Response to the Reviewer #3 (os-8-C1019-2012):

Specific comments (Reviewer #3)::

C01: Page 2272, line 3- starting with the abstract, you use the term phytoplankton functional types (PFT) while citing (page 2274, line 3) Nair et al 2008. The concept of PFTs as outlined by Nair et al 2008, however, groups algae with respect to their role in the biogeochemical cycle of the ocean, which often does not comply with taxonomic grouping. You refer to taxonomic groups instead and do not use the term PFT correctly. If you would like to keep the term PFT, please explain from the start (abstract and introduction) how your taxonomic groups can be grouped into PFTs. As an example: in Nair et al 2008, diatoms are grouped in both, nitrogen- fixers and silicifiers. E. huxleyi is a calcifier and a DMS producer.

R01: That's true. Some taxonomic groups (e.g., diatoms and coccolithophores) belong at the same time to different PFTs. Nevertheless the detection of the most important taxonomic groups is a necessary step towards understanding the PFT distribution in the global ocean (because PFT is a concept, while taxonomic group is the entity). However, we agree that the explanation given at the beginning of the manuscript had to be improved. Therefore we have added the following statement in the introduction:
"Even though some taxonomic groups (e.g., diatoms and coccolithophores) at the same time belong to different PFTs, the detection of the most important taxonomic groups is a necessary step towards the understanding of the PFT distribution in the global ocean (because PFT is a concept, while a taxonomic group is an entity)."

C02: Page 2273, line 25 – "chl-a is a common pigment among all phytoplankton species"- yes, all but prochlorophytes.

R02: The respective sentence has been accordingly modified in the revised manuscript as follows:
"chl-a is a common pigment among all phytoplankton species (divinyl chl-a for prochlorophytes only, and monovinyl chl-a for all others)"

C03: Page 2274, line 4- Check citation:You cite Millie et al 1997 for the space-borne detection of algal blooms. Please have a look at this publication! It is not about space-borne detection of algal blooms, but on the use of photo-pigments and absorption signatures for detection of Kareniabrevis (Gymnodiniumbreve) in the laboratory, but not from space. There is a lot of appropriate literature for the satellite-borne detection of algal blooms available, please use one of these.

R03: We removed the above mentioned citation and cite now an appropriate one:
Kahru, M., B.G. Mitchell, A. Diaz, M. Miura. MODIS Detects a Devastating Algal Bloom in Paracas Bay, Peru. EOS, Trans. AGU, Vol. 85, N 45, p. 465-472, 2004.

C04: Page 2280, line 1- "scattering of CDOM"? CDOM is dissolved, how does it scatter?

R04: We corrected this sloppy mistake accordingly.

C05: Page 2283, line 24- please include discussion, on how appropriate a pixel size of 30 km x 60 km

is for the delineation of algal groups in natural waters (e.g. in comparison to MODIS and MERIS pixel sizes).

R05: The reviewer is right that a better spatial resolution than 30 km by 60 km will resolve better phytoplankton dynamics. Still on the global scale, as stated by *Aiken et al.* (2007) and already discussed in *Bracher et al.* (2009) phytoplankton blooms in the open ocean are often larger than 50 km by 100 km and persist over a few days to several weeks. The SCIAMACHY PhytoDOAS PFT data set can be used to study phytoplankton dynamics in specific regions over longer time scale (here eight years) and is useful for parameterizing and evaluating biogeochemical models, as shown in the recently published paper by *Sadeghi et al.* (2012) and *Ye et al* (2012).
We modified as stated above accordingly the conclusions:
"Surely, a better spatial resolution than 30 km by 60 km will resolve better phytoplankton dynamics. Still on the global scale, as stated by Aiken et al. (2007) and already discussed in Bracher et al. (2009) phytoplankton blooms in the open ocean are often larger than 50 km by 100 km and persist over a few days to several weeks. As shown in the recently published papers by Sadeghi et al. (2012) and Ye et al (2012), the SCIAMACHY PhytoDOAS PFT data-set can be used to study phytoplankton dynamics in specific regions over longer time scale and for parameterizing and evaluating biogeochemical models. However, opposed to other PFT satellite data sets with PhytoDOAS not only the dominant groups within a pixel are identified from their optical imprint on the satellite data (e.g., Alvain et al. 2005, 2008), but also several PFT can be quantified with their specific chl-a conc.. The abundance-based PFT satellite methods (e.g., Hirata et al. 2011) also give chl-a conc. for various PFTs but these methods are purely based on empirical relationships within regionally biased in-situ data-sets and are not using the optical satellite information to infer the optical signatures of specific PFTs; so with these methods the unexpected cannot be detected."

C06: Page 2284, line 16- you are planning to validate model data on E. huxleyi as an indicator for coccolithophores with a model of PIC as another indicator for coccolithophores. Please discuss how appropriate this is and please also include in situ data to confirm both model outcomes.

R06: In the revised manuscript statements and citations have been given on the accuracy of MODIS PIC data, and NOBM modeled coccolithophores (see sec. 3.2). Moreover, as another data source for validating PhytoDOAS coccolithophores, we have used the global distribution of haptophytes obtained from a PFT method developed by *Hirata et al.* (2011). In this PFT algorithm the pigment-derived synoptic relationships are applied to the SeaWiFS level-3 chl-a products to reach the information of different PFTs. The accuracy of this data-set has been also included in revised manuscript.
We agree that comparing the PhytoDOAS results with in-situ data will be the most appropriate validation, but there have been the following limitations for PhytoDOAS coccolithophores data (as already mentioned to Reviewer #1 and introduced into the revised manuscript under section 2.4):
Since the spatial resolution of in-situ point measurements and the large size of SCIAMACHY pixel is too different, collocations will hardly match the same optical average of phytoplankton signatures sampled for both methods. This makes it generally difficult to validate phytoplankton retrievals extracted from SCIAMACHY data with in-situ measurements. However, in the case of coccolithophores this becomes even more difficult, because the different in-situ techniques are not encompassing the whole group of coccolithophores: Via the HPLC method, from marker pigments the biomass of the group of haptophytes are globally assessed only and the pigments of other haptophyte species (e.g., *Phaeocystis*) are spoiling the measurements of coccolithophores; with flow-cytometry only the larger groups of pico- or nanoeukarotic phytoplankton are identified; by microscopic counts

cells less than 5 micrometer cannot be identified properly. Hence, there are uncertainties in the determination of in-situ coccolithophore chl-a conc.

C07: Page 2284, line 17- you consider coccolithophores; what about dinoflagellates and diatoms?

R07: Motivated by some comments given by the reviewers, we became convinced that the focus of this paper, based on the existing evidences, must be on the group of coccolithophores only. This is because the particular configurations developed so far in our method improvement is targeting the PFT of coccolithophores, even though the results are also reasonable for diatoms (compared to the result of B*racher et al.* 2009). Therefore to adequately address the content work, opposed to the initial title chosen for the manuscript published in Ocean Science Discussion, we have modified the title as follows:
"Improvement to the PhytoDOAS method for identification of coccolithophores using hyper-spectral satellite data."
This was also motivated by the lack of an appropriate in-situ or satellite dinoflagellate product to evaluate the PhytoDOAS dinoflagellate data set (more about that you find in R13).

C08: Page 2284, line 26,27- "It must be mentioned that as E. huxleyi is the dominant species of the coccolithophores, it has been used in this study as the spectral indicator of this PFT target". Please add a reference for this statement. Further, E. huxleyi is both, a calcifier and a DMS producer (two groups in the concept of PFTs, as summarized by Nair et al 2008). To which PFT do you assign the species? As you include in total two more taxonomic groups to PhytoDOAS, coccolithophores and dinoflagellates, please discuss with relevant literature, why the use of a single species as marker species for the delineation of one of these two groups is appropriate.

R08: We now introduced an appropriate citation to the above mentioned statement (Tyrrell & Merico, 2004). The second point ("*to which PFT do you assign the species?*") was already explained in R01. Regarding the third point, in R09 we give details why we had to use a spectrum from a single species (*E. huxleyi*) and why we still regard this spectrum to be representative for the whole group of coccolithpohores. This was also now added to the revised manuscript (see sec. 2.3).

C09: Page 2285, line 1- Measurement of the reference absorption spectrum for the two new groups (coccolithophores and dinoflagellates): If I understand you right, you used for the group coccolithophoresonly one culture with one strain of E. huxleyi, without paying attention to the physiological state or age of the culture. For dinoflagellates you used only one natural sample, at a bloom situation. And so you proceeded for diatoms. Especially dinoflagellates are quite diverse with respect to pigment content and absorption spectra. These absorption spectra are the backbone of you approach and need to be selected and discussed more carefully! Please compare the derived spectra also with relevant literature.

R09: Of course, the priority would have been utilizing only natural samples for measuring all absorption spectra and selecting and measuring all spectra as elaborated as possible. But, as answered to Reviewer #1, we have been constrained by limitations to obtain an appropriate natural sample for coccolithophores where it was at least dominating the overall phytoplankton biomass by over 50%.

Nevertheless, even though the specific absorption spectrum of coccolithophores used in this study was obtained from an *E. huxleyi* culture sample, its spectral shape is very similar to the specific absorption of natural samples measured by *Siegel et al* (2007) in a coccolithophore bloom off the Namibia Coast (Benguela Upweling). This spectrum by *Siegel et al* (2007) was also well comparable to the absorption spectra obtained from coccolithophore cultures and the coccolithophore-dominated natural samples in the Kattegat. However, the natural sample of *Siegel et al.* (2007), does not have detailed HPLC analysis to prove the domination via chl-a conc. of coccolithophores among the total phytoplankton biomass and its absorption spectrum. This paragraph was now introduced in the manuscript in section 2.3.
It is also true that the biodiversity of dinoflagellates might cause a serious problem for a global retrieval. But, as pointed out in R07, so far the retrieval has only been optimized for the retrieval of coccolithophores. In the future natural samples obtained from the major bio-geographical provinces (according to *Longhurst* 1998) will be used to establish a regional-based PhytoDOAS.

C10: Page 2285, line 9- was this a monospecific bloom? Is the dinoflagellate species representative? How have other studies solved the problem of dinoflagellate diversity?

R10: The dinoflagellate bloom was identified by the HPLC pigment composition only. We have no microscopic data to clarify what different species of dinoflagellates were contributing.

C11: Page 2286, line 20- the triple target fit includes E. huxleyi together with diatoms and dinoflagellates. Why did you not include cyanobacteria?

R11: As mentioned before in response to Reviewer #1: Cyanobacteria are spectrally more different as compared to other PFTs incorporated in the current multi-target fit-mode. Technically, putting a cyanobacteria spectrum in the simultaneous fit does not help to reach the optimal fit quality for this group and cyanobacteria have to be fitted in a different wavelength window in order to be retrieved optimal. In addition, the global distribution of cyanobacteria, as shown by instance by *Bracher et al.,* (2009) is also quite different from the other PFTs of interest, which is due to their specific oceanic habitats resulting from their specific biological growth conditions.
To address this issue, we have already added this explanation in sec. 2.4, where we talk in detail about the different considerations for choosing the right PFT set, associated with the outcome of the "orthogonality tests" (the method is explained as *Appendix A* in the revised manuscript).

C12: Page 2287, line 14-17- The comparison with in situ data is a crucial aspect that deserves more discussion. Are there public datasets available that you can refer to? The question of how to match the large satellite ground pixels to in-situ data needs to be addressed here.

R12: This issue has been now addressed (as a whole paragraph) in section 2.4 in the revised manuscript:
"*Although the most reliable option for the quality test of retrieval will be, of course, validating the results by comparing them with the available high quality in-situ measurements, however, it cannot always be fulfilled. The general reason for that is the very low availability of in-situ data with respect to the global distributions of major PFTs. In particular, in the case of coccolithophores there is a complexity pertaining to in-situ measurng the whole group: via HPLC method and flow-cytometry the pigments of other haptophyte species (e.g., Phaeocystis) are spoiling the measurements of coccolithophores; by microscopic techniques (as they cannot detect cells less than 5µm) part of the*

coccolithophore cells are not accounted in the measurement. Hence, there are uncertainties in determination of coccolithophore concentrations, which limit the validation of the respective satellite retrievals with in-situ measurements. Moreover, there is a specific difficulty associated with the collocation (matching) of SCIAMACHY ground pixels to the existing in-situ data due to its large pixel size (30×60 km^2), which limits strongly the available match-up points."

C13: Page 2289 onwards, 3.2- you compare model data with the retrieved coccolithophore and diatom data. What about dinoflagellates?

R13: As mentioned in R07, in order to address limitations to verify the retrieval for dinoflagellates, we changed the title of the revised manuscript and partly the content (now focusing on the achievement of the improved PhytoDOAS for detection of coccolithophores). This was partly due to the lack of appropriate data sources (in-situ and satellite-based) for comparing the dinoflagellates' results. Moreover, even the abundance-based PFT algorithm of *Hirata et al.* (2011), which has been used as another data source for validating PhytoDOAS coccolithophores, is not suitable for dinoflagellates. It was shown in *Hirata et al.* (2011) that the currently available global HPLC-based data set on dinoflagellates is not normal distributed and a significant abundance-based relationship for dinoflagellates chl-a to total chl-a could not been inferred (which can then be used to derive a satellite-based estimate of dinoflagellate distribution).

C14: Page 2291, line 1- "..validity test should be done..": yes.

R14: In rewriting this section, this statement has been removed. Instead, the accuracy of MODIS PIC algorithm has been addressed according to *Balch et al* (2005).
In order to verify our PhytoDOAS results for coccolithophores we now added a direct comparison of the monthly mean values over eight years for a region in the North Atlantic of the PIC MODIS satellite product to PhytoDOAS (Fig. 9). The selected region, within the North Atlantic Ocean, was one of the three selected in *Sadeghi* et al. 2012. Within this publication, three oceanic regions where coccolithophores blooms are frequently forming, phytoplankton dynamics were studied using PhytoDOAS products in conjunction with other satellite products characterizing phytoplankton and various geophysical parameters.

C15: Page 2292, line 20, 21- generally yes, phytoplankton blooms could provide you the opportunity to test the retrieval method under realistic conditions. But how many phytoplankton blooms have a spatial dimension which corresponds to 30 km x 60 km?

R15: We already answered to that in our response to R07.
In particular, coccolithophore *E. huxleyi* blooms have been reported to form very large blooms (e.g., Holligon et al., 1993; *Brown and Yoder, 1994;* Sukhanova and Flint,1998; etc.).

Holligan et al., 1993: A biogeochemical study of the coccolithophore Emiliania huxleyi in the north Atlantic. Global Biogeochem Cycles 7: 879-900

Brown and Yoder (1994): Coccolithophorid blooms in the global ocean. Journal of Geophysical Research 99, 7467-7482.

Sukhanova and Flint (1998) Anomalous blooming of coccolithophorids over the eastern Bering Sea shelf. Oceanology 38: 502-505

C16: Page 2293, line 2, 3- why would this method be a better alternative to more accurately retrieve chl-a from satellite data, especially with respect to the not yet included algal taxonomic groups and the large pixel size?

R16: We answered and changed the manuscript accordingly as pointed in R05.

C17: Page 2294, line 4- "challenge to overcome spectral correlation between absorption spectra of target PFTs which arises from their common pigments"- not only from common pigments, but also from similar absorption regions of most other pigments than chl-a.

R17: That's true, we changed that accordingly.

Technical corrections:

Figure 11: please include colourbars with both lower panels.
Page 2286, line 9- "This approach, called as multi-target fit"- delete "as"
Page 2286, line 13- "targets are ïtted"- fitted
Page 2287, line 22, 25- fourth instead of forth
Page 2291, line 17- these instead of this
Page 2293, line 13, 14- Sentence not complete?
Page 2294, line 6- spectra?
Page 2294, line 21- global for "globla"
Page 2295, line 5- global distribution for "globladisribution"
Page 2295, line 22- lower case: dimethylsulphide instead of "Dimethylsulphide"

All technical corrections have been applied to the revised manuscript.