

[The reviewer's questions and comments are written in normal font and the answers are written in bold. The use of italic fonts refers to changes in the text]

General Comments: This study is a timely and valuable contribution to our understanding of the budget of OCS. I agree with all of the comments of Referee #2 and will not repeat them here but I would like to bring up a few more points:

Overall, there is a lot of discussion of what is higher/lower but not enough quantification of the disagreement nor a discussion of the causes. I wonder if the overall range in OCS emission (which seems unreasonable large) could be better defined by constraining the model to the observation of OCS concentrations that have been mentioned. There are many unphysical emissions discussed in the text and the range seems larger than will be useful in future work.

Thank you for the time and effort spent on this review. Most of your comments could be directly addressed and we believe that the clarity of the paper has been improved, especially that of section 2 (methods). We considerably expanded the section devoted to the comparison of modeled and observed OCS concentrations, despite (as pointed out by the other referee) the small number of sea-surface OCS measurements and the problem associated with the comparison of monthly mean values at a model grid-cell scale to discrete data.

Specific points (generally excluding Referee # 2 points):

Pg 20679, line 25: How much have the soil and vegetation fluxes changed since the Watts or Kettle budgets? Montzka et al (2007) and Suntharalingham et al (2008) updated the budget before Berry et al 2013.

The suggested references were added, and the re-estimated values (especially the relative changes compared to previous estimates) were made explicit: “*The uptake of OCS by plants was modeled to be no more than 240 GgS yr⁻¹ by Kettle et al. (2002), but it has been recently revised upwards, with new estimates of 490 GgS yr⁻¹ (Suntharalingam et al., 2008), of 738 GgS yr⁻¹ in the work of Berry et al. (2013) and even reaching up to 1500 GgS yr⁻¹ in Montzka et al. (2007). Soils could also play a role in the budget of OCS. It is still a strong matter of debate but recent estimates suggest that much more OCS is taken up by soils than proposed by Kettle et al. (2002) (355 GgS yr⁻¹ in Berry et al., 2013, compared to an estimate of around 130 GgS yr⁻¹ in Kettle et al., 2002).*”

Pg 20680, line 6: All of these references are modelling studies. You should reference the actual DMS-> OCS lab measurements instead (Barnes et al 1994, 1996, Patroescu et al 1999) and include the product yield (0.7% DMS -> OCS). These references suggest that the DMS -> OCS product yields are negligible due to titration by NO. Have the authors considered recalculating the emission flux without?

The reference to the DMS--> OCS d CS2--> OCS product yields have been changed and now expressed as: “*The ocean is believed to be the largest source of atmospheric OCS (Chin and Davis, 1993; Kettle et al., 2002; Berry et al., 2013). It contributes to OCS in the troposphere by direct emission of this gas, and by large emissions of carbon disulfide (CS₂) and dimethylsulfide (DMS) quickly oxidized into OCS (with an approximate lifetime of 1 day) (Barnes et al., 1994; Kloster, 2006). Barnes et al. (1994) suggests that OCS accounts for 0.7% of the oxidation products of DMS, and that 87% of the marine emissions of CS₂ are converted into OCS.*”

For the NO titration effect, we indeed did not take it into account. It does not affect the OCS fluxes towards the atmosphere, but it is of interest for the companion paper which includes these indirect oceanic OCS sources (<http://www.atmos-chem-phys-discuss.net/14/27663/2014/acpd-14-27663-2014.pdf>).

Pg 20680, line 13: Are there any observations to verify the suggested high and mid latitude OCS emissions in Chin and Davis, 1993; Watts, 2000?

Kettle et al. (2002) indicated large mid and high latitude emissions, while the emissions suggested by Chin and Davis (1993) and Watts (2000) are actually more homogeneous through latitudes. The end of the paragraph has been corrected, and now stands as “*Kettle et al. (2002) simulated direct global oceanic OCS fluxes from -110 GgS yr⁻¹ (a sink) to 190 GgS yr⁻¹ (a source to the atmosphere), while previous estimates based on field observations suggested global direct oceanic OCS emissions from 160 to 640 GgS yr⁻¹ (Chin and Davis, 1993; Watts, 2000). The Kettle et al. (2002) study suggested that direct sea-air OCS emissions mainly take place at mid and high latitudes, during the respective periods of maximum irradiance.* “

Pg 20680, line 29: Methods used to measure soil fluxes were found to be faulty (around 2000) and recent analyzer advances have shown that OCS can be emitted from rubber/neoprene and

some plastics. Were the sampling volumes used in the von Hobe (2001, 2003) studies free of these materials?

We went back to the materials and methods sections of both manuscripts. The authors used materials made of glass and did not mention the use of rubber/neoprene and plastics.

Pg 20683, line 5: that cloud cover is used as the surface irradiance input?

The irradiance used is the ISCCP-FD as described in Zhang et al. (2004).

Zhang Y, Rossow W, Lacis A, Oinas V, Mishchenko M (2004) Calculation of radiative flux profiles from the surface to top-of-atmosphere based on ISCCP and other global data sets: refinements of the radiative transfer model and input data. J Geophys Res 109. doi:10.1029/2003JD004457

Pg 20684, line 1: I don't fully follow this paragraph. Can you better explain how you use the light absorption of CDOM at 350nm to represent the CDOM concentration. You don't know the concentration of CDOM so you are using the absorption coefficient at 350nm. Does this need to be a function of CDOM to be used? I think a little more information here would help with that. Also, why have you chosen 350nm, when the two parameterization use 440nm and MODIS uses 320 nm?

As shown by Para et al. (2010), CDOM absorbance at 350nm follows CDOM quantities, while the slope of the reflectance (S_{cdom}) is primarily influenced by CDOM quality. Therefore, yes, a_{350} is considered as a function of CDOM quantity, and it is this property that allows linking OCS dark-production to a_{350} .

CDOM absorbance was not necessarily primarily deduced at 350nm. It was converted to the corresponding absorbance at 350nm, since both dark- and photo-productions are expressed as functions of a_{350} only, following:

$$a_{CDOM}(\lambda) = a_{CDOM}(ref) * e^{(-S*(ref-\lambda))} \quad (\text{eq 1})$$

Pg 20684, line 24: "has been" should be was... And what remote sensing products were used? Needs more details.

More details (SeaWiFS products and time-period) are now provided: “Products from SeaWiFS monthly global composites for the 2002-2007 period were used, and led to the following relation between CDOM absorption coefficient and chlorophyll concentration:”

Pg 20686, line 12: Need some references for this range of AQY. What is the range of AQY? What causes the variability?

AQY ranges for the quoted studies were added, and causes of the variability were indicated (especially the changes in CDOM quality, thus changes in its absorbance): “A few AQY for OCS have been published, but they exhibit considerable variability, with values varying by a factor of >7 depending on the environment considered (quantum yields ranging from $9.3 \cdot 10^{-8}$ to $6.4 \cdot 10^{-7}$ in the Sargasso Sea for Weiss et al., 1995a and Zepp et al., 1994, respectively). The quantum yields depend both on the location and the season of the measurement, especially because CDOM quality and its absorption coefficient might vary through time (Kettle et al., 2002; Weiss, 1995b; Cutter et al., 2004).”

Pg 20684, line 16: What data are you using for the calculation of equation 7. Why was this data chosen? How different is the calculated value in different waters?

The fact that this equation and normalization process were taken from Uher et al. (1997) has been made more explicit: “To compensate for part of this natural variability, Uher et al. (1997) normalized the measured AQY by the absorption coefficient of CDOM available for the reaction at the same location. Therefore, the new relation, implemented in NEMO-PISCES, is the following:

$$P = a_{350} UV \frac{P}{a_{350}} = k a_{350} UV \quad “$$

The use of the “offshore” pool of water was made more explicit too. “The k coefficient is retrieved from the normalization of measured photoproduction constants to measured CDOM absorption coefficient values at 350 nm. For offshore waters (the majority of globe waters), k was found to be close to a value of $2.1 \text{ fmol L}^{-1} \text{ s}^{-1} \text{ W}^{-1} \text{ m}^3$. “

The relation is based on AQY values, which were normalized to the absorption coefficient of CDOM available at the site location, to dampen the natural variability observed in the AQY values as presented. As discussed in the paper, this normalization provided a mean value of 2.1 for offshore waters and 2.8 for inshore waters. As we

considered the offshore value only in the current model, this likely leads to an under-estimation of the OCS production in coastal waters.

Pg 20687, line 1-14: The theory of how the dark production can be related to the light absorption of DOM really needs more explanation. (see Pg 20684, line 1 comment above)

This remark was also a concern of the other reviewer,

In the introduction section, we just simplify it as “*This pathway is therefore called dark-production. Measurements by Von Hobe et al. (2001) indicate that its rate is proportional to the amount of organic material, and it has therefore so far been linked to the chromophoric dissolved organic matter (CDOM) absorption coefficient (Von Hobe et al., 2001 and 2003).*” [...] “*The dark-production rate implemented in the NEMO-PISCES model follows the formulation of Von Hobe et al. (2001, 2003). Therefore, the dark-production rate, even if supposed to be light-independent, is also linked to the chromophoric dissolved organic matter absorption coefficient at 350nm (a_{350}), as the variable provides an indirect estimate of the seawater richness in organic matter.*”

We are aware that linking the dark production pathway with a variable which is light-dependent is not intuitive. Therefore, in the paragraphs where the dark-production parameterization is detailed, we explicitly pointed out that the a_{350} variable also gives information about the CDOM concentrations.

We also added the following paragraph, to emphasize the link with a_{350} : “*OCS production pathways are either dependent on irradiances in the UV domain (photo-production) or on CDOM and organic matter concentrations (dark-production). As a_{350} allows a link with both variables, it is a key parameter in our parameterizations of OCS production. Sensitivity tests were performed using NEMO-PISCES and three different formulations of a_{350} .*”

We further insist on this point on the dedicated paragraph describing the dark-production rate estimates: “2.2.4 Parameterization of OCS dark-production rates

Measurements of large OCS concentrations well below the photic zones have proven that OCS can be produced when no light is available. The so-called dark-production pathway was shown to largely depend on available organic matter. The presence of organic matter is quantified by the a_{350} parameter, following Para et al. (2010), as explained in section 2.2.2.

Microbial activities are suggested as main precursors for the OCS dark-production pathway,[...]”

Pg 20689: It might be better to include to combine Section 2.3 and 2.2.3. That will help give sufficient detail about the AQY.

Since section 2.2.3 describes parameterizations used in NEMO-PISCES and section 2.3 concerns an independent estimation of photoproduction rates (without using NEMO-PISCES), we decided to keep them separated. However, some of the information from section 2.3 was moved to section 2.2.3 when relevant for the parameterization used in NEMO-PISCES.

More specifically, the following sentence now appears in section 2.2.3: « OCS photo-production is primarily induced by the interaction of UV radiation and natural photosensitizers in CDOM (Ferek and Andreae, 1984; Flöck et al., 1997). “

[...]

$$P = p UV \quad (8a)$$

This expression was established using strong assumptions, such as considering that no other source or sink of OCS affects OCS concentrations in seawater. The authors found mean values for the photoproduction constant around $1.3 \pm 0.3 \text{ fmol L}^{-1} \text{ s}^{-1} \text{ W}^{-1} \text{ m}^2$ on offshore samples and values twice as high in inshore waters. “

Pg 20691, line 5: Can you quantify the effect of the underestimate of the chlorophyll concentration in the oligotrophic subtropical zones?

The impact of this underestimate was made more explicit in section 3.3.1, for subtropical waters. The quantification of the over-/under-estimation is, however, difficult at a yearly/global scale. Thus, we re-wrote this paragraph: “As these are regions of warm ocean waters favorable to OCS dark-production, the consequence might be an underestimation of OCS production in these regions. In regions showing low chlorophyll concentrations, this underestimation translates to an approximately 30% underestimation of the a_{350} value (depending on the a_{350} formulation used), which directly translates to an equivalent underestimation of OCS dark- and photo-production, since both parameterization linearly depend on a_{350} . “

Pg 20691, line 10: Are there no other OCS depth profiles from other areas that could be used for comparison?

As the comparison of figures 3 and 4 in the study of von Hobe et al. (2003) shows, the reproduction of the OCS depth profiles by their models was generally less accurate than that of surface data because the models were tuned to fit the surface concentrations. In our study, the model was not tuned to fit surface or depth concentrations. As NEMO-PISCES provides gridded monthly mean concentrations of OCS on the entire water column, monthly mean concentrations of OCS data series should, ideally, be used to evaluate the global simulations.

Unfortunately, a global database of sea surface OCS measurements and a procedure to calculate sea surface OCS as a function of latitude, longitude, and month are not available in the literature as, for example, for DMS (e.g. Kettle et al. (1999), Lana et al. (2011)). The assemblage of a global OCS database was not achievable in the framework of this project. The evaluation of the modeled oceanic OCS concentrations that had been carried out is unsatisfactory because we implicitly accepted to compare modeled monthly mean concentrations and discrete measurements.

With these caveats in mind, the results of the comparison of modeled and observed OCS concentrations are displayed in a figure in the supplementary information (Fig. A1), reproduced below.

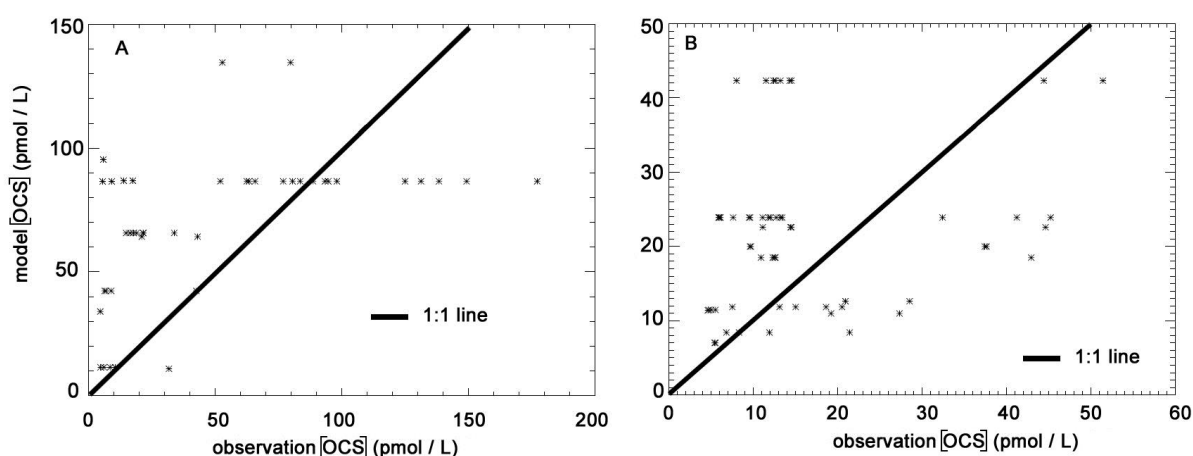


Figure A1: Comparison of modeled and observed marine OCS concentrations from (A) sea surface samples (0 to 10 m depth) and (B) depth profiles.

As added in the core of the article : *“150 OCS measurements classified according to location, date and depth were gathered from the literature (Weiss et al., 1995a ; Ulshofer et al., 1996 ; Cutter et al., 2004 ; Von Hobe et al., 2001 and 2003). Figure A1 shows that the outputs of the model generally overestimate the measured concentrations by a factor of two to four at the sea surface (first 10m, A) , especially at sites where low concentrations were measured. In seawaters with high OCS concentration measurements (higher than 100 pmol L⁻¹), the corresponding simulated concentrations were generally underestimated, up to a factor of two. A better agreement between modeled and observed concentrations is found with the subsurface data (below 10m, B).*

The previous model-data comparison suggests that simulated OCS concentrations might be overestimated in a significant way in surface waters, which might lead to an overestimation of the simulated OCS outgassing fluxes (up to factors of two to four). However, the limited spatial (many measurements were done around 40°N) and temporal (many measurements in July and August) distribution of the measurements severely reduced the possibility for an exhaustive model validation and for the identification of concentration biases in the model. Furthermore, a large range of concentrations were measured even for sites close in latitude and/or for measurements realized around the same period of the year.”

Pg 20692, line 28: Can you quantify the agreement between the simulated and observed OCS profiles? Can the observed data be added to Figure 5?

Horizontal bars showing the ranges of variation of observed OCS concentrations were added in Fig. 5D to better compare modeled and observed data. An envelope corresponding to the minimal and maximal values measured at this site for the same period has been added to the figure and in the text: “When using the a_{350} formulas derived from the studies of Morel and Gentili (2009) or Preiswerk (2000), the simulated vertical profiles of OCS concentrations in the Sargasso Sea in August (Fig. 5D) fall into the range of measured OCS concentrations reported by Cutter et al. (2004). This is however not the case when using the a_{350} based on MODIS-aqua data which lead to the highest simulated OCS concentrations (270 pmol L⁻¹ at the sea surface) and seem to overestimate the natural variability of the OCS concentrations, as measured in these waters.”

Pg 20694, line 1: What is the overall southern hemisphere overestimate in chlorophyll and, therefore, OCS. Is there anything that can be done to correct for this overestimate? There are a

number of places where the authors discuss an over/underestimate. Is there a way to quantify the magnitude of these over/underestimates?

Dark- and photo-productions are linear functions of a_{350} , thus any bias in a_{350} results in a proportional bias in OCS production. However, a_{350} is not a linear function of [Chl]. Thus, depending on the formula chosen to express $a_{350}=f([\text{Chl}])$, an under-/over-estimate of [Chl] will translate to a more or less large bias in the calculated a_{350} value. This bias is not easy to quantify. An indication (to give the order of magnitude of the change) was added in the paragraph 3.3.1, based on the example of subtropical oligotrophic regions: *“As these are regions of warm ocean waters favorable to OCS dark-production, the consequence might be an underestimation of OCS production in these regions. In regions showing low chlorophyll concentrations, this underestimation translates to an approximately 30% underestimation of the a_{350} value (depending on the a_{350} formulation used), which directly translates to an equivalent underestimation of OCS dark- and photo-production, since both parameterization linearly depend on a_{350} . “*

Pg 20695, line 13-15: These sentences should be clarified. They appear to contradict each other.

There was a difference between yearly totals and monthly rates, and the relevant sentences were clarified: *“[...] subtropical regions are the major contributors in terms of yearly total photo-production of OCS, because the photo-production rates were roughly constant through the entire year, whichever model was used. However, the highest monthly photo-production rates were found in mid-latitude regions (40-60°N and 40-60°S) during the period of maximum irradiance, with rates twice as large as the nearly constant rates obtained in tropical regions“*

Pg 20696, line 1: Why is the Sargasso sea photoproduction so much higher than the total ocean simulation? I am not surprised at this result given how clear the water is in the sargasso but some suggestions as to the reason for this result would be useful.

Indeed, at least in the simulations, the high simulated OCS concentrations are possible due to the combination of large a_{350} and elevated UV exposure during most of the year.

Pg 20696, line 4: "appears"? or is? Have you done an analysis of the main drivers of OCS dark production in the model?

Dark production is a function of a_{350} (linear dependence, where the dark production increases with a_{350}) and of temperature (dark production increases with temperature). As the dark production is reaching its maximum values in tropical regions (with low a_{350} and high sea surface temperature values) and displays clear latitudinal variations, we can infer that the temperature effect on the dark production rate is larger than that of a_{350} variations in the simulation.

Pg 20696, line 20: Should the model be tuned to the few observations that are available? If more than Cutter et al. (2004) is available, this should be used in the initial analysis.

The proportion of OCS produced through the “dark production” pathway, estimated by Von Hobe et al. (2001, 2003) was obtained using measurements performed during a single campaign, therefore during a short time period and only on few sites close to each other. Thus, both model-measurement comparisons and model tuning are severely limited by the sparse data.

Discussion: Overall, the paper might be easier to follow if the Results and Discussion were rolled into one. Some of the discussion would be much more useful earlier on in the text! Discuss the implications of the results of the model parameters as they are brought up initially.

The second reviewer had the same concern. Details from the discussion were moved to the Results section and, in some cases, to the Methods section (see previously-indicated changes). We believe that these changes improve the clarity of the text.

Pg 20703, Line 5: The Kamyshny et al paper states that their hydrolysis estimates are in line with the Elliott estimate. How does this tie in with this statement?

Figure 2 presents the hydrolysis constant calculated using the Elliot and Kamyshny's parameterizations, respectively (using a constant pH value). The differences are far from negligible, especially for sea surface temperatures around 290K, which represent zones of high productivity. The respective k_{hydr} values vary by a factor of 2 in these waters depending on the parameterization used.

Such differences do have a significant impact in our global simulation, as expressed in the text: “Simulations run with two different hydrolysis parameterizations (based on Eq. 11a or Eq. 11b) provide global OCS emissions diverging by a factor of 2.5 (see Fig. 10).”

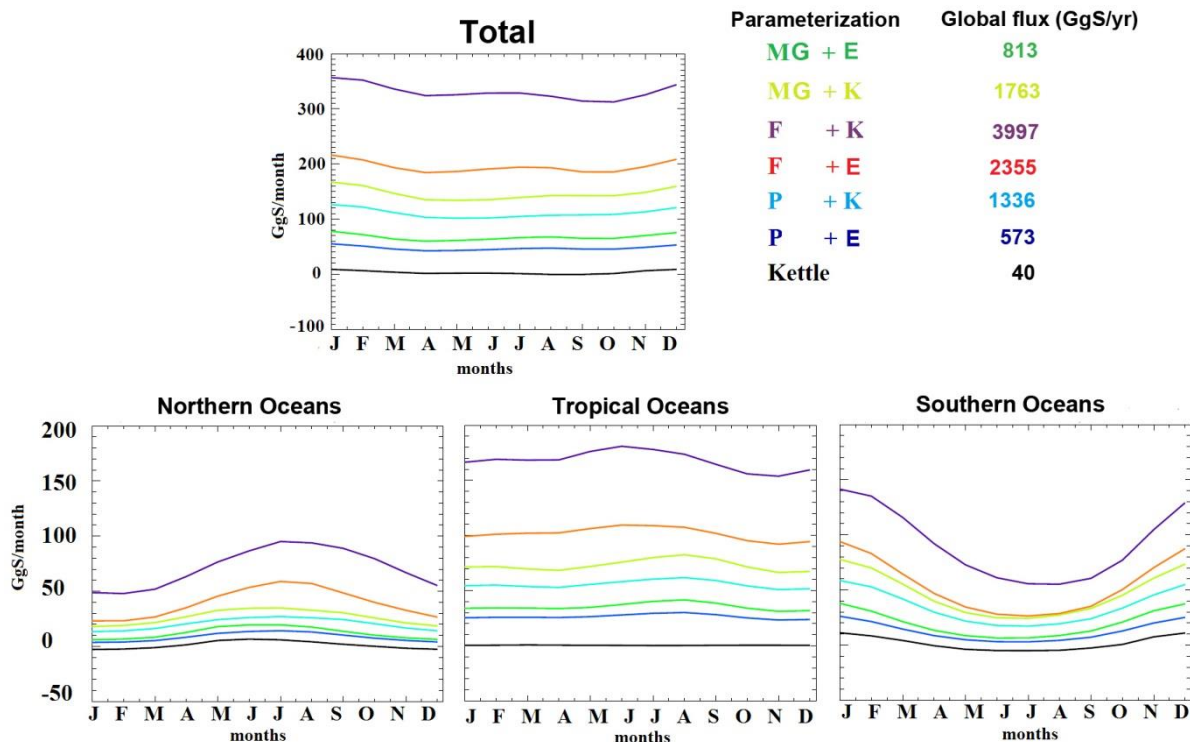


Figure 10: Global and regional monthly mean sea-air fluxes for 6 different parameterizations of the NEMO-PISCES model. Kettle et al. 2002 (black line) is shown as a reference. Each colored line represents a set of parameters: first name refers to the equation used to calculate the UV absorption coefficient of CDOM at 350 nm and the second name refers to the hydrolysis constant formulation. Global fluxes on top row, Northern Oceans (30°N-90°N, bottom left), Tropical region (30°S-30°N, bottom center), Southern Oceans (30°S-90°S, bottom right). F: a_{350} relation assembled in this study; MG: a_{350} relation from Morel and Gentili (2009); P: a_{350} relation from Preiswerk et al. (2000); E: hydrolysis constant from Elliott et al. (1989); K: hydrolysis constant from Kamyshny et al. (2003)

The following clarity/grammatical issues were also fixed in the article. We thank the reviewer for pointing them out.

Pg 20679, line 26: "Berry et al suggests"

Pg 20679, line 29: "levels" -> mixing ratio

Pg 20697, line 3: "levels"? Do you mean concentrations?

Pg 20691, line 19: "twice as low".. replace with "half as much"

Pg 20692, line 2: "important" replace with "high"

Pg 20695, line 6: Full stop missing.

Pg 20683, line 17: important? In what way?

Pg 20680, line 1; reword: "dark-production rate is also linked..."

Pg 20702, Line 5: Are these references correct? Berry and Suntharalingam studies suggest a terrestrial sink much larger than 300 Gg S yr⁻¹ as far as I remember?

Pg 20688, line 16: [COS] should be [OCS]