Using solar FTIR spectrometry to investigate the sources and sinks of carbonyl sulfide and its application to the carbon cycle

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Abstract

Understanding carbon dioxide (CO$_2$) biospheric processes is of great importance because the terrestrial exchange drives the seasonal and inter-annual variability of CO$_2$ in the atmosphere. Atmospheric inversions based on CO$_2$ concentration measurements alone can only determine net biosphere fluxes, but not differentiate between photosynthesis (uptake) and respiration (production). Carbonyl sulfide (OCS) could provide an important additional constraint: it is also taken up by plants during photosynthesis but not emitted during respiration, and therefore is a potential means to differentiate between these processes.

Solar absorption Fourier Transform InfraRed (FTIR) spectrometry allows for the retrievals of the atmospheric concentrations of both CO$_2$ and OCS from measured solar absorption spectra. Here, we exploit the FTIR measurements of OCS and CO$_2$ to study their atmospheric relationship. The OCS columns are retrieved from the measured spectra at twelve stations spanning both Northern and Southern Hemisphere. The CO$_2$ FTIR data in the Northern Hemisphere are also used.

The OCS measurements were compared to forward simulations using a chemical transport model (GEOS-Chem) driven by different land biosphere fluxes to reproduce the seasonality of the measurements. Increasing the plant uptake of Kettle et al. (2002a) by a factor of three resulted in the best comparison with the measurements. The simulation with OCS land fluxes from the simple biosphere model (SiB) underestimated the seasonal amplitude in the high latitudes of the Northern Hemisphere, indicating that the latitudinal flux distributions in SiB need to be adjusted. There are discrepancies in the low latitudes when comparing with HIPPO (HIAPER Pole-to-Pole Observations) data spanning both hemispheres, which implies a missing source in that region.

OCS flux inversions were performed to gain better flux maps. The inversion with SiB land fluxes and Campbell et al. (2015) anthropogenic emissions leads to the best agreement with the measurements. However, the validation with HIPPO measurements shows mismatches in the tropics as well as Northern temperate region, where the measurements are too sparse to constrain the fluxes. Inclusion of FTIR measurements did not improve the inversion, because there is an offset between these two data sets, which makes it not straightforward.

The simple biosphere model (SiB) simultaneously calculates the biospheric fluxes of both OCS and CO$_2$. Therefore the CO$_2$ biosphere fluxes in SiB can be evaluated with the help
of OCS. The CO$_2$ simulation with SiB fluxes agrees with the measurements well, while the OCS simulation reproduced a weaker drawdown than the measurements at selected Northern Hemispheric sites, and a smaller latitudinal gradient in the Northern Hemisphere during growing season. It suggests that the photosynthesis is underestimated in the boreal region in SiB. An offset in the timing of the seasonal cycle minimum between SiB simulation and measurements is also seen in both CO$_2$ and OCS. These phase differences offer another aspect that can be used to evaluate the photosynthesis and respiration in SiB. The OCS was also used to study the contributions of photosynthesis and respiration on the inter-annual variation of atmospheric CO$_2$. The heatwave event in 2010 was taken for a case study. The analysis of OCS indicates that the photosynthesis decreased during the heatwave, which is underestimated in SiB. Using OCS as a photosynthesis proxy can help to understand how the biospheric processes are reproduced in models and to further understand the carbon cycle in the real world.
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I would like to thank Professor Justus Notholt, who gave me the opportunity to conduct my PhD work in his working group in the University of Bremen. I am grateful for his support during my whole research and for the time he spend on reviewing this thesis.

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Publications

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Presentations at conferences

- EGU 2016, Vienna, Austria, April, 2016, PICO-presentation: Using NDACC column measurements of carbonyl sulfide to estimate its sources and sinks.

• NDACC IRWG and TCCON Meeting, Bad Sulza, Germany, May, 2014, oral presentation: Investigating the atmospheric relationship between carbonyl sulfide and carbon dioxide using solar FTIR spectrometry and a chemical transport model.

• Ny-Ålesund Science Managers Committee 11th Seminar, Rome, Italy, October, 2013, oral presentation: Investigating the atmospheric relationship between carbonyl sulfide and carbon dioxide using solar FTIR spectrometry and a chemical transport model.

• 9th International Carbon Dioxide Conference, Beijing, China, June, 2013, poster: Investigating the atmospheric relationship between carbonyl sulfide and carbon dioxide using solar FTIR spectrometry and a chemical transport model.

• NDACC IRWG and TCCON Meeting, Wengen, Switzerland, June, 2012, poster: Retrieval of the seasonal and diurnal variation of NO₂ above Ny-Ålesund and comparison to DOAS measurements.
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Chapter 1

Motivation and outline

1.1 Motivation

Understanding the carbon dioxide (CO\textsubscript{2}) biospheric processes within the carbon cycle is of great importance, because (1) the land carbon sink absorbs more than a quarter of the CO\textsubscript{2} emissions released by human activities, which mitigates the increase of atmospheric CO\textsubscript{2} concentration; and (2) terrestrial exchange drives CO\textsubscript{2} variability in the atmosphere on seasonal and inter-annual timescales. The total biospheric CO\textsubscript{2} flux (net ecosystem production, NEP) is the sum of two much larger terms with different seasonality and drivers: the carbon uptake of gross primary production (GPP) and the release via respiration (Re). These fluxes are co-located, therefore, typically only information about their sum (the NEP) is available when they are quantified. To improve our knowledge of CO\textsubscript{2} biospheric processes, in particular how ecosystems will respond to a changing climate, we would ideally like to understand the individual contributions of these two fluxes.

Laboratory experiments (e.g. Goldan et al., 1988) have studied the pathway for carbonyl sulfide (OCS) uptake by plants, which is similar to the uptake mechanism of CO\textsubscript{2} during photosynthesis. Unlike CO\textsubscript{2}, OCS uptake is a one-way process, and it is not emitted during respiration. Therefore OCS could be used to differentiate between photosynthesis and respiration fluxes of CO\textsubscript{2} (Campbell et al., 2008). Flask measurements of OCS in the Northern Hemisphere show a clear seasonal variation with a maximum in early spring and minimum in autumn, which is similar to the seasonality of CO\textsubscript{2} (Montzka et al., 2007) as biospheric fluxes are the main driver of the seasonal cycles for both species (Kettle et al., 2002a).
However, the estimates of OCS sources and sinks still have significant uncertainties. To use OCS as a photosynthetic tracer, it is necessary to first improve our knowledge of the OCS fluxes with the help of more measurements at different latitudes and ecosystem regions. Until now, the measurements used for OCS studies are sparse. The typical measurements involved, such as the NOAA/ESRL/GMD network, include ground-based and aircraft flask sampling data. These ground-based in-situ measurements are only at limited sites and aircraft measurements cover relatively short time periods. The satellite data, though provide a wide distribution of OCS, are mainly sensitive in the upper troposphere and stratosphere (Barkley et al., 2008, Glatthor et al., 2015, Kuai et al., 2014), and therefore provide little help on constraining the land fluxes.

Ground-based solar absorption Fourier Transform InfraRed (FTIR) spectrometry measures the absorption of both CO$_2$ and OCS. They can be used to retrieve the total and/or partial atmospheric columns of these two gases. Compared to satellite retrievals, the FTIR OCS retrievals are sensitive at both high and low altitude and can capture the variations due to the biospheric processes. Additionally, when interpreted by models, total column measurements are much less sensitive to assumptions on the boundary layer mixing, because every molecule in the atmospheric column is detected, independent of whether it is at the surface or in the upper troposphere. In order to obtain realistic fluxes by inverse models, assumptions must be made on the vertical mixing in the atmosphere, which is currently a large uncertainty in the transport of most models (Keppel-Aleks et al., 2011, Wunch et al., 2011, Yang et al., 2007). Therefore, column measurements of OCS and CO$_2$ could provide additional information for evaluating their terrestrial exchange.

The FTIR networks have been existing for more than 20 years, but have never been used for this topic before. The aim of this work is to exploit the ground-based FTIR measurements of OCS to evaluate its sources and sinks, and further to use OCS as a tracer of photosynthesis.

### 1.2 Aims

The final goal of this study is to separate the photosynthesis and respiration contributions to land biosphere-atmosphere carbon exchange processes and to improve the estimation of gross primary production (GPP) of the biosphere. To reach this goal, we will first consider the following objectives:
1. evaluation the estimates of OCS sources and sinks.

2. Investigation of the atmospheric relationship between CO$_2$ and OCS.

3. Application of OCS to study the response of photosynthesis and respiration to climate variabilities.

After the above work, we can be more confident of the usage of OCS to separate the photosynthesis and respiration. Based on the relationship between OCS and CO$_2$, atmospheric inversions with both gases can be made to estimate the GPP.

### 1.3 Outline

This work is presented in the PhD thesis in the following order:

Chapter 2: First of all, the roles of CO$_2$ on the climate change and the importance of understanding the CO$_2$ biosphere processes is described. Then the ways to separate the photosynthesis and respiration including using OCS as the photosynthesis tracer are introduced. After that, an overview of the properties of OCS is given. The previous researches on the relationship between OCS and CO$_2$ are reviewed.

Chapter 3: This chapter introduces the measurements and models used in this study. First the theories of FTIR measurements and the trace gases retrieval methods are described, then the in-situ measurements (both surface and aircraft measurements) are also introduced. The models including the forward and inversion model as well as the biosphere model used in the study are described.

Chapter 4: The selection of the FTIR sites and the OCS retrievals are shown in this chapter. The OCS is retrieved from the FTIR spectra using different setups. The results are compared to choose the best retrieval approach.

Chapter 5: In this chapter, forward simulations of OCS are performed using different surface fluxes. By the comparison between the simulations and measurements, the sources and sinks of OCS are evaluated.

Chapter 6: In order to obtain better OCS flux estimations, the flux inversions are conducted. Different prior flux fields are used to test the impact on the results. The inversions
are first performed with the flask measurements only, and then the FTIR measurements are included.

Chapter 7: After the evaluation of the OCS fluxes, the application of OCS as an photosynthesis tracer is tested in two aspects: the GPP amount and seasonal cycle simulated in the biosphere model are evaluated with the help of OCS; the contributions of photosynthesis and respiration to the inter-annual variations of CO$_2$ are analyzed by combining the variations of OCS and CO$_2$.

Chapter 8: This chapter summaries the results of this work. The future plans are given in the outlook.
Chapter 2

Scientific background

2.1 Climate change

This section is largely adopted from the contribution of Working Group 1 to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC, 2013a).

Climate change has been observed from direct or remote sensing measurements in the atmosphere, ocean, cryosphere, and at land surface. The temperature of the lower atmosphere and the upper part of ocean have increased (e.g. Brönnimann et al., 2007, Cicerone et al., 2001, Salinger, 2005); the ice sheets of Greenland and Antarctic have been losing mass, the glaciers over worldwide have continued to shrink, and Arctic sea ice has decreased in extent (Serreze et al., 2007); the sea level has risen; the atmospheric circulation has changed (e.g. Diaz and Bradley, 2004); the concentrations of greenhouse gases (GHGs) such as carbon dioxide (CO$_2$), methane (CH$_4$), and nitrous oxide (N$_2$O) have increased; the intensity and frequency of extreme events such as droughts, floods, heat waves, heavy precipitation, and strong hurricanes have increased (e.g. Alexander et al., 2006, Brönnimann et al., 2007, Easterling et al., 2000, Thornton et al., 2014).

The Earth’s climate system is powered by solar radiation (Figure 2.1). About 30% of the incoming solar shortwave radiation (SWR) is reflected back to space by atmosphere (clouds, gases and aerosols) and Earth’s surface (albedo); about a half of SWR is absorbed by the Earth’s surface; and approximately 20% is absorbed in the atmosphere (Kiehl and Trenberth, 1997). The Earth’s surface emits longwave radiation (LWR) to the atmosphere and part of it is absorbed by greenhouse gases (GHGs) such as water vapor (H$_2$O), CO$_2$,
Chapter 2. Scientific background

Figure 2.1: The Earth’s mean energy balance and the main drivers of climate change (Cubasch et al., 2013).

\[CH_4, \text{ and } N_2O. \] The GHGs and clouds trap the energy that is trying to escape to space, thus heating the Earth surface. These GHGs and clouds also emit LWR into atmosphere and space, the latter is called outgoing longwave radiation (OLR). In a steady state, the incoming SWR minus the amount reflected by the atmosphere should be in balance with the OLR. Therefore the Earth’s temperature can stay constant.

The climate system is influenced by many natural and anthropogenic substances and processes such as the Sun, clouds, GHGs, aerosols, land use and land cover (Baede et al., 2001, IPCC, 2013a) (see Figure 2.1). These substances and processes, which alter the energy budget of the Earth, are called the drivers of climate change, including both natural and anthropogenic. The main natural drivers are the solar fluctuations and the Earth’s orbit variations, which can change the solar radiation. The land use, combustion of fossil fuels and biomass burning are the main human activities which have effects on the climate change. The biomass and fossil fuel burning changes the concentration of the GHGs and aerosols in the atmosphere, altering the radiation budget.

For studying how much the climate drivers (natural and anthropogenic substances and processes) affect the climate change, IPCC calculated the radiative forcing (RF) of different factors to quantify the change in energy flux at tropopause or at the top of the atmosphere caused by a driver. When the RF of a factor is positive, the energy of the climate system will increase, and results in a warming of the system in average. In the
## Scientific background

### Radiative forcing estimations and aggregated uncertainties for the main drivers of climate change (IPCC, 2013b)

The values represent the forcing in 2011 relative to 1750 (the beginning of the industry revolution).

<table>
<thead>
<tr>
<th>Emitted compound</th>
<th>Resulting atmospheric drivers</th>
<th>Radiative forcing by emissions and drivers</th>
<th>Level of confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>CO₂</td>
<td>1.68 [1.33 to 2.03]</td>
<td>VH</td>
</tr>
<tr>
<td>CH₄</td>
<td>CO₂, CH₃OH, CH₃Cl, CH₄, Cl₂</td>
<td>0.97 [0.74 to 1.20]</td>
<td>H</td>
</tr>
<tr>
<td>Halo-carbons</td>
<td>O₃, CFCs, HCFCs</td>
<td>0.18 [0.01 to 0.30]</td>
<td>H</td>
</tr>
<tr>
<td>N₂O</td>
<td>N₂O</td>
<td>0.17 [0.13 to 0.21]</td>
<td>VH</td>
</tr>
</tbody>
</table>

- **Anthropogenic**
  - CO
  - NMOVC
  - NOₓ
  - Aerosols and precursors (e.g., SO₂, NOₓ, NH₃, Organic aerosol)
  - Cloud adjustments due to aerosols
  - Albedo change due to land use
  - Changes in solar irradiance

- **Natural**
  - Total anthropogenic RF relative to 1750

<table>
<thead>
<tr>
<th>Year</th>
<th>Radiative forcing relative to 1750 (W m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>2.29 [1.13 to 3.33]</td>
</tr>
<tr>
<td>1980</td>
<td>1.25 [0.64 to 1.98]</td>
</tr>
<tr>
<td>1950</td>
<td>0.57 [0.20 to 0.85]</td>
</tr>
</tbody>
</table>

Figure 2.2: Radiative forcing estimations and aggregated uncertainties for the main drivers of climate change (IPCC, 2013b). The values represent the forcing in 2011 relative to 1750 (the beginning of the industry revolution).

opposite, a negative RF represents a decrease of the energy in the Earth-atmosphere system and a system cooling. The estimates of the RF of the main climate change factors are shown in Figure 2.2. For the natural drivers, the total RF of solar radiation is small. Among the human-influenced drivers, the land use induced albedo change has a negative RF, which is a small amount compared to the RF of the gases and aerosols (e.g., Cicerone et al., 2001). The total RF of CO₂ (1.68 W/m²) is the highest positive value compared to other natural or anthropogenic drivers (e.g., IPCC, 2013b, Shindell et al., 2009), meaning that CO₂ is the most important anthropogenic GHG. The increased aerosols in the atmosphere due to human activities directly block the solar radiation to surface, leading to a surface cooling. This cooling effect is much smaller than the warming effect caused by anthropogenic GHGs emissions, thus the total anthropogenic RF is positive and the climate system is becoming warmer. Since the Industrial Revolution, the impact of human activities on global climate change is large and obvious. The total anthropogenic RF increases rapidly from 0.57 W/m² in 1950 to 2.29 W/m² in 2011 relative to 1750, of which about 63% are due to CO₂ emissions (IPCC, 2013b). Therefore the monitoring and studying of the atmospheric CO₂ is essential for predicting the climate change.
2.2 The carbon cycle

CO₂ is the most important anthropogenic greenhouse gas. Its contribution to radiation forcing largely affect the climate change (Cicerone et al., 2001). The global atmospheric CO₂ concentration has increased from about 280 ppm before industrial era to 400 ppm nowadays (Oh, 2010). The comparison of the observed atmospheric CO₂ record since 1959 from Mauna Loa Hawaii (Figure 2.4) and the high resolution Antarctic ice core records (Figure 2 in Lüthi et al. (2008)) shows that the atmospheric CO₂ concentration after industrial times is significantly higher than any time during the past 800,000 years. It indicates that the atmospheric CO₂ concentration increase since 1750 is largely due to human activities, which include fossil fuels combustion (the largest and direct influence), biomass burning, and land use and land cover change (LULCC).

![Atmospheric CO₂ at Mauna Loa Observatory](http://www.esrl.noaa.gov/gmd/ccgg/trends/full.html)

**Figure 2.3:** Monthly mean atmospheric carbon dioxide at Mauna Loa Observatory, Hawaii. http://www.esrl.noaa.gov/gmd/ccgg/trends/full.html

The carbon cycle is the transfer and exchange process of carbon among the atmosphere, biosphere, geosphere, hydrosphere, and pedosphere (Archer et al., 2009, Post et al., 1990). This occurs on many temporal and spatial scales. The basic processes of natural carbon cycle, which are the carbon fluxes before 1750, are shown in the black arrows in Figure 2.4 from the 5th IPCC report. On large scale of over millions of years, CO₂ is removed from the atmosphere by weathering of rocks and deposit in sediments in the Earth’s crust. The deposited CO₂ can be released again through volcanoes. On shorter time scale of years, CO₂ natural fluxes occur between the atmosphere and terrestrial biosphere, and the atmosphere and oceans. Terrestrial takes up CO₂ from the atmosphere through photosynthesis, and then releases the CO₂ again to the atmosphere by respiration. The oceans continuously exchange carbon with atmosphere. CO₂ enters the surface ocean and
Figure 2.4: The simplified schematic of the global carbon cycle (IPCC, 2013a). The black arrows and numbers show the natural processes and amount before the industrialization; the red arrows and numbers represent the changes by human activities.

reacts with water to form bicarbonate ($\text{HCO}_3^-$) and carbonate ($\text{CO}_3^{2-}$). Cold and dense water, enrich with $\text{CO}_2$, sinks at high latitudes from the surface to the ocean depths (Post et al., 1990). Over time, it is balanced by a diffuse upward transport into warm surface water. In addition to the dissolution, phytoplankton takes up carbon through photosynthesis. Part of these carbon sinks from the surface to the deeper layers in the form of dead organisms and particles, most of which is recirculated to the surface again. The natural carbon flows are fairly balanced, resulting in a stable concentration of $\text{CO}_2$ in atmosphere before the industrialization.

However, human activities add $\text{CO}_2$ to atmosphere and break the balance of the natural carbon cycle. These activities significantly change the carbon stocks in the reservoirs and the exchange between these reservoirs. The red arrows and numbers in Figure 2.4 show the annual mean human-caused carbon changes during 2000-2009. Every year, about 7.8 Pg C and 1.1 Pg C was released to the atmosphere in the form of $\text{CO}_2$ through fossil
Figure 2.5: Annual anthropogenic CO$_2$ emissions and their partitioning among the atmosphere, land and ocean (PgC year$^{-1}$) from 1750 to 2011 (IPCC, 2013a).

fuel combustion and LULCC, respectively. Of this amount, a quarter was absorbed by the Ocean, and a quarter was taken up by the terrestrial biosphere, and the rest a half stays in the atmosphere (Figure 2.5), resulting a CO$_2$ concentration increase by about 2 ppm per year (Raupach, 2011). The atmospheric increase in CO$_2$ leads to increased radiation forcing, and hence global warming. Ballantyne et al. (2012) calculated the changes in global CO$_2$ sources and sinks during the past 50 years and showed that the global carbon uptake had been doubled between 1960 and 2010, with an increase rate of about 0.05 Pg C year$^{-1}$. The net uptakes of CO$_2$ in the ocean and biosphere moderate the global climate change. However, the enhanced CO$_2$ in the ocean results in an increased hydrogen ion (H$^+$) concentration and a lower surface ocean pH. The biosphere behavior was also changed by the CO$_2$ fertilization. Analyses indicate that the magnitude and spatial distribution of the land carbon sink has increased over the past 30 years (Gurney and Eckels, 2011, Pan et al., 2011).

Among the components in the carbon cycle, several terms have a higher degree of certainty than others. Fossil fuel emissions, based on international energy statistics (Andres et al.,
are probably the best known term in the global carbon budget. The atmosphere CO$_2$ growth rate is obtained from the atmospheric measurements at a lot of sites all over the world, as well as the ice core observations, which is quite certain too. The Oceanic carbon uptake has been estimated from many different ocean models based on observations, which were assessed a medium confidence level (Le Quéré et al., 2015). So far, the land carbon sink is the most uncertain term in the global carbon cycle, and is calculated as the residual of the other components – that is the sum of the anthropogenic emissions minus the atmospheric increase and the ocean uptake (Le Quéré et al., 2015). Additionally, the land carbon sink has most variabilities compared to the other sources and sinks, and drives the CO$_2$ variations in the atmosphere. Therefore, it is important to understand the processes of CO$_2$ exchanges between the biosphere and atmosphere. This is the key point to predict the capability of the land continuously removing the extra burden of atmospheric CO$_2$ in the future, which is critically important to estimate the carbon trend and climate change.

2.3 The biospheric processes of CO$_2$

2.3.1 Some ecological terms used in carbon accounting

There are several processes that exchange CO$_2$ between the biosphere and the atmosphere. CO$_2$ enters the plants through the leaf stomata, and is then converted to organic compounds, which are used for the plant growth, through photosynthesis. Plants release CO$_2$ back to the atmosphere through respiration too, which is called as Autotrophic Respiration (Ra). Besides the plants, soils also respire CO$_2$, known as Heterotrophic Respiration (Rh). These CO$_2$ biospheric process can be described by the following concepts:

Gross Primary Production (GPP) represents the total amount of carbon fixed during the process of photosynthesis by plants in an ecosystem. It was estimated that the global GPP is around 123 Pg C year$^{-1}$ (Beer et al., 2010).

Net Primary Production (NPP) is GPP minus the amount of carbon respired by plants themselves, which is Ra:

$$NPP = GPP - Ra \quad (2.1)$$

NPP refers to the net production of organic carbon by the plant. This part is used for the plants growth and reproduction, and quantifies as the amount of biomass that can be
used by heterotrophic organisms including humanity. The estimation of NPP is about 60 Pg C year\(^{-1}\), approximately half of GPP. Recent calculations of global NPP from satellite data show an annual mean value of 53.1 Pg C year\(^{-1}\) from 2000 to 2010 (Smith et al., 2012).

Net Ecosystem Production (NEP) is the balance between carbon photosynthesis production and ecosystem respiration. It is NPP minus the carbon losses in Rh:

\[
NEP = NPP - Rh = GPP - (Ra + Rh) = GPP - Re
\] (2.2)

The sum of Ra and Rh is the total ecosystem respiration, Re.

Net Ecosystem Exchange (NEE) is somewhat equal to NEP, with NEE more refers to the fluxes observed from measurements of gas exchange rates over hours, while NEP more used for measurements based on ecosystem carbon stock changes, usually over time scales of at least one year. NEE can be expressed as:

\[
NEE = -NEP = Re - GPP
\] (2.3)

### 2.3.2 The components in CO\(_2\) variations

On seasonal scale, photosynthesis is larger than total respiration in summer, and causes a net uptake, while in winter photosynthesis is smaller than respiration, which leads to a net flux from the land to the atmosphere. This results in the seasonal cycle of CO\(_2\) in the atmosphere. The seasonal amplitude of CO\(_2\) can be explained by the seasonality of NEP (Köhler et al., 2006). On a scale of years, the natural biosphere carbon cycle is balanced, in another words, the average of NEP or NEE over many years is close to zero. However, the CO\(_2\) extra emissions from human activities altered this balance to a net land sink. The processes that dominating this change are still open question. One major source of the uncertainty is the difficulty to distinguish between photosynthesis and respiration, which response to physical and biological drivers. Stoy et al. (2005, 2009) analyzed the relationship between CO\(_2\) variation and climate at multiple time scales using orthonormal wavelet transformation, and showed that the short time variation (e.g. daily) is largely determined by physical controls, while longer time variability (e.g. seasonal and inter-annual) is mainly driven by biological responses to climatic variability. The global pattern in GPP shows a clear dependency on temperature and precipitation. Climatic conditions explain 71% of the GPP variability, while only explain 36% and 5% of the
variability in NPP and NEP respectively (Luyssaert et al., 2007). This indicates that the respiration and photosynthesis responses independently to climatic drivers. In order to improve the understanding of the biospheric feedback to climate change, we must separate the photosynthesis and respiration.

Figure 2.6: Processes and feedbacks triggered by extreme climate events (Reichstein et al., 2013). The plus sighs stand for positive impact and the minus sighs represent negative impacts. Solid arrow show direct impacts and dashed arrow show indirect impacts. The relative importance of the impacts is shown by arrow width (broader arrows are more important).

In addition to the mean climate change, climate extremes have clear impacts on ecosystems by altering the stable state rapidly. For example, the droughts and storms can lead to a decrease in regional ecosystem carbon stocks, and change the balance of carbon exchanges (Reichstein et al., 2013). Therefore studying the biospheric responses to climate extremes is important, since the extreme events become more frequency under the climate change condition. On the other hand, this will also help to understand the biosphere processes because the reactions are amplified than the mean state. Figure 2.6 summarized the biosphere responses to the extreme climate events. From the Figure, we can see that the processes are complex. Firstly, one extreme event can cause changes in
several factors that control the biosphere behaviors. Secondly, photosynthesis and respiration responses independently to the control factors. Additionally, some of the factors have both impacts on photosynthesis and respiration, which make it difficult to separate the processes. Although the mechanisms triggered by different climate extremes can be described in concepts, their specific impact is difficult to quantify, because it highly depends on the ecosystem type. Therefore it is necessary to separate the photosynthesis and respiration to help estimate the individual impact on those processes.

2.3.3 The means to separate photosynthesis and respiration

The only CO$_2$ flux of the biosphere that can be measured directly above leaf scale is NEE. GPP and Re, which cannot be measured directly, must be estimated using additional information. Extrapolating the night-time NEE measurements to daytime ecosystem respiration is the most common method to partitioning the GPP and Re. This method usually use a temperature response function that is derived from long-term data sets, however, this temperature sensitivity of Re does not reflect the short-term temperature sensitivity that is effective for extrapolating from night-time to daytime, which leads to a large bias in the calculation (Reichstein et al., 2005). In addition, the low turbulence and advection in the night time can introduce problems to NEE measurements (van Gorsel et al., 2009).

There are some other approaches can be used to the separation, like scaling-up measurements made in leaf, stem, and soil chambers, prediction of Re from light response models, calculation from ecosystem process models, and stable isotope approaches (Blonquist et al., 2011). But these methods are all with large uncertainties and challenges.

Recent studies showed that the measurements of carbonyl sulfide (OCS) and CO$_2$ in the northern hemisphere have some similarity in their seasonal variation, because the terrestrial exchange is the main driver for both species. Moreover, OCS is only taken up by plants during photosynthesis but not emitted during respiration, and therefore is a potential means to differentiate between photosynthesis and respiration.

In this study, the potential method of using OCS as a photosynthesis tracer is tested. In the next sections, an overview of carbonyl sulfide is first given.
2.4 Carbonyl sulfide

OCS is the most abundant sulfur-containing compounds in the atmosphere. OCS has a nearly constant burden of around 5.2 Tg, of which 4.63 Tg can be assigned to the troposphere and 0.57 to the stratosphere (Chin and Davis, 1995). Because OCS is inactive in the troposphere, it has a relatively long life time of 2-7 years (Chin and Davis, 1995, Griffith et al., 1998, Johnson, 1981, Montzka et al., 2007), which allow it to be well mixed in the troposphere and transported to the stratosphere, where it is photodissociated and oxidized to sulfur dioxide and further form sulfate aerosol, thus affect the earth’s radiation balance (Crutzen, 1976, Svoronos and Bruno, 2002) and stratosphere ozone chemistry (Solomon et al., 1993).

2.4.1 Sources and sinks

Our knowledge about the sources and sinks of OCS is limited, and therefore there are still a lot of uncertainties. The generally identified OCS sources include ocean emissions (direct emission and indirect emission via oxidation of carbon disulfide (CS$_2$) and dimethyl sulfide (DMS), anthropogenic releases (direct emission and indirect emission via oxidation of CS$_2$), biomass burning, and volcanoes. The sinks are plant uptake, soil uptake, reaction with hydroxyl radicals (OH), reaction with oxygen atoms (O), and photolysis in the stratosphere. OCS is mainly produced in the biosphere. The sulfate reduction by biological processes can form organosulfur compounds, from which OCS can be produced and released to the atmosphere through air-sea or air-biosphere fluxes (Andreae, 1990).

2.4.1.1 Plant uptake

Plant uptake has been commonly recognized as the main sink of OCS. The ability of vegetation for taking up OCS was first reported by several laboratory studies (Kluczewski et al., 1985, Taylor et al., 1983), and later, the vegetation was proposed to be the major global sink (Brown and Bell, 1986, Goldan et al., 1988). Kesselmeier and Merk (1993) reported that OCS exchange depend highly on the ambient OCS mixing ratios, and deposition occurred for all studied plant species under ambient OCS mixing ratio larger than 150 ppt, and emission only took place for rapeseed with OCS low than 90 ppt. Brown and Bell (1986) calculated the flux of OCS to the vegetation using the land surface vegetation productive area, the annual average leaf area index of the productive land,
### Table 2.1: Annual global OCS sources from previous studies (fluxes in Gg S year\(^{-1}\))

<table>
<thead>
<tr>
<th>Sources</th>
<th>Estimations</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocean (direct)</td>
<td>320±106</td>
<td>Rasmussen et al. (1982)</td>
</tr>
<tr>
<td></td>
<td>464</td>
<td>Ferek and Andreae (1984)</td>
</tr>
<tr>
<td></td>
<td>320(160-480)</td>
<td>Khalil and Rasmussen (1984)</td>
</tr>
<tr>
<td></td>
<td>171(85-341)</td>
<td>Chin and Davis (1993)</td>
</tr>
<tr>
<td></td>
<td>169±133</td>
<td>Watts (2000)</td>
</tr>
<tr>
<td></td>
<td>41±154</td>
<td>Kettle et al. (2002a)</td>
</tr>
<tr>
<td></td>
<td>639</td>
<td>Berry et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>813(573-3997)</td>
<td>Launois et al. (2015a)</td>
</tr>
<tr>
<td>Ocean (via CS(_2))</td>
<td>84 ± 54</td>
<td>Kettle et al. (2002a)</td>
</tr>
<tr>
<td>Ocean (via DMS)</td>
<td>53-149</td>
<td>Barnes et al. (1994)</td>
</tr>
<tr>
<td></td>
<td>91±21</td>
<td>Watts (2000)</td>
</tr>
<tr>
<td></td>
<td>154±37</td>
<td>Kettle et al. (2002a)</td>
</tr>
<tr>
<td>Anthropogenic (direct)</td>
<td>74(27-240)</td>
<td>Khalil and Rasmussen (1984)</td>
</tr>
<tr>
<td></td>
<td>22(14-31)</td>
<td>Chin and Davis (1993)</td>
</tr>
<tr>
<td></td>
<td>66±32</td>
<td>Watts (2000)</td>
</tr>
<tr>
<td></td>
<td>90±37</td>
<td>Campbell et al. (2015)</td>
</tr>
<tr>
<td>Anthropogenic (via CS(_2))</td>
<td>106</td>
<td>Chin and Davis (1993)</td>
</tr>
<tr>
<td></td>
<td>116±58</td>
<td>Kettle et al. (2002a)</td>
</tr>
<tr>
<td></td>
<td>190±70</td>
<td>Campbell et al. (2015)</td>
</tr>
<tr>
<td>CS(_2) convection (all)(^a)</td>
<td>320(0-1067)</td>
<td>Khalil and Rasmussen (1984)</td>
</tr>
<tr>
<td></td>
<td>181(91-325)</td>
<td>Chin and Davis (1993)</td>
</tr>
<tr>
<td></td>
<td>224±64</td>
<td>Watts (2000)</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>112</td>
<td>Crutzen et al. (1979)</td>
</tr>
<tr>
<td></td>
<td>75(21-139)</td>
<td>Chin and Davis (1993)</td>
</tr>
<tr>
<td></td>
<td>69(32-112)</td>
<td>Nguyen et al. (1995)</td>
</tr>
<tr>
<td></td>
<td>144(75-277)</td>
<td>Chin and Davis (1993)</td>
</tr>
<tr>
<td></td>
<td>11±6</td>
<td>Watts (2000)</td>
</tr>
<tr>
<td>Volcano</td>
<td>11</td>
<td>Cadle (1980)</td>
</tr>
<tr>
<td></td>
<td>11(5-26)</td>
<td>Khalil and Rasmussen (1984)</td>
</tr>
<tr>
<td></td>
<td>3-48</td>
<td>Belviso et al. (1986)</td>
</tr>
<tr>
<td></td>
<td>11(3-48)</td>
<td>Chin and Davis (1993)</td>
</tr>
<tr>
<td>Precipitation</td>
<td>69±32</td>
<td>Watts (2000)</td>
</tr>
</tbody>
</table>

\(^a\)The CS\(_2\) convection is not separated to ocean and anthropogenic emissions in some references
Table 2.2: Annual global OCS sinks from previous studies (fluxes in Gg S year\(^{-1}\))

<table>
<thead>
<tr>
<th>Sinks</th>
<th>Estimations</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant</td>
<td>1067-2667</td>
<td>Brown and Bell (1986)</td>
</tr>
<tr>
<td></td>
<td>128-315</td>
<td>Goldan et al. (1988)</td>
</tr>
<tr>
<td></td>
<td>229(85-533)</td>
<td>Chin and Davis (1993)</td>
</tr>
<tr>
<td></td>
<td>459-533</td>
<td>Kesselmeier and Merk (1993)</td>
</tr>
<tr>
<td></td>
<td>298 ± 53</td>
<td>Watts (2000)</td>
</tr>
<tr>
<td></td>
<td>238 ± 30</td>
<td>Kettle et al. (2002a)</td>
</tr>
<tr>
<td></td>
<td>368-747(NPP)</td>
<td>Sandoval-Soto et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>730-1500(GPP)</td>
<td></td>
</tr>
<tr>
<td>Oxic soil</td>
<td>490±416</td>
<td>Watts (2000)</td>
</tr>
<tr>
<td></td>
<td>130±56</td>
<td>Kettle et al. (2002a)</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td>Berry et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>510(255-770)</td>
<td>Launois et al. (2015b)</td>
</tr>
<tr>
<td>OH oxidation</td>
<td>427(53-800)</td>
<td>Khalil and Rasmussen (1984)</td>
</tr>
<tr>
<td></td>
<td>69(11-427)</td>
<td>Chin and Davis (1993)</td>
</tr>
<tr>
<td></td>
<td>94 ± 12</td>
<td>Kettle et al. (2002a)</td>
</tr>
<tr>
<td>O oxidation</td>
<td>16</td>
<td>Khalil and Rasmussen (1984)</td>
</tr>
<tr>
<td></td>
<td>8(5-14)</td>
<td>Chin and Davis (1993)</td>
</tr>
<tr>
<td></td>
<td>15(11-21)</td>
<td>Chin and Davis (1993)</td>
</tr>
</tbody>
</table>

Goldan et al. (1988) conducted laboratory measurements of the OCS uptake by several kinds of crops under conditions of controlled illumination, temperature, and CO\(_2\) concentration, indicating that the major pathway for OCS uptake was through open stomata, which is similar to CO\(_2\). The consumption of OCS in the cells is by the enzyme carbonic anhydrase (CA), which is co-located with the enzyme that consumes CO\(_2\) – Rubisco (Protoschill-Krebs and Kesselmeier, 1992, Protoschill-Krebs et al., 1996). This result provided a potential method to estimate the plant uptake of OCS (U\(_{OCS}\)) by scaling the global CO\(_2\) plant uptake (U\(_{CO_2}\)),

\[
U_{OCS} = U_{CO_2} \times \frac{[OCS]}{[CO_2]} \tag{2.4}
\]

where [OCS] and [CO\(_2\)] are the ambient concentrations of OCS and CO\(_2\) respectively. Based on this, Goldan et al. (1988) calculated the total terrestrial uptake of OCS to be 128–315 Gg S year\(^{-1}\). Later studies such as Chin and Davis (1993), Kesselmeier and Merk (1993), Kettle et al. (2002a), Sandoval-Soto et al. (2005), Watts (2000), applied this relationship between OCS and CO\(_2\) plant uptake and obtained various amounts as
shown in Table 2.2. The different estimations are partly resulted from the assumptions of the relative uptake rate between OCS and CO$_2$, and partly from the usage of NPP or GPP. Kesselmeier and Merk (1993) indicated that some plants showed a preference for OCS over CO$_2$. Sandoval-Soto et al. (2005) obtained the deposition velocity ratios for OCS and CO$_2$, VdOCS/VdCO$_2$, in the range of 1.3 $\sim$ 5.5 by chamber measurements and summarizing the other publications. Considering that OCS is consumed by plant irreversibly, while CO$_2$ is also released through respiration, GPP was proposed to replace NPP in the estimation (Sandoval-Soto et al., 2005). Berry et al. (2013) calculated the OCS plant uptake based on the mechanistic parameterization in a simple biosphere model, and got the annual total plant uptake of 765 Gg S.

### 2.4.1.2 Ocean fluxes

The ocean is believed to be the most important source of OCS via both direct and indirect fluxes, and makes the biggest contribution to the seasonality of OCS in the Southern Hemisphere (Kettle et al., 2002a). Seawater contains plentiful of sulfur and usually supersaturated with sulfur containing gases such as CS$_2$ and DMS (Bruehl et al., 2012). Ferek and Andreae (1984) first reported the dial variation of OCS in the ocean, with maximum in the middle of afternoon and minimum in the morning, which leading to a suggestion of photochemical production mechanism. Flock and Andreae (1996) measured the dissolved OCS in the water column of Northeast Atlantic, and showed that the OCS concentration decreases with increasing depth, but still present in measurable concentration below the photic zone, which suggested a non-photochemical mechanism of OCS production. Pos et al. (1998) indicated that the key sulfur intermediary is a sulfur-centered radical (thiyl or sulfhydryl) generated in seawater, and this sulfur radical pathway could also produce OCS in dark. Experimental and model studies show that the photoproduction is still the main source of seawater OCS. OCS can be also removed from seawater by hydrolysis to CO$_2$ and H$_2$S, downward mixing, and exhalation. This means the ocean could also be a sink for OCS. Actually the ocean was speculated only to be the sink of atmospheric OCS (Johnson, 1981), then it was doubted based on the measurements showing that the seawater was supersaturated with OCS, and the OCS concentrations in seawater are always higher than those in the overlying atmosphere, thus the entire ocean acts as a net source (Andreae, 1990). However, these measurements were all made under the conditions suiting high OCS production, such as low latitudes and warm season. Later results indicated that parts of the ocean can be undersaturated (Flock and Andreae, 1996, Xu et al., 2001), which confirm that the ocean could also
act as an OCS sink. The balance between OCS production and removal leads to the temporal and spatial variations in the ocean. Generally the summer and autumn for each hemisphere are the period when the ocean acts as a source, while winter to spring are the sink period, and the tropical and subpolar region are with higher OCS production than the rest, and coastal water are richer with OCS than the open sea (Watts, 2000).

The direct ocean source was estimated by many studies based on the seawater measurements in different regions and seasons or general circulation models (Table 2.1). Since recent studies (Berry et al., 2013, Suntharalingam et al., 2008) indicated that the previous plant uptake estimation is too small, and therefore a corresponding increase in sources is necessary to maintain the annual balance in the OCS budget. The disagreement between measurements and simulations of OCS indicated that the missing sources are mainly in the tropical region (Berry et al., 2013). Berry et al. (2013) added a missing ocean sources of 600 Gg S in the model, and resulted in better agreement with the atmospheric measurements. Launois et al. (2015a) calculated the direct ocean emissions using an ocean general circulation and biogeochemistry model, and estimated a source of about 813 Gg S year\(^{-1}\). However, the ocean fluxes have large uncertainties. The direct ocean flux has large temporal and spatial variations, and under certain conditions could also act as a sink for OCS (Xu et al., 2001). Seawater measurements in some regions of the ocean suggested that the open ocean could be a small source of OCS (Weiss et al., 1995, Xu et al., 2001), and that indirect ocean emissions may play more important roles.

### 2.4.1.3 Soil

Soil acts as both source and sink for OCS, because the microbial processes and chemical reactions in the soil can both produce and consume OCS. This emission or uptake is dependent on the soil type, which can be roughly divided to anoxic soil and oxic soil (Watts, 2000). Earlier studies considered soil as a source only. Khalil and Rasmussen (1984) estimated the source strength to be 213 Gg S year\(^{-1}\). These investigations were all using sulfur-free air as the carrier gas in their dynamic enclosure system, so that could not measure uptake (Chin and Davis, 1993). Some later measurements showed that the soil is mainly a sink of OCS instead of source (Andreae and Crutzen, 1997, Kesselmeier et al., 1999, Kuhn et al., 1999). Watts (2000) estimated the fluxes for anoxic soil and oxic soil separately and gain a source of 11 Gg S year\(^{-1}\) for anoxic soil and a sink of 490 Gg S year\(^{-1}\) for oxic soil, with large uncertainties. However, the overall role of soils is as a sink of OCS, with very different uptake rates between soil types and other physical parameters.
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(Sun et al., 2015, Van Diest and Kesselmeier, 2008). Kettle et al. (2002a) calculated the soil uptake using an empirical algorithm with the parameterization determined for one arable soil type, and obtained 130 Gg S year\(^{-1}\). Since the current information on soil CA activity is limited, Berry et al. (2013) calculated the soil uptake as a function of Rh, because measurements show that the OCS soil uptake is proportional to Rh (Yi et al., 2007). Another method to calculate the soil uptake is to use the similarity of deposition to soils between molecular hydrogen (H\(_2\)) and OCS (Belviso et al., 2013). This estimation yields a sink of about 510 Gg S year\(^{-1}\), largely dependent on the H\(_2\) spatial distribution (Launois et al., 2015b). Recent studies indicated that the soil sink of OCS could turn to a source under very high temperature, high radiation, and low soil moisture, while the underlying processes are unclear (Commane et al., 2015).

2.4.1.4 Biomass burning

Biomass burning, which is mainly caused by human activities, produces various emissions of trace gases and aerosol particles, among which OCS is one of the important gases. Crutzen et al. (1979) estimated the OCS flux from biomass burning using the emission ratio OCS/CO\(_2\) of 15.8 \times 10^{-6} in the range of 5.4 \times 10^{-6} \sim 28.6 \times 10^{-6}, and gained a strength of 112 Gg S year\(^{-1}\), however, this emission ratio had a large variability (more than 100%). Nguyen et al. (1995) found a high correlation between OCS and CO in the smoke samples collected close to the fires with a slope of 8.5 \times 10^{-5} and a correlation coefficient of 0.96, indicating that OCS is produced during the smoldering stage, not the flaming stage when CO\(_2\) is produced. Based on this theory and CO emission from biomass burning calculated by Crutzen and Andreae (1990), Nguyen et al. (1995) estimated the OCS flux to be 69 Gg S year\(^{-1}\) with a uncertainty of about 60%. Although this is only a small value compared to the global total OCS source strength, biomass burning can affect the OCS level dramatically in certain region and period, such as tropical dry season. Notholt et al. (2003) measured an enhanced OCS mixing ratio of 20% to 50% larger than assumed in upper tropical troposphere, and suggested that it caused by biomass burning and upward transport.

2.4.1.5 Anthropogenic source

Anthropogenic activities may also play an important role in the current global budget. The measurement of OCS in firn air collected near South Pole suggested an annual mean
mixing ratio between 300 and 400 ppt during 1650 – 1850, which is lower than the 500 ppt observed nowadays, and a continuous increase through most of the 20th century (Montzka et al., 2004). This indicated that the anthropogenic sulfur emissions might contribute to the OCS increase in the atmosphere. The identified direct anthropogenic sources include coal combustion, automobiles, sulfur recovery processes, aluminum production, fish processing, combustion of refuse and plastics, manufacture of petroleum, synthetic fibers, starch and rubber (Chin and Davis, 1993, Harnisch et al., 1995a,b, Khalil and Rasmussen, 1984, Pos and Berresheim, 1993, Watts, 2000). Only the first four sources can be evaluated, but the others were suggested to be not important and have a very small contribution to the OCS budget. The estimations of the direct anthropogenic sources were shown in Table 2.1. Besides the direct sources, there is an additional indirect anthropogenic source via CS$_2$ oxidation. CS$_2$ is released during the chemical production, which was estimated to be around 261 Gg S year$^{-1}$ by Chin and Davis (1993), more than a half of the global total CS$_2$ emission. The corresponding OCS flux is nearly twice of the direct anthropogenic emission.

2.4.1.6 CS$_2$ conversion

The oxidation of CS$_2$ is thought to be an important source of OCS. The key reaction is the oxidation by the OH radical,

$$CS_2 + OH \rightarrow OCS + HS$$

$$HS + O_2 \rightarrow OH + SO$$

$$\rightarrow SO_2 + H$$

CS$_2$ has a short lifetime of several days. Once it is released to the atmosphere, it is rapidly converted to OCS and SO$_2$ (Blake et al., 2004). The main sources of CS$_2$ are ocean emission and anthropogenic production. So the oxidation of CS$_2$ can also be classified to the indirect ocean and anthropogenic sources for OCS. Similar to OCS, CS$_2$ is also generally supersaturated in the ocean, thus can be released to the atmosphere through air-sea exchange. The anthropogenic source is suggested to be stronger than the ocean, because the measurements show a relatively high concentration above continents (Blake et al., 2004). Khalil and Rasmussen (1984) first gave an estimation of about 320 Gg S year$^{-1}$. Then Chin and Davis (1993) calculated the molar conversion efficiency from the
laboratory study as $0.81 \pm 0.06$. Based on this, the OCS flux from CS$_2$ estimated from the CS$_2$ flux times the conversion efficiency is 181 Gg S year$^{-1}$. Watts (2000) revised this value to 224 Gg S year$^{-1}$, because the changes of CS$_2$ flux estimation. In Kettle et al. (2002a), the indirect OCS flux via CS$_2$ from the ocean and anthropogenic pollution were calculated to be 84 Gg S year$^{-1}$ and 116 Gg S year$^{-1}$ respectively.

2.4.1.7 DMS conversion

The oxidation of DMS is considered to be another source of OCS. It is first proposed by Barnes et al. (1994) from their laboratory study. OCS was observed in the experiment of the OH initiated oxidation of DMS under NO$_X$ free conditions, and a value of 0.7% S for the OCS formation yield was measured. Because DMS is the most abundant sulfur compound emitted from the ocean, this pathway for OCS flux could be large. Barnes et al. (1994) estimated this OCS source strength in the range of 53 to 149 Gg S year$^{-1}$. This value was revised to $91 \pm 21$ Gg S yeas$^{-1}$ by Watts (2000) according to the new estimation of DMS fluxes. Kettle et al. (2002a) calculated the indirect OCS flux as DMS from ocean as 154 Gg S year$^{-1}$.

2.4.1.8 Photochemical loss

OCS can be photochemically decomposed in the atmosphere by the following reactions,

$$OCS + hv \rightarrow CO + S \quad (2.8)$$

$$OCS + O \rightarrow CO + SO \quad (2.9)$$

$$OCS + OH \rightarrow CO_2 + HS \quad (2.10)$$

The photolysis of OCS by solar ultraviolet (UV) radiation mainly takes place in the stratosphere, and requires radiation having a wavelength of 388 nm or shorter (Chin and Davis, 1995). The OCS sink by photolysis was calculated to be 53 Gg S year$^{-1}$ by Khalil and Rasmussen (1984). Chin and Davis (1993) presented 14 and 1 Gg S year$^{-1}$ in the stratosphere and troposphere respectively. The OCS loss by reactions with OH was estimated to be 427 Gg S year$^{-1}$ by Khalil and Rasmussen (1984) using a constant reaction rate, while it was 69 Gg S year$^{-1}$ calculated by Chin and Davis (1995, 1993) using a temperature dependent rate coefficient. Kettle et al. (2002a) applied another OH concentration field, and calculated it to be 94 Gg S year$^{-1}$. The oxidation by O
removes much less OCS than OH, which was estimated to be 16 Gg S year\(^{-1}\) by Khalil and Rasmussen (1984) and 8 Gg S year\(^{-1}\) by Chin and Davis (1995).

### 2.4.1.9 Volcanoes and precipitation

Volcanoes have a small contribution to the OCS budget. The volcanic emission was estimated between 5 and 48 Gg S year\(^{-1}\) with a large uncertainty (Belviso et al., 1986, Cadle, 1980, Khalil and Rasmussen, 1984). OCS was reported supersaturated in the rain waters by Belviso et al. (1987), indicating that the precipitation might be an additional sources for OCS. However, the formation mechanism is unclear. Watts (2000) proposed the organic matter in the precipitation as the precursors, and estimated the strength of this source to be 69 ± 32 Gg S year\(^{-1}\).

### 2.4.2 Global budget

<table>
<thead>
<tr>
<th>References</th>
<th>Total source</th>
<th>Total sink</th>
<th>Net</th>
</tr>
</thead>
<tbody>
<tr>
<td>Khalil and Rasmussen (1984)</td>
<td>1067 (&lt;2667)</td>
<td>496 (53-800)</td>
<td>571 (&lt;2614)</td>
</tr>
<tr>
<td>Chin and Davis (1993)</td>
<td>608 (293-1168)</td>
<td>309 (101-944)</td>
<td>299 (-651-1067)</td>
</tr>
<tr>
<td>Kettle et al. (2002a)</td>
<td>525 (170-1010)</td>
<td>490 (380-597)</td>
<td>35 (-36-185)</td>
</tr>
<tr>
<td>Berry et al. (2013)</td>
<td>1192.5</td>
<td>1195</td>
<td>-2.5</td>
</tr>
</tbody>
</table>

The global budget of OCS sources and sinks is difficult to assess, because of the limited knowledge. However, a lot of work has been done to evaluate the global budget of OCS. Khalil and Rasmussen (1984) calculated the sources and sinks of OCS identified by that time, and obtained 1067 Gg S year\(^{-1}\) and 496 Gg S year\(^{-1}\) for sources and sinks respectively, which is totally imbalanced, since they considered soil as a source and the photochemical losses as the only sinks. In the work of Chin and Davis (1993), the plant uptake was included as the major sink of OCS, leading the source and sink strength to be 608 (range of 293 – 1168) Gg S year\(^{-1}\) and 309 (range of 101-944) Gg S year\(^{-1}\). Watts (2000) reviewed the sources and sinks of OCS, and counted the anoxic soils as source and oxic soils as sink separately, and presented the total source of 699 ± 133 Gg S year\(^{-1}\) and the total sink of 885 ± 421 Gg S year\(^{-1}\). Kettle et al. (2002a) analyzed the OCS fluxes monthly, then calculated the global annual source and sink to be 525 Gg S year\(^{-1}\) and 490 Gg S year\(^{-1}\), which is nearly in balance. Since the new studies indicated that the
plant uptake is underestimated in Kettle’s fluxes, and therefore the budget balance is challenged again. The Ocean is suggested to be the missing source, but this is still open question. Berry et al. (2013) calculated the land uptake using a biosphere model and added an extra ocean source in the budget, and obtained a total source of 1192.5 Gg S year$^{-1}$ and a total sink of 1195 Gg S year$^{-1}$.

2.4.3 Variability of OCS

Measurements from firn air and ice core provided a long term time series of OCS mixing ratios. Aydin et al. (2002) observed the OCS mixing ratios of 322.6 to 442.3 ppt during 1616 – 1694 A.D. from Antarctic ice core, which are much lower than the 500 ppt at present. Additional measurements from both firn air and air trapped in ice reported a longer period between 1650 and 1850 A.D. and suggested the annual mean OCS mixing ratios in the range of 300 to 400 ppt during that period (Montzka et al., 2004). Based on the measurements and model calculations, Montzka et al. (2004) derived the atmospheric history for OCS, implying that the OCS concentrations decreased during the 1600s and reached the minimum in the 1700s, and increased significantly after 1850, then decreased again from 1990.

Multi-decade infrared measurements of atmospheric OCS also provide information for its long term trend. The observations at all the ground stations, such as Jungfraujoch, Kitt Peak, Wollongong and Lauder, showed that OCS columns have remained nearly constant with a slow decline of less than 1% year$^{-1}$ (Notholt et al., 2006). The satellite measurements from ATMOS and ACE found no statistically trend in the lower stratospheric OCS (Rinsland et al., 2008). Recent measurements showed that the OCS concentration increased again from about 2002, and the this increase was mainly in the troposphere, suggesting that this trend may caused by an increasing source, likely the anthropogenic emissions (Kremser et al., 2015, Lejeune et al., 2016).

Previous measurements of OCS showed no significant seasonality (Mihalopoulos et al., 1991) or only very small seasonality with a summer maximum and a winter minimum for the total columns (Rinsland et al., 1992). Griffith et al. (1998) reported a peak-to-peak seasonal cycle in OCS total column of 18% at Wollongong and 6% at Lauder, respectively, with peak values in late summer, and suggested 5-6% of the amplitude was caused by the tropopause height variation. Atmospheric OCS measured at the Taunus Observatory on the summit of Kleiner Feldberg, Germany from 1993 to 1999 showed a strong seasonal
cycle with a minimum in September and maximum in March and an averaged peak-to-peak amplitude of about 100 ppt. This seasonal type had a high correlation with CO₂ assimilation, which leading to a speculation that this seasonality of OCS was caused by vegetation uptake (Xu, 2001). Later observations across the globe suggested that strong seasonality were common in both hemispheres (Montzka et al., 2007, 2004, Notholt et al., 2006). Kettle et al. (2002a) analyzed the seasonal variation of surface fluxes of OCS, and indicated that terrestrial vegetation uptake was the dominate driver in the Northern Hemisphere, while ocean fluxes were the main influence in the Southern Hemisphere.

### 2.5 The progress of using OCS to separate the photosynthesis and respiration

A lot of work has been made to study the similarity of OCS and CO₂. The earlier research (e.g. Kettle et al., 2002a, Watts, 2000) used the NPP-based model to estimate the plant uptake of OCS and assumed the uptake rates for OCS and CO₂ were the same, then laboratory studies showed some plants favored OCS over CO₂ (Kesselmeier and Merk, 1993). Taking into account that OCS is consumed by plant during photosynthesis, but not released by respiration, a GPP-based model was suggested to replace the NPP-based model (Sandoval-Soto et al., 2005). Comparison between measurements and model simulations with different terrestrial fluxes confirmed that the NPP-based model underestimated the plant uptake of OCS, while the GPP-based model improved the model ability of catching the seasonal amplitude and vertical gradient of OCS during the growing season (Campbell et al., 2008, Suntharalingam et al., 2008). Analysis of measured CO₂ and OCS seasonal amplitude showed a high correlation with a regression r² of 0.9 and a slope of 6 ± 1 (Montzka et al., 2007).

Blonquist et al. (2011) for the first time conducted the OCS approach to estimate GPP at the Harvard Forest AmeriFlux site, following the equation,

$$GPP = NEE \times ERU \times \left( \frac{1}{LRU} \right)$$  \hspace{1cm} (2.11)

Where LRU is leaf relative uptake of OCS to CO₂, which is estimated to about 1.4-4.0 (Sandoval-Soto et al., 2005, Seibt et al., 2010, Stimler et al., 2010, 2012). ERU is defined
as ecosystem relative uptake of OCS to CO$_2$ (Campbell et al., 2008),

\[ ERU = \frac{RG_{OCS}}{RG_{CO_2}} = \frac{G_{OCS}}{C_{aOCS}} / \frac{G_{CO_2}}{C_{aCO_2}} \]  \hspace{1cm} (2.12)

Where $RG_{OCS}$ and $RG_{CO_2}$ are the relative gradients of OCS and CO$_2$ at the flux tower scale. They are the near- or within-canopy OCS and CO$_2$ mole fraction gradients, $G_{OCS}$ and $G_{CO_2}$, respectively, normalized by ambient OCS and CO$_2$ mole fraction, $C_{aOCS}$ and $C_{aCO_2}$. Blonquist et al. (2011) calculated the LRU to be 3 for deciduous forests and C3 species, and applied it to estimate GPP and compared to GPP estimated by extrapolating night time respiration to day time with temperature relationship from Reichstein et al. (2005). The results were similar for both methods, which confirmed the potential utility of OCS.

Asaf et al. (2013) estimated GPP directly from OCS flux measurements by the following equation,

\[ GPP = F_{OCS} \times \left( \frac{C_{aCO_2}}{C_{aOCS}} \right) \times \left( \frac{1}{LRU} \right) \]  \hspace{1cm} (2.13)

Where $F_{OCS}$ is the measured OCS flux, LRU was taken to be 1.6 from a estimation by Stimler et al. (2010). The calculated GPP from different field campaigns were all comparable to those from a more traditional method (extrapolating night time respiration to day time) within an error of 15%.

Berry et al. (2013) employed a Simple Biosphere Model (SiB3) to estimate CO$_2$ and OCS land fluxes and designed a simulation experiment to examine the different responses in photosynthesis and respiration under different soil hydrology and water stress. By comparing the drawdown of CO$_2$ and OCS, the results indicated that additional information could be provided on separating the responses of photosynthesis and respiration to environmental forcing.
Chapter 3

Measurements and models

This chapter will introduce the fundamental methods for this study. First, the measurements of OCS and CO$_2$ are described. The solar absorption FTIR measurement (Davis et al., 2001) and retrieval technique (Rodgers, 2000) are introduced. The in-situ measurements are also included as a complement to have a better coverage on the site map, and also to validate the latitudinal distribution. Secondly, the models used in the study are described, including the forward model, the inversion model as well as the biosphere model. Finally, the methods for comparing between different remote sensing measurements and between measurements and models are introduced.

3.1 Ground-based solar absorption FTIR spectrometry

Ground-based solar absorption FTIR spectrometry has been established as a powerful tool to measure the composition of the earth atmosphere. It uses the sun as a light source, and measures the solar spectrum in the infrared region. The gas molecules absorb solar radiation at certain frequency, so that we can determine the abundances (either total columns or profiles) of the atmospheric trace gases from the measured spectrum.
Figure 3.1: Solar irradiance spectrum above atmosphere and at surface (from Wikipedia: https://en.wikipedia.org/wiki/Sunlight). The yellow part shows the solar spectrum above atmosphere, and red part is the spectrum at surface.

3.1.1 Solar spectrum

The radiance $I$ emitted by a black body with a temperature of $T$, dependent on wavelength $\lambda$ is described by Planck’s law,

$$I(\lambda) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

(3.1)

where

Planck’s constant $h = 6.626 \times 10^{-34} Js$

light speed $c = 2.998 \times 10^8 ms^{-1}$

Boltzmann’s constant $k = 1.381 \times 10^{-23} JK^{-1}$

The $\lambda_{\text{max}}$, at which the Planck curve reaches its maximum, can be calculated using Wien’s displacement law,

$$\lambda_{\text{max}} = \frac{2.897 \times 10^{-3}}{T}$$

(3.2)

The surface temperature of the sun is about 5778 K, so the solar spectrum on the top of the atmosphere is similar to that of a 5778 K blackbody (Figure 3.1). The maximum intensity is at about 500 nm wavelength. The solar spectrum mainly consists of ultraviolet rays (200 – 400 nm), visible light (400 – 700 nm), and infrared radiation (700 nm – 1mm).
3.1.2 Radiation transfer

When the solar rays pass through the atmosphere, a proportion of the total energy is scattered or absorbed, and some molecules also emit energy from transitions, so the solar spectrum at the earth’s surface is different from that at the top of the atmosphere. The change of the intensity $I$ along the light path $l$ can be expressed as:

$$\frac{\partial I}{\partial l} = -\alpha I + \alpha J_{\text{emission}} - \alpha_{\text{scatter}} I + \alpha_{\text{scatter}} I J_{\text{scatter}} \quad (3.3)$$

The four parts on the right hand side of the Equation 3.3 are the absorption, emission, scattering in, and scattering out terms, respectively. $\alpha$ is the absorption coefficient, and $\alpha_{\text{scatter}}$ is the scattering coefficient. $J_{\text{emission}}$ and $J_{\text{scatter}}$ are the sources of emission and scattering, respectively. In the infrared region, the scattering can be neglected if there is no cloud in the light path. The atmospheric emission can also be neglected in the infrared region when measuring the solar absorption. Therefore, the Equation 3.3 simplifies to:

$$\frac{\partial I}{\partial l} = -\alpha I \quad (3.4)$$

Which can be solved using Beer-Lambert law as:

$$I = I_0 \exp(-\int_0^\infty \alpha(l) dl) \quad (3.5)$$

where $I_0$ is the intensity at the position of the light source. The absorption coefficient $\alpha$, which depends on frequency $\nu$, can be calculated by the molecular number density $n$, the line strength of the molecular transition $S$, and the line shape factor $f$:

$$\alpha(\nu) = nSf(\nu - \nu_0) \quad (3.6)$$

where $\nu_0$ is the frequency of the central position of a line. The molecular transition $S$ and the line shape factor $f$ will be further discussed in the next section.

3.1.3 Molecular spectroscopy

The molecules only absorb discrete and specific wavelengths, because only radiation that equal to the molecular energy state gaps can be absorbed or emitted. Therefore the absorption lines are assigned to certain molecules. The molecular spectra are divided into electronic transitions, vibrational transitions, and rotational transitions. The energy
resulted from the three molecular transitions are summarized in Table 3.1. The electronic transition has the highest energy, and can be observed in the UV and visible region. The vibrational transition happens in the infrared region. The rotational transition has the lowest energy and it is in the microwave region. Additionally, the electronic, vibrational, and rotational transitions can occur at the same time. In the infrared region, the vibrational transitions are mostly accompanied by the rotational transitions, and result in rotational-vibrational transitions.

<table>
<thead>
<tr>
<th>transition</th>
<th>energy (eV)</th>
<th>wavenumber (cm(^{-1}))</th>
<th>spectral range</th>
</tr>
</thead>
<tbody>
<tr>
<td>electronic</td>
<td>1-10</td>
<td>(10^4-10^7)</td>
<td>UV, visible</td>
</tr>
<tr>
<td>vibrational</td>
<td>0.1</td>
<td>(10-10^4)</td>
<td>infrared</td>
</tr>
<tr>
<td>rotational</td>
<td>0.001</td>
<td>(0.01-10)</td>
<td>microwave</td>
</tr>
</tbody>
</table>

In general, a linear molecule with \(N\) atoms has \(3N - 5\) normal vibrational modes, while a nonlinear molecule has \(3N - 6\) normal modes. OCS is a linear molecule with three atoms, and therefore it has four vibrational modes: a symmetric stretch \((\nu_1 = 859 \text{ cm}^{-1})\), two equal-energy bending vibrations in two planes \((\nu_2 = 520 \text{ cm}^{-1})\), and an asymmetric stretch \((\nu_3 = 2062 \text{ cm}^{-1})\). These modes are illustrated in Figure 3.2. CO\(_2\) has the same vibrational modes with OCS because of the similar molecular structure, but the associated band frequencies are different \((\nu_1 = 1388 \text{ cm}^{-1}, \nu_2 = 667 \text{ cm}^{-1}, \nu_3 = 2349 \text{ cm}^{-1})\). Because the vibrational and rotational transitions usually occur together and the energy of the rotational transition is much lower than the vibrational transition, the spectrum of the combined transitions is a series of rotational lines grouped around the vibrational line.

The molecular spectroscopy is usually collected in large databases (e.g. HITRAN) based on laboratory measurements.

![Figure 3.2: The fundamental vibration modes of OCS. The arrows indicate the directions of motion. The plus sigh represents the motion into the paper, and the minus sigh means the motion out of the paper.](image)

Spectral lines are not infinitely narrow because of the line broadening determined by several factors. In the infrared region, the most important factors are the natural line width, the Doppler broadening, and the pressure broadening. The natural line width is
because of the finite lifetime of the exited state of an atom or molecule. The shorter the lifetime of the state, the broader the spectral line. The Doppler broadening is caused by the Doppler shift of the detected frequency depending on the moving of the source towards or away from the detector. The velocities of the molecules depend on the temperature, so that the Doppler broadening is also called thermal broadening. Additionally, the Doppler broadening is also increasing with frequency. The pressure broadening is a result of intermolecular collisions, which lead to a decrease of the lifetime of a exited state. The line width increases with the pressure, from which the altitude dependent information can be retrieved from the spectra. The maximum altitude that can be reached is determined by the altitude at which the pressure broadening dominates the Doppler broadening.

3.1.4 The principle of the FTIR spectrometry

Solar absorption FTIR spectrometry uses the sun as the light source. The sunlight is directed by a solar tracker, which follows the position of the sun during the measurement (Figure 3.3). The spectrum containing the absorption information along the sunlight path is recorded by the spectrometer. A FTIR spectrometer is basically a Michelson interferometer. The main components of a FTIR spectrometer are shown in Figure 3.4. After the sunlight goes to the instrument, it is split into two light beams by a beamsplitter, where the input radiation is partly transmitted and partly reflected. One beam goes to a fixed mirror, while the other one travels to a movable mirror, which brings in an optical path difference (OPD) between the two paths the beams travel. The reflected lights from both mirrors are recombined at the beamsplitter and passed to a detector that measures the light intensity.

The measured pattern of intensity, which is called interferogram, is as a function of OPD. Considering an input monochromatic light of wavenumber $\sigma$ and intensity $B(\sigma)$, the interferogram intensity $I$, dependent on the OPD $x$, is given by the familiar two-beam interference relation:

$$I(x) = B(\sigma)[1 + \cos(2\pi\sigma x)]$$

When a source is polychromatic, the measured intensity is a superposition of all wavenumbers:

$$I(x) = \int_{0}^{\infty} B(\sigma)[1 + \cos(2\pi\sigma x)]d\sigma$$

The first term in the equation 3.8 is the DC term of the interferogram, depend on the intensity of the source; the second term represents the AC signal, containing the sinusoidal
wavenumber dependent information. Ignoring the DC term, the equation 3.8 becomes:

\[ I(x) = \int_{0}^{\infty} B(\sigma) \cos(2\pi \sigma x) d\sigma \] (3.9)

\( I(x) \) is the Fourier Transform of \( B(\sigma) \). The spectrum of the intensity \( B \) as a function of wavenumber \( \sigma \) can be computed by applying an inverse Fourier Transform:

\[ B(\sigma) = \int_{0}^{\infty} I(x) \cos(2\pi \sigma x) dx \] (3.10)

The Fourier transformation also produces the mirror image \( B(-\sigma) \). An even spectrum \( B_e(\sigma) \) can be produced by:

\[ B_e(\sigma) = \frac{1}{2} [B(\sigma) + B(-\sigma)] \] (3.11)

\[ I_e(x) = \int_{-\infty}^{\infty} B_e(\sigma) \cos(2\pi \sigma x) d\sigma \] (3.12)

\[ B_e(\sigma) = \int_{-\infty}^{\infty} I_e(x) \cos(2\pi \sigma x) dx \] (3.13)

### 3.1.5 Retrieval of the gases

From the solar spectra measured by the FTIR spectrometry as described above, vertical columns and/or mixing ratio profiles of atmospheric tracers can be obtained through the
gas retrieval procedure. The retrieval is usually only performed in small spectral windows, which is so called micro-windows (MW). In the MWs, only a few gas absorption lines are included, which reduces the sources of errors. Except the target gas, all the other species that are considered in the retrieval are called interfering species.

In the gas retrieval, a forward model $F$ is used to map the atmospheric state vector $x$ to a measurement vector $y$, with measurement error $\epsilon$.

$$ y = F(x) + \epsilon $$ (3.14)

The forward model describes the physics of the measurements, which is constructed with the information of the light path through the atmosphere calculated using the measurement time, location, and measured or modeled temperature and pressure profiles, together with the spectra line data usually from the HITRAN (high-resolution transmission) spectral database. The forward model has to be inverted to obtain the information of the atmospheric state $x$. Unfortunately the most inverse problems are ill-conditioned, because the measurements have errors, which can be greatly amplified, and the solution can be meaningless, even it agrees with the measurements. To solve this problem, several regularization methods can be performed, such as the optimal estimation method (OEM) (Rodgers, 2000) and the Tikhonov regularization. Because the OEM is used in the retrieval of OCS, this method is described in this section.

The forward model (Equation 3.14) can be described in terms of probability density functions ($PDF$) as $PDF(y|x)$. The knowledge of the atmospheric state before measuring is called a priori, which can be also written in the form of probability density as $PDF(x)$. According on the Bayes’ theorem, the two terms can be combined by:

$$ PDF(x \mid y) = \frac{PDF(y \mid x)PDF(x)}{PDF(y)} $$ (3.15)

where $PDF(x|y)$ is the a posteriori $PDF$ of the state when the measurement is given, which is what we are aiming for. $PDF(y)$ is the $PDF$ of the measurement before it is made, and it is often not needed in practice.

Consider a linear problem, the Equation 3.14 can be written as:

$$ y = F(x) + \epsilon = \frac{\partial F}{\partial x} x + \epsilon = K x + \epsilon $$ (3.16)

where $K$ is defined as the weighting function matrix.
Assuming that all the measurement error, the a priori state, and the a posteriori have Gaussian distributions, the PDF of the measurement, the a priori, and the a posteriori can be expressed as:

\[-2 \ln PDF(y|x) = (y - Kx)^T S^{-1}_e (y - Kx) + c_1\]  

where \(S_e\) is the measurement error covariance. \(c_1\) is a constant.

\[-2 \ln PDF(x) = (x - x_a)^T S^{-1}_a (x - x_a) + c_2\]  

where \(x_a\) is the a priori value of \(x\). \(S_a\) is the a priori covariance. \(c_2\) is a constant.

\[-2 \ln PDF(x|y) = (x - \hat{x})^T \hat{S}^{-1} (x - \hat{x}) + c_3\]  

where \(\hat{x}\) is the expected value. \(\hat{S}\) is the associated covariance. \(c_3\) is a constant. The Equation 3.15 becomes:

\[-2 \ln PDF(x|y) = (y - Kx)^T S^{-1}_e (y - Kx) + (x - x_a)^T S^{-1}_a (x - x_a) + c_1 + c_2\]  

From the Equation 3.19 and Equation 3.20, the estimation of the true state can be found:

\[\hat{x} = x_a + (K^T S^{-1}_e K + S^{-1}_a)^{-1} K^T S^{-1}_e (y - Kx_a)\]  

Defining \(G\) as the contribution function, it is given by

\[G = (K^T S^{-1}_e K + S^{-1}_a)^{-1} K^T S^{-1}_e\]  

The Equation 3.21 becomes:

\[\hat{x} = x_a + G(y - Kx_a) = x_a + G(K(x - x_a) + \epsilon)\]  

Usually the forward model is nonlinear, and therefore an iteration procedure has to be used to find the maximum probability state \(\hat{x}\). The Gauss-Newton method is commonly used to find the solution by equating the derivative of Equation 3.20 to zero:

\[\nabla_x (-2 \ln PDF(x|y)) = \nabla_x ((y - Kx)^T S^{-1}_e (y - Kx) + (x - x_a)^T S^{-1}_a (x - x_a)) = 0\]  

\[\hat{x}_{i+1} = x_a + (K_i^T S^{-1}_e K_i + S^{-1}_a)^{-1} K_i^T S^{-1}_e (y - F(\hat{x}_i) + K_i (\hat{x}_i - x_a))\]
where $K_i$ are calculated for each $x_i$. The best guess of the state \( \hat{x} \) will be obtained when the iteration converges.

The retrieved gas concentration from the FTIR spectrum is not simple expression of the true atmospheric state, but rather a estimated state \( \hat{x} \), which can be derived from the true atmospheric state \( x_T \) and the a priori state \( x_a \) through the information of the retrieval contribution, which is presented by the averaging kernel matrix \( A \),

\[
\hat{x} = x_a + A(x_T - x_a) + \epsilon
\]  

The averaging kernel matrix is the sensitivity of the retrieval to the true atmospheric state, and it can be expressed as:

\[
A = \frac{\partial \hat{x}}{\partial x_T} = GK
\]  

To evaluate how much information is obtained from the retrieval, the degree of freedom for signal (DOF) can be calculated from the averaging kernel matrix by

\[
DOF = \text{trace}(A)
\]

It expresses the number of pieces of independent information in the retrieval.

The fitting of the spectrum can be performed in different ways. One way used in the well established retrieval software GFIT (Wunch et al., 2010) is scaling the a priori profile by a constant number while minimizing the root mean square (RMS) value between the measurement and the synthetic spectrum. The total columns of the trace gases can be retrieved from this method. Another way is varying the mixing ratio profile independently in different atmospheric layers, using the OEM method described above, as performed in SFIT-2 and SFIT-4. The information at different layers can be obtained because the line width depends on the pressure, which decreases with altitude.

### 3.1.6 Retrieval uncertainties

The uncertainties are calculated using contributions from measurement uncertainties \( S_m \), and forward model parameter uncertainties \( S_l \) based on Rodgers (2000). The interference uncertainties \( S_{\text{int}} \) are calculated as described by Rodgers and Connor (2003).
The uncertainty in total columns ($S_{\text{total}}$) was determined by adding these three components at each atmospheric layer (i) in quadrature:

$$S_{\text{total}} = \left( \sum_{1}^{n} (S_{m}(i)^2 + S_{f}(i)^2 + S_{\text{int}}(i)^2) \right)^{1/2}. \quad (3.29)$$

### 3.1.7 FTIR networks

**Figure 3.5:** Map of sites that measure both NIR and MIR regions. The green stars are the current sites, and the yellow stars are the future sites.

There are two networks of ground-based Fourier Transform InfraRed Spectrometers, both recording high resolution solar absorption spectra: the Total Carbon Column Observing Network (TCCON) (http://www.tccon.caltech.edu; Wunch et al., 2011) is concentrating on CO$_2$ and methane in the near-infrared (NIR); and the Network for the Detection of Atmospheric Composition Change InfraRed Working Group (NDACC-IRWG), measuring spectra in the mid-infrared (MIR). CO$_2$ total columns are retrieved from NIR spectra, while OCS profiles and columns can be calculated from MIR spectra. CO$_2$ could also be retrieved from MIR spectra, but the retrieval sensitivity dominates in the stratosphere, and therefore the CO$_2$ seasonal cycle cannot be well captured (Barthlott et al., 2015, Buschmann et al., 2015). We will only use the TCCON CO$_2$ product in this study. Additionally, some sites measure in both NIR and MIR spectral regions, and therefore provide co-located and quasi-simultaneous CO$_2$ and OCS measurements (Figure 3.5).
3.1.8 TCCON standard CO$_2$ retrieval

CO$_2$ total columns as well as O$_2$ total columns were retrieved from near-infrared spectra using GFIT, following the TCCON standard procedure (Wunch et al., 2011). The CO$_2$ column is retrieved from two bands centered at 6228 cm$^{-1}$ and 6348 cm$^{-1}$, while O$_2$ is retrieved from the electronic band centered at 7882 cm$^{-1}$. CO$_2$ column-averaged dry-air mole fractions (DMF) were calculated by the following equation:

$$x_{CO_2} = \frac{CO_2}{O_2} \times 0.2095$$  \hspace{1cm} (3.30)

3.2 In-situ measurements

3.2.1 Ground-based flask sampling

The OCS are measured from flasks filled with ambient air at multiple sites (Figure 4.1) in the NOAA’s Halocarbons and other Atmospheric Trace Species (HATS) program (Montzka et al., 2007). The sites samples are collected as paired flasks 1 to 5 times per month, and analyzed in NOAA’s Earth System Research Laboratory, Global Monitoring Division (NOAA/ESRL/GMD) using gas chromatography and mass spectrometry detection.

<table>
<thead>
<tr>
<th>Site</th>
<th>Code</th>
<th>Latitude (°N)</th>
<th>Longitude (°E)</th>
<th>Altitude (m a.s.l.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alert</td>
<td>ALT</td>
<td>82.5</td>
<td>-62.3</td>
<td>210</td>
</tr>
<tr>
<td>Barrow</td>
<td>BRW</td>
<td>71.3</td>
<td>-156.6</td>
<td>8</td>
</tr>
<tr>
<td>Summit</td>
<td>SUM</td>
<td>72.6</td>
<td>-38.4</td>
<td>3200</td>
</tr>
<tr>
<td>Mace Head</td>
<td>MHD</td>
<td>53.3</td>
<td>-9.9</td>
<td>42</td>
</tr>
<tr>
<td>Wisconsin</td>
<td>LEF</td>
<td>45.6</td>
<td>-90.3</td>
<td>868</td>
</tr>
<tr>
<td>Harvard Forest</td>
<td>HFM</td>
<td>42.5</td>
<td>-72.2</td>
<td>340</td>
</tr>
<tr>
<td>Trinidad Head</td>
<td>THD</td>
<td>41.0</td>
<td>-124.1</td>
<td>120</td>
</tr>
<tr>
<td>Niwot Ridge</td>
<td>NWR</td>
<td>40.1</td>
<td>-105.5</td>
<td>3475</td>
</tr>
<tr>
<td>Mauna Loa</td>
<td>MLO</td>
<td>19.5</td>
<td>-155.6</td>
<td>3397</td>
</tr>
<tr>
<td>Cape Kumukahi</td>
<td>KUM</td>
<td>19.5</td>
<td>-154.8</td>
<td>3</td>
</tr>
<tr>
<td>American Samoa</td>
<td>SMO</td>
<td>-14.2</td>
<td>-170.6</td>
<td>77</td>
</tr>
<tr>
<td>cape Grim</td>
<td>CGO</td>
<td>-40.7</td>
<td>144.7</td>
<td>164</td>
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<tr>
<td>Palmer Station</td>
<td>PSA</td>
<td>-64.6</td>
<td>-64.0</td>
<td>10</td>
</tr>
<tr>
<td>South Pole</td>
<td>SPO</td>
<td>-90.0</td>
<td>-24.8</td>
<td>2837</td>
</tr>
</tbody>
</table>
3.2.2 HIPPO aircraft flask sampling

The HIPPO (HIAPER Pole-to-Pole Observations) study of carbon cycle and greenhouse gases provides pole-to-pole measurements of meteorology, atmospheric chemistry, and aerosol content over the Pacific Ocean. HIPPO flew five month-long missions between January 2009 and September 2011 at different seasons. In this work, we use the NOAA flask sample data product of HIPPO (Wofsy et al., 2012), which provides additional information on the latitudinal distribution of the OCS and CO$_2$. The OCS data used in the work were measured by the NOAA “Whole Air Sampler-Montzka Mass Spectrometer #2” (NWAS-M2), while CO$_2$ concentrations were measured by the NOAA “Whole Air Sampler-Measurement of Atmospheric Gases that Influence Climate Change” (NWAS-MAGICC).

<table>
<thead>
<tr>
<th>Mission</th>
<th>Date</th>
<th>Latitudes</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIPPO 1</td>
<td>2009/01/09 – 2009/01/30</td>
<td>67°S – 80°N</td>
</tr>
<tr>
<td>HIPPO 2</td>
<td>2009/10/31 – 2009/11/22</td>
<td>66°S – 83°N</td>
</tr>
<tr>
<td>HIPPO 3</td>
<td>2010/03/24 – 2010/04/15</td>
<td>66.8°S – 85°N</td>
</tr>
<tr>
<td>HIPPO 4</td>
<td>2011/06/14 – 2011/07/10</td>
<td>58°S – 84°N</td>
</tr>
<tr>
<td>HIPPO 5</td>
<td>2011/08/09 – 2011/09/08</td>
<td>67°S – 87°N</td>
</tr>
</tbody>
</table>

Figure 3.6: Map of the NOAA flask sites included in this work.
3.3 Models

In this study, two global atmosphere transport models – GEOS-Chem and TM3 – were used. GEOS-Chem was used in the forward simulations of OCS (Chapter 5) and CO$_2$ (Chapter 7), and TM3 was used in the OCS flux inversions (Chapter 6). A simple biosphere model was also introduced because it simulates the coupled OCS and CO$_2$ land fluxes based on the biosphere processes.

3.3.1 GEOS-Chem

The GEOS-Chem global 3-D chemical transport model (version v9-01-03) is used in this study to simulate the concentrations of OCS in the global atmosphere. It is driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling Assimilation Office (GMAO) (Bey et al., 2001). There are several meteorological data products available covering different time periods. The most recent one is GEOS-FP ($0.25^\circ \times 0.3125^\circ$, 72 levels), which starts from 2012.
The previous data product is GEOS-5 \((0.5^\circ \times 0.666^\circ, 72\) levels), providing the temporal coverage from 2004 to 2012.

There are different simulations in GEOS-Chem including the standard full chemistry (NO\(_X\)-O\(_X\)-Hydrocarbon-aerosol) simulation and other offline tracer simulations, such as CO\(_2\), CH\(_4\), and CO. GEOS-Chem uses the TPCORE advection algorithm of Lin and Rood (1996). The convection transport in GEOS-Chem is computed from the convective mass fluxes in the meteorological archive, as described by Wu et al. (2007). For the standard full chemistry simulation, the HO\(_X\)-NO\(_X\)-VOC-O\(_3\)-BrO\(_X\) troposphere chemistry and aerosols interactions are built in chemistry solver package – SMVGGEAR and KPP (Eller et al., 2009). The stratosphere chemistry is coupled with the troposphere chemistry through the Universal tropospheric-stratospheric Chemistry eXtension (UCX, Eastham et al., 2014). Furthermore, the GEOS-Chem model consists of several emission inventories, such as fossil fuel combustion inventory from the Carbon Dioxide Information Analysis Center (CDIAC), biomass burning from the Global Fire Emission Database (GFED).

The CO\(_2\) simulation module in GEOS-Chem was developed by Suntharalingam et al. (2003, 2004), and updated by Nassar et al. (2010). The CO\(_2\) fluxes used in GEOS-Chem version v9-01-03 include monthly fluxes of fossil fuel emissions from the Carbon Dioxide Information Analysis Center (CDIAC) inventory; biomass burning from the Global Fire Emission Database (GFED3); ocean exchange from Takahashi et al. (2009); and annual biofuel fluxes from Yevich and Logan (2003). GEOS-Chem uses CO\(_2\) biospheric fluxes calculated from the Carnegie-Ames-Stanford Approach (CASA; Olsen and Randerson, 2004) model for the year 2000 as a standard input, so that the biospheric fluxes do not have interannual variability. The CASA biospheric fluxes are balanced to zero at every grid, and therefore another terrestrial flux, which is referred to as the residual annual terrestrial exchange, is added to the simulation (Baker et al., 2006).

### 3.3.2 SiB biospheric model

To have process-based calculation of OCS land fluxes, we used the SiB biosphere model. SiB was developed as a lower boundary for atmospheric models (Baker et al., 2013, Sellers et al., 1986), and has been coupled to general circulation models (Randall et al., 1996, Sato et al., 1989) as well as mesoscale models (Corbin et al., 2008, Denning et al., 2003, Nicholls et al., 2004, Wang et al., 2007). Berry et al. (2013) incorporated the calculation
of OCS uptake through stomata and in ground into SiB3 based on the biochemical mechanism for uptake of OCS by leaves and soils. This version of SiB is called SiB3-COS, and provides coupled simulations of CO$_2$ and OCS biospheric fluxes, including OCS plant uptake, OCS soil uptake, GPP, and CO$_2$ respiration. For this research, SiB3 simulations were performed on a $1.0^\circ$ by $1.25^\circ$ (latitude by longitude) grid, with meteorology provided by the Modern-Era Retrospective analysis for Research and Applications (MERRA; Rienecker et al., 2011). Precipitation fields were scaled to match Global Precipitation Climatology Project (GPCP; Adler et al., 2003) amplitudes globally. Respiration is scaled in SiB3, following Denning et al. (1996), to match productivity on a long-term basis; individual years are not in exact balance. Phenology (leaf area index (LAI), fractional photosynthetically active radiation (fPAR)) is determined prognostically following Stöckli et al. (2008, 2011).

In SiB, the OCS plant uptake is not scaled from GPP using a single factor, but estimated by mechanistic parameterization, consisting of several steps (Berry et al., 2013). OCS first diffuses from the boundary layer to the canopy, then from the canopy to the stomata, the stomata to the cells, and then is consumed in the cells. In the first step, the diffusion amount depends on the boundary layer concentration and diffusion conductance. The subsequent diffusion steps also depend on the conductance. The consumption of OCS in the cells is by the enzyme carbonic anhydrase (CA), which is co-located with the enzyme that consumes CO$_2$ – Rubisco (Protoschill-Krebs and Kesselmeier, 1992, Protoschill-Krebs et al., 1996). CA activity and mesophyll conductance are suggested to be proportional to the $V_{\text{max}}$ of Rubisco by some studies (Badger and Price, 1994, Berry et al., 2013, Evans et al., 1994), and this relationship is used in SiB to simulate the OCS uptake.

Soil uptake of OCS is a function of the activity of CA, as well as the condition of the soil (Berry et al., 2013, Van Diest and Kesselmeier, 2008). Due to the lack of information on soil CA activity, the soil uptake is instead calculated as a function of heterotrophic respiration (Rh), because measurements show that the OCS soil uptake is proportional to Rh (Yi et al., 2007). In Berry et al. (2013), the entire soil column was considered when scaling OCS soil uptake to Rh. Subsequent model versions have modified this treatment to consider only the top 20 cm of soil. Additionally, $J(\theta)$ (Equation 4 in Berry et al., 2013) is no longer monotonically increasing from wet to dry soil, but rather follows a function (as Rh does in SiB) that peaks at an “optimum” soil wetness based on soil character...
(Raich et al., 1991). Soil OCS uptake in SiB has been reduced from approximately one-half to around one-quarter of the uptake rate of the canopy, which is more in line with observations.

### 3.3.3 TM3 inversion system

The TM3 model is a global atmospheric tracer transport model. The advection is calculated using the "slopes scheme" developed by Russell and Lerner (1981). The vertical diffusion is calculated based on the stability of the air using the formula given by Louis (1979). The vertical transport by sub-grid scale cumulus clouds is based on the massflux scheme of Tiedtke (1989). It has been used in a couple of inversion studies for both CO₂ and CH₄ (Mikaloff Fletcher et al., 2004, Rödenbeck et al., 2003). Here a short description is given, which is mainly based on Rödenbeck (2005).

In an atmospheric transport model, the modeled concentrations $C_{\text{mod}}$ is calculated from the transport matrix $A$, the flux field $f$, and the initial concentration $C_{\text{ini}}$:

$$C_{\text{mod}} = Af + C_{\text{ini}} \quad (3.31)$$

Then the mismatch $m$ between modeled concentration $C_{\text{mod}}$ and observation $C_{\text{obs}}$ is:

$$m = C_{\text{obs}} - C_{\text{mod}} \quad (3.32)$$

The aim of the inversion is to find the flux $f$ that minimizes the mismatch $m$. However the atmospheric measurements are not sufficiently dense to provide a unique solution: the inverse problem is underdetermined. Thus one must either reduce the number of unknowns (by estimating fluxes for only a few regions at coarse temporal resolution (Ciais et al., 2000, Tans et al., 1990)) or by further constraining the problem through the addition of prior (or prior) knowledge of the system, using a classical Bayesian approach (Kaminski and Heimann, 2001, Tarantola, 1987). This exploits available prior knowledge of the flux distribution, with a description of its spatial and temporal correlations and a plausible range of uncertainty. The flux $f$ can be written as:

$$f = f_{\text{fix}} + f_{\text{ad}} \times p \quad (3.33)$$
where $f_{fix}$ is the fixed flux term, $f_{ad}$ is the adjustable flux, $p$ is the parameter vector, which is assumed to have zero mean and unit variance for the prior. That is:

$$
\langle P_{pri} \rangle = 0 \text{ and } \langle P_{pri} P_{pri}^T \rangle = \mu_1
$$

Based on the Bayesian approach as described in Section 3.1.5, the cost function can be obtained:

$$
J = \frac{1}{2} m^T Q_m^{-1} m + \frac{\mu}{2} p^T p + C
$$

where $Q_m$ is the error covariance matrix of the mismatch $m$. The first term of the equation represents the data constraint, the second term represents the prior constraint, the additional constant $C$ subsumes all parameter independent terms. The cost function minimum is calculated from:

$$
\frac{\partial J}{\partial p^T} \bigg|_{p=\langle p_{post} \rangle} = 0
$$

Initially this was done using matrix inversions, but such an analytical solution is only possible for a limited spatial and temporal resolution. (Consider that the size of the 2-D matrix representing the transport operator is defined by the number of flux components in one dimension and the number of observations in the other, and this becomes unwieldy as the number of observations and/or the spatial-temporal resolution of the fluxes increases.) In recent years this problem has been overcome through adjoint inversions, which can resolve fluxes at the resolution of the underlying transport model, combined with iterative or 4D-var approaches to minimize the cost function (Chevallier et al., 2010, Gurney et al., 2008, Peters et al., 2007, Rödenbeck et al., 2003). As satellite measurements and total-column measurements from ground-based sensors have become available, these observations have also been exploited to better constrain surface sources and sinks (Basu et al., 2013, Chevallier et al., 2011, 2014, Deng et al., 2014).

### 3.4 Inter-comparison between remote sensing measurements and models

Since remote sensing instruments do not measure the true state of the atmosphere as described above, it is necessary to take the different characteristics (a priori and averaging kernels) of these observing systems into account when comparing the measurements between different instruments and between measurements and models (Rodgers and Connor,
2003). Assuming two retrieved profiles ˆ\(x_1\) and ˆ\(x_2\), the retrieval 1 needs to be simulated with retrieval 2, that is:

\[
\hat{x}_{21} = x_{a2} + A_2(\hat{x}_1 - x_{a2})
\]  

(3.37)

where ˆ\(x_{21}\) is the smoothed profile 2, \(x_{a2}\), and \(A_2\) are the a priori and averaging kernel matrix of retrieval 2, respectively. When comparing the retrievals with model simulations, ˆ\(x_1\) will be replaced by the model profile.

For CO\(_2\) column retrievals, Equation 3.37 is modified by Wunch et al. (2010) to yield

\[
C_s = C_a + h^T \times a^T \times (X_m - X_a),
\]  

(3.38)

where \(C_s\) and \(C_a\) are the smoothed and a priori CO\(_2\) column-averaged DMFs, \(h\) describes the vertical summation, and \(a\) is the TCCON absorber-weighted column averaging kernel. TCCON averaging kernels are largely dependent on the solar zenith angle. Here we use the standard TCCON averaging kernel product, which provides the averaging kernels at 5° solar zenith angle intervals. The averaging kernels used here are interpolated to the solar zenith angle at the time the measurement was made.
Chapter 4

The retrieval of OCS from FTIR spectra

The FTIR OCS total column measurements were used to estimate hemisphere-integrated OCS flux and confirmed their understanding of OCS global budget (Kettle et al., 2002b). However, the measurements could not put constraints on the relative magnitude of vegetative uptake and ocean-related emissions. Lejeune et al. (2016) has improved the OCS retrieval, with a better accuracy on seasonal amplitude, which is important for studying the carbon cycle and resolving temporal variability of OCS fluxes. In this chapter, an approach based on Lejeune et al. (2016) was first tested at the selected sites, spanning both the Northern and Southern Hemisphere. The performances of the retrievals at different sites are discussed.

4.1 FTIR sites included in this study

Twelve measurement sites spanning both Northern and Southern Hemisphere are used in this study to retrieve OCS atmospheric abundances (summarized in Table 4.1). Eureka, Ny-Ålesund, Bremen, Tsukuba, La reunion, Wollongong, and Lauder belong to both TCCON and NDACC networks, and measure both CO$_2$ and OCS. Paramaribo is not a TCCON site because the instrument is different from the TCCON standard ones, but it also measure in NIR region and can obtain CO$_2$ columns. Jungfraujoch, Toronto, Mauna Loa, and Arrival Heights only measure in the MIR spectral region, and therefore TCCON-type CO$_2$ data are not available. The locations of the included FTIR sites are
Chapter 4. *Retrieval of OCS from FTIR spectra*

### Table 4.1: FTIR sites used in this study

<table>
<thead>
<tr>
<th>Site</th>
<th>Code</th>
<th>Latitude (°)N</th>
<th>Longitude (°)E</th>
<th>Altitude (m a.s.l.)</th>
<th>Network</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eureka</td>
<td>EUR</td>
<td>80.1</td>
<td>−86.4</td>
<td>610</td>
<td>NDACC&amp;TCCON</td>
</tr>
<tr>
<td>Ny-Ålesund</td>
<td>NYA</td>
<td>78.9</td>
<td>11.9</td>
<td>21</td>
<td>NDACC&amp;TCCON</td>
</tr>
<tr>
<td>Bremen</td>
<td>BRE</td>
<td>53.1</td>
<td>8.8</td>
<td>27</td>
<td>NDACC&amp;TCCON</td>
</tr>
<tr>
<td>Jungfraujoch</td>
<td>JFJ</td>
<td>46.5</td>
<td>8.0</td>
<td>3580</td>
<td>NDACC</td>
</tr>
<tr>
<td>Toronto</td>
<td>TOR</td>
<td>43.7</td>
<td>−79.4</td>
<td>174</td>
<td>NDACC</td>
</tr>
<tr>
<td>Tsukuba</td>
<td>TSU</td>
<td>36.1</td>
<td>140.1</td>
<td>31</td>
<td>NDACC&amp;TCCON</td>
</tr>
<tr>
<td>Mauna Loa</td>
<td>MLO</td>
<td>19.5</td>
<td>−155.6</td>
<td>3397</td>
<td>NDACC</td>
</tr>
<tr>
<td>Paramaribo</td>
<td>PMB</td>
<td>5.8</td>
<td>−55.2</td>
<td>7</td>
<td>NDACC</td>
</tr>
<tr>
<td>La Reunion</td>
<td>RUN</td>
<td>−20.9</td>
<td>55.5</td>
<td>87</td>
<td>NDACC&amp;TCCON</td>
</tr>
<tr>
<td>Wollongong</td>
<td>WOL</td>
<td>−34.4</td>
<td>150.9</td>
<td>31</td>
<td>NDACC&amp;TCCON</td>
</tr>
<tr>
<td>Lauder</td>
<td>LAU</td>
<td>−45.0</td>
<td>169.7</td>
<td>370</td>
<td>NDACC&amp;TCCON</td>
</tr>
<tr>
<td>Arrival Heights</td>
<td>ARH</td>
<td>−77.8</td>
<td>166.7</td>
<td>250</td>
<td>NDACC</td>
</tr>
</tbody>
</table>

shown as black stars in Figure 4.1. The including of the FTIR sites doubles the number of the ground-based OCS measurement sites, and fills in some gaps in the globe.

**Figure 4.1**: Map of the flask and FTIR ground-based sites included in this work. The red dots are the flask measurements sites, and black stars are the FTIR sites.
4.2 Setup of OCS retrieval

OCS profiles and total columns were retrieved using the SFIT-4 (v0.9.4) fitting algorithm, as described in Chapter 3. A mixed spectroscopy based on the HITRAN 2012 database was used in the retrievals. The original a priori profile of OCS was provided by G. Toon (personal communication). Considering that the OCS profiles vary at different latitude because of the differences in tropopause height, the a priori profiles were modified according to the average tropopause height above each site (constant in the troposphere, and decrease above tropopause). The temperature and pressure files are computed by the National centers for Environmental Prediction (NCEP) and extracted according to the locations of each sites. I adopted a prefixed signal to noise ratio (SNR) of 300 for the retrievals to optimize the fitting residuals as well as avoiding the unphysical oscillations in the retrieved profiles. Before fitting, spectra with a signal-to-noise ratio (SNR) of less than 100 were discarded. Post fitting, retrievals with a root-mean-square (RMS) residual of greater than 0.5% were excluded before subsequent analysis. The retrieval parameters are summarized in Table 4.2. The OCS column-averaged dry-air mole fractions (xOCS) were derived using Equation 4.1.

\[ x_{\text{OCS}} = \frac{C_{\text{OCS}}}{C_{\text{air}}} \]  

(4.1)

where \( C_{\text{OCS}} \) is the retrieved total column of OCS. \( C_{\text{air}} \) is the air mass total column, derived from the pressure \( (P_i) \) and temperature \( (T_i) \) at each atmospheric layer \( i \):

\[ C_{\text{air}} = \sum_1^n \left( \frac{P_i \delta h_i}{RT_i} \right) \]  

(4.2)

<table>
<thead>
<tr>
<th>Retrieval code</th>
<th>Spectroscopy</th>
<th>A priori OCS profiles</th>
<th>A priori Sa matrix</th>
<th>SNR</th>
<th>Pressure, Temperature profiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFIT4-v0.9.4</td>
<td>Based on HITRAN 2012</td>
<td>Provided by Geoff Toon over communication, modified by tropopause height</td>
<td>In-situ measurements variability below 9 km, ACE-FTS measurements variability above 9 km</td>
<td>300 pre-fixed</td>
<td>NCEP</td>
</tr>
</tbody>
</table>

Table 4.2: Summary of the retrieval parameters for OCS
where $\delta h_i$ is the thickness of each layer. $R = 8.315 \text{Jmol}^{-1} \text{K}^{-1}$ is the ideal gas constant.

### 4.3 Four micro-windows retrieval

<table>
<thead>
<tr>
<th>OCS target line</th>
<th>OCS line position</th>
<th>Micro-windows(cm$^{-1}$)</th>
<th>Interfering species</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(32)</td>
<td>2048.017611</td>
<td>2047.78-2048.22</td>
<td>$\text{O}_3$, $^{13}\text{CO}_2$</td>
</tr>
<tr>
<td>P(28)</td>
<td>2049.925642</td>
<td>2049.75-2050.12</td>
<td>$\text{O}_3$, $^{18}\text{CO}$, $\text{H}_2^{18}\text{O}$</td>
</tr>
<tr>
<td>P(25)</td>
<td>2051.331396</td>
<td>2051.18-2051.48</td>
<td>$\text{O}_3$, $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>P(18)</td>
<td>2054.527142</td>
<td>2054.33-2054.67</td>
<td>$\text{O}_3$, $\text{H}_2\text{O}$, $\text{H}_2^{18}\text{O}$, $^{13}\text{CO}_2$</td>
</tr>
</tbody>
</table>

**Figure 4.2:** One example of profiles and averaging kernels of the OCS retrievals. This measurement was taken at 10 UTC, April 17th, 2009. The left plot shows the a priori and retrieved profiles. The right plot shows the normalized averaging kernels.

Lejeune et al. (2016) compared 21 spectral Mws containing OCS lines, and selected four best MWs to retrieve OCS at Jungfraujoch station. These four MWs contain the OCS $\nu 3$ band P32, P28, P25, and P18 lines, respectively. The details of the MWs are summarized in Table 4.3. They were used in this study to retrieve OCS at the selected FTIR sites at different locations.

One example of the profile and the averaging Kernels of the OCS retrievals at Ny-Ålesund is shown in Figure 4.2. The averaging kernels indicate that the retrievals are sensitive
from the surface to about 30 km, where the OCS mainly distributes. This confirms the ability of the FTIR spectrometry to measure the OCS variations in both troposphere and stratosphere. In total, approximately 2.5 DOFs for total columns were obtained for all the sites. The average uncertainties in the total columns from 2005 to 2012 are about 3% for all the sites.

![Figure 4.3: The fitting of the gases in the selected MWs in a dry day. This measurement was taken at 10 UTC, April 17th, 2009. The observed spectra are shown in black dots. The fitted gases are shown in different colors as listed in the legend.](image)

<table>
<thead>
<tr>
<th>Date</th>
<th>Description</th>
<th>RMS (%)</th>
<th>DOFs</th>
<th>RMS (%)</th>
<th>DOFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007/04/17</td>
<td>dry</td>
<td>0.22</td>
<td>2.49</td>
<td>0.21</td>
<td>2.32</td>
</tr>
<tr>
<td>2007/08/28</td>
<td>humid</td>
<td>0.27</td>
<td>2.45</td>
<td>0.22</td>
<td>2.30</td>
</tr>
</tbody>
</table>

The gases fitting of the four MWs of the example is illustrated in Figure 4.3. We can see that the fittings are quite well for this measurement, through small structures remain in
Chapter 4. Retrieval of OCS from FTIR spectra

Figure 4.4: The fitting of the gases in the selected MWs in a humid day. This measurement was taken at 10 UTC, August 28th, 2009. The observed spectra are shown in black dots. The fitted gases are shown in different colors as listed in the legend.

the residuals, which are mainly caused by the ozone lines. The mean RMS of this four MW fittings is 0.22%, and the DOFs is 2.49. However, the four MWs spectra fittings are worse for some measurements, such as the one in Figure 4.4. This measurement was taken in the summer, when is usually more humid than spring (the example in Figure 4.3). There are a lot of water absorption in the P(18) window, which resulted in the mismatches. While in the dry day, the fitting is good in P(18) window. The mean RMS and the DOFs of this retrieval is 0.27% and 2.45, respectively, a little worse than those from the measurement in spring (summarized in Table 4.4). Ny-Ålesund is a general dry site located in the Arctic, and therefore the measurements are affected by the water absorption less than the humid sites.
4.4 Three micro-windows retrieval

I tested the retrieval of OCS without the P(18) MW, that is only using the P(32), P(28), and P(25) MWs. The results from the 4 MWs and the 3 MWs retrievals at Ny-Ålesund and Lauder, which stands for dry and humid site respectively, are shown in Figure 4.5. The first row is direct comparison of the retrieved OCS time series. I applied the averaging kernels of 3 MWs retrievals to smooth the 4 MWs retrievals to get rid of the influence from different averaging kernels, as described in Equation 3.37, and the comparison is
Figure 4.6: Mean differences of the xOCS between 4 MWs and 3 MWs retrievals at different site. The red dots are the differences between the original retrieved xOCS. The green dots are the differences after smoothing with averaging kernels as described in Figure 4.5.

shown in the second row. For Ny-Ålesund, the results are quite similar in the xOCS time series. The RMS are small in the 3 MWs retrievals, especially in the summer time, when the water absorption is strong in the P(18) window. The DOFs of the 3 MWs retrieval reduces a little, because the weight of the measurements decreased using less MWs. I check the fitting with 3 MWs at those two measurements shown above. The RMS for the dry day changes little, and the DOFs gets smaller. For the humid day, the RMS decreases to the number that is similar to the dry day, and so is the DOFs. This indicates that the 3 MWs retrieval is less sensitive to the perturbation of water lines.

The differences between these two retrievals at Lauder are much larger than Ny-Ålesund, probably because Lauder is generally more humid than Ny-Ålesund. In the direct comparison, both the mean values and seasonal cycles are different from the two retrievals, and the 4 MWs result is noisier than the 3 MWs. After the smoothing, the differences get smaller, but still larger than the differences at Ny-Ålesund. Unlike in Ny-Ålesund, the differences of RMS at Lauder is consistent in the whole year, implying that the water influence in the P(18) window is generally large in different seasons.

The mean xOCS differences between the two retrievals at all the sites are shown in Figure 4.6. The differences at dry sites, such as Eureka, Ny-Ålesund, Jungfraujoch, and Arrival Heights are small, while the differences are bigger at the humid sites. The smoothing with averaging kernels decreases the differences, which means the retrieval sensitivities change with the selection of the MWs.

In the following study, the 3 MWs retrievals are selected, because the spectrum fittings are better than the 4 MWs retrievals. However, the retrievals need to be calibrated using independent measurements. Because OCS has large variability at the high altitudes too, the calibration must be done with profile measurements up to the stratosphere, which
has not been performed before. The AirCore measurement has the potential capability to achieve this task. This needs to be designed and performed in the future work.

4.5 Summary

In this Chapter, the retrievals of OCS from FTIR spectra were conducted using two setups – the 4 MWs and 3MWs setups – at different sites. The water absorption line in P(18) window has a large influence on the retrievals, and affects both the mean values and seasonal cycles of the OCS time series. The differences between the two retrievals are bigger at the humid sites than the dry sites. To minimize the perturbation of the water line, the 3MWs retrievals are chosen in the study, however, the OCS retrievals need to be calibrated with independent measurements to evaluate the OCS latitudinal distribution and seasonal cycles.
Chapter 5

Evaluate the OCS sources and sinks through model comparison

There are large uncertainties in the OCS sources and sinks and the global budget. In order to use OCS as a photosynthetic tracer, we need to first evaluate its sources and sinks. In this Chapter, we use a chemical transport model (GEOS-Chem) to conduct the forward simulation of OCS, using different fluxes. Through comparison between simulations and observations, one can get an idea of how well the sources and sinks reproduce the variations of OCS in the atmosphere.

5.1 Setup of OCS simulation

The OCS simulation is not included in the current version of GEOS-Chem (v9-01-03). I developed the OCS module from the version of Suntharalingam et al. (2008), and added it to GEOS-Chem v9-01-03. Both the surface fluxes and the chemical reaction in the atmosphere are included to the OCS simulation. The basic version of the surface fluxes is based on the gridded flux inventories of Kettle et al. (2002a), hereafter referred to as K2002. The input fluxes from K2002 include monthly fluxes of ocean emissions (both direct emission and indirect emissions via CS$_2$ and DMS), anthropogenic emissions (both direct emission and indirect emission via CS$_2$), plant uptake, soil uptake, and biomass burning. In this study, the OCS biomass burning in K2002 was replaced by the year-dependent calculation using a fire database. The OCS biomass burning emission ($BB_{OCS}$) is calculated from CO emissions ($BB_{CO}$, from GFED3 database, described in Chapter 3)
using a scale factor (C):

\[ BB_{OCS} = C \times BB_{CO} \]  \hspace{1cm} (5.1)

where the factor C is \(8.5 \times 10^{-5}\) from Nguyen et al. (1995).

\[ K(T) = A \times \exp(-E/T) \]  \hspace{1cm} (5.2)

where the constant A is \(1.1 \times 10^{-13}\), and E is 1200 (Atkinson et al., 1997, DeMore et al., 1997). Then the OCS loss by OH oxidation \(L_{OH}\) is calculated by:

\[ L_{OH} = [OCS] \times [OH] \times K(T) \]  \hspace{1cm} (5.3)

where \([OCS]\) and \([OH]\) are the concentrations of OCS and OH, respectively.

In the stratosphere, all the reactions (reaction with OH, O, and photolysis, Equation 2.8, 2.9, 2.10) are combined in the simulation. Inclusion of the stratosphere loss reproduces the
slope of the OCS profile above the troposphere. This stratospheric loss $L_{\text{stra}}$ is computed using the altitude-dependent loss rate $K_{\text{stra}}$ from Chin and Davis (1995):

$$L_{\text{stra}} = [\text{OCS}] \times K_{\text{stra}}$$  \hspace{1cm} (5.4)

Chin and Davis (1995) used a box model with a fixed height of tropopause (14 Km) as the bottom and 50 Km as the top height. In this work the loss rate is adjusted by monthly mean tropopause height at several latitudinal bins to represent the seasonal differences. An example of the calculated OCS chemical sink is shown in Figure 5.1.

In this study, the simulations were run using GEOS-5 meteorology from 2004 to 2012 on a horizontal grid resolution of $2^\circ$ by $2.5^\circ$ (latitude by longitude), with 47 vertical levels from surface up to 0.01 hPa. Taking 2004 as a 1-year spin-up, we analyze the results from 2005 to 2012 based on hourly model output.

The hourly model vertical profiles were selected at the nearest grid point to the measurement sites and at measurement hours. The OCS profiles were smoothed by the FTIR a priori and averaging kernels of each measurement by Equation 3.37, as described in Chapter 3. The $x\text{OCS}$ was then calculated using Equation 4.1.

In this work, different versions of the surface fluxes were used to test their impact on the results. In addition to the K2002 surface fluxes described above, the OCS land fluxes calculated from SiB (details in Chapter 3) were used to replace the plant and soil uptake in K2002, and the anthropogenic fluxes from Campbell et al. (2015) were included too. In this chapter, all the simulations were run using the GEOS-Chem transport model. Different versions of the OCS fluxes used in the OCS simulations are summarized in Table 5.1. In the analysis, the simulations with different fluxes will be referred to as the names of the fluxes, as shown in Table 5.1.

### 5.2 Simulation of OCS with Kettle fluxes

#### 5.2.1 Initial simulation

As a starting point, we assess the accuracy of the OCS fluxes from Kettle et al. (2002a). The simulation with K2002 is referred to as the initial simulation.
The simulations of OCS with K2002 are shown as blue asterisks in Figure 5.2 and Figure 5.3. This simulation poorly reproduces the latitudinal distribution and seasonal cycle of the measurements. For the Northern Hemisphere, it underestimates the seasonal amplitude, as reported by previous studies (Berry et al., 2013, Suntharalingam et al., 2008). Plant uptake is thought to be the dominant driver of seasonal variation in the Northern Hemisphere, so increasing the plant uptake should increase the seasonal amplitude. K2002 used a model based on NPP (described in Chapter 2) to calculate the plant uptake of OCS, assuming the relative uptake rates for OCS and CO$_2$ were the same (Kettle et al., 2002a). That is,

$$OCS \text{ uptake} = NPP \times \frac{[OCS]}{[CO_2]}$$  \hspace{1cm} (5.5)

where $[OCS]$ and $[CO_2]$ are the atmospheric concentrations of OCS and CO$_2$, respectively. Considering that OCS is taken up by plants irreversibly, while CO$_2$ is also released through respiration, and plants favor OCS over CO$_2$, a model based on GPP (described in Chapter 2) has been suggested to replace the NPP-based model (Sandoval-Soto et al., 2005):

$$OCS \text{ uptake} = GPP \times \frac{[OCS]}{[CO_2]} \times LRU$$  \hspace{1cm} (5.6)

GPP is about 2 times as large as NPP, and the global averaged LRU (described in Chapter 2) is in the range of 1.3–3.1 (Berkelhammer et al., 2014, Seibt et al., 2010, Stimler et al., 2012), so that in the GPP-based model, the OCS plant uptake is increased by a factor of 2.6 to 6.2 from the NPP model. Therefore the plant uptake in K2002 needs to be increased to match the seasonal cycle of the measurements.

In the northern low latitudes, the simulation with K2002 underestimates the mean OCS value (such as in situ sites Mauna Loa and Cape Kumukahi, FTIR sites Tsukuba and Mauna Loa), implying a missing source at low latitudes. Berry et al. (2013) indicated that the missing source after increasing the land sinks is likely from the ocean, and distributed mainly in the tropical region. While in the Southern Hemisphere, the model shows higher seasonal amplitudes than the measurements. Suntharalingam et al. (2008) conducted test simulations with decreasing the OCS emissions in the Southern Ocean, and got better match to the measurements with a scaling factor of 0.5.

Additionally, the differences between the FTIR measurements and the K2002 simulation in the Southern Hemisphere are bigger than those between the flask measurements and the simulation. This is either because the atmospheric transport in the model is wrong, or the retrieved mean values have biases as discussed in Chapter 4.
Figure 5.2: Comparison of flask measurements of OCS to model simulations. The plots show weekly means from 2005 to 2012. The flask measurements are shown in black dots. The model simulations are driven by K2002 (blue asterisks), K2002x3 (green stars), and SiB (magenta triangles).
Figure 5.3: Comparison of FTIR measurements of OCS to model simulations. The plots show weekly means from 2005 to 2012. The FTIR retrievals are shown in black dots. The model simulations are driven by K2002 (blue asterisks), K2002x3 (green stars), and SiB (magenta triangles).
Chapter 5. *Evaluate the OCS sources and sinks*

5.2.2 Simulations with rescaled K2002 fluxes

Table 5.1: Annual global atmospheric OCS budget used in the forward simulations (fluxes in Gg S year\(^{-1}\))

<table>
<thead>
<tr>
<th>Source</th>
<th>K2002(^a) Mean (Range)</th>
<th>K2002x3 Revisions</th>
<th>SiB Revisions</th>
<th>SiB+Campbell Revisions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic</td>
<td>182 (90-266)</td>
<td>182</td>
<td>182</td>
<td>256</td>
</tr>
<tr>
<td>Ocean</td>
<td>280 (39-520)</td>
<td>754</td>
<td>870</td>
<td>800</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>35 (25-38)(^b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plant</td>
<td>238 (210-270)</td>
<td>713</td>
<td>765</td>
<td>765</td>
</tr>
<tr>
<td>Soil</td>
<td>130 (74-180)</td>
<td>130</td>
<td>178</td>
<td>178</td>
</tr>
<tr>
<td>Tropospheric OH oxidation</td>
<td>96 (95-98)(^b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stratosphere loss</td>
<td>43(^b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net</td>
<td>-10</td>
<td>-11</td>
<td>5</td>
<td>9</td>
</tr>
</tbody>
</table>

\(^a\)Modifications include biomass burning, tropospheric OH oxidation, and stratospheric loss. (see text)

\(^b\)The range for biomass burning and tropospheric OH oxidation is the range calculated in the model from 2005 to 2012; the calculated stratospheric loss varies little.

In order to improve the OCS simulation, we rescaled the OCS fluxes to find a better match to the measurements. Following Suntharalingam et al. (2008), we rescaled the fluxes in K2002 by increasing the plant uptake. To balance the global budget, the ocean emissions were modified based on previous studies, which include increasing the ocean emissions in the tropical region, and decreasing the ocean emissions in the Southern Ocean (Suntharalingam et al., 2008). Multiplying the plant uptake by a factor of 3 (K2002x3, Figure 5.2 and Figure 5.3 green stars) agrees with the measurements best. The details of the rescaled OCS sources and sinks are shown in Table 5.1.

The simulations with rescaled fluxes increased the seasonal cycle amplitudes, and decreased the peak and mean values at the measurement sites in the Northern Hemisphere. The rescaled plant fluxes mainly increased during growing season, causing a larger OCS drawdown. Combined with a small increase in the uptake during Northern winter, this leads to a decrease in the mean values. The increased ocean emissions result in a higher OCS concentrations in the tropics, thereby changing the latitudinal distribution. The simulation also produces smaller seasonal amplitude in the Southern Hemisphere, which caused by scaling down the Southern Ocean emissions, and agree with the measurements at South Pole, Cape Grim and Palmer Station well. In general, the simulation with
Chapter 5. Evaluate the OCS sources and sinks

K2002x3 matches the measurements better than the original Kettle fluxes. This scaling, while not realistic, provides an idea of the sensitivity of the simulations to these processes.

5.3 OCS simulation with SiB land fluxes

Different from K2002, SiB provides the OCS land fluxes through process based simulation, and therefore can be used to improve the understanding of these biospheric processes by comparison between model and measurements. The OCS simulation results with SiB fluxes are shown as magenta triangles in Figure 5.2 and Figure 5.3. The mean values at the Northern Hemispheric sites are higher than those with the original or rescaled K2002 fluxes, especially at Arctic sites (Eureka, Ny-Ålesund, Alert, and Barrow). In contrast, the SiB simulated OCS concentrations at Southern Hemisphere sites are lower than the simulations with original and rescaled Kettle fluxes, and agree with measurements better. The simulated seasonal amplitudes with SiB fluxes at the Northern sites are smaller than those simulated with K2002x3. Table 5.1 shows that the plant uptake of SiB is about 3 times that of K2002, and the soil uptake is also bigger than K2002. With identical distributions of these fluxes, one would expect a similar drawdown during growing season in the Northern Hemisphere from SiB compared to K2002x3. The fact that this is not consistently present at the selected sites indicates that the latitudinal distribution of the land fluxes between SiB and Kettle is different.

![Figure 5.4](image)

**Figure 5.4**: Difference between SiB OCS plant uptake and K2002x3 (left, SiB – K2002x3), and difference between OCS soil uptake and K2002 (right, SiB – K2002) in July.

I compared the difference between SiB and the scaled K2002 plant uptake and soil uptake in July, shown in Figure 5.4. For the plant uptake, SiB is much smaller than K2002x3 in the boreal forest region, causing a smaller drawdown, while it is stronger in the tropical region. Figure 5.5 (top) shows the monthly plant uptake of different fluxes summed
Evaluate the OCS sources and sinks

Figure 5.5: Monthly totals of OCS plant uptake (top) and soil uptake (bottom) of K2002 (blue), K2002x3 (green), and SiB (magenta) for global, 30° N - 90° N, 30° N - 30° S, and 30° S - 90° S.

globally, and in three latitude bands: 30°N to 90°N (North); 30°S to 30°N (Equatorial); and 90°S to 30°S (South). In the North region, the total amount and seasonal variation of the SiB plant uptake are smaller than K2002x3. The plant uptake of K2002 in the North region accounts for 42% of the global total uptake in a year, while for SiB plant uptake, it contributes only 24%. In Equatorial region the uptake in SiB is much larger than that in K2002x3. In the South, the plant uptake of SiB shows stronger seasonal variation than K2002x3. Globally, the SiB plant uptake is most consistent with K2002x3, though with a smaller seasonality, resulting from the strong uptake in the tropics and Southern Hemisphere. The difference in soil uptake between SiB and K2002 in July shows a similar pattern to the difference in plant uptake: larger uptake in the tropics and smaller uptake in the remaining regions. This latitudinal distribution of SiB OCS land fluxes leads to a higher mean value and smaller seasonal amplitude in the northern high latitudes, as seen from Arctic sites. The seasonal amplitude is better represented by SiB at lower latitudes.
5.4 Using HIPPO to validate the latitudinal and vertical distribution of the simulations

To evaluate the latitudinal distribution of the fluxes, we compared the model simulations with HIPPO-OCS (Figure 5.6). The latitudinal distribution of the simulation with K2002 poorly matches the HIPPO-OCS. The K2002 simulation results in OCS concentrations that are too low in the tropics and too high in the Southern Hemisphere compared to the measurements from all five campaigns. In late northern summer (HIPPO-5) and autumn (HIPPO-2), the model is higher than the measurements in the boreal region, because the modeled plant uptake is too weak. After rescaling the plant uptake and ocean emissions, the latitudinal distribution of the simulation shows better agreement with HIPPO-OCS. The latitudinal gradient in the boreal region is sensitive to plant uptake. Increasing the

![Figure 5.6: Comparison of HIPPO OCS measurements and model simulations. The five campaigns are compared separately to show the latitudinal gradient in different seasons. To minimize the influence of the stratosphere, only the measurements lower than 9km are used. The model outputs are selected at the nearest measurement location and time. The measurements and model output are averaged in five degree bins. The HIPPO data are shown in black dots. The model simulations are in the same colors with those shown in Figure 5.2 and Figure 5.3.](image-url)
Figure 5.7: Vertical distribution of HIPPO observations and simulations. The five rows are the five HIPPO campaigns in different seasons. The first column shows the observations; the second column shows the model simulation with K2002; the third column shows the simulation with K2002x3; the fourth column shows the simulation with SiB.
plant uptake gives a steeper latitude gradient towards the Arctic. The simulation with K2002x3 reproduced the strong gradient in summer and autumn, but the values are lower than the measurements – in agreement with the comparison with FTIR measurements. The mean values of the simulation with K2002x3 at the Northern boreal stations are lower than the measurements.

There are mismatches in the tropical and northern temperate regions during HIPPO-2 and HIPPO-3, likely because sources in this region are too low in the model. This is also seen in Tsukuba and Mauna Loa comparison between simulations and measurements. Increasing the ocean emissions in the Northern Hemisphere by a factor of 2 (not shown) results in a simulated increase in OCS in northern summer, at the time that ocean fluxes are greatest, while winter is hardly affected. Simply rescaling the fluxes based on the distribution (temporal and spatial) of K2002 is not sufficient to reproduce the latitudinal gradient of OCS: the seasonal cycles of the fluxes also need to be reconsidered. In this part of work, the ocean emissions were only modified at certain latitudes by a single regionally specific factor. Because the role of ocean direct emissions is a subject of debate (Berry et al., 2013, Launois et al., 2015a, Weiss et al., 1995, Xu et al., 2001) and the temporal variations of the direct and indirect ocean emissions are similar (Kettle et al., 2002a), we take all ocean emissions as a whole when rescaling, similarly to the method in Suntharalingam et al. (2008). For the simulations with K2002x3 and SiB, a value of 0.5 was applied for the Southern Ocean (30–90° S), while in the tropics (30° N–30° S), values of 5.1 and 6.1 were used for K2002x3 and SiB, respectively, to balance the global budget. Other studies used atmospheric inversions (Berry et al., 2013, Kuai et al., 2015) or an ocean general circulation and biogeochemistry model (Launois et al., 2015a) to access the ocean fluxes. The global amount and general latitudinal distribution are consistent with this study. The inversion of OCS fluxes is presented in Chapter 6. New studies have also shown that the anthropogenic sources of OCS have been underestimated (Campbell et al., 2015). This could be another reason for the mismatch.

The simulation with SiB fluxes shows similar pattern in the Southern Hemisphere to the rescaled Kettle fluxes. However the values are slightly lower from SiB than K2002x3. SiB has a stronger plant uptake in the tropics and Southern Hemisphere, while the ocean emissions are also higher than K2002x3 in order to maintain the balanced budget. For the Northern Hemisphere, the low OCS concentrations in the low latitudes and mid latitudes (HIPPO-2, HIPPO-3) are due to a combination of sources and/or transport, as are the simulations with Kettle’s fluxes. SiB did not capture the strong latitudinal gradient during growing season (HIPPO-5), indicating that the plant uptake of OCS in SiB in the
boreal forest is too small, at least for the year (2011) in question.

The vertical patterns of the HIPPO measurements and the simulations are shown in Figure 5.7. There are clear vertical variations in the observations. OCS concentration decreases above the tropopause, resulted from strong photolysis and oxidation with oxygen atom. OCS is relatively well mixed in the troposphere, because of its long life time and dynamic transport. In the growing season, the rapid uptake by the plant leads to a decrease in the low altitudes, which can be seen in the late summer and autumn HIPPO measurements (HIPPO-2 and HIPPO-5). The tropopause is high in the tropic region because of the strong convection, so the HIPPO measurements hardly show vertical variation in this region. All the simulations reproduce the structure in the high atmosphere well, meaning that the chemical loss rate in the stratosphere is reasonable. The differences between simulations and measurements are bigger in the lower levels, especially in the high latitudes, which could be caused by the wrong surface sources and sinks. In some regions such as the Southern Ocean from HIPPO-1, the simulation with K2002 overestimates the OCS near the surface, while underestimates the concentration between 5 and 10 Km, implying the vertical transport in that region is too weak in the model. In general, the simulations show similar vertical pattern to the measurements, therefore the surface fluxes can be evaluated from comparing the between models and observations.

5.5 Simulation with new anthropogenic emissions

The anthropogenic emissions of OCS calculated in Kettle et al. (2002a) was based on the estimations of Chin and Davis (1993), Watts (2000), which are from 20 years ago. New studies suggested that the total amount and global distribution of these emission have differed with the location change of the rayon industry (Blake et al., 2004, Campbell et al., 2015). Blake et al. (2004) showed high OCS and CS$_2$ concentrations in Japan and south China during the TRACE-P campaign, suggesting strong anthropogenic emissions in that region. Campbell et al. (2015) developed a new estimation of the anthropogenic sources based on new industry data and measured emission factor. The distribution of this emission is shown in Figure 5.8. This version of data is only calculated from rayon production, which is the dominant anthropogenic source of OCS, base on the year 2013. It shows that the emission is concentrated in the southeast of Asian and Europe, which is different from the Kettle’s inventory. The annual total amount of this estimation if 256 Gg S, about 50% more than K2002.
Chapter 5. Evaluate the OCS sources and sinks

Figure 5.8: The Distribution of anthropogenic emission (annual totals) from K2002 and Campbell et al. (2015).

Figure 5.9: Comparison between simulations with different anthropogenic emissions at Tsukuba. The left plot shows the simulations with the anthropogenic emissions from K2002, and the right plot are the simulations with the anthropogenic emissions from Campbell et al. (2015). The black dots are the measurements; the green stars are the simulation with K2002x3; the magenta triangles are the simulation with SiB.

The model simulation with the new anthropogenic fluxes (Figure 5.9) shows higher value at Tsukuba, Japan, and agree with the mean value of the measurements better than the old simulations. The measurements show a increasing trend, which is not shown in the simulation. Campbell et al. (2015) showed that the anthropogenic emission was increasing in the recent years. This can be a possible reason of the positive trend at Tsukuba.

Figure 5.10 shows the comparison of HIPPO-OCS data to the simulations with the new anthropogenic emissions. Including the new anthropogenic fluxes increases the simulated OCS in northern low and mid latitudes, which in the latitude of southern Asian, and agrees with the HIPPO measurements better, though mismatches remain. It indicates
Figure 5.10: Comparison of HIPPO OCS measurements and model simulations with new anthropogenic fluxes. The five campaigns are compared separately to show the latitudinal gradient in different seasons. To minimize the influence of the stratosphere, only the measurements lower than 9km are used. The model outputs are selected at the nearest measurement location and time. The measurements and model output are averaged in five degree bins. The HIPPO data are shown in black dot lines. The simulations with K2002x3 are shown in green lines; the simulations with K2002x3 but replaced anthropogenic emissions with Campbell et al. (2015) are shown in yellow lines; the simulations with SiB are shown in magenta lines; the simulations with SiB but replaced anthropogenic emissions with Campbell et al. (2015) are shown in blue lines.

that the anthropogenic emissions play an important role in the OCS global budget. Improving the estimation of OCS sources and sinks is important for applying the study of carbon cycle. The remaining disagreements can result from several possible reasons: the anthropogenic emissions are still underestimated; the ocean sources need to be increased; the land uptake is too strong in that region. This will be further evaluated by flux inversion in Chapter 6.
5.6 Summary

I compared the OCS FTIR and flask measurements to simulations with different fluxes to evaluate the estimations of OCS sources and sinks. The original fluxes of Kettle et al. (2002a) poorly reproduce the seasonal cycle and global distribution of OCS. The rescaling of the fluxes indicates that increasing the plant uptake, increasing the tropical ocean emissions, and decreasing the Southern Ocean sources improves the comparison.

The SiB process-based land fluxes are used to replace the plant and soil uptake in Kettle. The simulation with SiB shows better agreement with the measurements than K2002, but smaller seasonal amplitude than K2002x3. The mean values at high latitudes are also overestimated by SiB simulation. It indicates that the SiB land uptake in the Northern boreal region is too small. The SiB and K2002 land fluxes have different patterns: SiB shows more uptake in the tropics and less in the high latitudes compared to K2002. Substituting the anthropogenic emissions by the estimation of Campbell et al. (2015) increases the simulated OCS concentration in Asian, which can be seen at Tsukuba.

The OCS simulations were also compared to HIPPO in situ measurements to validate the latitudinal and vertical distribution of the simulations. The K2002 simulation shows little latitudinal variation. Increasing plant uptake leads to a stronger latitudinal gradient in the Northern Hemisphere during growing season and better agreement with HIPPO-OCS. However, the latitudinal distribution of the rescaled fluxes mismatches the HIPPO-OCS measurements in the tropical and northern temperate zone, implying a missing source in that region. The SiB simulation also underestimated the slope in the Northern Hemisphere during growing season. The new anthropogenic emissions improves the comparison with HIPPO, but mismatches remain. Further studies are needed to optimize the OCS sources and sinks. All the simulations captured the vertical structure of HIPPO measurement well, indicating the chemical sink and the vertical transport is in good behavior.
Chapter 6

OCS fluxes estimated from atmospheric measurements

From the forward simulations in Chapter 5, the OCS sources and sinks are evaluated. It indicates that there are large uncertainties remaining in the fluxes. Therefore we need to improve the flux estimation to gain a better distribution and variations before using OCS as photosyntheses tracer. One direct way to do this is to use a process-based approach to calculate the fluxes, which is so called "bottom-up" method. However, there are a lot of unknowns in the OCS productions and removal, such as in the ocean and soil, making it difficult to conduct.

Over the last years, the atmosphere inversion approach has been established to gain information of sources and sinks of greenhouse gases (e.g. CO$_2$ and CH$_4$, Mikaloff Fletcher et al., 2004, Rödenbeck et al., 2003). Because the atmospheric tracer transport is linear, a model of atmospheric transport can be used in an "inverse" mode to estimate the distribution of surface sources and sinks from atmospheric observations (Rödenbeck, 2005). This is the so-called "top-down" modeling. Here we apply the atmosphere inversion for OCS to evaluate its sources and sinks.

6.1 Setup of OCS inversion

TM3 inversion system is used to inverse OCS fluxes. A statistical linear flux model describing OCS is developed for use in the TM3 inversion system base on the version from J. Marshall (personal communication, 2015), following the approach described in Rödenbeck
Chapter 6. OCS flux inversion

(2005). The atmospheric transport is driven by ERA–Interim reanalysis meteorological fields, with a horizontal resolution of approximately $4^\circ \times 5^\circ$ (latitude x longitude) and 26 vertical levels.

The surface flux is separated into four components: land fluxes (combination of plant uptake and soil uptake), ocean fluxes (combination of direct and indirect emissions), anthropogenic emissions (direct and indirect emissions), and biomass burning. The biomass burning is the output from the GEOS-Chem, which is calculated from the CO biomass burning emissions in GFED3 database as described in Chapter 5, and it is not optimized by the inversion. Different land, ocean, and anthropogenic fluxes are used as prior fields in the inversions. The details of these fluxes are summarized in Table 6.1. The chemical sink of OCS is added in the inversion system, which is the same as described in Chapter 5.

For the flask measurements, an uncertainty of 6.3 ppt is assumed based on the pair differences (Montzka et al., 2007). For the FTIR measurements, the uncertainty is chosen to be 3% for all the sites, because the error estimations performed at some of the sites gave similar values of 3%, as described in Chapter 4. The covariance matrix of each adjustable flux term is calculated from the standard deviation of the prior field and a scaling factor which represents the flux uncertainty. The scaling factors are base on the estimations of Kettle et al. (2002a).

6.2 Inversion with only in-situ data

The inversion was first performed with NOAA flask measurement, since these in-situ data are well established. The inversions were run several times with different prior fluxes – land fluxes from K2002 and SiB, and anthropogenic fluxes from K2002 and Campbell et al. (2015) – which are summarized in Table 6.1. Then the forward simulations were run with the prior fluxes and optimized fluxes, respectively.

6.2.1 Inversion with K2002

The comparison between the simulations and measurements are shown in the left column of Figure 6.1. As found in Chapter 5, K2002 fluxes underestimate the seasonal amplitude in the Northern Hemisphere and overestimate the seasonal cycle in the Southern Ocean region. The flux inversion with K2002 fluxes increases the seasonal amplitude all
Figure 6.1: Comparison of inversion with different priors. The left column shows the inversion with K2002 as the prior fluxes; the middle column shows the inversion with SiB as the prior fluxes; the right column shows the inversion with SiB and Campbell et al. (2015) anthropogenic emission as the prior fluxes. The measurements are shown in black dots; the simulations with the prior fluxes are shown in red dots; the simulation with the inversed fluxes are shown in green.
Chapter 6. OCS flux inversion

Continued. Comparison of inversion with different priors.
over the Northern Hemisphere. The simulation with the optimized fluxes matches with the measurements well at Northern high latitudes (ALT, BRW, SUM, and MHD), however, the seasonal amplitude is still smaller than the measurements at Northern mid and low latitude sites (LEF, HFM, THD, NWR, MLO, and KUM). The seasonal amplitude at Southern Hemisphere decreases after inversion, and agree with the measurements better. The comparison between HIPPO and simulations (Figure 6.2) shows that the inversion improves the simulation of OCS in the Southern Hemisphere, however, the mismatches are large in the tropics. The simulation does not reproduce the latitudinal gradient from the Southern Hemisphere to the tropics, especially for HIPPO-3 and HIPPO-4, implying a missing source in the tropics. For the Northern Hemisphere, the inversion results in a better slope during the growing season (HIPPO-5), which agrees with the measurements well. However, the latitudinal pattern in the other season is not reproduced well.

Table 6.1 lists the annual totals of the 3 adjustable terms before and after inversions. The Inversion with K2002 increases all the three fluxes: the land uptake increases to less than 2 times of the prior, which is not as discussed in Chapter 5 – increasing the plant uptake by three results in the best agreement with the measurements; the ocean increases about one and a half; the anthropogenic emission amount is doubled. The distribution of the prior and posterior of the inversion with K2002 are shown in Figure 6.3. The inversion increases the land uptake all over the continent. The ocean emission only becomes larger in the tropics and decreases in the high latitudes in both Hemisphere, in consistent with the discussion in Chapter 5. However both total amounts of the optimized land and ocean fluxes are lower than expected. This may be the reason for the underestimation of the seasonal cycle in the Northern mid latitudes and mean concentration in the tropic region.

The seasonal variations of the land and ocean fluxes before and after inversion are shown in Figure 6.4. Both the amount and seasonal amplitude of the global land uptake increased after inversion. In the Northern Hemisphere, the seasonal amplitude of the land uptake increased more than one time of the prior. In the tropics and Southern Hemisphere, the seasonal variation is small, but the total amount increases. For the ocean fluxes, there is little seasonal variation in the tropics, and the tropical region contributes a large proportion to the global amount, and therefore the ocean variation is small in the global total. The ocean flux variation is opposite in the Northern and Southern Hemisphere, because the ocean emissions vary with temperature. The inversion decreases the seasonal amplitude of the ocean fluxes in both hemisphere. But the decrease in the Northern Hemisphere enlarges the net seasonal cycle, because the ocean has a negative effect on it, while the smaller ocean variation in the Southern Hemisphere, where the ocean is the
main driver of the atmospheric OCS variation, leads to decreased OCS seasonal cycle.

Table 6.1: Annual global atmospheric OCS budget before and after inversions (fluxes in Gg S year⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>K2002</th>
<th>SiB</th>
<th>SiB+Campbell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocean prior</td>
<td>280</td>
<td>870</td>
<td>800</td>
</tr>
<tr>
<td>Ocean posterior</td>
<td>445</td>
<td>898</td>
<td>844</td>
</tr>
<tr>
<td>Land prior</td>
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<td>938</td>
<td>938</td>
</tr>
<tr>
<td>Land posterior</td>
<td>686</td>
<td>930</td>
<td>927</td>
</tr>
<tr>
<td>Anthropogenic prior</td>
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<td>182</td>
<td>256</td>
</tr>
<tr>
<td>Anthropogenic posterior</td>
<td>357</td>
<td>216</td>
<td>267</td>
</tr>
</tbody>
</table>

6.2.2 Inversion with SiB land fluxes

The SiB land fluxes are used in the inversion to substitute those in K2002. The Ocean fluxes are rescaled as the same with that done in Chapter 5 to keep the prior in balance. The simulation with the prior and posterior fluxes are shown in the middle column of Figure 6.1. The simulation with the optimized fluxes agrees with the measurements well. The simulation at Northern high latitudes is similar to that from the inversion with K2002. The simulation at the mid latitudes in the Northern Hemisphere (LEF, HFM, THD) is improved by the SiB inversion compared to the measurements, which is better than the K2002 inversion. There are still some mismatches at NWR, MLO, and KUM – the simulations are lower than the measurements, though it is better than the K2002 inversion. The comparison with HIPPO (middle column of Figure 6.2) shows better agreement than K2002 inversion too. Latitudinal gradient is better captured in both Northern and Southern Hemisphere, especially for the summer campaign (HIPPO-4), the strong slope in represented well because of the increased ocean sources in the prior. The mismatch in the tropics and the Northern temperate region still remains, implying the ocean emission need to be further increased or the other sources are too small.

The total amount of the Ocean source increased a little after the inversion (Table 6.1), and the global distribution is also similar to the prior (Figure 6.5). The land total uptake does not change much after inversion, however, the distribution is different from the prior – the optimized fluxes lead to more uptake in the Northern boreal forest and less uptake in the Northern low latitudes and Southern Hemisphere. This changed distribution results in larger seasonal cycle in the Northern Hemisphere, and agrees better with the measurements.
Figure 6.2: Comparison of inversion with different priors to HIPPO. The left column shows the inversion with K2002 as the prior fluxes; the middle column shows the inversion with SiB as the prior fluxes; the right column shows the inversion with SiB and Campbell et al. (2015) anthropogenic emission as the prior fluxes. The colors are the same as those in Figure 6.1.
Figure 6.3: Comparison of annual mean prior and posterior distributions from inversion with K2002. The left column shows the land fluxes, and the right column shows the ocean fluxes. Notice the different scales of the colorbars. The three rows show the prior fluxes, the posterior fluxes, and the changes by the inversions (the posterior minus prior), respectively.
Figure 6.4: Monthly totals of OCS land (top) and ocean (bottom) fluxes of the priors and posteriors for global, 30° N - 90° N, 30°N - 30° S, and 30° S - 90° S. The K2002 prior is shown in red; the K2002 posterior is shown in green; the SiB prior is magenta; the SiB posterior is blue.

Figure 6.6 shows the differences of the land and ocean posterior global distributions between the K2002 inversion and SiB inversion. The SiB inversion results in more biosphere uptake in Europe and the east of North America, which are the locations of MHD, LEF, and HFM. The stronger uptake in those regions lead to bigger seasonal amplitude at the three sites, more consistent with the measurements. The land uptake in the Northern low latitudes and Southern Hemisphere are smaller from the SiB inversion than those from the K2002 inversion, while the uptake in the tropics are stronger from SiB inversion. These structures come partly from the distribution of the priors, since the measurements are sparse in these regions. The ocean sources are generally larger from SiB inversion, especially in the tropics and Northern Hemisphere.

The SiB inversion does not change the seasonal variation much in the global scale. The global seasonal amplitude is similar to the posterior of K2002 inversion, but the uptake amount is bigger than K2002 optimized land fluxes. In the Northern Hemisphere, the prior land fluxes of SiB and K2002 have a one month time difference between the strongest uptake points. After inversion the SiB posterior flux changes to the shape of the a priori of K2002 land uptake. This will be further discussed in Chapter 7. The seasonal cycles of the land fluxes in the tropics and Southern Hemisphere change a lot after inversion, the
Figure 6.5: Comparison of prior and posterior distributions from inversion with SiB. The left column shows the land fluxes, and the right column shows the ocean fluxes (Notice the different scale of the colorbar from Figure 6.3). The three rows show the prior fluxes, the posterior fluxes, and the changes by the inversions (the posterior minus prior), respectively.
structure of the variation even becomes the opposite of the prior. Similar to the K2002 inversion, the seasonal cycles of ocean fluxes in the tropics and global sum change little by the inversion. The seasonal amplitude of the ocean fluxes in the Northern Hemisphere decreases by the inversion and the phase shifts too. This phase shift leads to less net uptake in the spring, and more net uptake in the late summer, which enlarges the shape change in the total fluxes of OCS. In the Southern Hemisphere, the seasonal amplitude of the ocean fluxes decreases a lot, however, the simulated OCS with the posterior is similar to that with K2002 posterior. This can be explained by the optimized land fluxes in the Hemisphere. The measurement sites in the Southern Hemisphere are most in the coast region, and affected by both land and ocean fluxes. The inversion may not separate the two terms with the information from the measurements, and therefore the land fluxes take part of the variation away from the ocean fluxes.

### 6.2.3 Inversion with Campbell anthropogenic emission

The inversion with Campbell anthropogenic emissions are shown in the right column of Figure 6.1. At most of the sites, the simulation with Campbell inversed fluxes is similar to that with SiB inversion, because the OCS seasonal cycle is mainly driven by land and ocean fluxes. However, at NWR, MLO, and KUM, the simulated OCS concentrations are higher than SiB inversion, and match the measurements better. it indicates that the anthropogenic emissions mainly affect the mean value of OCS in the Northern mid and low latitudes. The inversion with Campbell anthropogenic sources does not improve
the comparison with HIPPO measurements a lot, though better than the SiB inversion. The slight improvement is more come from the prior than the inversion. This is not surprising because there is no NOAA measurement site in the region affected most by the anthropogenic production. The total amount of the anthropogenic production increases little after inversion, and the land and ocean fluxes are not changed much either. The distribution of the land and ocean fluxes from the inversion with Campbell anthropogenic emission are very similar to those from the SiB inversion, since the anthropogenic flux is smaller than the other two fluxes.

Through the several inversions with different priors, one can see that the inversions are affected by the priors a lot. The OCS measurements are much less than the CO$_2$ and CH$_4$, therefore the information we can get from the measurements are less too. In the Northern Hemisphere, where there are more measurements than the rest of the globe, the fluxes are better constrained, especially the land uptake. While in the tropics, the mismatches still remain when comparing with HIPPO measurements, which means that the estimation of fluxes in this region needs to be further improved. To obtain better OCS fluxes maps, more measurements are needed, especially in the Asia, tropics and Southern Hemisphere, where there are still measurement caps.

### 6.3 Inversion with both in-situ and FTIR measurements

As discussed above, the measurement sites of OCS are too sparse to provide enough information to gain proper flux distributions. Through the validation of the inversion using HIPPO measurements, there are mismatches at all latitudes, with most disagreements in the tropics and Northern temperate region. We hope the inversion will be improved with inclusion of more measurements. Here the first try of including FTIR measurements into the OCS inversion is conducted. The inclusion of FTIR measurements will not only increase the number of measurement sites, but also bring in additional information at different layers of the atmosphere. Since we get the best results with SiB land fluxes and Campbell anthropogenic emission as the prior input, the inversion with FTIR sites uses this version of the prior too.

The simulations with prior and posterior fluxes at the flask measurements sites are shown in Figure 6.7. Generally, the simulation with the optimized fluxes from the inversion with FTIR measurements is similar to that from the inversion with only flask measurements. The mean simulated OCS concentrations are lower, especially at Northern high
latitude, such as ALT, BRW, SUM, and MHD. The comparison with FTIR measurements is shown in Figure 6.8. The simulation with optimized fluxes from inversion with flask measurements shows higher value than the measurements at most of the FTIR sites. After inclusion of FTIR measurements into the inversion, the simulated OCS with the posterior of the new inversion decreases toward the measurement values, but still higher than the measurements. Figure 6.9 shows the comparison with HIPPO OCS measurements. The simulation with posterior from FTIR inversion gains lower OCS concentration than the flask only inversion. The differences between these two inversions get bigger from the tropics to the polar regions.

The differences of obtained land and ocean flux distributions between inversion with only flask measurements and inversion with both data sets are shown in Figure 6.10. The land uptake increases in the Northern boreal region and Amazon forest after including FTIR data, while the land fluxes decrease in the rest of the continents. The annual total amount of the land uptake decreases by about 70 Gg S from the prior (Table 6.2). The ocean fluxes from FTIR inversion are smaller than flask only inversion too. The decreased ocean fluxes are mainly in the Northern Hemisphere and some regions in the tropics. Besides of the land and ocean fluxes, the anthropogenic emission gets about 20 Gg S bigger after inversion with FTIR measurements.

Figure 6.11 shows the seasonal variation of the land and ocean fluxes from FTIR inversion. The two inversions result in similar pattern of the land seasonal cycles in both the Northern and Southern Hemisphere. The seasonal shape of the land fluxes in the tropics is similar to the flask only inversed fluxes, but the amount decreases after including FTIR sites. The ocean fluxes from FTIR inversion show smoother seasonal cycles than the flask only inversion, more alike to the prior.

In general, the inclusion of FTIR measurements in the inversion does not improve the model simulation comparison with the measurements, and at some site even worse than the flask only inversion. The most probable reason is that the FTIR retrievals have an offset with the flask measurements. The FTIR measurements can not be compared to the flask measurements directly, because the FTIR measures the total/partial columns while the flasks are collected in the surface. Additionally the a priori and averaging kernels must be taken into account when comparing a remote sensing measurement. However, the offset can be partly assessed through the model simulation. I calculated the differences between the FTIR measurements and the model simulation with optimized fluxes from inversion with flask measurements, which is shown in Figure 6.12. The offsets at each
Figure 6.7: Comparison of flask measurements with inversion with FTIR measurement. The measurements are shown in black; the simulations with prior fluxes are shown in red; the simulation with the optimized fluxes from inversion with only flask measurements are shown in green; the simulation with the optimized fluxes from inversion with both flask and FTIR measurements are shown in blue.
Figure 6.8: Comparison of FTIR measurements with inversion with FTIR measurements. The measurements are shown in black; the simulations with prior fluxes are shown in red; the simulation with the optimized fluxes from inversion with only flask measurements are shown in green; the simulation with the optimized fluxes from inversion with both flask and FTIR measurements are shown in blue.
Figure 6.9: Comparison of inversion with HIPPO measurements. The measurements are shown in black; the simulations with prior fluxes are shown in red; the simulation with the optimized fluxes from inversion with only flask measurements are shown in green; the simulation with the optimized fluxes from inversion with both flask and FTIR measurements are shown in blue.

Figure 6.10: Comparison of optimized fluxes from inversion with and without FTIR measurements. The differences are posteriors from inversion with FTIR measurements minus posteriors from inversion without FTIR measurements.
sites vary from 10 to 30 ppt, which is not consistent. The differences with simulation with FTIR inversed fluxes get smaller, but still different from site to site. Therefore, the FTIR measurements cannot be included directly in the inversion. The OCS retrieval need to be calibrated using independent measurements.

<table>
<thead>
<tr>
<th></th>
<th>Prior</th>
<th>Inversion with flask only</th>
<th>Inversion with FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocean</td>
<td>800</td>
<td>844</td>
<td>773</td>
</tr>
<tr>
<td>Land</td>
<td>938</td>
<td>927</td>
<td>865</td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>256</td>
<td>267</td>
<td>287</td>
</tr>
</tbody>
</table>

Table 6.2: Annual global atmospheric OCS budget from inversions with FTIR measurements (fluxes in Gg S year⁻¹)

Figure 6.11: Monthly totals of OCS land (top) and ocean (bottom) fluxes of the posteriors from inversion with and without FTIR measurements for global, 30° N - 90° N, 30°N - 30° S, and 30° S - 90° S. The prior is shown in red; the posterior from inversion without FTIR measurements is shown in green; the posterior from inversion with FTIR measurements is blue.

6.4 Summary

TM3 inversion system is used in this study to do the OCS flux inversion using atmospheric concentration measurements. The OCS flux inversions were first conducted with only
NOAA flask measurements using different flux fields as prior. Then the inclusion of FTIR data into the inversion was tested.

The inversion with K2002 increases the land uptake, ocean sources, and the anthropogenic emissions. The simulation with the optimized fluxes agrees with the measurements better than that with the original fluxes, but still underestimated the seasonal amplitude at Northern temperate region. The comparison with HIPPO shows big mismatches in the tropics. Replacing the K2002 land fluxes with SiB improves the comparison with the measurements, and reproduces better latitudinal gradient. The inversion with Campbell anthropogenic emission further improves the simulation at Northern mid to low latitude sites, and decreases the differences with HIPPO measurements in that region.

The OCS inversions with different priors result in different distributions of the optimized fluxes. However, the seasonal variations of the fluxes are similar in the Northern Hemisphere. The disagreements between inversions are concentrated in the tropics and the Southern Hemisphere, where the measurements are sparse.

The inversion with both flask and FTIR measurements does not improve the results, because there are offsets between these two data sets. To exploit the full potential use of the FTIR measurements, the errors must be evaluated by independent measurements as discussed in Chapter 4.
Chapter 7

Using OCS to study the biospheric processes of CO₂

In this Chapter, the application of OCS as a photosyntheses tracer is utilized to investigate the carbon cycle. Although there are still uncertainties in the OCS sources and sinks, apart from the land uptake, their effect on the seasonal cycle in the northern high latitudes is small. Therefore we focus on the Northern Hemisphere in the following study. Two parts of work have been done: evaluate the GPP and Respiration estimation in SiB from the mean seasonal cycles of OCS and CO₂; understanding the biosphere responses to climate factors from analyzing the inter-annual variations.

SiB calculates OCS and CO₂ uptake simultaneously. Through using the coupled land fluxes of OCS and CO₂ from SiB, we simulate the atmosphere concentration of OCS and CO₂ with their seasonal cycles connected via the same modeled processes. By looking at the comparison of both species to the measurements, we can evaluate the GPP and Re in the biosphere model.

The carbon processes in the biosphere are sensitive to the environmental factors, especially the climate extremes, and contribute significant uncertainties in the climate models. Therefore it is important to understand the biosphere feedbacks to climate change. The IAV in the atmospheric CO₂ concentrations, which is mainly driven by the biosphere responses to the climate variability, provide a way to quantifying the biosphere feedbacks. However, the analysis of CO₂ alone can only determine the effect of NEP. As mentioned in Chapter 2, the photosynthetic uptake and respiration emission acts independently to different climate drivers. Studies of photosynthesis have identified canopy development
Chapter 7. Using OCS to study the biospheric processes of CO$_2$

and nutrient status, light, temperature, ambient humidity, CO$_2$ concentration, and soil moisture as controlling factors; while respiration is controlled by temperature, soil moisture, nutrient availability, living and dead biomass, ecosystem productivity, and seasonal carbon allocation. Therefore the separation of photosynthesis and respiration is one of the key points for improving the understanding of the biospheric processes.

In 2010, Europe and Russia was stricken by outstanding heatwave. Atmospheric CO$_2$ from the measurements shows weaker drawdown in the growing season. Previous studies (Guerlet et al., 2013, Wunch et al., 2013) have indicated that the biosphere has a large contribution to the IAV. However, how the photosynthesis and respiration responded to the extreme conditions respectively is unclear. In this study, the year 2010 is taken for a case study to investigate the biosphere behavior under extremes with the help of OCS.

7.1 Similarity between OCS and CO$_2$ from retrieved time series

I choose three FTIR sites in the Northern Hemisphere measuring both OCS and CO$_2$ to analyze the relationship of the two gases. The weekly mean of retrieved xCO$_2$ and xOCS timeseries are shown in Figure 7.1. Both CO$_2$ and OCS show clear seasonal variation with a maximum in spring and a minimum in autumn. At the selected stations, OCS reaches its minimum about one month later than CO$_2$. The drawdown of CO$_2$ results from the sum of the photosynthesis uptake and respiration emission. When respiration exceeds photosynthesis, CO$_2$ starts increasing, while OCS is still decreasing due to the contribution of photosynthesis.

The FTIR measurements show a relative seasonal amplitude (relative to the mean value) of OCS of about six times that of CO$_2$, which is similar to the ratio derived from in-situ measurements (Montzka et al., 2007). The different magnitudes of the seasonal amplitudes are attributed to the absence of respiration, and to the leaf-scale relative uptake (LRU) rate of OCS to CO$_2$. Some experiments have shown that plants prefer OCS to CO$_2$, and obtained a LRU in the range of 1.3 - 5.5 for different species (Sandoval-Soto et al., 2005, Seibt et al., 2010, Stimler et al., 2010). If the LRU rate is known, the seasonal cycle of GPP can be determined from the OCS seasonal cycle, and measurements of OCS can be used to quantify GPP.
Chapter 7. Using OCS to study the biospheric processes of CO₂

7.1 Seasonal Amplitudes

The seasonal amplitudes of both CO₂ (approximately 3%) and OCS (approximately 17%) in Ny-Ålesund and Eureka are bigger than those in Bremen (approximately 2 and 12% for CO₂ and OCS, respectively). This is caused by the effect of the boreal forest combined with advective transport. The photosynthesis in the boreal forest is strong during the polar day, leading to the rapid drawdown of both CO₂ and OCS, which can be clearly seen in the measurements at the Arctic sites.

7.2 Implication of GPP in SiB from OCS comparison

The aim is to gain additional information on the CO₂ biospheric fluxes with the help of OCS. Since the CO₂ and OCS uptake by photosynthesis is coupled in SiB, one can calculate the GPP using the OCS uptake amount. This evaluation is complicated, however, because OCS and CO₂ go through the diffusion and consumption steps independently in
SiB. The LRU is a diagnostic quantity that comes out of the simulations following explicit calculation of CO₂ and OCS fluxes. LRU varies by vegetation type, season, and time of day with uncertainties (Berry et al., 2013). However, these fluxes can still be evaluated by combining the comparison of OCS and CO₂ between simulations and measurements.

7.2.1 CO₂ simulation

In this study, two CO₂ runs were performed. The first CO₂ simulation used the original fluxes from GEOS-Chem standard inventory. In the second CO₂ run, we substitute the CASA biospheric fluxes with those calculated by the Simple Biosphere model (SiB; detail in Chapter 3) to connect the OCS and CO₂ in the model simulation, because the OCS and CO₂ land fluxes are coupled in SiB. Global GPP for the years 2000–2012 averages 120 Gt C year⁻¹, in reasonable agreement with flux tower-based estimates (Beer et al., 2010, Jung et al., 2011), although the spatiotemporal distribution of carbon uptake and efflux is uncertain.

The comparison of the CO₂ simulations and FTIR measurements are shown in Figure 7.2. The seasonal amplitude of CO₂ simulation in GEOS-Chem (with CASA NEP fluxes) is too small compared to the measurements. It is indicated by Messerschmidt et al. (2013) that the CO₂ uptake in CASA in the boreal forest region is too weak. After substituting the CASA NEP with SiB NEP in the CO₂ simulation, the seasonality of CO₂ increased and matches the measurements better. This is consistent with the previous studies (e.g. Messerschmidt et al., 2013).

As discussed in Chapter 5, SiB underestimated the OCS drawdown at Northern Hemispheric sites (e.g. Eureka and Ny-Ålesund), and poorly represented the latitudinal gradient in the Northern Hemisphere. This indicates that the photosynthetic production could be underestimated in northern high latitudes. However, the simulation of CO₂ with SiB fluxes represents the seasonal cycles at selected well (Figure 7.2), unlike with the OCS comparison in Chapter 5.

I also compared the CO₂ latitudinal distribution between HIPPO measurements and model simulations (Figure 7.3). The difference in the Southern Hemisphere between CASA and SiB is very small and both agree with the measurements well. The main disagreement between the two simulations and between simulation and measurements is in the boreal region. In spring (HIPPO-3), the SiB simulation is higher than the HIPPO measurements as well as CASA simulation in the Arctic. Previous studies showed that
SiB3 performed well in the forest region of North America (Schwalm et al., 2010), while did a poor job in some Arctic tundra regions, caused by an over-sensitivity to very low temperature (Fisher et al., 2014). While in late autumn (HIPPO-2), SiB gives lower values than both the measurement and CASA simulation in the boreal forest. That means that the rebound of CO$_2$ after growing season in SiB is slower. During the northern growing season (HIPPO-5), the SiB simulation resulted in a stronger drawdown in CO$_2$ concentration and a bigger latitudinal gradient, which matches the measurements better than CASA, inconsistent with the conclusion that the CO$_2$ uptake in the growing season in SiB is larger than that in CASA. The comparison with HIPPO measurements illustrates that the net CO$_2$ fluxes in SiB have a reasonable latitudinal distribution, unlike the OCS simulation with SiB.
7.2.2 Combining CO$_2$ and OCS

The seasonal cycle of OCS is mainly influenced by the plant uptake, which is connected with GPP, while CO$_2$ seasonality results from the sum of both GPP and Re. Huntzinger et al. (2012) have shown that models can get similar NEP with gross fluxes (GPP and Re) that differ by a factor of two or more. If OCS plant uptake is used as a proxy for GPP, one can infer that the GPP estimated in SiB is low in the northern boreal region, which can not be seen in the CO$_2$ simulation driven by NEP. Assuming a reasonable LRU, this means that the Re in SiB must also be low, so that the weak uptake is canceled out in the net flux. However, the LRU is still uncertain. If the LRU is low in general in the Northern Hemisphere, a reasonable GPP estimate could occur together with a small OCS uptake. Therefore the relationship of OCS and CO$_2$ in SiB needs to be further verified, but these results indicate that while the NEP is reasonably modeled, its individual component
Chapter 7. Using OCS to study the biospheric processes of CO$_2$

fluxes might be in error. This inference is made possible through the combination of OCS and CO$_2$ measurements.

Figure 7.4: Comparison of the mean seasonal cycles of FTIR measurements and model simulations at selected sites. The upper panels show the OCS seasonal cycles, and the bottom row shows the CO$_2$ seasonal cycles. The dots are the monthly mean relative xOCS and xCO$_2$ (relative to annual mean) averaged for multiple years. The error bars are the standard deviations of each month. The FTIR retrievals are shown in black dots. The OCS model simulations are driven by K2002 (blue), K2002x3 (green), and SiB (magenta). The CO$_2$ simulations are driven by CASA (blue) and SiB (magenta) land fluxes.

The mean seasonal cycles of the FTIR measurements and model simulations for both OCS and CO$_2$ are shown in Figure 7.4. Although there is no TCCON CO$_2$ measurements at Jungfraujoch, its OCS data are plotted here complimenting the Bremen OCS data, since the retrieval in Jungfraujoch is more certain than Bremen because it is affected less by water vapor, and the two sites are near. From the Figure, the phase differences can be seen between the measurements and the model simulations with SiB land fluxes in both OCS and CO$_2$.

For the OCS comparison, the phase differences are clear at Bremen and Jungfraujoch between the simulations with SiB fluxes and FTIR measurements. Due to the gap during polar winter, these cannot be evaluated at Eureka and Ny-Ålesund. The simulation with SiB shows higher values in the wintertime, which are also seen in the simulations with original and rescaled Kettle’s flux. SiB, however, does not have a mechanism for OCS efflux, so the mean overestimation of OCS concentration in winter is a function of source location/magnitude and/or transport. The simulation with SiB fluxes reaches the minimum earlier than the measurements. If we discard transport errors, this indicates
that there is more OCS uptake (either from plants or soils) in the real world than that calculated in the model in the autumn. The minimum offset is not seen in the simulations with K2002 and K2002x3, and the seasonal variations of plant uptake are similar in SiB and K2002x3 in the Northern Hemisphere (Figure 7.5, left), so the early minimum in SiB may result from the smaller soil uptake in autumn compared to K2002, which is shown in the middle plot of Figure 7.5. As mentioned in Chapter 5, the soil uptake used in this work is smaller than that in Berry et al. (2013). This could mean that the actual soil uptake is stronger or continues longer. However, the temporal and spatial pattern of K2002 fluxes has large uncertainties. The plant uptake is estimated from the NPP base model; the soil uptake is calculated using an empirical algorithm with the parameterization determined for one arable soil type only, which is a likely source of error (Kettle et al., 2002a). Therefore, the early minimum in SiB cannot be attributed to soil uptake through the comparison to K2002. Further investigation is needed to understand the minimum shift.

In the flux inversions we used the sum of the plant and soil uptakes as one term and optimized it accordingly, and therefore the seasonal cycles of the two fluxes cannot be separated in the inversion. However, the two inversions with Kettle and SiB as prior result in similar seasonal cycles of the land fluxes in the Northern Hemisphere, shown in the right plot of Figure 7.5. The Kettle inversion only changes the amount of the land fluxes, while the shape stays the same. In contrast, the inversion with SiB changes the seasonal shape of the land fluxes, which is towards the shape in Kettle fluxes. It confirms that the minimum offset between measurements and SiB simulations is likely due to the weak land uptake in the autumn in SiB.

From the mean seasonal cycles of CO$_2$ (Figure 7.4, bottom panels) the minimums of the seasonal cycles are later in the simulation than those in the measurements, indicating that the rebound of CO$_2$ after growing season is slower. This in already seen from the HIPPO comparison in the campaign in autumn (HIPPO-2). Since the seasonal cycle of CO$_2$ is the combined effect from both photosynthesis and respiration, it is difficult to decide if the photosynthesis is too strong or the respiration is smaller than the actual amount in SiB.

If we look at the phase differences in OCS and CO$_2$ together, the minimum offsets to the measurements for the two species are the opposite. There are several possibilities: (1) If the early minimum of OCS in the SiB simulation compared to the measurements is caused by an early canopy shutdown, CO$_2$ assimilation would also stop early, leading to a
shorter period of CO$_2$ drawdown in the simulation, which is the opposite of what is shown in Figure 7.4. (2) The soil uptake is too small in SiB in the autumn, which is more likely. Because the OCS soil uptake in SiB is proportional to Rh, the respiration could also be too small. This would explain the late minimum in the CO$_2$ simulation. (3) Another possibility is that the LRU becomes very large in the autumn, so the OCS uptake is still strong while CO$_2$ uptake nearly stops. Experiments have shown that the LRU increases under low light condition (Stimler et al., 2010). We do not have sufficient information at this time to determine the most likely reason for SiB to show a shift in the seasonal cycle minimum between the OCS and CO$_2$ simulations and the measurements. However, the combination of OCS and CO$_2$ atmospheric measurements opens some new avenues to explore how the biospheric models reproduce the carbon cycle in the real world.

### 7.3 IAV of CO$_2$ and OCS

#### 7.3.1 Correlation of CO$_2$ and OCS in IAV from the measurements

Since OCS could be used as a photosynthesis tracer, the IAV of OCS should provide the information of the role of photosynthesis. Here the time series of both gases from 2000 to
Chapter 7. Using OCS to study the biospheric processes of CO$_2$

2012 are analyzed using the NOAA curve fitting method (Thoning et al., 1989). A function consisting of a polynomial term and a harmonic part is fitted to the measurements:

$$f(t) = a_0 + a_1 t + a_2 t^2 + ... + a_{(k-1)} t^{(k-1)} + \sum_{1}^{n} c_n (\sin(2\pi t + \varphi_n))$$

(7.1)

where $k$ is the number of polynomial terms, and $n$ is the number of harmonics in the function. Here we chose $k=2$ to represent a linear growth rate for OCS and CO$_2$, and $n=4$ to use four harmonics to fit the mean seasonal cycle.

![Graphs of OCS and CO2](Figure 7.6: IAV of OCS and CO$_2$ from NOAA flask measurements at six Northern Hemispheric sites. The red lines are the variation of CO$_2$, and the blue lines are the variation of OCS. The OCS variations are divided by 7 to get same magnitude with CO$_2$, because the OCS seasonal amplitude is about 6 to 7 times of CO$_2$.)

After the function fitting, the residuals of the data are filtered using a Fast Fourier Transform method to smooth out the short time variations (here the variations in one month are removed) and to define the inter-annual variations.
Chapter 7. Using OCS to study the biospheric processes of CO$_2$

The obtained inter-annual variabilities are shown in Figure 7.6. The OCS variations are divided by 7 to get same magnitude with CO$_2$, because the OCS seasonal amplitude is about 6 to 7 times of CO$_2$. Both OCS and CO$_2$ vary a lot inter-annually, suggesting that the biosphere is sensitive to the environmental factors. From the long time series, there is no clear relationship between the variations of the two species. If only considering the biosphere contributions, it implies that the IAV of CO$_2$ is not only driven by the photosynthesis uptake differences every year – the respiration also plays an important role. The biospheric processes are complex because both photosynthesis and respiration react to some climate factors such as temperature and soil moisture, and therefore these responses can differ under same extreme event but with different levels and various accompanying effects. Therefore the biosphere responses must be investigated for each event respectively. The correlation can be seen if the time series are divided to several parts: 2003 – 2004 and 2009 – 2012 OCS and CO$_2$ show positive correlation; 2005 – 2008 the correlation is negative. In theory, the positive correlation indicates that the photosynthesis dominates in the variations, on the contrary, the respiration has a larger effect on the inter-annual variabilities. In the following study, we take the year 2010 to investigate the roles of the photosynthesis and respiration in the heatwave event.

7.3.2 Case study for 2010 Europe-Russia heatwave

Europe and Russia experienced a warmer summer, with temperature increasing to 4 standard deviations above the reference mean. Figure 7.7 (left column) shows the temperature abnormals from May to September. The temperature in the Arctic region was relatively high in spring (May), and the east of Europe and west of Russia was warmer too, while the west of Europe was still cool. From June, the heatwave moved south, and the area extended to whole Europe as well as the north of Asia. The temperature abnormals further increased in July, and reached more than 5°C in the west of Russia and lasted for two months (July and August). The temperature came back to normal in September, and the heatwave event ended. The soil moisture abnormals are shown in the right column of Figure 7.7. In spring, the soil water is more than usual in the Europe, while the soil in the west of Russia is dryer. When the heatwave enhanced in July, most of the places in Europe and Russia became dryer, where the heatwave affected. Then soil in the Europe was back to normal again, but the Russia continued dry even after the temperature got back to normal.
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Figure 7.7: Monthly climate abnormals in 2010 (relative to the average of 2001 to 2015) from May to September. The left columns are averaged temperatures at 2 m; and the right columns are soil moistures at 0 - 7 cm. The temperature and soil moisture fields are from the ERA-Interim Reanalysis.
Several studies (e.g. Basu et al., 2013, Wunch et al., 2013) have shown smaller seasonal amplitude in atmospheric measurements of CO$_2$ at Northern Hemisphere sites in 2010, for which the heatwave should be responsible. The previous studies suggested three possible reasons for this CO$_2$ anomaly: (1) the atmosphere transport changed in 2010; (2) the biosphere responded to the extreme heatwave, and took up less CO$_2$ than the other years; (3) the heatwave induced more wildfire, which released more CO$_2$. Wunch et al. (2013) tested the contribution of the dynamics with simulating the CO$_2$ concentration with fixed flux fields, but inter-annual meteorological data. It showed that the transport explained approximately 40% of the differences between 2009 and 2010. The biosphere was believed to be the biggest contributor, and accounted for more than 60% of the IAV in 2010. The role of the fire in the CO$_2$ anomaly was not significant from the analysis of CO data (Wunch et al., 2013) and the fire database (Basu et al., 2013). However, this is uncertainty because CO has a short life time, and the fire database is considered to underestimate the fire emissions in the heatwave event.

In this study, we concentrate on the biosphere processes under this extreme condition. As mentioned above, the biosphere was considered to be the largest contributor on the IAV of CO$_2$, however, the individual roles of photosynthesis and respiration can not be separated. Here we analyzed the biosphere fluxes calculated in SiB, and evaluated the behavior of SiB model to the climate extremes. Figure 7.8 shows the monthly differences of NEE between 2009 and 2010 calculated in SiB. It shows less net land fluxes in the south of Europe and the west of Russia in May of 2010, but more NEE in the north of Europe. When the heatwave started to extend in June, the NEE in the Europe continues to be low, while the NEE in Russia increased. In July, the NEE began to increase in some region of Europe, and decreased again from August. Different from Europe, the NEE in Russia continued to increase during the whole heatwave event. The sums of the NEE in the Northern Hemisphere in 2009 and 2010 are shown in the upper left plot of Figure 7.11. The NEE is bigger in 2010 than 2009 from June to September, in other words, the net land uptake is less in 2010 during the heatwave event. The smaller land uptake results in the weaker drawdown in atmospheric CO$_2$ in 2010.

Since NEE is the sum of two much larger fluxes: photosynthesis (GPP) and respiration (Re), the larger NEE could have been resulted from smaller GPP or more Re. The biosphere respiration increases with the temperature ($T$) with the $Q_{10}$ temperature coefficient:

$$Re = R_0 Q_{10}^{(T-208)/10} g(m)$$  \hspace{1cm} (7.2)
Chapter 7. Using OCS to study the biospheric processes of CO$_2$

Figure 7.8: Monthly differences of NEE (Re - GPP, positive means fluxes from land to atmosphere) calculated in SiB between 2009 and 2010 (2010 - 2009) from May to September. The positive value (red) means more net fluxes to the atmosphere in 2010 than 2009.

where $R_0$ is base level of the respiration, and $g(m)$ is the soil moisture term. The photosynthesis increases with the temperature too when there is no stress. However, at extremely high temperature, the photosynthetic production may decrease under water stress. As shown in Figure 7.7, the soil moisture decreased during the heatwave, and therefore the GPP could be decreased in 2010. To further investigate the biosphere responses to the heatwave, the GPP and respiration differences between 2009 and 2010 are plotted separately in Figure 7.9. The GPP in Europe is smaller in spring of 2010 than that in spring of 2009, while the GPP in the west of Russia is bigger in 2010. This is positively correlated with the temperature anomaly. When the heatwave event strengthened in June, the GPP was still increasing, implying that the plants were not under stress. From July, when the temperature reached the peak, the GPP started to decrease from the west of Russia, which experienced the highest temperature and lowest soil moisture.
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Figure 7.9: Monthly differences of GPP (left) and Respiration (right) calculated in SiB between 2009 and 2010 (2010 - 2009) from May to September.
The GPP declined further in August and also in September after the temperature back to normal. It indicates that there is a time lag between the heatwave event and the weakening of the photosynthetic production. The respiration basically increased during the whole extreme event, and the spatial pattern highly correlated with the pattern of the temperature abnormal, which confirmed the relationship in Equation 7.2. The Northern Hemisphere sum of the GPP (Figure 7.11) in 2010 is slightly bigger than 2009 from June to August, and it is similar to 2009 in September. The sum of Re in the Northern Hemisphere is larger in 2010 than 2009 in summer. It indicates that the increased respiration during the heatwave plays more important role for the weaker CO\textsubscript{2} drawdown in the Northern Hemisphere scale.

In SiB the land uptake of CO\textsubscript{2} and OCS is calculated simultaneously, and therefore they are affected by the same environmental conditions, which means the OCS uptake should also be influenced by the heatwave event. As described in Chapter 3, SiB simulates the soil uptake of OCS in relation to Rh, thus the soil uptake increases with temperature in SiB. However, the soil uptake is less than one quarter of the plant uptake, which is unlike the CO\textsubscript{2} respiration. Here we first take the OCS plant and soil uptake as a whole to look at how it changes in this event. The left panel of Figure 7.10 shows the monthly differences of the OCS land uptake between 2009 and 2010. The distribution of the OCS uptake differences is similar to the distribution of GPP differences, because of the relationship between these two fluxes. The Northern Hemisphere monthly totals of the OCS land uptake for 2009 and 2010 are plotted in Figure 7.11 (upper right). It shows that the land uptake of OCS is larger in 2010 than 2009, meaning that the photosynthesis increased during the heatwave event.

In order to check if the SiB well reproduces the biosphere processes under the 2010 heatwave event, the atmospheric concentrations of CO\textsubscript{2} are simulated with SiB biospheric fluxes, and compared to the measurements at several Northern Hemisphere sites affected by the event, which is shown in the left panel of Figure 7.12. Generally, the simulations agree with the measurements well at selected sites. However, the simulation with SiB only reproduces part of the IAV – the simulation at ALT, SUM, and LEF overestimates the seasonal amplitude in 2010. MHD is located in Ireland, which is affected by the heatwave event directly. The simulation at MHD matches the CO\textsubscript{2} seasonal cycle well, indicating that the NEE differences are captured by SiB. The CO\textsubscript{2} measurements at LEF also show strong IAV in these two years, since it is influenced by the heatwave too. The simulation underestimates the IAV at LEF, implying that the net uptake in that region is too big in SiB. Different from MHD and LEF, ALT and SUM are located in
Chapter 7. Using OCS to study the biospheric processes of CO$_2$

Figure 7.10: Monthly differences of OCS land fluxes in SiB between 2009 and 2010 (2010-2009) (left), and those optimized from OCS flux inversion with FTIR and flask measurements (right) from May to September.
Figure 7.11: Differences of the Northern Hemisphere flux seasonal cycles in SiB between 2009 and 2010. The fluxes are summed up from 30°N to 90°N. The upper left shows the CO$_2$ fluxes (GPP, Re, and NEE); the upper right are the OCS land uptakes from SiB; the bottom plots show the optimized OCS land uptakes from the inversion with only flask measurements (bottom left, inversion 1) and from the inversion with both flask and FTIR measurements (bottom right, inversion 2), respectively. The blue lines are the seasonal cycles in 2009, and the red lines are those in 2010.
Figure 7.12: Comparison between measurements and model simulations for 2009 and 2010. The left column is the CO$_2$ simulation with SiB land fluxes; the middle column is the OCS simulation with SiB land uptakes; the right column is the OCS simulation with optimized fluxes from inversion with both flask and FTIR measurements. The measurements are shown in black dots; the simulations with original SiB fluxes are shown in magenta dots; the simulations with optimized fluxes are in green dots.
the remote region, where the measurements represent the fluxes in a larger scale through atmospheric transport. The simulation shows a smaller seasonal amplitude in 2010 at both sites, however, still bigger than the measurements. The comparison indicates that in SiB the biosphere has some reaction during the heatwave, but not strong enough. There are two possibilities: the respiration in SiB increases less than the reality, or the photosynthesis should be reduced more. To test the hypothesis, the simulation of OCS with SiB fluxes is compared to the measurements at the same sites (Figure 7.12 middle column). The OCS simulations are scaled up to match the mean seasonal amplitude of the measurements, because SiB underestimates the land uptake in the Northern High latitude as discussed in Chapter 5 and Chapter 6. The simulation does not agree with the IAV of the measurements – the seasonal amplitude is bigger in the simulation than the measurements. As discussed above, the reduced net uptake of CO$_2$ is more due to the increased respiration according to SiB, and the photosynthesis did not change much through there are decrease in some region. However, the OCS measurements show a weaker drawdown in 2010, implying that the photosynthesis plays more important role than what is shown by SiB.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7_13}
\caption{Gradient against time of OCS and CO$_2$ from NOAA flask measurements. The blue lines are the gradients in 2009; the red lines are the gradients in 2010; the black lines are the zero lines.}
\end{figure}

The gradients of CO$_2$ and OCS are calculated to further investigate the IAV in the measurements. The same filtering method as in the curve fitting is used to smooth out
the short term variations in one month. Then the gradient $g$ against time $t$ is calculated as:

$$g(t) = \frac{\delta C}{\delta t}$$

(7.3)

where $C$ is the atmospheric concentration of CO$_2$ or OCS. The calculated gradients are shown in Figure 7.13. The positive gradients mean the concentrations are increasing, and the negative values stand for the decrease of the concentrations, and the zero crossing points are the concentration turning points, which are peak and bottom value respectively. The minimum values show the biggest net uptake rates. The areas below zero line stand for the total amounts of the net uptake. From the CO$_2$ gradients, we can see that the area in 2010 is smaller than 2009, consistent with the weakened drawdown in 2010. The net CO$_2$ uptake rates in the first half year are similar in 2009 and 2010, but the maximum of the uptake rate, which takes place in July, is smaller in 2010 than that in 2009. Additionally, the gradients reach the second zero points earlier in 2010 than in 2009 at ALT, SUM, and LEF, implying that the respiration took over the photosynthesis early in 2010. This CO$_2$ pattern indicates that the heatwave decreased the net uptake rate during the event, and also shortened the length of the growing season.

The OCS gradient at LEF has more variations than at the other sites, because the LEF measurements are influenced by the local processes. The gradients of OCS show bigger (ALT and MHD) or similar (SUM) uptake rate in spring in 2010 than 2009, and the maximum of the uptake rate in 2010 is even bigger than that in 2009, which means that the photosynthesis increased because of the warmer temperature at the beginning of the heatwave event. The increase of the respiration canceled out the differences in CO$_2$ net uptake. From July the OCS uptake in 2010 became smaller than that in 2009, implying that the photosynthesis decreased under stress and also stopped early. The OCS gradient at SUM shows a different structure – the photosynthesis decreased first in July but recovered again after the event and lasted longer than 2009. Generally speaking, the photosynthesis did contribute to the IAV between these two years, which implies that the impact of the heatwave event to the photosynthesis may be underestimated.

The OCS flux inversion can be used to check how much the photosynthesis are underestimated by SiB. The model simulation with optimized OCS fluxes is compared to the measurements (right column of Figure 7.12). The simulation agrees with the measurements better than the original SiB fluxes, and the IAV is reproduced well too. The differences of the land OCS uptake between 2009 and 2010 from the OCS inversion are shown in the right column of Figure 7.10. The inversion leads to a strong reduction of OCS uptake in 2010, especially in the west of Russia. The uptake decreasing region is
extended by the inversion from June, and the differences between these two years are increased. In addition to Europe and Russia, the OCS uptake in the east of US in 2010 is decreased by the inversion too. The monthly sums of the Northern Hemisphere OCS uptake after inversion are shown in the bottom of Figure 7.11. Both inversions decrease the land uptake of OCS in 2010, opposite to the original SiB fluxes. This supports the hypothesis that the photosynthesis reduction in the heatwave is too weak in SiB, implying that the limitation of the environmental stress may be too loose in SiB.

7.4 Summary

OCS and CO$_2$ retrieved from FTIR spectra at the Northern Hemisphere sites confirmed their similarity in the seasonal cycles. Simulations using coupled SiB land fluxes of CO$_2$ and OCS show good agreement of CO$_2$ with FTIR measurements at Northern Hemisphere sites, but underestimated OCS drawdown. Using OCS as a GPP proxy, the GPP estimation in the Northern Hemisphere could be too low in SiB. However, the relationship between OCS plant uptake and GPP in the model needs to be further verified.

The seasonal cycle minimum offset between simulation and measurements is not consistent for OCS and CO$_2$. The simulation presents an early minimum for OCS but a late minimum for CO$_2$ when compared to the measurements. These phase differences offer another aspect that can be used to evaluate the photosynthesis and respiration in SiB. Several possibilities which could cause this inconsistency have been discussed, but further research is needed before reaching a conclusion.

The correlation of the IAV between OCS and CO$_2$ is not constant because the photosynthesis and respiration react differently for each climate event. The Heatwave in 2010 was studied to separate the responses of photosynthesis and respiration under extreme event. The respiration played more important role in the SiB simulation. However, with the help of OCS, it indicates that the contribution of photosynthesis is underestimated in SiB. Looking at OCS and CO$_2$ together inspires some new thoughts in how the biospheric models reproduce the carbon cycle in the real world.
Chapter 8

Summary and outlook

8.1 Summary

This is the first time that column measurements from FTIR networks are used to study the relationship between OCS and CO$_2$. The objective of my PhD is to test the application of OCS as a photosynthesis tracer, and to exploit the usage of FTIR measurements for this topic. The OCS columns are retrieved from the measured spectra at twelve stations spanning both Northern and Southern Hemisphere. Forward simulations of OCS and CO$_2$ were performed and compared with the measurements, and the current flux estimations were evaluated. Then the OCS flux inversions were conducted to obtain better flux maps from the atmospheric measurements. After the flux evaluation, the use of OCS to study the carbon land cycles were tested.

Two sets of micro-windows were used in the OCS retrievals and resulted in different mean values and seasonal cycles, especially at the sites with high atmospheric water vapor content. It indicates that the water absorption lines have large impact on the OCS retrievals. The micro-window affected by the water vapor most is rejected in the retrievals to minimize the influence by water, however, the OCS retrievals need to be calibrated with independent measurements to evaluate the OCS latitudinal distribution and seasonal cycles.

The comparisons between OCS measurements and forwards simulations driven by various fluxes show that the land uptake, ocean sources, and the anthropogenic emissions are all underestimated in the Kettle inventory. Upscaling the plant uptake by three and
ocean sources in the tropics in K2002 results in better agreement with the measurements. Simulation with SiB OCS land fluxes underestimated the seasonal amplitude in the high latitudes of Northern Hemisphere, indicating that the latitudinal flux distributions in SiB need to be adjusted.

The OCS flux inversions were performed with different prior fields. The inversion with SiB land fluxes and Campbell et al. (2015) anthropogenic emissions leads to the best agreement with the measurements. The SiB land fluxes are increased in the Northern boreal region and decreased in most of the rest regions by the inversion, while the total amount is not changed much. The validation with HIPPO measurements shows mismatches in the tropics as well as Northern temperate region, where the measurements are too sparse to constrain the fluxes. Inclusion of FTIR measurements does not improve the inversion, because there is an offset between these two data sets, which makes it not straightforward.

Although there are uncertainties in the OCS fluxes in some regions, the Northern Hemisphere fluxes are well constrained and the OCS seasonal cycle is affected little by ocean fluxes in the tropics. The CO$_2$ biosphere fluxes in SiB were evaluated in the Northern Hemisphere with the help of OCS on two aspects. The comparison of the mean seasonal cycles of OCS and CO$_2$ suggests that the GPP is underestimated in the boreal region. The phase differences of the two gases imply several possibilities, which are inferred from the combination with OCS. The OCS was also used to study the contributions of photosynthesis and respiration on the IAV of atmospheric CO$_2$. The heatwave event in 2010 was taken for a case study. The analysis of OCS indicates that the photosynthesis decreased during the heatwave, which is underestimated in SiB.

8.2 Outlook

The FTIR OCS retrievals need to be calibrated using independent measurements to make them comparable with in-situ measurements. After that, the FTIR column data can be included into the flux inversion again. Besides of the variations in the troposphere, OCS profiles also vary a lot at the tropopause and the lower stratosphere resulting from both chemical reactions and the transport. The calibration of OCS needs to be done with profile measurements up to the tropopause. The AirCore profile measurement is considered in the next plans.
The OCS inversions indicate that the OCS measurements included in this study are not dense enough to constrain the flux distribution. More FTIR sites will be added in the future. Additionally, the satellite OCS data (such as ACE (Barkley et al., 2008) and TES (Kuai et al., 2015)) can be included to constraint the ocean fluxes in the tropics, where the ground based sites are sparse.

The relationship between OCS and CO$_2$ uptake in SiB can be further verified by field measurements for more plant types and at different times. This will increase the confidence for making conclusions on GPP distribution and time variation from the view of OCS.

Based on the relationship between OCS and CO$_2$ assessed using SiB, OCS measurements will be added into the CO$_2$ inversion to provide an extra constraint on GPP, allowing estimation of the separate GPP and Re fluxes.
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</tbody>
</table>
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>CA</td>
<td>Carbonic Anhydrase</td>
</tr>
<tr>
<td>CASA</td>
<td>Carnegie-Ames-Stanford Approach</td>
</tr>
<tr>
<td>CDIAC</td>
<td>Carbon Dioxide Information Analysis Center</td>
</tr>
<tr>
<td>CFC</td>
<td>Chlorofluorocarbon</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>CO₃⁻</td>
<td>Carbonate</td>
</tr>
<tr>
<td>CS₂</td>
<td>Carbon Disulfide</td>
</tr>
<tr>
<td>DMF</td>
<td>Dry-Air Mole Fractoins</td>
</tr>
<tr>
<td>DMS</td>
<td>Dimethyl Sulfide</td>
</tr>
<tr>
<td>DOF</td>
<td>Degree of Freedom</td>
</tr>
<tr>
<td>ERU</td>
<td>Ecosystem Relative Uptake</td>
</tr>
<tr>
<td>ESRL/GMD</td>
<td>Earth System Research laboratory/Global Monitoring Division (NOAA)</td>
</tr>
<tr>
<td>fPAR</td>
<td>Fractional Photosynthetically Active Radiation</td>
</tr>
<tr>
<td>FTIR</td>
<td>Solar Absorption Fourier Transform InfraRed</td>
</tr>
<tr>
<td>GEOS</td>
<td>Goddard Earth Observing System</td>
</tr>
<tr>
<td>GFED</td>
<td>Global Fire Emission Database</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse Gase</td>
</tr>
<tr>
<td>GMAO</td>
<td>Global Modeling Assimilation Office (NASA)</td>
</tr>
<tr>
<td>GPCP</td>
<td>Global Precipitation Climatology Project</td>
</tr>
<tr>
<td>GPP</td>
<td>Gross Primary Production</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen Atoms</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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</tr>
<tr>
<td>H⁺</td>
<td>Hydrogen Ion</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water Vapor</td>
</tr>
<tr>
<td>H₂S</td>
<td>Hydrogen Sulfide</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>Bicarbonate</td>
</tr>
<tr>
<td>HATS</td>
<td>Halocarbons and Other Atmospheric Trace Species</td>
</tr>
<tr>
<td>HIAPER</td>
<td>High-Performance Instrumented Airborne Platform for environmental research</td>
</tr>
<tr>
<td>HIPPO</td>
<td>HIAPER Pole-to-Pole Observations</td>
</tr>
<tr>
<td>HITRAN</td>
<td>High Resolution Transmission</td>
</tr>
<tr>
<td>IAV</td>
<td>Inter-Annual variation</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>KPP</td>
<td>K-Profile Parameterization</td>
</tr>
<tr>
<td>LAI</td>
<td>Leaf Area Index</td>
</tr>
<tr>
<td>LRU</td>
<td>Leaf-Scale Relative Uptake</td>
</tr>
<tr>
<td>LULCC</td>
<td>Land Use and Land Cover Change</td>
</tr>
<tr>
<td>LWR</td>
<td>Longwave Radiation</td>
</tr>
<tr>
<td>MERRA</td>
<td>Modern-Era Retrospective Analysis for Research and Application</td>
</tr>
<tr>
<td>MIR</td>
<td>Mid-Infrared</td>
</tr>
<tr>
<td>MW</td>
<td>Micro-Window</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration (U.S.)</td>
</tr>
<tr>
<td>NCEP</td>
<td>National Centers for Environmental Prediction (U.S.)</td>
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<tr>
<td>NDACC-IRWG</td>
<td>Network for the Detection of Atmospheric Composition Change -InfraRed Working Group</td>
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<tr>
<td>NEE</td>
<td>Net Ecosystem Exchange</td>
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<tr>
<td>NEP</td>
<td>Net Ecosystem Production</td>
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<tr>
<td>NIR</td>
<td>Near-Infrared</td>
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<tr>
<td>N₂O</td>
<td>Nitrous Oxide</td>
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<tr>
<td>NOx</td>
<td>Nitrogen Oxide</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration (U.S.)</td>
</tr>
</tbody>
</table>
Abbreviations

NPP  Net Primary Production
NWAS-M2  NOAA Whole Air Sampler-Montzka Mass Spectrometer #2
NWAS-MAGICC  NOAA Whole Air Sampler-Measurement of Atmospheric Gases that Influence Climate Change
O  Oxygen Atoms
O₂  Oxygen
O₃  Ozone
OCS  Carbonyl Sulfide
OH  Hydroxyl Radical
OEM  Optimal Estimation Method
OLR  Outgoing Longwave Radiation
OPD  Optical Path Difference
Ra  Autotrophic Respiration
Re  Ecosystem Respiration
RF  Radiative Forcing
Rh  Heterotrophic Respiration
RMS  Root Mean Square
S  Sulfide Atoms
SO  Sulfer Monoxide
SO₂  Sulfer Dioxide
SiB  Simple Biosphere Model
SMVGEAR  Spares-Matrix Vectorized Gear Code
SNR  Signal to Noise Ratio
SWR  Shortwave Radiation
T  Temperature
TCCON  Total Carbon Column Observing Network
UCX  Universal Tropospheric-Stratospheric chemistry Extension
UTC  Coordinated Universal Time
UV  Ultraviolet
xCO₂  CO₂ Column-Averaged Dry-Air Mole Fractions
xOCS  OCS Column-Averaged Dry-Air Mole Fractions