A spectral light absorption-based approach for detecting changes in the phytoplankton community size structure at the BOUSSOLE site (Mediterranean Sea)

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I. INTRODUCTION

Temporal variations in the taxonomic and size structure of algal communities play a key role in understanding many marine biogeochemical processes. Thanks to the advances in the remote sensing field, the analysis of space-derived or *in situ* optical properties (IOPs and AOPs) is today largely dedicated to identify different phytoplankton types and analyze synoptically the changes in the algal communities, so that biogeochemical models can possibly be refined (Nair et al., 2008).

In the framework of the BIOCAREX (BIOoptics and CARbon Experiment) and BOUSSOLE (BOUée pour l'acquiSition d'une Série Optique à Long termE) projects, we elaborated a new algorithm based on the multivariate Partial Least Square (PLS) technique in order to retrieve information on phytoplankton pigments and size structure from a long-time series of hyperspectral phytoplankton absorption measurements monthly collected at the BOUSSOLE site (Ligurian Sea, Mediterranean Sea) since 2003.
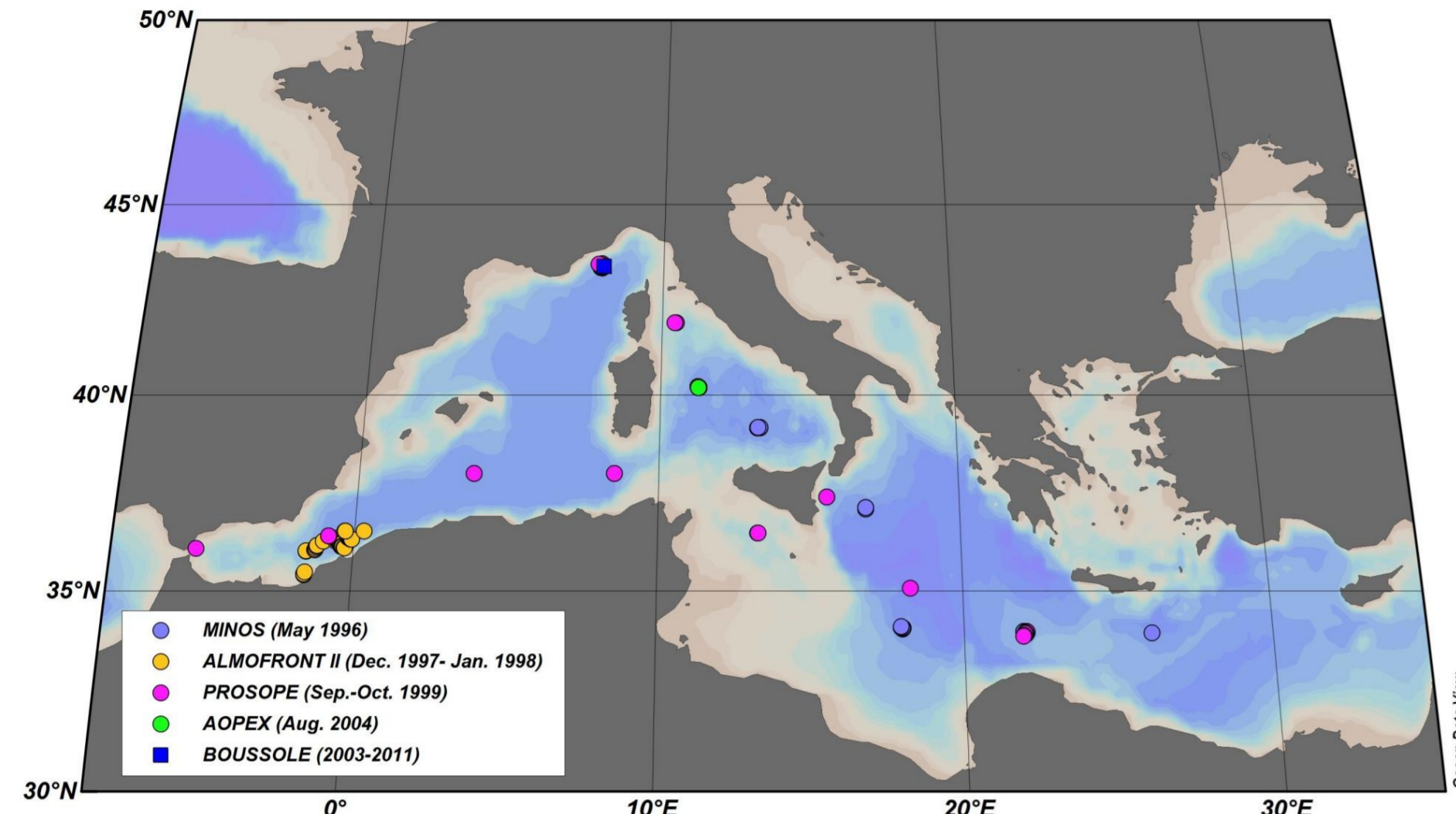

Figure 1. Map of the sampling sites (circle= stations for model calibration; square= BOUSSOLE mooring site). Schlitzer, R., Ocean Data View, http://odv.awi.de, 2012.

II. BIO-OPTICAL ANALYSES

HPLC pigment and light absorption measurements used to develop calibration model were collected during 4 oceanographic cruises in the Mediterranean Sea between 1996 and 2004 (Fig.1). At the BOUSSOLE mooring site (7°54'E, 43°22'N, Mediterranean Sea; Fig.1) samples were monthly collected between 2003 and 2011. Phytoplankton absorption spectra ($a_{ph}(\lambda)$) were measured every 1 nm in the range 400-700 nm. HPLC pigment measurements were performed according to Vidussi et al. (1996). All data considered here, belong to the first optical depth ($Z_{eu}/4.6$) of Case 1 waters.

III. PARTIAL LEAST SQUARE (PLS) REGRESSION: CALIBRATION AND VALIDATION

PLS is a multivariate analysis technique that relates a data matrix of predictor variables to a data matrix of response variables by regression. Thus, the PLS method can be used for the prediction of one or several dependent variables from several independent variables (Martens and Næs, 1989). In this study:

PREDICTOR VARIABLES: Fourth-derivative of phytoplankton absorption spectra (Fig.2).

RESPONSE VARIABLES: Biomarker pigments (DP) of the three phytoplankton size classes (Uitz et al., 2006) and Tchl *a* (see Table 1 for details).
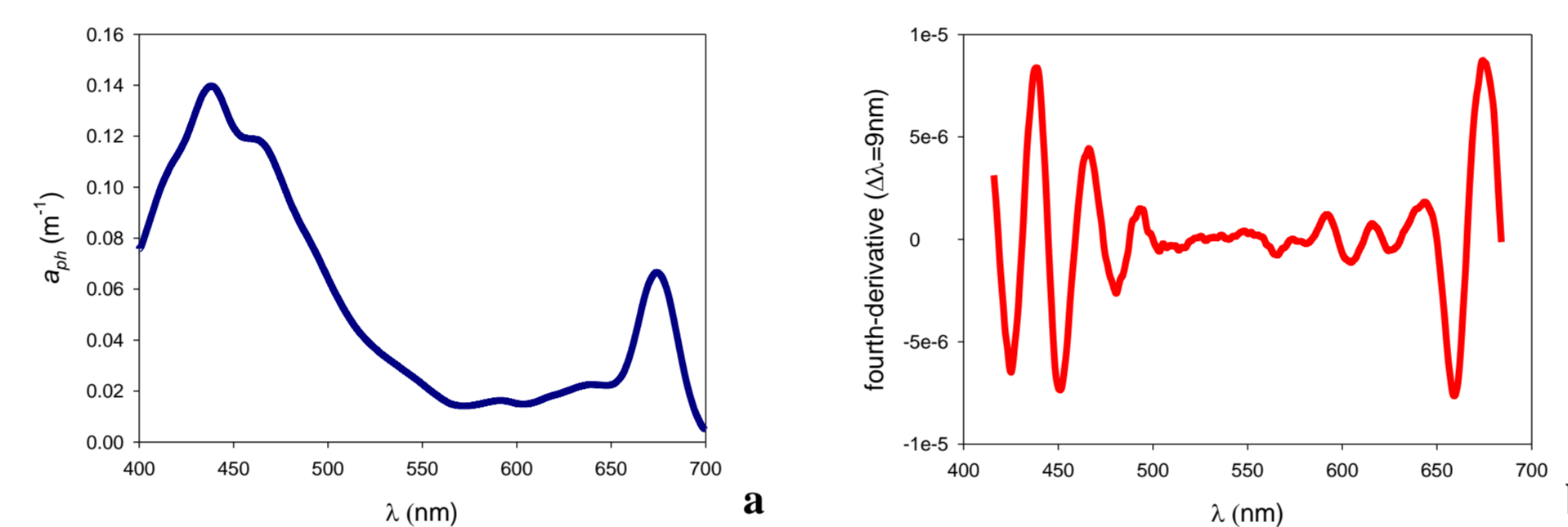

Figure 2. Example of a phytoplankton absorption spectrum (a) and its fourth-derivative (b). The fourth-derivative method computes the changes in curvature of a given spectrum over a pre-fixed sampling interval (Δλ=9nm). The fourth-derivative absorption spectrum is composed of 269 spectral values.

Table 1. Symbols, comments, formulae for phytoplankton pigments and sums used as dependent variables in the PLS multivariate analysis.

Variable	Pigments	Comment	Formula
Tchl *a*	Chlorophyll *a*, Divinyl-chlorophyll *a* and Chlorophyllide *a*	Phytoplankton biomass index	[Chl *a*] + [DV Chl *a*] + [Chlide *a*]
Micro	Fucoxanthin and Peridinin	DPs of microphytoplankton	1.41[Fuco]+1.41[Perid]
Nano	19'-HF, 19'-BF and Alloxanthin	DPs of nanophytoplankton	1.27[19'-HF]+0.35[19'-BF]+0.60[Allo]
Pico	Chlorophyll b+Divinyl-chlorophyll b and Zeaxanthin	DPs of picophytoplankton	1.01[Tchl b]+0.86[Zea]
DP	All DPs	Total Marker Pigments	Micro+Nano+Pico

CALIBRATION: Models were developed using samples (n=239) collected during the Mediterranean Cruises (Fig.1). The optimal number of components was selected for the lowest Root Mean Square Error of Prediction (RMSEP; see example in Fig.3). Two and three components were sufficient for Tchl *a* and DP variables respectively, while at least four PLS components were required to minimize the prediction error of Micro, Nano and Pico (Table 2).
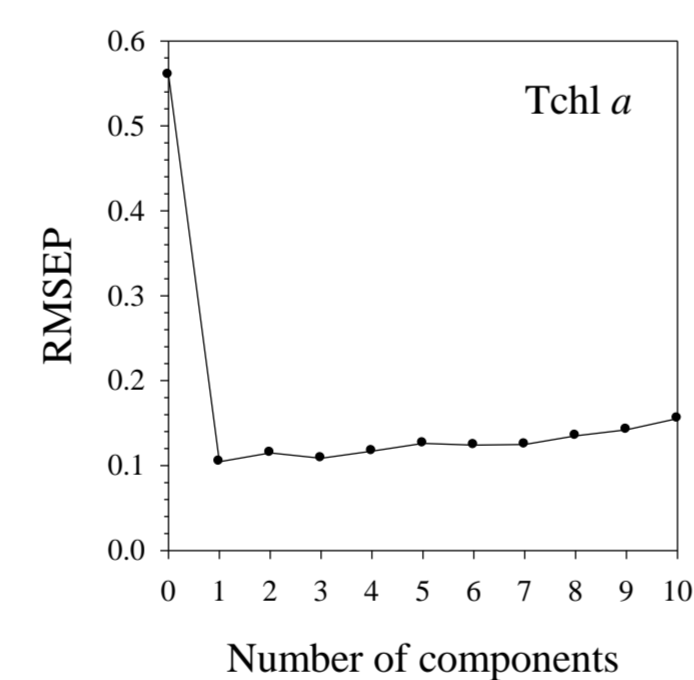
Table 2. PLS parameters of $a_{ph}(\lambda)$-models, from left to right: number of components (N comps), Root Mean Square Error of Prediction (RMSEP, in mg m^{-3}), the explained variance (%) for independent (R^2X (%)) and dependent (R^2Y (%)) variables.

	N comps	RMSEP	R^2X (%)	R^2Y (%)
$a_{ph}(\lambda)$ models				
Tchl *a*	3	0.1086	95.63	98.56
DP	2	0.0857	95.18	97.12
Micro	4	0.1085	96.31	96.56
Nano	4	0.0832	96.24	95.06
Pico	5	0.0207	97.29	95.62

Figure 3. Variation of the Root Mean Squared Error of Prediction (RMSEP in mg m^{-3}) as a function of the number of components for PLS model built using the fourth-derivative of phytoplankton absorption spectra and [Tchl *a*].

VALIDATION: At the BOUSSOLE site the most accurate PLS predictions (n=484) are obtained for Tchl *a* and DP (R^2=0.91, Fig. 4a, b). More importantly, PLS models evidenced their ability in predicting the concentrations of DPs associated to micro-, nano-, and pico-phytoplankton size classes (Fig.4c, d, e) as observed from high R^2 values (0.52-0.75) and regression slopes (b>0.90).
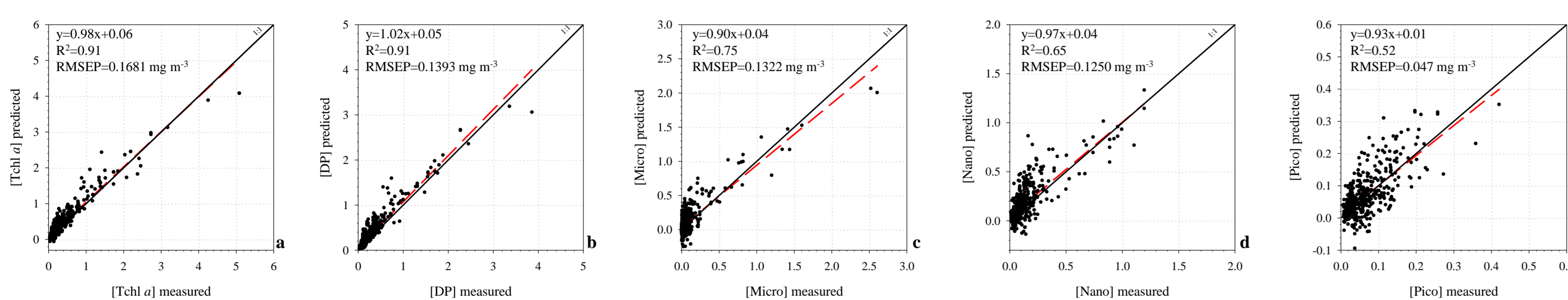

Figure 4. Relationships between the HPLC measured and PLS predicted concentrations (in mg m^{-3}) of the 5 variables (Tchl *a*, DP, Micro, Nano and Pico) for the BOUSSOLE data set (n=484). The 1:1 ratio is shown as a solid line (black). Linear regressions between measured and predicted concentrations are shown as a dashed line (red). Statistical parameters of linear relations and Root Mean Square Error of Prediction (RMSEP, in mg m^{-3}) are also reported.

IV. PLS PREDICTED TEMPORAL CHANGES

The $a_{ph}(\lambda)$-PLS model predicted concentrations of Tchl *a*, DP Micro, Nano and Pico reproduced well those obtained from HPLC pigment measurements over the entire BOUSSOLE time series (Fig.5).
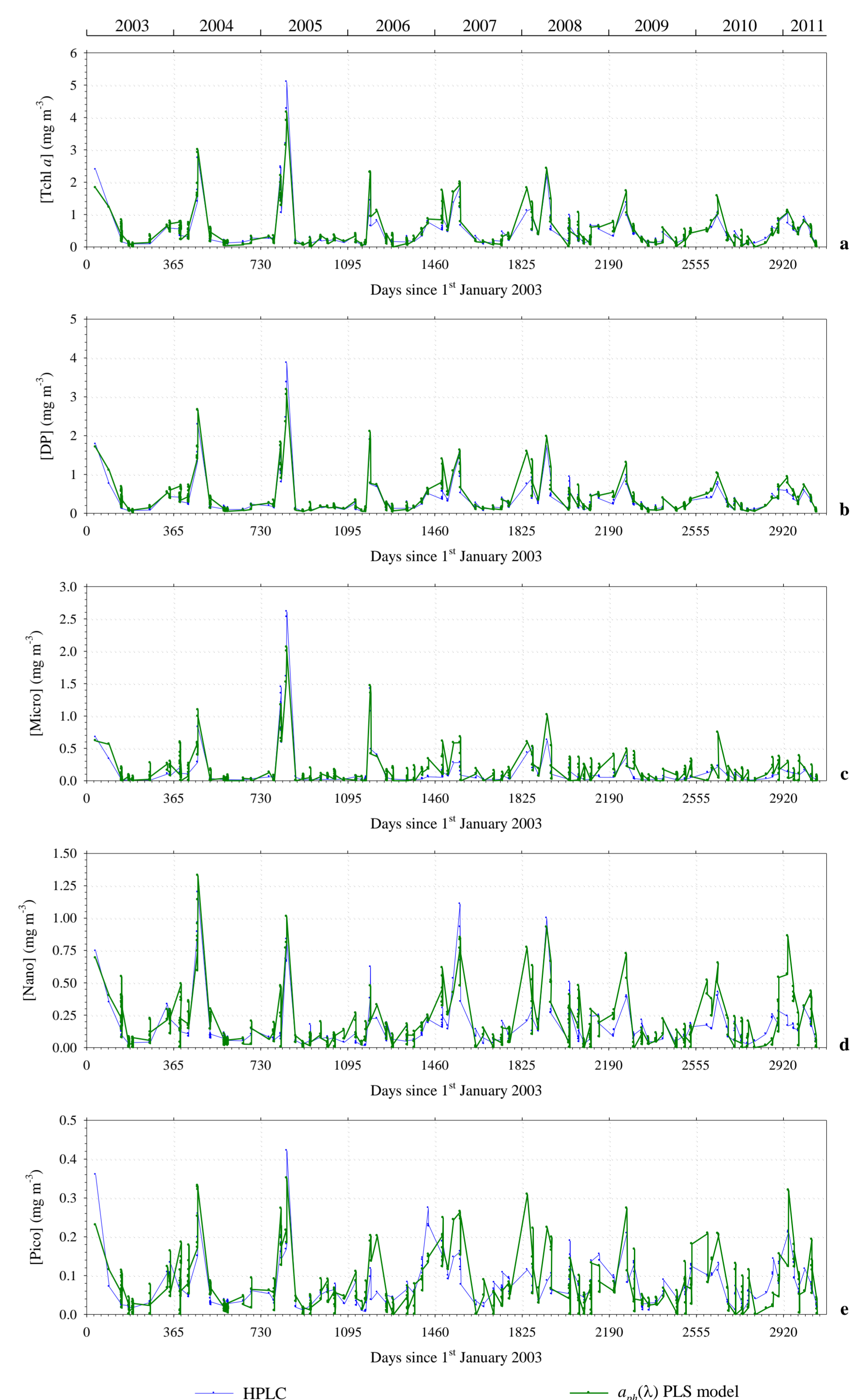

Figure 5. The entire BOUSSOLE time series (January 2003-May 2011) of pigment concentrations as derived by HPLC pigment measurements (blue line) and $a_{ph}(\lambda)$-PLS models (green line).

V. CONCLUSIONS

The PLS technique represents an encouraging method for retrieving algal biomass and size structure from *in situ* absorption properties. Future work will be focused on the application of the PLS method to space-derived optical properties, so that the continuous monitoring of the algal community structure can become possible.

References

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