[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]

This study presents a new estimate of direct marine emissions of carbonyl sulfide (OCS) calculated using parameterizations implemented in the NEMO-PISCES global ocean biogeochemistry model. The analysis aims to address the recently highlighted discrepancy in the global OCS budget between the estimates of identified sources and sinks to the atmosphere. Recent studies have suggested that ocean sources may need to be revised upwards to balance increases in the estimates of OCS uptake by terrestrial vegetation and soils.

The analysis is generally well-founded, and appropriate sensitivity analyses have been conducted on some of the key parameters underlying the biogeochemical production and loss parameterizations, in order to provide a range of uncertainty for the ocean emissions. In this study, several of the OCS production and loss pathways implemented in the NEMO-PISCES model are based on previously derived parameterizations (e.g., as outlined by von Hobe et al. 2001, 2003). A new contribution of this work is the use of a global ocean biogeochemistry model to provide the organic matter cycling fluxes underlying the derivation of the OCS production and loss terms, in deriving a revised estimate of global ocean direct emissions of OCS.

This study is a useful addition to the field, and addresses an open question on the magnitude and nature of oceanic OCS emissions. I suggest the authors address the concerns outlined below before publication.

Specific areas of concern as outlined below in ‘Specific Comments’ include:

(a) the lack of a more comprehensive and detailed evaluation of the modeled oceanic OCS concentrations (e.g., for their preferred ‘standard model run’ of section 4), as has been done in previous estimates of this type;

(b) lack of clarity in some sections on model development, validation of the individual components, and discussion. These could be improved by a clearer discussion and more detail on the underlying assumptions and methods.

Thank you for the useful comments all along the manuscript and for qualifying this work as a valuable contribution to the field. Your specific comments have all been addressed and taken into account. As recommended, the revised version now includes a more comprehensive evaluation of the modeled oceanic OCS concentrations. Most of the

comments regarding a lack of clarity have been addressed by simplifying/completing the information presented in section 2 (Methods).

SPECIFIC COMMENTS

- 1) Evaluation of modelled OCS: A more systematic evaluation of modelled OCS concentrations against available ocean measurements would improve the manuscript. A significant concern I have is that the current validation of modelled OCS is minimal, and limited to a few sentences in the text comparing ocean model results to summary values from a few previous measurement campaigns. I recognize that ocean OCS measurements are sparse, however for a model development exercise as presented here, it is important to present as comprehensive a validation as possible. It would have been good to have seen a more detailed evaluation using a larger database of the available ocean OCS measurements (in figure or table form, as was presented, for example, by previous studies such as von Hobe et al. 2003). This would be especially useful to assess the validity of the 'standard model run' of section 4, which incorporates their chosen 'best-guess' parameterizations. In the current manuscript version, for example, modeled OCS concentrations are shown in Figures 5 and 9, but no observed values are shown as points of comparison. Without such an evaluation of OCS against observations, it is difficult to assess the validity of the proposed total model for oceanic OCS that is presented here (i.e., the combined effect of parameterizations for production, hydrolysis and air-sea exchange components on modeled surface ocean OCS levels, and hence on ocean emissions).

When using the MODIS-Aqua-based a_{350} formulation (Eq. (6)) which gives the best representation of a_{350} in the region (Fig.6), simulated OCS concentrations near shores only reached values from 30 pmol L^{-1} in winter to 100 pmol L^{-1} in summer (Fig. 9). NEMO-PISCES matches correctly the seasonal amplitude of OCS concentrations measured in these areas and represents quite accurately the absolute values measured near the shores. However, as expected, the lack of resolution of the model translates into an under-estimation of the estuarine concentrations.

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 not fully satisfactory 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.

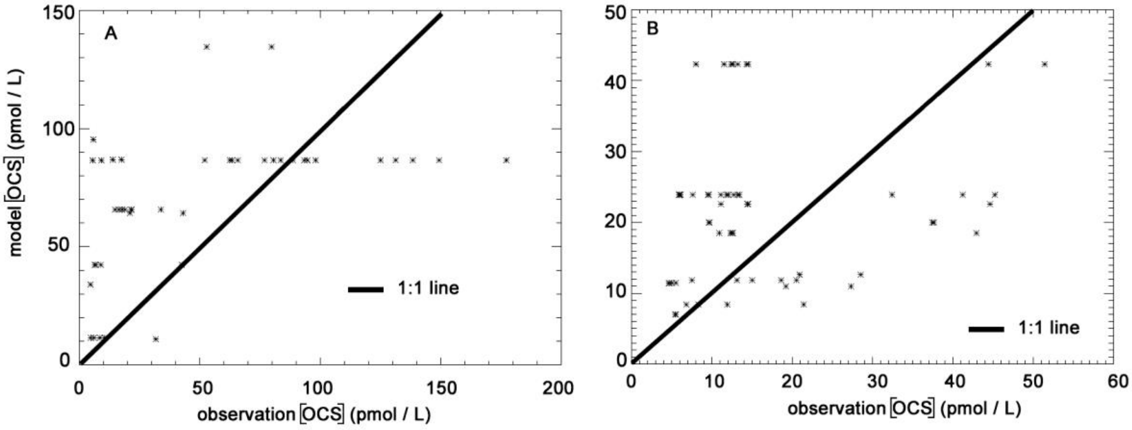

Figure A1: Comparison of modeled and observed marine OCS concentrations from (A) sea surface samples (0 to 10 m depth) and (B) depth profiles.

We added the following sentences in section 3.3.5: "*150 OCS measurements classified according to location, date and depth were gathered from the literature (Weiss et al., 1995a ; Ulshöfer 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 (top 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).*

This 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.”

The modeled depth profile at BATS was also evaluated against observations carried out by Cutter et al. (2004) in the Sargasso Sea. Following your suggestion, Fig. 5D was also adjusted to provide this indication of the minimal and maximal values reported by Cutter et al. (2004).

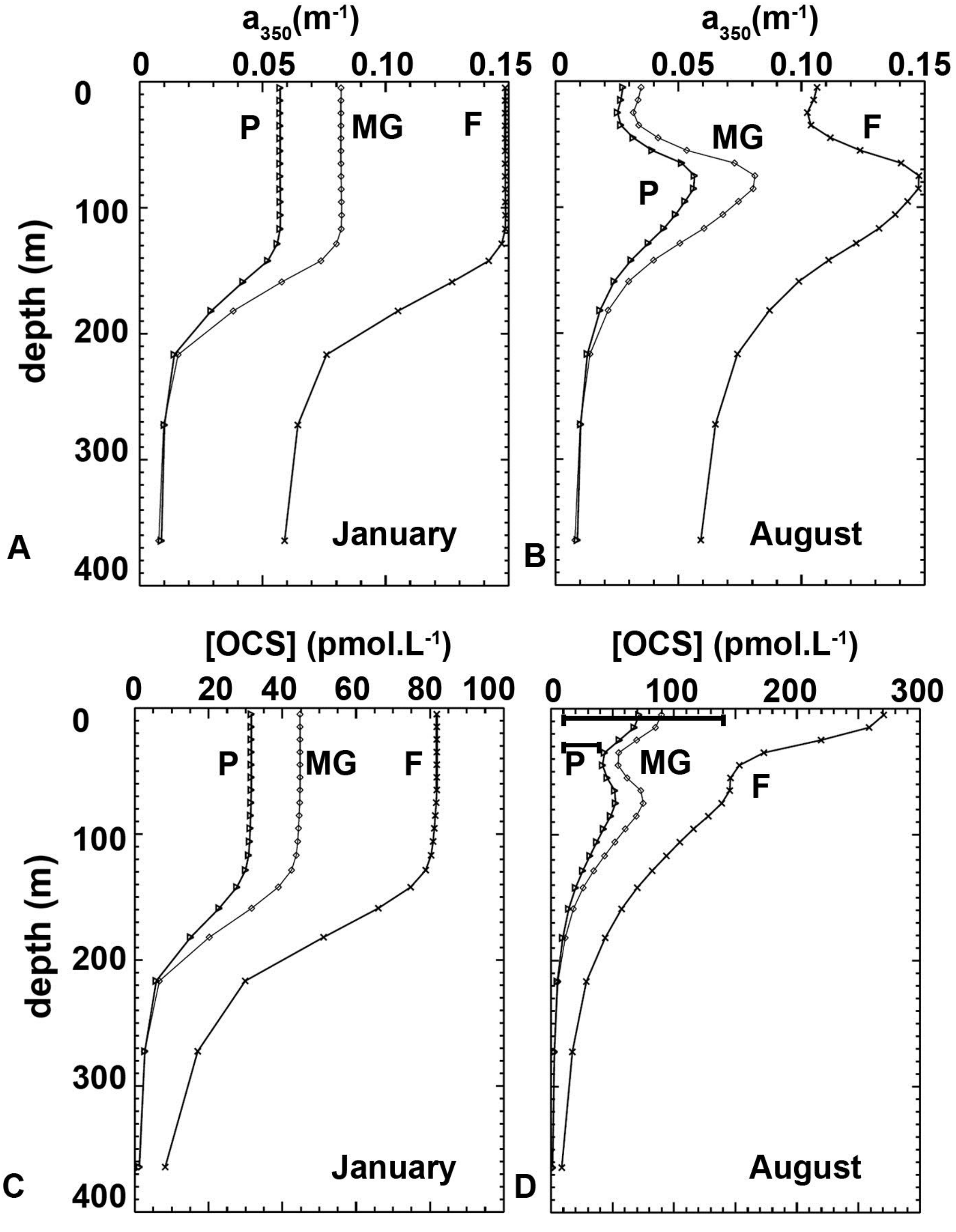

Figure 5: Monthly mean vertical profiles of a_{350} (top row) and OCS concentration (bottom row) in January (left column) and August (right column) simulated by NEMO-PISCES in a 1-D run at the Bermuda Atlantic Time Series (BATS) site. The thick lines in subfigure D cover the range between minimal and maximal values as measured by Cutter et al. (2004). The different a_{350} profiles are calculated using the formulations of Morel and Gentili (2009) (MG, diamonds), Preiswerk et al. (2000) (P, triangles) or based on MODIS-*aqua* data (F, black line). Symbols used on the OCS concentration profiles on the bottom row indicate which a_{350}-chlorophyll relation was used in the simulation.

As described in paragraph 3.2.2 : "*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.* "

2) Clearer more detailed discussion: Certain aspects of the description of model components and parameterizations in section 2 would also benefit from a clearer discussion and additional detail to clarify the methods used. For example, more detail is needed on the following:
a) The analysis underlying the normalization of the Apparent Quantum Yield of OCS production outlined in section 2.2.3, as this is a key quantity in the derivation of OCS production.

Section 2.2.3 has been modified to explicitly quote Uher (1997)'s method to normalize the expression of AQY by UV irradiance absorption, since we use the same approach. This normalization aims to transform a highly time- and site-dependent factor (AQY) into a more constant-through-conditions variable. The new paragraph has become: "*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 10^{-8} to 6.4 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). 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:*"

$$P = a_{350}\, UV \frac{p}{a_{350}} = k\, a_{350}\, UV \qquad \textbf{(8b)}$$

where P is the OCS photo-production rate (pmol m^{-3} s^{-1}), UV is the incident irradiance integrated from 295 to 385nm (W m^{-2}). 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 fmol L^{-1} s^{-1} W^{-1} m^3." **Note that the k coefficient deduced from inshore water samples was found to be 2.8 *fmol* L^{-1} s^{-1} W^{-1} m^3 on average. The smaller difference between the two k values justified the choice to use this normalized expression rather than Eq. 8a which showed more sample-dependence.**

b) The implementation of the dark matter production pathway in conjunction with NEMO-PISCES; in particular, lines 1-12 of page 20687 (section 2.2.4) need more explanation.

A general description of the dark-production pathway had already been provided in Section 1 (Introduction). However, Section 2.2.4 was improved to make it more understandable, in a stand-alone paragraph. More specifically, key points about the dark-production pathway appearing in the Introduction are now also recalled in Section 2.2.4 where necessary. We also simplified the description of the method used by Von Hobe et al. (2001). Section 2.2.4 has been rewritten as follows:

"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 pool 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, but their exact nature and the mechanisms underlying this process are poorly known. Von Hobe et al. (2001, 2003) calculated dark-production rates assuming that after dawn OCS concentrations were reaching a steady-state when dark-production was compensating for the parallel hydrolysis. Equation 9 was established using measurements from a campaign in the Sargasso Sea and hydrolysis rates were calculated following the Elliott et al. formulation (1989).

The formulation from Von Hobe et al. (2001) relating OCS dark-production rates to the CDOM absorption coefficient was implemented in NEMO-PISCES following:

$$Q = a_{350} e^{\left(55.8 - \frac{16200}{T}\right)} \qquad (T \text{ in } K) \qquad (9)$$

where Q is the dark-production rate in pmol m^{-3} s^{-1}, and a_{350} is the CDOM absorption coefficient which is used here to describe the CDOM/organic matter concentration."

c) Section 2: A clearer identification is needed of (i) the specific parameterizations relating to modification of NEMO-PISCES, vs. (ii) independent parameterizations of OCS production and loss pathways. Reading through section 2, it is not always clear which parameterizations relate to NEMO-PICSES modules, and which are independent estimates derived from other (e.g., remote sensing) data.

Explicit indications were added as to which parameterizations are/are not part of the standard NEMO-PISCES model and which ones are/are not new additions in the model developed for the present paper. In particular, we made it clear that every paramaterization described in Section 2.2 was an addition in NEMO-PISCES necessary for the present paper.

[about a350 parameterization] « ***Equation 6 was then added in NEMO-PISCES*** **to complete the sensitivity tests of the OCS concentrations on the different** a_{350} **expressions tested."**

[about photoproduction] « Therefore, ***the new relation implemented in NEMO-PISCES*** **is the following:**

$$P = a_{350} UV \frac{p}{a_{350}} = k\, a_{350} UV$$ **"**

"The formulation from Von Hobe et al. (2001) relating OCS dark-production rates to CDOM absorption coefficient ***was implemented in NEMO-PISCES*** **following..."**

« ***We performed sensitivity tests in NEMO-PISCES by using two different hydrolysis parameterizations*** **to study the impact of the choice of the hydrolysis constant formulation ...."**

"Through H, the Henry's law constant, the sea-air OCS flux also depends on temperature, ***and was implemented in NEMO-PISCES following the expression established by Johnson et al. (1986)*****"**

Paragraph 2.3 provides an approach independent from the use of NEMO-PISCES and now starts with "***Independently from NEMO-PISCES, the photochemical model of Fichot and Miller (2010) was used to calculate monthly climatologies of depth-integrated photo-production rates of OCS in the global ocean.*****".**

3) Indirect ocean sources of OCS: This study presents revised estimates of direct ocean emissions of OCS. The study of Kettle et al. 2002 also suggested there were large indirect

fluxes of OCS associated with ocean emissions of CS2 and DMS. These indirect sources were previously estimated to be significantly larger than the direct ocean source of OCS. Since the authors now present revised estimates of the ocean direct source, does their analysis suggest any new constraints on the indirect oceanic sources, within the overall limits of the global budget ? The authors should provide some discussion of this, if possible.

We are aware of the current large uncertainties on the global flux estimates from main OCS sinks and sources. The present paper is actually a preliminary study which helped in the construction and constraint of the global OCS budget. This global budget is described in a companion paper, currently in online discussion (http://www.atmos-chem-phys-discuss.net/14/27663/2014/acpd-14-27663-2014.html).

More precise estimates of some of the OCS sinks and sources would lead to better constraints on all the different fluxes composing the global cycle of OCS, including the indirect oceanic OCS sources, as the reviewer underlines it. However, recent large re-estimates of the major sinks of atmospheric OCS (by soils, by vegetation…) have been provided by studies such as Montzka et al. (2007), Suntharalingam et al. (2008), Berry et al. (2013), up to a tripling of the soil and vegetation sinks compared with the budget from Kettle et al. (2002). Thus, at the moment, the high remaining uncertainties over the different flux estimates limit the constraint obtained on the indirect OCS oceanic fluxes. This is especially true as these indirect fluxes only represent 20% of the oceanic OCS emissions in the new direct OCS outgassing proposed in this paper.

The companion paper uses the oceanic OCS source presented hereby in an inverse optimization scheme. Estimates of the global sinks and sources were allowed a 30% variation around their a priori values in the optimization scheme. The set of fluxes leading to the best fit between simulated and observed OCS concentrations led to a new set of global fluxes with negligible changes in the indirect oceanic OCS sources (see Fig. 3 of the companion paper), thus supporting the estimates provided in this paper.

4) Figure of OCS production/loss pathways : Figure 1 should be improved to provide a clearer schematic of the linkages between upper ocean processes and OCS production and loss pathways. The legibility of the figure should also be improved (e.g., by being converted to a B/W schematic, rather than a grey-scale or color figure). Some of the figure's text, especially towards the bottom, is hard to read.

The figure is now set in B&W and the text which was hard to read has been modified:

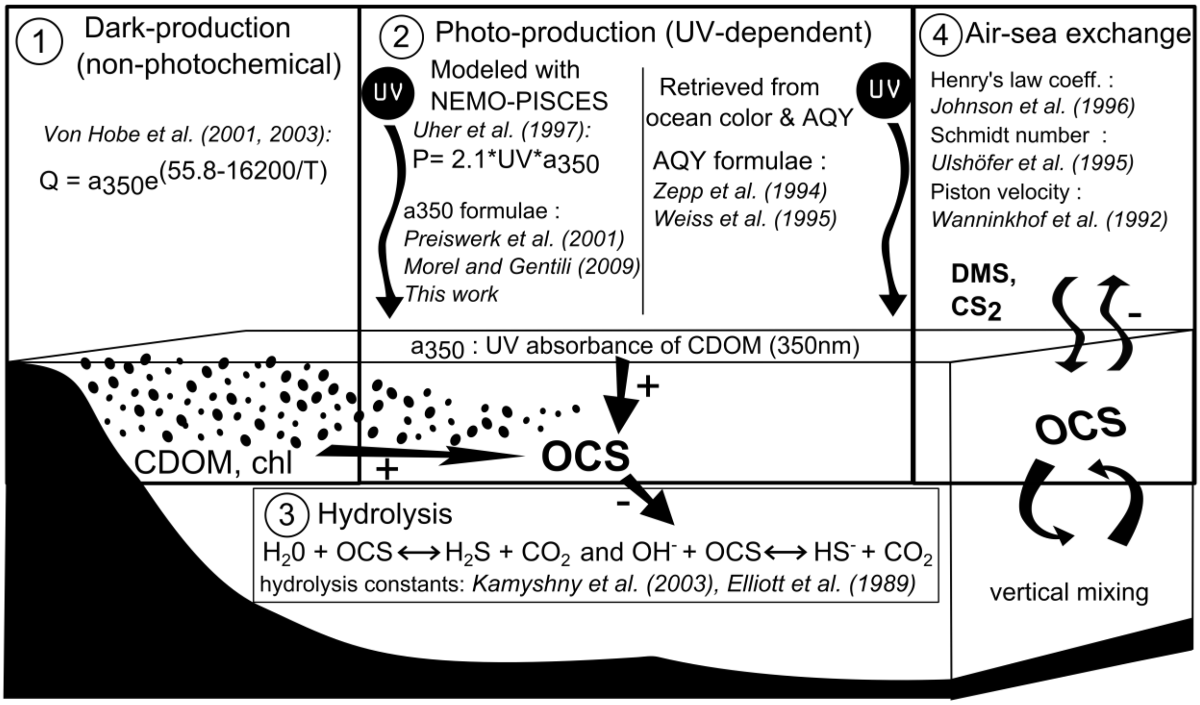

Figure 1: Main production and removal processes implemented in the NEMO-PISCES OGCM to simulate the marine OCS cycle: dark-production, photo-production and hydrolysis. Of central importance is the UV absorption coefficient at 350 nm of chromophoric dissolved organic matter (CDOM) which is derived from modeled Chl concentrations using three different relationships linking a_{350} to Chl. The simulated photo-production rates of OCS were evaluated independently using the model of Fichot and Miller (2010) and published apparent quantum yields (AQY). Aqueous OCS is removed by hydrolysis (two different formulations of the hydrolysis rate are used), lost or absorbed at the air-sea interface and mixed both vertically and horizontally. Studies relevant for sensitivity tests and model parameterization presented in this paper are displayed in italic. Oceans also emit DMS and CS_2 which are later oxidized in OCS in the atmosphere. These indirect sources of OCS are not detailed in the present study but in the companion paper (Launois et al., 2014b).

5) Introduction: p. 20679, Lines 11-20: Please improve the discussion of the vegetation and soil uptake of OCS with a more detailed quantification of the fluxes involved, and more relevant references for the soil fluxes (e.g., see Van Diest and Kesselmeier, 2008, and references therein).

The numbers (comparing Kettle et al., 2002 and Berry et al., 2013) are now explicitly expressed: "*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}, according to Berry et al., 2013, compared with an estimate of around 130 GgS yr^{-1} in Kettle et al., 2002)*"

We did not quote Kesselmeier et al. (2008) or Van Diest and Kesselmeier (2008), since their approach is providing a site-scale estimate, and, as they suggested, experiments on a more exhaustive list of soil types must be realized before any global modeling can apply their results/parameterizations to provide a first estimate of the soil OCS uptake at a global scale based on their work.

6) Introduction : p. 20679, Lines 23-25 : There are earlier global budgets of OCS than Kettle et al. 2002 (e.g., in Chin and Davis, 1993), therefore this cannot be the 'initial global budget'. Please reword.

Any reference to the work of Kettle et al. (2002) as the "initial" global OCS budget has been erased. (*"much more OCS is taken up by soils than proposed by Kettle et al. (2002)", "Kettle et al. (2002) proposed a global budget of OCS* " ...)

TECHNICAL CORRECTIONS

All technical corrections have been taken into consideration

Abstract

p. 20678 : Line 4 : Change to 'uptake'

Line 12 : 'using the UV absorption..'(add 'the')

Line 21 : change to 'uptake'

Introduction

Pg. 20679: line 3: Grammar issues, so reword sentence; e.g., ‘: : :it is a major contributor to the stratospheric: : :’

Pg 20680: Line 4 : Missing reference : ‘Kettle et al. 2002 ‘?

Pg 20681: Line 7 : Change to ‘results’

Pg. 20683: line 16 : Change to ‘ranging’

Pg. 20683: line 23 : Change to ‘impacts’

Pg. 20683: lines 24-25 : Grammar issues : change to ‘.. has been identified as one of the most influential factors: : :’

Pg 20684: lines 5 and 7 : Use of the word ‘primordial’ is not clear. Do you mean ‘fundamental’ or ‘necessary’ ?

Pg. 20684: line 23 : Change to ‘The deduced: : :’

Pg. 20684: line 24 : ‘..has been established by remote sensing: : :’ : Please provide more detail on the remote sensing sources.

Pg. 20687: lines 1-3 : Please make clearer the sentence beginning ‘Therefore the formulation:’

Pg. 20691: lines 24 : Change to ‘translated to a ..’

Pg. 20691: lines 25 : Reword : change ‘quick’ to ‘abrupt’ or ‘sharp’