Response to Reviewer #2

We appreciate very much the time and effort that the reviewer put into this paper and the very careful and thorough review. We respond to all comments below and thank the reviewer for his/her comments that have helped to improve the manuscript. For convenience, we show the reviewer comments in italics and response in plain font.

General Comments: This is a timely paper which discusses the methods for the retrieval of chlorophyll red fluorescence from satellite-borne spectrometer data. In general it can contribute to the rapidly growing amount of publications in this field. Especially as it is connected closely to the work of Wolanin et al. (2015) who recently published first spectrometer retrievals of red Solar Induced Fluorescence (SIF) over land and ocean. Even though rather recently such similar studies have been published I feel that the results of this paper can anyway be very helpful for the community in absence of feasible validation sources. As long as such sources do not exist I am convinced that this paper can provide useful research information and data for future intercomparisons. Especially because some of the approaches taken here appear to be sufficiently different compared to the previous work of Wolanin et al. (2015) and provide novel research.

Thank you for these positive comments.

However, I was surprised that this manuscript is considered to be suitable for a journal focusing on atmospheric measurement techniques (nomen est omen). Only marginal relation to such atmospheric measurement techniques can be found except that the devices used for the retrieval algorithms were designed to measure atmospheric parameters. As two related papers led by the first author1 and two papers as a co-author2 have already been published in AMT it is only fair to publish this one as well. Accordingly its acceptance by the editors for a peer-review is comprehensible. Especially, as content and quality of the manuscript is, after revision, certainly worth to publish. However, as long as scientific journals are published in a themed fashion, readers continue to select them according to their foci. Thus, for the future I recommend to the editorial board of this journal (of which the first author is a member of) to either (1) reject such manuscripts and recommend a more appropriate one; (2) extend the topical focus of AMT (thus changing the title) or (3) probably create a new journal having an appropriate focus under the umbrella of “Copernicus Publications.”

For the first of the above-mentioned papers led by the lead author, we had submitted first to Biogeosciences, which we thought to be a more appropriate journal than AMT(D). However, it was rejected as out of scope (too heavy on the technical nature of the retrieval), and AMT(D) was recommended instead. We responded to the Biogeosciences editor, saying that we would submit to AMT(D), but that we were disappointed that Biogeosciences would not consider the paper. For the second paper, there was an open special issue on GOME-2 so the paper could be justified to be placed in this issue. We also had statements in both papers about how fluorescence can affect atmospheric retrievals, especially for the bands that were specifically placed on these instruments for sensitive trace-gas measurements. After that, more papers on fluorescence were submitted to and published in AMT(D), and it seemed to become common practice to accept these technical type of papers in AMT(D) (so long as they used traditionally atmospheric instruments). But this is certainly an important point and since the lead author is on the editorial board, the issue has been formally raised at that level. It was agreed that this type of paper is considered in the “gray zone” and subsequent similar papers will be considered on a case-by-case basis. It was decided that papers that use measurements made with traditionally atmospheric sensors or that use atmospheric techniques to derive other parameters (like here using oxygen bands to derive a surface parameter) would be acceptable for publication in AMT(D).

Coming to the scientific general comments:

1) I see one general shortcoming of the presented study which is related to the justification of several decisive settings. I found many places in the manuscript on hand where scientific reasoning is missing. Wherever I have found such unexplained decisions/settings I have asked for justification (see “Detailed Comments”).

See responses below under detailed comments.
2) In general I think that the introduction of the O2 - γ absorption band provides a potential constrain (probably a more appropriate term than “anchor”) to the O2 - B absorption used for the red SIF retrieval. However, for the sake of trace-ability (and if required also of reproducibility) the reader needs more information how precisely this has been done! In this respect and most others I cannot agree more with anonymous referee #1. I am not satisfied with the answer given to 1. referee as it mainly broaches the wording instead of explaining the underlying principle of how the use of O2 - γ is beneficial.

Please see answer to comment regarding p. 6 below.

3) The same general criticism is related to zero-offset correction (Sect. 4.4.4): Here the reader seemingly receives guidance but the instructions remain vague. Of particular importance (see further comments) is the necessity that principle components (PCs) are not affected by the zero-offset effect.

This comment is mostly addressed in detail below. In addition, we added some discussion in this section on how additive effects impact the principal components.

4) Another general, though less critical, aspect is the fact, that the maps (or their color scales) should show units wherever applicable — satisfying solution already proposed to referee #1.

5) All comparisons of your results are qualitative. I admit that a quantitative comparison might be difficult with datasets of other non-institutional groups (for example Wolanin et al., 2015). However, at least the comparison of your nFLH retrievals and MODIS is feasible on a quantitative level. If there are no important technical obstacles please provide such quantitative comparison (by means of histogram or scatter-plot analysis).

We address this in the similar comment below.

6) Please discuss the potential impact of Vibrational Raman Scattering (VRS). You are only indicating this in Sect. 6.5. — satisfying answer already given to referee #1.

7) To my understanding, when introducing the O2 - γ band to constrain the O2 - B retrieval an important goal was to ensure that the impact of SIF shall be reduced to the latter, as the O2 - γ is (correctly) assumed to be free of impact from SIF. However, no information is given how large the impact of the zero-offset and Rotational Raman Scattering (RRS) on the O2 - γ band is expected. This is of importance, as the effects of both aspects cannot be discriminated spectrally from the effect of SIF (at moderate spectral resolutions).

This is addressed below (comment on p. 6, line 103).

8) Several times rather definite conclusions about the ability of the presented algorithms are given. I feel that these conclusions are coming too early, as most of the findings are coming from qualitative comparisons with others and visual inspections of monthly maps. I agree, that the proposed approaches seem to have promising potential, but announcing that “Our approach offers noise reduction” based on these comparisons and bearing in mind that the above mentioned open issues are not yet solved you should refrain from such statements (see further comments).

Addressed below.

Detailed Comments:

Page 1

Line 8: You state: “Our approach offers noise reductions ...” I suggest to remove this sentence, as substantiation is based on visual inspection, which can come also to other conclusions (see comments below).
We modified statement and added to it; it is explained that the simulations show the potential for noise reduction and that our approach is an extension of previously implemented methods.

*line 10: anchor → constrain (?) biases due to … → biases most likely due to …*

In response to the previous review, we had changed “anchor” to “estimate absorption within”. We made the other suggested change.

*line 18: I do not understand the connection: soil moisture and what? Furthermore, soil moisture is mentioned only here in the abstract and is not subject of discussion any more*

We changed “sensitive to soil moisture” to “drought-sensitive”.

*Page 2*

*line 29: Add Khosravi et al. (2015)*

It was already added here per response to reviewer #1.

*line 47: Many different terms have been used in this manuscript for retrievals utilizing solar Fraunhofer lines. It would be helpful to introduce a common term/description (or even abbreviation) for solar Fraunhofer line based retrievals used throughout the paper.*

We have modified the paper to use the abbreviation SFL for solar Fraunhofer line (retrievals).

*line 48: Add Koehler et al. (2015), Wolanin et al. (2015) and Khosravi et al. (2015)*

done

*line 50: Why is “surface reflectance” not listed in the enumeration?*

Thank you for pointing this out. We added “surface reflectance” as it was an unintended omission.

*Page 3*

*line 58: Please use the full information available about the ESA report.*

We are not sure what exactly is meant by this comment.

We added some text here on aircraft measurements that used a non-fluorescing target (reference to Rascher et al., 2009) and that do not require a non-fluorescing target (Rascher et al. 2015); these are mentioned in the ESA report.

Regarding the reference itself, we had used the recommended citation from page ii of the report. There is additional information on that page. We have now included some of that in the reference.

*line 9: biochemistry → biochemistry*

fixed, thank you.

*line 12: quantaties → quantities*

fixed, thank you

*line 14: use oxygen → use of oxygen*

fixed, thank you
Is no impact of SIF on cloud top height retrievals using O2 – A expected? If not, it should be added as this retrieval was one of the first exploiting the O2 – A in such a way and has been proposed by Yamamoto and Wark already in the early 60ies and applied by Kuze and Chance first time to satellite spectrometer data.

Thank you for pointing out this omission. We added “cloud pressure” to this sentence with references to Kuze and Chance (1994), Koelemeijer et al. (2001), Kokhanovsky et al. (2003), and Loyola et al. (2007).

remove “straightforward”. Even though I am sure I have understood what you mean by “straightforward” approach, interested readers without specialized knowledge will (at this point) have difficulties why this approach is more straightforward than the O2 – B/A retrievals.

done

Page 4

line 28: effects of → instrumental effects such as

done

line 34: a single month → two months

done

You state: “While promising, the monthly averages appear to be noisy, and a significant offset between GOME-2 and SCIAMACHY red SIF magnitudes was shown.”

- Obviously the GOME-2 results over ocean in Wolanin et al. (2015) show a similar pattern as the ones from SCIAMACHY (Fig. 9/page 253 compared to Fig. 13/page 256) but the scale seems to be different and compared to your results (Fig. 15/page 40) they are in fact more noisy and do not appear to be on a mature level.

- When looking into the land or ocean results based on SCIAMACHY in Wolanin et al. (2015) (maps in Fig. 14/page 257) these values are not showing particularly noisy or patchy features. You are repeating this statement in section 6.5 where you explain in more detail: “Results from GOME-2 and SCIAMACHY, using the full wavelength range between 660 and 713 nm, are less noisy than those obtained by Wolanin et al. (2015) with a smaller fitting window that includes only solar Fraunhofer lines.” Your result for SCIAMACHY seems to me not (yet) conclusive, as you are also mentioning in section 6.5: “SCIAMACHY, which alternated between limb and nadir mode observations, is gridded at a resolution of 1° so as not to show too many gaps between grid boxes.” As your SCIAMACHY land or ocean results show similar “unsmooth” features as shown in Wolanin et al. (2015) poorer statistics (in terms of less pixels per gridcell compared to GOME-2) is another very conceivable possibility.

To summarize, either remove your statement or adapt it in a way to that GOME-2 and SCIAMACHY results for land and ocean are individually judged.

We agree that less sampling with SCIAMACHY may lead to poorer statistics. This is why we show both standard deviations and standard errors in Figure 9. We changed this part to “While promising, the monthly averages show a significant offset between GOME-2 and SCIAMACHY red SIF magnitudes over both land and ocean (Wolanin et al., 2015). Yearly averages of normalized fluorescence line height over ocean from SCIAMACHY appear noisy as compared with averages from MODIS.”

the sentence is more easily understood when you would bold-face the word “nearby”.

(I think line 51 is meant here). We’re not sure if bold-face is allowed in this context in AMT. For now, we put “nearby” in italics.

anchor → constrain (?)
In response to reviewer 1, we had removed “essentially as an anchor”. We used “to estimate” which is similar to “constrain”.

line 50: For the sake of completeness: PCA-based approaches in remote sensing have been used earlier to retrieve aquatic parameters from satellite borne instrumentation (Bracher et al., 2009).

We added “PCA has also been used to identify different phytoplankton groups with SCIAMACHY (Bracher et al., 2009).”

Page 5

line 60: Again you assert that the results of Wolanin et al (2015) are of poor quality. As mentioned above, you should explain better what you mean or remove the sentences. In fact, Wolanin et al.’s results for GOME-2 are debatable but the SCIAMACHY results seem to have the similar quality as those shown in your manuscript. To be more precise: The results of your Fraunhofer line retrieval leads to very similar global features while the O2 - B band retrievals appear to be smoother. But several issues of the latter are not well explained (see below), so that the quality of these results seem to be promising but remain worth discussing.

We removed the last two sentences of this paragraph.

line 68: “GOME-2 and SCIAMACHY measurements. Application of our approach leads to unprecedented precision and accuracy for red SIF data sets that span more than a decade.” Please remove this sentence and as you cannot prove this quantitatively.

done

Page 6

line 101: Which solar spectrum have you used (please give reference).

We added, “As in Joiner et al. (2013), we use solar data from kurucz.harvard.edu/sun/irradiance2005/irradthu.dat, similar to Chance and Kurucz (2010) but more highly sampled.

line 103: Guanter et al. (2010) and Vasilkov et al. (2013) discuss thoroughly spectral features in the O2 - A/B bands or nearby. None of them discuss the effect of RRS on the O2 - γ band. Please give information why you think that RRS is negligible.

We changed and added to this part. It now reads: “RRS is relatively small at the O2 B-band wavelengths (Vasilkov et al., 2013). We expect that RRS will also be small within the less deep feature of the O2 γ-band even though the amount of RRS increases with decreasing wavelength. We also expect that with real data, the effects of RRS will be accounted for within our principal component analysis (PCA) retrieval framework discussed below as they are not purely additive, but also contain a multiplicative component.

line 1cont.: As already recommended by referee #1, please explain how mathematically and technically the O2 - γ band absorption is taken into account. Your answer to the referee is already leading to a better explanation. However, it is still not completely clear to me how precisely the O2 - γ band information is used in the O2 - B retrieval.

We have added more discussion in this section, going more into detail.

line 9: the selection of the spectral window for ocean SIF is not justified. Why exactly this window? Or you relying on previous works or defined it based on own findings? (and if so, how?)
We reorganized and added to this paragraph, pulling some of the material from the results section to here in order to better explain why we selected this window.

*Page 7*

*line 16:* I doubt that the effects of aerosol scattering can certainly be ignored but I suppose you are taking it into account through the PCs(?)

Correct. To be more clear, we added here that we were referring to atmospheric Rayleigh scattering in line 16. In the last part of this paragraph, we state (with additions in green) “\(q_s(\lambda)\) and SIF(\(\lambda\)) represent TOA spectral components of surface reflectance and fluorescence modified by atmospheric scattering (cloud, aerosol, and Rayleigh) that is spectrally smooth. In other words, atmospheric scattering is implicitly incorporated into these terms. As both Rayleigh scattering and aerosols are included in our simulation data set, we can evaluate their impact on the retrievals.”

Eq (1): This relation has been derived phenomenologically in Joiner et al. (2013). It is not strictly valid in case of Bidirectional Reflectance Distribution Function (BRDF) like reflectance behavior. It would be helpful if the authors discuss the implications on the retrieval results.

In the above-mentioned section, we explain that the equation was derived for the assumption of a Lambertian surface and then say that the implications will be discussed below. Then in Sect. 4.3 we added the following:

“The polynomial model for surface reflectivity can account for atmospheric scattering; the polynomial coefficients represent an effective surface reflectivity rather than the true surface reflectivity. This effective surface reflectivity includes the spectrally smooth effects of atmospheric scattering. In addition, this formulation can also account for the effects of non-Lambertian surface reflectance. In this case, the retrieved coefficients will produce a reflectivity either higher or lower than that of a Lambertian surface. The resulting interaction with atmospheric scattering will still produce a spectrally smooth function of wavelength that can be represented with a polynomial function. There should be virtually no impact on the retrieved SIF in this case. For non-Lambertian SIF, we will simply retrieve and report the SIF radiance for the given geometry. This value may be different from a retrieval obtained for a different viewing geometry.”

Eq (2): You also model transmittances for later analyses (not only use the PCA for application to experimental data only). In such a case the canopy-to-satellite transmittance that you create using radiative transfer must be created using the correct lower boundary condition. Can you please elaborate (not needed in the manuscript).

We are not sure what is asked here and what is meant by “correct lower boundary condition.” The lower boundary in the simulations was a Lambertian surface; it was stated that directional effects are not simulated.

Eq (3): Such a relation would lead to unitless SIF. Your answer to referee #1 is not sufficient, as a (formal) substitution of Eq (3) into Eq (1) is not leading (overall) to the right units. A sentence like “SIF ...is given in radiance units” is not correcting the formal mistake. The simple introduction of a factor having the right units would help.

Thank you for pointing out this omission. We added a factor \(A\) in this equation and state that it is “the SIF magnitude at the peak emission given in radiance units.”

*Page 8*

*line 43:* I clearly see a need in emphasizing advantages of a developed method/methodology from the author’s perspective but from the perspective of the reader I prefer a better balanced discussion. Please
add a discussion of the disadvantage as well (the danger of: improper selection of the underlying multivariate dataset or loss of interpretability of the individual orthonormal PC etc.)

We added “On the other hand, the PCs may mix instrumental effects with real atmospheric phenomena in the orthogonal PCs. This does not allow for a clean analysis of instrumental artifacts or accuracy of the radiative transfer. In addition, the approach may not work well if an unrepresentative sample is used to generate the PCs.”

line 52: I suppose, that the polynomial fits produce “envelope” polynomials(?)

We are not sure what exactly is meant by “envelope” polynomials. If it means bracketing the wavelengths of interest, then yes.

line 62: PCA in → PCA is

not sure about this, it is “PCA is” on my copy from http://www.atmos-meas-tech-discuss.net/amt-2015-387/amt-2015-387.pdf

line 64: anchor → constrain (?)

From the previous review, we had changed “as an anchor to estimate” to “to disentangle”.

line 69: and well as → as well as
these window → these windows

fixed, thank you.

Page 9
line 82: Eqs. (1-???)

As stated for reviewer 1 response, this was a problem with the last LaTeX compilation. It has been fixed.

line 86: As this is rather general information it would be good for the reader to have a decent reference (Rodgers?)

We added a reference to Rodgers (1990).

line 100: “good fits”: this needs further explanation: what are “good” fits? The assessment of goodness might differ to mine or any other reader.

We changed this sentence to “By trial and error, we found that these parameter values provide an adequate fit to the observed radiances over ocean.”

line 2: Please check: GOME-2 measures the solar irradiance once per day, SCIAMACHY does it once per orbit.

We are not sure if we have a complete SCIAMACHY data set of the solar irradiance, because we have repeated solar irradiance on many orbits. Never-the-less, we use one single SCIAMACHY solar measurement per day. This is now made more clear in the revised manuscript.

line 5: I suppose “cloudy data” and the removal of “biases” refer to subsections 4.4.2 and 4.4.1, respectively. If so, please refer to the section. If not, what kind of “biases” are you referring to in this line? Zero-offset biases?

We have made adjustments to this part. It now reads, “Quality assurance checks (see Sects. 4.4.2-4.4.3) are
then conducted to filter out noisy radiance data, cloudy data, and failed retrievals (see also Joiner et al., 2013). Adjustments are also made to remove biases (see Sects. 4.4.1 and 4.4.4).”

Page 10

done

line 31 cont.:  
- I have checked the reference “Joiner et al. (2013)” to which the reader is guided in order to understand more about the “effective cloud fraction” used here. From there the reader is directed to Joiner et al. (2012) which is discussing SCIAMACHY cloud fractions, but provided that the analysis is done near 866 nm? Please make it more convenient for the reader to have everything on hand, for both GOME-2 and SCIAMACHY.

Firstly, we changed the reference to Joiner et al. (2012). Secondly, we now provide the equation used to compute the effective cloud fraction and more details about the wavelengths that are used here.

- Furthermore, specify the used thresholds (if different from the one given here), and if differing from the original manuscripts (Joiner et al., 2012/2013), please provide reasons why.

We added “…, a more stringent threshold than was used in Joiner et al. (2013). This provides improved cloud filtering at the cost of somewhat noisier results owing to a decrease in sampling.”

- One interesting finding of Koehler et al. (2015) was that the retrievals of far-red SIF are not significantly “suffering” from cloud cover. They stated: “On this basis, a cloud fraction threshold of 0.5 is a reasonable compromise between the loss of measurements and changes in the SIF average.” Please explain why SIF retrievals are only shown for fc < 0.3.

We added that our choice was “consistent with that used in version 26 far-red GOME-2 SIF provided on http://avdc.gsfc.nasa.gov.us. The choice of the cloud threshold is empirical. Our choice of 0.3 is a more stringent threshold than that used by Joiner et al. (2013) and Köhler et al. (2015) and results in somewhat noisier results owing to a decrease in sampling. Köhler et al. (2015) showed that magnitudes of gridded SIF decrease with increases in the cloud cover threshold, but that the overall temporal variations remain consistent.”

- You eliminate solar zenith angles (SZA) > 70°. Which is consistent with your statements in Joiner et al. (2013) but why is this threshold different from the one used for the PCA (see page 8/line 48). As far as I could figure out this is in line with your approach from 2013 but was not explained there as well.

Thank you for pointing out this inconsistency. We mentioned on page 9/line 4 that we use SZA < 70° for the PCA which was inconsistent with the threshold listed on page 8/line 48 (75°) and in the flow diagram figure. The latter was incorrect (we in fact use a threshold of 70° for both the PCA and for gridded of the level 3 data sets). This has been corrected in the revised manuscript. In checking this, we realized that we had omitted one more filtering check for the PCA. This is now included in the text and flow diagram.

Page 11 and Page 12
line 40: Why “particularly for GOME-2 measurements”? and not for SCIAMACHY? Is this based on own findings our on Wolanin et al. (2015) or/and Koehler et al. (2015)? Both are explicitly mentioning the problems of the SAA for GOME-2 retrievals.
We added references here to Wolanin et al. (2015) and Koehler et al. (2015) and added “but also present in SCIAMACHY radiances” to be more clear. Also, our plots of standard deviation confirm that it is more of a problem for GOME-2.

line 53: “Koehler et al. (2015) found that GOME-2 and SCIAMACHY far-red SIF retrievals exhibited biases, ...” Koehler et al. (2015) showed that the bias for GOME-2 can almost be a factor of two to three larger than for SCIAMACHY (see Fig. 17/page 2604). For the effect on SCIAMACHY results they state: “Nevertheless, a slight offset of about 0.1 mW m$^{-2}$ sr$^{-1}$ nm$^{-1}$ is introduced in latitudes above 40° N.”

- According to your maps in Fig. 10 the adjustment for SCIAMACHY is neither simple nor following a simple latitudinal dependence.
- While you were writing the article, you were obviously not aware that Khosravi et al. (2015) provided a thorough analysis of the zero-offset for SCIAMACHY far-red SIF retrievals. In their Fig. 2/page 7 they show that the difference between the retrievals for SIF for vegetated and non-vegetated regions can be in the range of a factor of two. To summarize: please add a more comprehensive discussion on what has been done in the field of zero-offset correction so far and the main findings.

We added a more comprehensive discussion as suggested, focusing on the above-mentioned points. In doing this we realized that we had left out one term (latitude) in the description of our bias adjustment scheme. This is now included.

line 64 cont./section 4.4.4: The description of your developed zero-offset correction scheme is not clear. Please revise this section by taking into account the following questions:

- “SIF retrievals over ocean” - The whole oceans or only selected parts?

Added “all areas of the ocean” to clarify. However, in doing this we realized that we left out an important part of the PCA, namely that we do not use all parts of the ocean, only selected parts away from continental coastlines. A map of these is now included in the supplemental material and more discussion was added.

- What is a “clear sky solar irradiance?”

We changed clear sky to “top-of-atmosphere”

- Why is SIF/cos($\theta$) a valid approximation?

This was a typo. It should be $\cos(\theta_0)$ and has been corrected. We clarified that “SIF has been normalized by $\cos(\theta_0)$ to remove its dependence upon the top-of-atmosphere solar irradiance.” (This ignores only small variations at ~the 1 percent level due to changes in the Earth-sun distances.)

- How do you define the continuum radiance and

Here we changed “continuum” to “at a wavelength not impacted by strong O$_2$ absorption (e.g., 682.5 nm)”. We referred to “continuum SIF emission” throughout the manuscript to describe the broadband emission. So as not to be confusing, we removed the word “continuum” elsewhere as we did here when used in a similar context.

- why do you think is the dependence on $\theta_0$ and continuum radiance yield the intended result? And how exactly are you relating both to the regression?

We added that “We found empirically that this model accounts for much of the variations in the bias.” We revised this section to express more clearly how the regression works. For example, we now express the regression equation mathematically instead of in words.

- How do you exactly “apply the derived coefficients?”

We hope that our clarifications now address this point.
• Why have you introduced latitude bins at these particular positions?

As stated on p. 12, line 72, “The ranges were chosen empirically to minimize discontinuities at the boundaries and maximize the ability to remove zero-level offsets.” We added that they “were chosen empirically (by trial and error) for each instrument and retrieval type…”

Please provide also illustration of your regression coefficients or similar.

We have provided additional figures in the supplement and corresponding discussion in the main text with many example plots of the zero-level bias as a function of latitude, radiance, and solar zenith angle, before and after adjustment, for different days and the different instruments and retrieval types.

line 86/Page 12: You state: “We also have not added barren land…” As long as there are no illustrations of the dependence of the zero-offset on “continuum radiance” and θ₀ it is hard to decide whether ignoring barren land has no impact on the quality of your regression coefficients. Background: I tend to doubt that clouds can represent land spectral features.

The objective here is to determine the zero-level offset, an additive effect that produces a false filling-in of solar or atmospheric lines that are present whether over land or ocean. We do not believe that the relatively smooth reflectance features of land and ocean (they can be different) will significantly impact the zero-level bias adjustment (we are not trying to represent land spectral features here, only the zero-level offset). We have added more discussion here on the remaining bias over the bright land surfaces (such as the Sahara) during certain seasons.

line 94 cont.: For those having experience in the field of sensitivity studies the terms “true” and “retrieved” might be clear. For interested third parties it might not be obvious. Please add a short explanation.

We added a short explanation as suggested.

line 97/Section 5:

• According to your response to referee #1 you seem to have already fixed the wavelength range selection already. This was indeed important. Thank you for that. However, using the fourth order polynomial for the synthetic data set while for real data (according to 4.3) you fit a third order polynomial makes me doubt that the surface treatment in the radiative transfer is representative.

As stated in the section “4.3 Solving the non-linear problem”, we used a 3rd order polynomial for the solar line red retrievals (that have a narrow fitting window) and 4th order polynomials for each of the wider fitting windows in the oxygen band retrievals. The paragraph you refer to above starts by saying that that we are focusing here on the oxygen band retrievals, so we are consistent.

• I appreciate very much the depth and thoroughness of the sensitivity study but I am clearly missing an important dependence analysis for zero-offset adaption. I do understand that it is most likely an instrumental spectral feature but even without precise knowledge it is possible to assess its impact. Please add, or justify why this is not needed.

We added, “We checked that the addition of a constant value to the simulated radiances in order to produce a zero-level offset results in a retrieved bias of the same amount. We note below that the derived zero-level offset with real satellite data is not a constant, but in fact has complex dependences on time, latitude, geometry, and radiance. We did not attempt to add this complexity to the simulations.”

• Scenario “Line 6” is not discussed. Please add discussion or remove scenario.
Thank you for noticing this. We had left out a reference to Line 6 where it was relevant to the discussion. That reference has now been added.

Page 13 line 9: Eq. ?? → correct reference.

As stated in the response to the first review, this was due to a problem with the last LaTeX compilation before submission. It has been fixed.

Page 15 line 74-76: Makes more sense as part of the introduction of Section 5.

We removed these sentences as they were not needed. We also had neglected to update this section when Figure 5 was revised in response to reviewer 1. We have now made the adjustments.

line 80: You state: “This implies that reasonable red SIF retrievals should be obtained using our new approach with existing instruments (provided they behave as expected) ...” Bearing in mind that your findings are based on self-consistent theoretical data analyses (end-to-end simulations) it is clearly too early to state that. The sensitivity study gives you at best guidance rules. Please keep in mind, that you excluded aspects like zero-offset correction, RRS (especially in the O2 - γ bands) or VRS. Please remove this sentence or weaken the statement.

We removed this statement.

line 6: The selection of this wavelength range is not explained/justified. This is unfortunate as a rather thorough sensitivity study has obviously not been used to support a wavelength window change from either Wolanin et al. (2015) or the window used in the sensitivity study (682 – 686.7 nm). Please justify!

We have rerun the simulations to make the results consistent with the range used here (682 – 686.5 nm). This did not make much difference to the results (see Table 1 with updated results). We also ran simulations for the fitting window used by Wolanin et al. (2015), and the results are now included in Table 1. We added corresponding text to go along with that addition. While bias increased somewhat, the RMS error significantly decreases with our somewhat larger fitting window as compared with the one used by Wolanin et al. (2015).

Page 17
line 60-61: I recommend to mention individual sensitivities of your algorithm(s) on the factors. Currently the list can be perceived as completely disconnected to your retrievals. For instance, the solar Fraunhofer line retrieval might be more/less affected by poor SNR values than the O2 - B retrievals.

We rearranged this paragraph and added some discussion as suggested.

Page 18
line 79: Please mention explicitly that this leads actually to a better spatial coverage.

done

line 89: there are some some … → there are some

fixed, thank you.

line 90 cont.: I cannot follow this argument. Koehler et al. (2015) show clearly stronger biases for GOME-2 than for SCIAMACHY while you are showing the opposite. Also the latitudinal dependence shown here is obviously more complex in case of SCIAMACHY than for GOME-2. Please explain in more detail or remove related sentences.

We removed this sentence.
Section 6.4: Please give reasons for the selection of these boxes.

We added “These areas were selected because they display significant interannual variability.”

Furthermore explain why you have decided to use a 3°x3° box.

We added “This resolution was selected in order to reduce the effects of instrumental noise in order to focus on the interannual variations.”

Page 19
line 3: Why are you only focusing on GOME-2 now? Explain.

We added an explanation at the beginning of this section, explaining that we focus on GOME-2 because we want to compare results with the high quality far-red GOME-2 retrievals.

Why more grid resolutions and why these values and no others?

We added that the grid resolution for the far-red retrievals is the standard resolution used for the publicly available level 3 data sets. We stated that the resolution for red retrievals shown here is lower to reduce the impact of noise.

line 25: You state: “This demonstrates the ability of the GOME-2 monthly red SIF at the box resolution to resolve signals of the order of +/-0.1 mw/m2/nm/sr.” I think, that an important “ingredient” to reach such signal levels is not mentioned which is the deseasonalization/anomaly analysis. Please rephrase.

We rephrased to “The deseasonalization performed here allows us to demonstrate that the ability of the GOME-2…”

line 33: I understood, that RRS is not that much of importance in this wavelength region (which has been well justified in other papers) but why is VRS not playing a role?

The sentence stated that our approach allows for a clean separation of the SIF and Raman scattering in the atmosphere (RRS) and ocean (VRS). This implies that VRS may play a role. We have tried to clarify this sentence (which was moved to the “Retrieval Methodology” section).

line 35: Why is no further “zero-level offset adjustment” performed? On page 12/line 82 you showed such a correction. Why not here?

We removed this sentence here and added near the old line 82 on page 12, “In fact, we did not find significant a zero-level offset in the ocean SIF retrievals as we did with the terrestrial retrievals. This is because the ocean retrievals rely more on the broadband emission rather than filling-in of solar lines that is more sensitive to false filling-in by effects such as stray light, dark current, and Raman scattering (oceanic or atmospheric). We therefore do not apply any zero-level adjustment over ocean.”

Page 20
line 40: “GOME-2 provides superior …” → “The reader is reminded that GOME-2 provides superior …” (makes sense when applying proposed change Page 18/line 79).

Changes made as suggested.
While this is true for GOME-2 this does not hold for SCIAMACHY. The results in Fig. 15/page 40 in this manuscript compared to Fig. 9/page 253 in Wolanin et al. (2015) are not directly comparable, as (1) the latter are shown for one year of data, while in this manuscript monthly data are shown and (2) the difference in color scales makes it impossible to compare reliably. A thorough quantitative comparison of both SCIAMACHY results could help. As long as you do not provide such a comparison please refrain from such statements or separate the qualitative comparison into two parts: one for GOME-2 and one for SCIAMACHY.

Here, we were speaking about the noisiness or patchiness rather than making a quantitative comparison. The reason we made this statement is that averaged over a year, the data should look smooth like the MODIS data. Our monthly data (at least GOME-2) look more smooth than Wolanin’s yearly data and also more similar to MODIS. Therefore, we have modified this statement to discuss only GOME-2 results.

“Our monthly means from GOME-2, using the full wavelength range between 660 and 713 nm, appear to be less noisy (patchy) than a GOME-2 yearly mean shown by Wolanin et al. (2015) that was obtained with a smaller fitting window that included only SFLs.”

You state that magnitude and patterns agree excellently. Please show this quantitatively and provide histogram of differences or a scatterplot.

We have modified the text and now show two types of difference maps (we think this provides more information than a scatterplot): absolute difference and percent different, where a scale factor was applied to MODIS in order to show that the differences are not simply a single scale factor. We added text to explain these figures.

As above, we changed “help anchor” to “estimate absorption within”.

We demonstrate that use of the O2 γ- and B-bands can increase red SIF retrieval precision as compared with approaches that utilize a smaller fitting window confined to regions outside the O2 B-band where the SIF signal is obtained solely by filling in of solar Fraunhofer features.”

As indicated before, assuming a better performance using additional spectral information suggests such an improvement. However, bearing in mind, that you have not yet elaborated on the impact of inelastic scattering (RRS and potentially VRS) and zero-offset:

• on the O2 - γ “constrain”
• on the creation of PCs
I doubt the conclusiveness of the present study to allow such a statement.

First, we changed this statement to reflect only the results of the simulations and added the caveats mentioned above: “Our simulations suggest that use of the O2 γ- and B-bands can increase red SIF retrieval precision over land as compared with approaches that utilize a smaller fitting window confined to regions outside the O2 B-band where the SIF signal is obtained solely by filling in of SFLs. However, we did not simulate the effects of complex biases in the simulations.”

We also added in the simulation section a statement that “The effects of vibrational Raman scattering (VRS) in the atmosphere are expected to be much smaller than those of RRS at these wavelengths and therefore not important (Lampel et al., 2015).”

Maybe I missed something but where in the manuscript can I find the analysis leading to the mentioned uncertainties? If this is not yet included please add or remove the statement.
We removed the statement.

**Comment 6 of referee #1 and your answer**
The results shown in Fig. 6 and 16 in your answer to referee #1 are very interesting and improving the reader’s understanding. I suggest to add “nm” to the annotation of the wavelength axis.

done

Furthermore I recommend to remind the reader that “b)” is referring to the full (and “constrained”) O2 - B retrieval while “c)” shows the results for the solar Fraunhofer line retrieval. I suppose that “d)” is the residual for the full O2 - B retrieval.

Thank you for noticing this. We have clarified the figure caption. It now reads “(a), observation and spectral fits of top-of-atmosphere (TOA) reflectance with and without SIF for the O2 band retrieval in (b) and (c); c) is a spectral zoom of b), and residual of the reflectance spectral fit in (d).”

Furthermore I’d like to reassure: the reflectances shown there are given as reflectances at top of atmosphere(?)

Yes, we have added to the caption that these are top-of-atmosphere reflectances.
New methods for the retrieval of chlorophyll red fluorescence from hyper-spectral satellite instruments: simulations and application to GOME-2 and SCIAMACHY

J. Joiner1, Y. Yoshida2, L. Guanter3, and E. M. Middleton1

1NASA Goddard Space Flight Center, Greenbelt, MD, USA
2Science Systems and Applications, Inc., Lanham, MD, USA
3Helmholtz Centre, Potsdam, Germany

Correspondence to: J. Joiner (joanna.joiner@nasa.gov)

Abstract.

Global satellite measurements of solar-induced fluorescence (SIF) from chlorophyll over land and ocean have proven useful for a number of different applications related to physiology, phenology, and productivity of plants and phytoplankton. Terrestrial chlorophyll fluorescence is emitted throughout the red and far-red spectrum, producing two broad peaks near 683 and 736 nm. From ocean surfaces, phytoplankton fluorescence emissions are entirely from the red region (683 nm peak). Studies using satellite-derived SIF over land have focused almost exclusively on measurements in the far-red (wavelengths > 712 nm), since those are the most easily obtained with existing instrumentation. Here, we examine new ways to use existing hyperspectral satellite data sets to retrieve red SIF (wavelengths < 712 nm) over both land and ocean. Red SIF is thought to provide complementary information to that from the far-red for terrestrial vegetation. Terrestrial SIF has been estimated with ground-, aircraft- or satellite-based instruments by measuring the filling-in of atmospheric and/or solar absorption spectral features by SIF. Our approach makes offers noise reductions as compared with previously published solar Fraunhofer line filling retrievals by making use of the oxygen (O2) γ-band that is not affected by SIF. The SIF-free O2 γ-band helps to estimate absorption within the spectrally variable O2 B-band which is filled in by red SIF. SIF also fills in the spectrally stable in conjunction with solar Fraunhofer lines (SFLs) at wavelengths both inside and just outside the O2 B-band which further helps to estimate red SIF emission that provide additional information on red SIF. Our approach is then an extension of previous approaches applied to satellite data that utilized only the filling-in of solar Fraunhofer lines by red SIF. We conducted retrievals of red SIF using an extensive database of simulated radiances covering a wide range of conditions. Our new algorithm produces good agreement between the simulated truth and retrievals and shows the potential of the O2 bands for noise reduction in red SIF retrievals as compared with approaches that rely solely on SFL filling. Biases seen with existing satellite data, most likely due to instrumental artifacts that vary in time, space, and with instrument, must be addressed in order to obtain reasonable results. The satellite instruments that we use were designed to make atmospheric trace-gas measurements and are therefore not optimal for observing SIF; they have coarse spatial resolution and only moderate spectral resolution (∼0.5 nm). Nevertheless, these instruments offer a unique opportunity to compare red and far-red terrestrial SIF at regional spatial scales. Our eight year record of red SIF observations over land with the Global Ozone Monitoring Instrument 2 (GOME-2) allows for the first time...
reliable global mapping of monthly anomalies. These anomalies are shown to have similar spatio-temporal structure as those in
the far-red, particularly for drought-prone regions. There is a somewhat larger percentage response in the red as compared with
the far-red for these areas that are drought-sensitive to soil moisture, although the differences are within the specified
uncertainties that are dominated by systematic errors. We also demonstrate that high quality ocean fluorescence line height
retrievals can be achieved with GOME-2 and similar instruments by utilizing the full complement of radiance measurements
that span the red SIF emission feature.
1 Introduction

Measurements of chlorophyll fluorescence over both land and ocean are related to photosynthetic function and thus the carbon cycle and climate feedbacks. Observations of solar induced fluorescence (SIF) from chlorophyll, obtained from specialized satellites, can provide global coverage within a few days at spatial scales relevant to global models (≈ 0.5° × 0.5° grid cells).

Satellite instruments that have been utilized to measure chlorophyll SIF over land include the MEdium Resolution Imaging Spectrometer (MERIS) (Guanter et al., 2007), the Japanese Greenhouse gases Observing SATellite (GOSAT) (Joiner et al., 2011, 2012), Frankenberg et al. (2011b), Guanter et al. (2012), the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) (Joiner et al., 2012, Köhler et al., 2015, Wolanin et al., 2015, Khosravi et al., 2015), the Global Ozone Monitoring Experiment-2 (GOME-2) (Joiner et al., 2013), and the Orbiting Carbon Observatoy 2 (OCO-2) (Frankenberg et al., 2014). Terrestrial SIF derived from these satellites has been used for studies focused on tropical dynamics (Parazoo et al., 2013, Guan et al., 2015a), primary productivity (Guenter et al., 2014, Parazoo et al., 2014, Zhang et al., 2014, Lee et al., 2015, Guan et al., 2015b), the carbon uptake period (Joiner et al., 2014, Walther et al., 2015), and responses to drought (Lee et al., 2013, Yoshida et al., 2015, Sun et al., 2015, Wang et al., 2016). Oceanic SIF measurements have been made with MERIS (Gower and King, 2007), SCIAMACHY, GOME-2 (Wolanin et al., 2015), the MODerate-resolution Imaging Spectroradiometer (MODIS) (Abbott and Letelier, 1999), and the Korean Geostationary Ocean Color Imager (GOCI) (O’Malley et al., 2014). MODIS has been used to detect red tides (e.g., Hu et al., 2005) and to conduct studies related to the physiology, phenology, and productivity of phytoplankton (e.g., Behrenfeld et al., 2009, Morrison and Goodwin, 2010, Gower and King, 2012, McKibben et al., 2012, Westberry et al., 2013, O’Malley et al., 2014, Gower, 2015).

In terrestrial vegetation, chlorophyll fluorescence is emitted at red to far-red wavelengths with two broad peaks near 685 and 740 nm, known as the red and far-red emission features, respectively, as shown in Fig. 1. Oceanic SIF is emitted in the red emission feature. The primary method used to measure the small terrestrial fluorescence signal from passive ground- and aircraft- remote sensing instrumentation makes use of dark features in spectra of reflected sunlight from oxygen absorption bands in the Earth’s atmosphere (see e.g., Meroni et al., 2009, Rascher et al., 2009, 2015, Damm et al., 2015 and references therein). The strong O₂ A-band (≈ 760 nm) and its somewhat weaker counterpart, the O₂ B-band (≈ 690 nm), are conveniently located near the peaks of the far-red (but displaced ∼20 nm) and red (≈ 5 nm) chlorophyll fluorescence emission features, respectively (see Fig. 1).

Solar Fraunhofer lines (SFLs), also shown in Fig. 1, have also been used to measure SIF from the ground (e.g., Guanter et al., 2013) and from space (Joiner et al., 2011, 2012, Frankenberg et al., 2011b, 2014, Guanter et al., 2012, Joiner et al., 2013, Köhler et al., 2015, Wolanin et al., 2015, Khosravi et al., 2015). Use of the filling-in of SFLs for satellite retrievals has several advantages as compared with that from oxygen absorption features. Firstly, the spectral structure of SFLs is not modified by clouds, aerosols, surface pressure, surface reflectance, or temperature as is the case with atmospheric oxygen absorption features (e.g., Preusker and Lindstrot, 2009, Joiner et al., 2011, Frankenberg et al., 2011a). Secondly, SIF emissions are partially absorbed in the atmosphere as they travel towards a satellite sensor at wavelengths where oxygen (and water vapor) are radiatively active. Satellite SIF retrieval algorithms that rely mostly or exclusively on the filling in of SFLs tend to...
be less complex than those that rely primarily on measurement of the signal in the O$_2$ A- and B-bands. To effectively utilize these O$_2$ bands, both the downward and upward transmittance through the atmosphere must be accurately estimated. Satellite SIF studies to date that rely primarily on these bands have either required an on-ground non-fluorescing target as applied to aircraft- (Rascher et al., 2009) or satellite-based data (Guanter et al., 2007) or have used simulated conditions to retrieve some of all of the parameters affecting the bands, as but have only been tested with simulated data (Guanter et al., 2010; Sanders and de Haan, 2013; ESA, 2015; Cogliati et al., 2015) and aircraft observations (Rascher et al., 2015).

Nearly all scientific studies utilizing space-based terrestrial SIF have thus far focused entirely on retrievals from the far-red fluorescence feature. While far-red SIF has been shown to be useful for several applications, having the combination of both red and far-red SIF observations may offer additional information. For example, the relative magnitudes of the red and far-red peaks and their emission intensities are sensitive to nitrogen uptake (Corp et al., 2003, 2006, 2010; Campbell et al., 2007, 2008; Zarco-Tejada et al., 2003) and responses to stresses including but not limited to low temperature and high salinity (Agati et al., 1995, 1996, 2000; Lichtenthaler, 1987, 1988, 1996; Rinderle and Lichtenthaler, 1988; Rossini et al., 2015; Ać et al., 2015) conducted meta-analysis of stress responses to red and far-red passively and actively sensed fluorescence signals for both leaf and canopy measurements. Their results indicate, for example, a higher detectability of water stress in the far-red as compared with the red fluorescence, consistent with observations of Daumard et al. (2010), Fournier et al. (2012), Middleton et al. (2015) and references within that showed influences of canopy architecture on far-red fluorescence signals. As noted, red and far-red canopy fluorescence measurements may reflect information from different layers of a canopy or leaf (Gitelson et al. 1998; Porcar-Castell et al., 2014) owing to higher amounts of reabsorption at red wavelengths. This may lead to higher sensitivity of the far-red signal to deeper layers of the canopy (Verrelst et al., 2015). While most fluorescence is emitted from photosystem II (PS II), a protein complex involved in photosynthesis, Agati et al. (2000) discuss the impact of photosystem I (PSI) and temperature sensitivity on the ratio of far-red to red fluorescence emissions. The PSI contribution grows with wavelength and is considered to be unaffected by biochemistry while the PSII contribution is affected by both physiological regulation as well as leaf structure and chemical composition (Verrelst et al., 2015). In a canopy radiative transport model, Verrelst et al. (2015) then show that the carboxylation capacity ($V_{cma}$), related to photosynthetic capacity, has its greatest influence in the red emission peak. They further suggest that when trying to relate SIF to photosynthetic quantities such as gross primary productivity (GPP), it would be more beneficial to exploit the full broadband emission flux as compared with a single band in the far-red.

SIF emissions must be understood and accounted for in order to make the best possible use of oxygen bands for atmospheric applications. For example, the O$_2$ A-band has been used to estimate cloud pressure (e.g., Kuze and Chance, 1994; Koelemeyer et al., 2001; Kokhanovsky et al., 2003; Loyola et al., 2007) and aerosol plume height (e.g., Sanders et al., 2015). The O$_2$ A-band has also been used to assess photon pathlength for trace-gas retrievals including CO$_2$ (e.g., O’Dell et al., 2012). It is for this purpose that the A-band spectral region is specifically observed with several atmospheric satellite sensors. Unfortunately for SIF retrieval, some of these instruments, such as GOSAT and OCO-2, include only the O$_2$ A-band and not the B-band. However, GOME-2 and SCIAMACHY include both bands.
Terrestrial SIF retrievals near the red peak can have larger errors than those near the far-red peak for several reasons. Firstly, SFLs are not as wide and deep in the red region as those in the far-red; this makes the red SFLs less sensitive to filling-in by SIF, particularly at the moderate spectral resolution (full width at half maximum, FWHM, $\sim 0.5 \text{ nm}$) of current satellite sensors such as GOME-2 and SCIAMACHY that have spectral coverage in the red region. Secondly, the $\text{O}_2$ B-band covers a fairly large section of the SIF near the peak within the red fluorescence emission feature. Therefore, less spectral range near the red peak is available for the straightforward SFL retrieval approach as compared with the far-red. Thirdly, the sharp upturn of the red-edge in reflectance (see Fig. [1]) may complicate red SIF retrievals. For example, it may necessitate the use of smaller rather than larger spectral fitting windows for SFL retrievals. Finally, at lower reflectances of the red band as compared with the far-red, instrumental artifacts such as effects of dark current and stray light may constitute a larger percentage of the overall observed radiance leading to larger systematic errors.

Results of simulated red SIF retrievals performed for the TROPOspheric Monitoring Instrument (TROPOMI), a hyperspectral grating instrument to be launched in 2016, show that it should have capability to retrieve red SIF using relatively small spectral fitting windows ([Guanter et al. 2015], [Wolanin et al. 2015]) showed that a red SIF signal can be detected from SCIAMACHY and GOME-2 over both land and ocean using a spectral fitting window of 681.8–685.5 nm that is located close to the red SIF emission peak but just outside the $\text{O}_2$ B-band. Results over land for two months show spatial patterns similar to those of the Enhanced Vegetation Index (EVI). While promising, the monthly averages show a significant offset between GOME-2 and SCIAMACHY red SIF magnitudes over both land and ocean was shown ([Wolanin et al. 2015]). Yearly averages of normalized fluorescence line height over ocean from SCIAMACHY appear noisy as compared with those from MODIS. Some of these difficulties in retrieving red SIF should be overcome with the higher spectral resolution instruments designed specifically for fluorescence retrievals ($\leq 0.3 \text{ nm}$) planned with the Fluorescence Explorer (FLEX) mission, as recently shown with modeling studies ([Cogliati et al. 2015]).

Here, we develop new methodology to retrieve terrestrial red SIF using space-based hyper-spectral measurements, especially useful for implementation with moderate spectral resolution data currently available. The approaches make use of SFL filling and absorption in and around the $\text{O}_2$ B- (or A-) bands. Absorption of sunlight in atmospheric absorption bands is complicated due to photon path modulation by aerosol and cloud profiles, surface pressure, and surface effects such as the bi-directional reflectance distribution function (BRDF). Our new methodology additionally makes use of the relatively weak $\text{O}_2$ $\gamma$-band spectral region, near 627 nm, essentially as an additional anchor to estimate the amount of absorption that will be present in the $\text{O}_2$ B- (or A-) bands. The $\text{O}_2$ $\gamma$-band occurs in a spectral valley between red and blue-green fluorescence features (e.g., [Lichtenthaler and Schweiger 1998]) and so has a minimal sensitivity to vegetation fluorescence. This band also has a minor sensitivity to water vapor absorption as is the case for the $\text{O}_2$ B-band (see Fig. [1]). Both bands are affected by clouds and aerosol, in a related and predictable way. As will be shown below, principal component analyses of cloudy observations over ocean show that a large fraction of the spectral variability in both bands ($> 99.96\%$) is described by just two modes, one dominated by $\text{O}_2$ absorption and the other by $\text{H}_2\text{O}$ absorption. Therefore, the fluorescence-free $\text{O}_2$ $\gamma$-band can be used to estimate the amount of absorption in the fluorescence-contaminated $\text{O}_2$ B-band under all-sky conditions. Reflectance in between the continuum surrounding both bands is very similar for cloudy conditions. Over land, there are small differences in
continuum reflectance surrounding the two bands that may produce small errors (see e.g., Fig. 1) when using the O$_2 \gamma$-band to estimate B-band absorption. Fluorescence also produces filling-in of SFLs shown in Fig. 1 both inside and outside the O$_2$ B-band. This provides additional information to disentangle the spectral signature of absorption from fluorescence within O$_2$ B-band. Use of the O$_2$ B-band may help to reduce noise in retrievals of the very small red fluorescence signal.

Our methodology is similar to approaches developed for ground- and satellite-based instruments in that radiative transfer in atmospheric absorption bands is approximated using a data-driven principal component analysis (PCA) approach (Ganter et al., 2012; Joiner et al., 2013; Köhler et al., 2015). Similar PCA methods have also been applied to retrievals of atmospheric trace gases (Li et al., 2013, 2015) and have been used to identify different phytoplankton groups with SCIAMACHY (Bracher et al., 2009). While our approach does not require a nearby non-fluorescing target, it does make use of a representative sample of observations over non-fluorescing scenes in order to generate a comprehensive set of fluorescence-free principal components (PCs). For this purpose, we use desert and snow- or ice-covered data over land as well as cloudy observations over ocean covering a large range of latitudes and conditions. While our approach is generally applicable to either the O$_2$ A- or B-band spectral regions, we focus here on the B-band. The O$_2$ A-band has more non-linear absorption (saturated lines) and tends to be brighter than the O$_2$ B- or $\gamma$-bands over vegetated land (see Fig. 1); this may lead to complex photon path differences for the O$_2$ A-band as compared with the B-band in the presence of cloud and aerosol. In addition, SIF can be accurately retrieved with existing satellite instrumentation in the far-red emission feature without need of the O$_2$ A-band by utilizing the filling-in of SFLs (Joiner et al., 2013). In contrast, current moderate spectral resolution satellite retrievals using SFLs near the red emission peak suffer from high noise and systematic errors (Wolanin et al., 2015). Our methods offer a potentially more sensitive approach.

We conduct simulations to demonstrate the applicability of our approach to current and future satellite instruments. We then apply our technique to data from SCIAMACHY on the European Space Agency (ESA) Environmental Satellite (Envisat) and GOME-2 on the European Meteorological Satellite (EuMetSat) first operational MetOp-A satellite. The primary function of these instruments was and is to make measurements of atmospheric trace gases. While not optimal for fluorescence retrievals owing to their relatively large ground footprints and moderate spectral resolution, their excellent ground sampling, large spectral coverages, and high signal-to-noise ratios enable red SIF retrievals. Near-global coverage is provided within a few days from GOME-2 and SCIAMACHY measurements. Application of our approach leads to unprecedented precision and accuracy for red SIF data sets that span more than a decade. We also show that these sensors can be used to make high quality measurements of fluorescence line height over the ocean by utilizing their full spectral content covering the range of red SIF emissions.

2 GOME-2 and SCIAMACHY satellite data

We use data from GOME-2, a nadir-viewing cross-track scanning spectrometer that measures radiances at wavelengths from the ultraviolet to the near-infrared (240–790 nm) (Munro et al., 2006). It flies on the series of European Meteorological Satellites (EUMETSAT) as part of the Polar System (EPS) MetOp mission. GOME-2 measures the solar irradiance and backscattered radiance from the Earth in four detector channels. Here, we use revision R2 level 1B data from channel 4 that covers wave-
lengths 590–790 nm with a spectral resolution of approximately 0.5 nm \cite{Callies2000}. The signal-to-noise ratio (SNR) in this channel is fairly high (\(>1000\)). The footprint size on the Earth’s surface at nadir view is approximately 40 km \(\times\) 80 km in its nominal mode with a swath width of 1920 km. In this mode, it takes about 1.5 days for a single GOME-2 instrument to provide coverage of Earth’s surface globally.

The first GOME-2 instrument was launched on the MetOp-A satellite 19 October 2006. MetOp satellites are in a polar orbit with an equator crossing local time near 09:30 LT. The second GOME-2 was launched 17 September 2012 on the MetOp-B platform that has a similar equator crossing time but is 180° out of phase with respect to the first flight model. Therefore, one or the other of the GOME-2 instruments is making observations of the sunlit part of the Earth. Near daily global coverage is provided by the two instruments. Since 15 July 2013, GOME-2 onboard MetOp B makes observations in the nominal mode, while the MetOp A GOME-2 measures in a reduced swath of 960 km with a nadir pixel size of \(\sim\)40 km by 40 km.

SCIAMACHY is a similar grating spectrometer that makes measurements in both limb- and nadir-viewing geometries from ultraviolet to near-infrared wavelengths (212–2386 nm) in eight separate channels \cite{Lichtenberg2006}. It was launched in February 2002 on Envisat and took measurements until 8 April 2012 when communication with the host satellite was suddenly lost. Envisat flew in a sun-synchronous orbit with a descending node equator crossing time near 10:00 LT. In this work, we use channel 4 that covers wavelengths between 595 and 812 nm at a spectral resolution of 0.48 nm. The nadir ground footprint size is approximately 30 km by 60 km in the along and across track directions, respectively, for latitudes between 60 N and 60 S. Note that for the fitting windows that have been used to retrieve far-red SIF with SCIAMACHY, coadding of pixels was done on board, resulting in a degraded spatial resolution of 240 km cross track by 30 km along track. We use the SciaL1c command-line tool software package \cite{DLR2006} to apply all available corrections and calibrations to generate level 1B data.

3 Simulated radiances and irradiances

To test the algorithm and accurately quantify retrieval errors, we use radiance simulations over a wide range of conditions similar to that used by \cite{Joiner2013} and \cite{Ganter2015} but now including wavelengths in and surrounding the O\(_2\) \(\gamma\) band. Here, we provide a brief overview of the simulated data. Top-of-the-atmosphere (TOA) radiances are computed using the Matrix Operator Model (MOMO) radiative transfer model \cite{Fell2001,Preusker2009} with absorption line parameters from the high-resolution atmospheric radiance and transmittance model code (HITRAN) 2008 dataset \cite{Rothman2009}. The monochromatic sun-normalized radiances are sampled at 0.005 nm. They are then multiplied by a solar spectrum sampled in the same way and finally convolved with various instrument line shape functions and resampled. As in \cite{Joiner2013}, we use solar data from kurucz.harvard.edu/sun/irradiance2005/irradthu.dat, similar to \cite{Chance2010} but more highly sampled.

Neither rotational-Raman scattering (RRS) nor O\(_2\) A-band dayglow emissions are included in the simulation. RRS is as they are relatively small at the O\(_2\) B-band wavelengths \cite{Vasilkov2013}. We expect that RRS will also be small within the less deep feature of the O\(_2\) \(\gamma\)-band even though the amount of RRS will increase somewhat with the decrease in wavelength. We also expect that with real data, the effects of RRS may be partially accounted for within our PCA retrieval.
framework discussed below as they are not purely additive, but also contain a multiplicative component of interest. The effects of vibrational Raman scattering (VRS) in the atmosphere are expected to be much smaller than those of RRS at these wavelengths and therefore not important \cite{Lampel2015}. Directional effects of the vegetation reflectance and fluorescence are also not simulated, but the impact on SIF retrievals is expected to be limited as discussed below.

Radiantces are computed for a range of view and solar zenith angles (SZAs), atmospheric temperatures, humidities, aerosol profiles, and surface pressures as discussed in \cite{Joiner2013}. Two separate data sets are created, one without fluorescence intended for principal component analyses (referred to as “training”), and one containing fluorescence intended to examine retrieval performance (referred to as “testing”). There are sixty possible top-of-canopy fluorescence spectra from various combinations of chlorophyll content and leaf area index (LAI) as shown in \cite{Joiner2013}. We used only combinations that produced fluorescence values of $<1 \text{ mW/m}^2/\text{nm/sr}$ at 682 nm, consistent with GOME-2 and SCIAMACHY satellite observations shown below. There are a total of 38 400 and 15 655 different samples in the training and testing data sets, respectively.

4 Retrieval methodology

We performed several types of red SIF retrievals using both real satellite data and simulations. The first type of retrieval relies solely upon the filling-in of SFLs by SIF. This approach was similar to that used by \cite{Joiner2013} for far-red SIF retrievals and \cite{Ganter2015} for simulated TROPOMI red SIF retrievals employing a relatively small fitting window (682–686.5 nm). This window is similar to the one used by \cite{Wolanin2015} in a differential optical absorption spectroscopy (DOAS) type of retrieval applied to GOME-2 and SCIAMACHY. We refer to this approach as the SFL red SIF retrieval.

The second type of retrieval, referred to as the O$_2$ band red SIF retrieval, is used to estimate terrestrial red SIF and expands the spectral fitting windows of the SFL retrievals to encompass the O$_2$ $\gamma$- and B-bands. The difficulty in using these absorption bands for satellite retrievals is that their depth (in the absence of SIF filling-in) must be accurately characterized in order to estimate the filling-in due to SIF. Their depth can be altered by aerosols, clouds, surface pressure, and the surface reflectance. The FLEX approach for utilizing these bands is to perform an atmospheric correction to estimate the bottom of atmosphere (BOA) radiance using data from FLEX itself as well as measurements from the Sentinel-3 satellite that will fly in tandem \cite{Cogliati2015}. Here, we provide an alternative method.

We propose to use the O$_2$ $\gamma$-band, that is not affected by SIF filling-in, to characterize the depth of the O$_2$ B-band in the absence of SIF. As will be demonstrated below, principal component analyses show that in the absence of SIF, the depths of the O$_2$ $\gamma$- and B-bands are highly correlated; a very high fraction of the spectral variability of both bands can be described by just a couple of principal components, representing absorption from both O$_2$ and H$_2$O columns in the atmosphere. This is aided by the fact that over land (as is the case for clouds over ocean), the reflectance of both bands is very similar, leading to a predictable B-band depth if that of the $\gamma$-band is measured. In the presence of SIF, additional information on the filling-in effect on the B-band can be gleaned from the filling-in of SFLs. Therefore, both the $\gamma$-band and filling-in of SFLs can be used
to estimate the band depth of the B-band and disentangle this from the filling-in effect of SIF. The potential advantage of using the O$_2$ bands is that this may offer some noise reduction as compared with what can be achieved by using only the filling-in of SFLs. This is important for the difficult measurement of the very small red SIF signal. As described below, both O$_2$ bands may be additionally filled in by rotational and vibrational Raman scattering. However, this filling-in may be small to negligible in these bands and even if measurable may be at least partially accounted for by our principal component analysis approach. The fitting windows for our O$_2$ band retrievals are 622–640 nm for the O$_2$ γ and two different windows between 682 and 698 nm for the O$_2$ B-band, either 682–692 nm or 682–698 nm. This approach is applicable to terrestrial SIF retrievals.

Oceanic red SIF can be retrieved using the filling-in of SFLs (Wolanin et al., 2015), the continuum red SIF emission which can be measured above the dark ocean surface (Hu et al., 2005), or both, as will be shown here. Here, we selected the Our approach for ocean retrievals uses the full spectral window of 660–713 nm for ocean SIF retrievals. Our approach for ocean retrievals primary exploits the continuum SIF emission that includes both sides of the 683 nm feature. This emission can be cleanly detected over the relatively dark ocean surface as proven by the use of the broadband MODIS sensor to measure it. Use of the large fitting window encompassing the red SIF emission feature is not only feasible for oceanic fluorescence retrievals, owing to the otherwise relatively dark ocean surface, but also beneficial. Firstly, fitting the peak as well as both shoulders of the red SIF emission feature allows for a clean separation of its spectral structure with that of monotonically decreasing or otherwise independent spectral effects such as those produced by water leaving radiance, atmospheric scattering and absorption, rotational Raman scattering (RRS) in the atmosphere, and vibrational Raman scattering (VRS) in the ocean. Secondly, use of this large fitting window also reduces the impact of instrumental noise and other artifacts such as non-linearity effects that impact the small radiance levels typically measured over ocean. The O$_2$ γ-band is not needed or used here for the oceanic SIF retrievals.

4.1 General approach

The basic idea behind our approach is similar that used by Joiner et al. (2013). The key is to separate the spectral features of sun-normalized top-of-atmosphere (TOA) radiances ($\rho_{\text{tot}}$) as a function of wavelength $\lambda$ related to 1) atmospheric absorption (i.e., the total irradiance transmittance $T$ and the spherical transmittance from surface to TOA, $\overline{T}$; 2) surface reflectivity ($\rho_s$); and 3) SIF radiance emitted at the surface. Neglecting the effects of atmospheric Rayleigh scattering, which was shown to be appropriate in this context (Joiner et al., 2013), we have

$$\rho_{\text{tot}}(\lambda) = \rho_s(\lambda)T(\lambda)\overline{T}(\lambda) + \frac{\pi\text{SIF}(\lambda)}{E(\lambda)\cos(\theta_0)},$$

(1)

where $\theta_0$ is the solar zenith angle (SZA), and $E(\lambda)$ is the observed extraterrestrial solar irradiance. Joiner et al. (2013) showed that $\overline{T}(\lambda)$ could be estimated using

$$\overline{T}(\lambda) = \exp\left(\ln[T_2(\lambda)]\frac{\sec(\theta)}{\sec(\theta) + \sec(\theta_0)}\right),$$

(2)

where $\theta$ is the view zenith angle, and $T_2(\lambda) = T(\lambda)\overline{T}(\lambda)$ is the sun to satellite (2-way) atmospheric transmittance. This amounts to the assumption of the so-called geometrical air mass factor within the DOAS formulation that is appropriate
for a non-scattering, linearly absorbing atmosphere. With atmospheric scattering \( \rho_s(\lambda) \) and SIF(\( \lambda \)) represent TOA spectral components of surface reflectance and fluorescence modified by atmospheric scattering (cloud, aerosol, and Rayleigh) that is spectrally smooth. In other words, atmospheric scattering is implicitly accounted for within these terms. As both Rayleigh scattering and aerosols are included in our simulation data set, we can evaluate their impact on the retrievals. Equation 1 also assumes a Lambertian surface. The implications of this assumption are discussed below.

Here, we model the fluorescence red emission feature as a function of wavelength as having a Gaussian shape similar to e.g., Subhash and Mohanan (1997) and Zarco-Tejada et al. (2000), i.e.,

\[
\text{SIF}(\lambda) = A \exp\left(\frac{(\lambda - \lambda_0)^2}{2\sigma^2}\right),
\]

where \( A \) is the SIF magnitude at the peak emission given in radiance units. For the red fluorescence emission feature, we use \( \lambda_0 = 683 \) nm. Over ocean, we found that a value for the Gaussian standard deviation, \( \sigma \), of 9.55 nm provided a good fit to observations. Over land, we found that interference from the far-red SIF emission feature may necessitate the use of different values of \( \sigma \) depending on the size of the spectral fitting window as discussed below.

As in Joiner et al. (2013), we assume that \( \rho_s(\lambda) \), within our limited spectral fitting window, is spectrally smooth and model it as a low order polynomial in \( \lambda \). While other representations for fluorescence and reflectance have been explored (e.g., Mazzoni et al., 2010, 2012), small errors in the assumed shape of the fluorescence emission will likely have little impact on the estimated peak fluorescence value (Daumard et al., 2010; Fournier et al., 2012; Guanter et al., 2013). We estimate the spectral structure of \( T_2 \) using principal components (PCs) as described below.

### 4.2 Generation of atmospheric PCs

Here, we use a data-driven approach to estimate \( T_2(\lambda) \) in Eq. 2. We perform a principal component analysis (PCA) to represent \( T_2(\lambda) \) similar to the approach of Joiner et al. (2013) and Köhler et al. (2015), i.e.,

\[
T_2(\lambda) = \sum_{i=1}^{n} a_i \phi_i(\lambda) + 1,
\]

where \( \phi_i(\lambda) \) are the principal components (PCs) and \( a_i \) are the coefficients of the PCs. In place of laboratory-measured absorption cross-sections as is typical in the DOAS approach, we are essentially using atmospheric spectra (simulated or measured) to derive the spectral components of atmospheric absorption. This approach has the following advantages: 1) it does not require knowledge of the instrument response function and 2) it implicitly captures instrumental artifacts such as drifts and imperfections in the wavelength calibration. On the other hand, the PCs may mix instrumental effects with real atmospheric phenomena in the orthogonal PCs. This does not allow for a clean analysis of instrumental artifacts or accuracy of the radiative transfer. In addition, the approach may not work well if an unrepresentative sample is used to generate the PCs.

For comparison, we performed the PCAs with both the simulation training data and actual GOME-2 radiances. For the GOME-2 PCA, we use spectra from a single day consisting of observations over sea ice, snow/ice-covered land, the Sahara desert, and cloudy ocean (avoiding continental coastlines) for pixels with \( \theta_o < 70^\circ \) and geometrical air mass factors, GAMF...
\[ \sec(\theta) + \sec(\theta_o) < 5. \] The precise areas used are shown in the supplemental material. We compute the reflectance at 670 nm \((\rho_{670})\) and use ocean observations only for \(\rho_{670} > 0.7\) and Sahara pixels only for \(\rho_{670} > 0.52\).

Joiner et al. (2013) used the logarithm of the normalized radiance spectra as is typical in DOAS implementations. Here, we work with the normalized radiances rather than the logarithm of the normalized radiance as this works just as well. For both real and simulated data, we normalize the spectra with respect to second order polynomials fit to wavelengths not significantly affected by atmospheric absorption (i.e., \(620 < \lambda < 625\) nm, \(635 < \lambda < 640\) nm, \(680 < \lambda < 687\) nm, \(712 < \lambda < 713\) nm). This essentially produces atmospheric transmittance spectra. We then subtract unity before conducting the principle component analysis to produce values of zero in the absence of atmospheric absorption. The value of unity is then added back in the retrieval step once the coefficients of the PCs are determined in order to compute the two-way transmittance. In the strict implementation of PCA, a mean spectrum is computed and subtracted from each spectrum. We found that this is not necessary and in fact further complicates the approach. When the mean is not subtracted, the first PC represents the mean atmospheric transmittance.

Note that we use a slightly larger \(O_2\) B-band window for the PCA as compared with the retrieval. The larger PCA window is needed to fit the radiances not affected by strong \(O_2\) or \(H_2O\) absorption so that atmospheric transmittance may be accurately computed. The leading principal components are related to atmospheric absorption from oxygen and water vapor as well as instrumental effects such as wavelength shifts that span this full wavelength range. Testing with simulation data confirms that using a larger fitting window for the PCA as compared with the retrieval does not present problems. In other words, we are able to use smaller fitting windows for SIF retrievals that are contained within the larger one used for the PCA.

One key difference with respect to the approach used by Joiner et al. (2013) is that here we use two separate and disconnected spectral regions, encompassing the \(O_2\) \(\gamma\)- and B-bands, to retrieve SIF in the red emission feature over land. For these two fitting windows, a single PCA is performed that covers both fitting windows. The purpose of the PCA is to relate the absorption in the \(O_2\) \(\gamma\)- and B-bands in the absence of fluorescent emissions. Then, in the retrieval step the \(O_2\) \(\gamma\)-band can be used to disentangle the spectral structure of absorption and fluorescence within the \(O_2\) B-band. This is done simultaneously with the retrieval of red SIF and the surface spectral reflectance. Equation 2 is used to estimate how much of the SIF emission is absorbed within the atmosphere as it travels towards the satellite sensor.

Figure 2 shows the leading four PCs for the wavelength ranges 622-640 nm and 680-713 nm that encompass the \(O_2\) \(\gamma\)- and B-bands, respectively. The PCs are computed with simulated data for FWHMs of 0.5 nm (similar to GOME-2) and 0.3 nm as well as with actual GOME-2 data from 1 July 2012. The spectral variance in these windows is due to both oxygen and water vapor absorption. The variances explained (with respect to the total) as well as the cumulative variances explained are indicated. The PCs for the simulated data are similar for the two spectral resolutions with more fine-scale structure, particularly in the oxygen B-band, at the higher resolution. The variance explained by the leading PCs is similar for the simulated data at the two spectral resolutions and for GOME-2 data, with slightly more variance explained per PC for GOME-2 data. The first PC explains over 96% of the spectral variance. More than 99.97% of the variance is captured in the first four modes for both the simulated and GOME-2 data.
The PCs for simulated and real data are not expected to be identical. PCs from the real data may contain instrumental artifacts and processes not included in the simulated data (e.g., rotational-Raman scattering). In addition, the simulated data may not represent all of the conditions or the distribution of conditions that are present in the GOME-2 data. It is nevertheless remarkable how similar the leading PCs are in the simulated data as compared with the GOME-2 data.

4.3 Solving the non-linear problem

As described in [Joiner et al. 2013], we use a gradient-expansion algorithm to solve the non-linear estimation problem using a forward model based on Eqs. 1-4. The observation vector for each pixel consists of sun-normalized radiances in two separate windows, encompassing the O$_2$ $\gamma$ and B-bands. In general, the state vector consists of 1) coefficients of the PCs, 2) separate sets of coefficients for surface reflectance polynomials in the two windows, and 3) either the peak value of the red fluorescence feature centered at $\sim$683 nm for O$_2$ band retrievals or an averaged value of SIF over the SIF fitting window for SFL retrievals. For all results shown in the remainder of this paper, SIF represents a single value that refers to either the peak value or an average over the fitting window as appropriate for the red or far-red emission features. At convergence, the partial derivatives contained in the Jacobian $K$ matrix may be used to compute errors from an unconstrained linear error estimation, i.e.,

$$S_r = (K^T S_e^{-1} K)^{-1},$$

where $S_r$ is the retrieval error covariance matrix, and $S_e$ is the measurement error covariance (e.g., Rodgers 1990).

Specifically, the state vector of the SFL red SIF terrestrial retrievals consist of coefficients for a third order polynomial to model the surface reflectivity, coefficients for 3 PCs, and a mean value of SIF across the small fitting window (i.e., the Gaussian shape for SIF emission is not needed or used). In contrast, the state vector for the more complex O$_2$ terrestrial red SIF satellite retrievals includes coefficients of 15 PCs, coefficients of a fourth order polynomial for surface reflectivity in each O$_2$ fitting region, and the peak value of SIF at 683 nm assuming a Gaussian shape for SIF emissions at red wavelengths. The fitting windows used for GOME-2 and SCIAMACHY were 622–640 nm for the O$_2$ $\gamma$ band region and two different fitting windows between 682 and 692 nm for the B-band region. We used $\lambda_0 = 683$ nm and $\sigma = 10$ for the satellite retrievals. The selection of these parameters will be discussed in more detail below.

The polynomial model for surface reflectivity can account for atmospheric scattering (Rayleigh and aerosol); the polynomial coefficients represent an effective surface reflectivity rather than the true surface reflectivity. This effective surface reflectivity includes the spectrally smooth effects of atmospheric scattering. In addition, this formulation can also account for the effects of non-Lambertian surface reflectance. In this case, the retrieved coefficients will produce a reflectivity either higher or lower than that of a Lambertian surface. The resulting interaction with atmospheric scattering will still produce a spectrally smooth function of wavelength that can be represented with a polynomial function. There should be virtually no impact on the retrieved SIF in this case. For non-Lambertian SIF, we will simply retrieve and report the SIF radiance for the given geometry. This value may be different from a retrieval obtained for a different viewing geometry.

For oceanic retrievals, coefficients of 8 PCs are retrieved along with those of a second order polynomial to account for the spectral dependence of the water leaving radiance. The fitting window 660–713 nm spans the range of significant red SIF
emissions. We use Eq. 3 with $\lambda_0 = 683$ nm and $\sigma = 9.55$ for oceanic SIF emissions. By trial and error, we found that these parameter values provide adequate fits to the observed radiances over ocean.

### 4.4 Processing of GOME-2 and SCIAMACHY data

The overall processing of the satellite data follows the approach detailed in [Joiner et al. (2013)] which is augmented as described in this section. Figure 3 shows a flow diagram of the basic steps. One subset of radiance data is used to generate the PCs (chosen such that fluorescence is not present). We perform a PCA daily using a single measured solar irradiance spectrum per day. Similar to [Joiner et al. (2013)], we use pixels over highly cloudy ocean and snow- and ice-covered surfaces ($\rho$ at 670 nm > 0.7 and SZA < 70°) and the Sahara for the PCA. The derived PCs are then used for the fluorescence retrieval. Quality assurance checks (see Sects. 4.4.2-4.4.3) and bias adjustments are then conducted to filter out noisy radiance data, cloudy data, and failed retrievals (see also Joiner et al., 2013). Adjustments are also made to and remove biases (see Sects. 4.4.1 and 4.4.4) below in Finally, the quality controlled retrievals are gridded at a monthly temporal and 1° (or other as noted) spatial resolution to produce level 3 data sets.

Ideally, the last step is validation of the level 2 or 3 data sets. There are very few opportunities for validation available. [Yang et al. (2015)] compared ground-based data with far-red SIF from GOME-2 for a season over one forested location. But in general, it is difficult to compare ground-based data with large pixel satellite data owing to the spatial mismatch. Aircraft-based data are extremely limited at the current time. One of the few tools available for global validation is intercomparison of different satellite data sets as in [Joiner et al. (2013), Köhler et al. (2015), and Khosravi et al. (2015)] which is the approach undertaken here.

#### 4.4.1 Absolute solar calibration drift

Many instrumental calibration issues cancel out when using the ratio of the Earth radiance to the solar irradiance (i.e., reflectances) in Eq. 1. For example, the reflectance degradation factor at the wavelengths of interest for GOME-2 SIF retrievals is reported to be only a few percent over the course of the MetOp-A mission [Tilstra et al. (2012)]. Other types of degradation can also occur that may or may not cancel in the reflectances. Wavelength shifts and changes in the spectral bandpass can change over time [Dikty et al. (2012)]. For GOME-2, changes in the instrument bandpass occurred primarily in the ultraviolet (UV) channels of the instrument. Even so, this type of degradation should be handled within the our algorithm with use of the PCA. However, there are still some unexplained instrument behaviors for GOME-2, such as the dependence of the dark signal on temperature [Dikty et al. (2012)], that may not be fully accounted for within our algorithm or zero-level adjustment scheme and will lead to systematic errors in SIF retrievals. Various other instrumental effects that may produce false signatures in SCIAMACHY SIF retrievals are documented in [Lichtenberg (2006)]. Their potential impact on SIF retrievals is discussed in [Joiner et al. (2012)]. An approach to mitigate the resulting biases in SIF retrievals is detailed in Sect. 4.4.4.

As compared with pure DOAS retrievals used for trace-gas retrievals, SIF retrievals are more sensitive to the absolute calibration of the solar irradiance data (see Eq. 1). MetOp-A GOME-2 has encountered radiometric degradation over its lifetime. We have made adjustments to the SIF retrievals based on irradiance changes that occurred at 690 nm. We fit a second order
polynomial to these irradiances as a function of time after accounting for variations in the sun-Earth distance. These changes are of the order of 15% and occurred primarily over the first 6 years of the mission with stabilization after that.

4.4.2 Cloud filtering and quality control

As detailed in Joiner et al. (2012), we compute an effective cloud fraction $f_c$. Neglecting scattering, it is derived using

$$f_c = \frac{R_{\text{obs}} - R_s}{0.8 - R_s},$$

where $R_{\text{obs}}$ is the retrieved surface reflectivity (assuming no atmospheric scattering) at the shortest wavelength in the fitting window, and $R_s$ is the black-sky 16-day gridded filled-land surface albedo product from Aqua MODIS (MOD43B3) at 656 nm (Lucht et al., 2000). When computing monthly SIF averages, we eliminate data with $f_c > 0.3$, consistent with that used in version 26 far-red GOME-2 SIF level 3 product provided on http://avdc.gsfc.nasa.gov.us. The choice of the cloud threshold is empirical. Our selection of 0.3 is a more stringent threshold than that used by Joiner et al. (2013) and Köhler et al. (2015) and results in somewhat noisier results owing to a decrease in sampling. Köhler et al. (2015) showed that magnitudes of gridded SIF decrease with increases in the cloud cover threshold, but that the overall temporal variations remain consistent.

Simulations show that a substantial fraction of the satellite SIF signal can still be detected even through moderately cloudy conditions (Frankenberg et al., 2012). Use of more or less stringent limits on cloud contamination within a moderate range did not substantially alter the derived spatial and temporal patterns of red SIF. However, placing stricter limits decreases the number of samples included in a gridded average. This reduces coverage and increases noise in gridded SIF averages.

In the results shown below, we include all data passing gross quality assurance checks on the retrieval convergence and radiance residuals. These checks typically remove few observations. We also eliminate all data with SZA $> 70^\circ$.

4.4.3 Radiance spike removal

The South Atlantic Anomaly (SAA) increases noise in observed radiances in the vicinity of South America over southern Brazil and surrounding areas, particularly for GOME-2 measurements but also present in SCIAMACHY radiances (Köhler et al., 2015; Wolanin et al., 2015). In an effort to mitigate the effects of this noise, the following steps are taken. A first step PCA is conducted as outlined above. Then, for each observation, the spectrum is reconstructed using a reduced number of PCs. In this work, we use 20 PCs. The maximum error for each reconstructed spectrum is then computed. Any spectra with maximum errors $> 0.5\%$ are discarded from the sample. The PCA is performed again using only the spectra passing this quality control check. Typically, only a very small fraction of spectra are removed from the sample during this process.

A radiance outlier check is also performed during the retrieval process as follows. A first step retrieval is performed using all radiances within the specified fitting window. Following the retrieval, radiance residuals (observed minus computed from the retrieval) are calculated. If any radiances residuals are $> 0.5\%$, those wavelengths are then given a weight of zero in a second step retrieval. If for a given observation, more than half of the wavelengths have radiance residuals $> 0.5\%$, that observation is flagged. Again, only a very small percentage of spectra are flagged in this process.
4.4.4 Zero-level adjustment

Köhler et al. (2015) found that GOME-2 and SCIAMACHY far-red SIF retrievals exhibited biases, henceforth referred to as zero-level offsets, in the PCA training data set (expected to have a mean near zero) of the order of several tenths of a mW/m²/nm/sr with systematic dependences on latitude. The biases were higher for GOME-2 as compared with SCIAMACHY by a factor of 2 or more and the dependences on latitude for the two instruments were different. Joiner et al. (2012) also found zero-level offsets for SCIAMACHY at 866 nm. Khosravi et al. (2015) showed that for SCIAMACHY in the far-red wavelength range, an additive radiance signal that leads to the zero-level offsets was relatively stable over time and a fairly linear function of radiance. The bias was shown to be of the same order of magnitude as the SIF signal. These biases can be of the same order of magnitude as the SIF signal we are trying to measure. These artifacts result from unaccounted for dark current, stray light, so-called memory effects, and other non-linear responses (e.g., Joiner et al., 2012). All of these additive effects can produce a false filling-in of SFLs and absorption lines which can have a significant impact of terrestrial SIF retrievals. Because the effects are additive, they are not well captured by the leading principal components and this leads to biases with a spatial dependence.

We developed an empirical correction scheme to mitigate zero-level offsets. This scheme is implemented in version 26 GOME-2 data that are publicly available at http://avdc.gsfc.nasa.gov.us. We use the same correction scheme to adjust red SIF terrestrial retrievals here. The zero-level adjustment scheme is designed to account for instrumental non-linear radiance behavior that appears to slightly distort the spectra as a function of radiance. The scheme may also correct for small effects of rotational-Raman scattering in the atmosphere. As shown below, we find that the biases vary with time (on both daily and monthly time scales) and instrument.

The zero-level adjustment scheme has the following steps 1) Provide a training sample data set of SIF retrievals over all areas of the ocean passing all quality control checks except the cloud filtering check for a single day; 2) Within a given latitude range, using a least squares approach, determine coefficients (A through H) to the following apply a regression model:

\[
\frac{\text{SIF}}{\cos(\theta_0)} = A + B \theta_0 + C \theta_0^2 + D \theta_0^3 + E I_1 + F I_1^2 + G I_1^3 + H \text{lat},
\]  

(7)

where \(I_1\) is the radiance at a wavelength not impacted by strong O\(_2\) absorption (e.g., 682.5 nm), lat is latitude, and SIF has been normalized by \(\cos(\theta_0)\) to remove its dependence upon the top-of-atmosphere solar irradiance. We found empirically that this model accounts for much of the variability in the bias. The right hand side of Eq. 7 represents the zero-level bias. 3) Compute the zero-level bias using the derived regression coefficients (A through H) for each pixel over land, subtract from the normalized SIF retrieval over land, then multiply by \(\cos(\theta_0)\) to obtain the corrected estimate of SIF. The regression is not extrapolated beyond the range of \(I_1\) radiances and \(\theta_0\) values found in the training sample data set. The regression coefficients are generated and applied separately for different latitude bins. For GOME-2 v26 far-red SIF retrievals, we use latitude bins bounded by 90S, 45S, 0, 45N, and 90N. For SCIAMACHY red SIF retrievals, we use latitudes bins bounded by 90S, 0, and 90N and for GOME-2 red SIF retrievals 90S, 40S, 40N, and 90N. The ranges were chosen empirically (by trial and error) for each instrument and retrieval type to minimize discontinuities at the boundaries and maximize the ability to remove zero-level offsets.
The supplemental material shows examples of how biases over ocean vary as a function of latitude, $\theta_0$, and radiance ($I_1$) for two randomly selected days in July 2007. Also shown are the biases after the correction scheme is applied. Results are shown for SCIAMACHY SFL and O$_2$ band retrievals as well as O$_2$ band retrievals from GOME-2. The biases are shown to vary with day and instrument as well as the parameters in the correction scheme. The bias correction works well in most cases, but may not be effective at high radiance values that can be scarce over ocean in certain latitude bins (e.g., high latitudes) and thus do not receive much overall weight in the least squares fitting.

The zero-level adjustment scheme essentially uses ocean data with the assumption of negligible SIF emissions. While this is a good assumption for far-red SIF, there is significant SIF emission in the red SIF region in some areas over ocean as shown below. We did not make any attempt to avoid these areas for the zero-level adjustment scheme. Our regression model assumes that the zero-level adjustment is a smooth function of radiance. As radiance increases from the clear-sky dark to cloudy skies, the ocean SIF signal becomes more shielded. Note that reflectances over land tend to be higher than those over the dark ocean at red wavelengths, so that adjustments over land will typically be made using cloudy ocean data.

We found that after applying the derived regression model over ocean, the spatial patterns of oceanic SIF are still present; this indicates that our regression model has not removed these signals. However, there may be a slight overcorrection in our approach for the red SIF zero-level adjustment. Figure 10 of the supplemental material shows an example of red SIF retrievals for May 2007 with and without zero-level adjustment over both land and ocean. For comparison, we also show high quality oceanic SIF obtained with the full band retrievals that are less susceptible to zero-level offsets. In fact, we did not find significant a zero-level offset in the ocean SIF retrievals as we did with the terrestrial retrievals. This is because the ocean retrievals rely more on the broadband emission rather than filling-in of SFLs that is more sensitive to false filling-in by effects such as stray light, dark current, and Raman scattering (oceanic or atmospheric). We therefore do not apply any zero-level adjustment over ocean. For future versions of the zero-level offset scheme, we intend to explore a two step regression approach whereby we first remove the oceanic SIF signal using full band ocean retrievals before computing regression coefficients. We also have not added barren land to the regression scheme in the present version in order to test how well the scheme works using only cloudy ocean data; the addition of barren land data can easily be accomplished in a future version. As will be shown below, exclusion of barren land data from the bias adjustment parameter determination may lead to biases over very bright land surfaces, particularly over the Sahara where radiance levels are high. These high radiance values may not be well represented in the ocean data samples in a given latitude bin during certain months when convection is not prevalent within the bin.

5 Sensitivity analysis for terrestrial red SIF

In this section, we retrieve terrestrial red SIF using the radiances that were computed from the simulation testing data set that contains 15,655,230,400 different sets of conditions. This set of conditions includes the so-called true SIF that serves as the benchmark for the retrieved SIF. Instrument noise is added to the simulated radiances as indicated, where the noise is uncorrelated between channels and follows a Gaussian distribution. The nominal signal to noise ratio (SNR) (referred to as “nom.” in Table I), specified as a function of radiance, is similar to that used by Guanter et al. (2015) for GOME-2 with
SNR values of 673 and 4053 at radiances of 10 and 240 mW/m²/nm/sr, respectively, and is shown in Fig. 5. Table 1 provides statistics on the differences between the retrievals and the true states for several scenarios described below. To compare true and retrieved SIF, we average SIF over the wavelength range of the red spectral fitting window.

We checked that the addition of a constant value to the simulated radiances in order to produce a zero-level offset results in a retrieved bias of the same amount. We note below that the derived zero-level offset with real satellite data is not a constant, but in fact has complex dependences on time, latitude, geometry, and radiance. We did not attempt to add this complexity to the simulations. This constant zero-level offset would be detected and corrected by our bias adjustment scheme.

5.1 Sensitivity to number of PCs used

Here, we focus on O₂ band red SIF retrievals with an O₂ B-band fitting window between 682 and 692 nm and for an instrument with FWHM = 0.5 nm and sampling rate of 0.2 nm. The γ band fitting window was 622–640 nm. We use fourth order polynomials to model the surface reflectivity for each fitting window. Use of a higher order polynomial order does not significantly improve the results, while use of a lower order polynomial degrades results.

The first three lines of Table 1 show results for retrievals that use 5, 10, and 15 PCs. There are small biases in all cases with biases generally decreasing with increasing numbers of PCs. The improvement in both accuracy and precision is noticeable when increasing from 5 to 10 PCs and starts to level out with subsequent further increases. There is virtually no change in the results when we further continue to increase the number of PCs (not shown). There is a slight bias obtained with both the 10 and 15 PC results as also evidenced by the deviation of the fitted slope from unity. This bias is further discussed below.

We may also compute fluorescence errors using the linear estimation method (Eq. 5) by assuming random and uncorrelated wavelength-independent radiance errors (as was the case in our simulated data) as in Joiner et al. (2013). However, the linear estimation does not account for errors that may result from using an imperfect model for the SIF spectral emissions or an imperfect forward model (e.g., that does not account explicitly for atmospheric scattering). Here, we have assumed a Gaussian shape for SIF emissions as in Eq. 3. However, interference from far-red emissions in our spectral fitting range slightly distorts the Gaussian shape. We found that it was important to apply some constraint to the SIF emissions spectral shape in order to obtain accurate retrievals, and the Gaussian function provides a reasonable approximation. To accurately evaluate errors resulting from this approach, we show results from the full end-to-end simulation in this work rather than from the linear estimation.

5.2 Sensitivity to the fitting window and instrumental noise

In line 4 of Table 1, we use a larger smaller O₂ B-band fitting window (682–698 nm) than for results shown in lines 1–3. With this larger smaller fitting window, we specified σ = 107.5 in Eq. 3 as compared with σ = 7.510 that was used for the smaller larger fitting window. With this configuration biases increased/reduced (results are further from closer to the 1:1 line). This is likely because the assumed Gaussian shape for red SIF emissions is more applicable to the smaller fitting window. However as expected, the use of a smaller fitting window decreases retrieval precision (σ increases).
Line 5 shows results with the same O$_2$ B-band fitting window, but now without the benefit of the O$_2$ $\gamma$-band. Removing the $\gamma$ band decreases precision and increases bias. However, results with no instrument noise (lines 7 and 9) show that precision improves when the $\gamma$ band is not used. Also in contrast to the results with noisy data, lines 6 and 7 show that precisions are improved with the smaller O$_2$ B-band fitting window when noise is absent and the $\gamma$ band is included. We may therefore infer that the primary benefit of the larger fitting window in the O$_2$ B-band as well as the addition of the $\gamma$ band is to beat down the effects of instrumental noise.

In order to assess how much of an impact the SFL filling has on the results, we conducted simulations using a flat solar spectrum and no instrumental noise. Results shown in line 8 of Table 1 indicate that there is a substantial stabilizing effect of the SFL filling for the O$_2$ band retrievals. Note that SFL filling occurs both inside and outside the O$_2$ B-band. An additional experiment with a flat solar spectrum and without the $\gamma$-band included in the fitting resulted in poor performance with many non-convergent retrievals.

Line 10 shows results for a simulation with two times the nominal noise for the larger B-band fitting window. Precision decreased by approximately a factor of 2. Errors increased, but less than a factor of 2. This is consistent with the fact that errors are present even without noise, a consequence of small state-dependent errors.

### 5.3 Sensitivity to spectral resolution, sampling, and wavelength jitter

We performed simulations for O$_2$ band red SIF retrievals at a higher spectral resolution (FWHM = 0.3 nm, sampling of 0.1 nm) than in the previous simulations. Lines 11–12 of Table 1 show retrieval statistics at the higher spectral resolution with the nominal noise model for fitting windows of 682–692 nm and 682–698 nm, respectively. The precision significantly improves as compared with FWHM = 0.5 nm retrievals. This improvement results from 1) more spectral samples within the fitting window and 2) a larger filling-in signal from SIF in the deepest part of the O$_2$ B-band as well as within the SFLs. This is consistent with the simulations of expected FLEX performance for the red SIF (Cogliati et al., 2015).

We also performed simulations for SFL red SIF retrievals using a single small spectral fitting window that contains only SFLs, similar to that used by Wolanin et al. (2015) and Guanter et al. (2015) (682–686.5 nm, lines 13–16 of Table 1). Here we used the nominal noise model with FWHMs of 0.1, 0.2, 0.3 and 0.5 nm with sampling rates of 0.03, 0.075, 0.1, and 0.2 nm, respectively. When using only SFLs for the retrieval, a significant improvement is obtained at higher spectral resolutions for the same reasons given above for the O$_2$ B-band retrievals. Note that good performance can be achieved with a smaller number of PCs for this limited fitting window. The results obtained at FWHM values of 0.5 and 0.3 nm show that significant improvements are achieved when instrumental noise is simulated and the oxygen B- and $\gamma$-bands are included in the spectral fitting as compared with the use of the more limited fitting window that contains only SFLs.

We performed an additional experiment at 0.3 nm spectral resolution where we resampled the spectra at the same spacing as used for 0.5 nm spectral resolution (sampling rate of 0.2 nm). As expected owing to enhanced sensitivity, improvement is obtained at the higher spectral resolution with identical spectral sampling (line 17 of Table 1). This demonstrates the benefits of higher spectral resolution.
Additionally, finally, we simulated a random wavelength jitter with a normal distribution and standard deviation of 0.01 nm in both training and testing data sets at 0.3 and 0.5 nm spectral resolutions. Such a jitter may be expected due to changes in the instrument response function with inhomogeneous scenes (e.g., partial clouds). While there is a small degradation in the results, overall the impact of such jitter with our approach is relatively small (lines 18–19 of Table 1 compared with lines 15–16). The effects of the wavelength jitter should be at least partially accounted for by the use of principal components.

Finally, in line 20 we used the same fitting window in our simulations as that used by Wolanin et al. (2015) for SCIAMACHY and GOME-2 retrievals (681.8–685.5 nm); this is a bit more narrow than that used in lines 13–19. Results should be compared directly with line 16 that uses our fitting window that is 0.8 nm wider. While bias is reduced by about 0.07 mW/m²/nm/sr and the correlation increased from 0.51 to 0.59 with the smaller fitting window, the standard deviation and RMS error both increased by more than 0.3 mW/m²/nm/sr.

5.4 Radiance residuals from simulated data

Figure 4 shows the root-mean-squared (RMS) of the radiance residuals (observed minus calculated radiance) for an instrument with FWHM = 0.5 nm, with nominal noise, and for O₂ band retrievals using B-band fitting window of 682–698 nm when red SIF is and is not retrieved. The displayed values represent the RMS of the residual at each wavelength averaged over all conditions in the simulation testing data as a percentage of the observed radiance. Reductions in the residuals are shown on average when fluorescence is retrieved, as expected. The RMS reductions are not particularly apparent within the O₂ γ band portion of the fitting window where fluorescence is not present. However, Reductions are shown substantial in the O₂ B-band portion of the fitting window, both inside and outside the band. Residuals are substantially reduced outside the B-band (λ < 686.5 nm) where SFL filling from SIF occurs. Smaller, more subtle RMS reductions also occur inside the O₂ B-band, particularly at wavelengths between 687 and 693 nm. At longer wavelengths, filling-in of H₂O lines also occurs and some RMS reductions are seen. When SIF is fitted, the radiance residuals are relatively constant with wavelength at a level of around 0.1% or less, consistent with the noise levels in the simulation.

5.5 Discussion of simulation results

As described above and shown in Joiner et al. (2013), there are 60 distinct fluorescence spectra in the testing data set. For each fluorescence spectrum, the simulation contains a number of different observing conditions (e.g., SZAs, VZAs, surface pressures, temperature profiles, and aerosol parameters). Figure 5 shows results for O₂ band (smaller fitting window) and SFL retrievals with FWHM = 0.5 nm and nominal noise. This figure shows that negative biases are more prevalent for the O₂ band retrievals at higher levels of fluorescence and for certain simulation configurations. However, the improvement in terms of precision obtained with the O₂ band retrievals as compared with the SFL approach is also apparent. This implies that reasonable red SIF retrievals should be obtained using our new approach with existing instruments (provided they behave as expected) and that higher spectral resolution is not an absolute necessity for red SIF retrievals so long as both the O₂ γ and B-bands are available.
Our retrieval approach relies on several simplifying assumptions, such as that the geometrical air mass factor is an appropriate approximation and that the spectral structures of SIF and $\rho_s$ can be modeled reasonably well with a few parameters. The simulated data do not contain these assumptions; the radiances are generated monochromatically with atmospheric scattering before being convolved with the instrument response function, and the spectral dependences of SIF and $\rho_s$ are based on model and spectral libraries. Therefore, our simulation results should accurately reflect errors produced by our assumptions. As can be seen, the biases and errors produced by these simplifications are relatively small. Our simulation results provide confidence that our method can be used to successfully retrieve red SIF with satellite measurements from GOME-2 and SCIAMACHY provided that the instruments are performing in a linear and expected manner and that remaining biases can be effectively removed.

6 Results from GOME-2 and SCIAMACHY data

For GOME-2 and SCIAMACHY O$_2$ red SIF retrievals, we use a fitting window of 682–692 nm and 15 PCs. Although we obtain good results using simulated data that include wavelengths impacted by H$_2$O (vapor) absorption ($692 < \lambda < 713$ nm), we found unrealistic month-to-month variations in both far-red and red SIF magnitudes with real satellite data when using wavelengths impacted by H$_2$O absorption. These unphysical variations were drastically reduced when we restricted the retrievals to wavelengths with minimal H$_2$O absorption. Use of the 682–692 nm window was chosen to maximize wavelength range in order to minimize the impact of instrumental random noise while minimizing the impact of H$_2$O absorption. Similarly, in version 26 of far-red GOME-2 SIF retrievals we restricted the fitting window to 734–758 nm, a reduction as compared with that used in Joiner et al. (2013). This also reduced unrealistic month-to-month variations that were present in earlier versions.

For SFL red SIF retrievals, we use a window of 682–686.5 nm with 3 PCs. This is slightly larger than the fitting window used by Wolanin et al. (2015) (681.8–685.5 nm).

6.1 Radiance residuals from GOME-2 for terrestrial retrievals

Figure 6 shows a sample spectral fit for an observation over the southeast US. Improvements in the fit are visible only when the spectral range is reduced to limit the y-axis range. The reflectance residuals show that reductions over the entire spectral range are subtle owing to the small values of red SIF; the overall reduction in the RMS of the residuals is approximately 7%.

A relatively high signal-to-noise is necessary to retrieve the small red SIF signal. Figure 7 is similar to Fig. 4 but shows the spectral RMS of GOME-2 radiance residuals, obtained with and without fitting SIF. The residuals shown here were obtained on a single day (01 July 2007) and are averaged for each wavelength over all observations with SZA < 70° and the Normalized Difference Vegetation Index (NDVI) > 0.5 (i.e., moderately to highly vegetated pixels) that passed quality control and cloud filtering checks. Reductions in the residuals are modest and of roughly similar magnitude to those obtained using the simulated data in Fig. 4. RMS residuals are reduced on average 1% in the wavelength range 682–692 nm for the GOME-2 data used here and about 2% in the simulated data set. As will be shown below, we retrieve values of red SIF with GOME-2 and SCIAMACHY that are on average lower than those present in the simulation data set. We should therefore ex-
pect smaller reductions in residuals when SIF is fit with the GOME-2 data as compared with the simulated data. The largest reductions are in the SFLs near 684 nm and within the deepest part of O$_2$ B-band around 687-690 nm. Overall, RMS residuals have similar or slightly smaller magnitudes as compared with those shown in Fig. 4 for simulated data. This indicates that the noise model used in our simulations is appropriate for GOME-2. We note somewhat better performance of GOME-2 in the O$_2$ γ-band spectral region as compared with that near the B-band.

6.2 Comparison of GOME-2 and SCIAMACHY terrestrial red SIF

Global composites of red SIF derived from SCIAMACHY and GOME-2 for July and December 2009 are displayed in Fig. 8. For comparison, these are the same months displayed in Wolanin et al. (2015). Quality-filtered retrievals have been averaged in 1° latitude-longitude grid boxes in all cases. The filtering uses data only for SZA < 70°, where RRS effects should be relatively small (Joiner et al., 2012). A zero-level adjustment is made as described above for all cases. No other explicit account of rotational-Raman scattering is made.

The top panels show retrievals obtained using the SFL approach with a fitting window of 682–686.5 nm for SCIAMACHY. The fitting window is similar to that used by Wolanin et al. (2015). The main difference of our approach as compared with that used by Wolanin et al. (2015) here is that we use the PCA approach to account for H$_2$O absorption and our zero-level offset adjustment may account for the effects of RRS as well as other instrumental artifacts. Magnitudes are similar but perhaps slightly higher than those shown in Wolanin et al. (2015). Here, we display results over all land areas that meet our filtering criteria. Note that retrievals in many areas such as deserts and the Himalayan plateau were not shown in Wolanin et al. (2015) so that we are unable to compare results there.

Unrealistic high biases are seen over the Sahara and Arabian peninsula in July and to a lesser extent in December. These are cases of high surface reflectance and small amounts of vegetation. A simple filter for high reflectivities ( > 0.35) can remove these cases or alternatively they could be used in the training data set for the zero-level offset adjustment scheme. However, to examine potential instrumental effects and our ability to remove them, we have not filtered the data or included them in the zero-level offset regression training. Similar biases in SCIAMACHY data at the deep Ca II line at 866 nm were also discussed in Joiner et al. (2012). Zero-level adjustments are typically of the order of a few tenths of a mW/m$^2$/nm/sr. The adjustments do not completely remove biases at high radiance levels as shown here.

The middle and bottom panels show red SIF retrievals obtained using the O$_2$ band retrievals with SCIAMACHY and GOME-2, respectively. A generally good agreement of the SIF magnitudes and spatial patterns is observed between the satellite retrievals obtained with different instruments and fitting windows. High red SIF values are observed over vegetated areas, while low (or sometimes negative) values are obtained over deserts and sparsely vegetated areas. Spatial patterns of active regions are similar to those of far-red SIF retrievals (740–770 nm) obtained by GOME-2 and GOSAT. Values of red SIF are generally lower than those obtained in the far-red consistent with previous canopy-level ground-based measurements (Daumard et al., 2010; Cheng et al., 2013; Fournier et al., 2012).

Positive biases over bright desert areas are less prevalent in the O$_2$ band retrievals, particularly for SCIAMACHY. However, some biases are seen in the GOME-2 retrievals in December. Again, these can be removed with a simple high reflectance filter.
We also note that there are larger negative biases over non-vegetated areas obtained with SCIAMACHY as compared with GOME-2. The fact that similar results are obtained over vegetated areas suggests that the instruments are behaving differently over high reflectivity scenes. There are other differences between the retrievals even in vegetated areas. In the case where identical algorithms are applied, these differences are likely instrument related and will be explored in more detail below.

We note that biases (both before and after zero-level adjustment) vary over time. Figure 9 in the supplemental material shows similar results obtained in 2007. The unphysical high biases over the Sahara are much reduced for the SFL retrievals in July 2007 as compared with July 2009 and similarly for the GOME-2 O2 band retrievals in Dec. 2007 as compared with 2009. It should be noted again that these red SIF retrievals are derived using instruments that were not designed or optimized for such measurements.

6.3 Variability, biases, and estimated errors in GOME-2 and SCIAMACHY terrestrial red SIF retrievals

Standard deviations of the July 2007 red SIF retrievals in the left panels of Fig. 9 show the variability of the retrieved red SIF in 1° × 1° grid boxes for the three different retrievals in Fig. 8. SCIAMACHY retrievals show less variability in general as compared with GOME-2, particularly in the area impacted by the SAA (high variability over parts of South America). This indicates a better performance per pixel of the SCIAMACHY instrument in the red spectral region. Lower variability is shown for the SCIAMACHY O2 retrievals as compared with the SFL retrievals as may be expected from the use of additional spectral range. Additional variability affecting all retrievals results from the effects of instrumental noise, natural variability in vegetation activity within the month, cloud effects, the effects of different illumination and viewing geometries, and the different footprints from the satellite orbits. Clouds and aerosols can affect both types of retrievals by a blocking effect, but can additionally affect O2 retrievals by altering the depth of the O2 absorption features. There does not appear to be additional noise resulting from these cloud effects on the O2 retrievals.

In general for both instruments, higher standard deviations occur over brighter scenes (e.g., over Greenland and deserts) consistent with the higher noise expected at higher radiance levels. Interestingly, vegetation patterns are not obvious in the standard deviation maps, indicating that there is not much additional variability contributed by vegetation as compared with that from instrumental noise. This was not the case for far-red retrievals from GOME-2 and SCIAMACHY [Joiner et al., 2013; Köhler et al., 2015]. Variability due to noise (in radiance units) in sparsely vegetated areas is higher for GOME-2 in the red as compared with the far-red shown in [Joiner et al., 2013]. Variability in vegetated areas is similar.

The right panels of Fig. 9 show computed standard errors of the monthly mean (grid box standard deviations divided by the square root of the number of retrievals). Despite lower variability in the SCIAMACHY SFL red SIF retrievals, the GOME-2 retrievals show lower standard errors than SCIAMACHY SFL retrievals in all but a few areas owing to more observations per month. The SCIAMACHY O2 band red SIF retrievals provide slightly lower standard errors in most areas as compared with those of GOME-2. However, there is some block-like structure in the SCIAMACHY standard errors. The block-like structure results from alternating blocks of nadir and limb retrievals that were performed by SCIAMACHY. GOME-2 operates exclusively in the nadir mode which leads to a better spatial coverage.
Figure 10 shows monthly mean zero-level offset adjustments for July and December 2007 for the three red SIF retrievals. Both SCIAMACHY retrievals show positive and negative adjustments while GOME-2 shows mostly negative adjustments. SCIAMACHY adjustments for the $O_2$ band red SIF retrievals show alternating blocky spatial patterns; this results from day to day variation in the estimated zero-level adjustments. Adjustments for the two SCIAMACHY retrievals are different because they are using different retrieval approaches and fitting windows. The $O_2$ B-band is a deeper feature than the SFLs and may therefore behave differently. RRS increases rapidly with SZA at high SZAs (Joiner et al., 2012). The zero level adjustments do not clearly or consistently show this effect.

As can be seen, the zero-level adjustments are substantial in many areas. Uncertainties in the zero-level adjustment likely dominate the retrieval errors. The day-to-day and even at times orbit to orbit variation in the SCIAMACHY offsets lead to larger uncertainties than for GOME-2. Note that there are some discontinuities at the latitudes where the boundaries for the adjustments are defined. However, they are not very pronounced in the figures. The latitude dependences of the zero-level biases shown here are roughly consistent in terms of latitudinal dependence with those found by Köhler et al. (2015) for SCIAMACHY and GOME-2 far-red SFL retrievals. Based on the magnitude and stability of the adjustments, we estimate that uncertainties in monthly mean red SIF retrievals are in the range 0.1–0.3 mW/m$^2$/nm/sr for SCIAMACHY data and 0.1–0.2 mW/m$^2$/nm/sr for GOME-2 $O_2$ band retrievals.

### 6.4 Time series and mapped anomalies for terrestrial retrievals

We display time series of red and far-red SIF from GOME-2 for the boxes shown in Figure 11(a). We focus on GOME-2 so that we may compare the long time series of red SIF with the high quality GOME-2 far-red SIF data set. The boxed areas were selected because they display significant interannual variability. Each box is an average over an area of 3$\degree$ latitude by 3$\degree$ longitude. This resolution was selected in order to reduce the effects of instrumental noise in order to focus on the interannual variations. Figure 11(b) shows that red and far-red SIF display similar seasonality. Many of the boxes shown also display a fair amount of inter-annual variability (IAV). The IAV is similar for red and far-red SIF and in the areas shown is driven primarily by water availability. Yoshida et al. (2015) and Sun et al. (2015) showed that drought-related negative SIF anomalies (e.g., the 2011 low values shown for Box 1 in the Texas drought area) are driven by decreases in the fraction of absorbed photosynthetically-active radiation (fPAR) as well as decreases in fluorescence efficiency that is related to electron transport rate within leaves. There is a somewhat earlier autumn or dry season decline in the far-red SIF as compared with the red in some of the boxes (1 and 2). The seasonality of far-red SIF has been shown to closely match that of gross primary productivity (GPP) derived from flux tower eddy covariance measurements while greenness vegetation indices that are related to fPAR tended to decline later in autumn (Joiner et al., 2014).

To further assess the GOME-2 red SIF data set, we compute monthly mean anomalies and compare with those from the far-red. We should expect to see some similarities in the anomalies, particularly those driven by moisture stress (e.g., Daumard et al., 2010; Ać et al., 2015; Middleton et al., 2015). Showing consistency (or not) in the anomalies demonstrates the ability to resolve small signals and therefore provides a check on the estimated errors and sensitivities.
Figure 12 shows mapped gridded monthly anomalies for far-red and red SIF from GOME-2 for August 2010, 2011, and 2012. These months highlight the impact of droughts where SIF satellite observations have been studied previously (Yoshida et al., 2015; Sun et al., 2015; Lee et al., 2013). To generate the anomalies, monthly mean climatological maps averaged over the years between 2007 and 2014 are subtracted from the monthly means. The anomalies are then shown as a fraction of the climatological gridbox value for a particular month. Far-red SIF anomalies are gridded at a resolution of 0.5° resolution; this is the standard resolution used for publicly available level 3 gridded data set. To reduce the impact of retrieval noise, red SIF anomalies are shown at a lower resolution of 1°. Data are shown for gridboxes where the climatological NDVI from GOME-2 > 0.2.

Negative anomalies due to the Russian drought of 2010 are clearly shown in both red and far-red SIF anomaly maps while at the same time positive anomalies are shown in the western US and northeast Mexico. Smaller negative anomalies are also shown in southern Amazonia in 2010 and may be the result of the drought conditions (Lewis et al., 2011; Lee et al., 2013). Shown in terms of a percent of the monthly mean climatological values, the anomalies appear to be somewhat larger in the red SIF as compared with the far-red. However, the differences may be within the uncertainties of the zero-level adjustment scheme.

Negative SIF anomalies due to the Texas drought of 2011 are also shown in both red and far-red SIF in Texas and northern Mexico, while mostly positive anomalies are shown in the Russian grain belt during this year. Similarly, negative far-red and red SIF anomalies are shown in the region of the 2012 US great plains drought in the western US. Spatial patterns of red and far-red anomalies are consistent elsewhere such as just to the south of the Sahara and to the east of the Gobi desert.

Figure 13 shows time series of monthly anomalies (absolute magnitudes in radiance units, not fractional values) for boxes from Fig. 11(a). Overall, the temporal dependence of the anomalies is very similar, at least to within the uncertainties of the measurements. The deseasonalization performed here allows us to demonstrate that it demonstrates the ability of the GOME-2 monthly red SIF at the box resolution to resolve signals of the order of +/-0.1 mw/m²/nm/sr. Expected future work includes a closer examination of the anomalies.

6.5 Oceanic SIF retrievals

Here, we retrieve oceanic fluorescence line height (FLH) with GOME-2 and SCIAMACHY using the method discussed above. Normalized FLH (nFLH) Our results from SCIAMACHY and GOME-2 is, shown in Fig. 14 along with results from, compare well in terms of spatial variations with each other and with the simpler three broadband channel approach applied to the Terra MODIS. Aqua MODIS results, not shown, were similar, but we show Terra data here as the local overpass times are more similar to those of Envisat and MetOp). MODIS data, provided at a spatial resolution of 9 km, were downloaded from http://oceandata.sci.gsfc.nasa.gov.

Here, we apply a very simple adjustment to provide normalized fluorescence line height (nFLH, normalized with respect to incoming solar irradiance) to facilitate comparisons with MODIS nFLH. Our approach accounts only for \( \cos(\theta_0) \) (i.e., it does not account for the effects of atmospheric scattering and absorption or changes in the sun-Earth distance). We note that our results are referenced to 683 nm while MODIS uses slightly different wavelengths so that our magnitudes are expected to be
somewhat higher as is generally shown. Finally, it should be noted that a more liberal cloud filter is applied to the GOME-2 and SCIAMACHY retrievals as compared with that used for MODIS, particularly considering that MODIS has a much smaller footprint (of the order of 1 km²).

The reader is reminded that GOME-2 provides superior sampling as compared with SCIAMACHY as it operates in nadir mode exclusively. In Fig. [14] we display GOME-2 data gridded at a 0.5° spatial resolution. SCIAMACHY, which alternated between limb and nadir mode observations, is gridded at a resolution of 1° so as not to show too many gaps between grid boxes. MODIS data were regridded to the same resolution as GOME-2. Our monthly means from GOME-2 and SCIAMACHY, using the full wavelength range between 660 and 713 nm, appear to be less noisy (patchy) than a GOME-2 yearly mean shown those obtained by Wolanin et al. (2015) that was obtained with a smaller fitting window that included only SFLs.

Nevertheless, the agreement with MODIS in terms of the magnitude and spatial patterns, is excellent. Figure [15] shows maps of absolute and fractional differences in nFLH between SCIAMACHY and MODIS as well as GOME-2 and MODIS. For the fractional difference, we scale MODIS by a factor of 1.5 to show that the difference is not a simple scale factor (this factor brings the differences to near zero in the Pacific where nFLH values are generally larger than zero). Larger fractional differences are seen in the northern hemisphere and off the west coast of Africa. This may be related to the presence of absorbing aerosols that are common in these regions (i.e., smoke, dust, and industrial aerosols) that may affect the MODIS and GOME-2/SCIAMACHY retrievals differently. The spatial patterns of the difference in absolute amount of nFLH with respect to MODIS are similar for GOME-2 and SCIAMACHY. MODIS nFLH is higher than both GOME-2 and SCIAMACHY over large portions of the less productive ocean regions in the southern hemisphere. It appears that MODIS has a zero-level offset in the southern hemisphere as low values appear to have slightly positive values as compared with the northern hemisphere where values are closer to zero. GOME-2 and SCIAMACHY nFLH values are higher than those from MODIS in the upwelling coastal areas where nFLH has high values.

Figure [16] shows a sample GOME-2 spectrum and fit off the Mexican coast. Improvement in the fit can be seen to result from fitting the broad spectral feature of SIF emission, particularly at wavelengths 660–685 nm. The overall reduction in RMS of the reflectance residual is about 30%. Figure [17] shows the mean spectral residuals with and without fitting ocean fluorescence for GOME-2 on 01 July 2007 averaged over all pixels with FLH > 0.4 mW/m²/nm/sr. The spectral structure of the reduction in residuals further supports that most of the information in fitting for ocean FLH is coming from the broad SIF continuum emission as opposed to filling-in of telluric absorption features or SFLs. We note that some of the remaining fine structure in the residuals may be due to residual filling-in from atmospheric rotational or oceanic vibrational Raman scattering or instrumental effects that we did not attempt to account for in this work.

7 Conclusions

We have developed new approaches to retrieve SIF at red wavelengths over land from moderate spectral resolution satellite instruments. We also showed for the first time that red SIF can be retrieved over ocean with good fidelity with the same instruments by utilizing the full wavelength range of the SIF emission. Similar to previous works, we use a principal
component analysis (PCA) approach to estimate the spectral structure of atmospheric absorption. Our PCA approach as applied to land retrievals utilizes the O$_2$ γ-band, which is relatively free of SIF, as well as the filling-in of SFLs to estimate absorption within help anchor the O$_2$ B-band that is used to increase the precision of SIF retrievals. A simplified radiative transfer model based on the geometrical air mass factor approximation is used to determine how much of the emitted surface SIF signal is absorbed in the atmosphere.

We used simulated data computed with a full radiative transfer model for thousands of different scenarios to demonstrate that high quality red SIF retrievals may be obtained using satellite instrumentation with a relatively high SNR and moderate spectral resolution similar to GOME-2 and SCIAMACHY, provided that unmodelled effects, such as complex instrumental artifacts and Raman scattering, do not severely impact the retrievals. Retrieval errors depend upon the instrument SNR, the spectral fitting window used, and spectral resolution. Our simulations suggest We demonstrate that use of the O$_2$ γ- and B-bands can increase red SIF retrieval precision over land as compared with approaches that utilize a smaller fitting window confined to regions outside the O$_2$ B-band where the SIF signal is obtained solely by filling in of SFLs.

We applied our new approach to satellite measurements from GOME-2 and SCIAMACHY. The GOME-2 and SCIAMACHY retrievals that use the O$_2$ γ- and B-bands compare well with those from SCIAMACHY that use the less complex and also less sensitive SFL filling narrow window approach. Red SIF uncertainties for monthly mean gridded data are estimated to be ~0.1–0.3 mW/m$^2$/nm/sr and are a consequence of both random and systematic errors. Our long time series of red SIF from GOME-2 allows for the calculation of globally mapped monthly mean anomalies. These first maps of red SIF anomalies show similar temporal and spatial patterns as compared with far-red SIF anomalies though with somewhat larger fractional values.

Several satellite instruments with red spectral coverage and various spectral and spatial resolutions have flown, are currently flying, or are planned for launch in the next few years. The approach outlined here can potentially be applied to these instruments. The original GOME instrument, launched in 1995 on the ESA European Remote Sensing satellite 2 (ERS-2), can also be used for red SIF measurements, but with a larger pixel size (40 km × 320 km) in its nominal operating mode. GOME has the unique ability to extend the record of SIF measurements back to 1995.

In the future, the approach developed here may be applied to the US National Aeronautics and Space Administration (NASA) Earth Ventures 1 Tropospheric Emissions: Monitoring of Pollution (TEMPO) [Chance et al., 2013], a geostationary instrument designed primarily for air quality measurements planned for launched near the end of the decade. TEMPO should provide the first hourly terrestrial red SIF measurements throughout the day with coverage over much of the populated areas of North America and as well as hourly oceanic SIF over surrounding coastlines. With nearly continuous spectral coverage from the ultraviolet through approximately 740 nm and a spectral resolution of ~0.6 nm, it should obtain time-resolved far-red as well as red SIF retrievals at a substantially higher spatial resolution (native ground pixel of 2 km by 4.5 km at the center of the field of regard) than GOME-2 or SCIAMACHY. As mentioned above, TROPOMI will have the capability to measure both red and far-red SIF. It will be in an early afternoon orbit and will have a ground resolution of ~7 × 7 km$^2$ [Guanter et al., 2015].

The FLuorescence EXplorer (FLEX) [ESA, 2015], a selected ESA Earth Explorer 8 Mission, plans to utilize the O$_2$ A- and B-bands for SIF retrievals [Guanter et al., 2010; Cogliati et al., 2015] and other bio-spectral information across the visible-NIR
spectrum. FLEX will provide measurements at an even higher spatial resolution (~300 m) at approximately a monthly time scale.

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Table 1. Statistical comparison of retrieved versus true values of SIF obtained with the simulated testing data set for different experiments (Exp); all fluorescence radiance units (indicated by *) are mW m\(^{-2}\) nm\(^{-1}\) sr\(^{-1}\). Retrievals are performed for an instrument with a given full-width at half-maximum (FWHM) line shape function, signal-to-noise ratio (SNR), number of principal components (#PCs), and fitting window from starting wavelength \(\lambda_1\) to ending wavelength \(\lambda_2\). Statistics given are the root-mean-squared difference (RMS diff.), correlation coefficient (\(r\)), mean difference (bias) of retrieved minus truth, standard deviation (\(\sigma\)), and slope (B) and intercept (A) of a linear fit (retrieved fluorescence = A + B \cdot truth) (last two columns, respectively). Under the signal-to-noise ratio (SNR) heading, “nom.” refers to the nominal model described in the text.

<table>
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<th>Exp</th>
<th>FWHM (nm)</th>
<th>SNR</th>
<th>#PCs</th>
<th>(\lambda_1) (nm)</th>
<th>(\lambda_2) (nm)</th>
<th>(\gamma)-band incl.</th>
<th>RMS diff.</th>
<th>(r)</th>
<th>bias</th>
<th>(\sigma)</th>
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</table>

\(^a\)Used a flat solar spectrum

\(^b\)Sampling of 0.2 nm instead of 0.1 nm

\(^c\)Wavelength jitter of 0.01 nm simulated
Figure 1. Simulated typical terrestrial spectra (atmospheric transmittance, reflectance, SIF emissions, and solar irradiance as a function of wavelength) computed for an instrument with FWHM = 0.3 nm.
Figure 2. Leading principal components (PCs) of simulated (Sim.) and actual GOME-2 reflectance spectra (from 1 July 2012, black) for spectral windows encompassing the oxygen $\gamma$ band (left panels) and B-band (right panels). Simulated data are for a GOME-like instrument (red lines) with FWHM = 0.5 nm (red) and a higher spectral resolution instrument with FWHM = 0.3 nm (blue); numbers in the top titles are the variance explained in terms of percent of the total and cumulative percent of the total with numbers for GOME-2, simulated FWHM = 0.5 nm, and FWHM = 0.3 nm, respectively.
Radiance and irradiance data; Level 1B

[Over cloudy ocean \( (\rho_{670} > 0.7) \) or over snow/ice or Sahara] and SZA < 70° and GAMF < 5

Yes

Principal component analysis (generate PCs)

Retrieve SIF, atmospheric absorption (coefficients of PCs), and surface reflectance using simplified radiative transfer model

Residual check (and reflectance spike removal)

Other quality assurance checks (convergence, cloud filter, etc.)

Yes

Grid the SIF retrievals (Level 3)

Zero-level bias adjustment using ocean data and solar calibration adjustment (Level 2)

Evaluate (by inter-comparison with other satellite data sets)

Yes

Reconstruct reflectances using reduced set of PCs and remove spectra with large residuals

Figure 3. Flow diagram of the basic steps used to produce SIF data sets.
Figure 4. Root mean squared (RMS) of simulated radiance residuals (observed minus computed, in % of radiance) at wavelengths in and around the O$_2$ γ-band (left) and B-band (right) from the testing dataset with FWHM = 0.5 nm and nominal noise model when fluorescence (SIF) is fit/retrieved (red) and when it is not (black).
Figure 5. Fluorescence retrievals from simulated data (y-axis) using wavelengths between 682 and 692 nm along with wavelengths surrounding the $O_2 \gamma$-band (left) and using wavelengths between 682 and 686.5 nm (right) for an instrument with FWHM = 0.5 nm and with the nominal noise model. Fluorescence is averaged over the fitting window used in the retrieval (different for left and right panels) and compared with the “truth” (x-axis) averaged in the same way. Standard deviations are shown with vertical bars. Different symbols are shown for the various values of chlorophyll content and different colors are for the various values of leaf area index.
Figure 6. A sample GOME-2 observation made on 01 July 2012 at location specified in (a), observation and spectral fits of top-of-atmosphere (TOA) reflectance with and without SIF for the O\textsubscript{2} band retrieval in (b) and (c); c) is a spectral zoom of b), and residual of the reflectance spectral fit in (d). The retrieved SIF at reference wavelength 682 nm was 2.25 mW/m\textsuperscript{2}/nm/sr. RMS of the residual spectrum is 9.35e-5 when SIF is fit and 1.01e-4 when SIF is not fit.
Figure 7. Similar to Fig. 4 for actual GOME-2 radiance residuals (RMS) for pixels with moderate to high amounts of vegetation (NDVI > 0.5) for a single day (01 July 2007).
(a) SCIAMACHY solar Fraunhofer line (SFL) red SIF retrievals in mW/m²/nm/sr using fitting window 682-686.5 nm for July (left) and December (right) 2009.

(b) Similar to (a) but using fitting windows in O₂ γ (622–640 nm)- and B-bands (682–692 nm).

(c) Similar to (b) but using GOME-2.

Figure 8. Global composites of red SIF from SCIAMACHY and GOME-2 binned in 1° cell boxes with zero-level adjustment.
(a) Grid cell standard deviation (left) and standard error (right) for SCIAMACHY SFL red SIF retrievals in mW/m²/nm/sr (682–686.5 nm).

(b) Similar to (a) but for SCIAMACHY O₂ band red SIF retrievals (622–640 nm and 682–692 nm).

(c) Similar to (b) but for GOME-2.

**Figure 9.** Global maps of red SIF retrieval statistical parameters in 1° grid cells for July 2007.
(a) Zero-level adjustment for July (left) and December (right) 2007 for SCIAMACHY SFL red SIF retrievals in mW/m²/nm/sr (682–686.5 nm).

(b) Similar to (a) but for SCIAMACHY O₂ band red SIF retrievals (622–640 nm and 682–692 nm).

(c) Similar to (b) but for GOME-2.

**Figure 10.** Global maps of the zero-level adjustment July (left) and December (right) 2007.
Figure 11. Time series of monthly red (red, right axes) and far-red SIF (black, left axes) in mW/m$^2$/nm/sr from GOME-2 (b) for 8 boxes shown in (a). Axes are specified to align the maximum values.
Figure 12. Global SIF anomaly maps (in terms of fractional amount of climatological values) for August 2010, 2011, and 2012 (top to bottom) for GOME-2 far-red (left) and red (right) retrievals.
Figure 13. Similar to Fig. 11(b) but showing time series of red and far-red SIF monthly anomalies (in mW/m$^2$/nm/sr) from GOME-2 for 8 boxes shown in Fig. 11(a).
Figure 14. Monthly mean (simplified) normalized fluorescence line height (nFLH) from SCIAMACHY (top), GOME-2 (middle), and Terra MODIS (bottom) in mW/m²/sr/nm for May 2007. SCIAMACHY and GOME-2 are gridded to spatial resolutions of 0.5° and 1°, respectively. MODIS data were obtained at a 9 km spatial resolution, but regridded to the same resolution as GOME-2/SCIAMACHY. No zero-level adjustments are made to the retrievals.
(a) SCIAMACHY simplified nFLH differences from MODIS in terms of absolute amount (left) and fractional difference with respect to MODIS (right) only for gridboxes where MODIS nFLH > 0.05. MODIS values on the right have been scaled up by 1.5 to produce fractional differences near zero in the Pacific low latitudes in (b) below to show that differences are not a simple scale factor.

(b) Similar to (a) but for GOME-2.

Figure 15. Monthly mean (simplified) normalized fluorescence line height (nFLH) differences between SCIAMACHY and MODIS (top), and GOME-2 and MODIS (bottom) for May 2007 in terms of absolute (left) and fractional (right) amounts.
Figure 16. Similar to Fig. 6 but showing a GOME-2 observation on 01 July 2012 and spectral fits for an ocean pixel with retrieved FLH of 0.57 mW/m²/nm/sr. RMS of the residual spectrum is 1.04e-4 when SIF is fit and 1.35e-4 when SIF is not fit.
Figure 17. Similar to Fig. 7 but showing the mean of the residuals within the full band algorithm fitting window for ocean pixels with moderate to high amounts of ocean fluorescence (FLH > 0.4 mW/m²/nm/sr) for a single day (01 July 2007).
Supplemental material for “New methods for retrieval of chlorophyll red fluorescence from hyper-spectral satellite instruments: simulations and application to GOME-2 and SCIAMACHY”

J. Joiner¹, Y. Yoshida², L. Guanter³, and E. M. Middleton¹

¹NASA Goddard Space Flight Center, Greenbelt, MD, USA
²Science Systems and Applications, Inc., Lanham, MD, USA
³Helmholtz Centre, Potsdam, Germany

Correspondence to: J. Joiner (joanna.joiner@nasa.gov)

Figure 1. Regional boxes used for principal component analyses (PCA).
(a) SCIAMACHY biases over ocean (black with diamonds: before bias adjustment; red with triangles: after adjustment) for solar line retrievals for July 15 (left) and July 31 (right) 2007. Symbols denote mean bias and error bars are the standard deviations. Bins 1 and 2 refer to latitude bins between 0-90N and 0-90S, respectively.

(b) Similar to (a) but for SCIAMACHY O\textsubscript{2} band retrievals.

(c) Similar to (b) but for GOME-2. Bins 1-3 refer to latitude bins between 40-90N (bin 1), 40S-40N (bin 2), and 40S-90S (bin 3).

**Figure 2.** SCIAMACHY (upper two panels) and GOME-2 (lower panel) biases over ocean as a function of latitude before (black) and after (red) zero-level adjustment for July 15 (left) and July 31 (right) 2007.
Figure 3. SCIAMACHY solar line retrieval biases over ocean as a function of solar zenith angle before (black) and after (red) zero-level adjustment for July 15 (left) and July 31 (right) 2007 and two latitude bins (top and bottom).
Figure 4. SCIAMACHY $O_2$ band retrieval biases over ocean as a function of solar zenith angle before (black) and after (red) zero-level adjustment for July 15 (left) and July 31 (right) 2007 and two latitude bins (top and bottom).
(a) GOME-2 O$_2$ band retrieval biases over ocean (black with diamonds: before bias adjustment; red with triangles: after adjustment) for latitude bin 1 (40N-90N) for July 15 (left) and July 31 (right) 2007. Symbols denote mean biases and error bars are the standard deviations.

(b) Similar to (a) but for latitude bin 2 (40S-40N).

**Figure 5.** GOME-2 biases over ocean as a function of solar zenith angle (SZA) before (black) and after (red) zero-level adjustment for July 15 (left) and July 31 (right) 2007 and two latitude bins (top and bottom). The third latitude bin for GOME-2 is not shown because it contains only high SZAs.
Figure 6. SCIAMACHY solar line retrieval biases over ocean as a function of radiance (normalized, arbitrary units) before (black) and after (red) zero-level adjustment for July 15 (left) and July 31 (right) 2007 and two latitude bins (top and bottom).
(a) SCIAMACHY \( \text{O}_2 \) band retrieval biases over ocean (black with diamonds: before bias adjustment; red with triangles: after adjustment) for latitude bin 1 (40N-90N) for July 15 (left) and July 31 (right) 2007. Symbols denote mean biases and error bars are the standard deviations.

(b) Similar to (a) but for latitude bin 2 (40S-40N).

**Figure 7.** SCIAMACHY \( \text{O}_2 \) band retrieval biases over ocean as a function of radiance (normalized, arbitrary units) before (black) and after (red) zero-level adjustment for July 15 (left) and July 31 (right) 2007 and two latitude bins (top and bottom).
(a) GOME-2 O$_2$ band retrieval biases over ocean (black with diamonds: before bias adjustment; red with triangles: after adjustment) for latitude bin 1 (40N-90N) for July 15 (left) and July 31 (right) 2007. Symbols denote mean biases and error bars are the standard deviations.

(b) Similar to (a) but for latitude bin 2 (40S-40N).

(c) Similar to (b) but for latitude bin 3 (40S-90S).

Figure 8. GOME-2 O$_2$ band retrieval biases over ocean as a function of radiance (normalized, arbitrary units) before (black) and after (red) zero-level adjustment for July 15 (left) and July 31 (right) 2007 and three latitude bins (top, middle, and bottom).
Figure 9. Global composites of red SIF from SCIAMACHY and GOME-2 binned in 1° cell boxes with zero-level adjustment for July (left) and December (right) 2007.
Figure 10. Monthly mean fluorescence from different retrievals with and without corrections as noted in mW/m$^2$/str/nm for May 2007 gridded to spatial resolutions of 0.5° in (c) and 1° resolution in (a) and (b).