Towards understanding the variability in biospheric CO_2 fluxes: using FTIR spectrometry and a chemical transport model to investigate the sources and sinks of carbonyl sulfide and its link to CO_2

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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 investigate co-located and quasi-simultaneous FTIR measurements of OCS and CO_2 performed at five selected sites located in the Northern Hemisphere. These measurements are compared to simulations of OCS and CO_2 using a chemical transport model (GEOS-Chem). The OCS simulations are driven by different land biospheric 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 FTIR measurements. However, there are still discrepancies in the latitudinal distribution when comparing with HIPPO (HIAPER Pole-to-Pole Observations) data spanning both hemispheres. The coupled biospheric fluxes of OCS and CO_2 from the simple biosphere model (SiB) are used in the study. The CO_2 simulation with SiB fluxes agrees with the measurements well, while the OCS simulation reproduced a weaker drawdown than FTIR measurements at selected sites, and a smaller latitudinal gradient in the Northern Hemisphere during growing season. An offset in the timing of the seasonal cycle minimum between SiB simulation and measurements is also seen. 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.

1. Introduction

Understanding the carbon dioxide (CO_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_2 emissions released by human activities, which mitigates the increase of atmospheric CO_2 concentration; and (2) terrestrial exchange drives CO_2 variability in the atmosphere on seasonal and inter-annual time scales. The total biospheric CO_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_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_2 during photosynthesis. Unlike CO_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_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_2 (Montzka et al., 2007) as biospheric fluxes are the main driver of the seasonal cycles for both species (Kettle et al., 2002a).

However, our knowledge about the sources and sinks of OCS remains limited. The estimates for the global budget still have significant uncertainties. This makes it difficult to use OCS as a photosynthetic tracer. The 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. 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). Plant uptake is commonly recognized as the main sink of OCS, and is the dominant driver of seasonal variation in the Northern Hemisphere (Goldan et al., 1988). Kettle et al. (2002a) analyzed OCS monthly fluxes, and then calculated the global annual sources and sinks, which are in balance within uncertainties. More recent studies (Suntharalingam et al., 2008; Berry et al., 2013) indicated that the plant uptake in Kettle's estimation is too small, and therefore a corresponding increase in sources is necessary to maintain the annual balance in the OCS budget. New studies have also shown that the ocean and anthropogenic sources of OCS have been underestimated (Guo et al., 2010; Berry et al., 2013; Campbell et al., 2015; Cheng et al., 2015; Launois et al., 2015a) in Kettle et al. (2002a). The disagreement between measurements and simulations of OCS indicated that the missing sources are mainly in the tropical region (Berry et al. 2013). Anthropogenic emissions are unlikely to be the main reason for missing sources in that region,

and therefore ocean sources are likely to be responsible. Indeed, 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. 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 $year^{-1}$. In addition, OCS soil uptake still has large uncertainties. Some soil types act as a source (Whelan et al., 2013) or only a small sink (Xu et al., 2002; Steinbacher et al., 2004); however, the overall role of soils is as a sink of OCS, with very different uptake rates between soil types and other physical parameters (Van Diest and Kesselmeier, 2008; Sun et al., 2015). 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; H. Chen, private communication). This estimation yields a sink of about 500 Gg S $year^{-1}$, largely dependent on the H_2 spatial distribution (Launois et al., 2015b). Therefore, improving the estimation of the OCS sources and sinks is important when using it to investigate the biospheric fluxes of CO_2. To achieve this aim, more OCS measurements at different latitudes and ecosystem regions are needed to validate the estimates.

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 emerging of the remote sensing data, including ground-based (Notholt et al., 2003) and satellite (Barkley et al., 2008; Kuai et al., 2014; Kuai et al., 2015; Glatthor et al., 2015) measurements, will potentially increase the number of OCS measurements largely. The satellite data provide a wide distribution of OCS; however, they are mainly sensitive in the upper troposphere and stratosphere (Barkley et al., 2008; Glatthor et al., 2015) or mid troposphere (Kuai et al., 2014), and therefore have 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. This can be used to retrieve the total and/or partial atmospheric columns of these two gases. Compared to satellite retrievals, ground-based FTIR OCS retrievals are also sensitive to low altitude and can therefore more directly capture the variations due to the biospheric processes.

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), 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 using dedicated software packages. 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 TCCON CO_2 product in this study. The NDACC-IRWG sites provide a potential database of OCS, that could be used to assess its sources and sinks. Kettle et al. (2002b) used FTIR OCS total column measurements to estimate hemisphere-integrated OCS flux and confirmed their understanding of OCS global budget. However, the measurements could not put constraints on the relative magnitude of vegetative uptake and ocean-related emissions. B. Lejeune (private communication) 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. Additionally, some sites measure in both NIR and MIR spectral regions, and therefore provide co-located and quasi-simultaneous CO_2 and OCS measurements.

The aim of this work is to exploit ground-based FTIR measurements of OCS to evaluate its sources and sinks, and further to use OCS as a tracer of photosynthesis. This is the first time using total/partial column data from FTIR networks to study the relationship between OCS and CO_2. 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 (Wunch et al., 2011; Yang et al., 2007; Keppel-Aleks et al., 2011). Therefore, column measurements of OCS and CO_2 could provide additional information for evaluating their terrestrial exchange.

In section 2, 3, and 4, we will describe the measurements, models, and inter-comparison between FTIR and model, respectively. In sections 5, we first analyze the FTIR measurements of OCS and

CO_2 at selected sites. Then we compare OCS measurements to model simulations to evaluate the sources and sinks of OCS. Finally, we will discuss what can be learnt about CO_2 biospheric fluxes from OCS. The publication closes with the conclusion and outlook.

2. Measurements

2.1 FTIR

Five measurement sites are used in this study as a starting point for the research aim of using OCS to differentiate between photosynthetic and respiration fluxes of CO_2 (see details in Table 1). Ny-Ålesund and Bremen, which are operated by the University of Bremen, and Eureka, operated by the Canadian Network for the Detection of Atmospheric Change (CANDAC) and the University of Toronto, measure both OCS and CO_2. The Jungfraujoch and Mauna Loa, operated by the University of Liège and National Center for Atmospheric Research, respectively, only measure in the MIR spectral region, and therefore TCCON-type CO_2 data are not available.

OCS profiles and total columns were retrieved using the SFIT-4 algorithm, based on the optimal estimation technique (Rodgers, 2000). A mixed spectroscopy based on the HITRAN 2012 database was used in the retrievals. The a priori profile of OCS was provided by G. Toon (private communication), and modified according to the average tropopause height above each site (constant in the troposphere, and decrease above tropopause). Four spectral micro-windows were used in the fitting (B. Lejeune, private communication), containing the OCS $\nu 3$ band P32, P28, P25, and P18 lines, respectively. 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 2.

To minimize the influence of the variations in stratosphere, the tropospheric partial columns were calculated from the surface to 9.8 km, based on the structure of the averaging kernels. In total, approximately 2.5 degrees of freedom for signal (DOFS) for total columns were obtained for all three sites. The DOFS for 0 to 9.8km is about 1. To make the values comparable to the in situ measurements, the tropospheric OCS column-averaged dry-air mole fractions (xOCS) were derived using Eq. (1):

$$\text{xOCS} = \text{Tropospheric OCS partial column} / \text{Tropospheric dry} - \text{air partial column} \quad (1)$$

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

$$S_{\text{total\_tropo}} = \left(\sum_1^n (S_m(i)^2 + S_f(i)^2 + S_{int}(i)^2) \right)^{1/2} \quad (2)$$

The average uncertainties in the tropospheric partial columns from 2005 to 2012 are about 3% for all the sites.

The OCS retrievals from the FTIR spectra are not calibrated to account for biases due to the spectroscopy and other factors, therefore the means of the FTIR and in-situ measurements have an offset.

We use the GGG2012 version of the TCCON CO_2 data, available on http://tccon.ornl.gov/2012. 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:

$$xCO_2 = CO_2 \ / \ O_2 \times 0.2095 \quad (3)$$

2.2 HIPPO

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 (referred to as HIPPO-OCS) used in the work were measured by the NOAA "Whole Air Sampler-Montzka Mass Spectrometer #2" (NWAS-M2), while CO_2 concentrations (referred to as HIPPO-CO_2) were measured by the NOAA "Whole Air Sampler-Measurement of Atmospheric Gases that Influence Climate Change"

(NWAS-MAGICC).

3. Model simulations

3.1 GEOS-Chem and CO_2 simulation

The GEOS–Chem chemical transport model (version v9-01-03) is used in this study to simulate the concentrations of CO_2 and 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). The simulations were run using GEOS-5 meteorology from 2004 to 2012 on a horizontal grid resolution of 2 by 2.5 degrees (latitude by longitude), with 47 vertical levels. Taking 2004 as one year spin-up, we analyze the results from 2005 to 2012 based on hourly model output.

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 inter-annual 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). In this study, we substitute the CASA biospheric fluxes with those calculated by the Simple Biosphere model (SiB; detail in section 3.3).

3.2 OCS simulation

The OCS module is developed from the version of Suntharalingam et al. (2008), and added to GEOS-Chem v9-01-03. It is largely based on the gridded flux inventories of Kettle et al. (2002a), hereafter referred to as K2002. The input fluxes from K2002 include ocean emissions, anthropogenic emissions, plant uptake, and soil uptake. The OCS biomass burning emission is calculated from CO emissions (from GFED3) using a scale factor from Nguyen et al. (1995). The

tropospheric OH oxidation of OCS is calculated from OH monthly data (Park et al., 2004) and a temperature dependent rate (Atkinson et al., 1997). In addition, we included stratospheric loss (total loss from reaction with OH, O, and photolysis) in the OCS simulation to avoid the OCS accumulation above the troposphere. This stratospheric loss is computed using the altitude dependent loss rate from Chin and Davis (1995). The OCS simulation with K2002 provides a baseline for evaluating the sources and sinks of OCS.

3.3 The Simple Biosphere model (SiB)

To study the relationship between OCS and CO_2, we used the coupled fluxes from SiB. 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 (GCMs; Sato et al., 1989; Randall et al., 1996) as well as mesoscale models (Denning et al., 2003; Nicholls et al., 2004; Wang et al., 2007; Corbin et al., 2008). 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 by 1.25 degree (latitude by longitude) grid, with meteorology provided by the Modern-Era Retrospective analysis for Research and Applications (MERRA; Reinecker 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 (LAI, fPAR) is determined prognostically following Stöckli et al. (2008; 2011). 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.

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 diffusion pathway of OCS is the same as that of CO_2, but with different 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_{max} of Rubisco by some studies (Berry et al., 2013; Badger and Price, 1994; 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(θ) (Equation 4, 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.

In this work, all the simulations were run using GEOS-Chem transport model. Two OCS land fluxes were used, K2002 and SiB, in the OCS simulations, summarized in Table 3. In the analysis, the simulations with different fluxes will be referred to as the fluxes names, as shown in Table 3.

4 Comparison between FTIR retrievals and model

When comparing FTIR data with model simulations, the a priori and vertical sensitivity of the retrievals must be considered. We use the method described by Rodgers and Connor (2003). 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 following the equation.

$$X_s = X_a + A(X_m - X_a) \quad (4)$$

where X_s, X_a and X_m are smoothed, a priori and model vertical profile, respectively, and A is the

averaging kernel matrix. The tropospheric xOCS was then calculated using Eq. (1).

For CO_2 column retrievals, Eq. (4) is modified (Wunch et al., 2010) to yield:

$$C_s = C_a + h^T \times a^T \times (X_m - X_a) \quad (5)$$

where C_s and C_a are smoothed and a priori CO_2 column-averaged DMF, h describes the vertical summation, 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 five degree solar zenith angle intervals. The averaging kernels used here are interpolated to the solar zenith angle at the time the measurement was made.

5 Results

5.1 The relationship between OCS and CO_2 in FTIR measurements

Weekly mean calculated xCO_2 and xOCS are shown in Figure 1. Both CO_2 and OCS show clear seasonal variation with a maximum in late winter or early spring and a minimum in autumn. At Eureka, Ny-Ålesund and Bremen, 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 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 laboratory and field 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; Xu et al., 2002). 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.

The seasonal amplitudes of both CO_2 (approximately 3%) and OCS (approximately 18%) in Ny-Ålesund and Eureka are bigger than those in Bremen (approximately 2% and 13% for CO_2 and OCS, respectively), Jungfraujoch (approximately 10% for OCS) and Mauna Loa (approximately

9% for OCS). 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 CO_2 and OCS, which can be clearly seen in the measurements at the Arctic sites. For Jungfraujoch, the seasonal amplitude is smaller than that in Bremen, which partly results from its high altitude, so that the variation in the lower atmosphere is not captured. Eliminating altitudes below 3.5km (the altitude of Jungfraujoch) from the calculation of xOCS at Ny-Ålesund and Bremen decreases their seasonal cycle amplitude by approximately 10%.

5.2 OCS sources and sinks implied from FTIR measurements and model comparisons

5.2.1 Initial simulation of OCS

Prior to using the model relationship between OCS and CO_2, we assess the accuracy of the OCS fluxes, starting with fluxes of K2002, referred to as the initial simulation.

The simulations of OCS with K2002 are shown as orange plus signs in Figure 2. The initial simulation (K2002) underestimates the seasonal amplitude, as reported by previous studies (Suntharalingam et al., 2008; Berry et al., 2013). 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 Net Primary Production (NPP) 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,

$$OCS\ uptake = NPP \times [OCS]/[CO_2] \quad (6)$$

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 has been suggested to replace the NPP-based model (Sandoval-Soto et al., 2005):

$$OCS\ uptake = GPP \times [OCS]/[CO_2] \times LRU \quad (7)$$

GPP is about two times as large as NPP, and the global averaged LRU is in the range of 1.3 – 3.1 (Seibt et al., 2010; Stimler et al., 2012; Berkelhammer et al., 2014), 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.

Additionally, the simulation underestimates the mean OCS value at 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.

5.2.2 Simulations with rescaled K2002 fluxes

In order to improve the OCS simulation, we rescaled the OCS fluxes to find a better match to the measurements. This scaling, while not optimal, provides an idea of the sensitivity of the simulation to these processes. Following Suntharalingam et al. (2008) we modified the K2002 fluxes by increasing the plant uptake by factors of two (K2002x2, Figure 2. blue asterisks) and three (K2002x3, Figure 2. green stars). 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). This will be further discussed in section 5.2.3. The details of the rescaled OCS sources and sinks are shown in Table 3.

The simulations with rescaled fluxes increased the seasonal cycle amplitudes, and decreased the peak and mean values at the high latitude sites. The seasonal amplitude of the simulation with K2002x2 matches the measurements better than the original Kettle fluxes. K2002x3 further increases the seasonal cycle amplitude. There is no inter-annual variability in the fluxes, so these simulations cannot reproduce the yearly varying seasonal amplitudes. However, from the averaged seasonal cycles (Figure 2, right panels), the simulations with K2002x3 match the measurements better than K2002x2.

Mauna Loa is more affected by ocean fluxes than the other high latitude sites, indeed, on average, the simulated OCS amounts at Mauna Loa did not change with the rescaling of the fluxes. This is in contrast to the other sites, where the influence of the land sink dominates; at Mauna Loa, the increased tropical ocean sources negate the effect of the increased land sink. The simulated seasonal cycles show a peak in summer, which mainly results from the seasonality of the ocean fluxes. This is different from the measurements: the maximum measured OCS abundance occurs in spring, suggesting that the temporal variation of the ocean sources also needs to be adjusted.

5.2.3 HIPPO latitudinal distribution

To evaluate the latitudinal distribution of the rescaled fluxes, we compared the model simulations with HIPPO-OCS (Figure 3). To facilitate this comparison, the model mean was adjusted (by

adding an offset of 30 ppt) to match the mean of the HIPPO measurements. 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. In the Southern Hemisphere, the K2002x3 simulation has a higher value than K2002x2, caused by the larger ocean emissions in the tropics. There are still mismatches, especially 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 Mauna Loa comparison between simulations and measurements. Increasing the ocean emissions in the Northern Hemisphere by a factor of two (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 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 (Weiss et al., 1995; Xu et al., 2001; Berry et al., 2013; Launois et al., 2015a) 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 all simulations except K2002, a value of 0.5 was applied for the Southern Ocean (30° S - 90° S), while in the tropics (30° N - 30° S), values of 3.2, 5.1, and 5.2 were used for K2002x2, 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, and gain better distribution. The global amount and general latitudinal distribution are consistent with this study.

The latitudinal gradient in the boreal region is more sensitive to plant uptake. Increasing 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 selected stations are lower than the FTIR measurements.

5.3 Combination of OCS and CO_2 with SiB biospheric fluxes

Although there are still uncertainties in the OCS sources and sinks, apart from land uptake and ocean emissions, their effect on the seasonal cycle in the northern high latitudes is small. Since we only increased the tropical ocean emissions, the ocean effect on the seasonal cycle in the northern high latitudes is smaller than that from land sinks. We used the coupled land fluxes of OCS and CO_2 from SiB to simultaneously simulate OCS and CO_2 with their seasonal cycles connected via the same modeled processes. Through the comparison of both species to the measurements, we can evaluate the GPP and Re in the biosphere model.

5.3.1 OCS simulation with SiB land fluxes

The OCS simulation results with SiB fluxes are shown as magenta triangles in Figure 2. The mean values at the four high/mid latitude sites are higher than those with the original or rescaled K2002 fluxes, especially at Eureka and Ny-Ålesund. The seasonal amplitudes at Eureka, Ny-Ålesund and Bremen are similar to those simulated with K2002x2; and the seasonal amplitude at Jungfraujoch is between those of K2002x2 and K2002x3. From Table 3, shows that the plant uptake of SiB is about three times 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. 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.

We compared the difference between SiB and the scaled K2002 plant uptake and soil uptake in July, shown in Figure 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 (top) shows the monthly plant uptake of different fluxes summed 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 similar to K2002x2. 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 Eureka and Ny-Ålesund. The seasonal amplitude is better represented by SiB at the mid latitude site of Jungfraujoch.

Besides the seasonal amplitude, there are phase differences at Bremen and Jungfraujoch between the simulations with SiB fluxes and 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 by necessity a function of source location/magnitude and/or transport. The simulation with SiB fluxes reaches the minimum earlier than the measurements. If we discount 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 K2002x2 and K2002x3, and the seasonal variations of plant uptake are similar in SiB and K2002x2 in the Northern Hemisphere (Figure 5, top), so the early minimum in SiB may result from the smaller soil uptake in autumn compared to K2002, which is shown in Figure 5 (bottom). As mentioned in section 3.3, 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 is with 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.

The comparison between the SiB simulation and HIPPO-OCS measurements is shown in magenta lines in Figure 3. The simulation with SiB fluxes results in a lower value in the Southern Hemisphere than the rescaled Kettle fluxes. This matches the HIPPO-OCS better, because SiB has a stronger plant uptake in the tropics and Southern Hemisphere. For the Northern Hemisphere, the low OCS concentrations in the low 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 the plant uptake of OCS in SiB in the boreal forest is too small, at least for the year (2011) in question.

5.3.2 Implications for CO_2 fluxes in SiB from OCS comparison

We hope to gain additional information on the CO_2 biospheric fluxes with the help of OCS. Since the CO_2 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 CO_2 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 CO_2 and OCS fluxes. LRU varies by vegetation type, season, and time of day with uncertainties. However, these fluxes can still be evaluated by combining the comparison of OCS and CO_2 between simulations and measurements.

As discussed in section 5.3.1, SiB underestimated the OCS drawdown at Eureka and Ny-Ålesund, and poorly represented the latitudinal gradient in the Northern Hemisphere. This indicates that the photosynthetic uptake could be underestimated in northern high latitudes. We examine this further by comparing the CO_2 simulations with measurements.

The simulation of CO_2 with SiB fluxes represents the seasonal cycles at all the three sites well (Figure 6, left panels), unlike with the OCS comparison. From the mean seasonal cycles (Figure 6, right panels) the minima in the CO_2 seasonal cycles are later in the simulation than measurements, indicating that the increase of CO_2 after the growing season is slower in the model. We also compared the CO_2 latitudinal distribution between HIPPO-CO_2 and model simulations (Figure 7). The difference in the Southern Hemisphere between the HIPPO-CO_2 and model is very small, so the main disagreement is in the northern high latitudes. In late autumn (HIPPO-2), SiB gives lower values than the HIPPO data in the boreal region. This supports the late minimum in comparison to the FTIR measurements. In spring (HIPPO-3), the simulation is higher than the HIPPO measurements 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). During the northern growing season, the SiB simulation of CO_2 resulted in a strong latitudinal gradient, which matches the HIPPO measurements well (HIPPO-5), illustrating that the net CO_2 fluxes

have a reasonable latitudinal distribution, unlike with the OCS simulation.

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 and the LRU is reasonable, one can infer that the GPP estimated in SiB is low in the northern boreal region, which cannot be seen in the CO_2 simulation driven by NEP, meaning that the Re in SiB must also be low, so that the weak uptake is cancelled out in the net flux. However, the LRU is still uncertain. If 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. However, these results indicate that while the NEP is reasonably modeled, its individual component fluxes might be in error. This inference is made possible through the combination of OCS and CO_2 measurements.

The early minimum in SiB simulation of OCS compared to the measurements is indicative of weak uptake in the autumn. If this is caused by an weak OCS plant uptake, CO_2 assimilation would also be small, leading to a shorter period of CO_2 drawdown in the simulation, which is the opposite of what is shown in Figure 6. Therefore, it is more likely that OCS soil uptake is too small in SiB in the autumn. 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. Another possibility is that the LRU becomes very large in the autumn, so the OCS uptake is still strong while CO_2 decreases to a very small value. 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 simulation 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.

6 Conclusions

For the first time, FTIR measurements of OCS and CO_2 were used to study their relationship. OCS retrieved from FTIR spectra at the five sites showed clear seasonal cycles, and confirmed

the similarity to CO_2 variations.

We compared the OCS column measurements to simulations with original and rescaled versions of fluxes based on Kettle et al. (2002a). The results indicate that increasing the plant uptake and ocean emissions improves the comparison. For the five selected sites in the Northern Hemisphere, increasing plant uptake by a factor of three represented the OCS seasonality well. The OCS simulations were also compared to HIPPO in-situ measurements. 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. Further studies are needed to optimize the OCS sources and sinks.

Simulations using coupled SiB land fluxes of CO_2 and OCS show good agreement of CO_2 with FTIR measurements at selected sites, but underestimated OCS drawdown. Through the comparison with HIPPO-OCS measurements, a weaker gradient in the Northern Hemisphere during growing season can be seen in the simulation. Using OCS as a GPP proxy, the GPP estimation in the Northern Hemisphere could be 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. Looking at OCS and CO_2 together inspires some new thoughts in how the biospheric models reproduce the carbon cycle in the real world.

7 Outlook

This work will be extended to more sites, including some in the Southern Hemisphere, to evaluate the seasonal cycles of OCS and CO_2 in different regions. The FTIR networks will provide an additional database for using OCS to constraint GPP, which would be further improved if more frequency, simultaneous measurements of OCS and CO_2 where available at a greater number of sites.

Using coupled OCS and CO_2 land fluxes in a biospheric model and comparing to measurements of both gases provides the method to constrain GPP with the help of OCS. The relationship between OCS and CO_2 uptake in SiB can be further verified by field measurements for more plant types and at different time. This will increase the confidence for making conclusions on GPP distribution and time variation from the view of OCS.

Although the relationship between OCS plant uptake and GPP still has uncertainties, OCS could be used to study the biospheric processes driving the inter-annual variability. Some climate extremes have impacts on both photosynthesis and respiration; for instance, high temperature could decrease photosynthetic production and increase respiration. With the help of OCS, these biospheric feedbacks could be distinguished.

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Table 1. FTIR sites used in this study

Site	Latitude (°N)	Longitude (°E)	Altitude (m a.s. l.)	Instrument	Measurement years	Network
Eureka	80.1	-86.4	610	Bomem DA8	1993-2008	NDACC&
				125HR	2006-present	TCCON
Ny-Ålesund	78.9	11.9	21	120HR	1992-2012	NDACC&
				120-5HR	2013-present	TCCON
Bremen	53.1	8.8	27	120HR	2002-2003	NDACC&
				125HR	2004-present	TCCON
Jungfraujoch	46.5	8.0	3580	homemade	1984-2008	NDACC
				120HR	1990-present	
Mauna Loa	19.5	-155.6	3397	Bomem DA8	1991-1995	NDACC
				120M	1995-present	

Table 2. Summary of the retrieval parameters for OCS

Retrieval code	Spectroscopy	A priori OCS profiles	A priori S_a matrix	Microwindows (cm^{-1})	Interfering species	SNR	Pressure, Temperature profiles
SFIT4_v0.9.4	Based on HITRAN 2012	Provided by G. Toon over private communication, modified by tropopause height	In-situ measurements variability below 9 km, ACE-FTS measurements variability above 9 km	2047.78-2048.22 2049.75-2050.12 2051.18-2051.48 2054.33-2054.67	O_3, H_2O, CO, $H_2{}^{18}O$, $^{13}CO_2$, ^{18}OCO	300 (pre-fixed)	NCEP

Table 3. Annual global atmospheric OCS budget (fluxes in Gg S $year^{-1}$)

	K2002[a] Mean (Range)	K2002x2 Revisions	K2002x3 Revisions	SiB Revisions
Sources				
Anthropogenic	182 (90-266)			
Ocean	280 (39-520)	516	754	757
Biomass burning	35 (25-38)[b]			
Sinks				
Plant	238 (210-270)	475	713	688
Soil	130 (74-180)			159
Tropospheric OH oxidation	96 (95-98)[b]			
Stratosphere loss	28[b]			
Net	5	4	4	3

[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.

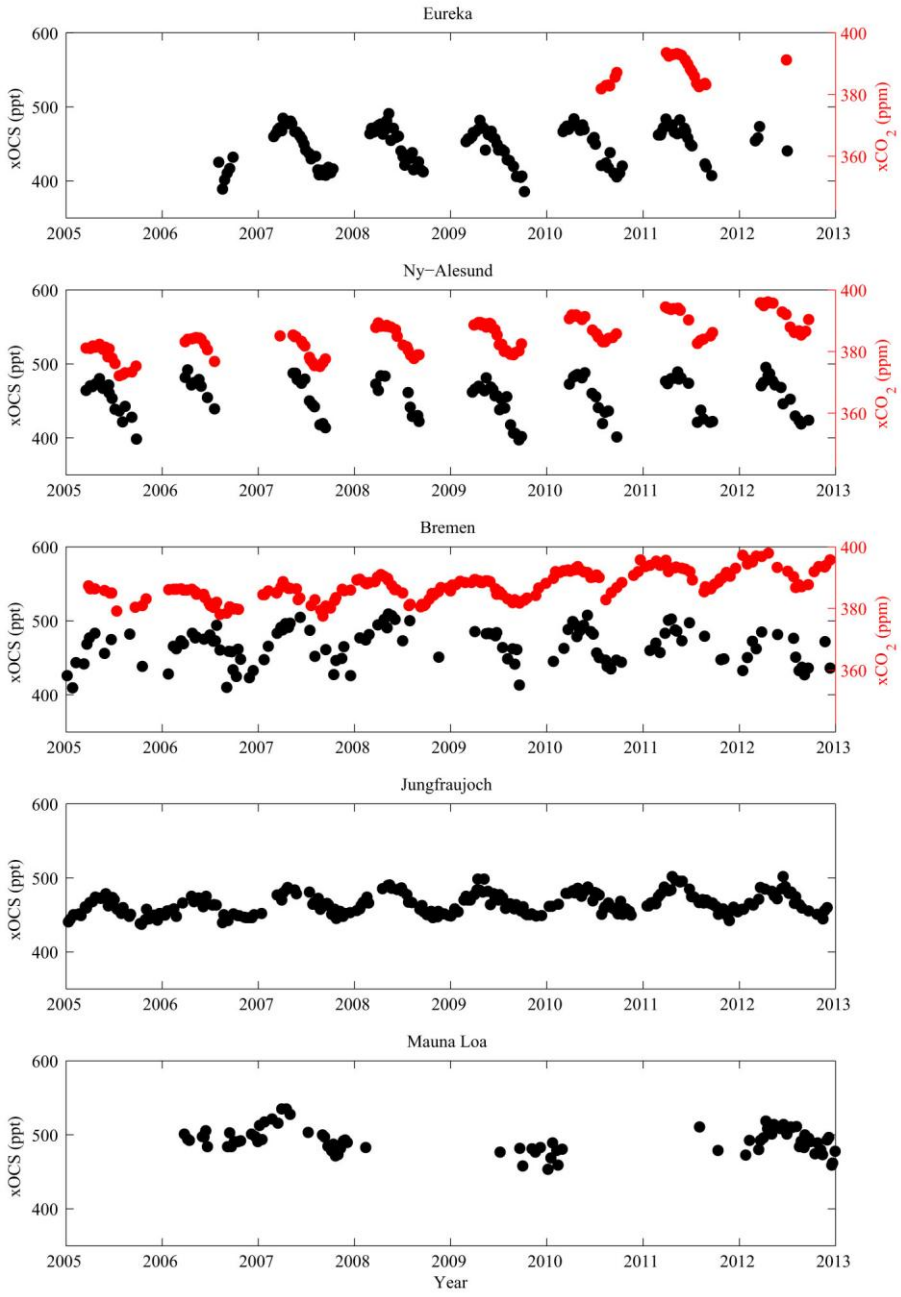

Figure 1. Weekly mean xOCS (black dots) and xCO_2 (red dots) retrieved from FTIR spectra at Eureka, Ny Ålesund, Bremen, Jungfraujoch and Mauna Loa.

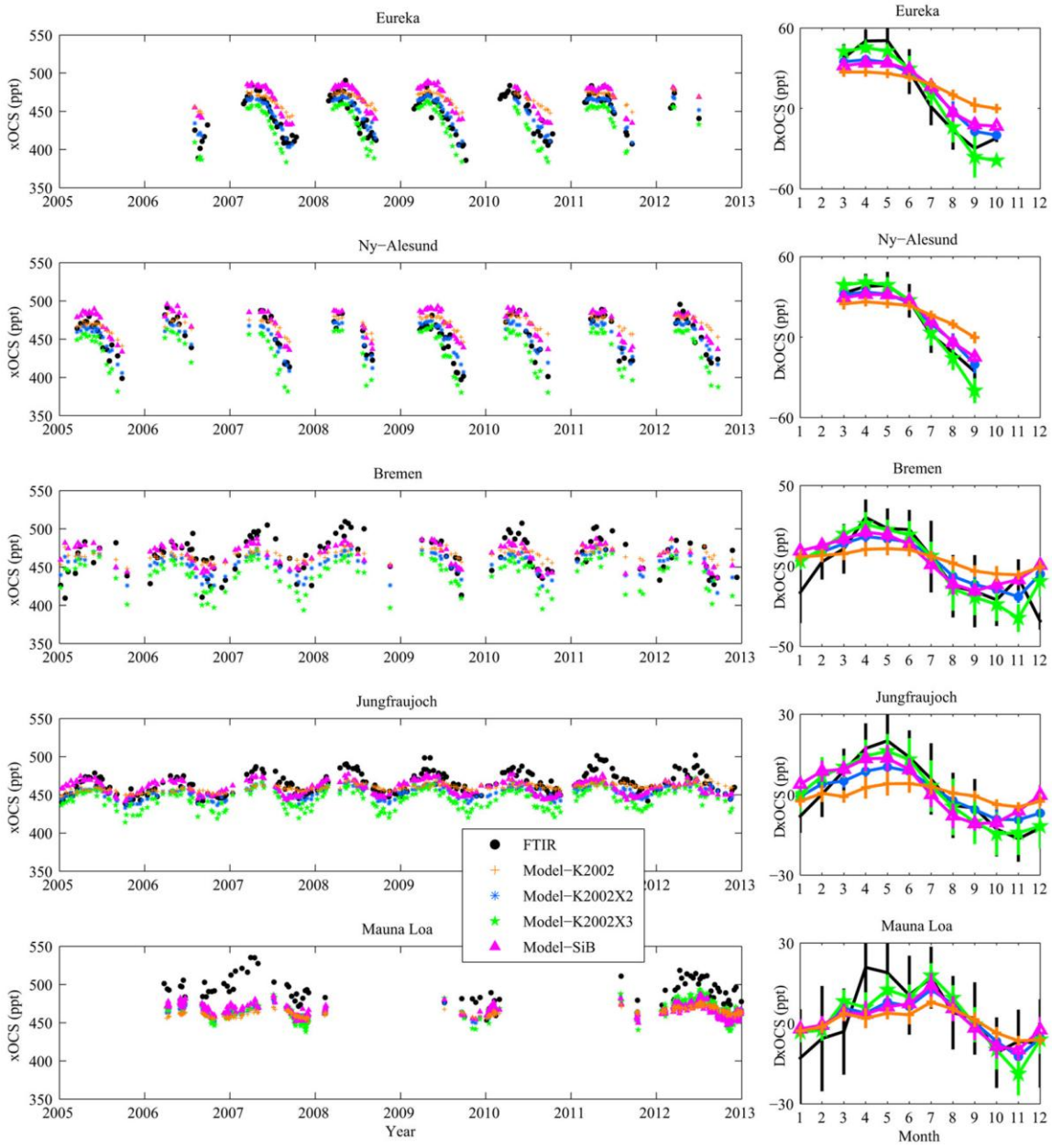

Figure 2. Comparison of FTIR measurements of OCS to model simulations at Eureka, Ny-Ålesund, Bremen, Jungfraujoch and Mauna Loa. The left panels show weekly means from 2005 to 2012. The right panels are the monthly mean relative xOCS (relative to annual mean) averaged for multiple years. The error bars are the standard deviations of each month. The FTIR retrievals are shown in black dots. The model simulations are driven by K2002 (orange plus signs), K2002x2 (blue asterisks), K2002x3 (green stars), and SiB (magenta triangles).

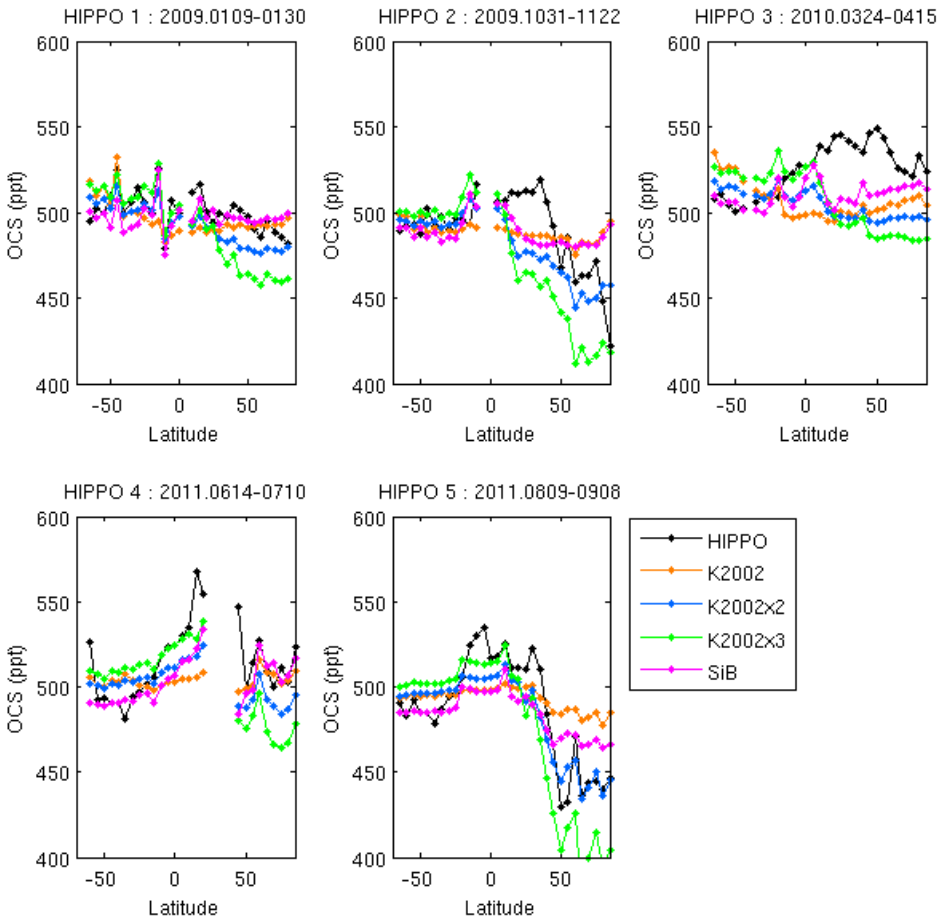

Figure 3. Comparison of HIPPO OCS measurements and model simulations. The five campaigns are compared separately to show latitudinal gradient at different seasons. To minimize the influence of the stratosphere, only the measurements lower than 9 km are used. The model outputs are selected at the nearest 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 2.

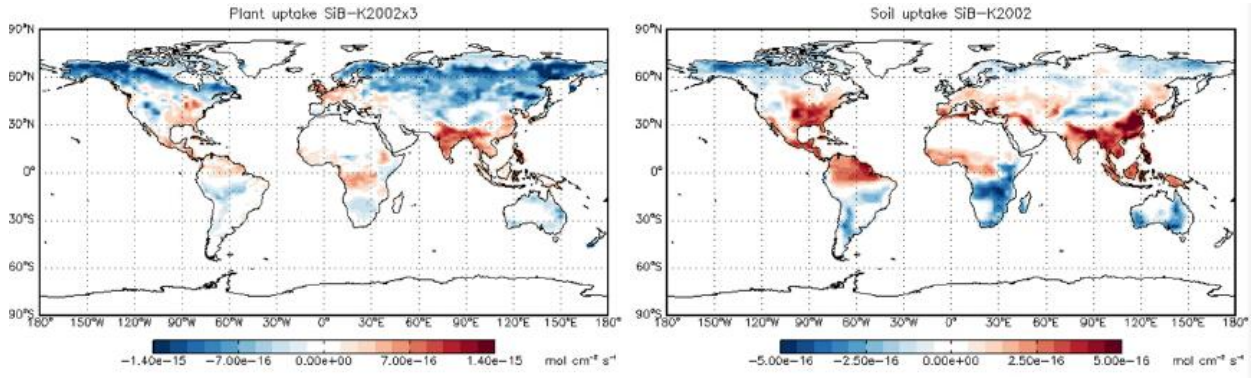

Figure 4. Difference between SiB OCS plant uptake and K2002x3 (left, SiB – K2002x3), difference between OCS soil uptake and K2002 (right, SiB – K2002)

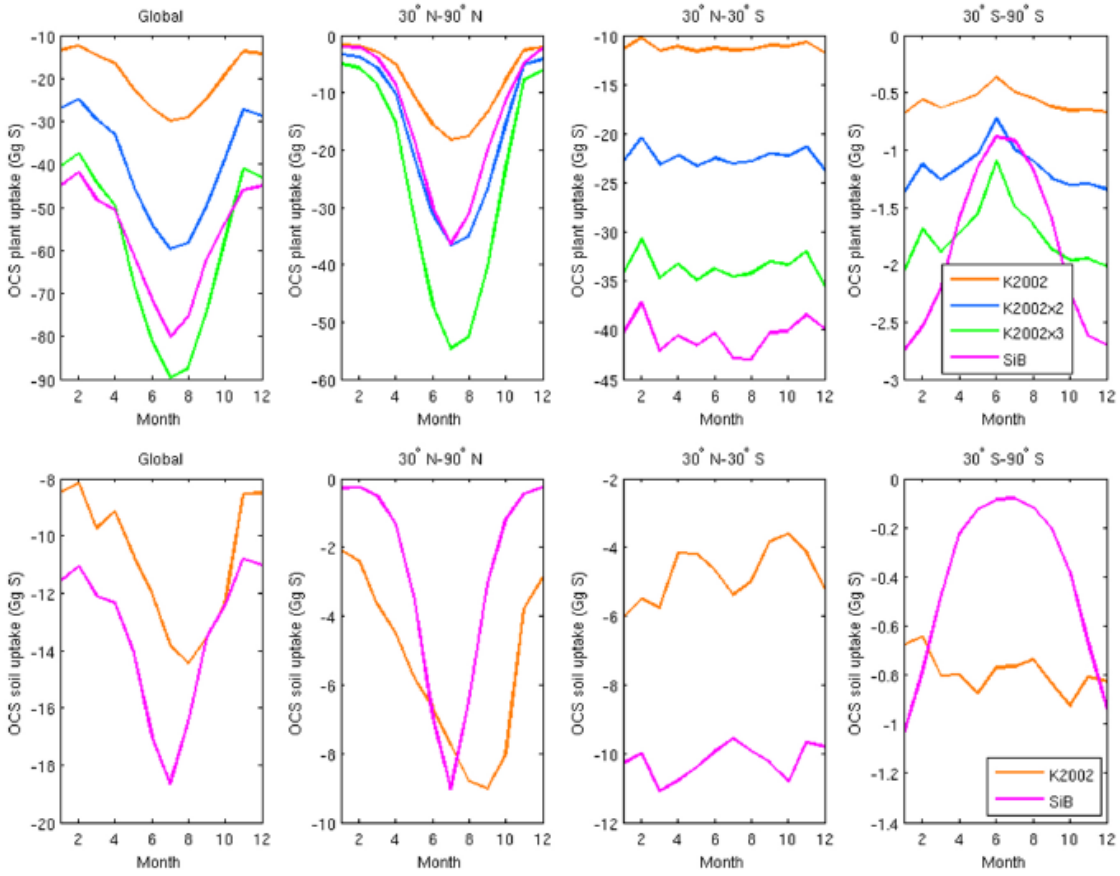

Figure 5. Monthly totals of OCS plant uptake (top) and soil uptake (bottom) of K2002 (orange), K2002x2 (blue), K2002x3 (green), and SiB (magenta) for global, 30° N - 90° N, 30°N - 30° S, and 30° S - 90° S.

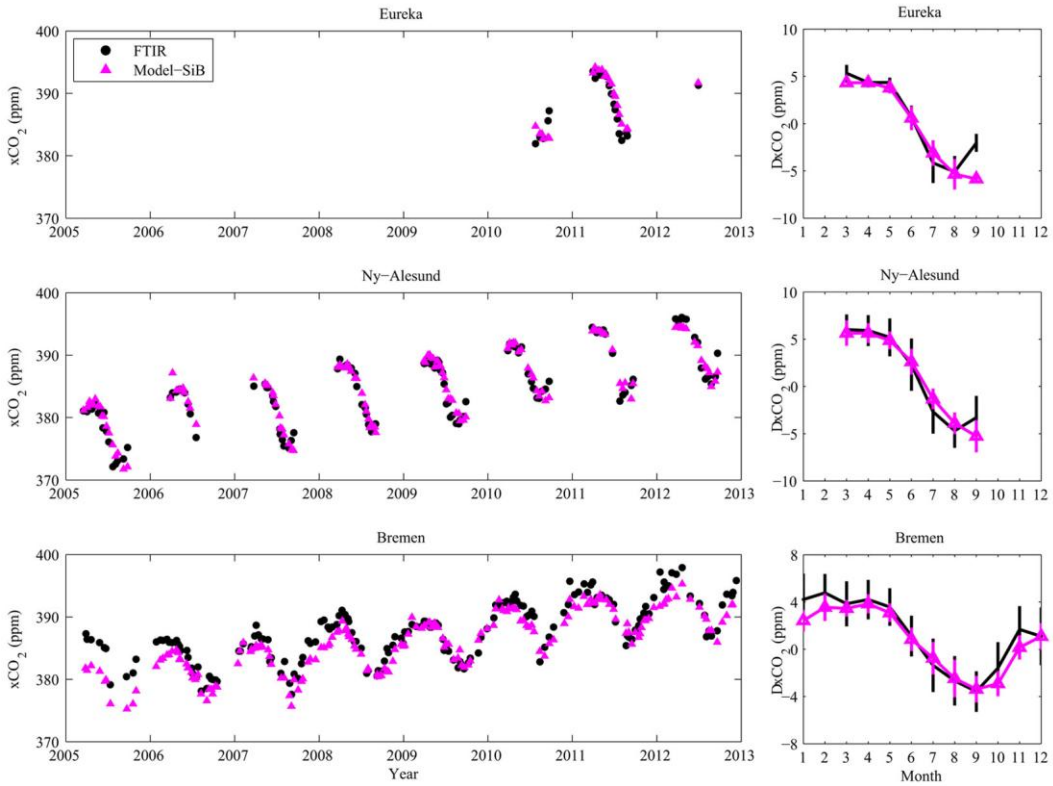

Figure 6. Comparison of FTIR measurements of CO_2 (black dots) to model simulations with SiB land fluxes (magenta triangles) at Eureka, Ny-Ålesund and Bremen. The left panels show weekly means from 2005 to 2012. The right panels show the monthly mean relative xCO_2 (relative to annual mean) averaged for multiple years. The error bars are the standard deviations of each month.

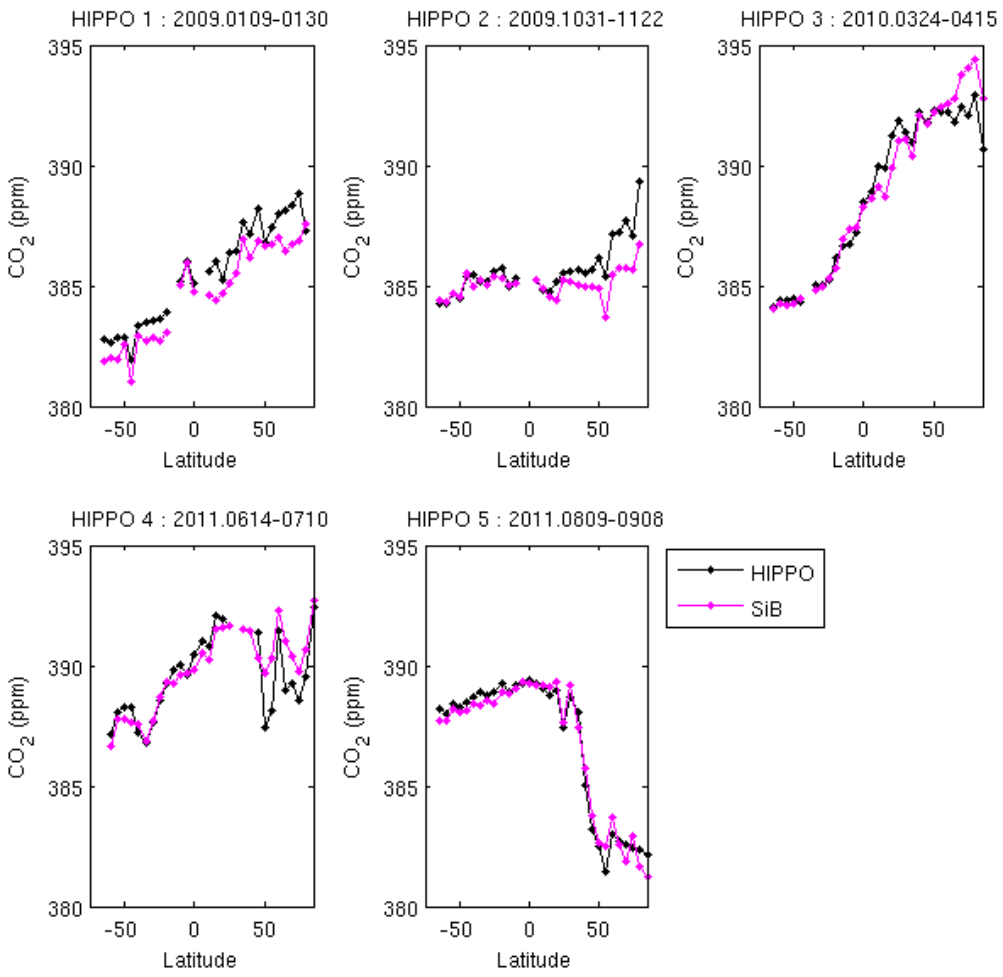

Figure 7. Comparison of HIPPO CO_2 measurements (black) and model simulations with SiB land fluxes (magenta).