Response to Editor

We thank Dr. Zaehle for his extensive suggestions to the manuscript. It is much improved for the attention. The text of the manuscript is now reduced by about one third through the removal of redundancies and considerable re-writing of some sections. We hope that this is clearer and more directly to the point, while still retaining the depth of information required to review the state of carbonyl sulfide research.

We have addressed each of the points Dr. Zaehle suggested as detailed below. The format is *editor comment* followed by author response. Thanks for the considerable effort.

Cheers,

Mary Whelan

I further do not understand the current structure of the manuscript, which presents available measurements AFTER the application of OCS. It would seem to me more logical to have Section 4 prior to Section 3, but I'm open to your ideas on this.
Most of the data is presented in review as it is needed for the discussion. The data available section is more of a resource for readers who would like to perform their own analysis now that they have been brought up to speed on the state of the science, rather than as the foundation of the discussion.

I would also appreciate if – especially in section 2 – would have a common format suggestion recommendations at the end of each section, possibly starting with "Recommendations: "
This has been done for Sections 2 and 3.

P4 L26-27: seems out of place for the introduction. There is a section on EC data where this should be mentioned.
This has been moved.

P5 L10-18: This is conclusion material, not the introduction. Merge with the Conclusion Section
These ideas have been merged with the conclusion

P5 L26-27. This is a common place and can be removed
Done

P6 L1-14: This is the introduction section to an extensive section of different Earth system compartments and their fluxes. No need to go into detail here. Focus on the essential (probably L9-14) and merge the remaining information with the relevant sections.
The details have been moved to appropriate sections.

P6 L15-16. This is a common place and can be removed

Done

P8 L7-9. This is a common place and can be removed
Done

P9 L5: Briefly explain reviewer #2 concern here and explain why you still use the concept.
We've now included an explanation of the "Ohm's Law" approach and why it is sufficient to side step for the studies presented here.
"The F_{CO2} to F_{OCS} relationship depends on the leaf conductance to each gas as it changes with the difference between concentrations inside and outside of the leaf. This requires further modeling to anticipate within leaf concentrations of OCS and CO_2, which cannot be observed directly. To keep the simplicity of the approach, especially when using OCS to evaluate models with many other built-in assumptions, the data-based LRU approximation is sufficient in many cases."

P10 L17-28: not directly relevant to the review. Shorten to make the key point.
Shortened.

P11 L9-10: repeats what was said in the sentences before. remove
Done.

P11 L22- P12 L16: Check for redundancies with the content of Section 2.3.1 and shorten (here or there) accordingly.
Content moved to Section 2.3.1.

P12 L21-23: Yes, but this is not a review on the EC technique, and OCS does not circumvent this problem. Can be removed.
Done.

P13 L14-15: Is a negative repetition of the previous sentence. Remove.
Done.

P13 L19: It is not immediately clear how modeling can side-step a fundamental problem with the observations. A subclause hinting at the main information source helping to side-step this problem would be warranted.
This idea was removed here and described further in Applications, section 3.1 instead.

P13 L20-22: It is a large step from resolving weekly GPP to climate carbon feedbacks. I would agree that this is a step towards better understanding the effect of synoptic meteorological variability on carbon fluxes, and therefore maybe the seasonal to interannual variability of the carbon fluxes. but not more.
The conclusion here was scaled back, "Additionally, OCS observing towers upstream and downstream of large forested areas could resolve the synoptic scale variability in forest carbon uptake (Campbell et al., 2017b). "

P14 L2-4 is redundant with L14 16-18.
Removed.

P15 L1-11: Why are such questions formulated here, whereas they aren't in the other sections. Why is there such an emphasis on model development, when this isn't the case for the other sections. This seems out of place to me, since in the other Sections there is also no focus on model development and future scenarios.
This section was removed.

P19 L 4-5 "We integrate…". Not necessary, remove
Done.

P20 L1 and following. covers abiotic processes also described in Section 2.3.4. I don't see the need for such a duplication.
The abiotic processes section is now reduced to the sorption and hydrolysis section. Redundancies have been removed.

P21 L12-14. Irrelevant for a review.
Removed.

Section 2.3.3. Given that not much is know, and most of the text does not concern OCS, I recommend to significantly shorten this section.
Section removed, relevant information absorbed into discussion of plant fluxes.

P24 L20-24: I don't see why this is relevant here. This has nothing to do with understanding real-world OCS sorption, as becomes clear in the following sentence.
This section has been reworked to be more concise.

P25 L 1-10: I suggest that this can be summarized in 2 sentences and added to the atmosphere section
Done.

P25 L11-P26-L28. I think the context should be merged with the soils section and reducing redundancies significantly shortened.
Done.

P26 L18-19. Unclear whether these number are global or regional estimates. I don't really see the need for giving these numbers here.
The numbers are presented in the budget section much later on instead.

P30 Paragraph beginning in L26: seems more a topic for 3.1.3. Merge with information there.
Done.

P31 L21- P 32 L 17: This entire section mostly summarizes findings of one manuscript. Please shorted to the essential findings and refer the reader to Belviso et al. 1986 for details on various modeling approaches etc.
Done.

Section 2.7: Misses important components of the budget (e.g. ocean, volcanoes). I would recommend moving the relevant sentences here (ie not need to repeating between 2.X and 2.7, but 2.7 should allow to understand Table 4 without having to read all of 2.X in detail. Otherwise, this section does not fit with table 4 and remains incomprehensive.
All discussions of budget have been moved to the budget section.

P 33 L7: There is no justification to assign the tropical biome as C4. Most tropical tree species are C3 and they contribute to a large fraction of global GPP.
Tropical zones are now calculated at C3.

P 33 L 8-10 Example of lack of adequate text editing in this manuscript. This can be significantly shortened. No need to mention Table 4 (see first sentence of Section)
Done.

P 33 L 15: Check the unit. This is a stock, not a flux. It cannot be used to calculate an OCS flux. Where does this LRU value come from?
The unit had a typo: it should be per year. The LRU value now has a citation.

P 33 L 17-21. Should have been part of the discussion in Section 2.2.4, and is probably partly redundant
Removed.

P34 L 12 Unit missing. The last sentence is not necessary.
Unit included; sentence removed.

P35 L4: Ciais et al. 2014 missing in the reference list. Also, I don't think that this is correct. It is a key source of uncertainty in carbon cycle prediction
This sentence was taken out. It wasn't adding much to the paragraph.

P35 L11-P36 L5: This introduction is unnecessarily lengthy, as it provides information that is then repeated in the following section. Shorten as much as possible
The introduction has now been reduced in size considerably.

P36 L27-P37 L10. This can be summarized more efficiently to focus on what was found. The reader can refer to Hilton et al. to see which data sources were used, and which modeling approaches were used. I also don't understand "By using multiple estimates of each uncertainty (these are not explained)… quantitatively assessed each uncertainty source …

The description of Hilton's work is now more concise and focusses more on conclusions than methods.

P37 L23-P38 L9. No need to explain the studies finding in all detail, in particular, which model did what.
The section has been reworked to be more concise.

P38 L8-9: This is a contradiction, please reword: A model bias cannot be only deducible by OCS, when it can also be seen in the CO2 record.
I see your point. This sentence is fixed.

Section 3.1.2. Does this not seem a bit hopeful, given the uncertainties in the overall OCS budget and findings discussed for instance in Section 2.5?
This section has been removed.

P42 / Section 3.2. I am surprised that is has taken 42 pages to arrive at this not insignificant fact, which is largely absent from any previous discussion.
Ideas from the introduction of Section 3.2 are now included in the Terrestrial Ecosystems introduction, Section 2.2.

P42 L 23-P43 L9: There is no need for such level of detail in a review&synthesis. Shorten to the essentials.
Shortened.

P43 L 25- P45 L6: I am missing the "Application" relevance of these paragraphs. The content seems to be more relevant for Section 2, in particular the soils section. This section also misses the review and synthesis character. I recommend it to be shortened to fit into this character.
This has been shortened to essentials and the relevant information transferred to the soils section.

Section 4.1.: This section is disproportionally long compared to the other Sections. Please be more synthetic here. There is no need to describe individual panels of figures in this level of detail. Describe the main features and strength (to the extent that they have not been presented before).
The satellite data section now describes the data instead of going into too much detail about interpretation.

P 50 L5: This sentence is redundant. Calibration was mentioned before.
Removed.

P50 L 2: Clarify or remove entire sentence.
Removed.

P51 L 19: Remove last sentence

Done

P52 L2: Available from where and whom? Give details or remove.
Removed.

P52 L8: This statement is not helpful, and inadequate given the other subsections in Section 4.
The ice cores data section has now been expanded to include more description and include firn data.

Section 5: This is a shopping list of things that may be interesting to do, but falls short of the aspiration of being a "community research plan". Either write is this such that it becomes a plan, or reduce the ambition stated in the introduction.
Ambition reduced.

P52 L11: This sentence is redundant with the following few sentences. remove.
Removed.

P52 L 25-26. If there are not enough measurements in desert (Table 4), why do you recommend not making any measurements there?
Good point. This is now included in the discussion.

P52 L26: Several boreal regions? This is somewhat imprecise a statement. Clarify.
Yes, there's only one Boreal region. Corrected.

P53 L9: As has been outlined very well in the preceding 53 pages, this is not as straightforward as one would have hoped. I think the presentation needs to be a bit more balanced here.
Sentence removed.

P53 L13: While I agree that such a data-base would allow to investigate global carbon / water / climate connections the data themselves will not generate a "massive advancement in our understanding", if they are not accompanied by improved process understanding to attribute observed sources and their variability. While I do not disagree that OCS may contribute to improved understanding, I do not think that the use of the word "massive" is appropriate here. Finally, I must have missed this in the manuscript, but as far as I understand from what has been said in the manuscript, OCS may potentially help to constrain the carbon-water exchanges in terrestrial ecosystems, but this is a long way from making inferences on the effect of carbon-cycle feedbacks on the global water cycles.
The idea here is that OCS observations would help evaluate ecosystem process-based models that would then be used to predict future scenarios. That is too many orders removed to make any sort of massive claim. This language is removed.

P53 L20-21. Acknowledgements should be focused on contributions to the manuscript, not the overall scientific community. If you want to highlight their contributions to the field in general, this should be done in the manuscript, at an appropriate place.

General contributors to the field are removed.

Tables
Arrange tables 1-3 to conform to a similar format
Region – Season – Flux estimate – Reference
Done

Table 4 misses an approximation of the current atmospheric imbalance (evidenced as the mean average growth rate). Otherwise, it is impossible to determine the magnitude of the budget gap.
Done.

Table 6: It would be good if you could separate somehow what is know from what needs to be known or measured.
A new column of "critical data gaps" has been added to Table 6.

Figures:
I did not assess the Figures, as they were not revised as requested.
They are revised in this new version.

Reviews and Syntheses: Carbonyl Sulfide as a Multi-scale Tracer for Carbon and Water Cycles

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Abstract. For the past decade, observations of carbonyl sulfide (OCS or COS) have been investigated as a proxy for carbon uptake by plants. OCS is destroyed by enzymes that interact with CO_2 during photosynthesis, namely carbonic anhydrase (CA) and RuBisCO, where CA is the more important. The majority of sources of OCS to the atmosphere are geographically separated from this large plant sink, whereas the sources and sinks of CO_2 are co-located in ecosystems. The drawdown of OCS can therefore be related to the uptake of CO_2 without the added complication of co-located emissions comparable in magnitude. Here we review the state of our understanding of the global OCS cycle and its applications to ecosystem carbon cycle science. OCS uptake is correlated well to plant carbon uptake, especially at the regional scale. OCS can be used in conjunction with other independent measures of ecosystem function, like solar-induced fluorescence and carbon and water isotope studies. More work needs to be done to generate global coverage for OCS observations and to link this powerful atmospheric tracer to systems where fundamental questions concerning the carbon and water cycle remain.

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1 Introduction

Carbonyl sulfide (OCS or COS) observations have emerged as a tool for understanding terrestrial carbon uptake and plant physiology. Some of the enzymes involved in photosynthesis by leaves also efficiently destroy OCS, so that leaves consume OCS whenever they are assimilating CO_2 (Protoschill-Krebs and Kesselmeier, 1992; Schenk et al., 2004; Notni et al., 2007). The two molecules diffuse from the atmosphere to the enzymes along a shared pathway, and the rates of OCS and CO_2 uptake tend to be closely related (Seibt et al., 2010). Plants do not produce OCS and consumption in plant leaves is straightforward to observe. In contrast, CO_2 uptake is difficult to measure by itself. At ecosystem, regional, and global scales, large respiratory CO_2 fluxes from other plant tissues and other organisms obscure the photosynthetic CO_2 signal, i.e. gross primary productivity (GPP). Measurements of OCS concentrations and fluxes can generate estimates of photosynthesis or of other leaf parameters, like stomatal conductance, at otherwise inscrutable temporal and spatial scales.

Several independent groups examined OCS and CO_2 observations and came to similar conclusions about links between the plant uptake processes for the two gases. Goldan et al., (1988) linked OCS plant uptake, F_{OCS}, to uptake of CO_2, F_{CO2}, specifically referring to GPP. Advancing the global perspective, Chin and Davis (1993) thought F_{OCS} was connected to net primary productivity, which includes respiration terms, and this scaling was used in earlier versions of the OCS budget, e.g. Kettle et al., (2002). Sandoval-Soto et al., (2005) re-introduced GPP as the link to F_{OCS}, using available GPP estimates to improve OCS and S budgets, which were their prime interest. Montzka et al. (2007) first proposed to reverse the perspective in the literature and suggested that OCS might be able to supply constraints on gross CO_2 fluxes, with Campbell et al., (2008) directly applying it in this way.

Since then, other applications have been developed, including understanding of terrestrial plant productivity since the last ice age (Campbell et al., 2017a), estimating canopy (Yang et al., 2018) and stomatal conductance and enzyme concentrations on the ecosystem scale (Wehr et al., 2017), assessment of the current generation of continental-scale carbon models (e.g. Hilton et al., 2017), and better tracing of large-scale atmospheric processes like convection and tropospheric-stratospheric mass

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Moved up [11]: This is particularly true at ecosystem, regional, and global scales, where the large respiratory CO_2 fluxes from other plant tissues and other organisms further obscure the photosynthetic CO_2 signal, i.e. gross primary productivity (GPP).

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transfers. Many of these applications rely on the fact that the largest fluxes of atmospheric OCS are geographically separated: most atmospheric OCS is generated in surface oceans and is destroyed by terrestrial plants. In practice, these new applications often call for refining the terms of the global budget of OCS.

An abundance of new observations have been made possible by technological innovation. While OCS is the longest-lived and most plentiful sulfur-containing gas in the atmosphere, its low ambient concentration (~0.5 ppb) makes measurement challenging. Quantification of OCS in air used to require time-consuming pre-concentration before injection into a gas chromatograph with a mass spectrometer or other detector. While extended time series remain scarce, 17 years of observations have been generated by the National Oceanic and Atmospheric Administration (NOAA) Global Air Sampling Network (Montzka et al., 2007). A system for measuring flask samples for a range of important low-concentration trace gases was modified slightly in early 2000 to enable reliable measurements for OCS. These observations allowed for the first robust evidence of OCS as a tracer for terrestrial CO_2 uptake on continental to global scales (Campbell et al., 2008). In 2009, a quantum cascade laser instrument was developed, followed by many improvements in precision and measurement frequency (Stimler et al., 2010a). Current instruments can measure OCS with < .010 ppb precision and a frequency of 10 Hz (Kooijmans et al., 2016). On larger spatial scales, many FTIR stations and 3 satellites have recently been used to retrieve spectral signals for OCS in the atmosphere.

This review seeks to synthesize our collective understanding of atmospheric OCS, highlight the new questions that these data help answer, and identify the outstanding knowledge gaps to address moving forward. First, we present what information is known from surface level studies. Then we develop a scaled up global OCS budget that suggests where there are considerable uncertainties in the flux of OCS to the atmosphere. We examine how the existing data has been applied to estimating GPP and other ecosystem variables. Finally, we describe where data is available and prioritize topics for further research.

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2 Global Atmospheric OCS budget

The sulfur cycle is arguably the most perturbed element cycle on Earth. Half of sulfur inputs to the atmosphere come from anthropogenic activity (Rice et al., 1981). OCS is the most abundant and longest-lived sulfur-containing gas. Ambient concentrations of OCS are relatively stable over month-long time scales. Trends observed from flask (Montzka et al., 2007), FTIR (Toon et al., 2018), and FTS measurements (Kremser et al., 2015) are <5% on decadal time scales. Over millennia, concentrations may reflect large-scale changes in global plant cover (Aydin et al., 2016, Campbell et al., 2017a).

Upscaling ecosystem estimates (Sandoval-Soto et al., 2005) and global transport models with atmospheric measurements (Berry et al., 2013, Suntharalingam et al., 2008) suggest that there may be a large missing source of OCS, sometimes attributed to the tropical oceans; however, individual observations from ocean vessels do not necessarily support this hypothesis (Lennartz et al., 2017). Anthropogenic emissions are an important OCS source to the atmosphere, but data for the relevant global industries are incomplete (Zumkehr et al., 2018). Here we analyze our current understanding of global surface-atmosphere OCS exchange and generate new global flux estimates from the bottom up, with no attempt at balancing the atmospheric budget (Fig. 1). We use the convention that positive flux represents emission to the atmosphere and negative flux represents removal.

2.1 Global Atmosphere

OCS in the atmosphere is primarily generated from ocean and anthropogenic sources. A portion of these sources are indirect, emitted as CS_2 which can be oxidized to OCS (Zeng et al., 2016). Within the atmosphere, major sinks of OCS are OH oxidation in the troposphere and photolysis in the stratosphere. Between large volcanic eruptions, OCS is a significant source of sulfur to the stratosphere and was briefly entertained as a geoengineering approach to promote global dimming (Crutzen, 2006). However, the global warming potential of OCS roughly balances whatever global cooling effect it might have (Brühl et al., 2012). Hydrolysis in the atmosphere plays a small role: while snow and rain were observed to be supersaturated with OCS (Belviso et al., 1989; Mu et al., 2004), even in the densest

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supersaturated clouds the OCS in the air would represent 99.99% of the OCS present (Campbell et al., 2017b). Multiple lines of evidence support hydrolysis in plant leaves as the dominant removal mechanism of atmospheric OCS.

The observed atmospheric OCS distribution suggests that seasonality is driven by terrestrial uptake in the Northern Hemisphere and oceanic fluxes in the Southern Hemisphere (Montzka et al. 2007). Improvements in the OCS budget were derived through inverse modeling of NOAA tower and airborne observations on a global scale (Berry et al., 2013; Launois et al., 2015b; Suntharalingam et al., 2008). Lower concentrations were generally found in the terrestrial atmospheric boundary layer compared to the free troposphere during the growing season, and amplitudes of seasonal variability were enhanced at low-altitude stations, particularly those situated in mid-continent.

Total column measurements of OCS from ground-based Fourier transform spectroscopy (FTS) show trends in OCS concentrations coincident with the rise and fall of global rayon production which creates OCS indirectly (Campbell et al., 2015). Kremser et al. (2015) found an overall positive tropospheric rise of 0.43–0.73%/y at three sites in the southern hemisphere from 2001 to 2014. The trend was interrupted by a sharply decreasing interval from 2008 to 2010, also observed in the global surface flask measurements (Fig. S2, Campbell et al., 2017a). A similar but smaller dip was observed in the stratosphere, indicating that the trends are driven by processes within the troposphere. Over Jungfraujoch, Switzerland, Lejeune et al. (2017) observed a decrease in tropospheric OCS from 1995 to 2002 and an increase from 2002 to 2008; after 2008 there was no significant trend observed. An increase in OCS concentrations from the mid-20[th] century with a decline around the 1980s were also recorded in firn air (Montzka et al., 2004), following historic rayon production trends.

Changes in terrestrial OCS uptake and possibly the ocean OCS source can be observed from the 54,000 year record from ice cores. Global OCS concentrations dropped 45 to 50 % between the last glacial maximum and the start of the Holocene (Aydin et al., 2016). By the late Holocene, concentrations rose and were the highest recorded in the 1980s (Campbell et al., 2017).

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Recommendations: Modern seasonal and annual variability of OCS can be validated with smaller vertical profile datasets, e.g. Kato et al. (2011) and data from flights e.g. Wofsy et al., (2011). Interhemispheric variability on millennia time scales requires ice core data from the Northern Hemisphere: all current ice core data is from the Antarctic (Aydin et al., 2016).

2.2 Terrestrial ecosystems

OCS uptake by terrestrial vegetation is governed mechanistically by the series of diffusive conductances of OCS into the leaf and the reaction rate coefficient for OCS destruction by CA (Wohlfahrt et al., 2012), though it can also be destroyed by other photosynthetic enzymes, e.g. RuBisCo (Lorimer and Pierce, 1989). CA is present both in plant leaves and soils, although soil uptake tends to be proportionally much lower than plant uptake. In soil systems, OCS uptake provides information about CA activities within diverse microbial communities. OCS uptake over plants integrates information about the sequential components of the diffusive conductance (the leaf boundary layer, stomatal, and mesophyll conductances) and about CA activity, all important aspects of plant and ecosystem function. Stomatal conductance in particular is a prominent research focus in its own right, as it couples the carbon and water cycles via transpiration and photosynthesis.

Terrestrial plant OCS uptake has typically been derived by scaling estimates of the plant CO_2 uptake with proportionality coefficients, such as the empirically-derived leaf relative uptake rate ratio (LRU; Sandoval-Soto et al., 2005):

$$F_{OCS} = F_{CO2}[OCS][CO_2]^{-1}\ LRU \qquad (1)$$

where F_{OCS} is the uptake of OCS into plant leaves, F_{CO2} is CO_2 uptake, [OCS] and [CO_2] are the ambient concentrations of OCS and CO_2, and LRU is the ratio of the OCS to CO_2 uptake, which is a function of plant type and water and light conditions. The concept of the LRU is a simplification of the leaf CO_2 and OCS uptake process. The F_{CO2} to F_{OCS} relationship depends on the leaf conductance to

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each gas as it changes with the difference between concentrations inside and outside of the leaf. This requires further modeling to anticipate within leaf concentrations of OCS and CO_2, which cannot be observed directly. To keep the simplicity of the approach, especially when using OCS to evaluate models with many other built-in assumptions, the data-based LRU approximation is sufficient in many cases. We have compiled LRU data (n = 53) from an earlier review and merged them with more recent published studies (Berkelhammer et al., 2014; Stimler et al., 2010b, 2011, 2012). The LRUs compiled in Sandoval-Soto et al., (2005) were partly re-calculated in Seibt et al., (2010) to account for the lower gas concentrations in the sample cuvettes. For C_3 plants, OCS uptake behavior is attributed to CA activity (Yonemura et al., 2005). As shown in Fig. 2, LRU estimates for C_3 species under well-illuminated conditions are positively skewed, with 95 % of the data between 0.7 to 6.2, which coincides with the theoretically expected range of 0.6 to 4.3 (Wohlfahrt et al. 2012). The median, 1.68, is quite close to values reported and used in earlier studies and provides a solid "anchor ratio" for linking C_3 plant OCS uptake and photosynthesis in high light. LRU data are fewer for C_4 species (n = 4) converging to a median of 1.21, reflecting more efficient CO_2 uptake rates compared to C_3 species (Stimler et al., 2011).

LRU remains fairly constant with changes in boundary layer and stomatal conductance but is expected to deviate due to changes in internal OCS conductance and CA activity (Seibt et al., 2010; Wohlfahrt et al., 2012). The primary environmental driver of LRU is light, and an increase in LRU with decreasing photosynthetically active radiation has been observed at both the leaf (Stimler et al., 2010b, 2011) and ecosystem scale (Maseyk et al., 2014; Commane et al., 2015; Wehr et al., 2017; Yang et al., 2018). This behaviour arises because photosynthetic CO_2 assimilation is reduced in low light whereas OCS uptake continues since the reaction with CA is not light dependent (Stimler et al., 2011). Note that since low light reduces CO_2 uptake, the flux-weighted effect of the variations in LRU on estimating F_{CO2} (or GPP) is also reduced on daily or longer time scales (Yang et al., 2018).

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An additional complication is introduced by soil and non-vascular plant processes that both emit and consume OCS, with a few studies reporting net OCS emission under certain conditions comparable in magnitude to net uptake rates during peak growth. Generally, soil OCS fluxes are low compared to plant uptake with a few exceptions (Fig. 3). In non-vascular plants, OCS uptake continues in the dark even when photosynthesis ceases (Gries et al., 1994; Kuhn et al., 1999; Kuhn and Kesselmeier, 2000; Gimeno et al., 2017; Rastogi et al., 2018). Unlike other plants, bryophytes and lichens lack responsive stomata and protective cuticles to control water losses. OCS emissions from these organisms seems to be primarily driven by temperature (Gimeno et al., 2017).

The yearly average land OCS flux rate in recent modeling studies of global budgets (i.e. plant and soil uptake minus soil emissions) ranges from -2.5 to -12.9 pmol m^{-2} s^{-1} (Fig. 3). The only study reporting year-round OCS flux measurements is from a mixed temperate forest, which was a sink for OCS with a net flux of -4.7 pmol m^{-2} s^{-1} during the observation period (Commane et al., 2015). Daily average OCS fluxes during the peak growing season are available from a larger selection of studies and cover the range from -8 to -23 pmol m-2 s-1, excluding Xu et al., (2002) which found a surprisingly high uptake (–97 ± 11.7 pmol m^{-2} s^{-1}) from the relaxed eddy accumulation method (Fig. 3). Despite the limited temporal and spatial coverage, these data suggest that some of the larger global land net sink estimates may be too high (Launois et al., 2015b).

Recommendations: Available observations are limited in time and do not cover tropical ecosystems, which contribute almost 60% of global GPP (Beer et al., 2010). More year-round measurements from a larger number of biomes, in particular those presently underrepresented, are required to provide reliable bottom-up estimates of the total net land OCS flux. The causes for the observed variability in Fig. 2 require more investigation because they hamper the specification of defensible plant functional type-specific LRUs (Sandoval-Soto et al., 2005) and the development of models with non-constant LRU (Wohlfahrt et al., 2012). Relatively little is known regarding using OCS to estimate CA activity (Wehr et al., 2017) which is a promising new avenue of OCS research. Within this context, plant physiological

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and enzymatic adaptations to increasing CO_2 and their effects on the exchange of OCS are of special interest.

2.2.1 Forests

OCS has the potential to overcome many difficulties in studying the carbon balance of forest ecosystems. To partition carbon fluxes, respiration is often quantified at night when photosynthesis has ceased and turbulent airflow is reduced (Reichstein et al., 2005). This method has systematic uncertainties, e.g. less respiration happens during the day than at night (Wehr et al., 2016). Partitioning with OCS is based on daytime data and does not rely on modeling respiration with limited nighttime flux measurements.

Forests are daytime net sinks for atmospheric OCS when photosynthesis is occurring in the canopy (Table 1). While the relative uptake of OCS to CO_2 by leaves appears stable in high light conditions, the ratio changes in low light when the net CO_2 uptake is reduced (Stimler et al., 2011; Wehr et al., 2017; Rastogi et al., 2018). Forest soil interaction with OCS has been found to be small with respect to leaf uptake (Fig. 3) and straightforward to correct (Belviso et al., 2016; Wehr et al., 2017). Sun et al. (2016) noted that litter was the most important component of soil OCS fluxes in an oak woodland. Otherwise, forest ecosystem OCS uptake appears to be dominated by tree leaves, both during the day and at night (Kooijmans et al., 2017).

Recommendations: Tropical forest OCS fluxes would be informative for global OCS modeling efforts and are currently absent from the literature. The OCS tracer approach is particularly useful in high humidity or foggy environments like the tropics, where traditional estimates of carbon uptake variables via water vapor exchange are ineffective. Additionally, OCS observing towers upstream and downstream of large forested areas could resolve the synoptic scale variability in forest carbon uptake (Campbell et al., 2017b).

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2.2.2 Grasslands

OCS observations can address the need for additional studies on primary productivity in grassland ecosystems. Grasslands generally are considered to behave as carbon sinks or be carbon-neutral but appear highly sensitive to drought and heat waves and can rapidly shift from neutrality to a carbon source (Hoover and Rogers, 2016). Currently OCS grassland studies are scarce (Fig. 3), but indicate a significant role for soils. Theoretical deposition velocities for grasses of 0.75 mm s^{-1} were reported by Kuhn et al. (1999) and LRU values of 2.0 were reported by Seibt et al. (2010). Whelan and Rhew (2016) made chamber-based estimates of ecosystem fluxes from a California grassland with a distinct growing and non-growing season. Total ecosystem fluxes averaged -26 pmol m^{-2} s^{-1} during the wet season and -6.1 pmol m^{-2} s^{-1} during the dry season. During the wet season, simulated rainfall increased the sink strength. Light and dark flux estimates yielded similar sinks, suggesting either a large role for soils in the ecosystem flux or the presence of open stomata under dark conditions. Yi and Wang (2011) undertook chamber measurements over a grass lawn in subtropical China. Ecosystem fluxes of -19.2 pmol m^{-2} s^{-1} were observed. They noted average soil fluxes of -9.9 pmol m^{-2} s^{-1} that were occasionally greater than 50% of the total ecosystem flux. The large contribution of soils to the grassland OCS flux was attributed to atmospheric water stress on the plants that led to significant stomatal closure and reduced midday uptake by vegetation. More recently, Gerdel et al. (2017) reported daily average ecosystem-scale OCS fluxes of -28.7 ± 9.9 pmol m^{-2} s^{-1} for a productive managed temperate grassland.

Solar radiation has been identified recently as a controlling factor of grassland soil OCS emissions. Kitz et al. (2017) highlighted that in grasslands, primary production is devoted to belowground biomass early in the growing season, leading to a situation where exposed soils may be emitting photo-produced OCS simultaneously with high GPP. If unaccounted for, this would lead to an underestimation of the plant component of the total ecosystem OCS flux (Kitz et al., 2017; Whelan and Rhew, 2016).

Recommendations: Grassland plants tend to include mixtures of C_3 and C_4 species with a relative abundance and importance to GPP evolving over the season. These different photosynthetic pathways are known to exhibit different LRU values. On the one hand, this poses a challenge to direct estimations

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of GPP from OCS; on the other hand, observations may provide a unique opportunity to study C_3 and C_4 contributions to GPP. Another pressing research question is the effect of the changing leaf area index of grasses on radiation and related soil emissions.

2.2.3 Wetlands and peatlands

Much of the early work on OCS terrestrial-atmospheric fluxes was conducted in wetlands, perhaps because of the large emissions observed there. Unfortunately, many of these first surveys were conducted with sulfur-free sweep air, significantly biasing the observed net OCS flux compared with that under ambient conditions (Castro and Galloway, 1991).

OCS fluxes have been measured in a variety of wetland ecosystems, including peat bogs, coastal salt marshes, tidal flats, mangrove swamps, and freshwater marshes. Observed ecosystem emission rates vary by two orders of magnitude and generally increase with salinity (Fig. 4). OCS emissions in salt marshes usually range from 10 to 300 pmol m^{-2} s^{-1} (Aneja et al., 1981; DeLaune et al., 2002; Li et al., 2016; Steudler and Peterson, 1984, 1985; Whelan et al., 2013), whereas freshwater marshes and bogs have mean emission rates below 10 pmol m^{-2} s^{-1} (DeLaune et al., 2002; Fried et al., 1993) or act as net sinks due to plant uptake (Fried et al., 1993; Liu and Li, 2008; de Mello and Hines, 1994).

Although plants are generally OCS sinks, wetland plants may appear as OCS sources. Emergent stems can act as conduits transmitting OCS produced in the soil to the atmosphere, or OCS may be a by-product of processes related to osmotic management by plants in saline environments. For example, in a *Batis maritima* coastal marsh, vegetated plots were found to have up to four times more OCS emission than soil-only plots (Whelan et al., 2013). Growing season OCS emissions may greatly exceed those in the non-growing season (Li et al., 2016), but whether this is caused by environmental factors like temperature and soil saturation or by the developmental stage of plants is unclear.

Recommendations: Assessing the role of plants in the wetland OCS budget would require careful investigation of OCS transport via plant stems and OCS producing capacity of aboveground plant

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materials and the rhizosphere. More work needs to be done on the evolution of OCS in soils with low redox potential. Additional experiments should aim to help scale up wetland OCS fluxes.

2.2.4 Lakes and rivers

The role of lakes and rivers in the global OCS budget is not well known. OCS production and consumption have been studied in ocean waters, and these processes most likely occur similarly in freshwater. In the ocean, OCS is produced photochemically from chromophoric dissolved organic matter (CDOM) (Ferek and Andreae, 1984) and by a light-independent production that has been linked to sulfur radical formation (Flöck et al., 1997; Zhang et al., 1998). A mechanism for OCS photo-production was recently described for lake water (Du et al., 2017). Dissolved OCS (Fig. 5) is consumed by hydrolysis at a rate determined by pH, salinity, and temperature (Fig. 6; Elliott et al., 1989).

OCS is present in freshwaters at much higher concentrations than those found in the ocean (Table 2). This might be due to more efficient mixing in the ocean surface waters compared to lakes. However, Richards et al. (1991) found that the concentration remained at the same throughout the water column and observed a midsummer OCS concentration minima in 8 of the 11 studied lakes. This latter point was surprising because photochemical production should be highest during the summer months. It has been demonstrated that ocean algae take up OCS, which might explain the low concentrations when light levels are high; however, Blezinger et al. (2000) concluded that the consumption term should be small compared to hydrolysis and photo-production.

To our knowledge, there have not yet been any studies on OCS fluxes using direct flux measurement methods over freshwaters. Richards et al. (1991) calculated OCS fluxes from different lakes in Ontario, Canada, based on concentration measurements and wind-speed-dependent gas transfer coefficients, resulting in fluxes of 2–5 pmol OCS m^{-2} s^{-1}. In another study, Richards et al. (1994) found fluxes of 2–34 pmol OCS m^{-2} s^{-1} in salty lakes. These fluxes are 5 to 75 times higher than those measured in the oceans (Lennartz et al., 2017). There is also an indirect atmospheric OCS source from carbon disulfide (CS_2) production (Richards et al., 1991, 1994), for which little data exists.

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Recommendations: Measurements in lakes are easier than on the open ocean while generating more information on the processes that may drive OCS production in both regions. Flux data by eddy covariance (EC) and floating chamber methods from lakes and rivers are suggested. Concurrent measurements should target understanding of the biotic and abiotic factors driving water–air exchange of OCS to provide the basis for upscaling aquatic OCS fluxes, including CS_2 concentrations.

2.3 Other terrestrial OCS flux components

2.3.1 Soils

Measurements show that non-wetland soils are predominantly a sink for OCS and wetland (anoxic) soils are typically a source of OCS. OCS production has also been observed in most non-desert oxic soils when dry, with particularly large emissions from agricultural soil (Fig. 7).

In the field, reported oxic soil OCS fluxes range from near zero up to -10 pmol m^{-2} s^{-1}, with average uptake rates typically between 0 and -5 pmol m^{-2} s^{-1}. Higher uptake fluxes of -10 – -20 pmol m^{-2} s^{-1} have been observed in a grassland soil (Whelan and Rhew, 2016), wheat field soils (Kanda et al., 1995; Maseyk et al., 2014), unplanted rice paddies (Yi et al., 2008) and bare lawn soil (Yi and Wang, 2011). However, under warm and dry conditions, fluxes approached zero in grasslands (Berkelhammer et al., 2014; Whelan and Rhew, 2016) and an oak woodland (Sun et al., 2016). The highest reported uptake rates are nearly -40 pmol m^{-2} s^{-1}, following simulated rainfall in a grassland (Whelan and Rhew, 2016). Sun et al. (2016) also reported a rapid response to re-wetting following a rainstorm in a dry Mediterranean woodland.

Variations in soil OCS fluxes measured in the field have been linked to temperature, soil water content, nutrient status, and CO_2 fluxes. Uptake rates have been found to increase with temperature (White et al., 2010; Yi et al., 2008) but also decrease with temperature such that OCS fluxes approached zero or shifted to emissions at temperatures around 15–20˚C (Maseyk et al., 2014; Steinbacher et al., 2004; Whelan and Rhew, 2016; Yang et al., 2018). It can be difficult to separate the effects of temperature and soil water content in the field, and seasonal decreases in OCS fluxes may also be associated with lower

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soil water content (Steinbacher et al., 2004; Sun et al., 2016). Uptake rates have also been found to be stimulated by nutrient addition in the form of fertilizer or lime (Melillo and Steudler, 1989; Simmons, 1999).

Several field studies have found that OCS uptake is positively correlated with rates of soil respiration, or CO_2 production (Yi et al., 2007), but these relationships also vary with temperature (Sun et al., 2016, 2017), soil water content (Maseyk et al., 2014), or high CO_2 conditions (Bunk et al., 2017). The relationship with respiration is attributed to the role of microbial activity in OCS consumption, and similar covariance has been seen between OCS and H_2 uptake (Belviso et al., 2013), a microbially driven process. Berkelhammer et al. (2014) and Sun et al. (2017) have found that the OCS/CO_2 flux ratio has a non-linear relationship with temperature, such that the ratio decreases (becomes more negative) at lower temperatures but is constant at higher temperatures. Kesselmeier and Hubert (2002) observed both OCS uptake and emission by beech leaf litter that was related to microbial respiration rates. Sun et al. (2016) determined that most of the soil OCS uptake in an oak woodland occurred in the litter layer, composing up to 90% of the small surface sink.

Extensive laboratory studies demonstrate that OCS uptake is mainly governed by biological activity and physical constraints. Kesselmeier et al. (1999), van Diest and Kesselmeier (2008), and Whelan et al. (2016) characterized the response of several controlling variables such as atmospheric OCS mixing ratios, temperature, and soil water content or water-filled pore space. Clear temperature and soil water content optima are observed for OCS consumption. These optima vary with soil type but indicate water limitation at low soil water content and diffusion resistance at high soil water content. Additionally, other organism-mediated or abiotic processes in the soil, such as photo- or thermal degradation of soil organic matter (Whelan and Rhew, 2015), can play an important role.

The strong activity of sulfate reduction metabolism in anoxic environments is thought to drive OCS production in anoxic wetland soils (see Fig. 4) (Aneja et al., 1981; Kanda et al., 1992; Whelan et al., 2013; Yi et al., 2008). Temperature probably drives the observed seasonal variation of OCS production,

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with higher fluxes in the summer than winter (Whelan et al., 2013). How much OCS escapes to the atmosphere depends on transport in the soil column. Tidal flooding may inhibit OCS emission from wetland soils due to decreasing gas diffusivity with increasing soil saturation rather than changes in OCS production rates (Whelan et al., 2013).

With high light or temperatures, OCS production in oxic soils can exceed rates found in wetlands. Substantial OCS production has been observed in agricultural fields under both wet and dry conditions (Kitz et al., 2017; Maseyk et al., 2014). OCS fluxes of up to +30 and +60 pmol m^{-2} s^{-1} were related strongly to temperature (Maseyk et al., 2014) and radiation (Kitz et al., 2017), respectively. While most ecosystems do not experience these conditions, most all soils produce OCS abiotically when air dried and incubated in the laboratory (Whelan et al., 2016; Liu et al., 2010; Sauze et al., 2018; Meredith et al., [in review]). Whelan and Rhew (2015) compared sterilized and living soil samples from the agricultural study site originally investigated in Maseyk et al. (2014), finding that all samples emitted considerable amounts of OCS under high ambient temperature and radiation, with even higher emissions after sterilization. Net OCS emissions can occur from agricultural soils at all water contents (Bunk et al., 2017), develops in summer (Yang et al., 2018), and OCS production rates do not differ significantly in moist and dry soils (Kaisermann et al., 2018). Meredith et al., [in review] found that OCS soil production rates are higher in low pH, high N soils that have relatively greater levels of microbial biosynthesis of S containing amino acids and concentrations of related S compounds.

Two mechanistic models for soil OCS exchange have been developed and can simulate observed features of soil OCS exchange, such as the responses of OCS uptake to soil water content, temperature, and the transition from OCS sink to source at high soil temperature (Ogée et al., 2015; Sun et al., 2015). Both models resolve the vertical transport and the source and sink terms of OCS in soil layers. OCS uptake is represented with the Michaelis–Menten enzyme kinetics, dependent on the OCS concentration in each soil layer, whereas OCS production is assumed to follow an exponential relationship with soil temperature, consistent with field observations (Maseyk et al., 2014). Although diffusion across soil

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layers neither produces nor consumes OCS, altering the OCS concentration profile affects the concentration-dependent uptake of OCS.

Recommendations: Additional experiments are required to understand OCS production in oxic soils. The mechanism of soil production and why some soils are more prone to high production rates is unknown. In wetlands, the interaction between OCS production and transport processes remains poorly understood. If OCS produced by microbes accumulates in isolated soil pore spaces during inundation, subsequent ventilation can lead to an abrupt release, which may appear as high variability in surface emissions. Field experiments using simple transport manipulation (e.g. straight tubes inserted into sediment) interpreted with soil modeling would clarify matters.

2.3.2 Microbial communities

The mechanism of OCS consumption in ecosystems is thought to be mediated by carbonic anhydrase (CA), a fairly ubiquitous enzyme present within cyanobacteria, micro-algae, bacteria and fungi. Purified from soil environments or from culture collections, bacteria and fungi show degradation of OCS at atmospheric concentrations. *Mycobacterium* spp. purified from soil and *Dietzia maris* NBRC15801[T] and *Streptomyces ambofaciens* NBRC12836[T] showed significant OCS degradation (Kato et al., 2008; Ogawa et al., 2016). Purified saprotrophic fungi *Fusarium solani* and *Trichoderma* spp. were found to decrease atmospheric OCS (Li et al., 2010; Masaki et al., 2016). Some free-living saprophyte *Sordariomycete* fungi and *Actinomycetale* bacteria, dominant in many soils, are also capable of degrading OCS (Harman et al., 2004; Nacke et al., 2011). Sterilized soil inoculated with *Mycobacterium* sp. showed ability to take up OCS (Kato et al., 2008). In addition, cell-free extract of *Acidianus* sp. showed significant catalysed hydrolysis of OCS (Smeulders et al., 2011). During OCS degredation, soil bacteria introduce isotopic fractionation (Kamezaki et al., 2016; Ogawa et al., 2017). Using different approaches, Bunk et al., (2017), Sauze et al., (2017), and Meredith et al., [submitted] showed that fungi might be the dominant player in soil OCS uptake.

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In addition, there exist hyperdiverse microbial communities that colonise the surface of plant leaves or the "phyllosphere" (Vacher et al., 2016). The phyllosphere is an extremely large habitat (estimated in 1 billion km^2) hosting microbial population densities ranging from 10^5 to 10^7 cells cm^{-2} of leaf surface (Vorholt, 2012). With respect to OCS, it has already been shown that plant-fungal interactions can cause OCS emissions (Bloem et al., 2012). It is undetermined if these epiphytic microbes are capable of consuming and emitting OCS.

Biotic OCS production is a possibility: in bacteria, novel enzymatic pathways have been described that degrade thiocyanate and isothiocyanate and render OCS as a byproduct (Bezsudnova et al., 2007; Hussain et al., 2013; Katayama et al., 1992; Welte et al., 2016). Evidence for OCS emissions following SCN^- degradation has been observed from a range of environmental samples from aquatic and terrestrial origins, indicating a wide distribution of OCS-emitting microorganisms in nature (Yamasaki et al., 2002). Hydrolysis of isothiocyanate, another breakdown product of glucosinolates (Hanschen et al., 2014), by the SaxA protein also yields OCS, as shown in phytopathogenic *Pectobacterium* sp. (Welte et al., 2016). Some *Actinomycetales* bacteria and *Mucoromycotina* fungi, both commonly found in soils, are also known to emit OCS, but the origin and pathway remains unspecified (Masaki et al., 2016; Ogawa et al., 2016).

Recommendations: Further studies should test the connection between the microorganisms that degrade OCS and the candidate enzymes that we assume are performing the degradation. In addition, the magnitude of biotic OCS production in soils is unknown. While sterilized soils exhibit higher OCS production than live soils (Whelan and Rhew, 2015), we have not determined if biotic production is universally insignificant in bulk soils.

2.3.4 Surface sorption and hydrolysis

Several abiotic processes can affect surface fluxes of OCS. OCS can dissolve in water and adsorb and desorb on solid surfaces. Hydrolysis of OCS in water occurs slowly relative to the time scales of typical flux observations (Fig. 6). The temperature dependence of OCS solubility was modeled and described

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by Equation 20 in Sun et al., (2015): For a OCS concentration in air of 500 ppt, in equilibrium at ambient temperatures, the OCS dissolved in water will be less than 0.5 pmol OCS/mol H_2O (Fig. 5). Some portion of the dissolved OCS is destroyed by hydrolysis, following data generated by Elliott et al. (1989). For the rate-limiting step of hydrolysis in near-room-temperature water, the pseudo-first order rate constant is around 2×10^{-5} s^{-1}. The hydrolysis of OCS gains significance over hours, and especially in ice cores (Aydin et al., 2014, 2016).

Under typical environmental conditions, OCS adsorption and desorption is near steady state. OCS adsorbs onto various mineral surfaces at ambient temperatures and can be desorbed at higher temperatures (Devai and DeLaune, 1997). In some ecosystems with large temperature swings, temperature-regulated sorption cannot be ruled out as playing a small role in the variability of observed fluxes.

Recommendations: Abiotic sorption has been overlooked in studies of OCS exchange. Observing fluxes while abruptly changing OCS concentrations over a sterile soil or litter substrate could reveal sorption's role. This information could be used to inform our mechanistic soil models and explain some of the variability in OCS soil fluxes we see in the field.

2.4 Ocean

The oceans are known to contribute to the atmospheric budget of OCS directly via OCS and indirectly via CS_2 (Fig. 8) (Chin and Davis, 1993; Watts, 2000; Kettle et al., 2002). Large uncertainties are still associated with current estimates of marine fluxes (Launois et al., 2015a; Lennartz et al., 2017, and references therein) and has led to diverging conclusions regarding the magnitude of their global role.

The range of observed OCS concentrations in surface waters informs **how the magnitude of direct oceanic emissions is calculated**. Observations of OCS in the surface water of the Atlantic, Pacific, Indian, and Southern Ocean revealed a consistent concentration range of ~10–100 pmol L^{-1} in the surface mixed

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layer on daily averages, across different methods. Largest differences are found between coastal and estuaries (nanomolar L^{-1} range) and open oceans (picomolar L^{-1} range) (Table 3).

2.4.1 Marine production and removal processes

The primary sources of OCS in the ocean are divided into photochemical and light-independent (dark) processes (Von Hobe et al., 2001; Uher and Andreae, 1997). The primary sink is hydrolysis (Fig. 6; Elliott et al., 1989). Evidence indicates that these processes can regulate OCS concentrations in the ocean surface mixed layer, with diverging conclusions on the magnitude and global significance of marine OCS emissions (Launois et al., 2015a). We use the Lennartz et al., (2017) budget here because the emission estimate based on a model consistent with the majority of sea surface concentration measurements.

Global estimates of photo-production for the surface mixed layer can range by as much as 40-fold depending on the methodology used (Fig. 9). The heart of the problem is a limited knowledge of the magnitude, spectral characteristics, and spatial and temporal variability of the apparent quantum yield (AQY).

There is evidence for the role of biological processes (Flöck and Andreae, 1996) and for the involvement of radicals (Pos et al., 1998). Independent of a mechanism, only one parameterization for dark production is currently used in models (Von Hobe et al., 2001). Neither the direct precursor nor the global applicability of this parameterization is known. Despite these unknowns, the current gap in the top down OCS budget (Sect. 3.1.2) is larger than the estimated ocean emissions, including uncertainties from process parameterization and in situ observations.

Recommendations: Further studies should focus on generating a biochemical model for estimating oceanic OCS fluxes. Refining uncertainty bounds for OCS photo-production could be facilitated by a comprehensive study of the variability of AQYs across contrasting marine environments; the use of a photochemical model that utilizes AQYs and facilitates calculations on a global scale; and the cross-

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validation of the depth-resolved modeled rates with direct in situ measurements. During night time, continuous concentration measurements from research vessels can be used to calculate dark production rates assuming an equilibrium between hydrolysis and dark production.

2.4.2 Indirect marine emissions

Indirect marine emissions from oxidation of the precursor gases CS_2 and possibly DMS were hypothesized to be on the same order as or larger than direct ocean emissions of OCS (Chin and Davis, 1993; Watts, 2000; Kettle et al., 2002). Production and loss processes of CS_2 in seawater are less well constrained than OCS production, and they include photo-production, evidence for biological production (Xie et al., 1998, 1999), and a slow chemical sink (Elliott, 1990).

Measurements of CS_2 in the surface ocean comprise several transects in the Atlantic and Pacific oceans with concentrations in the lower pmol L^{-1} range. Significantly larger concentrations have been found in coastal waters (Uher, 2006, and references therein). In laboratory experiments, Hynes et al. (1988) found that the OCS yield from CS_2 increases with decreasing temperatures, suggesting larger OCS production from CS_2 at high latitudes.

It is unclear if the ambient yield of OCS from DMS oxidation is globally important. The production of OCS from the oxidation of DMS by OH has been observed in several chamber experiments, all of which used the same technique and experimental chamber (Barnes et al., 1994, 1996; Patroescu et al., 1998; Arsene et al., 1999, 2001) with a molar yield of 0.7 ± 0.2%. These studies were carried out at precursor levels far exceeding those in the atmosphere (ppm), so the potential exists for radical–radical reactions that do not occur in nature. In addition, experiments took place in a quartz chamber on time scales that have potential for wall-mediated surface or heterogeneous reactions and using only a single total pressure and temperature (1000 mbar, 298 K). The mechanism and atmospheric relevance of OCS production from DMS remains highly uncertain.

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Moved down [22]: To better constrain oceanic emissions of OCS from CS_2, we suggest expanding surface concentration observations across various biogeochemical regimes and seasons; using field observations, laboratory studies, and process models to characterize production processes and identify drivers and rates; and applying a temporally and spatially varying conversion factor when calculating resulting OCS emissions.

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Recommendations: To better constrain oceanic CS_2 emissions, we suggest expanding surface concentration observations across various biogeochemical regimes and seasons. Using field observations, laboratory studies, and process models we could characterize production processes and identify drivers and rates when calculating OCS emission estimates. Elucidating the production pathway and validating the atmospheric applicability of the reported OCS yields from DMS would require experiments at lower concentrations in a system that eliminates (or permits quantification) of wall-induced reactions.

2.5 Anthropogenic sources

Anthropogenic OCS sources include direct emissions of OCS and indirect sources from emissions of CS_2. The dominant source is from rayon production (Campbell et al., 2015), while other large sources include coal combustion, aluminum smelting, pigment production, shipping, tire wear, vehicle emissions, and coke production (Blake et al., 2008; Chin and Davis, 1993; Du et al., 2016; Lee and Brimblecombe, 2016; Watts, 2000).

All recent global atmospheric modeling studies used the low estimate of 180 Gg S y^{-1} from Kettle et al., (2002), which did not capture significant emissions from China. Updated globally-gridded inventories are considerably higher: a bottom-up estimate of 223-586 Gg S y^{-1} for 2012 (Zumkehr et al., 2018), and a top-down assessment of 230 to 350 Gg S y^{-1} for 2011 to 2013 (Campbell et al., 2015). One reason for the gap between the two recent inventories is that the top-down study used an optimization approach in which the result was limited to the a priori range, 150 to 364 Gg S y^{-1}. Both datasets indicate that most anthropogenic sources are in Asia.

Biomass burning is generally accounted as a category separate from anthropogenic emissions.

Several airborne campaigns have observed increases in OCS concentrations in air masses from nearby burning events (Blake et al., 2008). The most recent estimate suggests that biofuels, open burning, and

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agriculture residue are 63%, 26%, and 11% of the total OCS biomass burning emissions (Campbell et al., 2015).

Recommendations: Anthropogenic OCS emissions experience large year to year variation (Campbell et al., 2017a). Ambient OCS monitoring and on site industry observations in Asia could observe the anthropogenic contribution over time. In particular, modern viscose-rayon factory emissions are necessary to capture the variability of emissions factors used to scale rayon production to OCS emissions using economic data.

2.6 Volcanic sources

OCS is emitted into the atmosphere by degassing magma, volcanic fumaroles, and geothermal fluids. OCS can be released at room temperature by volcanic ash (Rasmussen et al., 1982), and has been observed to be conservative in the atmospheric plume emitted by the Erebus volcano up to tens of kilometers downwind of the volcanic source (Oppenheimer et al., 2010).

Using the linear relationship between the logarithm of the OCS/CO_2 ratio in volcanic gases and temperature, the volcanic OCS contribution was determined from estimated CO_2 emissions (Belviso et al., 1986). Here we calculate a revised temperature dependence of log[OCS/CO_2] with additional data (Chiodini et al., 1991; Notsu and Toshiya, 2010; Sawyer et al., 2008; Symonds et al., 1992), as shown in Fig. 10. The compilation of measurements from 14 volcanoes shows that the former relationship from Belviso et al. (1986) overestimated the OCS/CO_2 ratio of volcanic gases with emission temperatures from 110°C to 400°C, typical of extra-eruptive volcanoes. Even with this improved estimate, extra-eruptive volcanoes OCS emissions are negligibly small and can definitely be discarded from the inventory of volcanic OCS emissions. Eruptive and post-eruptive volcanoes contribute almost all of OCS emissions from volcanism.

Recommendations: An updated inventory of eruptive volcanos and a better assessment of their CO2 emissions will refine our understanding at a regional scale of the contribution of OCS from volcanos.

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Special attention should be paid to the Ring of Fire off the Asian continent where satellites observed significant atmospheric OCS enhancements.

2.7 Bottom-up OCS budget

We calculate a "bottom up" global balance of OCS with several approaches presented in Table 4. Within the atmosphere, the tropospheric sink owing to oxidation by OH is estimated to be in the range 82–130 Gg S y^{-1} (Berry et al., 2013; Kettle et al., 2002; Watts, 2000), and the stratospheric sink is in the range 30–80 Gg S y^{-1}, or 50 ± 15 Gg S y^{-1} (Barkley et al., 2008; Chin and Davis, 1995; Crutzen, 1976; Engel and Schmidt, 1994; Krysztofiak et al., 2015; Turco et al., 1980; Weisenstein et al., 1997). OCS concentrations are increasing roughly 0.5-1ppt/year averaged over the last 10 years (Campbell et al., 2017a), suggesting approximately 2 to 5 Gg S y^{-1} remains in the atmosphere.

We build a budget for terrestrial biomes that relies on observations where available, and on estimates of carbon uptake where no data exists, as has been done previously (Campbell et al., 2008; Kettle et al., 2002; Suntharalingam et al., 2008). In Table 5, the estimated OCS uptake is first calculated from a GPP estimate and Eq. 1, then the net OCS flux is appraised by taking into account observed or estimated soil fluxes for each biome. The [CO_2] and [OCS] are assumed to be 400 ppm and 500 ppt, respectively, and LRU is 1.16 ± 0.2 for C_4 plants (Stimler et al. 2010b) and 1.99 ± 1.44 for C_3 plants (Fig. 2). We further assume a 150-day growing season with 12 h of light per day for the purposes of converting between annual estimates of GPP and field measurements calculated in s^{-1} units, though this obviously does not represent the diversity of biomes' carbon assimilation patterns. Additionally, we assume that plants in desert biomes photosynthesize using the C_4 pathway. Converting annual estimated F_{COS} in pmol m^{-2} y^{-1} to pmol m^{-2} s^{-1} is sensitive to our growing season assumption. The lack of soil OCS flux time series datasets makes a more sophisticated upscaling approach ineffective. Anticipated fluxes from soils and plants are therefore combined in this purposely simple method, scaled to the area of the biome extent, and presented in Table 4 as annual contributions to the atmospheric OCS budget.

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We use a range of OCS flux observations in pmol OCS m^2 s^{-1} for fresh and saline wetlands: -15 (de Mello and Hines, 1994) to +27 (Liu and Li, 2008) for freshwater wetlands and -9.5 (Li et al., 2016) to +60 (Whelan et al., 2013) for saltwater wetlands (Fig. 4). Marine and inland wetlands cover 552 and 9299 10^3 km^2, respectively (Dixon et al., 2016; Lehner and Döll, 2004). Performing a simple scaling exercise results in contributions of -140 to 250 and -5 to 33 Gg S y^{-1} for fresh and saltwater wetlands, respectively, yielding a total range of -150 to 290 Gg S y^{-1} (Table 4).

To determine the role of non-vascular plant communities to the atmospheric OCS loading, we leverage Eq. (1) and work that has already been done on their carbon balance. According to Elbert et al. (2012), the annual contribution is 3.9 Pg C y^{-1}. A [OCS] of 500 ppt, a [CO_2] of 400 ppm, and a LRU of 1.1 ± 0.5 (Gimeno et al., 2017), yields -8 – -21 Gg S y^{-1}.

To estimate the maximum possible source of lakes to the atmospheric OCS burden, we perform a simple estimation of the global OCS flux following the approach in MacIntyre et al. (1995) as

$$F_{OCS} = k(c_{aq} - c_{eq}) \qquad (2)$$

where gas transfer coefficient, k, is assumed to be constant 0.54 m d^{-1} (Read et al., 2012); OCS concentration in the water, c_{aq}, is 90 pmol L^{-1} to 1.1 nmol L^{-1} (Richards et al., 1991); and OCS concentration in the surface water if it was in equilibrium with the above air, c_{eq}, calculated using Henry's law at global average temperature of 15°C and global atmospheric OCS mixing ratio of 500 ppt. Accounting for the number of ice-free days in a year and total lake surface area per latitude (Downing et al., 2006), the range of possible COS burden from lakes to the atmosphere is reported here as 0.8 to 12 Gg S y^{-1}.

Lennartz et al. (2017) generated a direct estimate of direct OCS emissions from oceans as 130±80 Gg S y^{-1}. A molar yield of CS_2 to OCS of 0.81–0.93 was established by Stickel et al. (1993) and Chin and Davis (1993), resulting in ocean OCS emissions from CS_2 with an uncertainty of 20–80 Gg S y^{-1}. This uncertainty is from the emissions of CS_2, not the molar yield, for which a globally constant factor is

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Deleted: Lakes and rivers could be important for regional OCS studies, especially in the northern latitudes. Lakes cover only about 3% of the Earth's surface (Downing et al., 2006), but in the boreal zone lakes cover on average 7% of land area. In some parts of Finland (Raatikainen and Kuusisto, 1990) and Northern Canada (Spence et al., 2003) they occupy up to 20% and 30% of the landscape, respectively. Among the admittedly few studies, no observations support lakes and rivers as a consistent OCS sink.

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used. The global DMS oxidation source of OCS was estimated by Barnes et al. (1994) as 50.1–140.3 Gg S y^{-1}, and subsequent budgets contain only revisions according to updated DMS emissions (Kettle et al., 2002; Watts, 2000). We suggest that the uncertainty in the production of OCS from DMS is underestimated. Until these issues are resolved, we recommend that this term be removed as a source from future budgets, but retained as an uncertainty.

Bottom-up analysis of the global anthropogenic inventory indicates a source of 500 ± 220 Gg S y^{-1} for the year 2012 (Zumkehr et al., 2018). The large uncertainty is primarily due to limited observations of emission factors, particularly for the rayon, pulp, and paper industries. The most recent estimate of the biomass burning sources is 116 ± 52 Gg S y^{-1} (Campbell et al., 2015).

To calculate global volcanic OCS emissions, we first consider the range of global volcanic CO_2 emission estimates of the five studies reviewed by Gerlach (2011) of 0.15–0.26 Pg y^{-1}, or 0.205 ± 0.055 Pg y^{-1}. Assuming that the mean OCS/CO_2 molar ratio of gases emitted by eruptive and post-eruptive volcanoes is 2.3×10^{-4} (for emission temperatures in the range 525°C–1130°C, see Fig. 10), the revised annual volcanic input of OCS into the troposphere is estimated to be in the range 25–43 Gg S y^{-1}.

Examining Table 4, we find large uncertainties in many global estimates and some biome observations are completely absent. It has been suggested that ocean OCS production has been underestimated (Berry et al., 2013), and some research points to unaccounted anthropogenic sources (Zumkehr et al., 2018). The uncertainty on our ocean OCS production and/or the industry inventories do not necessarily capture the true range of OCS fluxes. Despite the large uncertainties of the global OCS budget, many applications of the OCS tracer have been attempted with success.

Recommendations: More observations in the ocean OCS source region and from industrial processes, particularly in Asia, are needed to further assess their actual magnitude and variation (Suntharalingam et al., 2008). Current leaf-based investigations need to be expanded to include water or nutrient-stressed

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plants. Measurements from biomes with a complete lack of data, such as deserts and the entirety of the tropics, are desperately needed.

3 Applications

3.1 Global and regional GPP estimates

Here we describe work using OCS observations to assemble more information about ecosystem functioning on different scales. Estimates disagree in their diagnoses of global (Piao et al., 2013) and regional (Parazoo et al., 2015) GPP magnitude and spatial distribution in North America (Huntzinger et al., 2012), the Amazon (Restrepo-Coupe et al., 2017), and Southeast Asia (Ichii et al., 2013). Feeding observations of OCS uptake over land into transport models informs the spatial distribution and magnitude of GPP. With the suite of OCS flask and satellite data available, we describe studies that examine OCS fluxes with the top-down approach. Finally, we examine GPP estimates on very long temporal scales using the OCS ice core record.

3.1.1 Evaluating biosphere models

There are many uncertainties in evaluating biosphere models using OCS observations. Hilton et al. (2017) showed that the spatial placement of GPP dominates other uncertainty sources in the GPP tracer approach on the regional scale. Land surface models that placed the largest GPP in the Upper Midwest of the United States produced OCS plant fluxes that matched well against aircraft observations for all estimates of OCS soil flux, OCS anthropogenic flux, and transport model boundary conditions. OCS plant fluxes derived from GPP models that place the largest GPP in the Southeast United States were not able to match aircraft-observed OCS for any combination of secondary OCS fluxes. Placement of the strongest North American GPP in the Upper Midwest is consistent with new ecosystem models from the Coupled Model Intercomparison Project Phase 6 (CMIP6) (Eyring et al., 2016) with space-based estimates from SIF (Guanter et al., 2014; Parazoo et al., 2014). This result is encouraging for the potential of OCS to provide a directly observable tracer for GPP at regional scales.

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Launois et al. (2015b) analyzed the potential of existing atmospheric OCS and CO_2 mixing ratio measurements to evaluate model GPP biases. They used the simulated GPP from three global land surface model simulations from the TRENDY intercomparison (Sitch et al., 2015) and an atmospheric transport model. The amplitude and phase of the seasonal variations of atmospheric OCS appear mainly controlled by the vegetation OCS sink. This allows for bias recognition in the spatial and temporal patterns of the GPP. For instance, the ORCHIDEE GPP at high northern latitudes is overestimated, as revealed by a too-large OCS seasonal cycle at the Alert station (ALT, Canada) (Fig. 11). These results highlight the potential of current in situ OCS measurement to reveal model GPP and respiration biases.

Recommendations: While current datasets can support or refute current land surface model GPP data products over North America, evaluating modeled surface GPP fluxes with OCS observations would benefit from a broader network of continuous OCS observations. Unfortunately, satellite data are not currently sensitive to concentrations at the surface. Maintaining a network of tall towers with continuous OCS measurements over more than one continent could, in conjunction with upper-troposphere measurements from satellites, provide the data needed to refine next generation land surface models.

3.1.2 Top-down global OCS budgets

Top-down estimates use observed spatial and temporal gradients of OCS in the atmosphere to adjust independent surface fluxes, called the prior estimate. Constraints can be introduced to the results, e.g. Launois et al. (2015b) used flask measurement observations to optimize surface OCS flux components to obtain a closed global OCS budget. Other top down estimates without this restriction found a missing source of about 600–800 Gg S y^{-1} in the atmospheric budget of OCS (Berry et al., 2013; Glatthor et al., 2015; Kuai et al., 2015; Suntharalingam et al., 2008; Wang et al., 2016). This could be the result of missing oceanic sources, missing anthropogenic OCS sources from Asia, overestimated plant uptake, or a combination of factors.

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Kuai et al., (2015) implied a large ocean OCS source over the Indo-Pacific region with the total ocean source budget consistent with the global budget proposed by Berry et al. (2013). The observations in Kuai et al., (2015) were estimated OCS surface fluxes from NASA's Tropospheric Emission Spectrometer (TES) ocean-only observations. A similar conclusion was obtained by Glatthor et al. (2015), who showed that the OCS global seasonal cycle observed by MIPAS was more consistent with the seasonal cycles modeled using the Berry et al. global budget than using the global budget proposed earlier by Kettle et al. (2002).

Most of the anthropogenic source is located in China, while most of the atmospheric OCS monitoring is located in North America (Campbell et al., 2015). The spatial separation allows regional applications of OCS to North America to control for most of the anthropogenic influence through observed boundary conditions (Campbell et al., 2008; Hilton et al., 2015, 2017). The anthropogenic source has large inter-annual variations (Campbell et al., 2015), which suggest that applications of the OCS tracer to inter-annual carbon cycle analysis will require careful consideration of anthropogenic variability.

Recommendations: The accuracy of OCS surface flux inversions can be improved by using simultaneous OCS observations from multiple satellites, e.g. TES and MIPAS, to provide more constraints on the OCS distribution in different parts of the atmosphere. Satellite products need to be compared to observations to determine how well the upper troposphere can reflect surface fluxes, e.g. long-term tower measurements, airborne eddy flux covariance, and atmospheric profiles. This effort is furthered by better estimates of surface fluxes, in particular observations of OCS emissions from the oceans where we assume a large source region might exist (Kuai et al., 2015) and where poorly described anthropogenic sources are located in Asia (Zumkehr et al., 2018).

3.1.3 Long-term changes in carbon uptake

Ice core samples from the West Antarctic Ice Sheet Divide were used to produce a 54,300 year OCS record and an order of magnitude estimate of the change in GPP during the last glacial/interglacial transition (Aydin et al., 2016). Atmospheric OCS declined by 80 to 100 ppt during the last

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glacial/interglacial transition. Interpretation of these measurements with a simple box model suggests that GPP roughly doubled during the transition. This order of magnitude estimate is consistent with an ecosystem model that simulates 44% growth in GPP over the same period (Prentice et al., 2011).

The ice core OCS record has also been used to explore variation in GPP over the past 2,000 years. Observations show relative maxima at the peak of the Little Ice Age (Aydin et al., 2008). These data were used to estimate growth in GPP and were combined with other information to estimate the temperature sensitivity of pre-industrial CO_2 fluxes for the terrestrial biosphere (Rubino et al., 2016).

Given that earth system model projections have highly uncertain carbon-climate feedbacks (Friedlingstein et al., 2013), understanding of GPP in the current industrial era is needed to provide a benchmark for future model development. Firn air measurements and one-dimensional firn models have been used to show an increase in atmospheric OCS during most of the industrial era, with a decadal period of decline beginning in the 1990s (Montzka et al., 2004, 2007). The trend in the firn record has been interpreted to largely reflect the increase in industrial emissions, but it also suggests an increase in GPP during the 20^{th} century of 31 ± 5%, which is consistent with some models (Campbell et al., 2017a).

Recommendations: Ice core measurements represent the only observational constraint on GPP variation over the glacial/interglacial transition, and the ability to provide such constraints provides powerful new stimulus for development and testing of paleoclimate and biosphere models. Additionally, examining the polar differences in OCS over glacial-interglacial periods would provide additional evidence to interpret changes in GPP. For such an analysis, ice core OCS observations from the Northern Hemisphere are needed.

3.2 OCS to probe variables other than GPP

OCS and CO_2 uptake within plant leaves is partly regulated by the opening of stomata on leaf surfaces. Stomatal conductance is typically determined from combined estimates of transpiration, water vapor concentration, and leaf temperature. That approach can be particularly challenging at the canopy scale,

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where transpiration is difficult to distinguish from non-stomatal water fluxes (i.e. evaporation from soil and canopy surfaces) and to upscale from sap flux measurements (Wilson et al., 2001). Use of OCS uptake involves the similar, but more tractable challenge of distinguishing the canopy OCS uptake from soil OCS uptake or emission, as in Wehr et al. (2017). OCS data can also look at changes in uptake activity when plants are grown under elevated CO2 environments (White et al., 2010; Sandoval-Soto et al., 2012). Use of OCS uptake may also be less sensitive to errors in leaf temperature, which is difficult to define and quantify at the canopy scale but may be improved by OCS measurements (Yang et al., 2018). However, leaf temperature may still enter the problem via estimation of mesophyll conductance and CA activity.

The use of OCS to study canopy and stomatal conductance is therefore promising, but it is so far represented mostly by very few studies (Wehr et al., 2017; Yang et al., 2018). Wehr et al. (2017) used OCS uptake to derive canopy stomatal conductance and hence transpiration in a temperate forest. Stomatal conductance was the rate-limiting diffusive step, and so its diel and seasonal patterns were retrievable from the canopy OCS uptake to within 6% of independent estimates based on sensible and latent heat flux measurements (Fig. 12). OCS would be especially useful in humid environments or at night, when transpiration is too small to use other methods that rely on sap flow or heat flux (Campbell et al., 2017b). However, an independent estimate of CA activity and mesophyll conductance would be required.

Recommendations: OCS observations should be used to link plant physiological variables together. OCS fluxes are related to GPP via all three diffusive conductances, CA activity, transpiration, and the ^{18}O isotope compositions of CO_2 and H_2O. The ^{18}O connection results from the fact that CA promotes the exchange of oxygen isotopes between CO_2 and liquid water in the leaves. Solar-induced fluorescence measurements could also be synergistic, as they relate to the photochemical aspect of photosynthesis, while OCS uptake relates to the gas transport aspect. So far, few research schemes have taken advantage of these relationships.

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4 Available datasets

4.1 OCS satellite data products

Global OCS concentrations have been retrieved from several satellite instruments, including NASA's TES (Kuai et al., 2014), the Canadian Space Agency's Atmospheric Chemistry Experiment–Fourier Transform Spectrometer (ACE-FTS) (Boone et al., 2005), the European Space Agency's MIPAS (von Clarmann et al., 2003; Glatthor et al., 2017) and the Infrared Atmospheric Sounding Interferometer (IASI) (Camy-Peyret et al., 2017; Vincent and Dudhia, 2017). Among these instruments, TES and IASI are nadir-viewing instruments (i.e. looking downwards from space towards the surface), while ACE-FTS and MIPAS are limb scanners (i.e. looking through the atmosphere tangentially). Nadir measurements are less prone to cloud interference and provide good horizontal spatial resolution but coarse vertical resolution. Limb measurements provide better vertical resolution and higher sensitivity to tracer concentrations, but they are subject to a higher probability of cloud interference and poorer line-of-sight spatial resolution. Currently there are no satellite measurements that are strongly sensitive to OCS concentrations near the surface, where they are most needed to evaluate surface fluxes.

The standard TES OCS product is an average between 200 and 900 hPa, with maximum sensitivity to the mid-tropospheric value (Kuai et al., 2014, Fig. 13a). Currently, the TES OCS retrievals are available over ocean only for latitudes below 40°, where the signal-to-noise ratio is higher (due to larger thermal contrasts) and the surface spectral emissivity can be easily specified. Comparisons with collocated airborne and ground measurements show that the current TES OCS data has an accuracy of 50–80 ppt, and the accuracy is improved to ~7 ppt when averaged over one month (Kuai et al., 2014).

MIPAS retrievals from 7 to 25 km characterize the average OCS concentration in a thin layer (a few kilometers thick) around the corresponding tangent height. Currently, the MIPAS OCS product (Fig. 13b) provides pole-to-pole OCS concentrations at multiple levels in the upper troposphere and the stratosphere, which show an accuracy of ~50 ppt against balloon-borne measurements. Fig. 14 shows the summertime (June–August) latitudinal distribution of OCS observed by MIPAS (Glatthor et al., 2017).

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To use the OCS GPP tracer to its full potential, surface OCS estimates over land and ocean are needed to evaluate ocean and ecosystem fluxes to the atmosphere at the global scale. Current satellite retrievals are sensitive to OCS concentrations much higher in the troposphere, and FTIR or tower data have limited coverage. Currently, the most used surface OCS dataset is from the NOAA Flask Network, where gas samples are often collected twice a day. Coordinating satellite retrievals with ground-based measurement efforts is important to realize greater data coverage and accuracy.

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IASI retrieves a single value for the total column OCS (Fig. 13c). Recently, Vincent and Dudhia (2017) reported the pole-to-pole global OCS retrieved from the IASI measurements. Their preliminary test showed that the seasonally averaged IASI OCS data vary consistently with ground measurements. The IASI OCS observations over land generally agree with the MIPAS observations, showing large sinks over South America and Africa. The high spatial resolution also reveals more clearly the land OCS sources over Asia, which are not seen in TES nor MIPAS observations. Furthermore, the relatively low OCS abundance over the Inter-Tropical Convergence Zone is only apparent in IASI data.

The ACE-FTS OCS reported concentrations in the lower stratosphere are known to be 15% lower than the balloon-borne measurements (Velazco et al., 2011) and ~100 ppt lower than MIPAS OCS (Glatthor et al., 2017).

4.2 FTIR data

Ground-based FTIR retrievals of OCS are sensitive to the altitudes between surface and 30 km, and can therefore more directly capture the variations near the surface compared to satellite data. There are two networks of FTIR spectrometers: the Network for the Detection of Atmospheric Composition Change (NDACC), recording the mid-infrared spectra including the OCS bands, and the Total Carbon Column Observing Network (TCCON), mainly focusing on the near-infrared with only some sites including the OCS bands. The FTIR remote sensing measurement is an indirect measurement, and therefore needs to be calibrated to in-situ observations to have the same scale when combining the datasets. For example, Wang et al.,(2016) added an offset when comparing FTIR retrievals and HIAPER Pole-to-Pole Observations (HIPPO) to the same model. Published datasets exist for the periods 1993–1997 (Griffith et al., 1998), 1978–2002 (Rinsland et al., 2002), 2001–2014 (Kremser et al., 2015), 2005–2012 (Wang et al., 2016), and 1995–2015 (Lejeune et al., 2017) and by an airborne Fourier spectrometer for the period 1978–2005 (Coffey and Hannigan, 2010). Balloon-borne FTIR data are available, starting in 1985 (Toon et al., 2018).

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4.3 Tower and airborne data

Data are available from two kinds of airborne sampling: survey flights, and atmospheric chemistry projects. OCS measurements from aircraft began in the late 1980s, using both *in situ* and flask collection with subsequent analysis by GC-MS (e.g. Bandy et al., 1992, 1993; Hoell et al., 1993; Thornton et al., 1996; Blake et al., 2008, etc). The airborne survey flight data are designed to sample background air at set locations on a regular basis over long time periods and are part of the NOAA ESRL GMD Carbon Cycle Aircraft Network (http://www.esrl.noaa.gov/gmd/ccgg/aircraft/index.html, an update of results published in Montzka et al., 2007). This data collection started in 1999 at a range of locations and have been used extensively in analysis of the continental US carbon budget (e.g. Campbell et al., 2008; Hilton et al., 2017). OCS has been measured at 10 globally distributed sites in the AGAGE network using the MEDUSA GC-MS. The data for the Jungfraujoch site is presented in Lejeune et al., (2017). Larger spatial scale/shorter time interval survey flights include the HIPPO (2009-2011) and ATom (2016-2018) airborne programs that predominantly sample OCS over remote marine locations. Atmospheric chemistry flights are designed to understand chemical processing and pollution transport and include sampling as part of pollution transport across the Pacific (e.g. Pacific Exploratory Mission-West A (PEM-A), Thornton et al., 1996) or Transport and Chemical Evolution over the Pacific experiment (TRACE-P), which sampled Asian outflow dominated by anthropogenic OCS emissions in 2001, (Blake et al., 2004). Other projects included sampling of OCS over continents (e.g. over the US in 2004; Blake et al., 2008).

OCS measurements have been made from tall towers using flasks and subsequent analysis by GC-MS. Most long-term tall tower observations have been conducted as part of the NOAA ESRL GMD Carbon Cycle Tower Network (Montzka et al., 2007). These data from 11-12 sites include continuous sampling from 2000 onward at a daily or twice daily time basis for most of the record.

4.4 Ecosystem-level data

Three approaches have been used to quantify ecosystem fluxes of OCS: chamber measurements, gradient measurements, and eddy flux covariance measurements. While researchers have been

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quantifying OCS measurements with chambers for decades, most field outings prior to 1990 used dynamic chambers with sulfur-free sweep air, artificially inducing high emissions (Castro and Galloway, 1991).

Measurements from towers have been made in a variety of ecosystems. An OCS analyzer capable of determining ambient OCS and CO_2 concentrations at 10 Hz is commercially available (Kooijmans et al., 2016; Commane et al., 2013; Stimler et al., 2010a) allowing for eddy flux covariance measurements (Asaf et al., 2013; Billesbach et al., 2014; Commane et al., 2015; Wehr et al., 2017). With this powerful new tool, traditional methods of partitioning carbon fluxes over ecosystems can be directly compared to using OCS data as a proxy for GPP in situ. A few studies have made use of the gradient method (Berresheim and Vulcan, 1992; Blonquist et al., 2011; Rastogi, et al, 2018).

4.5 Oceanic measurements

OCS measurements in the surface ocean comprise about 6,000 ship-based measurements. These samples are usually taken at a depth of 0–5m below the ocean surface and analyzed by gas chromatography with various detectors or off-axis integrated cavity output spectrometry. Table 3 gives an overview on available measurements. A central database for ship-based OCS measurements is desired to derive global patterns and facilitate model comparison. Measurements of the precursor gas CS_2 are scarcer than OCS measurements. Samples for CS_2 are taken usually in a similar way to OCS samples from the same depth range and analyzed using gas chromatography and mass-spectrometry detection.

4.6 Firn and ice core records

Different hydrolysis rates apply for OCS trapped in bubbly ice versus clathrate (bubble-free) ice. Some ice core material is not suitable for OCS analysis because the environment was too warm for long periods and OCS was hydrolyzed at high rates for thousands of years. Aydin et al. (2014, 2016) developed the necessary corrections to take into account OCS hydrolysis within the ice core bubbles. Corrected data is published for Taylor Dome, the West Antarctic Ice Sheet Divide, and Siple Dome

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(Aydin et al., 2016). Firn data is available for more recent time periods (Montzka et al., 2004, Sturges et al., 2001).

5 Conclusion

On the global scale, top-down estimates suggest a large missing source or overestimated sink of OCS. The available ocean water OCS measurements have not revealed a large enough OCS source to close the budget gap. This review concludes that the DMS source contribution for ocean OCS estimations should be considered only as a source of uncertainty until further experiments can be performed under conditions more similar to ambient air. Anthropogenic OCS estimates would benefit greatly from CS_2 and OCS observations from rayon factories, particularly in Asia. Unaccounted for domestic coal combustion in Asia may also play a significant role. To improve the robustness of the large plant sink estimate, observing OCS uptake in plants that are water or nutrient stressed may effect OCS exchange closer to the natural environment.

For regional scale studies, aircraft profiles or flux measurements could help substantially with the OCS budget. We will need to quantify soil OCS fluxes in periodically hot and dry regions. Boreal and Arctic regions must take into account OCS fluxes from freshwater as well as bryophytes. Studies in tall forests require a more in-depth treatment of canopy-dwelling organisms, such as mosses and lichen (Rastogi et al., 2018).

Our overall understanding of the elements of the budget are summarized in Table 6. Several types of observations are needed to link the observed ground fluxes and the atmospheric satellite data, for example, FTIR measurements and AirCore campaigns. Ground OCS observations can also be applied in regions where current satellite coverage is poor, such as the Tropics. Creating a global OCS data product and a coordinated tall tower network generating continuous, calibrated concentration data will provide the information we need to close the global OCS budget and create an OCS-based estimate of global GPP. Forwarding our process-based understanding with new observations will promote advancement in our understanding of global carbon feedbacks.

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Acknowledgements

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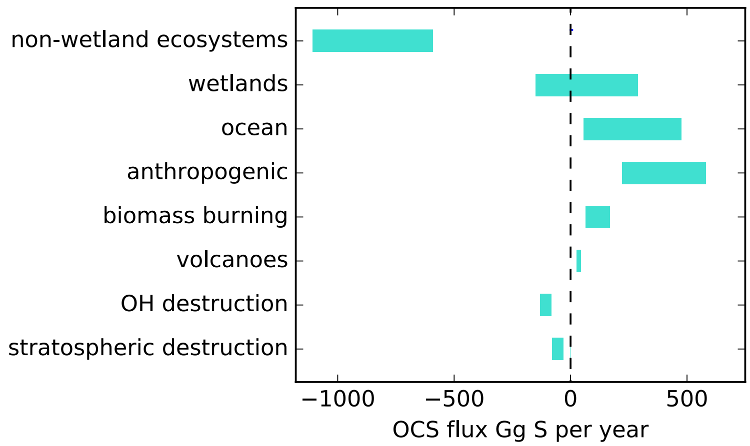
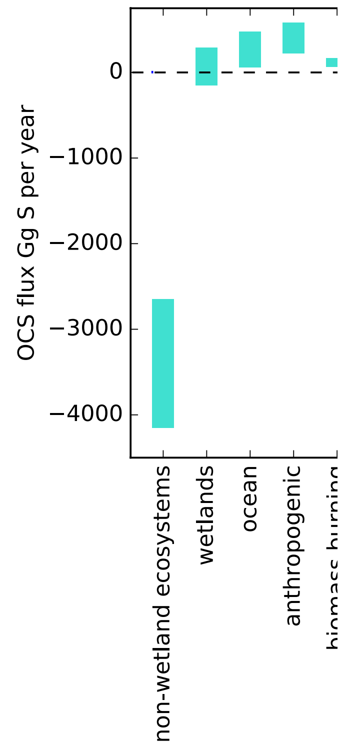


Figure 1. A bottom-up budget of atmospheric OCS on the global scale. Positive values indicate a source to the atmosphere. No attempt has been made to preserve mass balance. The contribution of lakes and non-vascular plants is included in the non-wetland ecosystem estimate.



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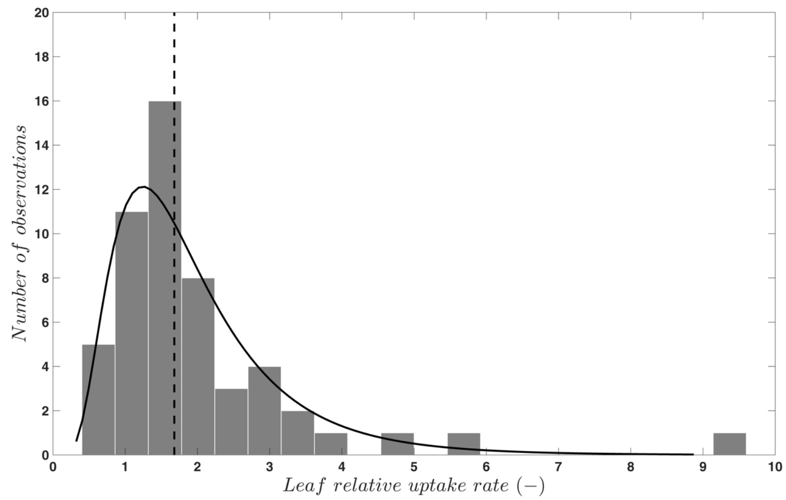

Figure 2. Frequency distribution (bars) and a log-normal fit (solid line) to published values (n = 53) of the leaf relative uptake rate of C3 species. The vertical line indicates the median (1.68). Published data are from Berkelhammer et al., (2014); Sandoval-Soto et al., (2005); Seibt et al., (2010); and Stimler et al., (2010b, 2011, 2012).

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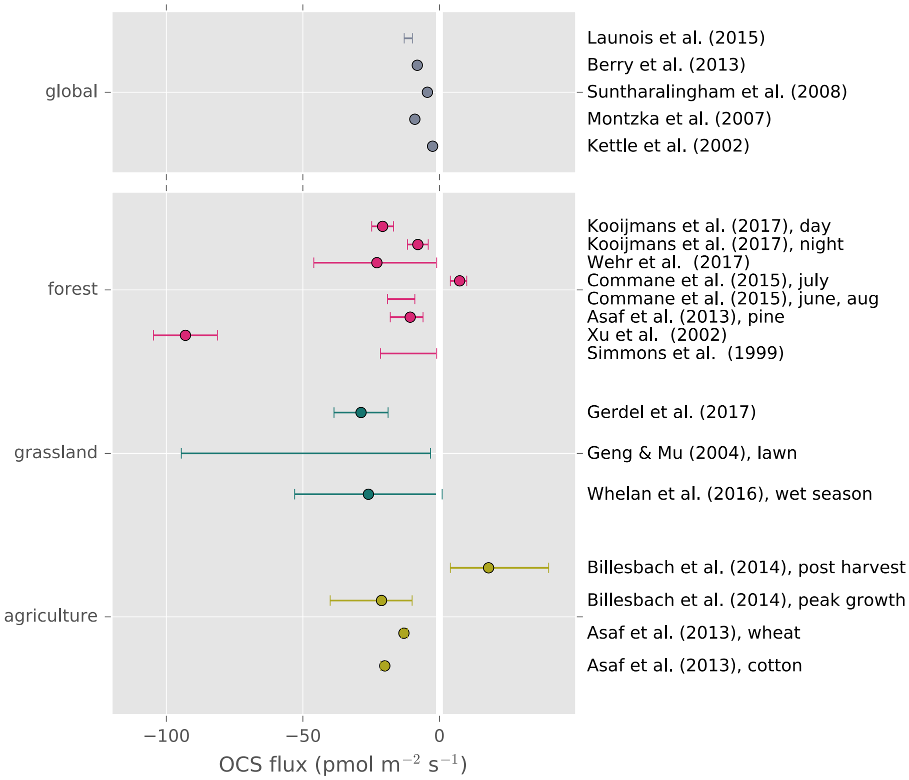
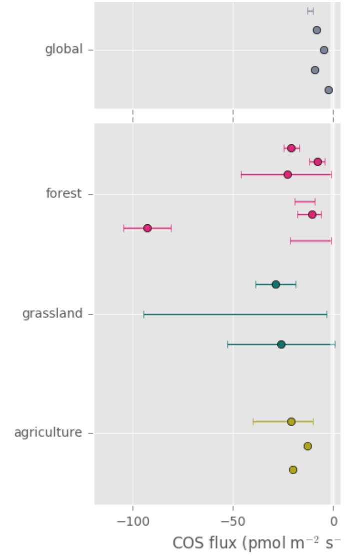


Figure 3. Top panel: Global average land OCS uptake from modeling studies. Bottom panel: reported averages and ranges of whole ecosystem, site-level OCS observations. Points represent reported averages, error bars show the uncertainty around the average, or the range of observed fluxes where no meaningful average was reported.



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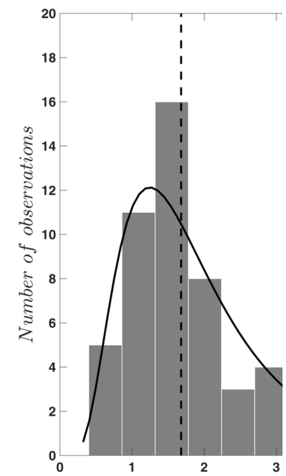

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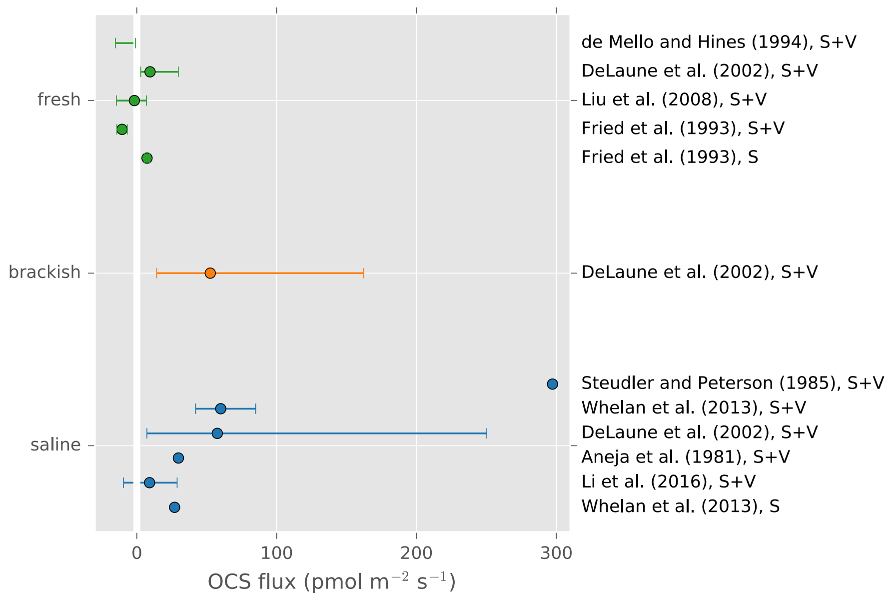
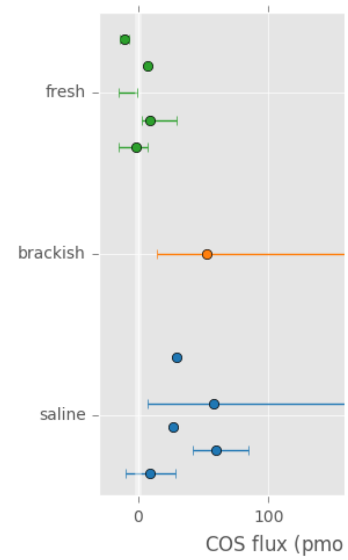


Figure 4. A summary figure for wetland OCS emissions. Lines indicate minimum to maximum ranges. Studies denoted "S" indicated a soil-only observation, and "S+V" denotes a soil and vegetation observation. Points show reported averages and error bars show either reported uncertainty or the full range of observations. Note that some earlier observations using sulfur-free air as chamber sweep air have been excluded due to overestimation (Castro and Galloway, 1991).



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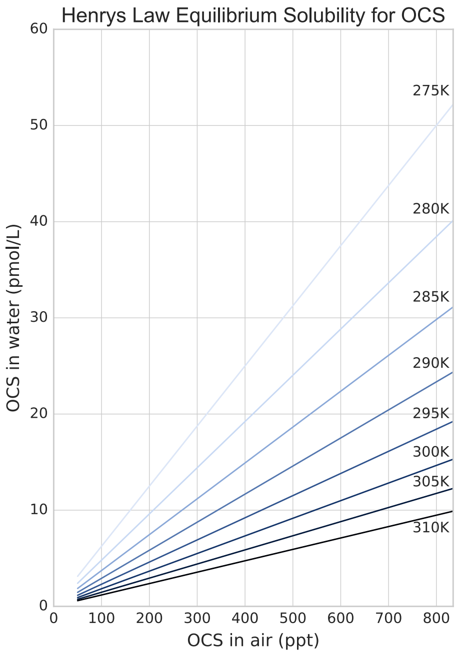
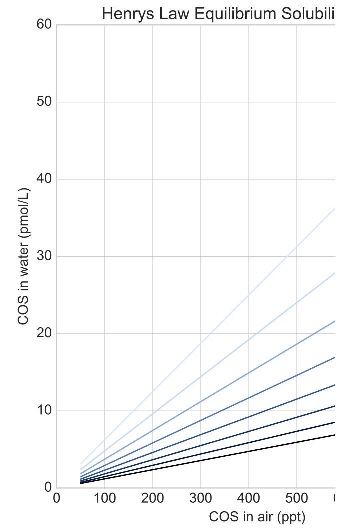


Figure 5. Solubility of OCS in water dependent on ambient OCS concentration and temperature as calculated in Sun et al., (2015).



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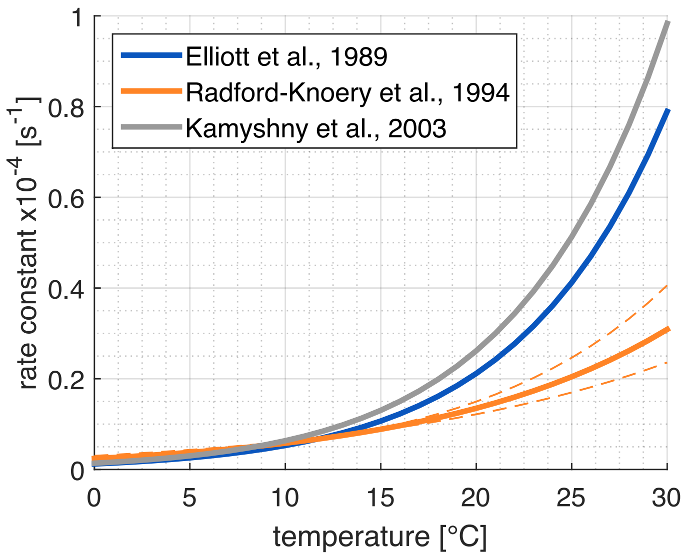

Figure 6. Comparison of published hydrolysis rates for OCS based on laboratory experiments with artificial water (Elliott et al., 1989; Kamyshny et al., 2003), and under oceanographic conditions using filtered seawater (Radford-Knoery et al., 1994). The graph is replotted using equations from original papers at a pH of 8.2.

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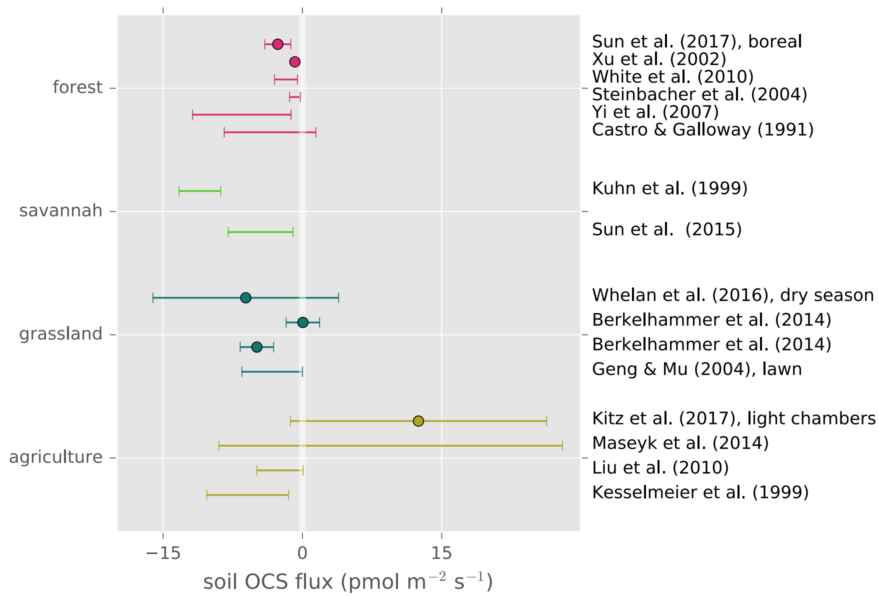
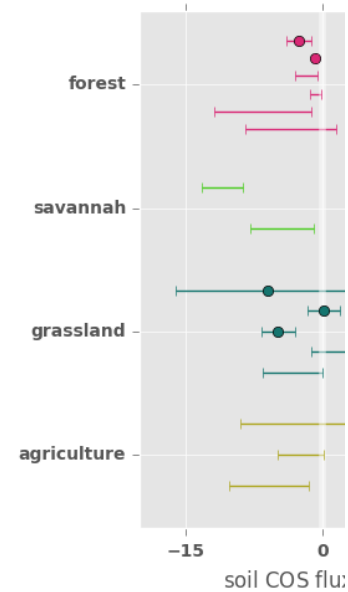


Figure 7. Field observations of soil OCS fluxes. Points are reported averages. Error bars are the reported range or the uncertainty of the average. Kuhn et al. (1999) represents an upper range due to under-pressurized soil chambers.



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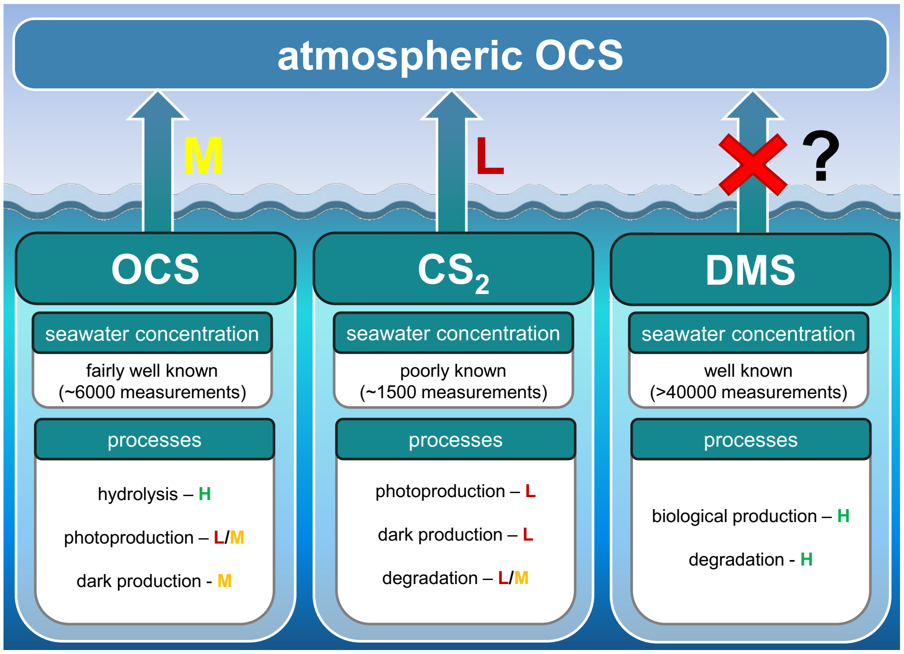
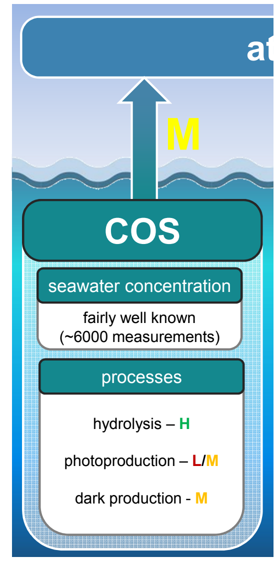


Level of understanding: H – high, M – medium, L - low

Figure 8. Marine contribution to the atmospheric OCS loading from direct and indirect (CS_2) emissions. The sea surface concentration determines the magnitude of the oceanic emissions, and the uncertainty in global emissions decreases with increasing numbers of measurements. The understanding of processes is important to extrapolate from small-scale observations to a regional or global scale and varies between a low level of understanding for CS_2 (i.e. few process studies available) to a medium level of understanding for OCS (i.e. several process studies available, but considerable spread in quantifications across different locations). We recommend reconsidering the contribution of oceanic DMS emissions.



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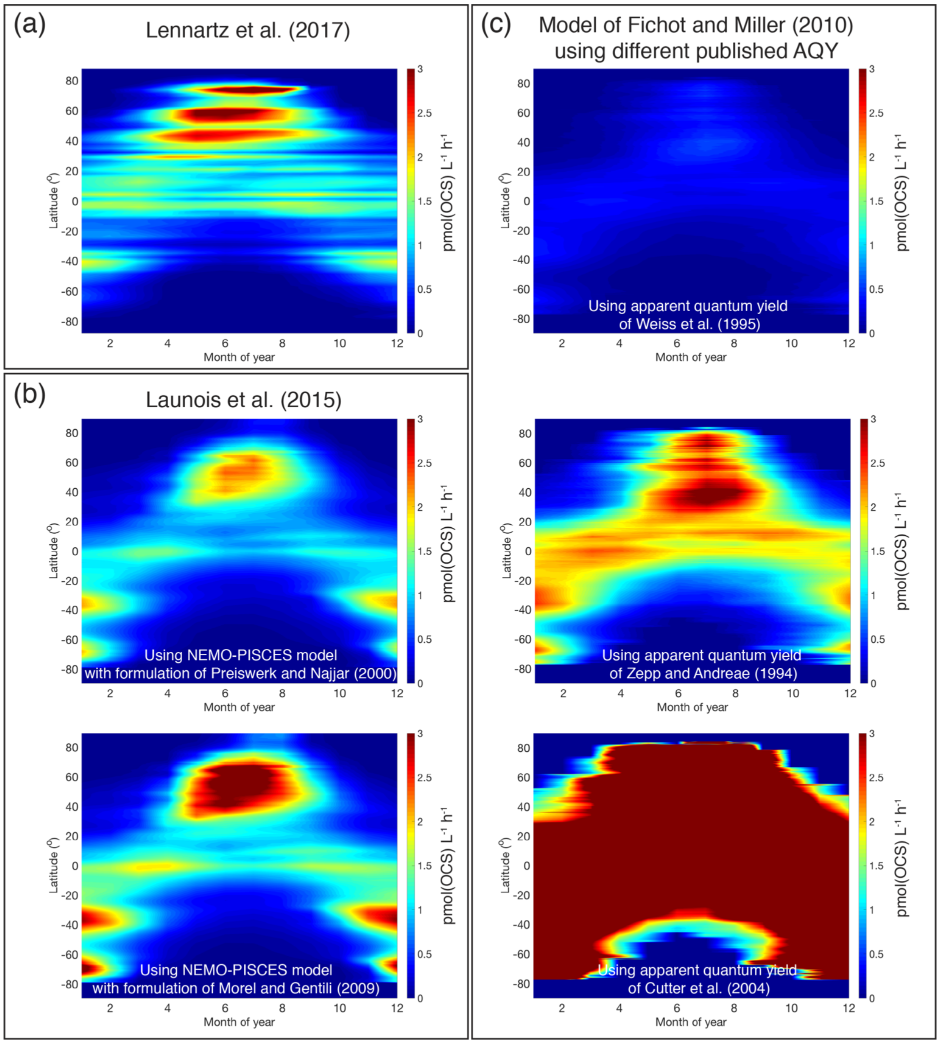
(a)
Lennartz et al. (2017)
(b)
Launois et al. (2015)
Using NEMO-PISCES model with formulation of Preiswerk and Najjar (2000)
Using NEMO-PISCES model with formulation of Morel and Gentili (2009)
(c)
Model of Fichot and Miller (2010) using different published AQY
Using apparent quantum yield of Weiss et al. (1995)
Using apparent quantum yield of Zepp and Andreae (1994)
Using apparent quantum yield of Cutter et al. (2004)
Latitude (°)
Month of year
pmol(OCS) L-1 h-1

Figure 9. Comparison of OCS photoproduction rates (averages for surface mixed layer, pmol(OCS) L^{-1} h^{-1}) modeled using different approaches and demonstrating discrepancies between methods: (a) Hovmöller (latitude-time) plot of rates calculated using the approach described in Lennartz et al. (2017). (b) Th same Hovmöller plot generated with the approach described in Launois et al. (2015) and two different formulations for CDOM absorption coefficients from Preiswerk and Najjar (2000) and Morel and Gentili (2004). (c) The same Hovmöller plots generated with the photochemical model of Fichot and Miller (2010) and the published spectral apparent quantum yields of Weiss et al. (1995), Zepp and Andreae (1994), and Cutter et al. (2004).

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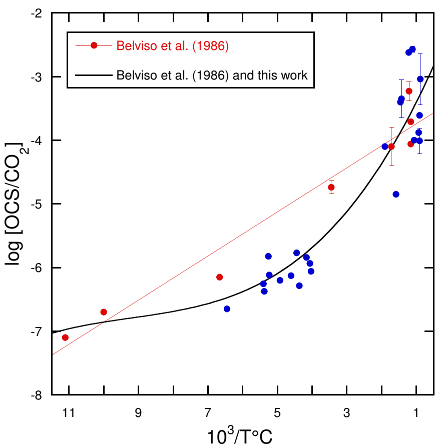
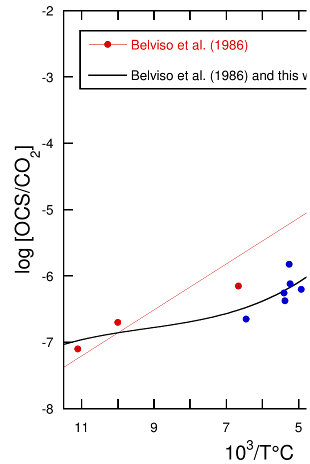


Figure 10. Decimal logarithm of the OCS/CO_2 ratios plotted against the reciprocal of the emission temperature of the gases for volcanos. The red dots refer to the analytical data published by Belviso et al. (1986) and the red line corresponds to the linear model used in that study to evaluate the volcanic contribution to the atmospheric OCS budget. The blue dots refer to measurements published by others since 1986 (Chiodini et al., 1991; Notsu and Toshiya, 2010; Sawyer et al., 2008; Symonds et al., 1992). The better fit through all measurements is obtained using a polynomial of the third order (R^2 = 0.89, n = 31).



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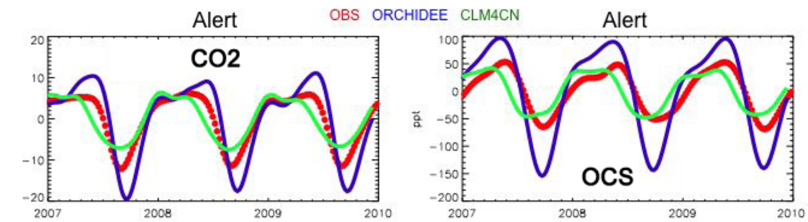
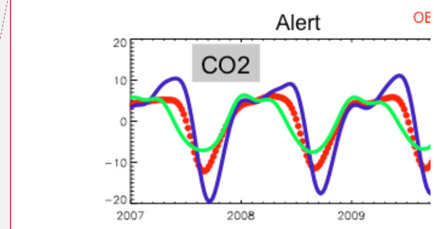


Figure 11. Smoothed seasonal cycles of OCS (right) and CO_2 (left) monthly mean mixing ratios, simulated at Alert station, Canada, obtained after removing the annual trends. Simulations are obtained with the LMDz transport model using two flux scenarios for the vegetation uptake of OCS, calculated with the GPP of ORCHIDEE and CLM4CN models; the other OCS flux components are identical (see Launois et al. (2015)). Observations (red) are from the NOAA-ESRL global monitoring network (Montzka et al., 2007) averaged from 2007 to 2010.



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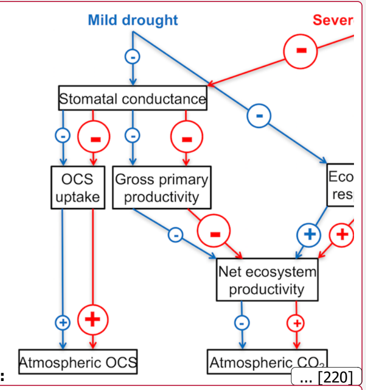

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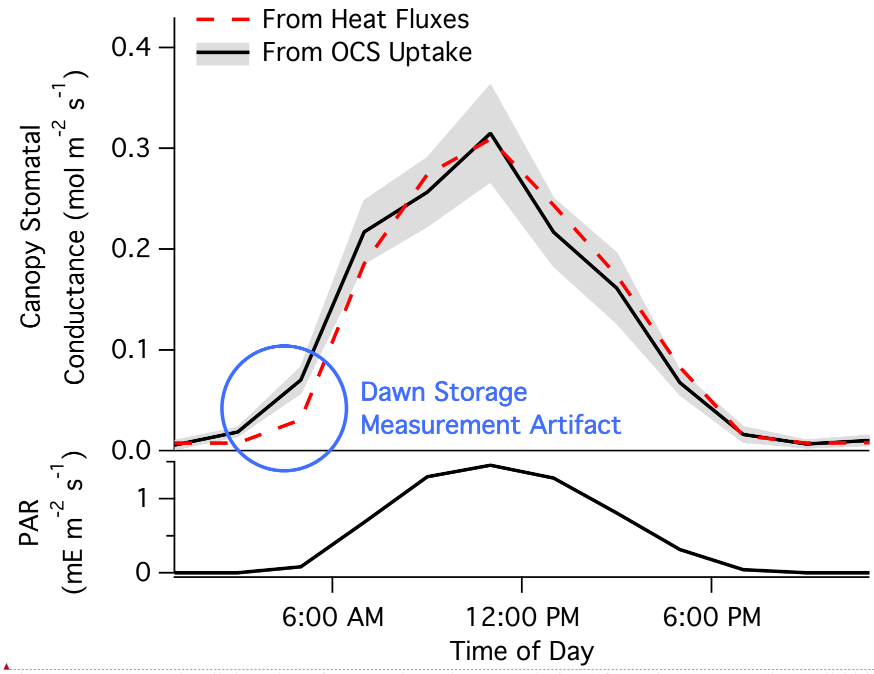

Figure 12. Composite diel cycles of stomatal conductance derived from the OCS uptake (solid black line with grey bands) and from the sensible and latent heat fluxes (red dashed line), along with photosynthetically active radiation (PAR, bottom panel) for context, including May through October of 2012 and 2013. Lines connect the mean values of each 2 h bin. The grey bands depict standard errors in the means as estimated from the variability within each bin. Adapted from Wehr et al. (2017), which discusses the dawn storage measurement artifact indicated here by the blue circle.

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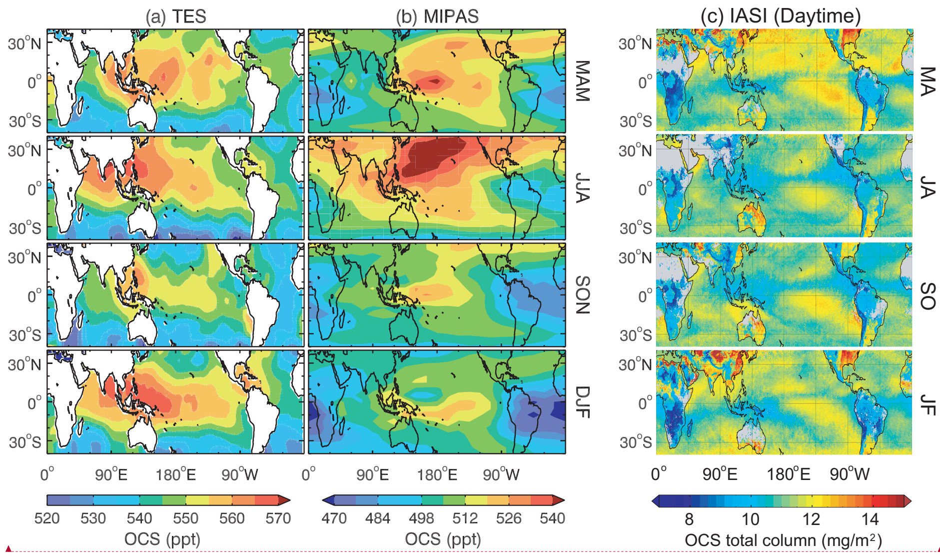

Figure 13. Comparisons of the seasonal horizontal distribution of OCS retrievals. (a) TES averaged between 200–900 hPa, obtained using TES Level-2 swath OCS retrievals in 2006, averaged over four seasons (March to May, June to August, September to November, and December to February). (b) MIPAS (250 hPa), using MIPAS Level-2 swath retrievals from 2002 to 2011. The data in (a) and (b) have been averaged to the same 5° longitude × 4° latitude grid boxes and have been smoothed to a 20°×20° spatial resolution. (c) Two month averages of IASI daytime OCS total column retrievals from 2014 with resolution 0.5° × 0.5°, extracted from Vincent and Dudhia (2017). Missing data are represented by white areas in panels (a) and (b) and by gray areas in panel (c).

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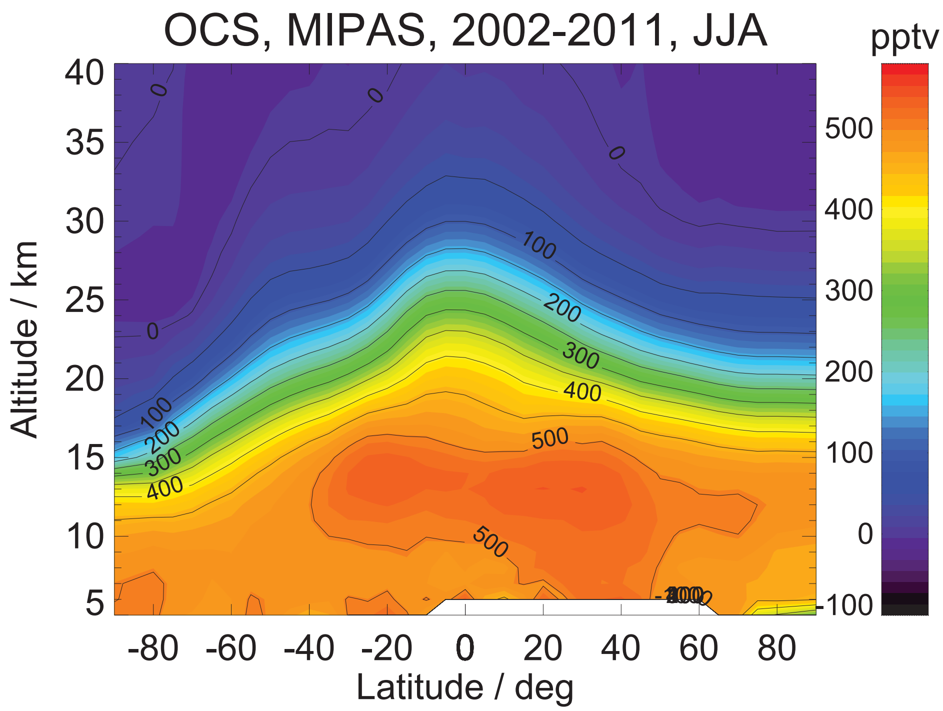

Figure 14. Latitudinal distribution of OCS, observed by MIPAS. Extracted from Glatthor et al. (2017).

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Table 1. In situ fluxes of forest ecosystems. Some of this data is plotted in Fig. 2.

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Cover; Location	Time	Reported fluxes (OCS pmol m^{-2} s^{-1})	Reference
Quercus, *Acer*; Harvard Forest, Massachusetts, USA	Jan–Dec 2011, May–Oct 2012,	Near 0 in winter and at night to ~-50 at peak leaf area and light. Anomalous emissions in summer found in the 2015 study were not	Wehr et al., (2017) and Commane et al., (2015)

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	May–Oct 2013	observed during subsequent summers.	
Populous, *Pinus*; Niwot Ridge, Colorado, USA	Aug 13–18, 2012	Leaf chamber flux near 0 at night to a peak at ~-50; soil flux between 0 and -7.	Berkelhammer et al., (2014)
Picea; Solling Mountains, Germany;	summer, fall, 1997–1999	Relaxed eddy accumulation, -93±11.7 uptake; large night time emissions	Xu et al., (2002)
Pinus; 3 sites Israel	growing season 2012	Eddy flux covariance, at 3 pine forests on a precipitation gradient, daylight averages were -22.9±23.5, -33.8±33.1, and -27.8±38.6.	Asaf et al., (2013)
Pinus; Boreal forest, Hyytiälä, Finland;	June-November 2015	Nighttime fluxes -6.8 ± 2.2 (radon-tracer method) and -7.9 ± 3.8 (eddy covariance), daytime fluxes -20.8 (eddy covariance).	Kooijmans et al., (2017)

Table 2. OCS concentrations observed in rivers and lakes compared to ocean observations in Lennartz et al. (2017).

Cover; Location	OCS concentration	Reference
lake, surface, Canada	1.1 nmol L^{-1}	Richards et al. (1991)
lake, surface, China	910 ± 73 pmol L^{-1}	Du et al. (2017)
river, 0.25 m depth	636 ± 14 pmol L^{-1}	Radford-Knoery and Cutter (1993)
river, 3.84 m depth	415 ± 13 pmol L^{-1}	Radford-Knoery and Cutter (1993)
lake, whole water column, Canada	90 to 600 pmol L^{-1}	Richards et al. (1991)
lake, hypolimnion, Antarctica	233 to 316 pmol L^{-1}	Deprez et al. (1986)
Eastern Pacific Ocean	28.3 ± 19.7 pmol L^{-1}	Lennartz et al. (2017)
Indian Ocean	9.1 ± 3.5 pmol L^{-1}	Lennartz et al. (2017)
lake, hypolimnion, Switzerland	detected “occasionally”	Fritz and Bachofen (2000)

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Table 3. Measurements of OCS water concentration at the ocean surface (0–5 m) in open ocean, coastal, shelf, and estuary waters. [a]Converted from ng L^{-1} with a molar mass of OCS of 60.07g. [b]Converted from ng S L^{-1} with a molar mass of S of 32.1g. [c]Continuous measurements.

Region	Time	Water concentration of OCS mean ±SD (pmol L^{-1})	No. of samples	References
Open Ocean				
Indian Ocean	Mar/May 1986 Jul 1987	19.9 ±0.5[a] 19.9 ±1.0[a]	20 14	Mihalopoulos et al. (1992)
Southern Ocean	Nov–Dec 1990	109[b]	126	Staubes and Georgii (1993)
North Atlantic Ocean	Apr/May 1992 Jan 1994 Sep 1994	14.9 ±6.9 5.3 ±1.6 19.0 ±8.3	118 120 235	Ulshöfer et al. (1995)
Northeastern Atlantic	Jan 1994	6.7 (4–11)	120	Flöck and Andreae (1996)
Western Atlantic	Mar 1995	8.1 ±7.0	323	Ulshöfer and Andreae (1998)
Northeastern Atlantic Ocean	Jun/Jul 1997	23.6 ±16.0	940	Von Hobe et al. (1999)
Atlantic (meridional transect)	Aug 1999	21.7 ±19.1	783	Kettle et al. (2001)
North Atlantic	Aug 1999	8.6 ±2.8	518	Von Hobe et al. (2001)
Atlantic (meridional transect)	Oct/Nov 1997 May/Jun 1998	14.8 ±11.4 18.1 ±16.1	306 440	Xu et al. (2001)
Indian Ocean	Jul/Aug 2014	9.1 ±3.5	[c]	Lennartz et al. (2017)

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Coastal, shelf, and estuary waters				
Western North Atlantic	Jun/Jul 1990			Cutter et al.
Shelf	Aug 1990	400	15	(1993)
Estuary		300–12,100	?	
Indian Ocean, Mediterranean Sea, French Atlantic Coast	Dec 1989-1990	400–70,300	336	Mihalopoulos et al. (1992)
	May 1987			
averages of several cruises (shelf+coast)	averages of several cruises	112	157	Andreae and Ferek (1992)
Mediterranean Sea (shelf)	Jul 1993	43 ±24	34	Ulshöfer et al. (1996)
North Sea (shelf)	Sep 1992	49.1 ±11.7	69	Uher et al. (1997)
Chesapeake Bay (coast)	Oct 1991–May 1994	320.0 ±351	23	Zhang et al. (1998)
Eastern tropical South Pacific (shelf)	Oct 2015	40.5 ±16.4	[c]	Lennartz et al. (2017)

Table 4. Total bottom-up atmospheric OCS budget.

Component	OCS global flux Gg S $year^{-1}$	Data source
Forests	-430 – -370	
Grasslands	-500 – -200	
Deserts	-24 (?)	No field data exists for deserts.
Agricultural, excluding rice	-150 – +13	
Freshwater	+0.8 – +12	
Fungus/Lichen/Mosses	-21 – -8	
Wetlands	-150 – +290	
Ocean	Total: +265 ±210 OCS direct: +130 ± 80 OCS from oc. CS_2: +135 ±130 OCS from oc. DMS: 0 (+80)	Lennartz et al., (2017), see Sect. 2.3
Anthropogenic	+400 ± 180	For the year 2012, Zumkehr et al., (2018)
Biomass Burning	+116 ± 52	Campbell et al., (2015)
Volcanoes	+25 – +43	
Tropospheric destruction by OH radical	-130 – -82	Berry et al., (2013), Kettle et al., (2002) and Watts (2000)
Stratospheric destruction by photolysis	-80 – -30 or -50 ± 15	Barkley et al., (2008), Chin and Davis (1995), Crutzen (1976), Engel and Schmidt (1994), Krysztofiak et al., (2015), Turco et al., (1980), and Weisenstein et al., (1997)
Remains in the atmosphere	2 – 5	
Total Range	-1100 – +900	

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Table 5. GPP and OCS exchange estimates by biome.

[a]For the purpose of this estimate, we use the soil fluxes from temperate forests.

[b]Range of values from Castro and Galloway (1991), Steinbacher et al., (2004), White et al. (2010), and Yi et al. (2007).

[c]The average reported here is the average and one standard deviation from non-vegetated plots in a boreal forest, defined as plots having less than 10% vegetation cover (Simmons, 1999).

[d]Range from Whelan and Rhew (2016). The error estimate here is different from the one reported because a different LRU was used. Kitz et al. (2017) found soil-only OCS production of +60 pmol m^{-2} s^{-1} in an alpine grassland.

[e]In a laboratory incubation study, Whelan et al. (2016) found that desert soils exhibit a very small uptake. No field measurements have been published to our knowledge.

[f]The smaller production is from De Mello and Hines (1994). The larger production is an average estimate from Fried et al. (1993).

[g]Post-harvest soil exchange estimate from the wheat field (Billesbach et al., 2014) investigated further in Whelan and Rhew (2015).

[h]See Table 1.

[i]From Simmons et al. (1999).

[j]Range from Whelan and Rhew (2016), encompassing observations of a grass field by Yi and Wang (2011).

[k]Range reported in DeMello and Hines (1994), encompassing values observed by a bog microcosm by Fried et al. (1993).

[l]High value for cotton, low value for wheat in Asaf et al. (2013). Daily fluxes for a wheat field investigated by Billesbach et al. (2014) were -21 during the growing season and +18 after harvest. Agricultural soils have been shown to emit a large portion of OCS compared to plant uptake under hot and dry conditions (Whelan et al., 2016; Whelan and Rhew, 2015).

Biome	GPP estimated by Beer et al. (2010) in Pg C y^{-1}	Biome area (10^9 ha)	Anticipated F_{OCS}, plants from GPP estimate (pmol m^{-2} s^{-1})	F_{OCS}, soil (pmol m^{-2} s^{-1})	F_{OCS}, ecosystem By GPP method (pmol m^{-2} s^{-1})	F_{OCS}, ecosystem Field observations (pmol m^{-2} s^{-1})

Tropical forests	40.8	1.75	-75	No data[a]	-83 - -73	No data
Temperate forests	9.9	1.04	-30	-8 to 1.45[b]	-38 - -29	~0 to 93[h]
Boreal forests	8.3	1.37	-19	1.2 to 3.8[c]	-18 - -16	0 to -22[i]
Tropical savannas and grasslands	31.3	2.76	-36	No data	-61 - -29	No data
Temperate grasslands and shrublands	8.5	1.78	-15	-25 to 7.3[d]	-40 - -8	-26 growing season; +6.1 non-growing season[j]
Deserts	6.4	2.77	-7	0 (?)[e]	-7 (?)	No data
Tundra	1.6	0.56	-9	5.27 to 27.6[f]	-4 - 18	-15 to -1[k]
Croplands	14.8	1.35	-35	-18 to 40[g]	-53 - 5	-22 to -16, +18 during non-growing season[l]
Total	121.7	13.38				

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Table 6. Components of the OCS budget and data gaps.

Component	Notes	Critical Data Gaps
Vascular plant leaves	Vascular plant leaves have a well-established exchange of OCS that follows stomatal conductance. OCS is destroyed by both RuBisCO and CA in plant leaves, though it most often encounters CA first. The point of destruction is different for OCS and CO_2, though the correlation between their uptakes is consistent under high light conditions.	Nocturnal uptake and role of phyllosphere is not well characterised and "mesophyll" conductance to COS is not well constrained
Non-vascular plants and lichen	Few studies have addressed non-vascular plants. Bryophytes and lichen have been found to take up OCS depending on their water content, sometimes regardless of light level.	Activities to support scaling up OCS fluxes for non-vascular plants are needed for the assessment of their importance to ecosystem fluxes
Soil	Most soils are generally small sinks of OCS, making up less than 10% of the total ecosystem flux Non-desert soils exhibit large OCS emissions under hot and dry conditions. These OCS-emitting soils include both agricultural soils and some uncultivated soils.	It is unknown what controls the magnitude of the soil source term.
Terrestrial ecosystem	Ecosystem-scale flux measurements are available only from a handful of studies on a limited number of ecosystems and during relatively short periods of time.	No studies from the tropics and only one study in boreal forests have been published.
Regional terrestrial	The highly mechanistic leaf-enzyme kinetic approach to modeling plant-atmospheric OCS exchange yielded similar results to the mechanistically simple LRU approach when focusing on the peak of the North American growing season. However, laboratory studies demonstrate that LRU is not constant.	The minimum spatial and temporal scales at which the constant LRU approximation is viable are unknown. Uncertainties in non-plant OCS fluxes, particularly from soils, remain under-constrained at regional spatial scales.
Surface ocean	While the surface ocean is generally thought to be a source of OCS to the atmosphere, surface measurements of OCS are relatively sparse.	More continuous measurements covering full diurnal cycles are needed especially for the Pacific, Indian, Southern, and Arctic oceans.

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Deep ocean	Concentration profiles have been reported from only very few stations in the Atlantic Ocean (e.g. Cutter et al., 2004; Flöck and Andreae, 1996; Von Hobe et al., 2001). Understanding deeper ocean OCS production could allow us to model OCS ocean surface fluxes more accurately.	More data is necessary to make clear predictions of the relationship between deep and surface ocean OCS fluxes.
Regional ocean	Surface measurements comprise different oceanic regimes including several meridional Atlantic transects and oligotrophic and upwelling regions.	Especially, data from the Arctic and Southern oceans are missing.
Freshwaters	There are few, quite small datasets of OCS concentrations in lakes and rivers.	No OCS fluxes from freshwater bodies currently exist.
Global, modern	Global satellite products currently lack coverage over the land, and the location of TCCON sites are purposely chosen to observe atmospheric background.	A new satellite and data product would be necessary to distinguish surface fluxes, e.g. anthropogenic and ocean OCS sources
Global, paleo	Recent advances have allowed better interpretation of OCS in firn and ice air. There are still only a handful of cores that have been analyzed for OCS.	OCS observations from ice cores in the Northern Hemisphere are critical to GPP interpolar comparisons

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Although OCS has been studied mostly as a proxy for photosynthesis, OCS uptake by vegetation is actually governed mechanistically by (i) the series of diffusive conductances of OCS into the leaf, and (ii) the reaction rate coefficient for OCS destruction by CA (Wohlfahrt et al., 2012). CA is present both in plant leaves and soils, although soil uptake tends to be proportionally much lower than plant uptake. Over soils, OCS uptake provides information about CA activities within diverse microbial communities. OCS uptake over plants integrates information about the sequential components of the diffusive conductance (the leaf boundary layer, stomatal, and mesophyll conductances) and about CA activity, all important aspects of plant and ecosystem function. Stomatal conductance in particular is a prominent research focus in its own right, as it couples the carbon and water cycles via transpiration and photosynthesis.

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Our understanding of the OCS balance in the atmosphere has evolved as new observations have become available. The major atmosphere-based sinks of OCS are reaction within the troposphere and photolysis in the stratosphere.

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Spatial and temporal trends of atmospheric OCS variations also reflect changes of OCS fluxes, including the oceanic and anthropogenic sources, and the biospheric sink.

The spatial and temporal variations in

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.The global atmospheric flask sampling network described in

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has served as a basis for understanding the distribution and seasonality of OCS concentrations in both hemispheres at Earth's surface and, from regular aircraft profiles, through much of the troposphere over North America.

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These lines of evidence all support the notion that OCS is primarily removed from the atmosphere via terrestrial plants during the growing season.

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. Within the accuracy of those measurements there was no significant trend detected in stratospheric OCS until 2005. Updates of these records, reanalyzed with methods to increase accuracy (Kremser et al., 2015; Lejeune et al., 2017) do suggest a trend in OCS columns.

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Smaller datasets of OCS vertical profiles could be used to validate these broader trends, e.g. Kato et al. (2011).

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The generally smaller trends in the stratosphere indicate that the trends are driven by processes within the troposphere (Lejeune et al., 2017). Campbell et al. (2015) presented an inventory of anthropogenic CS_2 (rayon industry) and OCS emissions. The OCS trends observed with FTIR column measurements show close resemblance with global rayon production, which decreased until 1990, then stayed mostly constant until 2002 and increased after that.

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With the commercially available quantum cascade laser spectrometer (Commane et al., 2013; Kooijmans et al., 2016; Stimler et al., 2010a), continuous atmospheric concentration measurements of OCS allow for regional source and sink studies (Belviso et al., 2016;

Kooijmans et al., 2016). In situ vertical profile measurements of OCS have been obtained in the altitude range from 14 to 30 km at tropical and polar latitudes using the SPIRALE, a tunable diode laser spectrometer (Krysztofiak et al., 2015). The uncertainty of the in situ OCS measurements increases with decreasing pressures (higher altitude), ranging from 3.3% below 18 km to more than 30% above 26 km. As more data become available, the OCS budget will become better understood, clarifying the in situ tropospheric and stratospheric sinks for OCS.

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Uptake by land plants is thought to represent the most important sink for OCS, estimated to account for 50–82% of the global sink strength, followed by soil (Launois et al., 2015b, and references therein). The yearly average net land flux rate in recent modeling studies of global budgets (i.e. plant and soil uptake minus soil emissions) ranges from -2.5 to -12.9 pmol m^{-2} s^{-1} (Fig. 2). Relative to the many published site-level studies, this is a small range (Fig. 2). The available observations are limited in time and do not cover tropical ecosystems, which contribute almost 60% of global GPP (Beer et al., 2010). The only study reporting year-round OCS flux measurements is from a mixed temperate forest, which was a sink for OCS with a net flux of -4.7 pmol m^{-2} s^{-1} during the observation period (Commane et al., 2015). Daily average OCS fluxes during the peak growing season are available from a larger selection of studies and cover the range from -8 to -23 pmol m-2 s-1, excluding Xu et al., (2002) which found a surprisingly high uptake (–97 ± 11.7 pmol m^{-2} s^{-1}) from the relaxed eddy accumulation method (Fig. 2).

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F_{CO2} is often equated with GPP, however photorespiration in C_3 plants confuses the matter (Wohlfahrt and Gu, 2015).

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Relatively little is known regarding CA activity (Wehr et al., 2017), while changes in stomatal and leaf internal conductances in response to environmental stresses are well known (e.g. Brilli et al., 2011).

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More year-round measurements from a larger number of biomes, in particular those presently underrepresented, are required to provide reliable bottom-up estimates of the total net land OCS flux (see Fig. 1).

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, whether reflective of differences in environmental conditions or differences between plant species (e.g. in leaf internal conductance for OCS or in carbonic anhydrase activity), are still poorly understood and

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, while changes in stomatal and leaf internal conductances in response to environmental stresses are well known (e.g. Brilli et al., 2011)

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Grasslands cover ~20% of the terrestrial surface and store ~30% of the world's soil carbon (Hungate et al., 1997; Scurlock and Hall, 1998). Although grasslands store less carbon per area than forests, they are more ubiquitous and contain a larger portion of the terrestrial carbon pool (Parton et al., 1995). Grasslands generally are considered to behave as carbon sinks or be carbon-neutral but appear highly sensitive to drought and heat waves and can rapidly shift from neutrality to a carbon source (Hoover and Rogers, 2016). Studies on the response of grasslands to elevated CO_2 suggest that the sink strength temporarily increases. Because much of this carbon is stored as labile pools, it is unclear whether the effect has long-term consequences (Hungate et al., 1997). The lability of these pools and their dynamics are difficult to study and point to important uncertainties and challenges in projecting the role these ecosystems will play in a changing carbon cycle. Existing work highlights the need for additional studies on primary productivity in grassland ecosystems, which could be addressed with OCS observations.

Studies of OCS exchange in native or restored grasslands have been limited (see Fig. 2).

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In an early field-based study on the topic, Mihalopoulos et al. (1989) noted uptake of OCS when winds passed over a coastal grassland in northwestern France. More recently,

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Individual flux estimates ranged from -75 pmol m^{-2} s^{-1} to +7 pmol m^{-2} s^{-1}, indicating a wide range of possible fluxes. During the dry season, simulated rain led to a reduced sink or an increased source.

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While this study did not separate soil and plant components of the flux, l

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used transparent chambers over a temperate grassland soil with plants removed. This study found high production of OCS (up to 60 pmol m^{-2} s^{-1}) and revealed the dominant influence of radiation, as opposed to moisture, on the soil flux. Although positive fluxes from grassland soils have been noted elsewhere with both opaque and transparent chambers (Berkelhammer et al., 2014; Maseyk et al., 2014; Whelan and Rhew, 2016), the magnitude of the OCS emissions from bare soils significantly exceeded measurements made elsewhere. Kitz et al. (2017)

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Existing studies suggest a pressing need to understand how soil OCS fluxes evolve in grasslands during seasonal changes in leaf area index (i.e. changes in surface exposure to radiation).

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This would involve sustained chamber measurements as well as total ecosystem flux measurements. An issue that has not been addressed in previous work, but is critical, is that g

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(see Sect. 2.1 introduction) and are expected to have unique ecosystem relative uptake (ERU) values. Therefore, with seasonal variations in climate, there will be changes in photosynthetic pathways and the relative rate that plants uptake OCS and CO_2

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2.2.2 Forests

Forests mediate land-atmosphere fluxes of carbon and water (Alkama and Cescatti, 2016) and how forests will respond to climate change is an area of active debate (Metcalfe et al., 2017). OCS has the potential to overcome many difficulties in studying the carbon balance of forest ecosystems. To make flux measurements using eddy flux covariance or vertical concentration gradients, tall forest canopies require even taller towers. To partition carbon fluxes, respiration is often quantified at night when photosynthesis has ceased and turbulent airflow is reduced (Reichstein et al., 2005). This method has important uncertainties, e.g. less respiration happens during the day than at night (Wehr et al., 2016). Partitioning with OCS is based on daytime data and does not rely on modeling respiration with limited nighttime flux measurements and associated uncertainty.

As expected, forests are daytime net sinks for atmospheric OCS when photosynthesis is occurring in the canopy (Table 1). While the relative uptake of OCS to CO_2 by leaves appears to be stable in high light conditions, the ratio changes in low light when the net CO_2 uptake is reduced (Stimler et al., 2011; Wehr et al., 2017). Forest soil interaction with OCS has been found to be small (Castro and Galloway, 1991; Steinbacher et al., 2004; White et al., 2010; Xu et al., 2002; Yi et al., 2007) and straightforward to correct (Wehr et al., 2017). Sun et al. (2016) noted that litter was the most important component of soil OCS flux in an oak woodland, composing up to 90% of the small surface sink. Otherwise, forest ecosystem OCS uptake appears to be dominated by tree leaves, both during the day and at night (Kooijmans et al., 2017).

The OCS tracer approach is particularly useful in high humidity or foggy environments like the tropics, where traditional estimates of carbon uptake variables via water vapor exchange are ineffective (Campbell et al., 2017b). So far, all forest OCS investigations on the ecosystem scale have been in the temperate and boreal zones. There are no published studies from the tropical latitudes, though some studies are underway. The application of the OCS tracer in tall canopies poses difficulties because turbulence can be limited in canopies and complicate many traditional methods of trace gas flux measurements (Blonquist et al., 2011; Kooijmans et al., 2017). A possible solution is using the "surface renewal" approach (Paw U et al., 1995), but it has not been attempted for OCS. Regional scale modeling with OCS appears to sidestep site-level problems, as in Hilton et al., (2017). With more OCS observing towers upstream and downstream of large forested areas, OCS may be able to resolve the daily or weekly carbon uptake by forest ecosystems, a large and crucial component in understanding future climate-carbon feedbacks.

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The contribution of soils to the atmospheric budget of OCS has been studied for a few decades in both the field and the laboratory. The soil–atmosphere exchange of OCS has been measured in a range of environments, and these m

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Soil redox potential is an indicator of soil oxidation-reduction status and is positively related to oxygen content in the soil column (Patrick and DeLaune, 1977).

OCS exchange rates in wetland soils may

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If OCS produced by microbes accumulates in isolated soil pore spaces during inundation, subsequent ventilation can lead to abrupt release of OCS, which may appear as high variability in surface OCS emissions. However, the interaction between production and transport processes in driving OCS exchange variability remains poorly understood. Known abiotic contributions, e.g. the role of solubility, are detailed in Sect. 2.3.3 Abiotic processes.

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Recent field and laboratory studies have shown that OCS production is also occurring in oxic soils. Substantial OCS production has been observed in a temperate grassland under both wet and dry conditions (Kitz et al., 2017) and in a wheat field under dry conditions (Maseyk et al., 2014). Related strongly to temperature (Maseyk et al., 2014) and radiation (Kitz et al., 2017), OCS fluxes of up to +30 and +60 pmol m^{-2} s^{-1} were Related strongly to temperature (Maseyk et al., 2014) and radiation (Kitz et al., 2017),observed in the wheat field and grassland, respectively. These production rates are similar, or even exceed, those seen in waterlogged environments. OCS fluxes from rice paddies were ca. +10 pmol m^{-2} s^{-1}, but sometimes exceeded +40 pmol m^{-2} s^{-1} (Kanda et al., 1992; Yi et al., 2008), and from vegetated salt marshes are +40–+120 pmol m^{-2} s^{-1} (Aneja et al., 1981; Whelan et al., 2013). However, saline wetlands cover a small portion of the Earth's surface (roughly 10^4 km^2) whereas agricultural areas are widespread (more than 10^7 km^2).

Soil OCS production has been investigated through laboratory incubations [MW1](Bunk et al., 2017; Whelan et al., 2016; Whelan and Rhew, 2015), revealing that most soils experience abiotic OCS emissions. Whelan et al. (2016) measured OCS soil fluxes from six disparate study sites: Soils from a temperate forest, a tropical forest, a savannah, and two agricultural fields > 800 km apart all exhibited net OCS emissions under hot and dry conditions. Desert soil samples generated no emissions and only small OCS uptake. Whelan and Rhew (2015) compared sterilized to living soil samples from the agricultural study site originally investigated in Maseyk et al. (2014), finding that all samples emitted considerable amounts of OCS under high ambient temperature and radiation, with even higher emissions after sterilization. Recently, Bunk et al. (2017) showed that net OCS emissions can occur from agricultural soils at all water contents.

The recent evidence of soil OCS emissions led Launois et al. (2015b) to include an emissions term in their soil flux estimates by upscaling biome-specific emissions. For global fluxes, Launois et al. (2015b) used ranges typically measured for anoxic soil emissions reported by Whelan et al. (2013), which had dependencies on temperature and flooded state. Using a map of estimated anoxic soils used for methane emission estimates (Wania et al., 2010), OCS production was assessed and allowed to vary by ±30% in optimization. Typically, peatlands were probable net emitters of OCS, with a mean value of 25 pmol m^{-2} s^{-1}. Some ecosystems, such as rice paddies, shift from a net source to net sink depending on the flooding state of the soil. Because the reported range of fluxes was centered on 0, Launois et al. (2015b) considered these fields to have net emissions of zero. Peatlands are mainly located in the northernmost regions (above 60˚ N) and were expected to contribute about 101 ±30% Gg S y^{-1} to total emissions combining the wetland extent from Wania et al., (2010) and the estimated mean peatland flux. Seasonality was also indirectly included in soil fluxes because frozen soil was assumed to have a 0 net OCS flux. In the simulation, emission estimates dominated in some extratropical regions of the Northern Hemisphere, turning them into a net source of OCS in late autumn and winter.

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Related strongly to temperature (Maseyk et al., 2014) and radiation (Kitz et al., 2017),

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using diffusion–reaction equations (Ogée et al., 2016; Sun et al., 2015)demonstrate good skill in

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The mechanistic models that resolve the diffusion process thus have the advantage over empirical models of more realistic evaluation of OCS exchange. The models demonstrate good skill in simulating observed features of soil OCS exchange, such as the responses of OCS uptake to soil water content (Ogée et al., 2016; Sun et al., 2015) and temperature (Ogée et al., 2015) and the transition from OCS sink to source at high soil temperature (Sun et al., 2015).

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demonstrate good skill in simulating observed features of soil OCS exchange, such as the responses of OCS uptake to soil water content (Ogée et al., 2016; Sun et al., 2015) and temperature (Ogée et al., 2015) and the transition from OCS sink to source at high soil temperature (Sun et al., 2015).

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However, the interaction between production and transport processes in driving OCS exchange variability remains poorly understood. Known abiotic contributions, e.g. the role of solubility, are detailed in Sect. 2.3.3 Abiotic processes.

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It is hoped that future studies may integrate the mechanistic frameworks of soil OCS exchange into global land models (e.g. Community Land Model or Simple Biosphere Model) to simulate soil OCS fluxes for a better estimate of the global soil OCS budget.

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Microbes are key drivers of OCS exchange in terrestrial ecosystem components such soil (Sect. 2.3.2) and in association with plants and other non-vascular photoautotrophic communities (2.3.1). Cyanobacteria, micro-algae, bacteria, and fungi can contribute to net OCS uptake (Gries et al., 1994; Kusumi et al., 2011; Ogawa et al., 2013; Protoschill-Krebs et al., 1995; Smith and Kelly, 1988, Bunk et al., 2017).

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Fusarium and *Trichoderma* spp. that have been isolated from the surfaces of sandstones from ancient monuments and forest soil exhibited OCS uptake (Li et al., 2010; Masaki et al., 2016). Cultured bacteria have been observed to consume OCS, including *Thiobacillus thioparus*, *Mycobacterium* spp., and *Streptomyces* spp. (Kusumi et al., 2011; Ogawa et al., 2016; Smith and Kelly, 1988). Some free-living saprophyte Sordariomycete fungi and *Actinomycetale* bacteria, dominant in many soils, are also capable of degrading OCS (Harman et al., 2004; Nacke et al., 2011). Bacterial OCS degradation in sterilized soil inoculated with *Mycobacterium* sp. showed surprising ability to take up OCS (Kato et al., 2008). In addition, cell-free extract of *Acidianus* sp. also showed significant catalysed hydrolysis of OCS (Smeulders et al., 2011). Performing fungi inhibition experiments in whole soils, Bunk et al., (2017) showed that fungi might be the dominant player in soil OCS uptake.

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purified from soil environments or from culture collections,

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In addition to the uptake of OCS at atmospheric concentrations, OCS degradation of ppm-level concentrations has been detected in various fungi and bacteria purified from various environments. For example, 38 out of 43 fungi isolated from soil degraded 30 ppm OCS in around 24 hours without any prior acclimation to the high OCS concentrations (Masaki et al., 2016). A change in activity between ambient or ppt-level and ppb-level OCS concentrations suggests that different microbial communities are responsible for OCS consumption in the high and low concentration regimes (Conrad and Meuser, 2000).

Fusarium and *Trichoderma* spp. that have been isolated from the surfaces of sandstones from ancient monuments and forest soil exhibited OCS uptake (Li et al., 2010; Masaki et al., 2016). Cultured bacteria have been observed to consume OCS, including *Thiobacillus thioparus*, *Mycobacterium* spp., and *Streptomyces* spp. (Kusumi et al., 2011; Ogawa et al., 2016; Smith and Kelly, 1988).

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Performing fungi inhibition experiments in whole soils, Bunk et al., (2017) showed that fungi might be the dominant player in soil OCS uptake.

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2.3.3 Non-vascular and epiphytic phototrophic communities

Many land surfaces host photoautotrophic communities known as cryptogamic covers, assemblies of bryophytes (mosses, liverworts, and hornworts), lichens, algae, and cyanobacteria. In contemporary terrestrial ecosystems, these communities contribute significantly to the biogeochemical cycling of carbon and nitrogen (e.g. Lindo et al., 2013; Maestre et al., 2013), but global estimates of OCS uptake by these communities currently do not exist. Unlike vascular plants, bryophytes and lichens lack responsive stomata and protective cuticles to control water losses. As a result, their tissue hydration and physiological activity oscillate more dramatically with variations in ambient moisture than neighbouring vascular plants. In these organisms, photosynthetic CO_2 uptake is limited by moisture availability and diel and seasonal variations in light. OCS uptake, on the other hand, continues in the dark even when photosynthesis ceases (Gimeno et al., 2017; Gries et al., 1994; Kuhn et al., 1999; Kuhn and Kesselmeier, 2000).

At the global scale, our findings so far suggest that quantifying the contribution of cryptogamic covers to the OCS budget is not a straightforward task. This is because CO_2 and OCS fluxes are not necessarily coupled in lichens and bryophytes, and therefore OCS exchange cannot be modeled following the same approach as for vascular plants. Fortunately, the emission component from these organisms seems to be primarily driven by temperature (Gimeno et al., 2017) and the geographical extent of their contribution is limited to areas where cryptogamic covers constitute a non-negligible biomass fraction or contribute significantly to other ecosystem biogeochemical cycles (Elbert et al., 2012). A first approach toward estimating the contribution of these communities would require compiling sensitivity parameters (to air moisture, temperature, and other variables as in Porada et al., 2014) to predict OCS exchange from climatic drivers for dominant species, functional types, or even whole communities from these regions.

In addition to the contribution of crypotogamic covers to OCS uptake, there exist hyperdiverse microbial communities that colonise the surface of plant leaves or the "phyllosphere" (Vacher et al., 2016). The phyllosphere is an extremely large habitat (estimated in 1 billion km^2) hosting microbial population densities ranging from 10^5 to 10^7 cells cm^{-2} of leaf surface (Vorholt, 2012). With respect to OCS, it has already been shown that plant-fungal interactions can cause OCS emissions (Bloem et al., 2012). Assuming that these epiphytic microbes are capable of consuming and emitting OCS, they likely play a role in ecosystem OCS budgets.

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Emission to the atmosphere can also be generated by swings in redox potential and thermal- or photo-degradation of organic matter, both in soil and in the surface ocean.

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OCS consumption and production in precipitation does not play a significant role in OCS ecosystem fluxes. Two precipitation studies found both snow and rain were supersaturated with OCS (Belviso et al., 1989; Mu et al., 2004). Mu et al. suggested that this excess OCS may be due to photochemical reactions with sulfur-containing compounds scavenged by the water droplets. These reactions can continue after the precipitation is deposited and re-generate the highly supersaturated OCS state after 24 hours of irradiation. The highest observed OCS concentration in precipitation was 48 ng OCS/L or 14 pmol OCS/mol H_2O. The densest cloud water content is about 3 $gH_2O\ m^{-3}$. For 1 m^3 of air, there are $2*10^{-12}$ excess moles of OCS. For 1 m^3 of dry ambient air at 500 ppt OCS, there are $2*10^{-8}$ moles OCS. This potential flux is described further in Campbell et al., (2017b). Even in the densest supersaturated clouds, the OCS in the air would represent 99.99% of the OCS present.

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Redox potential has long been known to play a role in the production of reduced sulfur gases, including OCS. All wetland soils observed in the field produced OCS (see Fig. 4). OCS was emitted from soils in lab studies where redox was manipulated (Devai and DeLaune, 1995). Watts (2000) divided all soils into “oxic” and “anoxic,” where low-oxygen soils generally produced OCS. However, recent studies question this simple framework.

Most oxic soils investigated act as small sinks of OCS (see review in Fig. 3 of Whelan et al., 2013), but a few oxic soils observed under field and laboratory conditions have released large amounts of OCS under high temperatures or light conditions (Kitz et al., 2017; Maseyk et al., 2014; Whelan et al., 2016). This is attributed to the thermal- and photo-decomposition of organic matter (Whelan and Rhew, 2015). Whelan et al. (2016) determined that dried soils will exhibit net OCS emission following an exponential curve with temperature. Of six soils from vastly different ecosystems, only the sample from a desert showed no emissions when air-dried and heated. Sterilized soils exhibited a higher baseline of OCS emissions, suggesting that OCS production was abiotic and some of the OCS produced was consumed by in situ microbes (Whelan and Rhew, 2015). It could be that soils containing organic matter will emit OCS under hot and dry conditions, but that most ecosystems never experience the low soil moisture and high temperature combination in the field. Regardless, it is necessary to take this flux contribution into account when modeling potential soil OCS fluxes (Sun et al., 2015).

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A missing source of about 600–800 Gg S y^{-1} in the atmospheric budget of OCS has recently been identified by several top-down approaches (Berry et al., 2013; Glatthor et al., 2015; Kuai et al., 2015; Suntharalingam et al., 2008; Wang et al., 2016). Satellite data have shown that tropospheric OCS is elevated above the North Indian and northwest tropical Pacific oceans, and inverse models using enhanced oceanic emissions reproduced a similar pattern (Kuai et al., 2015). Global oceanic emissions would need to amount to 800–1000 Gg S y^{-1} to fully account for this missing source.

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and, potentially, dimethyl sulfide (DMS), most likely photochemical products of biogenic compounds

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on whether oceanic emissions represent the missing source of OCS

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Bottom-up emission estimates from global oceans have been obtained from simulations with models of different levels of complexity. Lennartz et al. (2017, 130±80 Gg S y^{-1}) predict highest emissions in high latitudes consistent with previous observations, whereas Launois et al. (2015a, 813 Gg S y^{-1}) predict highest emissions in the tropical oceans with the 3D oceanic model NEMO-PISCES. The latter corroborates the emissions needed to account for the missing source, but requires OCS surface water concentrations one order of magnitude higher than the majority of open ocean observations. The discrepancies between bottom-up oceanic emission estimates, and between top-down and bottom-up approaches, indicate the need to reduce uncertainties in the global marine OCS flux from direct and indirect sources, requiring new field measurements and process studies.

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2.4.1 Surface ocean OCS measurements

Although in situ measurements of OCS in the surface ocean remain relatively scarce, they span a range of oceanic regimes and seasons.

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The OCS photo-production term remains poorly constrained.

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The OCS photo-production term remains poorly constrained.

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Here, we propose that refining estimates and uncertainty bounds for OCS photo-production could be facilitated by (1) a comprehensive study of the variability of the spectrally resolved AQYs across contrasting marine environments, determined using laboratory-based photochemical experiments done under very controlled illumination conditions; (2) the use of a photochemical model that utilizes AQYs, fully accounts for the spectral and depth dependence of photochemical processes in the surface ocean, and facilitates calculations on a global scale by capturing the variability in solar irradiance and chromophoric dissolved organic matter (Fichot and Miller, 2010); and (3) the cross-validation of the depth-resolved modeled rates with direct in situ measurements of photo-production rates and/or with rates derived from field observations of surface OCS concentrations (e.g. Lennartz et al., 2017).

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Dark production remains similarly poorly constrained.

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Dark production remains similarly poorly constrained.

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The acquisition of vertical profiles of OCS concentrations within and below the euphotic zone would help reduce this uncertainty. Continuous concentration measurements from research vessels can be used to calculate dark production rates assuming an equilibrium between hydrolysis and dark production during nighttime. Different processes undoubtedly require further dedicated process studies to assess their importance.

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Bottom-up analysis of the global anthropogenic inventory estimates a source of 500 ± 220 Gg S y^{-1} for the year 2012. The large uncertainty is primarily due to limited observations of emission factors, particularly for the rayon, pulp, and paper industries. An independent approach using a top-down method estimated that the average source for the years 2011 through 2013 was 230 to 350 Gg S y^{-1} (Campbell et al., 2015). One possible reason for the gap between these estimates is that the top-down study used a constrained optimization approach in which the optimization was limited to the a priori range, which at the time of that study was 150 to 364 Gg S y^{-1}. These two estimates are considerably larger than the older gridded inventory estimate of 180 Gg S y^{-1} (Kettle et al., 2002), which was used in all recent global atmospheric modeling studies. Also, the Kettle inventory failed to capture the concentration of global emissions in China that is revealed in the updated inventory. The upward revision of the anthropogenic source suggests that some of the missing source in the global budget could be accounted for by anthropogenic emissions.

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The spatial and temporal trends in these inventories have multiple implications for applying OCS as a carbon cycle tracer. First, most of the anthropogenic source is located in China, while most of the atmospheric OCS monitoring is located in North America (Campbell et al., 2015). The spatial separation allows regional applications of OCS to North America to control for most of the anthropogenic influence through observed boundary conditions (Campbell et al., 2008; Hilton et al., 2015, 2017). Second, the anthropogenic source has large inter-annual variations (Campbell et al., 2015), which suggests that applications of the OCS tracer to inter-annual carbon cycle analysis will require careful consideration of anthropogenic variability.

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Biomass burning is generally accounted as a separate category.

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has shown that OCS is also emitted into the atmosphere by volcanism

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This finding is consistent with our current understanding of the chemical reactivity of OCS in the troposphere.

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The first compilation of OCS/CO_2 ratios in volcanic gases of various volcanoes was published in the mid-1980s

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In light of the variability of the OCS/CO_2 ratio in volcanic gases, it was possible to evaluate

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. The authors gathered data from 11 volcanoes covering nearly the whole range of volcanic temperatures (100–1100°C) and encompassing the main types of terrestrial volcanisms. They reported a statistically significant linear relationship between the logarithm of the OCS/CO_2 ratios and the reciprocal of the emission temperature of the gases, and pointed out that this experimental relationship was consistent with thermodynamical calculations.

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Although most of the results showed that the OCS/CO_2 ratio of volcanic gases was closely related to their emission temperature, samples collected at Merapi Volcano did not match well with the linear model.

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, whereas for temperatures over 700°C, typical of eruptive and post-eruptive volcanoes, the former model underestimated the ratios by less than an order of magnitude

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. For a more complete description of the outgassing state of active volcanoes the reader is referred to Belviso et al. (1986). In the latter, the e

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already represented a negligible proportion of the total OCS volcanic source strength: now they

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This demonstrates a critical gap in understanding of the terrestrial carbon cycle and suggests a need for independent information, such as that provided by OCS observations, to further constrain models.

There are two approaches to performing this application. One uses a biosphere model to simulate the CO_2 and OCS biospheric fluxes with the mechanism described above, which is the so-called "bottom up" method. Berry et al. (2013) employed the Simple Biosphere Model (SiB3) to estimate coupled CO_2 and OCS land fluxes, and designed an experiment to examine the different responses in photosynthesis and respiration under different soil hydrology and water stress. Berry et al. compared the drawdown of CO_2 and OCS under different conditions and in different regions and the results indicated that additional information on separating the responses of photosynthesis and respiration to environmental forcing could be provided with the help of OCS.

Launois et al. (2015) and Campbell et al. (2017a) used a simpler approach to simulate OCS fluxes from several land surface models, based on the simulated GPP and LRU. They further used an atmospheric transport model to evaluate the potential biases in the simulated GPP and respiration fields, comparing simultaneously the simulated OCS and CO_2 concentrations to observed atmospheric mixing ratios (see Sect. 3.1.1). Recent work by Hilton et al. (2017) combined both approaches to constrain the spatial distribution of GPP in North America.

The second method relies on obtaining the biosphere fluxes of CO_2 and OCS from gradients in measured atmospheric concentrations using inverse modeling, which is the “top-down” method. Atmospheric inverse modeling with CO_2 measurements alone is only able to constrain the total net flux of CO_2 and it is unable to distinguish between the underlying fluxes arising from photosynthesis and respiration. Adding atmospheric OCS measurements to the analysis will allow gross carbon fluxes to be calculated, from which biospheric responses to climate variations can be better described. Currently, there is a need for more surface measurements to carry out this method on large spatial scales. Using satellite observations sensitive to the mid or upper troposphere cannot well distinguish spatial variations of surface fluxes, e.g. exactly where a potential ocean source is located.

There are uncertainties shared by both approaches. While OCS observations show promise as an independent GPP tracer, there are smaller terrestrial OCS sources and sinks from soils (Kesselmeier et al., 1999; Kettle et al., 2002; Maseyk et al., 2014; Ogée et al., 2016; Sun et al., 2015; Whelan et al., 2015) and industrial activities (Campbell et al., 2015; Kettle et al., 2002; Zumkehr et al., 2017) that must be considered (see Sect. 2). For studies relying on LRU, laboratory and field work has shown that LRU varies under different conditions, such as low light (Stimler et al., 2010b). Although there are uncertainties in the OCS sources and sinks, OCS observations are useful even with an unbalanced global budget because the uncertainty introduced by LRU variation and potential soil OCS emissions is much smaller than the uncertainty of our current understanding of regional carbon balance (Hilton et al., 2015).
Here we describe the work that is underway or has already been done to use OCS observations to glean more information about ecosystem functioning, specifically GPP, on different spatial and temporal scales. With the bottom up approach, generating maps

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, allowing us to evaluate the representation of carbon uptake in our current suite of biosphere models

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We also explore the potential of using OCS to understand carbon cycle changes under extreme events.

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without carefully chosen OCS component fluxes, especially at small spatial scales

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Using aircraft OCS observations from the NOAA Global Greenhouse Gas Reference Networks aircraft program (http://www.esrl.noaa.gov/gmd/ccgg/aircraft/index.html, an update of results published in Montzka et al., 2007),

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they derived OCS plant fluxes from differing GPP models' spatial placement of North American GPP and used a chemical transport model to compare these to the aircraft observations. The study used multiple estimates of OCS soil fluxes, OCS anthropogenic fluxes, and continental boundary fluxes, supporting three different approaches to modeling the relationship of OCS and CO_2 plant uptake. Each of these contributes uncertainty to using OCS as a GPP tracer. By using these multiple estimates of each uncertainty, Hilton et al. (2017) quantitatively estimated each uncertainty source as well as the sources' combined, comprehensive uncertainty.

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however, they rely on the robustness of the global OCS modeling framework and in particular the choice of the LRU values (assumed constant in time) and the parameterization of soil OCS uptake (i.e. with small seasonal variations).

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3.1.2 Extreme events and the carbon cycle

Climate extremes have strong impacts on ecosystems by rapidly altering the stable state (Reichstein et al., 2013). OCS observations can be used to discern how extreme events affect the carbon cycle. Taking drought as an example, the mechanisms affecting carbon balance triggered by droughts can be described conceptually; however, the individual processes are difficult to quantify with CO_2 measurements alone. Most studies conclude that drought ought to decrease an ecosystem's respiration rates and photosynthetic production. However, the net effect of drought is challenging to assess, and different studies can be contradictory (Phillips et al., 2009). Figure 12 shows the impacts of drought on the ecosystem CO_2 and OCS exchange. With a mild drought (Fig. 12, blue arrows), the soil surface might dry out, reducing soil respiration and thus total ecosystem respiration. Plant roots would still be able to reach enough water, GPP would be unchanged or decreases slightly, and the net ecosystem production would increase. For a severe drought (Fig. 12, red arrows), GPP would be reduced because plants close stomata in order to conserve water, and the net ecosystem production would likely decrease. Additionally, some studies have shown an increased GPP during drought events, resulting from increased availability of sunlight (Huete et al., 2006; Saleska et al., 2007), which makes the overall effect even more complex.

Adding OCS to climate extremes studies would provide additional information on the biospheric processes. During drought events (Fig. 12), the OCS uptake changes along with GPP, since both processes are controlled by stomatal conductance. That results in an unchanged or slightly decreased OCS uptake during a mild drought and a largely reduced OCS uptake in a severe drought. With a given ratio between GPP and OCS uptake, the changes in GPP can be quantified for both mild and severe droughts.

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(i.e. sources and sink that are compatible with the atmospheric budget)

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More precisely quantified OCS surface fluxes should improve our knowledge of terrestrial photosynthesis and hence GPP (Sandoval-Soto et al., 2005). Improved knowledge of the global OCS budget will help constrain OCS surface flux components (vegetation, soil, ocean, anthropogenic). Current OCS surface flux budgets are mostly bottom-up estimates derived from leaf-scale or terrestrial-scale experiments (Berry et al., 2013; Campbell et al., 2008; Kettle et al., 2002; Suntharalingam et al., 2008). In addition to a better global OCS budget, atmospheric OCS measurements can also be used to further constrain bottom-up or mechanistic estimates. Such "top-down" estimates use observed spatial and temporal gradients of OCS in the atmosphere to adjust an independent estimate of surface fluxes (usually called the "prior" estimate).

Only a few top-down attempts have been made with the sparse flask sampling network results (i.e. mainly from NOAA). Launois et al. (2015b) used the measurements at 10 surface stations to optimize global scalars of all surface OCS flux components in order to obtain a closed global OCS budget (i.e. sources and sink that are compatible with the atmospheric budget) and to highlight the main contributing surface flux components to the trend and seasonal cycle of atmospheric OCS as well as to the inter-hemispheric gradient.

Recent satellite-based OCS measurements can be used to derive top-down estimates at continental to regional scales. Kuai et al. (2015) proposed to estimate the OCS surface flux from NASA's Tropospheric Emission Spectrometer (TES) ocean-only observations using a Bayesian inversion technique, which can be thought of as a time-independent version of the 4D-VAR assimilation (Liu et al., 2016). Their results implied a large ocean OCS source over the Indo-Pacific region, and the total ocean source budget was consistent with the global budget proposed by Berry et al. (2013). A similar conclusion was obtained by Glatthor et al. (2015), who showed that the OCS global seasonal cycle observed by MIPAS was more consistent with the seasonal cycles modeled using the Berry et al. global budget than using the global budget proposed earlier by Kettle et al. (2002).

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Among the four satellite OCS products, only TES OCS data have been used for OCS surface flux inversions. As the TES OCS product is limited to over ocean only, the inversion of the OCS terrestrial sinks in Kuai et al. (2015) may be subject to large uncertainties. Thus, for consistency, TES OCS over land may be highly desired. Spectral retrieval over land requires exact details of surface properties, including surface altitude, temperature, emissivity, reflectance, snow cover, etc., which have been considered in the IASI OCS retrieval (Camy-Peyret et al., 2017; Vincent and Dudhia, 2017). A similar retrieval algorithm for TES OCS is currently under development. The accuracy of the surface flux inversion can be further improved by using simultaneous OCS observations from more satellites, e.g. TES and MIPAS, to provide more constraints on the horizontal and vertical OCS distribution in different parts of atmosphere. Satellite products need to be compared to tower or airborne data, perhaps determining how well the upper troposphere can reflect surface fluxes. This effort is furthered by better estimates of surface fluxes, in particular observations of OCS emissions from the oceans in areas where we assume a large source region might exist (Kuai et al., 2015). Thus better "bottom-up" surface flux estimates constrained by more numerous atmospheric observations can provide powerful constraints on OCS surface fluxes, and thus GPP.

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Measurements of OCS in Antarctic ice core and firn air samples have been used to explore long-term trends in GPP.

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Although OCS has been studied mostly as a proxy for photosynthesis, OCS uptake by vegetation is actually governed mechanistically by (i) the series of diffusive conductances of OCS into the leaf, and (ii) the reaction rate coefficient for OCS destruction by CA (Wohlfahrt et al., 2012). CA is present both in plant leaves and soils, although soil uptake tends to be proportionally much lower than plant uptake. Over soils, OCS uptake provides information about CA activities within diverse microbial communities. OCS uptake over plants integrates information about the sequential components of the diffusive conductance (the leaf boundary layer, stomatal, and mesophyll conductances) and about CA activity, all important aspects of plant and ecosystem function. Stomatal conductance in particular is a prominent research focus in its own right, as it couples the carbon and water cycles via transpiration and photosynthesis.

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A powerful and more general approach would be to combine OCS measurements with other constraints in an ecosystem model framework. OCS uptake can serve as a glue that binds other measurable quantities within a model, because

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To use the OCS GPP tracer to its full potential, surface OCS estimates over land and ocean are needed to evaluate ocean and ecosystem fluxes to the atmosphere at the global scale. Current satellite retrievals are sensitive to OCS concentrations much higher in the troposphere, and FTIR or tower data have limited coverage. Currently, the most used surface OCS dataset is from the NOAA Flask Network, where gas samples are often collected twice a day. Coordinating satellite retrievals with ground-based measurement efforts is important to realize greater data coverage and accuracy.

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Fig. 14a shows the tropospheric OCS patterns obtained using TES Level-2 swath OCS retrievals in 2006, averaged over four seasons (March to May, June to August, September to November, and December to February). The TES swath data have been averaged to 5° longitude × 4° latitude grid boxes, but due to low TES spatial sampling, these OCS patterns have been further smoothed to a 20° × 20° spatial resolution. Only those swath data that pass quality flags, such as high signal-to-noise ratio, cloud clearance, and high goodness-to-fit (Kuai et al., 2014), are used in the grid box averages. The tropospheric OCS variability ranges from 520 to 570 ppt over the latitudes between ±40°. There is constant high OCS abundance over the tropics for all seasons, especially over the Indo-Pacific region and the Caribbean Sea, indicating the effect of tropical convection, which brings high-OCS air near the ocean surface to the mid-troposphere and may be due to an OCS ocean source. In contrast, over the Cold Tongue region in the eastern Pacific, the observed OCS is low due to the strong subsidence over there.

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For comparison, Fig. 14b shows the seasonal upper tropospheric OCS patterns at 250 hPa obtained using MIPAS Level-2 swath OCS retrievals from 2002 to 2011. The MIPAS swath data have been averaged to the same TES 5° longitude × 4° latitude grid boxes and have also been smoothed to a 20°×20° spatial resolution

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. MIPAS also provides OCS abundance over the polar region, but we focus only on the tropical region to facilitate comparison. Similar to TES, the MIPAS retrievals also reveal high OCS abundance over the tropics. However, MIPAS also shows significantly higher OCS abundance in subtropical regions compared to the TES observations, indicating the effect of poleward transport in the upper troposphere. The MIPAS observations also reveal lower OCS abundance over the continents, especially over South America and Africa. These continental OCS-low areas strongly suggest the effects of vegetation sinks, which unfortunately are not seen in TES observations because of the unavailability of TES retrievals over land.

Fig. 14c shows two-month averages of the day-time total column OCS obtained using IASI OCS retrievals in 2014. IASI also provides total column OCS over the polar region, which we do not discuss here. IASI has much higher spatial sampling than TES, and the patterns shown in Fig. 14c have a high spatial resolution of 0.5° × 0.5°. The IASI OCS observations over land generally agree with the MIPAS observations, showing large sinks over South America and Africa. The high spatial resolution also helps reveal more clearly the land OCS sources over Asia, which are not seen in TES nor MIPAS observations. Furthermore, the relatively low OCS abundance over the Inter-Tropical Convergence Zone is only apparent in IASI data.

Figure 15 shows the summertime (June–August) latitudinal distribution of OCS observed by MIPAS (Glatthor et al., 2017). The distributions in other seasons are similar due to the long atmospheric OCS lifetime. In the troposphere, the tropical OCS is ~520 ppt, while the polar OCS is ~480 ppt. The vertical transport by convection over the Indo-Pacific region is clearly seen. The main source of OCS is in the troposphere and it is destroyed in the stratosphere; the abundance above the tropopause decreases rapidly as altitude increases. The mid-stratospheric OCS is significantly higher in the tropical region than in the polar region because of the upwelling Brewer-Dobson branch at the equator that transports OCS from the lower stratosphere upward.

Furthermore, the OCS abundance is significantly lower (close to zero) over the winter poles due to downwelling over the polar vortex.

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Fig. 14c shows two-month averages of the day-time total column OCS obtained using IASI OCS retrievals in 2014. IASI also provides total column OCS over the polar region, which we do not discuss here. IASI has much higher spatial sampling than TES, and the patterns shown in Fig. 14c have a high spatial resolution of 0.5° × 0.5°.

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OCS is an important tool to constrain GPP, and more resources are needed to improve the accuracy of current satellite products. Measurement campaigns need to be put in motion that will allow us to measure OCS reliably from space. The next generations of high-quality satellite instruments may target measuring OCS in the lower troposphere and/or near the boundary layer with better land surface coverage, which would improve the surface flux inversion. Optimal requirements of the instrumental designs (e.g. maximum spectral resolutions, maximum footprint dimensions, minimum signal-to-noise ratios, and choice of orbits) to achieve a lower tropospheric sensitivity can be tested using a set of representative atmospheric conditions, such as those provided by NASA's Observing System Simulation Experiments.

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OCS concentrations can be retrieved for all historical spectra and some additional data are available by request [to whom?].

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As with comparing in situ atmospheric observations, it is important to note how disparate datasets are calibrated.

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The discussion in Aydin et al. (2016) identifies the records that are derived from more ideal conditions.

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The ultimate goal of OCS tracer research is to constrain our estimates of global carbon-climate feedbacks. To this end, we need to perform the modeling studies necessary to determine the location, distribution, and feasibility of a tall tower network that would support regional-scale GPP estimates based on OCS uptake. In support of regional studies, our understanding of processes should be refined: in particular, lab-based studies with water or nutrient-stressed plants are needed. On the global scale, our understanding of the OCS budget needs to be reconciled, determining whether a large missing source is from the oceans or from anthropogenic activity. With these advances, OCS could become an essential tracer of plant CO_2 uptake that operates on temporal and spatial scales where there are currently large knowledge gaps.
There are many questions yet to be answered about OCS fluxes between the Earth surface and the atmosphere.

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This may be from incomplete knowledge of the tropical ocean source, incomplete observations of anthropogenic sources, or an unlikely overestimation of the plant sink.

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were intended to be conducted from many different sites across the U.S. If this were realized it

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, and inform us about COS from different processes that would likely be relevant on larger scales.

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While there is still much work to be done, our collective knowledge has developed enough to warrant substantial investment in infrastructure to make OCS measurements from a coordinated network of tall towers, supporting and supported by satellite observations.

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The OCS tracer gives us information on the instantaneous and integrated carbon flux into plants. For regional and global-scale studies, it can be used to answer questions about large-scale perturbations and carbon-climate feedbacks, e.g. regional droughts. Most importantly, t

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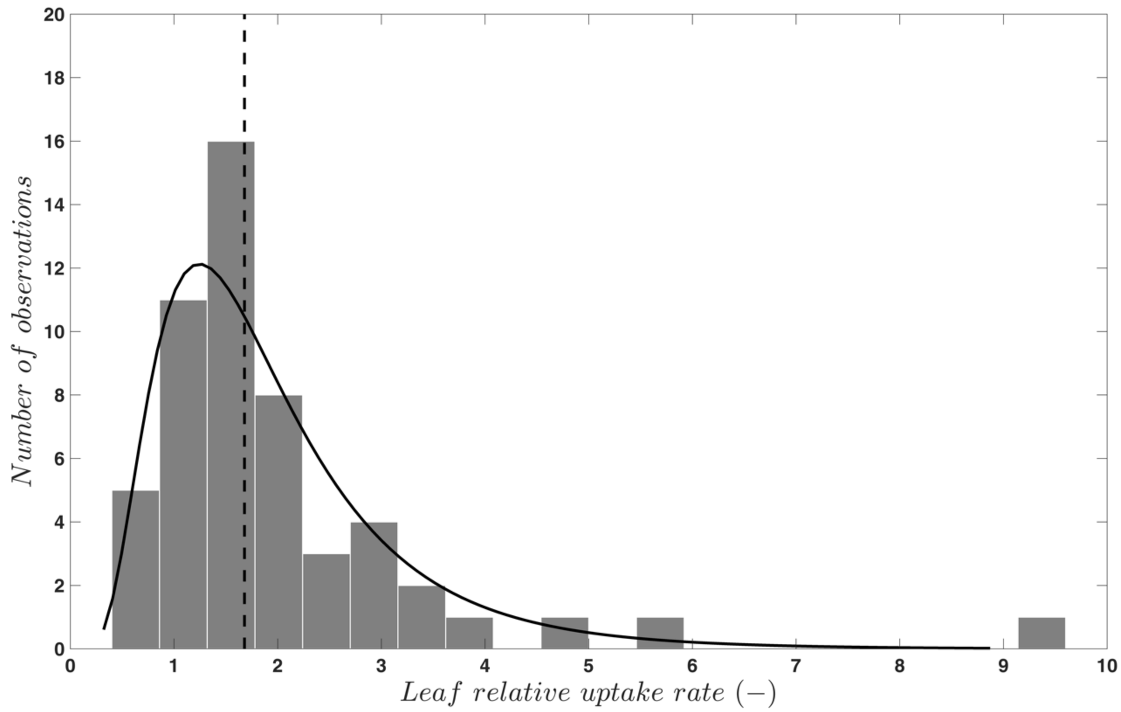

Figure 3. Frequency distribution (bars) of and log-normal fit (solid line) to published values (n = 53) of the leaf relative uptake rate of C3 species. The vertical line indicates the median (1.68). Published data are from: Berkelhammer et al., 2014; Sandoval-Soto et al., 2005; Stimler et al., 2010b, 2011, 2012.

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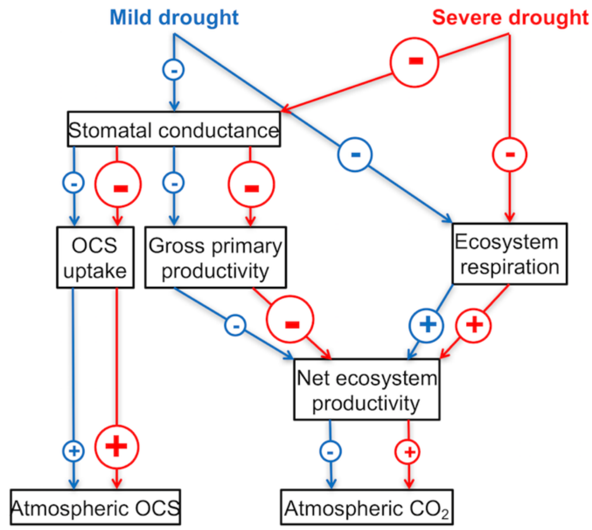

Figure 12. The impacts of droughts on biosphere processes and atmospheric CO_2 and OCS. Blue arrows show the impacts of mild droughts; red arrows show impacts of severe droughts. Plus signs show positive impacts; minus signs show negative impacts. The relative strength of the impacts is shown by the size of the signs.

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