$_2$. Several periods with zero growth and even periods with decreasing concentrations in the atmosphere were identified since the beginning of regular and global monitoring of CH$_4$ (Dlugokencky et al., 2009; Nisbet et al., 2014). After a pause of several years from 1999 to 2007, CH$_4$ concentrations in the atmosphere increased again. In 2014, growth was extreme with a rate of $12.5 \pm 0.4$ ppb (Nisbet et al., 2016).
Atmospheric carbon monoxide

CO is present in the atmosphere due to incomplete combustion processes such as natural and anthropogenic fires and burning of fossil fuels. It is considered to be a pollutant and it is toxic to humans. Furthermore, it plays a major role in tropospheric chemistry. It acts as an important sink for OH, forming CO₂ at the same time. It can be involved in formation of photochemical smog, depending on the simultaneous presence of nitrogen oxides (Seiler, 1974). CO can also be produced through oxidation of CH₄ (Seiler, 1974). According to the IPCC (2013), CO is a medium-lived gas with a lifetime of 2 to 3 months. Recent studies present conflicting results regarding the current trend of CO in the atmosphere. Worden et al. (2013) report a modest decreasing trend for both hemispheres, whereas Wai et al. (2014) state that the trend is positive at least in the southern hemisphere.

1.2 Atmospheric Observations of CO₂, CO and CH₄

To better understand and quantify how the Earth system and the global carbon cycle react due to anthropogenic GHG emissions, it is important to monitor GHGs and other carbon-containing gases like CO with a good temporal and spatial coverage. Continuous and regular monitoring started with the first high quality measurements of CO₂ concentrations in the 1950s on Mauna Loa in Hawaii. Measurements were performed under the supervision of Charles David Keeling and resulted in the famous Keeling curve showing the steadily increase of atmospheric CO₂ (Keeling, 1978). Over time, more and more measurement programs were launched to monitor trace gas concentrations and to detect long-term trends in the atmosphere. Today, three main categories of measurements can be distinguished. In situ measurements as they are performed by the National Oceanic and Atmospheric Administration (NOAA)/Earth System Research Laboratory and other research institutes provide high precision and accuracy but they are often spatially limited. Space-borne measurements offer high spatial coverage but they can suffer from a poorer precision and a limited temporal coverage. Ground-based remote sensing measurements like the ones performed within the Total Column Carbon Observing Network (TCCON) can provide a transfer standard between the locally limited in situ measurements and measurements from space. A unique data set is provided by data assimilation of measurements from all three different methods, resulting in an improved understanding of the global carbon cycle which could not be reached by only one method alone.

Remote sensing of GHGs and other carbon-containing gases like CO gases from space plays an important role for monitoring their changes in Earth’s atmosphere. The major advantage of this technique is the global coverage. The most prominent
past or current satellite missions dedicated to observe CO₂, CH₄ or CO concentrations from space are:

- the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) on the Environmental Satellite (ENVISAT) by the European Space Agency (ESA) (Burrows et al., 1995; Bovensmann et al., 1999). ENVISAT was launched in March 2002 and SCIAMACHY observed concentrations of CO₂, CH₄ and other trace gases as well as aerosol and cloud parameters until ENVISAT’s mission ended in May 2012.

- the Thermal and Near Infrared Sensor for Carbon Observation Fourier-Transform Spectrometer (TANSO-FTS) on the Greenhouse Gases Observing Satellite (GOSAT) belonging to the Japan Aerospace Exploration Agency (JAXA) (Kuze et al., 2009). Since its launch in January 2009, TANSO-FTS onboard GOSAT measures the concentrations of the two GHGs CO₂ and CH₄.

- the Orbiting Carbon Observatory-2 (OCO-2) owned by NASA (Crisp et al., 2004; Crisp, 2015). Successfully launched in July 2014, this satellite mission is purely dedicated to measure the total column of CO₂.

- the Tropospheric Monitoring Instrument (TROPOMI) onboard Sentinel-5 Precursor (Sentinel-5P) by ESA (Hu et al., 2016; Landgraf et al., 2016). Sentinel-5P was launched in October 2017 and among other quantities, TROPOMI observes concentrations of CO with an unprecedented spatial resolution.

Due to higher uncertainties, satellite data need to be corrected and validated using accurate and precise ground-based measurements. TCCON was formed in 2004 to serve that purpose mainly for the OCO-2 mission. It consists of ground-based Fourier transform spectrometers (FTSs) that provide high-resolution near-infrared spectral data. From these spectra, it is possible to retrieve total column dry-air mole fractions (DMFs) of CO₂, CH₄, CO, HF, H₂O, N₂O, O₂, and several other trace gases. Besides being the validation network for satellite missions, TCCON aims to improve our understanding of the carbon cycle with very precise and accurate data (Toon et al., 2009; Wunch et al., 2010, 2011a). Figure 1.2 shows a global map of all previous, current and planned measurement sites within TCCON.

1.3 Thesis Objectives

Gurney et al. (2002) already expressed the need for expanding the CO₂ observation network within the tropics to further reduce uncertainties in regional estimates of CO₂ fluxes when using atmospheric inversion modeling frameworks. But despite expanding in situ networks and a growing number of satellite missions, there are
still regions where precise and accurate measurements of the total column of trace gases provided by Fourier transform infrared (FTIR) spectrometry are sparse, e.g. in the southern hemisphere (SH) and especially in the tropics.

One of the main objectives of this thesis has been to establish an instrument in the tropics to help filling the data gap in this region of the world. Ascension Island (7.93°S, 14.39°W)* in the South Atlantic Ocean is located near the equator and in the middle between the two poorly sampled continents Africa and South America. Due to its unique location and its exposure to the trade wind inversion, Ascension has shown to be an important and interesting measurement site for performing ground-based total column measurements. A second goal within the project has been to characterize and monitor the instrument stability on Ascension to guarantee high quality measurements, and to use in situ profile measurements made onboard aircraft to tie the data from Ascension to the World Meteorological Organization (WMO) scale. Another objective has been to use total column measurements of CO₂ from Ascension and all other TCCON stations for comparisons to measurements from OCO-2 and to test different methods for collocating space-borne measurements with ground-based observations. Major goals of this work have been to investigate the time series of CO₂, CH₄ and CO measured in the total column above Ascension in order to learn about the seasonal cycle of these gases at this remote location, to compare these data sets to in situ measurements performed at the surface, and to show how total measurements from Ascension add valuable information to the carbon cycle research.

* In this work Ascension Island is often only referred to as Ascension for convenience.
This work is structured as follows: Chapter 2 gives an overview of the physical basis of spectroscopy in the infrared region of the electromagnetic spectrum, outlines Fourier transform spectrometry and contains a basic description on trace gas retrieval. Chapter 3 introduces the measurement site on Ascension Island, deals with atmospheric transport and dynamics around Ascension, mentions instrument specific issues and proofs the stability of the instrument by showing instrumental line shape parameters of the FTS. The calibration of the Ascension TCCON station with aircraft data is described in Chapter 4. Furthermore, this chapter presents the time series of total column measurements of CO$_2$ on Ascension and its comparison to surface data and model data. It also includes a comparison between observations from OCO-2 and TCCON data from Ascension and all other sites within the network by using different collocation methods. Chapter 5 deals with the time series of total column measurements of CH$_4$. It also includes the time series of the tropospheric partial column of CH$_4$. Moreover, these data sets are compared to surface data and modeled data from a model simulating methane concentrations in the atmosphere above Ascension are shown. In Chapter 6, the time series of total column measurements of CO is discussed and linked to biomass burning occurring on the African continent and elsewhere by showing results from tagged tracer simulations. Chapter 7 summarizes the results of Chapter 3 to Chapter 6 and gives an outlook regarding possible applications of the measurements in inverse modeling.
1.3 Thesis Objectives
Chapter 2
Fundamentals

2.1 Infrared Spectroscopy

This section summarizes the physical basis of spectroscopy in the infrared region of the electromagnetic spectrum. The content is adopted from Demtröder (2000), Haken and Wolf (2006) and Stephens (1994).

2.1.1 Molecular Transitions

Molecules consist of two or more atoms held together by chemical bonds such as covalent bonding or ionic bonding. They can absorb and emit electromagnetic radiation. These processes are associated with the transition of the molecules from one discrete energy state to another discrete state. When a molecule absorbs a photon, it reaches a higher energetic state. When it emits a photon, it relaxes back to its ground state or a state with less energy. Electronic, vibrational, and rotational transitions are possible. The spectral signatures associated with the transitions are characteristic to each kind of molecule. Therefore, they are used in spectroscopy to detect and identify different molecules. The total energy of a molecule \( E_{\text{tot}} \) in one specific state is the sum of its electronic energy \( E_{\text{el}} \), its vibrational energy \( E_{\text{vib}} \) and its rotational energy \( E_{\text{rot}} \):

\[
E_{\text{tot}} = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}} \quad (2.1)
\]

When a transition to another state occurs, the resulting energy difference \( \Delta E \) is a combination of the changes of the electronic, the vibrational and the rotational energy. Depending on the kind of transition, this energy difference can be quite large or relatively small. It holds that \( \Delta E_{\text{el}} > \Delta E_{\text{vib}} > \Delta E_{\text{rot}} \). Typically, electronic transitions are observed in the UV and visible spectral range. Pure rotational transitions result in spectral signatures in the microwave and far infrared.
2.1 Infrared Spectroscopy

Figure 2.1: Vibrational-rotational bands of CO$_2$ (black lines) according to the HITRAN 2012 database used within TCCON. The two main bands are due to the transitions (14$^{1}$1) ← (00$^{0}$0) and (21$^{2}$2) ← (00$^{0}$0). The weaker bands are due to absorption of excited states. The two reddish shaded regions are the retrieval windows of CO$_2$.

spectral region. Vibrational transitions usually generate spectral lines in the infrared region, and such transitions are often accompanied by rotational transitions. Together they form vibrational-rotational bands. An example of such bands is shown in Fig. 2.1. Here, the vibrational-rotational bands of CO$_2$ are depicted according to the high-resolution transmission molecular absorption (HITRAN) 2012 database (Rothman et al., 2013). These bands are used for retrieving CO$_2$ within TCCON. As vibrational-rotational bands in the infrared in general are the ones used within this work, the formation of such bands is explained in more detail below.

For describing transitions between different vibrational energy levels of a molecule, the concept of a harmonic oscillator with quantized energy levels can be used. In this model, energy levels are equidistant. It is found that for the vibrational quantum number, $\nu = 0, 1, 2,...$ only vibrational transitions with $\Delta \nu = \pm 1$ are allowed (Demtröder, 2000). However, the real potential of a molecule is not of symmetric parabolic shape. This is only a good approximation when the internuclear distance of the atoms within the molecule is close to the equilibrium distance $R_{eq}$. At smaller distances, repulsive forces occur and for distances larger than $R_{eq}$, the potential curve converges to the value of the dissociation energy for the given molecule. It is therefore more realistic to use an anharmonic oscillator described by a Morse potential.
The selection rule for allowed transitions can be extended for the anharmonic oscillator. It now holds that transitions with $\Delta v = \pm 1, \pm 2, \pm 3, \ldots$ are allowed (Demtröder, 2000). Furthermore, the energy levels are not equidistant anymore. They decrease with increasing $v$ leading to slightly different spectral lines, as $\Delta E = E_v - E_{v-1}$ gets smaller with increasing $v$. In case of absorption, the so-called fundamental transition from $(v = 0)$ to $(v = 1)$ is most likely. Transitions with $\Delta v = \pm 2, \pm 3, \pm 4, \ldots$ form overtone bands with rapidly decreasing intensities.

Every vibrational transition is accompanied by many additional rotational transitions resulting in many closely spaced lines which form the spectral band. Similar to the concept of the harmonic and anharmonic oscillator, the model of a rigid rotor could be used to describe the different possible rotational energy states of the system. It is found that for the rotational quantum number $J$ normally only transitions with $\Delta J = \pm 1$ are allowed. In special cases, $\Delta J = 0$ is also possible. In general, a vibrational-rotational absorption band can be divided into three different regions depending on the quantum numbers and the positions of the spectral lines according to the band origin. One region is called the P-branch. It is built by transitions with $\Delta J = -1$ and it is located on the low wavenumber side of the band origin $\nu_0$. These transitions are associated with smaller energy differences with increasing $J$. The second region is the R-branch. It is generated by transitions with $\Delta J = +1$. It is located on the high wavenumber side of the band origin. Transitions of this branch are associated with larger energy differences with increasing $J$. The third region, the so-called Q-branch, only occurs for pure vibrational transitions where $\Delta J = 0$. Figure 2.2 shows a schematic energy level diagram with possible vibrational-rotational transitions for the three different branches.

With this information, it is possible to understand the origin of the different CO$_2$ bands shown in Fig. 2.1 in more depth. Most prominent are two large absorption bands, both with a P-branch extending to the left and an R-branch extending to the right from the band origin. One band is centered at $\nu_0 = 6348$ cm$^{-1}$, the other band has its band origin at $\nu_0 = 6228$ cm$^{-1}$. Like all bands, these can be described as a linear combination of the fundamental vibrational modes of CO$_2$. As CO$_2$ is a linear triatomic molecule with the carbon atom in the center, it has four fundamental vibrational modes: the symmetric stretching mode with the corresponding line at $\nu_1 = 1337$ cm$^{-1}$, the bending mode with $\nu_2 = 667$ cm$^{-1}$ which is double degenerate and counts twice and the antisymmetric stretching mode with $\nu_3 = 2349$ cm$^{-1}$. The band at $\nu_0 = 6348$ cm$^{-1}$ is a linear combination of $2\nu_1, 1\nu_2$ and $2\nu_3$ and in HITRAN nomenclature the transition is $(21^\circ 2) \leftarrow (00^\circ 0)$. The band at $\nu_0 = 6228$ cm$^{-1}$ is a linear combination of $1\nu_1, 4\nu_2$ and $1\nu_3$ and in HITRAN nomenclature the transition is $(14^\circ 1) \leftarrow (00^\circ 0)$ (Yang et al., 2002).
The intensities of individual lines within the P- and R-branches vary due to the different population densities $N_J$ of the rotational energy levels. The population density $N_J$ for a rotational state $J$ is determined by the Boltzmann distribution in thermodynamic equilibrium and it holds:

$$N_J \propto (2J + 1) \exp \left( -\frac{Bhc(J + 1)}{k_BT} \right)$$

(2.2)

Here, $h$ denotes the Planck constant, $c$ the speed of light, $B$ the rotational constant, $k_B$ the Boltzmann constant and $T$ the absolute temperature. The term $2J + 1$ specifies the degeneracy of a rotational energy level. For small $J$, it is the dominating term. With increasing $J$, there are more degenerate levels and hence the line intensity gets stronger until a maximum is reached. There, the thermal distribution of the molecular states gets more important and energy levels with large $J$ are less populated. In other words, the second term of Eq. 2.2 dominates and the line intensities decrease again.

**Figure 2.2:** Schematic energy level diagram showing possible vibrational-rotational transitions. The P-branch is generated by transitions with $\Delta J = -1$ (green arrows). The R-branch is generated by transitions with $\Delta J = +1$ (blue arrows). The theoretically possible Q-branch with $\Delta J = 0$ is indicated by dashed black arrows. It can only be observed for molecules with an angular momentum parallel to their symmetry axis.
Chapter 2. Fundamentals

Figure 2.3: The 1.27 μm spectral band of O₂ (black lines) according to the HITRAN 2012 database used within TCCON. The greenish region indicates the retrieval window of O₂.

As a second example for a spectral band which is used within TCCON, the O₂ band for the transition $\alpha^1 \Delta_g \leftarrow X^3 \Sigma_g^-$ is shown in Fig. 2.3. The band origin is at $\nu_0 = 7882$ cm$^{-1}$ and the band is often also called the 1.27 μm band according to its central wavelength. Note that O₂ is a homonuclear diatomic molecule. Therefore, it has no electric dipole moment and should not be infrared active. The band originates from magnetic dipole transitions and electric quadrupole transitions (Gordon et al., 2010).

2.1.2 Spectral Line Shapes

Spectral lines are not determined by one single frequency. Instead, they are broadened and extend over a range of frequencies. The reasons for this are natural line broadening, Doppler broadening and pressure broadening. Natural line broadening leading to the natural line shape is caused by the finite lifetime of the excited states of the molecules. According to the uncertainty relation between energy and time, the energy associated with a finite lifetime can only be determined to a certain degree. This results in not entirely sharp energy levels of the excited states and broadening of the spectral lines around the line center with the frequency $\nu_0$. The line shape related to natural line broadening is a Lorentz profile. Typically, the full width at half maximum (FWHM) is in the order of $\Delta \nu \approx 10^{-8}$ cm$^{-1}$ (Hase, 2000). This value is very
small and natural line broadening can be neglected when considering processes in Earth’s atmosphere where the two mechanisms of Doppler broadening and pressure broadening, explained below, are mainly responsible for the line shape.

**Doppler broadening**

Doppler broadening of spectral lines is caused by the relative thermal motions of the molecules. The molecules move with different velocities along a given line of sight. If they absorb or emit a photon, the original wavenumber $\nu_0$ of the associated photon will be slightly shifted when reaching the observer. Due to the random motions of the molecules, these shifts are equally distributed in both directions. Hence, Doppler broadened spectral lines have the shape of a Gaussian distribution. The following equation describes the Doppler line profile by its shape factor $f_D(\nu - \nu_0)$ (see Stephens (1994), pp. 107):

$$f_D(\nu - \nu_0) = \frac{1}{\sqrt{\alpha_D \pi}} e^{-\left(\frac{\nu - \nu_0}{\alpha_D}\right)^2}$$

(2.3)

where $\alpha_D$ is the Doppler line width, $\nu$ is the wavenumber and $\nu_0$ is the central wavenumber. The line width $\alpha_D$ is dependent on several quantities and can be calculated as follows:

$$\alpha_D = \frac{\nu_0}{c} \sqrt{\frac{2k_B T}{M_r}}$$

(2.4)

where $c$ is the speed of light, $k_B$ is the Boltzmann constant, $T$ is the temperature and $M_r$ is the molecular mass. With rising temperatures the velocity distribution of the gas-phase molecules gets broadened and $\alpha_D$ increases. A typical value for $\alpha_D$ e.g. for the fundamental CO band with $\nu_0 = 2100 \text{ cm}^{-1}$ and $T = 270 \text{ K}$ is calculated to be $2.8 \cdot 10^{-3} \text{ cm}^{-1}$.

**Pressure broadening**

Pressure broadening is caused by a shortened lifetime of excited states due to collisions between the molecules. Pressure broadening is stronger in the lower levels of the atmosphere because the probability of collisions increases with the number density of molecules. The higher the atmospheric pressure, the more collisions occur. Similar to the natural line broadening, the line shape associated with pressure broadening has a Lorentz profile of the following shape $f_L(\nu - \nu_0)$:

$$f_L(\nu - \nu_0) = \frac{\alpha_L/\pi}{\alpha_L^2 + (\nu - \nu_0)^2}$$

(2.5)

where $\alpha_L$ is the Lorentz line width (see Stephens (1994), pp. 101). With kinetic theory describing molecular collisions, the following approximation can be made:

$$\alpha_L \approx \alpha_{L,s} \frac{p_s}{p} \sqrt{\frac{T_s}{T}}$$

(2.6)
with $\alpha_{L,s}$ being the half-width value at the standard temperature ($T_s = 273$ K) and the standard pressure ($p_s = 1000$ hPa). Typical values of $\alpha_{L,s}$ range between $0.01 \text{ cm}^{-1}$ and $0.1 \text{ cm}^{-1}$ for most gases of interest. Thus, pressure broadening dominates in the troposphere and Doppler broadening dominates from the middle stratosphere upwards.

The Voigt Profile

Doppler broadening and pressure broadening both contribute to the shape of an atmospheric spectral line. The actual shape of a line is described by the so-called Voigt profile $f_V$ which is a convolution of a Gaussian shape function and a Lorentz shape function and can be written as (Huang and Yung, 2004):

$$f_V(\nu - \nu_0) = f_L(\nu - \nu_0) \otimes f_D(\nu - \nu_0) = \frac{\alpha_L}{\alpha_D^2 \pi^{3/2}} \int_{-\infty}^{\infty} e^{-y^2} \left( \frac{(\nu - \nu_0)/\alpha_D}{\alpha_L^2 - y} + \frac{(\alpha_L/\alpha_D)^2}{\alpha_L/\alpha_D} \right) dy \quad (2.7)$$

Depending on the dominating broadening mechanism the Voigt profile can have different shapes. If $\alpha_L$ is much larger than $\alpha_D$, the associated Voigt profile will be very similar to the Lorentz profile (Huang and Yung, 2004).

2.2 Fourier Transform Infrared Spectroscopy

Remote sensing of atmospheric gases by measuring their absorption spectra plays an important role in monitoring the Earth’s atmosphere. Such measurements are performed with passive or active instruments. Passive instruments only detect electromagnetic energy from a natural source, e.g. from the Sun. Active instruments, on the other hand, provide their own electromagnetic energy and sense the atmosphere by measuring backscattered radiation. While passing through the atmosphere, parts of the electromagnetic energy are absorbed. By analysing the transmitted light with a spectrometer, it is possible to quantify the amount of gases of interest. Different types of spectrometers are used depending on the spectral region to be investigated. In the ultraviolet and visible spectral region, spectrometers with a dispersive element, e.g. a prism or a grating, are often favored to measure the frequencies associated with electron transitions of the molecules of interest.

In the infrared, which is the spectral region investigated within this work, a Fourier transform spectrometer (FTS) is frequently used. This instrument has three principle advantages over e.g. a grating spectrometer (Griffiths and de Haseth, 2007).

- **Connes’ or wavelength accuracy advantage:** An additional laser beam of known wavelength passes through the interferometer and acts as an internal reference. Due to the very accurately known wavelength of this laser, a
wavenumber scale can be derived which is much more accurate and has a better long term stability than the calibration of dispersive spectrometers.

- **Fellgett’s or multiplex advantage:** Information is collected simultaneously from all wavelengths, resulting in a higher signal-to-noise ratio.

- **Jacquinot’s or throughput advantage:** In a dispersive instrument, the amount of light entering the spectrometer is restricted by an entrance slit. Narrow slits are needed for a high resolution, resulting in a poor signal-to-noise ratio. An FTS also needs a circular aperture at the entrance of the interferometer to avoid convergence of the collimated light beam, but for a given resolution and wavelength more light can get into the instrument, resulting in a higher signal-to-noise ratio.

Figure 2.4 shows a schematic diagram of an FTIR spectrometer based on a Michelson interferometer. The basic concept of such an interferometer is the splitting of collimated light by a beamsplitter and its recombination after covering different distances. Ideally 50% of the incoming light is transmitted onto a moveable mirror and 50% is reflected onto a fixed mirror. From both mirrors, the partial beams are reflected back to the beamsplitter. The distance of the moveable mirror to the beamsplitter is varied by moving it with a defined and constant velocity. This introduces the so-called optical path difference (OPD) of the two partial beams, resulting in a destructive and constructive interference pattern after their recombination at the beamsplitter. The interference pattern, which is eventually recorded by the detector, is also called an interferogram. The spectrum of the incoming light can be derived from it by performing a Fourier transform.

The following mathematical treatment is carried out by consulting Wunch (2006), Griffiths and de Haseth (2007), Davis et al. (2001), Messerschmidt (2011) and Kiel (2016). By assuming that the incident radiation can be described as a plane wave of monochromatic light, its amplitude can be described with the following equation:

\[
A = A_0 e^{i(\omega t - kD)} \quad (2.8)
\]

where \( A_0 \) is the peak amplitude of the source, \( \omega \) is the angular frequency, \( t \) is the time, \( k \) is the angular wave number and \( D \) is the distance from the source.

After passing through the two different arms of the interferometer and traveling the distance \( D_1 \) or \( D_2 \), the two partial beams interfere with each other at the beamsplitter. The amplitude of the recombined light can be calculated as follows:

\[
A = A_1 + A_2 = A_0(e^{i(\omega t - kD_1)} + e^{i(\omega t - kD_2)}) = A_0e^{i\omega t}(e^{-ikD_1} + e^{-ikD_2}) \quad (2.9)
\]
Figure 2.4: Schematic diagram of an FTIR spectrometer based on a Michelson interferometer and used for remote sensing of the atmosphere. Figure reproduced from Buschmann (2018).
With the wave number $k = 2\pi \nu$, where $\nu$ is the reciprocal wavelength, Eq. 2.9 can be written as:

$$A = A_0 e^{i\omega t} (e^{-i2\pi\nu D_1} + e^{-i2\pi\nu D_2})$$

(2.10)

The intensity of the recombined light measured with the detector can be calculated by multiplying the amplitude function from Eq. 2.10 with its complex conjugate.

$$I = A \cdot A^* = A_0^2 (1 + e^{-i2\pi\nu(D_1-\nu D_2)} + e^{i2\pi\nu(D_1-\nu D_2)})$$

(2.11)

By using Euler’s formula, $e^{ia} = \cos(a) + isin(a)$, defining the OPD as $x = D_1 + D_2$ and with $S(\nu) = 2A_0^2$ as the spectral energy, Eq. 2.11 can be written as:

$$I = S(\nu) (1 + \cos(2\pi\nu x))$$

(2.12)

In case of a monochromatic light source, e.g. a laser, $I$ alternates between 0 and $2S$ and for an OPD $x = n/\nu$ with $n = 0, 1, 2, 3, ...$ constructive interference occurs while for $n = 1/\nu, 2/\nu, 3/\nu, ..., 2.5/\nu, ...,$ destructive interference occurs. In atmospheric research often the Sun or another polychromatic source is used and the detector records a superposition of the interferences of all different frequencies. In the case of a polychromatic source, Eq. 2.12 has to be integrated over all frequencies:

$$I = \int_0^{\infty} S(\nu) (1 + \cos(2\pi\nu x)) d\nu$$

$$= \int_0^{\infty} S(\nu) d\nu + \int_0^{\infty} S(\nu) \cos(2\pi\nu x) d\nu$$

(2.13)

The first integral on the right side of Eq. 2.13 has a constant value. It represents the total incoming radiation integrated over all frequencies and is also called the DC term. The second integral consists of a term which varies cosinusoidally. This term is called the AC term and it contains all spectral information of the measured interferogram which can be retrieved by extending the lower limit of the integral to negative infinity and performing a Fourier transform. It holds that:

$$S(\nu) = \int_{-\infty}^{\infty} I(x)e^{-\nu x} dx$$

(2.14)

The corresponding inverse transformation is:

$$I(x) = \int_{-\infty}^{\infty} S(\nu)e^{\nu x} d\nu$$

(2.15)
In case of an interferogram which is real and symmetric about the zero path difference (i.e. $I(x) = I(-x) = I \ast (x)$), the sine part of the integral vanishes and it remains a cosine Fourier transform of the following form:

$$S(\nu) = \int_{-\infty}^{\infty} I(x) \cos(2\pi \nu x) dx$$ (2.16)

$$I(x) = \int_{-\infty}^{\infty} S(\nu) \cos(2\pi \nu x) d\nu$$ (2.17)

With this equation, it is possible to calculate the spectrum of the radiation entering the FTS by computing the cosine Fourier transform of $I(x)$.

**Discrete sampling, resolution and aliasing**

Until now, it was assumed that the interferogram is recorded continuously as a function of the OPD. In reality, the interferogram is always sampled at discrete points being equidistantly spaced within the distance $\Delta x$. Furthermore, a real instrument always has a finite OPD. The integrals can be modified to being sums of $N$ terms where $N$ is the number of discrete sampling points and Eq. 2.16 and Eq. 2.17 become:

$$S(k) = \sum_{n=1}^{N} I(n) \cos \left( \frac{2\pi(k-1)(n-1)}{N} \right), \quad k = 1, 2, ..., N$$ (2.18)

$$I(n) = \sum_{k=1}^{N} S(k) \cos \left( \frac{2\pi(k-1)(n-1)}{N} \right), \quad n = 1, 2, ..., N$$ (2.19)

The spectral resolution $\Delta \nu$ is defined by the inverse of the maximum OPD, $OPD_{\text{max}}$.

$$\Delta \nu = \frac{1}{OPD_{\text{max}}}$$ (2.20)

According to the Nyquist theorem, a continuous signal can be reconstructed when the sampling frequency is at least as twice as high as the maximum frequency of the signal. The Nyquist frequency is defined as:

$$\nu_{\text{Nyq}} = \frac{1}{2\Delta x}$$ (2.21)

If the Nyquist theorem is not fulfilled an effect called aliasing occurs where spectral contributions from frequencies larger than the Nyquist frequency are folded back into the observed spectral range. In this work, an FTS with a HeNe metrology laser with a wavelength $\lambda = 632.8$ nm ($\nu = 15798 \text{ cm}^{-1}$) is used. As the indium gallium arsenide (InGaAs) detector in the FTS covers the spectral range from 3800 cm$^{-1}$ to
11000 cm$^{-1}$, the laser is sampled at $\lambda/2$ to uniquely resolve all frequencies. The corresponding Nyquist frequency is $\nu_{\text{Nyq}} = 15798$ cm$^{-1}$.

2.3 Trace Gas Retrieval

This section gives an overview regarding basics of trace gas retrieval from atmospheric solar absorption spectra and introduces the GGG software, which is the retrieval software used within TCCON. The content of Sect. 2.3.1 and Sect. 2.3.2 is based on the work of Rodgers (2000). The text in Sect. 2.3.3 largely follows the description of Wunch et al. (2011a) and Wunch et al. (2015).

2.3.1 Basics of the Radiative Transfer in Earth’s Atmosphere

The interaction between radiation and a medium is described by the radiative transfer equation (RTE). In the field of remote sensing of Earth’s atmosphere, the RTE forms the mathematical basis for applying the physical process of radiation propagating through the atmosphere within the forward model of the retrieval. While passing through the atmosphere the radiation is affected by processes such as absorption, emission and scattering due to aerosols and gas molecules. When assuming that Earth’s atmosphere is in local thermodynamic equilibrium and that the atmosphere is a thin medium, the RTE for a given wavenumber $\nu$ is:

$$L(\nu, s) = L(\nu, 0)\tau(\nu, 0, s) + \int_0^s J(s') \frac{d}{dz'} \tau(\nu, s', s) dz' \quad (2.22)$$

where $s$ is a distance coordinate along the path, $L(\nu, 0)$ is the radiance at the starting point, $L(\nu, s)$ is the radiance at the end of the path and $\tau(\nu, s', s)$ is the transmittance of the path from $s'$ to $s$. $J(s')$ represents the so-called source function depending on thermal emission as well as scattering.

In the case of remote sensing of atmospheric solar absorption spectra in the infrared spectral range, the second term of Eq. 2.22 can be neglected. As Rayleigh scattering is proportional to $\lambda^{-4}$, with $\lambda$ being the wavenumber of the radiation, this scattering process only plays a very minor role in the infrared region. The same holds for Mie scattering, which describes scattering by aerosols as the wavelengths in the infrared spectral area are in general large compared to the diameters of the aerosol particles. Furthermore, there exists no considerable thermal emission as source of infrared radiation when direct sun measurements are performed. Therefore, the first term of Eq. 2.22 is sufficient to describe measurements of solar absorption spectra...
in the infrared region. The transmittance can be related exclusively to the absorption coefficient $\kappa_i(\nu, s'')$ by:

$$\tau(\nu, s', s) = \exp \left( - \int_{s'}^{s} \sum_i \kappa_i(\nu, s'') \rho_i(s'') \, ds'' \right)$$  \hspace{1cm} (2.23)

As explained in Sect. 2.1.1, the absorption may be due to vibrational-rotational transitions with $i$ referring to the $i$-th absorber in the light path and $\rho_i(s'')$ being its density. The absorption coefficient can be expressed as the sum over a large number of spectral lines:

$$\kappa_i(\nu, s'') = \sum_j k_{ij}(T(s'')) f_{ij}(\nu, p(s''), T(s''))$$  \hspace{1cm} (2.24)

with $k_{ij}$ being the temperature-dependent strength of the $j$-th line of the $i$-th absorber and $f_{ij}(\nu, p(s''), T(s''))$ being its normalized shape that can be dependent on the temperature $T$ as well as the pressure $p$. Additionally, line mixing effects caused by e.g. rotationally inelastic collisions between molecules need to be taken into account. Therefore, it is necessary to treat the spectral lines of a molecular band in a more complex way than simple addition (Rosenkranz, 1975). The RTE is a part of the forward model for retrieving trace gas concentrations from atmospheric solar absorption spectra within an inverse modeling setup. This setup is described in more detail in the next subsection.

### 2.3.2 Retrieval Principle

In atmospheric science, inverse methods provide an established and widely used technique to retrieve information about measurement quantities for which direct measurements are very difficult or even impossible. Determining the concentration of a gas in Earth’s atmosphere from measuring an absorption spectrum is a typical example where inverse methods are applied. Inverse problems are often ill-posed. The quantity of interest can only be determined unambiguously when additional a priori information is added and a regularization must be performed. The regularization method used within the GGG software is the optimal estimation method which strives to determine the most likely solution for the quantity of interest by including a priori knowledge of the same quantity.

For solving an inverse problem, a forward model $F(x)$ is needed which includes all physics relevant for the measurement process. For example, in the case of retrieving a gas profile from solar absorption spectra, the forward model contains a solar model, an atmospheric model, a radiative transfer model and an instrument model. The measurement vector $y$ in this example is a recorded solar absorption spectrum. The
forward model $F(x)$ relates the measurement vector $y$ to the so-called state vector $x$:

$$y = F(x, b) + \epsilon \quad (2.25)$$

with $\epsilon$ being the associated measurement error and $b$ being model parameters such as the absorption coefficient of the gas or the pressure and temperature profile of the atmosphere. The retrieval aims to determine the true state of the atmosphere, expressed by the state vector $x$. This is done by a least-squares fitting algorithm which tries to minimize the error-weighted difference between the real measurement $y$ and the values modeled by $F(x, b)$. Additionally, the error-weighted difference between the a priori profile $x_a$ and the estimated profile $\hat{x}$ has to be minimized. In summary, the minimum of the following cost function has to retrieved:

$$\chi^2 = [y - F(\hat{x}, b)]^T S_\epsilon^{-1} [y - F(\hat{x}, b)] + [\hat{x} - x_a]^T S_a^{-1} [\hat{x} - x_a] \rightarrow \min \quad (2.26)$$

$S_\epsilon$ and $S_a$ are the covariance matrices of the measurement vector and the a priori profile, respectively. An important quantity of the retrieval is the so-called averaging kernel matrix $A$. It describes the sensitivity of the estimated state vector $\hat{x}$ with respect to the true state vector $x$.

$$A = \frac{\partial \hat{x}}{\partial x} \quad (2.27)$$

Under the assumption that there is no noise associated with the measurement, the estimated state vector $\hat{x}$ is a smoothed version of the true state vector $x$ and the averaging kernel matrix $A$ describes how the observing system (e.g. the FTS) smooths $\hat{x}$:

$$\hat{x} = x_a + A(x - x_a) \quad (2.28)$$

Thus, in the case of an ideal retrieval, the averaging kernel matrix would be the identity matrix ($A = I$), resulting in $\hat{x} = x$.

2.3.3 Retrieval Software

TCCON uses a nonlinear least-squares spectral fitting algorithm for analyzing solar absorption spectra. An open-source software package called GGG is used to compute dry-air mole fractions (DMFs) of gases of interest. GGG contains several individual subroutines. The subprogram interferogram-to-spectrum (I2S) converts raw interferograms to spectra. In doing so, it corrects for solar intensity variations (Keppel-Aleks et al., 2007) and laser sampling errors (Wunch et al., 2015). Furthermore, a phase correction (Mertz, 1967) and a fast Fourier transform (Bergland, 1969) are performed to calculate the spectra from the interferograms.
The GFIT algorithm is the main routine of the GGG suite. It is a nonlinear least-squares spectral fitting algorithm which tries to minimize the difference between the forward model and each measured spectrum within certain microwindows of the spectrum. The forward model consists of a theoretically computed atmospheric transmittance spectrum using molecular absorption coefficients, an assumed atmospheric ray path, assumed profiles of temperature and pressure and an a priori profile for the gas of interest in the given microwindow. In order to calculate the theoretical spectrum, the GFIT algorithm needs accurate information on the spectroscopic parameters (e.g. line intensities, self-broadening coefficients, air-broadening coefficients, temperature-dependent coefficients). This information is provided by an atmospheric line list which is mainly based on HITRAN 2012 (Rothman et al. (2013), see also Sect. 2.1.1). Some empirical changes were applied to the original HITRAN 2012 database so that the atmospheric line list better suits the real-world atmospheric scenario. For example, in the case of H$_2$O, Kitt Peak laboratory spectra were used to modify the 4000 to 6000 cm$^{-1}$ region. More details on the adaption of HITRAN 2012 for its use within GGG can be found in Wunch et al. (2015). The temperature and pressure profiles are based on the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) reanalysis (Kalnay et al., 1996). The a priori profiles of H$_2$O are obtained by using the same NCEP/NCAR reanalysis data. The a priori profiles of CO, CH$_4$ and N$_2$O are derived from ACE-FTS (Bernath et al., 2005) and MkIV-FTS (Toon, 1991) measurements. Additionally, the stratospheric a priori profiles of CH$_4$ and N$_2$O are constrained by the almost inverse relationship between HF and both CH$_4$ and N$_2$O in the stratosphere (Luo et al., 1995; Washenfelder et al., 2003). For the a priori profile of CO$_2$, an empirical model was developed which accounts for the latitudinal and seasonal variability of CO$_2$ and includes the long-term increase of that gas. The model is based on the GLOBALVIEW-CO2 product (GLOBALVIEW-CO2, 2013).

GFIT does not perform a full profile retrieval to retrieve vertical gas profiles. Instead, it scales the a priori profiles and computes one single value for the total column of the individual gases from the surface to the top of the atmosphere. The prime parameters which are adjusted within the fitting process are the volume mixing ratio scale factors (VSFs) for the various fitted gases and their isotopologues. The vertical column of a gas $G$, $\text{column}_{G}$, is calculated by:

$$\text{column}_{G} = VSF_{G} \int_{z_{s}}^{\infty} f_{G}^{\text{a priori}} n \, dz$$

(2.29)

Here, $VSF_{G}$ is the VSF for gas $G$, $f_{G}^{\text{a priori}}$ is the a priori mole fraction of the gas $G$, $n$ is the total number density, $z$ is the altitude and $z_{s}$ is the surface altitude.
To calculate the column-averaged dry-air mole fractions (DMFs) for particular gases, also denoted as $X_{\text{gas}}$, the total column of the gas has to be divided by the column of dry air. As the DMF of $O_2$ is known to be 0.2095, the column of dry air can be obtained by dividing the column of $O_2$ from the FTS spectrum with this known value:

$$column_{\text{dry air}} = \frac{column_{O_2}}{0.2095} \quad (2.30)$$

Using this method for the calculation of $column_{\text{dry air}}$ has an important advantage. Measurement errors like mis-pointing or intensity variations during a single measurement affect all target gases in a similar way. Therefore, these errors are much reduced by using the column ratio to calculate $X_{\text{gas}}$:

$$X_{\text{gas}} = \frac{column_G}{column_{\text{dry air}}} \quad (2.31)$$

With Eq. 2.30, the final equation to receive $X_{\text{gas}}$ can be written as:

$$X_{\text{gas}} = 0.2095 \frac{column_G}{column_{O_2}} \quad (2.32)$$

In a final step, an additional post-processing algorithm is applied. It applies an empirical airmass correction and airmass-independent correction factors to the retrieved $X_{\text{gas}}$ values and filters the data for unrealistic outliers before the data product becomes final and is released to the TCCON archive. The empirical airmass correction is important as the airmass-dependent artefacts change with the mean solar zenith angle (SZA) which varies seasonally. If not accounted for, they would be aliased into the seasonal cycle. These artefacts are most likely due to spectroscopic inadequacies, such as neglecting line mixing, incorrect line widths or inconsistencies in the relative strengths of weak and strong absorption lines, and instrumental problems, e.g. uncertainties in the instrumental line shape (ILS). Due to spectroscopic uncertainties, airmass-independent correction factors are necessary to tie the TCCON data to the WMO scale by using accurate and precise in situ measurements conducted onboard aircrafts or with AirCore sampling systems (Karion et al., 2010). Such aircraft calibrations have been performed by Wunch et al. (2010), Messerschmidt et al. (2011) and Geibel et al. (2012) and correction factors have been calculated which are consistent throughout the whole network. Section 4.2 describes the procedure of using aircraft profiles to determine the airmass-independent correction factors with aircraft profiles taken close to Ascension Island.
Chapter 3

The FTS System on Ascension Island

3.1 Introduction

In order to guarantee a good network density for TCCON, it is important to perform very precise and accurate ground-based measurements of $X_{gas}$ also at remote places. This was one of the reasons to set up a TCCON station on Ascension Island, since TCCON measurements in the southern hemisphere (SH) and specifically in the tropics are sparse compared to those in the northern hemisphere (NH). Measuring $X_{gas}$ between two continents, South America and Africa, promises to sample air from both regions and helps to gain insights into the tropical carbon cycle. Already Gurney et al. (2002) states how important it is to expand the CO$_2$ observation network within the tropics as carbon cycle modeling studies are often limited due to the lack of data in these dynamic regions.

Within the framework of my PhD project, a shipping container designed for performing TCCON measurements fully autonomous was deployed on Ascension in May 2012. Major improvements regarding the optical components, especially the solar tracker, and the handling of the data were established over time. In the following chapter, the measurement site as well as the atmospheric transport and dynamics around Ascension are described. Moreover, specifics of the system for the harsh environment on Ascension and the automatisation and performance of the instrument are detailed.

3.2 Measurement Site

Ascension Island (7.93°S, 14.39°W) is a small volcanic island (approx. 93 km$^2$) located in the South Atlantic Ocean about 1500 km southwest of the nearest mainland in Africa and about 2200 km east of the coast of South America. The population is
small, with only about 880 people living on the island. No significant local sinks and sources of GHGs of any kind exist on the island. It is perfectly situated to monitor and investigate the variability of gases related to the carbon cycle with no local influence on the signals. Furthermore, longterm transport phenomena of airmasses from Africa, South America and the NH can be studied. In May 2012, the measurement container was deployed at the European Space Agency (ESA) Downrange Telemetry Station (7.92°S, 14.33°W, 31 m.a.s.l.) at the North East Bay of the island. Figure 3.1 shows the location of the container at the ESA station. The station is only about 100 meters away from the shore. A close-up view of the container is shown in Fig. 3.2.

This site was chosen in part because of the already existing infrastructure which guaranteed access to electricity and an internet connection. Relative low cloud cover over that part of the island was a second reason for choosing the ESA station. In general, Ascension has a mild tropical climate with no strong seasonality regarding temperature and precipitation. Figure 3.3 shows the meteorological data from Ascension recorded by the Met Office, the United Kingdom’s national weather service, for the time period from 1986 to 2012. The data were received through personal communication with Jo Pitt, senior operational meteorologist, during a site visit in September 2013. The monthly mean air temperature on Ascension Island varies less

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**Figure 3.1:** Location of the measurement site. The measurement container is placed at the ESA Downrange Telemetry Station at the North East Bay of Ascension Island. The red arrow indicates the container.
than 4°C with a maximum of 27.9°C in March and a minimum of 24.2°C in September (see panel (a) in Fig. 3.3). Ascension Island is an arid ecosystem with only 5 to 13 mm average rainfall per month in austral summer (December, January, February) and 15 to 31 mm average rainfall per month in austral fall (March, April, May). This can be seen in detail in panel (b) of Fig. 3.3. Rain days are defined as days with 0.1 mm or more precipitation whereas wet days are defined as days with 1.0 mm or more precipitation. As can be seen in panel (c) of Fig. 3.3, there are only four to eleven rain days and only two to five wet days per month on average. The cloud cover which is also plotted in panel (c) of Fig. 3.3 varies little over the course of one year. It is below four oktas\(^\dagger\) on average for most months of the year except for austral fall where it can increase to more than five oktas.

\(^\dagger\) An okta is a unit of measurement used to describe the amount of cloud cover for the visible sky. It indicates how many eighths of the sky are covered by clouds. The measurement unit ranges from 0 oktas (completely clear sky) to 8 oktas (completely overcast).
Figure 3.3: Mean temperature, rainfall and cloud cover on Ascension Island for the years 1986 to 2012 measured at the Met Office site which is located close to the Wideawake Airfield. The upper left panel (a) shows the mean monthly air temperature which varies less than 4°C with a maximum in March and a minimum in September. The average rainfall per month is depicted in the upper right panel (b). The lower panel (c) shows rain days and wet days with the y-axis on the left side and the cloud cover measured in oktas with the y-axis on the right side.

3.3 Atmospheric Transport and Dynamics around Ascension Island

Signals seen in $X_{\text{gas}}$ (see Sect. 2.3.3) measured with the TCCON instrument on Ascension are the results of the corresponding fluxes of the gases as well as atmospheric transport and dynamics predominant around Ascension and at larger scales. Total column measurements often carry mixed signals from distant regions via long-range transport. It is therefore important to consider some general atmospheric transport
mechanisms to be able to interpret the measurements on Ascension correctly.

In each hemisphere, there are three large circulation cells which determine the global patterns of transport in the atmosphere: the Hadley cell, the Ferrel cell and the polar cell. The cell which is particularly relevant for the region around Ascension is the Hadley cell. Close to the equator, high solar radiation causes thermal convection...
3.3 Atmospheric Transport and Dynamics around Ascension Island

and air rising to the tropopause where it continues to flow poleward. On its way, it
cools down and sinks at a latitude of about 30°. The rising air close to the equator is
replaced by air flowing towards the equator at the surface. Due to the Coriolis force
the air is deflected westward resulting in the trade winds (Hadley, 1735; Roedel
and Wagner, 2011). The equatorial area where northern and southern trade winds
converge is also called Intertropical Convergence Zone (ITCZ). At high altitudes in
the ITCZ, the maximum exchange of air between the upper troposphere and lower
stratosphere takes place with the western Pacific being the most dominant region for
this exchange (Fueglistaler et al., 2004). The latitudinal position of the ITCZ in the
Atlantic shifts with the seasons. It has a minimum close to the equator in boreal
spring (March to May) and reaches its northernmost position of around 10° to 15°N
in late boreal summer (August) (Grodsky and Carton, 2003). Typically, the ITCZ
stays north of the equator because of demands of the global energy balance. South-
ward atmospheric heat transport compensates northward ocean heat transport to a
large extent. A shift of the tropical circulation pattern and its ITCZ northward is as-
sociated with this heat transport (Marshall et al., 2014). Hence, the ITCZ only rarely
moves as far south as Ascension Island. This can also be seen when considering the
average rainfall per month shown in panel (b) of Fig. 3.3. The narrow latitudinal
band of the ITCZ is associated with heavy rainfall whereas precipitation on Ascen-
sion is low and without a large variation throughout the year. Another important
atmospheric feature is the trade wind inversion, a strong and persistent tempera-
ture inversion which separates the marine boundary layer from the free troposphere
(Barry and Chorley, 2009). This phenomenon is especially important for interpret-
ing the differences found when comparing surface measurements to $X_{gas}$ measured
on Ascension (see e.g. Sect. 5.3).

In order to better understand the transport patterns and dynamics around Ascension
Island, backward trajectories were calculated using the HYbrid Single Particle La-
grangian Integrated Trajectory (HYSPLIT) 4 model (Stein et al., 2015; Draxler and
Rolph, 2015) for one example year, 2014. The results are summarized in Fig. 3.4.
At a pressure of 1000 hPa, which corresponds to the surface level, the air is highly
influenced by the trade winds and comes almost exclusively from the remote south-
ern Atlantic (see blue trajectories in all panels of Fig. 3.4). At a height of 800 hPa or
approximately 2000 m, the backward trajectories indicate that the air comes mostly
from Central Africa (see green trajectories in all panels of Fig. 3.4). At a height
of 400 hPa, which corresponds to approximately 7400 m and reflects the free tro-
posphere, the air comes mainly from South America in austral fall (March to May),
austral winter (June to August) and austral spring (September to November). In aus-
tral summer (December to February), the origin of air parcels reaching Ascension
at this height is relatively mixed between South America and Africa (see black tra-
jectories in all panels of Fig. 3.4). At 100 hPa or approximately 16300 m, which corresponds to the tropopause, the pattern also changes with the seasons. In austral summer, fall and winter (December to August) air parcels at this height come from South America and Africa, whereas in austral spring (September to November) the predominant origin is clearly South America (see red trajectories in all panels of Fig. 3.4).

3.4 Specifics of the System for the Environment on Ascension Island

3.4.1 Modifications of the System from Initial Setup

A major goal of the project has been to establish a station which measures autonomously in a remote place like Ascension Island with as little operator intervention as possible. A lot of effort was put into designing a stable and redundant system which can be operated easily by remote control. The initial system and its

Figure 3.5: Original gold-coated mirror from Bruker with damaged surface. The picture was taken on June 7, 2012, approximately three weeks after the setup of the measurement container on Ascension. Photo: Nicolas John.
3.4 Specifics of the System for the Environment on Ascension Island

Automation concept are detailed in Geibel et al. (2010) and Geibel (2011). Here, the modifications from this original setup, made after the deployment of the measurement container on Ascension Island, are described. By far the most profound change happened to the solar tracker, which guides the sunlight into the FTS. The Bruker A547 solar tracker is originally equipped with two gold-coated mirrors. In the harsh environment of Ascension Island, this coating was damaged only three weeks after installation of the system (see Fig. 3.5). The first replacement mirrors with a protected gold coating also lost about 80% of their reflectance within four weeks of installation (Feist et al., 2016). As a consequence, rugged mirrors made of stainless steel (Feist et al., 2016) and with sufficient optical properties were developed and installed during a maintenance visit in August/September 2013. The air around Ascension is full of dust and sea salt. The major advantage is that the stainless steel mirrors can be cleaned without noticeable surface damage. A technician on site cleans them once per week to guarantee stable reflectance properties of the mirrors. New mountings for both mirrors were also developed so that the mirrors can be changed easily without the need for realignment. Dimensional drawings of the mirrors and the mountings are shown in Appendix C. More details on the development of the mirrors and a detailed investigation of their performance can be found in Feist et al. (2016).

Transferring data from a remote place as Ascension is not trivial. Over the course of the project important modifications regarding the data transfer took place. In the early phase, the raw interferogram data were transferred on DDS-5 tapes which could easily be sent by post. One tape could hold up to 36 GB, which is sufficient for approximately 4 - 6 weeks of measurements in normal weather conditions. In February 2015, the tape drive broke and had to be replaced. An intermediate solution with compact flash cards that were also sent by post did not work well. Due to the low quality of the flash media, many cards arrived with unreadable data. Since August 2016, all data are transferred online via a satellite link. The data volume to be transferred could be reduced by performing the initial quality checks already on the local computer on Ascension. Furthermore, an increase of the monthly data volume limit from 8 to 10 GB and an additional limited time window at no charge between 00:00 and 06:00 UTC and with no restriction regarding the data volume made this possible. The extra time window at night allows for an additional effective data volume allowance of 20-25 GB per month. Additional facts regarding the data transfer are also explained in Sect. 3.5.1.

3.4.2 Technical Issues Specific to this Installation

During the years of operation on Ascension, several technical issues with the instrument were discovered which are described in more detail in the following subsection.
Some of them are related to the fact that the FTS instrument is operated in the tropics and in a harsh environment. Others are the results of design flaws in parts of the measurement system.

Discontinuity of the solar tracker’s coordinate system when sun is in zenith

A Bruker A 547 solar tracker is used to guide the sunlight into the FTS. This tracker has limitations which especially matter when using it in latitudes close to the equator like on Ascension, located at 7.92°S. Due to being between the Tropics of Cancer (23.4°N) and Capricorn (23.4°S), there are two days each year where the sun is in zenith over the site. Like all azimuth-elevation systems, the coordinate system of the Bruker A 547 solar tracker has a point of discontinuity at $\theta_{\text{elevation}} = 90.0^\circ$. If the tracker is perfectly well aligned and the elevation of the sun is 90°, a change in the azimuth angle $\theta_{\text{azimuth}}$ will not change the direction of the solar beam. However, it is very difficult to align the tracker so that it guides the solar beam into FTS completely perpendicular to the image plane of the FTS. An imperfect alignment of the tracker causes small errors, denoted as $\Delta x_{\text{align}}$ here, which lead to large deviations $\Delta \theta_{\text{azimuth}}$. 

**Figure 3.6:** Maximum elevation angle of the sun above Ascension for the year 2015 (blue, left y-axis) and corresponding deviation of the azimuth angle as calculated with Eq. 3.1 (red line with triangles, right y-axis).
when $\theta_{\text{elevation}}$ is close to $90^\circ$ according to Eq. 3.1 (personal communication with Axel Keens from Bruker, March 2013).

$$\Delta \theta_{\text{azimuth}} = \Delta x_{\text{align}} \frac{1}{\cos(\theta_{\text{elevation}})}$$  (3.1)

The maximum elevation angle of the sun per day is shown for the year 2015 in Fig. 3.6. The corresponding deviation $\Delta \theta_{\text{azimuth}}$ is also depicted. It was calculated with an alignment error of the tracker being estimated to equal $0.11^\circ$. As one can see in Fig. 3.6, for the case of the FTS instrument on Ascension, this limitation of the tracker leads to problems at times of the year when the sun is close to zenith at noon. The alignment error of the tracker $\Delta x_{\text{align}}$ propagates into the deviation $\Delta \theta_{\text{azimuth}}$ and the tracker is not able to point correctly into the direction of the sun. This results in no measurements around this time of the day.

**Difficulties to align the solar tracker for the two different flip states**

There exists a second issue with the Bruker solar tracker A 547 specific to latitudes close to the equator. The tracker has two so-called flip states to ensure that it can target every point of the sky irrespective of the azimuth position of the sun. The offset angles indicating the offset between the true geographical north and $0^\circ$ local position have to be adjusted for each flip state individually. These values are needed by the software of the solar tracker to transfer from the local coordinates of the two tracker axes to the absolute geographical coordinates. Ideally, the solar tracker base should be oriented such that the elevation mirror points roughly to the azimuth direction of the sun at noon to ensure a continuous tracking of the sun from sunrise to sunset without changing the flip state (see Bruker (2005), Solar Tracker A 547 - Accessory Manual, page 17). On Ascension, no such orientation of the tracker base is possible that would be valid throughout the whole year, as the sun passes over the tracker in the northern direction between March and mid-October and as it passes over in the southern direction between mid-October and the end of February. This results in a necessary change of the flip states during the day at least in some months of the year. It is difficult to achieve a good alignment of the tracker and its corresponding offset angles for both flip states at the same time. As a result, the tracker is sometimes not able to track the sun correctly even in good weather conditions because the alignment in one of the two flip states is not sufficient. During site visits, the offset angles were typically set for a good alignment of the tracker in the morning. However, the offset angle values were often not ideal in the afternoon and much less so for other days in the year.

Here, an attempt is made to quantify the problem with the guiding question: How often were there no measurements even though the conditions should have allowed for solar measurements? This was investigated by comparing the integrated signal of
the quadrant diode of the tracker with the direct solar radiation measurements taken at the weather station of the container. For the year 2015, a year with a good data coverage in general, isolated events where the tracker was not able to track properly were identified. To find such events, the following threshold was defined: the direct solar radiation within one hour had to be larger than 200 W/m² and the standard deviation of this quantity had to be smaller than 80 W/m², indicating stable and almost clear sky conditions. At the same time, the integrated signal of the quadrant diode was checked for hourly intervals. Values close to zero were regarded as a sign of no measurements. The results for 2015 are shown as a bar plot in Fig. 3.7. The number of events with no measurements is significantly larger around noon and in the afternoon, as the tracker and the offset angles for the software were adjusted in the morning. A possible solution for both tracker issues would be upgrading to a Camtracker system as described by Gisi et al. (2011). However, this is a costly addition to the system and it is not straightforward to find a good place for positioning.

Figure 3.7: Bar plot of events in 2015 where no measurements have been taken even though direct solar radiation measurements indicate good weather conditions, binned into hourly time intervals. There are significantly more such events around noon and in the afternoon. The alignment of solar tracker is best in the morning.
the camera in the source chamber of the FTS. Besides, the mechanical limitations of the tracker would still remain.

**Increasing leak rate of the FTS**

The instrument is operated under vacuum. It is evacuated with a rotary vacuum pump for 60 minutes every morning as part of its wake-up cycle before regular measurements start. Typical pressure values of around 0.05 hPa are reached at the end of the pumping. Figure 3.8 shows a time series of the calculated leak rate of the FTS. The leak rate of the instrument has been between approx. 0.1 hPa/hour and 0.7 hPa/hour since the beginning of taking measurements on Ascension. Already during a test campaign in Australia in 2010 it has been discovered that the leak rate increased over the course of the campaign. Until now, it is not clear why the leak rate increases over time. In an attempt to solve the problem, most O-ring seals on the chamber lids were changed on March 30, 2014. Only the seal of the small lid directly above the beam splitter was not replaced. This had little influence on the leak rate as one can see from Fig. 3.8. Despite this varying leak rate, it is assumed that no significant spectral contamination with water vapor occurs, as the absolute pressure inside the instrument at the end of a measurement day is still low.

![IFS125HR leak rate over time](image)

**Figure 3.8:** Leak rate of the FTS instrument. Red vertical lines indicate when the instrument was opened, dotted green lines indicate when the instrument was vented.
3.5 Automatisation and Performance of the Instrument

3.5.1 Data Acquisition, Processing and Filtering

Automated regular solar measurements on Ascension Island started on May 22, 2012. The acquisition of the data is automated accordingly to the concept detailed in Geibel (2011). The acquired interferograms are stored locally on a RAID system. As explained in Sect. 3.4.1, the transfer of the data from Ascension to Jena, Germany, where the final processing of the data is performed, was modified over the course of the project. After initially sending data tapes by post, from August 2016 it became possible to transfer all relevant data via internet by using a satellite link. To be able to transfer all data within the allowed volume of approx. 30 to 35 GB (regular 10 GB per month plus 20 to 25 GB at night per month at no charge, see Sect. 3.4.1), it became necessary to introduce a prefiltering of the data. Moving the initial post-processing and quality checking to Ascension and additional time-consuming compression of the data reduced the transferred data volume by about 30%. Measurements with poor tracking quality are discarded on site and are never downloaded to the server in Jena. In this context, poor tracking means that the solar tracker is in its active tracking mode less than 90% of the time needed for recording one measurement because the intensity of the signal on the quadrant diode dropped below the threshold to track the sun properly.

On average, 60-80 measurements can be transferred online per day. The number of measurements is between 0 and 180 per day. A backlog of several days may build up during good measurement periods. This backlog of data has to be transferred during periods with fewer measurements, for example due to bad weather or downtimes.

Figure 3.9 illustrates the three different steps of the data filtering. It also shows how many measurements pass the individual steps of the data processing and quality checking. Numbers were calculated for all data recorded between starting measurements on Ascension in May 2012 and the end of the year 2017. In total, more than 30% are already rejected within the first quality check performed on site and approximately 41% of recorded interferograms are transferred into valid TCCON data.

Since the beginning of performing TCCON measurements on Ascension, several longer time periods occurred where no data could be acquired due to instrument failures. The remote location of Ascension often made it difficult to react quickly to major problems of the instrument. Table 3.1 lists all periods lasting longer than 30 days.
Figure 3.9: Histogram showing the different amounts of measurements filtered out by the various steps of the acquired quality checks from May 2012 until the end of the year 2017. The left bar indicates that approximately 66% of the measurements pass the first quality check on Ascension. Those measurements are transferred to the server in Jena. Almost 31% of the measurements are discarded due to poor tracking. The bar in the middle shows how many data are filtered within the process of calculating spectra from the interferograms with the program called I2S (interferogram-to-spectrum). Approximately 5% of the data is discarded because the averaged solar intensity (SIA) is below a given, tracker-specific threshold which indicates reasonably stable clear sky conditions. The right bar indicates that about 41% of all recorded measurements are transferred into valid TCCON data and approximately 19% are flagged as invalid during the final, stringent post-processing within the software suite GGG.

3.5.2 Stability of the FTS on Ascension Island

A well aligned FTS instrument is crucial for retrieving $X_{gas}$ with high precision and accuracy. The FTS instrument on Ascension was initially aligned in May 2012 after its deployment on the island. To monitor the alignment and stability of the instrument, regular measurements of a gas cell filled with HCl at a low pressure of approximately 5 hPa have been conducted. The theoretically expected absorption lines within the spectrum are well-defined. They can be calculated from known pressure and temperature of the gas cell. A constrained fit of parameters describing the modulation efficiency of the FTS is performed to match the absorption lines observed
Table 3.1: Downtimes of instrument lasting longer than 30 days. The last column in the table gives some details regarding the technical problems which caused the downtimes.

<table>
<thead>
<tr>
<th>#</th>
<th>Date</th>
<th>Duration</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2012-09-01 to 2013-03-16</td>
<td>197 days</td>
<td>1st set of mirrors destroyed; solar tracker failure</td>
</tr>
<tr>
<td>2</td>
<td>2013-06-29 to 2013-09-10</td>
<td>74 days</td>
<td>2nd set of mirrors destroyed</td>
</tr>
<tr>
<td>3</td>
<td>2014-02-21 to 2014-03-27</td>
<td>35 days</td>
<td>solar tracker failure</td>
</tr>
<tr>
<td>4</td>
<td>2014-04-30 to 2014-06-20</td>
<td>52 days</td>
<td>laser failure</td>
</tr>
<tr>
<td>5</td>
<td>2015-12-19 to 2016-08-13</td>
<td>239 days</td>
<td>short circuit in the weather station followed by major problems of the Programmable Logic Controller (PLC)</td>
</tr>
<tr>
<td>6</td>
<td>2017-02-18 to 2017-08-03</td>
<td>167 days</td>
<td>worn-out belts of the dome needed to be replaced; solar tracker failure</td>
</tr>
</tbody>
</table>

In the measured cell spectrum. Then, the actual instrumental line shape (ILS) of the spectrometer is calculated from the modulation efficiency of the interferogram. Within TCCON, the retrieval code LINEFIT (Hase et al., 1999) is used for determining the modulation efficiency and the phase error. Both are indicators for the alignment quality of the FTS.

In the case of a perfectly aligned FTS, modulation loss only happens through inherent self-apodization of the spectrometer which is a result of the finite field of view (FOV) and the limited optical path difference. The ILS is a convolution of a sinc function and a rectangular function where the sinc function originates from the finite length of the interferogram and the rectangular function originates from the finite FOV of the FTS in the interferogram domain (see e. g. Davis et al. (2001), chapter 5). In case of misalignment, an additional component of the ILS is present due to the misalignment and optical aberrations of the spectrometer. As explained before, this additional component can be characterised by the modulation efficiency amplitude, which is related to the width of the ILS, and the modulation efficiency phase error, which quantifies the degree of ILS asymmetry (Hase et al., 2013). Both parameters can be retrieved from gas cell measurements.

The modulation efficiency and the phase error as a function of the optical path difference (OPD) for the FTS on Ascension are shown in Fig. 3.10. The TCCON data protocol allows for a variation of up to 5% in the modulation efficiency amplitude over the full OPD (Wunch et al., 2015) and a phase error exceeding not more than ± 0.04 rad is acceptable (Buschmann, 2018). In Fig. 3.10, the accepted range for the modulation efficiency as well as for the phase error according to the TCCON requirements are marked by white areas and gray bars mark the ranges where these limits are exceeded. The FTS on Ascension has fulfilled the TCCON requirements.
Figure 3.10: Modulation efficiency and phase error retrieved with LINEFIT version 14.5 from HCl cell gas measurements. Both quantities are indicators for the stability of the FTS on Ascension between May 2012 and August 2016. The dates of the individual gas cell measurements are color coded (see color bar on the right side of the figure).

since the beginning of the measurements in May 2012 and the instrument can be considered as a well aligned FTS. The increase in modulation efficiency with OPD indicates that the instrument suffers from a slight shear misalignment as overmodulation is an indicator for shear misalignment. Note that the modulation efficiency is normalized to 1.0 at zero OPD so that the ILS is area-normalized in the spectral domain (Hase et al., 2013).

3.6 Summary

The measurement site on Ascension was described and the atmospheric transport and dynamics around the island were investigated with the HYSPLIT model to be able to put the TCCON measurements into a larger context with respect to specific transport patterns around Ascension. Most striking in this context are the south easterly trade winds which transport relatively clean air from the remote Southern Atlantic to Ascension close to the surface all year round. Modifications from the initial setup of the system were specified. These adjustments mainly apply to the
solar tracker, which was equipped with stainless steel mirrors to withstand the harsh environment on Ascension, and the handling and transferring of the data, which was optimized to take into account the conditions offered by such a remote location. Furthermore, technical issues which are specific to the installation of the container on Ascension were detailed. Two of these issues are related to the fact that Ascension is close to the equator and the instrument therefore faces high solar zenith angles (SZAs) up to 90° in two periods of the year. Finally, the alignment and stability of the FTS were monitored with regular gas cell measurements and the measurements were analyzed with the retrieval code LINEFIT. The instrument proves to be well aligned within the TCCON requirements.
Chapter 4

Five Years of TCCON Observations on Ascension Island

4.1 Introduction

Measurements of $X_{\text{CO}_2}$, $X_{\text{CH}_4}$, and $X_{\text{CO}}$ sample a larger portion of the atmosphere than in situ measurements performed at the surface. They are also much less affected by spatial and temporal variability compared to surface in situ data which are heavily influenced by both, the exchange of carbon between the surface and the atmosphere as well as atmospheric transport on different time scales. Therefore total column measurements can help to separate the effects of atmospheric mixing from the surface exchange and to improve atmospheric transport models (Gerbig et al., 2008). As they are also very precise and accurate, ground-based total column measurements serve as the primary validation data set for space-borne measurements of the same quantity (e.g. Wunch et al. (2011b); Butz et al. (2011); Guerlet et al. (2013); Schepers et al. (2016); Inoue et al. (2016); Wunch et al. (2017)).

Within my PhD project, spectra were recorded at the TCCON site on Ascension since May 2012 and the retrieved time series of $X_{\text{CO}_2}$, $X_{\text{CH}_4}$, and $X_{\text{CO}}$ are presented here. The following chapter begins with describing the calibration of the TCCON station on Ascension with aircraft profile data. Then the time series of $X_{\text{CO}_2}$, $X_{\text{CH}_4}$, and $X_{\text{CO}}$ measured between May 2012 and December 2016 are introduced briefly. A more detailed investigation regarding the time series of $X_{\text{CO}_2}$ including a comparison with in situ data and model data from the Jena CarboScope is presented thereafter. Finally, the time series of $X_{\text{CO}_2}$ from Ascension and 24 other TCCON sites are compared to space-borne measurements made by OCO-2. This comparison also includes the application and performance check of three different methods for collocating ground-based measurements of $X_{\text{CO}_2}$ with those of OCO-2.
4.2 Calibration of the Ascension Island TCCON Station with aircraft data

Due to spectroscopic uncertainties, TCCON measurements need to be calibrated with respect to accurate and precise in situ measurements conducted onboard aircrafts or with AirCore sampling systems (Karion et al., 2010). Such aircraft calibrations have been made by Wunch et al. (2010), Messerschmidt et al. (2011) and Geibel et al. (2012). Calibration with very accurate and precise in situ measurements is the ideal for all sites within TCCON to provide site-to-site consistency of the data. Sampling of profiles close to the TCCON site on Ascension took place in the framework of the Atmospheric Tomography Mission (ATom).‡ Within this aircraft campaign profiles are collected over the Pacific and Atlantic Ocean basins during different seasons of the year to learn more about the impact of anthropogenic air pollution on GHGs and on chemically reactive gases. Some of these aircraft data have been used to add the TCCON site on Ascension to the calibration curves for $X_{\text{CO}_2}, X_{\text{CH}_4}$ and $X_{\text{CO}}$. In the following the data are described in detail and results are presented.

TCCON data from our instrument (Feist et al., 2014) for 2016-08-15 and 2016-08-17 have been compared to data from ATom-1. In total, two profiles measured with a Picarro (type: modified G2401m) operated by the NOAA/Earth System Research Laboratory could be used for the comparison. Details regarding both profiles are summarized in Table 4.1.

<table>
<thead>
<tr>
<th>Date</th>
<th>Species</th>
<th>Altitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 15, 2016</td>
<td>CO$_2$, CO, CH$_4$</td>
<td>0.0 - 12.6 km</td>
</tr>
<tr>
<td>August 17, 2016</td>
<td>CO$_2$, CO, CH$_4$</td>
<td>0.0 - 10.1 km</td>
</tr>
</tbody>
</table>

Figure 4.1 shows the profile for all three species measured during the descent before landing on Ascension on August 15, 2016 in the evening (approx. 19:30 until 20:00 UTC). The ascent after leaving Ascension again on August 17, 2016 in the morning (between 8:00 and 8:30 UTC) is shown in Fig. 4.2. Steep gradients around 1500 to 1700 m for the profile measured in the morning and between 1900 and 2200 m for the profile measured in the evening indicate the mixing height covering the marine boundary layer (MBL). The mixing height is slightly higher for the profile measured

‡ https://espo.nasa.gov/atom/, last access: 2018-06-27
Figure 4.1: Profiles measured by the Picarro during the last descent before landing on Ascension on the evening of August 15, 2016 for CO₂ (black), CH₄ (red) and CO (blue).

later during the day because the MBL grows deeper throughout the day due to turbulence driven by solar radiation. In Fig. 4.2 elevated signals for all three species between 2100 and 4000 m are very pronounced and indicate a layer carrying biomass burning signals from Africa. Striking in both figures are increased CH₄ values in the free troposphere compared to the values in the MBL. This phenomenon is driven by different transport patterns below and above the trade wind inversion (see Sect. 3.3) and it is described in detail in Brownlow et al. (2016).

4.2.1 Assessment of Collocation

Due to clouds on both days and the arrival time of the aircraft the time overlap between the aircraft profiles and the TCCON data has not been ideal. For a meaningful comparison quite a loose coincidence criteria has been allowed. For August 15, 32 individual spectra measured approx. 2.5 to 4 hours prior the end time of the profile have been used and for August 17, 8 individual spectra measured approx. 2.5 to 3 hours later than the end time of the profile have been used. More information regarding the chronology of the FTS measurements and the aircraft profiles is displayed in
4.2 Calibration of the Ascension Island TCCON Station with aircraft data

Figure 4.2: Profiles measured by the Picarro during the first ascent after leaving Ascension in the morning of August 17, 2016 for CO$_2$ (black), CH$_4$ (red) and CO (blue).

Fig. 4.3 and Fig. 4.4. The spatial coverage of the aircraft profiles can be seen in the three-dimensional Fig. A.1 (descent) and Fig. A.2 (ascent) in Appendix A. Allowing such a loose coincidence criteria seems to be reasonable for Ascension Island where diurnal variations are very small. Variations in the measured signals occur due to synoptic scale transport and happen on larger time scales. There are no large sources or sinks in the near field.

A comparison between data from radiosonde launches with data from ATom-1 supports the validity of such a loose coincidence criteria. In the framework of the Layered Atlantic Smoke Interactions with Clouds (LASIC) campaign a mobile Atmospheric Radiation Measurement (ARM) facility has been deployed on Ascension from 1 June 2016 to 31 October 2017 (Zuidema et al., 2016). Multiple radisondes have been launched per day (Holdridge et al., 2016). Data from launches closest to the aircraft profiles have been compared to measurements onboard ATom-1. Figure 4.5 shows how the H$_2$O volume mixing ratio (VMR) from ATom-1 measured with a diode laser hygrometer compares to data from two radiosondes launched closest to the time of the aircraft profile taken during the descent of the aircraft. Altogether
Figure 4.3: Timing of the aircraft profile measured during descending to Ascension and the TCCON measurements. The vertical black lines indicate the times of FTS measurements used for the comparison to the aircraft data. The last FTS measurement was taken at approx. 17:20 UTC. There is a break in the x-axis due to the time gap between the last FTS measurement and the start of the aircraft profile. Aircraft data are shown as blue dots.

Figure 4.4: Timing of the aircraft profile measured after leaving Ascension and the TCCON measurements. Aircraft data are shown as blue dots. The vertical black lines indicate the times of FTS measurements used for the comparison to the aircraft data. Similar to Fig. 4.3, the break in the x-axis indicates that there is a time gap between the end of the profile and the first FTS measurement symbolized by the first vertical black line at approx. 11:26 UTC.
Figure 4.5: Comparison between H$_2$O VMR from the NCEP/NCAR reanalysis, aircraft measurements and radiosonde data for August 15, 2016 (descent). Light blue dots show the radiosonde profile from the sonde launched at 17:50 UTC, black dots indicate data from the sonde launched at 20:29 UTC. Aircraft data are represented with red stars connected by a red line. Data from the NCEP/NCAR reanalysis are indicated by purple dots connected by a purple line.

aircraft and sonde data agree well. A sudden decline from approximately 15000 ppm to about 4000 ppm at 1500 m and a less pronounced drop from 4000 ppm to only several 100 ppm at 2000 m are visible in the aircraft data as well as in the sonde data. These steps match very well with the layering structure of the trace gases which can be seen in Fig. 4.2. For reference, the water profile from the NCEP/NCAR reanalysis closest to the aircraft profile is also shown. It matches the general shape of the measured profiles but the resolution is not sufficient to represent the variations on small spatial scales. The same comparison has been performed for the data of the aircraft profile taken during the ascent and data from radiosondes closest to the start of the aircraft. Findings are very similar, H$_2$O VMR from ATom-1 agrees well with radiosonde data also for that time period.
4.2.2 Data Analysis

Measurements performed onboard aircraft or with AirCore sampling systems cannot be compared directly to measurements of $X_{gas}$ performed by an FTS as they do not cover the same part of the atmosphere. While an FTS measures the whole atmosphere and delivers the total column $X_{gas}$ as final data product, aircraft measurements observe only a partial column of the atmosphere. Therefore those profiles have to be extended. For the profiles measured close to Ascension Island it is only necessary to extend the part above the aircraft ceiling as both profiles reach the ground. For this extension to the top of the atmosphere the a priori profiles of GFIT have been used (see Wunch et al. (2011a) and Wunch et al. (2015) for details on how the a priori profiles are calculated for the various species). Rodgers and Connor (2003) were the first describing how to compare measurements from two instruments while taking the differing characteristics of the observing systems into account. Wunch et al. (2010) adapted this approach for comparison of in situ aircraft profiles and FTS data (Wunch et al. (2010), their Eq. 3):

$$\hat{c}_s = \gamma c_a + a^T(x_h - \gamma x_a)$$

(4.1)

where $\hat{c}_s$ is the smoothed column-averaged DMF of the aircraft, $\gamma$ is the FTS retrieval scaling factor and $c_a$ is the FTS a priori column-averaged DMF. The vector $a$ contains the FTS dry pressure-weighted column averaging kernel, the vector $x_h$ is the extended aircraft profile and the vector $x_a$ describes the FTS a priori profile.

As mentioned in Sect. 2.3.3 GFIT is a scaling retrieval which calculates the averaging kernels for the scaled solution mole fraction profile. Hence, the linearization point of the Taylor expansion which yields Eq. 4.1 is $\gamma x_a$ and not $x_a$. According to Wunch et al. (2010) the vertical integration of the profiles is done most accurately on a pressure grid and by assuming that the atmosphere is in hydrostatic balance. Furthermore, the column averaging kernels have to be taken into account. Ultimately, the equation for the aircraft-derived $X_{gas}$ becomes:

$$\hat{c}_s = \gamma \frac{V C_{a \text{ priori}}_{gas}}{V C_{\text{dry air}}} + \left( \frac{V C_{\text{aircraft}}_{gas,ak} - \gamma V C_{\text{a priori}}_{gas,ak}}{V C_{\text{dry air}}} \right)$$

(4.2)

where $\hat{c}_s$ is the smoothed column-averaged DMF of the aircraft, $\gamma$ is the FTS retrieval scaling factor, $V C_{\text{dry air}}$ is the total column of dry air, $V C_{\text{a priori}}_{gas,ak}$ is the column averaging kernel-weighted vertical a priori and $V C_{\text{aircraft}}_{gas,ak}$ is the column averaging kernel-weighted vertical column of the aircraft.
4.2.3 Error Sources and Uncertainties

The uncertainty of the FTS measurements is the standard deviation of all measurements used in the comparison. The uncertainty of the aircraft measurements is a combination of the uncertainties of the in situ measurements conducted onboard the aircraft and the uncertainty due to the unknown gas profiles above the aircraft ceiling. For the aircraft data, twice the uncertainties provided by the NOAA/Earth System Research Laboratory after the post-flight analysis have been applied: CO₂: $2\sigma = 0.2$ ppm, CH₄: $2\sigma = 1.4$ ppb, CO: $2\sigma = 7.2$ ppb.

Above the aircraft ceiling two different sources of uncertainties exist. One is the uncertainty regarding the stratospheric profiles of the gases. The other is introduced by the part of the troposphere which is not covered by the aircraft. It is important to account for the fact that the tropopause on Ascension Island is high with typical values of around 16-17 km and only small variations of the tropopause height can be found in the tropics in general (Seidel et al., 2010). This means that only the lower three quarters regarding the height (descent) respectively only the lower two thirds regarding the height (ascent) of the whole troposphere has been covered by the aircraft during ATom-1. Since the density of the molecules decreases with altitude according to the barometric formula, the relative error contribution, $u_{rel}$, of the unmeasured part of the troposphere is nevertheless smaller than the uncertainty introduced by the aircraft data, see also Table 4.2.

To correctly extend the aircraft profiles above the aircraft ceiling several processing steps need to be applied. Firstly, temperature profiles from the two radiosonde launches being closest in time to the aircraft profiles have been used to correct the tropopause height calculated by the software GFIT. For the descent a shift of the tropopause of 300 meters upwards and for the ascent a shift of 180 meters upwards have been calculated. The a priori profiles have been corrected for the new tropopause heights before being used for the stratospheric extension of the aircraft profiles. Secondly, median values for each species have been calculated for the free troposphere. Measurements starting at a pressure of 600 hPa to the aircraft ceiling were used to calculate the medians. Those median values have been used to extend the aircraft profiles to the tropopause. The standard deviation of each set of data between 600 hPa and the aircraft ceiling has been used to estimate the uncertainty attributed to the extension of the aircraft profiles to the tropopause by medians. Thirdly, a priori profiles corrected for the true tropopause height have been used for the stratospheric extension of the profiles. Appendix A contains all extended aircraft profiles used for the calibration (see Fig. A.3 to Fig. A.8).
The stratospheric uncertainty for CO\(_2\) is calculated according to Wunch et al. (2010) who assumed the a priori profile used for the extension above the aircraft ceiling to be precise to 0.3\%. Furthermore, a 1 km shift is introduced. In total, the stratospheric error for CO\(_2\) is the sum, in quadrature, of shifting the a priori profile up by 1 km and adding a 0.3\% error. The stratospheric error for CO is calculated in the same way but with a much higher error of 12.5\% which is an estimation from ACE-FTS measurements (Clerbaux et al., 2008) because CO is highly variable. For CH\(_4\), the total stratospheric error is the sum, in quadrature, of a 1 km shift of the a priori and adding a conservatively estimated error of 2.0\%. The full error budget is summed up in Table 4.2.

**Table 4.2:** Aircraft integration error budget. This table lists all absolute and relative error contributions. The absolute error \(u_{abs}\) of the aircraft is twice the uncertainties of the aircraft measurements provided by the NOAA/Earth System Research Laboratory after post-flight analysis. The relative error contribution \(u_{rel}\) is estimated by adding the absolute error to the profile and re-integrating it. The absolute error \(u_{abs}\) for the unmeasured part of the troposphere is the standard deviation of all values used for the calculation of median value with which the profile is extended in the troposphere. The relative error contribution \(u_{rel}\) is calculated in the same way as with the aircraft data. The absolute error is added to the profile and then it is re-integrated. The relative contribution of the stratospheric uncertainty is calculated slightly different for all three gases. Details are described in Sect. 4.2.3. The total error is the square root from the sum of the squares of the relative errors \(u_{rel}\).

<table>
<thead>
<tr>
<th>profile</th>
<th>species</th>
<th>aircraft data</th>
<th>unknown part troposphere</th>
<th>stratospheric extension</th>
<th>total error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO(_2)</td>
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<td>0.2 ppm</td>
<td>1.2 ppm</td>
<td>0.1 ppm</td>
</tr>
<tr>
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<td>5.4 ppb</td>
<td>18.1 ppb</td>
<td>2.7 ppb</td>
</tr>
<tr>
<td></td>
<td>CH(_4)</td>
<td>1.4 ppb</td>
<td>1.1 ppb</td>
<td>9.9 ppb</td>
<td>1.0 ppb</td>
</tr>
<tr>
<td>descent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO(_2)</td>
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<td>0.1 ppm</td>
<td>0.8 ppm</td>
<td>0.2 ppm</td>
</tr>
<tr>
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<td>4.5 ppb</td>
<td>11.6 ppb</td>
<td>3.0 ppb</td>
</tr>
<tr>
<td></td>
<td>CH(_4)</td>
<td>1.4 ppb</td>
<td>0.9 ppb</td>
<td>8.4 ppb</td>
<td>1.7 ppb</td>
</tr>
</tbody>
</table>

### 4.2.4 Results

Results of the comparison between aircraft and FTS data are presented and updated versions of the various calibration curves are shown. The fitting is performed with a linear least-squares fitting algorithm and a zero intercept is forced because the GGG retrieval is assumed to be both linear and have a zero ordinate intercept (Wunch et al., 2010). Figure 4.6 shows the calibration curve for \(X_{CO\_2}\). Measurements from Ascension are perfectly in line with the rest of the data. The resulting calibration factor is \((0.9897\pm0.0004)\ ppm\) which is exactly the result presented by Kiel et al. (2016).
4.2 Calibration of the Ascension Island TCCON Station with aircraft data

Figure 4.6: Update of the standard TCCON calibration curve for $X_{\text{CO}_2}$ as presented earlier (and with fewer data) in Wunch et al. (2010) and Messerschmidt et al. (2011) including measurements from Ascension Island.

The same holds for the calibration curve for $X_{\text{CH}_4}$ shown in Fig. 4.7. Likewise, the result of $(0.976 \pm 0.001)$ ppb is in perfect agreement with what has been published by Kiel (2016).

For $X_{\text{CO}}$ the results for fitting of the calibration curves differ slightly which can be seen in Fig. 4.8. The result for the calibration factor without measurements from Ascension is $(1.068 \pm 0.030)$ ppb (black line). Adding data from Ascension Island changes the result to $(1.066 \pm 0.029)$ ppb (dashed line in cyan). Both results agree well within the errors and the overall difference for the resulting $X_{\text{CO}}$ is smaller than 0.5 ppb (estimated with an assumed high $X_{\text{CO}_2}$ of 200 ppb).

Measurements of $X_{\text{gas}}$ made on Ascension in the framework of TCCON have been compared to data from the ATom-1 mission. The different data sets agree very well within the uncertainty ranges. Adding data from Ascension to the calibration curves has not influenced the calibration factors for $X_{\text{CO}_2}$ and $X_{\text{CH}_4}$ at all. The calibration
Chapter 4. Five Years of TCCON Observations on Ascension Island

Figure 4.7: Update of the standard TCCON calibration curve for $X_{CH_4}$ as presented earlier (and with fewer data) in Wunch et al. (2010) and Geibel et al. (2012) including measurements from Ascension Island.

factor for $X_{CO}$ changed from $(1.068 \pm 0.030)$ ppb without data from Ascension to $(1.066 \pm 0.029)$ ppb. The calibration of TCCON data from Ascension Island with aircraft data from ATom-1 led to an upgrade of the site to a TCCON site with full TCCON status in May 2017. Finally, it should be noted that AirCore (Karion et al., 2010) measurements on Ascension Island would be a good additional source for profiles. With AirCore measurements, it is possible to sample the atmosphere up to an altitude of approx. 30 km. A long stainless steel tube is filled with ambient air as it descends from high altitudes. The layered structure of the air in the tube remains stable and so atmospheric profiles can be retrieved when analyzing the collected air in a laboratory. As the tropopause is high on Ascension (approx. 16-17 km), research aircraft are not able to cover the full troposphere. Fully coverage of the troposphere and sampling into the stratosphere could only be reached with AirCore measurements.
4.3 Time Series of $X_{\text{CO}_2}$, $X_{\text{CH}_4}$ and $X_{\text{CO}}$

In this section the time series of $X_{\text{CO}_2}$, $X_{\text{CH}_4}$ and $X_{\text{CO}}$ are introduced briefly. A comparison of $X_{\text{CO}_2}$ to flask data and data from the Jena CarboScope and an in depth discussion of the results follow in Sect. 4.4. $X_{\text{CH}_4}$ is compared to other data sets at length in Chapter 5 and the chapter is complemented by a detailed discussion and interpretation of the results. Eventually, $X_{\text{CO}}$ is discussed in the context of biomass burning in Chapter 6.

All data from the Ascension Island TCCON station presented in this work (Feist et al., 2014) have been retrieved with the software GGG2014 (Wunch et al., 2015). Details on the retrieval process can be found in Sect. 2.3.3 and the acquisition, processing and filtering of the spectra are described in Sect. 3.5.1.

Figure 4.9 shows the time series of daily medians for $X_{\text{CO}_2}$ measured on Ascension Island between May 2012 and December 2016. To isolate the trend and the seasonal

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**Figure 4.8:** Update of the standard TCCON calibration curve for $X_{\text{CO}}$ as presented earlier (and with fewer data) in Wunch et al. (2010) including Ascension Island.
Figure 4.9: Time series of daily medians of $X_{CO_2}$ retrieved from the FTS on Ascension Island. Blue circles show the calculated daily medians. The orange curve is a fit to the data.

cycle of the record, a simple function has been fitted to the daily medians of the time series:

$$X_{gas}(t) = a + b \cdot t + c \cdot \sin(2\pi(t + d)) + e \cdot \sin(4\pi(t + f))$$

Here, $a$ is a constant term, the offset at the beginning of the time series, $b$ is the linear trend, $c$ and $e$ are the amplitudes of the two harmonics and $d$ and $f$ allow for a phase shift.

The calculated growth rate for the complete time series of $X_{CO_2}$ is 2.4 ppm/year. That is in agreement with Dlugokencky and Tans (2017). Since Ascension Island is in the tropics and relatively close to the equator the instrument samples air masses from both hemispheres. Furthermore, the island is far away from strong sources and sinks for $CO_2$. In total, this makes it difficult to determine a clear seasonal cycle for $CO_2$. Compared to NH TCCON sites such as Park Falls and Bialystok, where seasonal cycle amplitudes can be up to approx. 9 ppm (Keppel-Aleks et al., 2012), the seasonal cycle is small on Ascension with an amplitude of approx. 2.5 ppm. Additionally, interannual variability seems to obscure the weak seasonal cycle. The small seasonal variability is in good agreement with Deutscher et al. (2014). They investigate the variability of $X_{CO_2}$ at the three SH TCCON stations Darwin, Wollongong and Lauder. Ascension Island seems to have a similar mean seasonal cycle as Darwin which is reasonable as both stations are close in latitude: Ascension is located...
at 7.92°S and Darwin at 12.4°S. The seasonal cycle shows a minimum in February and maximum in June. Another small minimum occurs in September followed by another less pronounced maximum in December. This bimodal seasonality is driven by signals from both hemispheres. The NH flux minimum is transported southwards and results in a small minimum in September. The minimum in February is produced by the biosphere in austral summer, see also Sect. 4.4.

The time series for $X_{\text{CH}_4}$ is shown in Fig. 4.10. The same fit function as described by Eq. 4.3 was used to derive a mean growth rate of 7.0 ppb/year for the time period between May 2012 and December 2016. In general, the annual global growth rate of CH$_4$ experiences much more variability than that of CO$_2$. According to Dlugokencky (2018), the global growth rate of CH$_4$ for the considered time period varied between 4.66 ppm in 2012 and an extreme growth of 12.5 ppb in 2014 being the largest growth rate in more than two decades. The seasonal cycle of $X_{\text{CH}_4}$ shows a bimodal seasonality with two maxima, one in February and one in September. This is caused by the reaction of CH$_4$ with hydroxyl (OH) radicals and long-range transport of CH$_4$ emissions. A detailed discussion on the seasonal cycle of $X_{\text{CH}_4}$ in comparison to in situ data can be found in Sect. 5.3.

Figure 4.11 shows the time series of $X_{\text{CO}}$ with a large dynamic range from 60 ppb up to approx. 125 ppm. Again, a fit function according to Eq. 4.3 was applied and two
clear maxima could be identified per year which have their origin in biomass burning occurring on the African continent. Chapter 6 contains a comprehensive discussion of $X_{CO}$ in the context of biomass burning.

### 4.4 $X_{CO_2}$ Time Series in Comparison to Flask Data and Data Retrieved by the Jena CarboScope

To investigate the variations seen in $X_{CO_2}$ on Ascension Island, the TCCON measurements have been compared to in situ measurements and CO$_2$ model results from the Jena CarboScope version s04_v3.8. Data from flask measurements are made available by NOAA (Dlugokencky et al., 2015b). In cooperation with the Met Office (United Kingdom), NOAA takes flask samples at the Wideawake airfield located at the south west of the island (7.97°S, 14.40°W, 87 m.a.s.l.) twice per week. The distance to the location of the TCCON measurements is 9.6 km.

A comparison between the mean CO$_2$ VMR of each flask pair and daily medians of $X_{CO_2}$ is shown in Fig. 4.12. Additionally, the same fitting method which has already been explained and used in Sect. 4.3 has been applied to the data. Fit functions including a constant term, a linear term and two harmonics have been fitted to the

![Figure 4.11: Time series of daily medians of $X_{CO}$ retrieved from the FTS on Ascension Island. Blue circles show the calculated daily medians. The orange curve is a fit to the data.](image-url)
daily median column values respectively to the mean of each flask pair. The main findings of this comparison are that the seasonal cycle of the in situ data is slightly smaller than that of the total column and its phase is shifted. The corresponding fit parameters according to Eq. 4.3 indicate a positive shift of three months. The seasonal amplitude of CO$_2$ measured on the surface is only approx. 2.0 ppm compared to an amplitude of approx. 2.5 ppm in the total column. The seasonal cycle of the flask data seems to be driven mainly by the SH land biosphere. The land mass in the SH is much smaller than in the NH and hence the contribution of the land biosphere to the seasonal cycle of CO$_2$ is smaller in this hemisphere.

The seasonal cycle of the in situ data has a minimum at the beginning of austral fall (March) and a period of elevated CO$_2$ in austral winter and austral spring (July to December). From approximately March to roughly July the concentration of CO$_2$ is smaller close to the surface than in the total column. The reason for this difference between in situ and total column measurements is caused by the higher CO$_2$ concentrations in the NH at the end of the NH winter. Air masses with higher CO$_2$ concentrations are transported southwards in higher altitudes due to the Hadley circulation (Sect. 3.3), see also individual subfigures of Fig. 4.16. Furthermore, the bimodal seasonality is much more apparent in the total column. In summary, Fig. 4.12 shows

![Figure 4.12: Time series of daily medians of $X_{\text{CO}_2}$ retrieved from the FTS on Ascension Island (light blue open circles) and means of flask pairs taken on Ascension Island (orange open circles). A blue line indicates a fit to the FTS data, a red line to the flask data.](image-url)
nicely how the surface layer is constrained by the SH while the total column is influenced by both hemispheres.

In the following subsection the FTS time series is compared to analyzed CO₂ fields based on TM3 model simulations using optimized fluxes from the Jena CarboScope inversion version s04_v3.8 (Rödenbeck, 2005). The Jena CarboScope is a Bayesian inversion framework. It serves to estimate trace gas fluxes at the surface of the Earth from measured mixing ratios of these gases and with knowledge and assumptions regarding atmospheric transport. Within the Jena CarboScope this transport is simulated by the global atmospheric tracer model TM3 (Heimann and Körner, 2003). All model simulations used or carried out within this thesis have been performed with a spatial resolution of approximately 4° in latitude by 5° in longitude with 26 vertical levels. ERA-Interim (European Centre for Medium-Range Weather Forcasts, ECMWF, Reanalysis) meteorological fields have been used to drive TM3.
Figure 4.14: Scatter plot showing $X_{\text{CO}_2}$ from TCCON versus $X_{\text{CO}_2}$ from Jena CarboScope.

For an accurate comparison between ground-based column measurements and model simulations the same mathematical approach is needed which has been explained in Sect. 4.2 regarding the comparison between aircraft measurements and total column measurements. This so-called smoothing follows the formulation of Rodgers and Connor (2003), Connor et al. (2008) and Wunch et al. (2010) and takes the TCCON a priori and averaging kernel into account. The smoothed $X_{\text{CO}_2}$ can be calculated by adding the column integrated a priori profile $c_a$ to the difference between model $x$ and TCCON a priori $x_a$ dry-air mole fractions weighted with the averaging kernel $a$ and the pressure weighting function $h$ defined in Connor et al. (2008):

$$c_s = c_a + h^T a^T (x - x_a)$$  \hspace{1cm} (4.4)

The results of the comparison between $X_{\text{CO}_2}$ from TCCON measurements and model simulations from the Jena CarboScope are depicted in Fig. 4.13. Daily medians of both data sets as well as fits to the data are shown. $X_{\text{CO}_2}$ from the model simulations is biased low which is even more evident in the scatter plot in Fig. 4.14. Furthermore, the model is not able to reproduce the bimodal seasonality of $X_{\text{CO}_2}$ measured with the FTS.
Figure 4.15: Time series of means of flask pairs taken on Ascension Island (orange open circles) and simulated mixing ratio of CO\(_2\) for the bottom layer of the model.

Figure 4.15 completes the comparison between flask measurements, TCCON measurements and results from the Jena CarboScope for Ascension. It shows the flask record and the simulated mixing ratio of CO\(_2\) for the bottom layer of the model. It is trivial that those two data sets agree very well as the modeled values of the Jena CarboScope inversion version s04_v3.8 are simulated by assimilating measurements from 61 surface stations including data from Ascension.

The discrepancy between the modeled values for X\(_{CO_2}\) and the FTS measurements is largest in the months May to July, see also upper panel of Fig. 4.13 where the difference between daily medians from FTS measurements and model simulations from the Jena CarboScope are displayed. One possible reason for this difference could be that the model underestimates the southwards transport of CO\(_2\) in higher levels of the troposphere at the end of the boreal winter (March) respectively in boreal spring (April to May/June), see Fig. 4.16 and especially the subfigures for March and April. This figure is an example for zonal monthly means calculated for the meridian at 15\(^\circ\)W. Ascension is located at 14.33\(^\circ\)W. Analyzed CO\(_2\) fields based on TM3 model simulations using optimized fluxes of the year 2015 have been used. Other years have been checked as well (not shown). The climatology is similar in all years.
Figure 4.16: Model studies showing zonal monthly mean plots of CO₂ (in ppm) for all months of the year 2015. The individual monthly means are calculated from analyzed CO₂ fields based on TM3 model simulations using optimized fluxes. The meridional cross-section is at 15°W. Ascension Island is located at 14.33°W. The black dashed line indicates the latitudinal position of Ascension Island at 7.92°S.
Figure 4.16: Model studies showing zonal monthly mean plots of CO$_2$ (in ppm) for all months of the year 2015 (continued).
The gradient between the surface layer and total column seen in the flask versus total column comparison in Fig. 4.12 can clearly be recognized in the zonal plots of the analyzed CO$_2$ fields (see subfigures: January to June). In agreement with the comparison between flask data and total column measurements, the gradient turns round for the months July to December.

To which amount the total column of air on Ascension Island is influenced by biomass burning of the African continent is described in details in Chapter 6. Here, it should only be briefly mentioned that the current version of the Jena CarboScope does not account for the varying injection heights of carbon-related trace gases through biomass burning. It is assumed that all emissions happen at the surface. In reality, the hot smoke and all gases released through the burning process are transported vertically very quickly due to intense heat and convective energy associated with the burning process. Paugam et al. (2016) summarizes how such fire plume injection heights are currently represented in other transport models such as the Weather Research and Forecasting Model with Chemistry (WRF-Chem, Grell et al. (2005)). Rémy et al. (2017) describes how the Global Fire Assimilation System (GFAS) has been updated lately to include injection heights of fire emissions. They find a better agreement of model profiles of aerosol extinction with observations when accounting for varying injection heights in the simulations. Results of a detailed analysis on the impact of accounting for the injection heights in the Jena CarboScope inversion framework can be found in Sect. 6.3.3.

4.5 X$_{CO_2}$ Time Series Measured on Ascension and at Other TCCON Sites in Comparison with OCO-2

One primary goal of TCCON is to serve as a validation network for NASA’s Earth-orbiting satellite OCO-2 and other satellite missions such as GOSAT and Sentinel-5P. Ground-based measurements of X$_{CO_2}$ are crucial for the validation of measurements from space, as they are more precise and accurate (see also Sect. 1.2). In the following section, data from OCO-2 are compared to TCCON and three different methods for collocating ground-based and space-borne measurements are evaluated. This study is also driven by the question how many collocated measurements of OCO-2 and TCCON can be found for the TCCON station on Ascension. Being a small island in the middle of the South Atlantic Ocean, Ascension proofs to be an important site for validating OCO-2 data in ocean glint mode.
4.5.1 Data and Methods

Data
In this study, version B8100r OCO-2 lite files have been used. Data are available from the Goddard Earth Sciences Data and Information Services Center (GES-DISC, OCO-2 Science Team/Gunson and Eldering (2017)). A documentation of the version B8 lite files can be found in Osterman et al. (2017). This version of the OCO-2 data contains additional information on the quality of the data, the warn levels, which range from 0 to 5. Data flagged with warn level = 0 belong to the best 50% of the data, a warn level of 5 includes all the data. The analysis of OCO-2 data from the daily lite files presented here has been restricted to data for which the warn level is zero and for which the “xco2_quality_flag” is zero. OCO-2 data are collected for three different observation modes of the satellite. One is target mode, in which the satellite scans about a certain point on Earth’s surface while passing overhead. Most of the ground locations that are targeted are stations belonging to TCCON. Data collected in this mode is mainly used for the bias correction of the raw OCO-2 data (Wunch et al., 2017) and therefore not considered in the following section. The second mode is the nadir mode, in which the satellite points straight downwards to ground, and the third mode is the glint mode, where the instruments points off the glint spot, i.e. the point of brightest solar reflection on Earth’s surface. The glint data can be divided into glint over land (“land glint”) and glint over ocean (“ocean glint”). In the following, analysis of the data is often split into the three modes “nadir”, “land glint” and “ocean glint” as there are different bias correction schemes derived and applied for the different modes.

For comparisons to OCO-2 and for evaluating the performance of three different collocation methods, TCCON data from 25 different stations have been used. Table 4.3 lists the basic information for all of them. All stations provide at least some data coverage for the two years 2015 and 2016. TCCON data were obtained from the TCCON Data Archive, hosted by CaltechDATA, California Institute of Technology, CA (US) (https://tccondata.org/).

A modeled $X_{CO_2}$ field is needed to apply the collocation method of Guerlet et al. (2013) which is described in detail in the next paragraph. Here, global Copernicus Atmosphere Monitoring Service (CAMS) CO$_2$ model data for the years 2015 and 2016 from the European Centre for Medium-Range Weather Forecasts (ECMWF) are used. The column-integrated CO$_2$ values have been retrieved from CO$_2$ forecasts constrained with the GOSAT $X_{CO_2}$ product from the Bremen Optimal Estimation Differential Optical Absorption Spectroscopy (BESD) algorithm (Reuter et al., 2016; Agustí-Panareda et al., 2014; Massart et al., 2016; Agusti-Panareda et al., 2017). The original 25 to 50 km resolution has been aggregated to 1° x 1°.
Table 4.3: Basic information on the TCCON sites used for the comparison between $X_{CO_2}$ from OCO-2 and ground-based measurements of $X_{CO_2}$, ordered by descending latitude.

<table>
<thead>
<tr>
<th>Site</th>
<th>Latitude (deg. N)</th>
<th>Longitude (deg. E)</th>
<th>Elevation (m)</th>
<th>Region</th>
<th>Data reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eureka</td>
<td>80.05</td>
<td>-86.42</td>
<td>610</td>
<td>Canada</td>
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<tr>
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<td>26.63</td>
<td>180</td>
<td>Finland</td>
<td>Kiwi et al. (2014)</td>
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<td>54.35</td>
<td>104.99</td>
<td>502</td>
<td>Canada</td>
<td>Wunch et al. (2016)</td>
</tr>
<tr>
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<td>23.03</td>
<td>180</td>
<td>Poland</td>
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<td>230</td>
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Methods

For comparing space-borne measurements of $X_{CO_2}$ with ground-based measurements of the same quantity, spatial and temporal collocation criteria have to be defined which help to select only those observations from both observing systems which are close in time as well as in space. There exist several different spatial collocation methodologies to match ground-based measurements with observations from space. A relatively simple approach is using a geographical collocation criterion where a spatiotemporal neighborhood region is defined around the location of interest (e.g. a TCCON site) and then all satellite observations within this region are considered as collocated. For example, this methodology is used by Inoue et al. (2013) who average all same-day satellite observations falling within $\pm 5^\circ$ of a location of interest and by Wunch et al. (2017) who calculate daily median $X_{CO_2}$ from OCO-2 which are within $\pm 2.5^\circ$ in latitude and $\pm 5^\circ$ in longitude of individual TCCON sites.

A more sophisticated approach which makes use of the mid tropospheric potential
temperature at 700 hPa ($T_{700}$) has been applied by Keppel-Aleks et al. (2011) and Wunch et al. (2011b). Additionally to a spatial criterion of $\pm 30^\circ$ in longitude and $\pm 10^\circ$ in latitude and a temporal criterion of $\pm 5$ days, this methodology uses $T_{700}$ as a proxy for dynamical patterns. It exploits the fact that the large-scale gradients in $X_{CO_2}$ are correlated with the potential temperature. Space-borne observations are considered to be collocated with measurements from the TCCON site of interest when they match the spatial and temporal criteria as well as $\pm 2$ Kelvin in $T_{700}$. This method works well in the NH where the large-scale gradients in $X_{CO_2}$ are strong, it is less effective in the tropics and in the SH in general. Nguyen et al. (2014) developed another more sophisticated approach by using a modified Euclidian distance with respect to latitude, longitude, time and $T_{700}$. The common goal of more advanced methodologies is to increase the number and accuracy of collocations.

In this study, two different well-established methods and one new method have been applied to find collocations of OCO-2 data with TCCON measurements. The first method is the geographical collocation method also used by Wunch et al. (2017). The second method is based on that which has been developed for the validation of $X_{CO_2}$ from GOSAT with TCCON data in Guerlet et al. (2013). This method accounts for the fact that observed $X_{CO_2}$ is influenced by surface fluxes as well as atmospheric transport. In a first step, a coarse geographical filter is applied which selects all satellite observations falling within $\pm 22.5^\circ$ longitude and $\pm 7.5^\circ$ latitude. In a second step, a contiguous area $A$ has to be identified in which the modeled $X_{CO_2,mod}$ values are identical to the modeled value at the location of interest, $X_{CO_2,mod,TCCON}$ within some tolerance $\delta$. Thus the following condition needs to be fulfilled:

$$|X_{CO_2,mod} - X_{CO_2,mod,TCCON}| \leq \delta.$$  \hspace{1cm} (4.5)

Here, the threshold $\delta$ is set to 0.5 ppm and modeled $X_{CO_2}$ with a $1^\circ \times 1^\circ$ resolution from the global CAMS CO$_2$ product are used. Figure 4.17 illustrates the concept of this method for the OCO-2 overpasses over the Ascension Island TCCON site on November 14, 2015. The modeled value $X_{CO_2,mod,TCCON}$ at Ascension is 401.7 ppm in this example and all modeled values $X_{CO_2,mod}$ between 401.2 and 402.2 ppm in the contiguous area $A$ fullfill the criterion according to Eq. 4.5. It should be mentioned that the performance of this collocation methodology does not depend on the absolute accuracy of the modeled $X_{CO_2}$. Only the spatial gradient of the modeled $X_{CO_2}$ has to be accurate within some tolerance over a few thousand kilometers. All OCO-2 measurements falling within $A$ are considered as collocated with the measurements of the respective TCCON site recorded $\pm 2$ hours of the mean OCO-2 overpass time. In case of measurements from two different OCO-2 orbits falling within $A$, the mean of both overpasses is taken as the mean OCO-2 overpass time.
Figure 4.17: Illustration of the different collocation methods. The modeled $X_{\text{CO}_2}$ fields around Ascension Island for November 14, 2015 at 12:00 UTC are color-coded in rainbow colors. The location of the Ascension Island TCCON site is marked with a black star. The red rectangle indicates the coarse geographical filter after Guerlet et al. (2013). The smaller black rectangle shows the geographical criterion after Wunch et al. (2017). Three orbits of OCO-2 data in green and orange circles are also shown. Orange circles indicate all OCO-2 data. Green circles indicate those soundings within the area $A$ where the values of the model fields have an absolute difference of not more than 0.5 ppm of the modeled value at Ascension Island. In this example, $X_{\text{CO}_2, \text{mod, TCCON}}$ is 401.7 ppm, values of $A$ range from 401.2 to 402.2 ppm and are shaded in light blue.

A third, new method has also been tested. This method is a combination of the spatial collocation method after Wunch et al. (2017) and the more dynamical collocation method after Guerlet et al. (2013). It is therefore called “combined method” hereafter. The coarse geographical filter has been reduced to the size of the rectangle used by Wunch et al. (2017) ($\pm 2.5^\circ$ in latitude and $\pm 5^\circ$ in longitude of individual TCCON sites) before filtering the OCO-2 data according to modeled fields of $X_{\text{CO}_2}$ by applying Eq. 4.5 with $\delta = 0.5$ ppm.

4.5.2 Results and Discussion

In a first check, it has been estimated how many potential collocations exist for each TCCON station for the given B8100r OCO-2 data set when filtering the satellite
Figure 4.18: Comparison of the Guerlet collocation method and the spatial boxes method. Shown are potential collocations of OCO-2 data with TCCON sites which are ordered by latitude from South to North for the two well-established collocation methods discussed in this section. The solid bars depict potential collocations according to the geographical collocation criterion whereas the bars with black dots show potential collocations for the method after Guerlet et al. (2013). The panels from top to bottom show potential matches for all OCO-2 data (top panel), only for ocean glint OCO-2 data (second panel), only for land glint OCO-2 data (third panel) and only for nadir OCO-2 data (bottom panel). Due to the larger spatial box applied for the southernmost two TCCON stations, Wollongong and Lauder have a lot more potential collocations for the geographical collocation criterion. For Wollongong, the number of potential matches exceeds the chart for all different modes. The equator is between Manaus (3.21°S) and Izaña (28.30°N). It is marked with a black line in all panels.

data according to the different collocation criteria. Note that the final number of collocations can be significantly smaller because of lacking TCCON data, e.g. due to longer instrument shutdowns. Figure 4.18 shows a comparison regarding such potential collocations for the two well-established collocation methods. Following Wunch et al. (2017), the boxes for the two TCCON stations south of 25° S (Wollongong and Lauder) have been made larger. The boxes span 20° in latitude and 120° in longitude with the TCCON sites in the center which is justified by the weak spatial variance in $X_{CO2}$ in the SH. These small differences in $X_{CO2}$ are also reflected in the
fact that the SH gets significantly more potential collocations compared to the NH (see Fig. 4.18, top panel, bars with black dots) when applying the method by Guerlet et al. (2013) because the criterion according to Eq. 4.5 is more often fulfilled in the SH. Apart from Wollongong and Lauder where the very large spatial boxes are applied, Ascension Island is the site with most potential collocations with OCO-2 ocean glint data when applying the collocation method after Wunch et al. (2017) (see Fig. 4.18, second panel, solid bars). For the collocation method according to Guerlet et al. (2013), the three islands Ascension Island, Reunion Island and Izaña have by far the most potential collocations with OCO-2 ocean glint data. Furthermore, Fig. 4.18 illustrates the unbalanced distribution of TCCON stations between the two hemispheres. As the station in Manaus (3.21°S), Brazil, has been shutdown in June 2015, Ascension Island is currently the station closest to the equator. There exists a large gap regarding the coverage of the latitudinal bands northwards from Ascension Island (7.92°S) to Izaña (28.30°N) which has been filled to some extent by the new TCCON station Burgos (18.52°N), Philippines, which started in operational mode in March 2017.

In a second step, actual collocated measurements of TCCON and OCO-2 have been determined for all TCCON stations listed in Table 4.3. For the method after Guerlet et al. (2013) and the combined method, measurements are considered as collocated when TCCON measurements have been recorded ±2 hours around the mean OCO-2 overpass time. For the spatial boxes method, daily medians for TCCON and for OCO-2 data falling into the coincidence box are considered to be collocated. Figure 4.19 shows an example of the results for the Ascension Island TCCON site for the method after Guerlet et al. (2013). For this collocation method, Table 4.4 summarizes the statistics of the comparison between OCO-2 and TCCON for all TCCON sites and all observation modes. Ascension Island is among the sites with the most collocations for ocean glint measurements (N=186) even though there was a longer data gap between December 2015 and August 2016 due to technical problems of the TCCON instrument (see Table 3.1 for details). The large collocation box used by the method after Guerlet et al. (2013) covers a small edge of Brazil (see purple rectangle in Fig. 4.17). OCO-2 data measured over this region lead to small numbers of collocations for land glint mode (N=12) and nadir mode (N=4), both with larger biases and RMS values than calculated for ocean glint collocations at Ascension Island.

Figure 4.20 shows the overall comparison between the two well-established collocation methods for ocean glint data. It is worth mentioning that Wunch et al. (2017) reported the coefficient of determination $R^2$ to be only 0.63 for ocean glint data when applying the spatial collocation method. This low correlation coefficient has been attributed to a known high bias for SH wintertime (June through September)
Figure 4.19: Comparisons between OCO-2 data collocated at Ascension Island using the method after Guerlet et al. (2013). In the upper left panel, the time series of TCCON daily medians from Ascension Island are shown in black circles and collocated OCO-2 measurements retrieved with the method after Guerlet et al. (2013) are shown by triangles colored differently for each viewing mode of the satellite. The difference between OCO-2 measurements and TCCON measurements are shown in the lower left panel. In the right panel, the scatter between $X_{CO_2}$ from OCO-2 for all three different viewing modes and $X_{CO_2}$ from TCCON are shown. The colored lines are the linear fits belonging to data points in the same color. The grey line shows the one-to-one line.

Ocean glint data in the version B7r OCO-2 files. The bias is related to a misrepresentation of stratospheric aerosols in the OCO-2 B7r retrieval algorithm (Wunch et al., 2017). It has been addressed in the latest available version of the data. Hence, $R^2$ for ocean glint data improved significantly for the spatial collocation method. It is 0.82 for the version B8100r OCO-2 lite files.
Table 4.4: Statistics of the comparison between X$_{\text{CO}_2}$ from OCO-2 for all three different viewing geometries and X$_{\text{CO}_2}$ from TCCON for the collocation method after Guerlet et al. (2013). For each TCCON station, the number of coincident measurements (N), the median bias (OCO-2 minus TCCON), its root-mean-square value (RMS) and the coefficient of determination ($R^2$) are listed in the table. For the calculation of the numbers in the last row (Total), all coincidences in the table have been considered as independent.

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Figure 4.21 and Fig. 4.22 show the comparison between the two well-established collocation methods for land glint data and nadir data respectively. The statistics for each individual TCCON site regarding the spatial collocation method after Wunch et al. (2017) are summarized in Table 4.5.

In total, both methods perform similarly well except for the number of collocations. For the collocation method after Guerlet et al. (2013) the differences between collocated X$_{\text{CO}_2}$ from OCO-2 and from TCCON are -0.10 ppm, -0.08 ppm and -0.02 ppm for ocean glint, land glint and nadir, respectively. The corresponding RMS values are 1.05 ppm, 1.31 ppm and 1.24 ppm. For the spatial collocation method differences are -0.14 ppm, 0.01 ppm and 0.07 ppm for ocean glint, land glint and nadir with corresponding RMS values 1.06 ppm, 1.18 ppm respectively 1.15 ppm. Correlations
Chapter 4. Five Years of TCCON Observations on Ascension Island

Figure 4.20: Scatter diagrams between ocean glint OCO-2 data and TCCON for the Guerlet collocation method and the spatial boxes method. The upper panel shows collocated measurements of ocean glint $X_{\text{CO}_2}$ from OCO-2 vs. $X_{\text{CO}_2}$ from TCCON determined with the method of Guerlet et al. (2013). The lower panel shows collocated measurements of the same quantity for the spatial boxes collocation method. In the upper panel each point represents a daily median of OCO-2 being coincident with TCCON measurements taken $\pm 2$ hours around the mean OCO-2 overpass time. In the lower panel each point depicts a daily median of collocated OCO-2 and TCCON measurements. In both panels the grey line is the linear fit to the data and $m$ is the corresponding slope of the fit. $R^2$ represents the coefficient of determination, $N$ is the total number of coincident measurements and RMS is the root-mean-square value of the differences between OCO-2 and TCCON $X_{\text{CO}_2}$. The dashed grey lines show the one-to-one line.
Figure 4.21: Scatter diagrams between land glint OCO-2 data and TCCON for the Guerlet collocation method and the spatial boxes method. The annotations are equivalent to those in Fig. 4.20.
Figure 4.22: Scatter diagrams between nadir OCO-2 data and TCCON for the Guerlet collocation method and the spatial boxes method. The annotations are equivalent to those in Fig. 4.20.
Table 4.5: Statistics of the comparison between $X_{\text{CO}_2}$ from OCO-2 for all three different viewing geometries and $X_{\text{CO}_2}$ from TCCON for the collocation method following Wunch et al. (2017). For each TCCON station, the number of coincident measurements (N), the median bias (OCO-2 minus TCCON), its RMS and the coefficient of determination ($R^2$) are listed in the table. For the calculation of the numbers in the last row (Total), all coincidences in the table have been considered as independent.

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calculated for the different collocation methods are also similar. For both methods, the best correlation has been calculated for ocean glint ($R^2 = 0.83$ for the method after Guerlet et al. (2013) and $R^2 = 0.82$ for the spatial collocation method), followed by nadir ($R^2 = 0.80$ for the method after Guerlet et al. (2013) and $R^2 = 0.80$ for the spatial collocation method.) The land glint mode data show the lowest correlation of all three modes ($R^2 = 0.78$ for the method after Guerlet et al. (2013) and $R^2 = 0.76$ for the spatial collocation method). Altogether, both collocation methods yield similar results. However, for the collocation method after Guerlet et al. (2013) the number of collocations is significantly higher for all three observation modes compared to the spatial collocation method: 147% more collocations for ocean glint, 57% more for land glint and 55% more for nadir, respectively.
Finally, the results of the third collocation method, the combined method, are presented. With the relative sparsity of GOSAT data, more sophisticated collocation criteria focussed on including as many data as possible, while applying additional constraints to ensure the comparability of the air mass (e.g. Keppel-Aleks et al. (2011); Wunch et al. (2011b); Nguyen et al. (2014); Guerlet et al. (2013)). The increased data density of OCO-2 over GOSAT allowed for the use of a smaller collocation method to account for the flux variations additionally. The upper panel shows collocated measurements of ocean glint $X_{CO_2}$ from OCO-2 vs. $X_{CO_2}$ from TCCON determined with the combined method. The lower left panel shows collocated measurements of land glint $X_{CO_2}$ from OCO-2 vs. $X_{CO_2}$ from TCCON determined with the same collocation method. The lower right panel shows the same for the nadir viewing mode of OCO-2. The other annotations are equivalent to those in Fig. 4.20.
Table 4.6: Summary of the statistics for all three different collocation methods. The table below lists the total number of measurements (N), the RMS of the difference between \( X_{\text{CO}_2} \) from OCO-2 and from TCCON, the coefficient of determination (\( R^2 \)) and the slope for all three different collocation methods which have been applied. Each row shows the calculated values for one of the three different viewing modes of OCO-2.

<table>
<thead>
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<th>combined method</th>
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<td>RMS</td>
<td>( R^2 )</td>
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The spatial criterion of Wunch et al. (2017) has been combined with filtering data according to modeled fields of \( X_{\text{CO}_2} \). Figure 4.23 shows the results for this combined method. A comparison of the total numbers for all three different collocation methods are given in Table 4.6. Going from the purely spatiotemporal collocation method to the one which combines spatiotemporal and dynamical criteria, the number of collocations (N) decreases by approximately 50% for each observation mode whereas \( R^2 \) increases significantly. Values are \( R^2 = 0.87 \), \( R^2 = 0.83 \) and \( R^2 = 0.85 \) for ocean glint, land glint and nadir, respectively. These are very interesting findings which highlight the importance of taking into account information about the local flux variability and airmass when collocating measurements. Wunch et al. (2017) reports that halving the spatial coincidence criteria over the TCCON sites does not significantly improve the correlation coefficients. Here, it is shown that an improvement in precision can still be gained by considering the local flux variability. Applying this method could potentially be of interest for other satellite missions like Sentinel-5P as well, which also have an increased data density due to using a push-broom type imaging spectrometer for sensing the Earth’s atmosphere.

### 4.5.3 Conclusions

\( X_{\text{CO}_2} \) from OCO-2 agree well with TCCON data for all three observation modes of the satellite. A significant improvement from the previous version B7r to the current version B8100r OCO-2 lite files is found, particularly for measurements taken in ocean glint mode. The results of the comparison can differ for different collocation methods being applied. The method after Guerlet et al. (2013) and the spatial collocation method after Wunch et al. (2017) yield similar statistics, apart from the fact that the former method provides a lot more collocations. For the third combined method, significantly better correlation coefficients are calculated.
Independent of the choice of the collocation method, the TCCON station on Ascension Island proves to be a very important validation site for ocean glint data. Furthermore, it is currently the TCCON station closest to the equator and the only station in the latitudinal band between 10°N and 10°S to be used for validation of satellite measurements.

### 4.6 Summary and Conclusions

Measurements from the TCCON site on Ascension were calibrated with aircraft profile data from the ATom-1 aircraft campaign. Perfect agreement with results published by Kiel et al. (2016) and Kiel (2016) has been found for $X_{\text{CO}_2}$ and $X_{\text{CH}_4}$, respectively. The results for $X_{\text{CO}}$ agree well within the errors. Due to this successful calibration the TCCON site on Ascension was upgraded to a station with full TCCON status in May 2017. $X_{\text{CO}_2}$ from Ascension carries a mixed signal from both hemispheres which makes it relatively difficult to attribute clear sources and sinks. On the other hand, $X_{\text{CO}_2}$ from Ascension could help to quantify the interhemispheric exchange between NH and SH. The seasonal cycle amplitude of $X_{\text{CO}_2}$ is calculated to be 2.5 ppm. It is an interesting finding that the seasonal cycle amplitude at the surface calculated from flask data is only 2.0 ppm and thus smaller than the variability measured in the total column. It is therefore likely that most of the variations measured in the total column above Ascension are due to long-range transport and occur above the MBL. Modeled $X_{\text{CO}_2}$ from the Jena CarboScope are biased low compared to TCCON and the model is not able to fully reproduce the bimodal seasonality. It is most likely that the model underestimates the southwards transport of $\text{CO}_2$ in the free troposphere, especially in the months March to June. Moreover, it has been demonstrated that $X_{\text{CO}_2}$ measured on Ascension plays an important role in validating observations from OCO-2 performed in ocean glint mode. Currently, it is also the only equatorial station within TCCON covering the latitudinal band between 10°N and 10°S.

From all these results it can be concluded that Ascension is a very important site for performing ground-based measurements of $X_{\text{CO}_2}$. Due to its unique location in the South Atlantic Ocean and due to facing the trade wind inversion, the TCCON site on Ascension proofs to provide an important time series of $X_{\text{CO}_2}$, both for improving atmospheric transport models as well as serving for the validation of satellite data.
4.6 Summary and Conclusions
Chapter 5

Comparison of Different Data Sets of Methane Measured on Ascension Island

5.1 Introduction

Global atmospheric CH$_4$ is rising again after a pause between 1999 and 2006. The annual growth rate between 2007 and 2013 has been $5.7 \pm 1.7$ ppb yr$^{-1}$. In 2014, the growth was extreme with a rate of $12.5 \pm 0.4$ ppb (Nisbet et al., 2016). Recent studies have proposed that emissions in the tropics from biogenic sources such as wetlands and agriculture are a major contributor to this recent growth (Nisbet et al., 2014; Schaefer et al., 2016).

Inverse modeling is one tool to assess which regions of the world act as a sink and which regions act as a source for CH$_4$. In recent years, huge progress has been made regarding the development of inverse modeling methods for estimating the global sources and sinks of CH$_4$ (Houweling et al., 2017). However, using different data products as input, e.g. from satellite measurements and surface stations, often yields diverging results. Especially in the tropics, where strong convection is present, total column measurements are able to see flux signals that are only weakly detected by surface measurements (Deutscher et al., 2010). One example for varying results of different inversion scenarios is given in Alexe et al. (2015). Global inversions of CH$_4$ using satellite data as input yield lower CH$_4$ fluxes across the Congo basin and higher emissions across tropical East Africa compared to the inversion scenario that only uses surface in situ data. It is therefore important to perform in situ as well as precise and accurate ground-based total column measurements of CH$_4$ in these key regions to better constrain CH$_4$ fluxes.
In this chapter, the time series of $X_{CH_4}$ as well as the tropospheric column-averaged CH$_4$ (denoted as $X^{tropo}_{CH_4}$) from Ascension are compared to surface in situ measurements. Furthermore, profiles of CH$_4$ sampled during the two aircraft campaigns ATom-1 and ATom-2 are shown. The investigation of CH$_4$ around Ascension is then completed by assessing the performance of the Monitoring Atmospheric Composition and Climate (MACC) CH$_4$ model (v10-S1NOAA_ra) in this area. Finally, the results of one other SH TCCON station, Reunion Island, are presented in comparison to the data sets from Ascension.

5.2 Data and Methods

**FTS data**

$X_{CH_4}$ has been retrieved using the standard TCCON processing which is described in detail in Sect. 2.3.3. The same fitting routine as described in Sect. 4.3 has been applied to daily medians of the $X_{CH_4}$ time series.

**In situ data**

The CH$_4$ data record from flask measurements is made available by NOAA (Dlugokencky et al., 2015a). Details on the sampling of the flasks and the location are already described in Sect. 4.4 for CO$_2$. The same flasks are analysed for CH$_4$.

**Tropospheric CH$_4$ derived with N$_2$O and HF**

Seasonal variability in the time series of $X_{CH_4}$ is determined by varying local sinks and sources which change the mixing ratio of CH$_4$ in the troposphere as well as a variable stratospheric contribution. These stratospheric dynamics sometimes mask trends and fluctuations of CH$_4$ in the troposphere. Several methods have been developed to deal with this problem. Washenfelder et al. (2003) were the first describing a method to disentangle the tropospheric and stratospheric part of CH$_4$ by using HF as a proxy. Warneke et al. (2006) used the same approach to retrieve the tropospheric column of CH$_4$ from FTIR measurements at Ny-Ålesund. This method was improved by Saad et al. (2014) by explicitly accounting for the CH$_4$ averaging kernels. Wang et al. (2014) examined the possibility of using nitrous oxide (N$_2$O) as a proxy for stratospheric CH$_4$. They found that the retrieved $X^{tropo}_{CH_4}$ has a smaller uncertainty when using N$_2$O instead of HF. Sepúlveda et al. (2012, 2014) describe a different approach where optimized profile retrievals have been performed in the mid-infrared spectral region to directly retrieve the tropospheric partial column of CH$_4$.

Here, $X^{tropo}_{CH_4}$ was retrieved by following the approach of Wang et al. (2014). As described in Wang et al. (2014), the quality of the HF retrieval in the NIR is influenced
by a nearby absorption line of H$_2$O. This results in larger daily variances due to higher HF errors especially for tropical sites like Ascension Island with a relatively high water content in the atmosphere. The impact of the inaccurately derived HF on the calculation of $X_{\text{CH}_4}^{\text{tropo}}$ is clearly visible in Fig. 5.1. This figure shows a comparison between both methods for retrieving $X_{\text{CH}_4}^{\text{tropo}}$ on Ascension Island. Due to the larger scatter of the derived values when using HF as a tracer it has been decided to only use data derived with N$_2$O.

**Aircraft data from ATom**
Aircraft profiles were collected in the framework of ATom (see Sect. 4.2) in August 2016 (ATom-1) and February 2017 (ATom-2). Here, the profiles of CH$_4$ measured closest to Ascension are shown. They were sampled with a Picarro (type: modified G2401m) operated by the NOAA Earth System Research Lab.

**MACC CH$_4$ model**
Simulations from the MACC CH$_4$ model (v10-S1NOAA-ra) are used (Bergamaschi et al., 2013) to assess the performance of a model around Ascension. The underlying inversion framework is the inverse modeling system TM5-4DVAR with a spatial
resolution of approximately 4° in latitude by 6° in longitude with 25 vertical levels. ERA-Interim meteorological fields provided by ECMWF are used to drive the model. The model is optimized using inversions of CH₄ surface emissions. Model data are available until the end of the year 2012.

5.3 Results and Discussion

A comparison between daily medians of X₇CH₄, daily medians of X₄tro₂ CH₄ and the mean CH₄ VMR of each flask pair from Ascension Island is shown in Fig. 5.2. The fitting method introduced in Sect. 4.3 was applied. Fit functions with a constant term, a linear term and two harmonics according to Eq. 4.3 were fitted to the data. The flask record at the surface shows the typical behavior of a marine background site. An average seasonal cycle of approx. 22 ppb has been estimated. The seasonal cycle is controlled mainly through oxidation of methane by OH radicals. OH itself is produced by the photolysis of ozone (O₃). In austral summer, when solar radiation is highest and therefore lots of OH is produced, the CH₄ time series has a minimum. In austral winter, the CH₄ data show a maximum because the sink through OH oxidation is smaller at this time of the year. In addition to the huge OH sink, CH₄ reacts with chlorine radicals from sea salt in the MBL. Kirschke et al. (2013) report this sink to be responsible for about 3% of the removal of CH₄ in the atmosphere.

Compared to the seasonal cycle at the surface, the seasonal variability of X₇CH₄ is much smaller on Ascension Island with an amplitude of approx. 10 ppb. Furthermore, the record shows a bimodal seasonality with two maxima, one in February and one in September. The seasonal cycle of X₇CH₄ is mainly driven by the reaction of CH₄ with OH radicals. However, CH₄ emissions occurring on continents and moving to Ascension via long-range transport influence X₇CH₄ as well. Thus, the signal seen in the total column above Ascension is a combination of both processes. The record for X₄tro₂ CH₄ is very similar to the one for X₇CH₄. This is expected as the stratospheric variability of CH₄ is very small in the tropics (Verma et al., 2017). Hence, almost all variability in X₇CH₄ is determined by the tropospheric variability (in X₄tro₂ CH₄).

The most striking feature of this comparison between in situ data, X₇CH₄ and X₄tro₂ CH₄ is the large difference between in situ and X₄tro₂ CH₄, with in situ data showing lower values. This positive gradient of CH₄ with increasing height is very special. In most regions of the world, concentrations of CH₄ are highest at the surface where most emissions occur. Higher up in the atmosphere, CH₄ gets mixed and diluted with other atmospheric constituents, resulting in a negative gradient with increasing height. However, on Ascension, the concentration of CH₄ at the surface is lower.
than in the free troposphere all year round. Depending on the time of the year, the differences between $X_{\text{CH}_4}^{\text{tropo}}$ and the surface values are between approx. 50 ppb (in February) and approx. 25 ppb (in September). These findings for a longer time series are in very good agreement with aircraft profiles of CH$_4$ measured during the two aircraft campaigns ATom-1 (see Fig. 5.3) and ATom-2 (see Fig. 5.4). As indicated by Fig. 5.2, the difference between CH$_4$ concentrations in the MBL and in the free troposphere are higher during ATom-2 because this campaign took place in February which is the month where the seasonal cycle of CH$_4$ at the surface has its minimum. The maximum difference sampled during the investigated ATom profiles occurred during the ascent on February 15, 2017 (see Fig. 5.4, right panel). CH$_4$ VMRs measured at ground level were around 1790 ppb while the values in the free troposphere reached 1870 ppb and higher. Furthermore, both figures showing data from ATom depict clearly the distinct separation between the MBL and the free troposphere indicated by a very steep gradient in the CH$_4$ VMR. Brownlow et al. (2016) were the first publishing these results regarding CH$_4$ below and above the trade wind inversion at Ascension Island.

Figure 5.2: Comparison between the time series of in situ measurements (orange open circles), $X_{\text{CH}_4}^{\text{tropo}}$ derived from N$_2$O (grey open circles) and $X_{\text{CH}_4}$ (light blue open circles) on Ascension Island. A red line indicates a fit to the flask data. A black line shows the fit to the tropospheric columns of CH$_4$, a blue line the fit to the total columns of CH$_4$. 
This feature of low values of CH₄ at the surface and elevated signals in the free troposphere is due to the unique location of Ascension in the middle of the South Atlantic. On the one hand, there are no larger sources of CH₄ in the surrounding area. On the other hand, the origin of air is quite different in different altitudes above Ascension as shown with backward trajectories terminating on Ascension, see Fig. 3.4. Close to the surface, the origin of air is determined by the southeasterly tradewinds. The air is coming from the deep South Atlantic all year long and carries no CH₄ signals from continents. In the free troposphere, the backward trajectories show that the air comes mainly from Africa, and sometimes also from South America, carrying e.g. biomass burning signals and signals of wetland emissions. Furthermore, the evaluation of zonal monthly means from TM3 (not shown) suggests inflow of CH₄ in higher layers of the troposphere from the NH.
A first step towards answering the question to which extend atmospheric models are able to reproduce the positive gradient of \( \text{CH}_4 \) VMRs with increasing altitude on Ascension Island is taken by assessing model simulations from the MACC \( \text{CH}_4 \) model. Figure 5.5 shows the time series of daily averages of the lowest level of the model, daily averages of the pressure-weighted mean of all vertical levels, denoted as \( \chi_{\text{CH}_4} \), and daily averages of the pressure-weighted mean of all levels belonging to the troposphere, denoted as \( \chi_{\text{tropo}}^{\text{CH}_4} \). The pressure weighting function according to Connor et al. (2008) (Appendix A) was applied. The general pattern is similar to the one of the TCCON and flask measurements shown in Fig. 5.2. Nevertheless, the difference between \( \text{CH}_4 \) values in the lowest level of the vertical grid and in the total column as well as only in the tropospheric column is not as high as indicated by the mea-
Figure 5.6: Comparison between the time series of in situ measurements (orange open circles), $X_{\text{tropo}}$ derived from N$_2$O (grey open circles) and $X_{\text{CH}_4}$ (light blue open circles) on Reunion Island. A red line indicates a fit to the flask data. A black line shows the fit to the tropospheric columns of $\text{CH}_4$, a blue line the fit to the total columns of $\text{CH}_4$.

Measurements. The most likely cause is that the model underestimates the southwards transport of $\text{CH}_4$ from the NH in higher levels of the atmosphere. It is important to mention that averaging kernel smoothing of the model output should be performed for a more rigorous and meaningful comparison between the model and the TCCON data.

For comparison, different data sets of $\text{CH}_4$ measured at another SH TCCON station, Reunion Island (20.90°S, 55.48°E, 87 m.a.s.l.), were investigated. The island is located east of Madagascar in the Indian Ocean, see Fig. 1.2. Figure 5.6 shows daily medians of $X_{\text{CH}_4}$ (data from De Mazière et al. (2014)), daily medians of $X_{\text{tropo}}$ and the daily means of $\text{CH}_4$ measured with a Picarro (type: G2301). The Picarro is operated by the Laboratoire des Sciences du Climat et de l’Environnement (LSCE). Data was provided by Michel Ramonet through personal communication.

The surface data show a distinct seasonal cycle with a clear maximum in September and an amplitude of 30 ppb. The seasonal variability in the tropospheric column is
larger than that in the total column. At the same time, it is expected that the seasonal cycle of stratospheric methane also has a higher influence on the total column than on Ascension Island. The lower values of the in situ data compared to $X_{tropo}^{CH_4}$ are consistent with the observations seen on Ascension even though the absolute differences are not as high as measured on Ascension. On Reunion Island, the prevailing winds on the surface are from the east and south-east. Like on Ascension Island, Reunion Island receives mostly clean air from the ocean, while in higher layers of the troposphere the air carries signals from continents such as wetland emissions and pollution from biomass burning.

### 5.4 Summary and Conclusions

The time series of $X_{CH_4}$ on Ascension Island has been shown in comparison to in situ data. Additionally, $X_{tropo}^{CH_4}$ has been retrieved. A striking difference of up to approx. 50 ppb can be measured between $CH_4$ values at the surface and $X_{CH_4}^{tropo}$. Aircraft profiles from ATom-1 and ATom-2 support these findings very well. They all show a large positive gradient of $CH_4$ with increasing altitude. This positive gradient can be attributed to transport from the continents and the trade wind inversion occurring on Ascension Island. A similar pattern can be found for another island in the SH, Reunion Island, where meteorological conditions are comparable to those on Ascension. The comparison for in situ data, $X_{CH_4}^{tropo}$ and $X_{CH_4}$, highlights how important it is to perform complementary measurements on Ascension Island as only in conjunction they provide a comprehensive overall picture for $CH_4$ at this location.

It is expected that incorporating these findings could help to enhance the performance of atmospheric models in this domain. Furthermore, using the complementary data sets from Ascension could lead to improved results of inversions for tropical Africa where satellite inversions yield lower $CH_4$ fluxes compared to inversions with surface data (Alexe et al., 2015). $X_{CH_4}$ measurements performed on Ascension Island and on Reunion Island can help to constrain $CH_4$ fluxes of the African continent and help to improve the knowledge in a key region of the world regarding source and sink processes of $CH_4$. 
Chapter 6

Biomass Burning Signals Seen at Ascension Island

6.1 Introduction

The interannual variability of CO$_2$, CH$_4$ and CO is influenced by the variability in biomass burning (BB) (Langenfelds et al., 2002) with variability in CO being most pronounced due to its comparatively short lifetime of two to three months. Variability of $X_{\text{CO}_2}$ and $X_{\text{CH}_4}$ from the same source are often obscured by other signals such as transport and natural variability. BB is the combustion of organic matter. It is known to be a major source for trace gases in the atmosphere (Crutzen and Andreae, 1990). According to Akagi et al. (2011), BB is the second largest source of trace gases in the global troposphere. Approximately 70 to 80% of BB occurs in the tropics (Crutzen and Andreae, 1990; van der Werf et al., 2010; Akagi et al., 2011).

The following chapter includes a detailed discussion on the time series of $X_{\text{CO}}$ from Ascension Island. The data of $X_{\text{CO}}$ are compared to surface flask measurements performed biweekly on the island. Furthermore, the relationship between the time series of $X_{\text{CO}}$ on Ascension and the El Niño Southern Oscillation (ENSO) is shown. To investigate in more detail from which regions signals of BB can be expected on Ascension, tagged tracer simulations were performed for CO$_2$ and results of these simulations are presented in comparison to one other SH TCCON site, Darwin (Australia).

6.2 Methods

**FTS data**

$X_{\text{CO}}$ was retrieved using the standard TCCON processing which is described in de-
tail in Sect. 2.3.3. As explained in Sect. 4.3 a model was fitted to the daily medians of the $X_{\text{CO}}$ time series to isolate the trend and the seasonal cycle of the record. The model includes a constant term, a linear term and two harmonics, see also Eq. 4.3.

**In situ data**
The CO data record from flask measurements is made available by NOAA (Novelli and Masarie, 2015). In cooperation with the Met Office (United Kingdom), NOAA takes flask samples at the Wideawake airfield located at the south west of the island ($7.97^\circ$S, 14.40$^\circ$W, 87 m.a.s.l.) twice per week. The distance to the location where TCCON measurements are performed is 9.6 km. The same model as for the FTS time series was fitted to the means of flask pairs.

**The Global Fire Assimilation System**
The Global Fire Assimilation System (GFAS) uses observations of the fire radiative power (FRP) made from space (Kaiser et al., 2012). With these observations of FRP daily emissions of various gases are calculated while taking the varying combustion rates of different land cover types and specific emission factors into account. The intense heat of fires leads to fire-induced convection. That is why BB can release a huge amount of aerosols and trace gases above the planetary boundary layer. The recent version of the GFAS data (GFAS v1.2, described in Rémy et al. (2017)) bear for this rapidly occurring thermal lift of air which happens within a fire plume. It additionally contains information on injection heights of the emissions based on a plume rise model. The GFAS v1.2 data are available on a global 0.1° by 0.1° grid. In order to perform tagged tracer simulations the data have been regridded to match the resolution of the so-called fine grid of TM3 (approx. 4° in latitude by 5° in longitude with 26 vertical levels, see Sect. 4.4 for more details on TM3).

**Tagged tracer simulations**
Tagged tracer model simulations as they are for example accomplished in Deutscher et al. (2014) are a powerful tool in atmospheric modeling. Tracers can be separated by process and/or by source regions to better understand which individual processes and/or regions contribute to a total signal. In this work, tagged tracer simulations for CO$_2$ have been performed to answer the following two questions:

1. Does the explicit consideration of the parameter *injection height* lead to a different result when performing tagged tracer simulations? If so, how big is this difference between simulations with injection height and without injection height?
2. Which regions of the world contribute most to the CO emissions which can be measured on Ascension?
To answer the first question two different kinds of simulations have been performed. In a first scenario all emissions were only released at the surface. A second set-up was more realistic. It takes the information of the varying injection heights of the emissions into account. Instead of surface fluxes volumetric fluxes were implemented into TM3.

At the same time and in order to answer question 2 the emissions were split into different regions according to TransCom3 regions (Gurney et al., 2002). Those regions are shown in Fig. 6.1. TM3 in fine grid resolution was used to transport the emissions forward in space and time. In total, tagged tracer simulations for CO₂ emissions from biomass burning for all 11 land regions of TransCom3 were carried out.

It has been a straight forward task to perform tagged tracer simulations for CO₂ with the existing model framework. It should be mentioned that CO₂ has a much longer lifetime than CO which belongs to medium-lived gases with a lifetime of 2 to 3 months (IPCC, 2013). Depending on the type of fire the ratio between emitted CO₂ and CO can also vary. Tagged tracer simulations of CO₂ are therefore considered to give qualitative results regarding CO emissions through BB. They do not allow for a quantification.
6.3 Results and Discussion

6.3.1 Time Series of $X_{CO}$ and Comparison to Flask Data

$X_{CO}$ measured on Ascension Island varies mainly due to BB occurring on the African continent. While elevated signals due to BB can clearly be seen in $X_{CO}$, variations in $X_{CO_2}$ and $X_{CH_4}$ from the same source are obscured by other signals such as transport and natural variability. Figure 6.2 shows the time series of $X_{CO}$ in comparison to in situ data. For each flask pair a mean is calculated. Especially for the two years 2014 and 2015 where there is good data coverage regarding the FTS measurements two different periods of higher CO values can be distinguished. Those two periods correspond to the two different burning seasons of Africa which are depicted in Fig. 6.3. Shown are CO emissions from GFAS v1.2 data for the years 2012 until 2016. Between approximately July and November there are large emissions of CO in Southern Africa, approximately between December and April in Northern Africa. Interestingly, the in situ measurements are also elevated in Fig. 6.2 for the time when higher values of BB in Southern Africa can be measured. This is indicated by the

![Figure 6.2: Time series of daily medians of $X_{CO}$ retrieved from the FTS on Ascension Island (light blue open circles) and means of flask pairs taken on Ascension Island (orange open circles). A blue line indicates a fit to the FTS data, a red line to the flask data.](image)
peak of the fit curve in red which is in good temporal agreement with the peak of the FTS measurements belonging to the BB season of Southern Africa. One possible explanation for this could be that CO being emitted through BB over the southern part of Africa is transported to Ascension more easily and to a larger amount also in the low layers of the troposphere. In contrast, CO being emitted close to the surface over the northern part of Africa moves not so easily to Ascension due to opposing northeasterly and southeasterly trade winds. The findings regarding the different transport patterns for emissions from Northern and Southern Africa especially for surface measurements are in very good agreement with tagged tracer simulations performed for surface data and column data. Results of these simulations will be presented in Sect. 6.3.3.

6.3.2 $X_{\text{CO}}$ on Ascension in the Context of the El Niño Southern Oscillation

Next to the two peaks belonging to the two different burning seasons of the African continent another striking feature can be found in the $X_{\text{CO}}$ time series. It shows significantly higher values in the second half of 2015 in comparison to the same time periods of 2013 and 2014, see Fig. 6.2. It is assumed that the ENSO is the driver
for this elevated measurements. The multivariate ENSO index (MEI (Wolter, 1987)) indicates that there has been a strong El Niño event in 2015-2016 (see Fig. 6.4, upper panel). This strong El Niño event has led to severe droughts in several parts

\[ \text{Figure 6.4: Upper panel: Multivariate ENSO index (Wolter, 1987). The peaks of two strong El Niño events in 1998 and 2015/16 are very pronounced. Lower panel: MEI in comparison to } X_{CO} \text{ from Ascension Island. The grey line with dots represents the MEI, light blue open circles are daily medians of } X_{CO}, \text{ a blue line indicates a fit to the FTS data.} \]
of the world. As a consequence the fire seasons in these regions happened to be stronger than usual which resulted in stronger BB emissions. Several studies have been published recently in this context. For example, a case study by Parker et al. (2016) investigates the enhancements of $X_{\text{CH}_4}$ and $X_{\text{CO}_2}$ measured with GOSAT due to stronger fires over Indonesia in September and October 2015. Heymann et al. (2017) estimates CO$_2$ emissions from fires for the same region and from July to November 2015 by using data from OCO-2.

The time series of $X_{\text{CO}}$ is assumed to be influenced by these strong fire activities. In the last quarters of the years 2013 and 2014 $X_{\text{CO}}$ measured on Ascension Island declined towards the end of the BB season of Southern Africa. On the contrary, $X_{\text{CO}}$ values of up to 125 ppb per day can be measured in the last quarter of 2015. On average, total column values measured in the air above Ascension Island are significantly higher than in the two preceding years. This is in good agreement with the MEI indicating the strong El Niño event in 2015-2016 (see Fig. 6.4, lower panel). Results from tagged tracer simulations for CO$_2$ which are presented in the next section (Sect. 6.3.3) support the hypothesis that a large part of the elevated CO signal in the second half of 2015 can be tracked down to burning in tropical Asia.

6.3.3 Tagged Tracer Simulations with GFAS Data

Firstly, it has been investigated in which altitudes most of the fire emissions are released according to GFAS v1.2 data. An analysis of the data for the years 2011 until 2016 yields that approximately 67% of the emissions are emitted above the very first level of TM3. This is also illustrated in Fig. 6.5. The figure depicts the CO$_2$ emissions for the year 2015. The pattern is similar for other years.

**Tagged tracer simulations with only surface fluxes vs. tagged tracer simulations with volumetric fluxes**

Interestingly, the large portion of fire emissions being released above the first model layer does not lead to significantly different results when explicitly considered in tagged tracer simulations. One of the key findings of performing the tagged tracer simulations has been that the influence of releasing volumetric fluxes instead of surface emissions is relatively small. Figure 6.6 shows this difference in CO$_2$ emissions which could be detected at Darwin and Ascension. Darwin was chosen for comparison because this SH TCCON site is also strongly influenced by BB. For Darwin the emissions from Australia are considered as Australia is the TransCom3 land region which has the strongest influence on the signals measured at Darwin. Likewise for Ascension the difference in emissions from Southern Africa are shown. It is obvious that at Darwin a much greater difference can be detected than on Ascension Island.
Figure 6.5: Total emissions of CO$_2$ released through BB in 2015. Plotted is GFAS v1.2 data. Panel $c$ shows a map indicating in which regions of the world large emissions of CO$_2$ have occurred due to BB in that year. Panel $a$ shows the same data but with the vertical injection included. The CO$_2$ emissions have been meridionally averaged in this panel. Zonally averaged CO$_2$ emissions for the same year are shown in panel $c$. Note that in panel $a$ as well as in panel $c$ large amounts of the emissions happen in altitudes corresponding to approx. 600 to 950 hPa.
Figure 6.6: Difference in CO$_2$ detectable by models at Darwin and Ascension for releasing fire emissions as volumetric fluxes instead of fluxes released only at the surface. The figure shows the particular regions which have the most influence for the corresponding TCCON stations: South Africa for Ascension Island, Australia for Darwin. Difference at Darwin is shown in dark green dots, difference on Ascension Island is shown in orange triangles. There are some timegaps because the simulations have only been sampled where real measurements were available.

For Darwin a difference up to 0.2 ppm is simulated for times which correspond to the BB season of Australia. It is important to mention that Darwin, which is located at the northern coast of Australia lies in the middle of that part of Australia, where most of the burning takes place, see Fig 1.2 and Fig. 6.5. Ascension Island is more than 1500 km away from the source region of southern Africa. Vertical mixing of the tracer while being transported from the source region to Ascension diminishes the difference between volumetric fire fluxes and fluxes released only at the surface by almost a factor of ten in comparison to Darwin. There were a lot more simulations performed for other TransCom3 land regions and as a third SH TCCON station Reunion Island has also been included in the study. Results are not shown here as they agree with the above mentioned findings. In summary, all simulations performed for volumetric fire fluxes instead of fluxes only at the surface support the same conclusion: Only close to the fires does injection height seem to matter.
Conflicting results regarding the effect of considering the injection height in modeling fire emissions have been reported in the past. The findings presented here are similar to those of Chen et al. (2009). They found the total effect of considering injection heights for simulating the North American boreal fire emissions in 2004 to be small. On the other hand, Freitas et al. (2006) show a comparison between a model and measurements with best agreement when most of the fire emissions are directly incorporated into the middle troposphere. As the difference between simulations with and without incorporated injection heights are quite small in the simulations presented in this work, it has been decided to only perform more simulations for fire emissions without volumetric fluxes.

Results of simulations for different TransCom3 regions
Figure 6.7 shows the annual CO$_2$ emissions for the six southernmost TransCom3 land regions based on GFAS v1.2 data. It is obvious that some regions have relatively constant emissions from year to year, e.g. Southern Africa, while particularly the emissions from tropical Asia and Australia vary from year to year. Interannual variability in precipitation rates partly control the variability in fire-driven emissions.

![Graph showing CO$_2$ emissions for the six southernmost TransCom3 regions](image)

**Figure 6.7:** Estimated CO$_2$ emissions for the six southernmost TransCom3 regions in the time period from 2011 to 2016 based on GFAS v1.2. Shown are total estimated CO$_2$ emissions in Pg Carbon per year for these regions: Southern Africa (green), Northern Africa (blue), tropical Asia (red), Australia (light green), tropical America (cyan), South America (purple).
This effect is notably important for tropical Asia where annual variability in precipitation is strongest (van der Werf et al., 2008). As mentioned in Sect. 6.3.2 the strong El Niño event in 2015-2016 led to more fires in Indonesia which results in almost three times higher CO$_2$ emissions in 2015 compared to the average of the years 2011, 2012, 2013 and 2016, see Fig. 6.7. Likewise, the emissions for Australia have been higher in 2011 and 2012 compared to later years shown.

The main qualitative results for performing tagged tracer simulations with GFAS v1.2 data as input for the two TCCON sites Ascension Island and Darwin are shown in Fig. 6.8 and Fig. 6.9. By far the most fire signal in the total column on Ascension can be measured for the two regions Southern Africa and Northern Africa (see Fig. 6.8, lower panel). Interestingly, the peaks corresponding to the two different

![Figure 6.8: Detrended tagged tracer simulation for Ascension Island. Shown are emissions from the four TransCom3 regions with the most influence on Ascension Island; blue dots: Northern Africa, dark green dots: Southern Africa, cyan dots: tropical America, red dots: tropical Asia. The upper panel depicts the detrended simulated CO$_2$ time series which could be detected in surface measurements. The lower panel shows the same time series for total columns.](image-url)
burning seasons of the African continent match better for the total column measurements whereas not so much emissions seem to be transported from Northern Africa close to the surface (see Fig. 6.8, upper panel). In the zone around the equator, northeasterly trade winds meet southeasterly trade winds. The ITCZ (see also Sect. 3.3) acts like a natural border between the two regimes, not allowing for mixing of gases close to the surface. Instead, thermal convection associated with transport of air molecules upwards occurs due to intense solar radiation heating the surface in the ITCZ. This difference between simulated signals measured at surface from Northern and Southern Africa is in good agreement with the comparison between $X_{CO}$ measurements and flask measurements, see Fig. 6.2.

Furthermore, performing tagged tracer simulations for CO$_2$ proof that besides BB

![Figure 6.9: Detrended tagged tracer simulation for Darwin. Shown are emissions from the three TransCom3 regions with the most influence at Darwin; light green dots: Australia, dark green dots: South Africa, red dots: tropical Asia. The upper panel depicts the detrended simulated CO$_2$ time series which could be detected in surface measurements. The lower panel shows the same time series for total columns.](image-url)
signals from Southern Africa and Northern Africa the TCCON station on Ascension Island also detects signals from tropical Asia. The strong peak from El Niño-induced fires in Indonesia is clearly visible for the region tropical Asia in Fig. 6.8 in the last three months of 2015. To a small amount even CO$_2$ from BB in tropical America can be detected in the column above Ascension Island. For the TCCON station at Darwin the highest fire signals come obviously from the region Australia (see Fig. 6.9, lower panel). Likewise on Ascension the strong fires in Indonesia in 2015 also show up significantly at Darwin. To a smaller but regular amount signals from Southern Africa can be detected in the column above Darwin. The surface measurements are clearly dominated by the region Australia (see Fig. 6.9, upper panel). This is evident because those measurements are performed in the middle of area where strongest BB occurs in Australia. In Appendix B detrended simulations for the six southernmost TransCom3 regions are shown for the three sites Ascension Island, Darwin and Reunion Island.

Figure 6.10 shows a direct comparison between the modeled simulations for the six southernmost TransCom3 regions being sampled on Ascension with the seasonality in the CO time series measured on Ascension. The two different data sets agree very well and it is shown once more that the most influence in the CO time series comes from the African continent.

![Figure 6.10](image)

**Figure 6.10:** Detrended tagged tracer simulation for Ascension in comparison to the seasonal signal of CO measured with the FTS. Shown are CO$_2$ emissions for the six southernmost TransCom3 regions (left y-axis) vs. the seasonality of CO measured with the FTS (right y-axis).
6.4 Summary and Outlook

6.4.1 Summary

The $X_{CO}$ time series from the TCCON site on Ascension allows the detection of the two different BB seasons of the African continent. The CO flask data yield elevated signals of BB only from Southern Africa. Another main finding is that the higher $X_{CO}$ values in the second half of 2015 can be attributed to stronger, El Niño-induced fires in Indonesia. Performing tagged tracer simulations with explicitly taking the injection height of the fire emissions into account did not yield significantly different results than tagged tracer simulations with fire emissions being released at the surface. In addition, the tagged tracer simulations for CO$_2$ support the hypothesis that the TCCON instrument on Ascension sees mainly signals from Southern Africa. The influences from Northern Africa, tropical Asia and tropical America are also visible, but to a minor extent.

6.4.2 Outlook

As a closing remark for this chapter, it should be mentioned that Africa and the South Atlantic were studied intensively in the context of BB with two field campaigns recently (Zuidema et al., 2016). The LASIC campaign (see also Sect. 4.2.1) took place between June 2016 and October 2017. A mobile ARM facility from the Department of Energy of the United States has been deployed on Ascension to mainly study aerosols with both in situ and remote sensing techniques (see also Sect. 4.2). It is supposed that a very valuable data set could be created of measurements made on Ascension Island spanning two BB seasons of Southern Africa as continuous in situ CO measurements and regular radiosonde launches have been part of the campaign, too. The second campaign, ObseRvations of Aerosols above CLouds and their intErActionS (ORACLES), is an aircraft campaign. It is based in Namibia with regular flights to Ascension during the BB season of Southern Africa in 2016, 2017 and 2018. Even though this campaign focuses on the interactions between aerosols, radiation and clouds, one instrument package onboard measures CO$_2$ and CO, too. It is assumed that results from these two field campaigns will add a lot of knowledge to the investigation of BB above Africa and the South Atlantic, especially in the context of how BB signals from Southern Africa are incorporated into the surface layer around Ascension again. This phenomenon could be detected within this thesis by the comparison of $X_{CO}$ from TCCON and surface CO data from flasks and is supported by tagged tracer simulations of CO$_2$ but there are still open questions regarding the detailed mechanism of the down mixing.
Chapter 7

Summary and Outlook

7.1 Summary

The objective of my PhD project was to establish a ground-based remote sensing observatory for performing high-resolution FTIR measurements on the remote island Ascension Island in the South Atlantic Ocean. This was done successfully and the time series of the total column measurements of CO$_2$, CH$_4$ and CO now comprise more than five years. The measurements are performed in the framework of TCCON, a global network of ground-based stations serving for validation of GHG measurements made from space. Within this network and within carbon cycle research in general, the SH and especially the tropics are an undersampled region. Therefore, the time series of $X_{CO_2}$, $X_{CH_4}$ and $X_{CO}$ from Ascension provide valuable input, both for validating satellite data as well as for gaining deeper insight into the tropical carbon cycle.

In this thesis, the measurement site and the performance of the FTS since the beginning of its operation on Ascension in May 2012 were described. Especially the demands on the optical components which are placed outside are challenging due to the harsh environment on Ascension. Mirrors made from stainless steel were developed to overcome these issues. After equipping the solar tracker with these rugged mirrors, the operation of the instrument and the data coverage improved significantly (Feist et al., 2016). The development of such mirrors is of further interest to the scientific community using ground-based FTS instruments for remote sensing of the atmosphere. Furthermore, the alignment and stability of the FTS were investigated by analyzing gas cell measurements and retrieving ILS parameters.

Measurements of $X_{CO_2}$, $X_{CH_4}$ and $X_{CO}$ performed on Ascension were calibrated by using profile data from the aircraft campaign ATom-1 which took place in August.
2016. Due to this successful calibration the station gained status as full TCCON station in May 2017. By comparing the time series of $X_{CO_2}$ with in situ measurements performed at the surface, a slightly smaller seasonal cycle has been determined for the surface data than for the column data. This indicates that most of the variability measured in total column above Ascension takes place due to long-range transport and occurs above the MBL. A comparison between measured $X_{CO_2}$ and modeled $X_{CO_2}$ from the Jena CarboScope was accomplished and the model was found to be biased low against the measurements by approx. 1 ppm. It was also shown that measurements of $X_{CO_2}$ on Ascension make an important contribution to validation of observations from OCO-2 performed in ocean glint mode.

The main finding regarding the detailed investigation of the time series of $X_{CH_4}$ in comparison to $X_{CH_4}^{tropo}$, which could also be retrieved from the acquired spectra, and surface measurements is the unusual positive gradient of CH$_4$ concentrations with altitude. These results are in agreement with aircraft profile measurements of CH$_4$ sampled during the two campaigns ATom-1 and ATom-2. In February, concentrations of CH$_4$ in the MBL are lowest because of depletion by OH radicals is strongest. During this time of the year, the differences between lower values at the surface and higher values in the free troposphere can amount to more than 50 ppb. The positive gradient with altitude is caused by different origins of the air. At the surface, clean air is coming from the deep South Atlantic Ocean all year round. Due to the trade wind inversion, this pattern is very stable. In the free troposphere, polluted air masses from the continents, mainly Africa, are transported towards Ascension.

The time series of $X_{CO}$ is mainly determined by the two different BB seasons on the African continent. On the other hand, the surface flasks capture only elevated signals of BB from Southern Africa. It was demonstrated that the TCCON station on Ascension is also able to detect fire emissions from more distant regions of the world. Higher $X_{CO}$ values in the second half of 2015 could be attributed to stronger, El Niño-induced fires in Indonesia by performing tagged tracer simulations. Altogether, these simulations showed that the measurements of $X_{CO}$ on Ascension are mainly influenced by BB signals from Southern Africa and to a minor extent also by BB signals from Northern Africa, tropical Asia and tropical America.

7.2 Outlook

Surface measurements of CO$_2$, CH$_4$ and CO performed by NOAA on Ascension and total column measurements of the same gases conducted within this work show very interesting differences. It is obvious that in situ measurements at ground level and measurements spanning the total column of the atmosphere yield different results
because the surface measurements are much more affected by local influences. The total column measurements, on the other hand, have a larger footprint meaning they sample a large area surrounding the measurement site. On Ascension, this situation is amplified due to the trade wind inversion. The air parcels landing on Ascension close to the surface and in the total column have different origins, which is especially evident when comparing the different data sets of CH4. The pattern is similar on Reunion Island which is located east of the African continent. Similar differences between surface and total column measurements can be detected there. Using the ground-based total column measurements of XCO2 and XCH4 from Ascension, and ideally also from Reunion Island, in inverse modeling could provide a better constraint on emissions of the African continent than using only in situ measurements. It would be highly interesting to perform regional inversions and to compare the results of the different inversion set-ups.

Thus, the continued operation of the TCCON station on Ascension is important, especially as the measured time series of XCO2, XCH4 and XCO proof to be useful data sets from an understudied region of the world. To continue performing total column measurements at this remote place will be even more challenging in the future as the access to the island has recently been made more difficult by the airport closure for larger airplanes. At the moment, Ascension can only be accessed via the island Saint Helena onboard an Embraer jet once every month. This makes regular maintenance visits more difficult. As the value of such time series of atmospheric trace gases increases with the length of the record, I can only hope that the TCCON station on Ascension is operated for many more years despite the challenges that arise from the remote location of the island.

Appendices
Appendix A

Flight Tracks of ATom-1 and Extended Aircraft Profiles

Figures A.1 and A.2 show three-dimensional flight tracks of ATom-1 before landing on Ascension and after leaving Ascension in August 2016.

Figures A.3 to A.8 show the extended aircraft profiles used for the calibration of the TCCON station on Ascension Island (see also Sect. 4.2).
**Figure A.1:** Flight track of aircraft before landing on Ascension Island on August 15, 2016.

**Figure A.2:** Flight track of aircraft after leaving Ascension Island on August 17, 2016.
Figure A.3: Extended CO$_2$ profile taken during landing on August 15, 2016. The aircraft started its descent at a height of 12.6 km. Aircraft measurements are given as green dots. Blue squares represent the GFIT a priori profile which has been shifted upwards by 300 meters to match the tropopause retrieved from radiosonde data. The red line with red dots shows the full profile which is used for the integration. It is interpolated where aircraft data are available and extended with a median value representing the free troposphere above the aircraft ceiling. 1 km before reaching the tropopause, it smoothly turns toward the shifted a priori profile with which it is extended in the stratosphere. The thin black line indicates the tropopause from radiosonde data.
Figure A.4: Extended CH₄ profile taken during landing on August 15, 2016. Details and colors are the same as in Fig. A.3.

Figure A.5: Extended CO profile taken during landing on August 15, 2016. Details and colors are the same as in Fig. A.3.
Figure A.6: Extended CO₂ profile taken after the start on August 17, 2016. The aircraft measured up to a height of 10.1 km after takeoff. Aircraft measurements are given as green dots. Blue squares represent the GFIT a priori profile which has been shifted upwards by 180 meters to match the tropopause retrieved from radiosonde data. The red line with red dots shows the full profile which is used for the integration. It is interpolated where aircraft data are available and extended with a median value representing the free troposphere above the aircraft ceiling. 1 km before reaching the tropopause, it smoothly turns toward the shifted a priori profile with which it is extended in the stratosphere. The thin black line indicates the tropopause from radiosonde data.
Figure A.7: Extended CH$_4$ profile taken after the start on August 17, 2016. Details and colors are the same as in Fig. A.6.

Figure A.8: Extended CO profile taken after the start on August 17, 2016. Details and colors are the same as in Fig. A.6.
Appendix B

Tagged Tracer Simulations

In this appendix detrended simulations for the six southernmost TransCom3 regions (South Africa, North Africa, temperate South America, tropical South America, Australia, tropical Asia) are shown for the three measurement sites Ascension Island (Fig. B.1), Darwin (Fig. B.2) and Reunion Island (Fig. B.3). More information can also be found in Sect. 6.3.3.
Figure B.1: Detrended tagged tracer simulation for Ascension Island. Shown are emissions from the six southernmost TransCom3 regions (purple dots: South America, cyan dots: tropical America, green dots: Southern Africa, blue dots: Northern Africa, red dots: tropical Asia, light green: Australia). The upper panel depicts the detrended simulated CO$_2$ timeseries which could be detected in surface measurements. The lower panel shows the same time series for total columns.
Figure B.2: Detrended tagged tracer simulation for Darwin. Details and used colors are the same as in Fig. B.1.
Figure B.3: Detrended tagged tracer simulation for Reunion Island. Details and used colors are the same as in Fig. B.1.
Appendix C

Dimensional Drawings of Mirrors and Mountings

The following figures (Fig. C.1 to Fig. C.4) show dimensional drawings of the stainless mirrors and mountings used with the Bruker A547 solar tracker on Ascension Island (see also Sect. 3.4.1).
Figure C.1: Dimensional drawing of the stainless steel mirror. On the left side the side view is shown. The front view can be seen on the right side. It is important to note that the two mirrors which are needed for the elevation and the azimuth direction are identical. They fit on both mountings (see Fig. C.2 and Fig. C.3). The elevation mirror typically suffers more because it is upward looking during operation most of the time which results in more scratches on the surface. Being able to change the mirrors among themselves leads to a more uniform wear and tear of the mirrors.
**Figure C.2:** Dimensional drawing of the mounting for the elevation mirror. On the left side the side view is shown. The front view can be seen on the right side.
Figure C.3: Dimensional drawing of the mounting for the azimuth mirror. On the left side the side view is shown. The front view can be seen on the right side. The dashed red lines mark the area where the mounting is attached to solar tracker.
Figure C.4: Dimensional drawing of azimuth mirror with mounting as it is attached to the solar tracker (side view).
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<th>Full Form</th>
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<tr>
<td>ACE-FTS</td>
<td>Atmospheric Chemistry Experiment-Fourier Transform Spectrometer</td>
</tr>
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<td>ARM</td>
<td>Atmospheric Radiation Measurement</td>
</tr>
<tr>
<td>ATom</td>
<td>Atmospheric Tomography Mission</td>
</tr>
<tr>
<td>BB</td>
<td>Biomass Burning</td>
</tr>
<tr>
<td>BESD</td>
<td>Bremen Optimal Estimation Differential Optical Absorption Spectroscopy</td>
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<tr>
<td>CAMS</td>
<td>Copernicus Atmosphere Monitoring Service</td>
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<tr>
<td>DMF</td>
<td>Dry-Air Mole Fraction</td>
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<tr>
<td>ECMWF</td>
<td>European Centre for Medium-Range Weather Forecasts</td>
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<tr>
<td>ENSO</td>
<td>El Niño Southern Oscillation</td>
</tr>
<tr>
<td>ENVISAT</td>
<td>Environmental Satellite</td>
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<tr>
<td>ESA</td>
<td>European Space Agency</td>
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<tr>
<td>FRP</td>
<td>Fire Radiative Power</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>FTS</td>
<td>Fourier Transform Spectrometer</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GFAS</td>
<td>Global Fire Assimilation System</td>
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<tr>
<td>GHG</td>
<td>Greenhouse Gas</td>
</tr>
<tr>
<td>GOSAT</td>
<td>Greenhouse Gases Observing Satellit</td>
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<tr>
<td>HITRAN</td>
<td>High-Resolution Transmission Molecular Absorption</td>
</tr>
<tr>
<td>HYSPLIT</td>
<td>Hybrid Single Particle Lagrangian Integrated Trajectory</td>
</tr>
<tr>
<td>IMECC</td>
<td>Infrastructure for Measurement of the European Carbon Cycle</td>
</tr>
<tr>
<td>ILS</td>
<td>Instrumental Line Shape</td>
</tr>
<tr>
<td>InGaAs</td>
<td>Indium Gallium Arsenide</td>
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<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<td>--------------</td>
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<tr>
<td>IPCC</td>
<td>International Panel on Climate Change</td>
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<tr>
<td>ITCZ</td>
<td>Intertropical Convergence Zone</td>
</tr>
<tr>
<td>I2S</td>
<td>Interferogram-to-Spectrum</td>
</tr>
<tr>
<td>JAXA</td>
<td>Japan Aerospace Exploration Agency</td>
</tr>
<tr>
<td>LASIC</td>
<td>Layered Atlantic Smoke Interactions with Clouds</td>
</tr>
<tr>
<td>LSCE</td>
<td>Laboratoire des Sciences du Climat et de l’Environnement</td>
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<tr>
<td>MACC</td>
<td>Monitoring Atmospheric Composition and Climate</td>
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<tr>
<td>MkIV</td>
<td>JPL Mark IV Ballon Interferometer</td>
</tr>
<tr>
<td>NCAR</td>
<td>National Center for Atmospheric Research</td>
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<tr>
<td>NCEP</td>
<td>National Centers for Environmental Prediction</td>
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<tr>
<td>NH</td>
<td>Northern Hemisphere</td>
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<tr>
<td>NIR</td>
<td>Near-Infrared</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration</td>
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<tr>
<td>OCO-2</td>
<td>Orbiting Carbon Observatory-2</td>
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<tr>
<td>OPD</td>
<td>Optical Path Difference</td>
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<td>ORACLES</td>
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<td>PLC</td>
<td>Programmable Logic Controller</td>
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<tr>
<td>RTE</td>
<td>Radiative Transfer Equation</td>
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<td>SCIAMACHY</td>
<td>Scanning Imaging Absorption Spectrometer for Atmospheric Chartography</td>
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<tr>
<td>SH</td>
<td>Southern Hemisphere</td>
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<tr>
<td>SIA</td>
<td>Solar Intensity Average</td>
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<tr>
<td>SZA</td>
<td>Solar Zenith Angle</td>
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<tr>
<td>TANSO-FTS</td>
<td>Thermal and Near Infrared Sensor for Carbon Observation - Fourier Transform Spectrometer</td>
</tr>
<tr>
<td>TCCON</td>
<td>Total Carbon Column Observing Network</td>
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<tr>
<td>TROPOMI</td>
<td>Tropospheric Monitoring Instrument</td>
</tr>
<tr>
<td>VMR</td>
<td>Volume Mixing Ratio</td>
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<tr>
<td>VSF</td>
<td>Volume Mixing Ratio Scale Factor</td>
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<tr>
<td>WMO</td>
<td>World Meteorological Organization</td>
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