BIO-OPTICAL CHARACTERIZATION OF ASINARA GULF SEA WATER IN SARDINIA (ITALY) USING BOTH LASER SPECTROFLUORIMETER AND REMOTE SENSING DATA.

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ABSTRACT

The general objective of this research is to calibrate MODIS bio-optical algorithm for better more accurate estimates of phytoplanktonic Chlorophyll a (Chl-a) in the Asinara Gulf (Northern Sardinia, Italy) using and exploring the suitability of the new laser spectrofluorometric apparatus CASPER (Patent ENEA) as a fast and accurate method to obtain “sea truth” values of Chl-a and other bio-optical parameters from simultaneous in situ measurements. The accuracy and reliability of data (in particular Chl–a) obtained by CASPER have been evaluated comparing them with standard measurements. CASPER has proved to be a valid instrument also for the investigation of polycyclic aromatic hydrocarbons (PAHs) and oil pollution (dispersed or in film) in water bodies. At the moment “sea truth” data of Chl-a have being compared to the imagery collected by MODIS. But in order to reach better results, the bio-optical algorithm is going to be recalibrated according to the measurements of CASPER, thus providing new estimates of phytoplanktonic Chl-a in the Asinara Gulf.

INTRODUCTION

Marine phytoplankton is recognized as one of the major climate driver, able to play an important role in climate regulation of the entire planet. It is capable to influence chemical and biological dynamics in the coastal zone because it directly affects water quality, biogeochemical cycling of reactive elements, and food supply to consumer organisms (1). Chl-a is considered a useful descriptor of the amount of phytoplankton in the aquatic ecosystems. The general objective of this research (financed by L.R. 7 “Promotion of scientific research and information technologies” of the Autonomous Region of Sardinia, Italy for the period 31 May 2010 – 31 May 2012) are:

to calibrate MODIS OC3 bio-optical algorithm for better more accurate estimates of phytoplanktonic Chl-a in the Asinara Gulf, an area located in Northern Sardinia (Western Mediterranean);

to explore the suitability of the new laser spectrofluorometric apparatus CASPER (Compact and Advanced laser SPEctrometeR – Patent N° RM2005A000269) as a fast and accurate method to

obtain “sea truth” values of Chl-a and other bio-optical parameters from simultaneous in situ measurements.

METHODS

Study area and sampling

The selection of sampling stations in the Asinara Gulf (Figure 1) was principally made in order to collect fluorescence excitation spectra considering sites with different degree of pollution. The northern coast of Sardinia is one of the most dynamic and vulnerable environments in the Western Mediterranean. It comprises the National Park of Asinara Island, is a part of the Sanctuary of the Cetaceans of the Mediterranean Sea and is well known for many beautiful tourist places. However, important civil and industrial activities, both on the coastline (harbours, power plants and industrial areas), and in the catchment coexist, certainly not without difficulties, with these aspects of very high naturalistic quality and with fishery.

Sea water samples from different depths (0 m and 10 m with a Niskin bottle) were collected at 18 stations every four months since August 2010. The stations are located along six transects perpendicular to the coastline, respectively from less impacted areas to more impacted ones (from Cala Reale, in the Asinara Island, to Porto Torres, in the central part of the gulf). Each transect comprises three stations, respectively at 500 m, 1500 m and 3000 m from the coast. Temperature, salinity, dissolved oxygen ,pH and fChl-a along vertical profiles were measured in situ with a multiparameter probe (Idronaut/YSI 6600V2) at each station. Transparency was also measured a Secchi disk

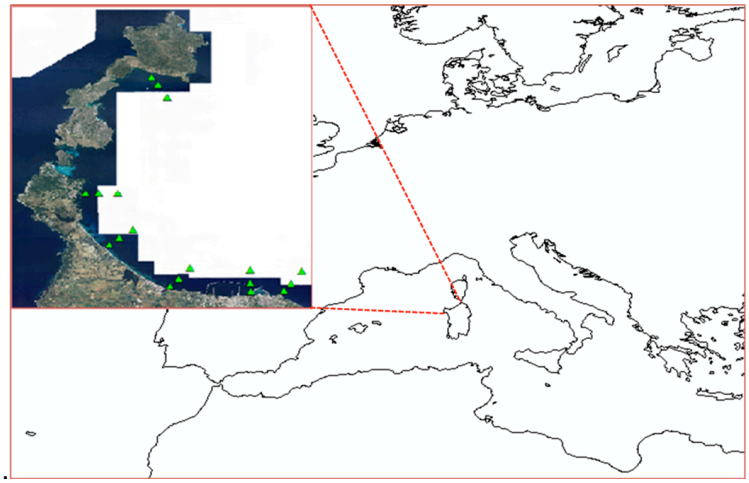

Figure 1: Area of study

Fluorescense measurements

The spectrofluorimeter CASPER was used to collect emission spectra of natural and filtered water samples. CASPER is based on double laser excitation of water samples in the UV (266 nm) and Visible (405 nm) spectral region and a double filtration in order to detect both quantitative data, such as chromophoric dissolved organic matter (CDOM), proteins-like components (tyrosine, tryptophan), algal pigments (phycoerythrin, phycocyanin, different pigments belonging to the carotenoid groups, Chl-a), and qualitative data on the presence of hydrocarbons and oil pollution (Table 1).

Fluorescence spectra were processed with a background subtraction, an integration of peaks within a 10 nm bandwidth and a deconvolution of overlapping structures. A successive normalisation to the relevant water Raman peak permitted to release data in “Raman units”. Fluorescence intensi-

ties in these relative units were converted in absolute value of concentrations by calibrating them with reference samples. Examples of fluorescence spectra obtained at different excitation wavelengths for sea water samples are reported in Figure 2.
The accuracy and reliability of data (in particular Chl–a) obtained by CASPER (Figure 3) were evaluated comparing them with standard measurements of water samples filtered through Whatman GF/C filters and analysed by spectrophotometry, after pigment extraction in 90% acetone (2). These measurement permitted also to calibrate frequently a multi-parameter probe (Idronaut and YSI 6600 V2) used in situ to obtain fluorimetric measured values of Chl-a (fChl-a) along vertical profiles.

Table 1: Wavelength bands analysed with CASPER

Wavelength	**λexc [nm]**	**λem [Nm]**
Laser	266	266
Raman		291
Tyrosine		305
Tryptophan		345
Cdom		450
Carotenoids		490
Laser	405	405
Raman		468
Phycoerythrin		575
Phycocyanin		645
Chlorophyll-A		680

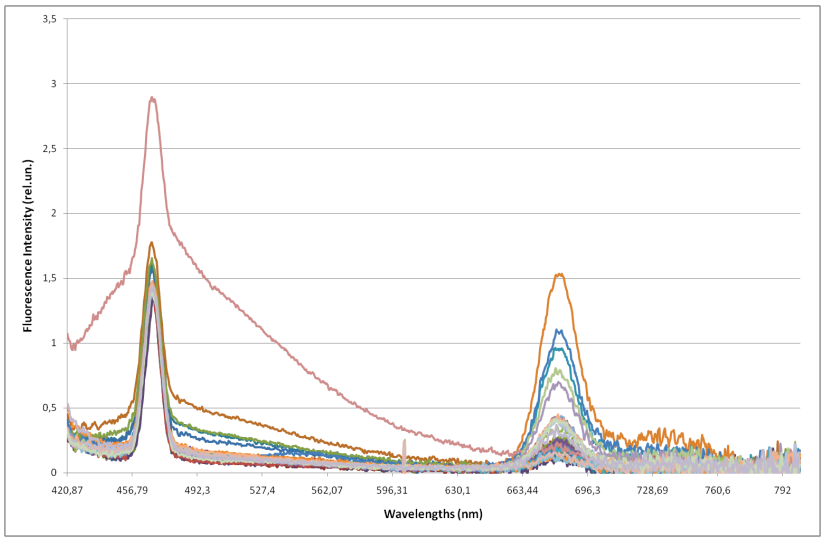

Figure 2: Examples of fluorescence spectra obtained with CASPER for water samples

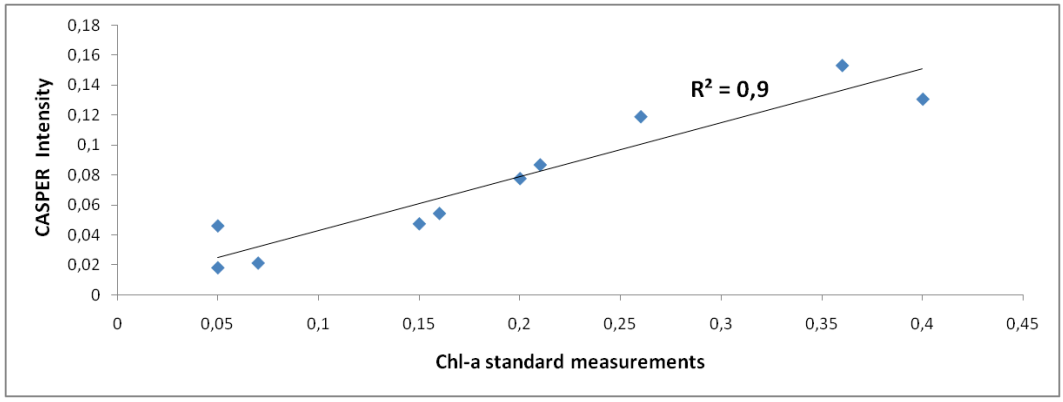

Figure 3: Calibration of CASPER intensities with Chlorophyll-a standard measurements

Laboratory measurements

Evaluation of total phytoplankton abundance, in terms of cell density (3) and class composition, and measure of chemical (main nutrients - N, P, Si - and oxygen) and physical variables (salinity and pH) were performed in the surface water samples from the stations nearest to the coastline (500 m on the transects Balai, Fiume Santo, Stintino, Cala Reale) to permit a better comprehension of the total algal pigment data recorded and of the state of the coastal marine environment.

Oil spill detection

On 11 January 2011, an incident occurred in the Asinara Gulf during fuel unloading operations of Fiume Santo power plant in the Porto Torres industrial area, causing the loss into the sea of about 50 ton of fuel oil. CASPER was used to investigate on the presence PAHs and oil pollution (dispersed or in film) just after a month after the event.

RESULTS

The level 2 data of MODIS sensor installed on board of the AQUA satellite contain estimates of chlorophyll-a concentration obtained through the application of a standard algorithm (OC3).

At the moment “sea truth” data of Chl-a were just compared to standard chlorophyll products of MODIS AQUA (obtained from MODIS website http://oceancolor.gsfc.nasa.gov/).

A relatively cloud-free images were obtained only for chlorophyll measurements of 3August 2010 **and 29 April 2011.** Matching between field measurements and MODIS chlorophyll-a concentrations was performed using statistical regression model and Root Mean Square Error (RMSE). The results are illustrated in Table 2.

Table 2: Result of comparison between field measurements of Chl-a and remote sensing data

Total days :	**R2**	**RMSE**
Superficial Chl-a	0,625	0,279
Depth Chl-a (10 m)	0,360	0,050
Maximum value along vertical profile	0,704	0,321
3 August 2010:		
Superficial Chl-a	0,8145	0,359
Depth Chl-a (10 m)	0,607	0,055
Maximum value along vertical profile	0,812	0,392
29 April 2011		
Superficial Chl-a	0,489	0,129
Depth Chl-a (10 m)	0,829	0,041
Maximum value along vertical profile	0,9155	0,137

CASPER has proved to be a valid instrument also for the investigation of polycyclic aromatic hydrocarbons (PAHs) and oil pollution in water bodies, thanks to the double filtration system that discriminates oil fluorescence from dissolved organic matter signal that usually interferes with oil (Figure 5).

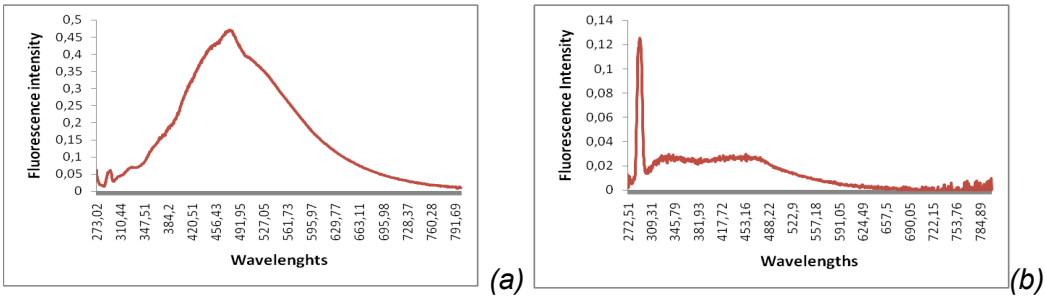

Figure 5: Emission spectra of oil first (a) and after (b) filtration

As regards phytoplankton, the temporal and spatial dynamics of cell density and class composition indicate that Bacillariophyceae, Dinophyceae and Cryptophyceae were the most important class in the first and second sampling, whereas Bacillariophyceae and Cyanophyceae were the most important in the last. Density maximum (160 x 103 cell l-1) was observed at Balai station in December 2010.

CONCLUSIONS

In order to reach better results, the bio-optical algorithm is going to be recalibrated according to In order to reach better results, the bio-optical algorithm is going to be recalibrated according to the measurements of CASPER during the next year, thus providing new estimates of phytoplanktonic Chl-a in the Asinara Gulf. Another interesting perspective will be the correction of satellite data for the effects of CDOM presence, which can reduce the depth range seen by the satellite. in particular in turbid coastal areas.

ACKNOWLEDGEMENTS

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