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Deliverable 2.5: Description of the in-situ measurements.

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V. Martinez-Vicente and G.H. Tilstone

Plymouth Marine Laboratory (PML) – UK.



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Description of in-situ data in ISECA

1. SUMMARY

The in-situ data in the ISECA Web Application Server (WAS), are the result of cross-border collaboration within the project. Overall, they constitute a combination of historical data (pre-ISECA) and data collected during the project life (2011-2014). In order to provide a comparable tool across the different partners, that at the same time fulfil the user requirements for Eutrophication detection; a sub-set of variables has been selected to be included in the WAS. The variables selected by the consortium for eutrophication monitoring and detection were: temperature, salinity, phytoplankton chlorophyll-a concentration, total suspended matter concentration, dissolved nutrients (NO₂, NO₂+NO₃, NH₄, SiOH₄, PO₄) and phytoplankton counts of species indicating of eutrophication. For the ISECA region, *Phaeocystis globosa* and the sum of all Phaeocystis were selected. In addition to the basic set of variables, an extended range of variables was monitored by PML following recommendations from users (D.1.2 User Requirements for the Remote sensing of Eutrophication in the 2Seas coastal waters).

The first part of this report summarises the overall sampling techniques and basic data processing steps for the new data collected during ISECA by PML. Detailed methods description and quality control are described in other parts of this Deliverable (Protocols and Quality Control Guidelines).

The second part of this report summarises the cross-border data that were used in the WAP.

2. BIOLOGICAL AND BIO-OPTICAL SAMPLING DURING ISECA

In-situ sampling activities at L4 and E1 have two different strategies. One is long term monitoring of the vertical biological and optical properties of the water column. Another is the ad-hoc above water reflectance sampling attempting to obtain matching data with satellite overpasses. The time series approach is intended as a part of a long term effort to monitor trends in ecosystem behaviour and to test in-water algorithms. The opportunistic above water sampling is focused on obtaining a dataset useful to test adjacency effect algorithms and atmospheric correction schemes.

A summary of the available datasets, the sampling methodology and processing is summarised in this report, and is based on precedent published studies [1-3]. The area of study is off the Plymouth coast (UK) (Figure 1).

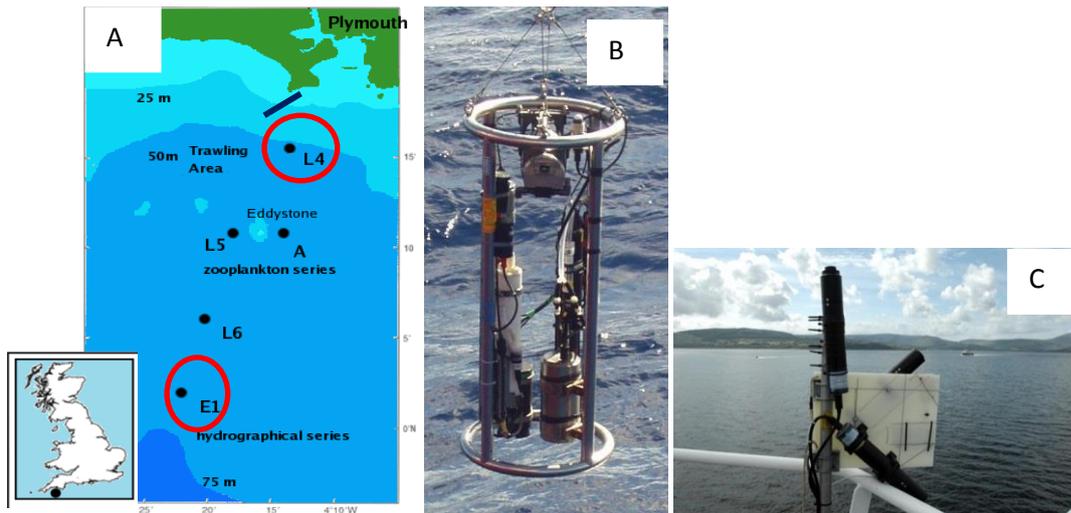


Figure 1: A) Map showing the position of the L4 and E1 stations as well as the opportunistic above water transects (dark blue line). B) Electronic in-situ optical measurements deployment cage. C) Above-water reflectance measurements in transect

2.1. METHODS

2.1.1. Sampling of a time series at L4 and E1

In situ sampling was undertaken on-board RV Plymouth Quest weekly at station L4, approximately monthly at E1 and comprised vertical profiles of hydrographic, biological and optical parameters. A summary of the samples collected since 1989 and with a focus on 2008-2012 years is given in Box 1.

Water for laboratory analysis was collected near-surface in 10 L carboys and returned to the laboratory in a cool box. Samples for coloured dissolved organic matter (CDOM) determination were kept in 0.5 L dark glass bottles also transported in the cool box.

Hydrography: Vertical temperature, salinity and fluorescence profiles were measured with a SeaBird SBE19 CTD coupled with a Chelsea Technology MINITracka fluorometer.

Phytoplankton pigments: Phytoplankton pigments have been measured using High Performance Liquid Chromatography (HPLC) systematically at the surface at L4 since 2000. Since 2007 at L4 pigments have been also collected at depth (0, 10, 25 and 50 m). At E1 pigments have been analysed at 0, 10, 20, 30, 40 and 60m since 2002. On board, approximately 1–2 L of seawater was filtered onto a GF/F and stored in liquid nitrogen until analysis. Pigments were extracted into 2 mL methanol containing an internal standard apocarotenoate (Sigma-Aldrich Company Ltd.) using an ultrasonic probe (30 S, 50 W) following the standard PML methods [4]. Pigments were identified using retention time and spectral match using PDA [5] and pigment concentrations calculated using response factors

generated from calibration using a suite of pigment standards (DHI Water and Environment, Denmark).

Phytoplankton primary production Phytoplankton photosynthetic parameters were calculated from photosynthesis-irradiance (P-E) curves measured using linear photosynthetrons illuminated with 50 W tungsten halogen lamps following the methods described by Tilstone et al. (2003)[6]. For each depth, 15 aliquots of 70 ml seawater within polycarbonate bottles (Nalgene) were inoculated with 5 to 10 μCi of ^{14}C -labelled bicarbonate. Incubations were maintained at in situ temperature for a 1.5 h period, after which the samples were filtered onto GF/F under a vacuum pressure no greater than 27 kPa. The filters were then exposed to 37% fuming hydrochloric acid for ~ 12 h and immersed in 4 ml scintillation cocktail for 24 h, and beta-activity was counted on a TriCarb 2910 scintillation counter (PerkinElmer). Correction for quenching was performed using the external standard and the channel ratio methods. Total inorganic carbon fixation within each sample was calculated following Tilstone et al. (2003)[6] and normalized to chl a, and the curves were then fitted using the equation given by Platt et al. (1980):

$$PB = PB_m [1 - \exp(-a/PB_m)] \exp(-bI/PB_m) \quad (1)$$

where a is the light-limited slope, b is the parameter representing the reduction by photoinhibition, and the maximal light photosynthetic rate (PB_m) is calculated as follows:

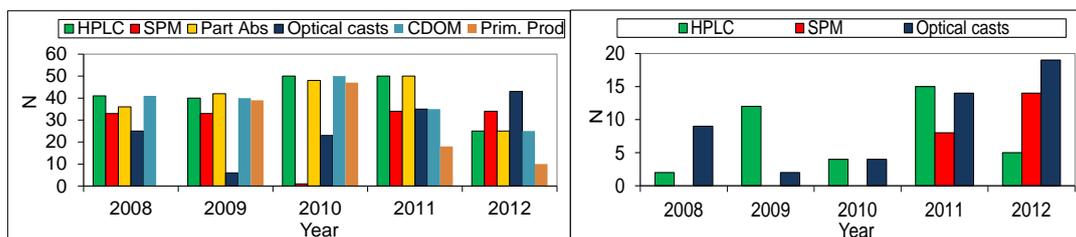
$$PB_m = PB_m [a/(a + b)] [b/(a + b)] b/a \quad (2)$$

Full details of this method and analysis of the results have been recently published in Xie in press [7].

Particulate, phytoplankton, detrital and coloured dissolved organic matter absorption (CDOM) coefficients: Measurements of absorption coefficients have been made of L4 surface water since 2001. The absorption coefficients of total particulate and detrital material retained on 25 mm GF/F filters were measured before and after pigment extraction using NaClO 1% active chloride from 350 to 750 nm at a 1 nm bandwidth using a dual beam Perkin- Elmer Lambda-2 spectrophotometer retro-fitted with an integrating sphere. Concerning CDOM, replicate seawater samples were filtered through 47 mm diameter 0.2 μm Whatman Anopore membrane filters using pre-ashed glassware. The first two 0.25 L of the filtered seawater were discarded. The absorption properties of the third sample were determined immediately on the spectrophotometer and a 10 cm quartz cuvette from 350 to 750 nm, relative to a bi-distilled MilliQ reference blank. Spectral CDOM absorption ($a_{\text{CDOM}}(\lambda)$, where λ refers to wavelength) was calculated from the optical density and the cuvette pathlength and baseline offset was subtracted from a_{CDOM} . Data have been processed using published methods [8].

BOX 1: Historical summary of variables sampling (Table) and recent sampling per year (Bar Charts)

Measurement	< 1999	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
HPLC																	
PABS																	
CDOM																	
SPM																	
POC - CHN																	
Chla(fluoro)																	
Primary production																	
FRRF																	
Ed, Lu																	
ac9																	
bb6																	
VSF.bb3																	
Above water RSR																	
PAR																	
Transmissometer																	
Flow cytometry																	
Coulter Counter																	
Phytoplankton counts																	
CTD																	



In-situ absorption and backscattering coefficients: In-situ optics at L4 combined a WETLabs ac-9+ (to derive the particle scattering (b_p) and total absorption (a)) and a WETLabs VSF-3 to measure particle backscattering (b_{bp}).

The ac-9+ measures absorption- a and attenuation- c at nine wavelengths (412, 440, 488, 510, 555, 630, 650, 676 and 715 nm) with a spectral resolution of 5nm and a measurement accuracy 0.005 m^{-1} . The calibration has been checked using pure water calibrations and by the manufacturer. The data processing included the correction of measurements using the pure water offsets, the temperature and salinity correction (using data from the SeaBird CTD) and the scattering correction (using the “Zaneveld method”), following the recommendations from the manufacturer. b_p can then be obtained by subtraction of the absorption from the attenuation.

The VSF-3 measures the volume scattering function ($\beta(\theta)$) at three angles (100°, 125°, and 150°) and three wavelengths (470, 530 and 660 nm). The processing of the data from the VSF meter was done in three steps. Firstly, conversion of digital counts into $\beta(\theta)$ done using the calibration parameters supplied by the manufacturer. Secondly, a pathlength correction in turbid or very absorbing water ($c > 5 m^{-1}$). Given the geometry of the sensor and the characteristics of the water sampled, the pathlength correction was neglected, implying an error not greater than 5% of the measurement. Finally, calculation of b_b from $\beta(\theta)$ at three angles. This was done by fitting a third order polynomial through all the measurements points of $[2\pi\beta(\theta)\sin(\theta)]$ including $\theta = \pi$, where $\beta(\theta)\sin \pi = 0$. Then the area under the

polynomial was integrated using the Newton method. To obtain b_{bp} , seawater backscatter (b_{bw}) was subtracted to measured b_b .

Only the upcast of each deployment was selected and all data were median filtered to eliminate “salt and pepper” noise and binned to 0.5m. After a visual quality control and elimination of the individual profiles following manufacturer’s guidelines, data presented here correspond to a depth of 5m.

2.1.2. Sampling at a transect

Transect sampling took place on the *Plymouth Quest* between 5th - 7th Sept. 2012. The objective was to collect radiometric data in a transect from offshore to the harbour, as the vessel carried out other routine tasks as a pilot test for future deployment. Unsupervised sampling of above water radiometric quantities was done using a hyperspectral Satlantic HyperSAS system composed of three sensors measuring, simultaneously, downwelling irradiance (E_d), sky radiance (L_i) and water leaving radiance (L_t). This system also included a Satlantic tilt, heading and roll sensor (THR) and GPS. The three sensors were mounted on a pole on the bow of the vessel at 5 m off the water surface. L_t was measured pointing to the water surface with an angle of $\sim 40^\circ$ from the nadir and the crew was instructed to measure away from the sun (azimuth) at 135° when possible during other routine operations [9]. A new algorithm to filter and process R_{rs} from radiance spectra was tested [10]. Results have been presented in a paper [11].

3. DATASETS IMPORTED IN THE WAS

Data were collected by ISECA partners through their interactions with relevant national agencies which hold data repositories. Tables 1 and 2 provide the time span and describes the sources of the different data variables.

Table 1 : Data sources and reference web-sites per project partner.

	Time Span	Link to data source	Main person of contact
PML (UK)	1988-2012	http://www.westernchannelobservatory.org.uk/	Victor Martinez Vicente vmv@pml.ac.uk
IFREMER (FR)	1998-2013	http://wwz.ifremer.fr/lerpc/Activites-et-Missions/Surveillance/REPHY	Francis Gohin Francis.Gohin@ifremer.fr
NIOZ (NL)	1990-2011	http://live.waterbase.nl/waterbase_wns.cfm?wbwns1=en	Jacco Krokamp Jacco.Kromkamp@nioz.nl
VITO (BE)	2003-2013	http://www.vliz.be/vmdcdata/midas/	Francisco Hernandez francisco.hernandez@VLIZ.fr

Overall, 25 stations were selected for inclusion in the WAS, covering a period of over 20 years. Spatial coverage of the selected stations is shown in Figure 2

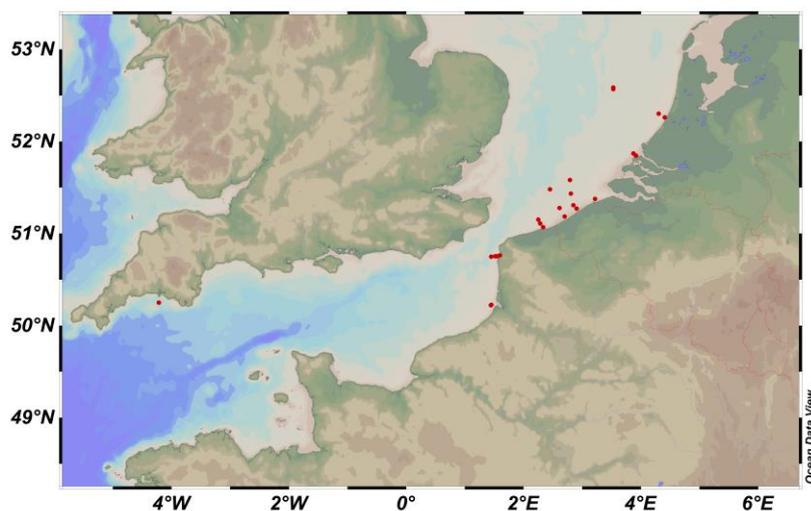


Figure 2 : Location of the stations selected for input into the WAS.

Extended documentation on the methodology used for each variable by each data provider can be found in the relevant internet link or by contacting the person provided in Table 1.

Table 2 : Data parameters and availability per partner shown by shadowed cells.

	PML (UK)	IFREMER (FR)	NIOZ (NL)	VITO (BE)
Temperature				
Salinity				
Chl-a				
SPM/Turbidity				
Nutrients				
Phaeocystis spp.				
Phaeocystis all				

Data from individual data providers were formatted into a common data format at PML, using IDL code. An example of the common data format agreed with VITO for ingestion into the WAS is provided here:

