WHITE BOOK ON

OCEANIC AUTONOMOUS PLATFORMS FOR BIOGEOCHEMICAL STUDIES: INSTRUMENTATION AND MEASURE

(PABIM)

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Abstract

This document is a synopsis of the joint work of the PABIM (Platforms for Biogeochemical studies: Instrumentation and Measure) project team, which groups more than 20 scientists strongly involved in scientific activities related to the exploitation and the use of autonomous platforms for biogeochemical oceanic observations. The present white book summarizes about 5 years of efforts of the involved scientists as well as the continual "brainstorming" experienced by the PABIM team during the lifetime of the project.

Firstly, a discussion on the scientific pertinence of the five biogeochemical parameters treated in the white paper is given. Then, the three main groups of autonomous platforms considered in this document are described (profiling floats, gliders and animals), specifically focusing on their use for biogeochemical studies. After that, the two main parameters ("The Chlorophyll Concentration" and the "Dissolved Oxygen Concentration") are described. In particular, some propositions for a Quality Control system are suggested, on the basis of the existing data processing chain implemented by the PABIM participants. Finally, a description of the different sea operations achievable with the biogeochemical autonomous platforms is given.

Three appendixes conclude the document: a detailed description of the commercially available sensors for the Chlorophyll and Oxygen concentrations (updated to December 2009); a presentation of three additional parameters (CDOM concentration, Particulate Organic Carbon, Nitrates Concentration), as well as of the sensors and the techniques to estimate it from autonomous platforms; a Quality Control procedure for the Chlorophyll Concentration, mainly for the Real Time Mode. Some propositions for the Adjusted and Delayed Modes, and for the Dissolved Oxygen parameter are also introduced.

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THE PABIM WHITE BOOK

1. INTRODUCTION

From the Argo-Oxygen White Paper, by Gruber et al. 2007:

« If only 20% of the 3000 Argo floats were equipped with biogeochemical/biological sensors, more than 20,000 profiles with 1,500,000 or more measurements in the upper 2000m could be made in a single year. In one year, the number of biogeochemical/biological profiles collected would reach the number of CTD stations occupied during the WOCE one-time hydrographic survey ».

What will be the response of oceanic ecosystems to the dramatic climatic changes predicted for the next years?

A broad unanimity exists among the oceanographers that answering the above question is one of the critical challenges for the XXI century oceanic sciences. Meanwhile, scientists recognize that the task will be hard. Climatic changes will modify the physical environment of the ecosystems, impacting the spatio-temporal structuration of the trophic webs, with evident, though not easily predictable, consequences for the higher trophic levels (i.e. resources). However, our knowledge of the physical-biological interactions in the oceans is still limited. Numerical simulations of oceanic ecosystems are an essential tool to provide some answers and they begin furnishing realistic results. However, models are still far to obtain the expected accuracy, as they are still inadequately constrained by observations. Furthermore not all the processes involved in the physical-biogeochemical coupling are accounted for.

Manifestly, oceanic biogeochemistry lacks in observations. The number of *in situ* biogeochemical observations is 2-3 orders of magnitude lower than the number of observations for the physical compartment. Ocean color satellites greatly improved our knowledge of biomass distribution, though they are limited 1. to the biological compartment only 2. to the surface and near surface layers.

Autonomous measuring platforms represent the "*deux ex machina*" to unblock the impasse.

More than 3000 T/S profiling floats, organized through the world-wide international program Argo, are currently monitoring the oceans. The obtained data are transmitted to land in real-time, and they are available, through dedicated data center (i.e. Coriolis, Data Center), to be directly assimilated in numerical operational systems, in order to simulate and predict ocean state (i.e. MERCATOR). Argo data centers processes and stores also data collected by CTD sensors mounted on Sea Elephants, which furnish inestimable observations of the Southern Ocean physical dynamics. Recent large-scale experiments (i.e. European Glider Observatory, Testor et al, 2010) demonstrated that glider technology is definitively mature to assure continuous and automatic observations of the ocean dynamics. The assimilation of the glider data in numerical models is one of the key priorities for oceanographic modelers.

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In brief, physical oceanography cumulates huge benefits from the use of autonomous measuring platforms. It indicates the way to the biogeochemical ocean sciences, which should evolve towards autonomous systems in order to enhance their observation capacity.

What is the present day status of autonomous platforms for biogeochemical ocean sciences?

Biological and chemical measurements are intrinsically more complex than the physical ones. Traditionally based on laboratory analysis of water samples, biogeochemical observations were dependent on ship-based sampling. Even when automatic sensors were developed (i.e. fluorometers), they were still too large and too energy consuming to be effectively mounted on autonomous platforms .

However, things are changing. Miniaturized, low energy consuming, biogeochemical sensors are being developed. Several companies have begun to commercialize instrumental biogeochemical pucks specifically designed for autonomous platforms. More and more performing batteries allow sustain highly energy demanding instruments. New generation telecommunication satellites ensure high rate transmission all over the world, multiplying by 10 the quantity of data, which is possible to transmit.

Importantly, the feedback with scientists has been constant and productive. Several RD projects have been funded in the last years, federalizing technological manufacturers with scientific institutions. An "Argo-Oxygen" White Paper (Gruber et al., 2007) resumed the advancements in the development and in the scientific exploitations of profiling floats equipped with sensor measuring oxygen (a key parameter for oceanic biogeochemical sciences). A special issue of the main journal "Limnology and Oceanography" was devoted to the biogeochemical observations collected by all kind of platforms (Limnology and Oceanography, Vol. 53, September 2008). During the OceanObs09 meeting, held in Venise in September 2009, a large emphasis has been dedicated to the biogeochemical autonomous platforms (Claustre et al., 2010).

In this framework, the Group Mission Mercator Coriolis (GMMC) funded a dedicated project, PABIM, with a two-fold objective:

1. To implement a set of automatic quality control tests for the oxygen and chlorophyll-a data collected with autonomous platforms.
2. To write a "White Book" on the present day status of the biogeochemical oceanic observations performed with autonomous platforms.

This document is devoted to the second PABIM objective. It represents the collective work of six French laboratories strongly involved in scientific activities related to the exploitation and the use of autonomous platforms for biogeochemical oceanic observations. The rationale was to provide biogeochemical oceanographers with a "user's manual" on the autonomous platforms, with the declared aim of sharing the experiences of the authors towards an enlarged community. The text is mainly based on the know-how acquired on the field by the authors and represents about 5 years of efforts within the French community. The authors tried to be as exhaustive as possible, however the topic is continuously evolving and it cannot be *a priori* excluded that some issue is missing or partially treated.

2. PLAN OF THE DOCUMENT

The PABIM white paper is the result of the discussions achieved during the 2 years lifetime of the homonymous project. The document is consequently organized in four main sections, which outline the different topics developed by the project activities.

In the first section ("The Core Parameters"), we justified the selection of 5 biogeochemical parameters, which constituted the object of the white paper. Considering the extent of the topic

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and the continuous technological advancement, a selection of the parameters was mandatory to fix a starting point. We explained in this chapter, why and how we limited our field of discussion. Additionally, we explained here why two of them (Chlorophyll-a Concentration and Dissolved Oxygen Concentration) were analyzed in more details in this white book.

In the second section ("The Platforms"), the three main groups of autonomous platforms object of the document are described (profiling floats, gliders and animals). Without explaining all the possible applications of these instruments, we focused our discussion on their use for biogeochemical studies. Also, we try to discuss on their possible coordination and their complementarity with other platforms (i.e. satellite).

In the third and fourth sections, the two main parameters ("The Chlorophyll Concentration" and the "Dissolved Oxygen Concentration") are described. In these sections, the scientific rationale, the available measurement techniques and the identified problems with the autonomous platforms are explained. There, we discuss also the way to perform a "right" measurement of the two parameters with a specific autonomous platform. Moreover, some propositions for a Quality Control system are suggested, on the basis of the existing data processing chain implemented by the PABIM participants.

In the last section, "Implementation", a (tentative) list of the different sea operations concerning biogeochemical autonomous platforms is given. Again, most of the considerations depicted in this section originate from the know-how and from the experience of the authors.

In the first appendix ("The Sensors"), for the two main core parameters, a detailed, although not omni-comprehensive, description of the commercially available sensors is presented. Only instruments commercially available and already used on autonomous platforms are described, excluding thus sensors that are still at the prototype phase. The general specifications of the instruments are furnished, and, if different methods of measurements exist, they are analyzed separately. This section is principally a summary of the information obtained by manufacturers, although they were modulated/commented/modified, on the basis of the field experience and the know-how acquired by the authors during the last 4 years.

In the second appendix ("The additional parameters"), three additional parameters are presented (CDOM concentration, Particulate Organic Carbon, Nitrates Concentration), as well as the sensors and the techniques to estimate it from autonomous platforms. We are convinced that, for these parameters, the number of data collected with autonomous platforms will dramatically increase in the next years. However, they don't match entirely the criteria that we fixed for a "core parameter". For this reason, they are described in appendix.

Finally, in the last appendix, a detailed Quality Control (QC) procedure for the Chlorophyll Concentration is proposed. Only the real time mode is considered, although some propositions for the Adjusted and Delayed Modes are presented. A similar procedure for the Dissolved Oxygen Concentration is presently under study, although the autonomously estimation of this parameter is still affected by hardware/sensor problems (clearly described in this document), which made still premature the definition of a QC.

3. THE CORE PARAMETERS

For autonomous platforms, the choice of the measured variables was initially guided by the available technology. Technology is, however, continuously evolving and now the miniaturized instruments commercially available make possible the measurement of a vast set of biogeochemical parameters (i.e. chlorophyll concentration, dissolved oxygen concentration,

backscattering, CDOM concentration, underwater light transmittance, nitrate concentration etc.). In the near future, technological advancements in the fields of the miniaturization, energetic power and transmission will certainly allow a wider list of available parameters.

It is obvious that every parameter is (or has to be) considered scientifically relevant, as its evaluation always adds a piece of information to the knowledge of the marine ecosystem functioning. However, practical, economical, and logistic arguments could reduce the number of the instruments mounted on an autonomous platform, with a consequent impact on the quantity of acquired parameters. Additionally, scientific reasons could determine the decision to include or not a specific measure for an autonomous platform based experiment. Finally, the type of the experiment could also influence the selection of the sampled parameters, as a basin-scale/long-term experiment of monitoring has different constraints to that of a specific, more process focused sea operation. In conclusion, the field of application of autonomous platforms for biogeochemical studies is vast enough that a first set of parameters (the "core parameters") needs to be defined.

In this document, we decided then to fix four criteria to define a core parameter. They are necessarily arbitrary, as they are specifically defined for the purpose of the white paper (i.e. to constitute a "user manual" of the biogeochemical observations with autonomous platform). Moreover, they derive directly from the author's experiences (which are obviously limited) and, as such, need to be considered as a starting point for further discussions.

The 4 requirements proposed here are:

1. A core parameter should be a robust **proxy of a biogeochemical oceanic process or variable**.
2. The measurement of a core parameter with an autonomous platform should be **cost effective** and **low energy** consuming.
3. A core parameter should have **already been measured extensively and for a long time** with referenced methods.
4. A core parameter obtained from autonomous platforms should be **easily comparable with observations collected with classical methods** (i.e. ships, satellites, moorings). If climatologies are produced from previous observations, data from autonomous floats should be easily incorporated

Among the present day possibilities (i.e. sensors commercially available), only the Chlorophyll-a concentration and the Dissolved Oxygen concentration meet all the four requirements, with points 3 and 4 being the most limiting requirements. Nevertheless, we have selected 3 others parameters, which, in our opinion, will meet the full set of requirements in the near future: the Particulate Organic Carbon (POC), the Colored Dissolved Organic Matter (CDOM) and the Nutrients Concentration. It is a matter of fact, however, that the simultaneous collection of additional variables could relevantly improve the calibration and the validation of the Chlorophyll-a and of the Dissolved Oxygen data, as well as, they allow a better ecological interpretation. In other terms, although the present day availability of additional parameters avoids their widespread utilization as core parameters, the situation could rapidly evolve, resulting in an increased scientific relevance of the ensemble of the data collected by bio-geochemical autonomous platforms.

Consequently, these parameters (CDOM, POC, Nutrients) are discussed in the appendix, although less in details than for the Chlorophyll-a Concentration and for the Dissolved Oxygen Concentration.

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4. THE PLATFORMS

4.1 THE BIOGEOCHEMICAL PROFILING FLOATS

Profiling floats are passive and automatic buoys drifting at fixed depths and following oceanic currents. They can be programmed to change their buoyancy using a hydraulic pump, which, by modifying the total volume of the device, allows for vertical displacements within the water column. Equipped with scientific instruments, profiling floats can then autonomously acquire vertical profiles of oceanographic parameters. Collected data are transmitted on land in real-time, through satellite communications.

A typical profiling float cycle of measure is composed by 4 phases:

1. float is placed at a fixed depth (parking depth), where it stay for most of his lifetime;
2. after a pre-determined and user-programmed time interval (typically from 1 to 10 days), float loss floatability, reaching a deeper layer (i.e. profiling depth);
3. from the profiling depth, float starts to increase volume (i.e. gaining floatability), slowly mounting on surface. During this phase, data are acquired and stored.
4. at surface, float transmits the collected data and the Argos or Iridium or GPS position; afterward, parking position is once more reached (point 1).

The most important and the best known profiling floats network is organised in the international Argo project, which has disseminated more than 3000 buoys in the global ocean (www.argo.ucsd.edu). Argo floats are specifically devoted to physical oceanography (only Temperature and Salinity are collected), and Argo data are directly assimilated in the numerical systems to ocean prevision.

Floats are easily deployed from a boat, also in difficult (although not extreme) sea state conditions. For this reason, floats could be deployed by opportunities ships. To minimize errors in the sensors calibration, a CTD cast is required just before the float deployment (i.e. Argo protocol for floats deployment).

In recent years, floats equipped with biogeochemical sensors (in addition to T and S sensors) have been developed and successfully deployed (LeReste et al. 2009; Bishop et al. 2009; Boss et al. 2008). Compared to the physical floats (i.e. Argo), the biogeochemical buoys presented additional issues that required more sophisticated systems, resulting in advanced technical solutions. These modifications increased the overall potentiality of the platform for oceanographic studies. Firstly, biogeochemical sensors demanded an increased amount of available energy, which lead to the generalised use of more performing piles (i.e. Lithium). Secondarily, the augmented quantity of collected data required the use of more efficient data transmission systems (i.e. IRIDIUM), which, in addition, allowed a two-way communication (i.e. commands could be sent to the buoy). This technical solution impacted also on the scientific potentialities of the profiling buoys, giving the possibility to change, in real time, the sampling strategy. In addition, the two-way transmission systems could allow a recuperation operation when problems are detected or when float's batteries are down. Generally, profiling floats are not recuperated, as the surface position is known only during the transmission phase. In addition, as a recuperation cruise is virtually impossible to schedule, floats are then considered losable devices. Floats equipped with two-way transmission systems should be provided with an "end-of-life" protocol, consisting in 1) a loss of floatability to remain on surface; 2) the periodic (i.e. each hour) transmission of the geographical position to allow the recuperation. Importantly, the "end-of-life" protocol should be reversible, in the case of the operation of recovery is not possible.

Presently, the most developed biogeochemical floats network (in terms of number of buoys) concerns profiling floats equipped with oxygen sensors (Gruber et al, 2007). Additionally, a float with a chlorophyll calibrated fluorometer acquired more than 2 years of observations (Boss et al., 2008) in the North Atlantic. In 2008, 8 PROVBIO floats (LeReste et al, 2009), with fluorometers

(calibrated for chlorophyll and CDOM), irradiance sensors, transmittance and backscattering meters, were deployed in 4 different oceanic regions (Mediterranean, North Atlantic, North Pacific) by the LOV-CNRS (PI H. Claustre). Two PROVBIOs have been recuperated and redeployed in 2008.

4.2 THE BIOGEOCHEMICAL GLIDERS

Gliders enhance the capabilities of profiling floats by providing some level of maneuverability and hence navigational control. Also, in contrast to profiling floats, gliders are designed to be recovered and redeployed.

Gliders are propelled by a buoyancy engine, along slightly inclined paths. No propeller is required. A change in volume (generated by filling an external oil bladder) creates positive and negative buoyancy. Because of the fixed wings, the buoyancy force results in forward velocity as well as vertical motion. So gliders move on a saw-tooth pattern, gliding downward when denser than surrounding water and upward when buoyant. Pitch and roll are controlled (by modifying the internal mass distribution) to achieve desired angle of ascent/descent and heading. The gliders perform its saw-tooth trajectories from the surface to depths of 1000-1500m, along reprogrammable routes using hourly to daily two-way satellite link. When diving to 1km depth, there is around ~2-6 km between two surfacing. They achieve forward speeds of up to 40 km/day and have an endurance of a few months. The efficiency of the propulsion system enables gliders to be operated for several months during which they may cover thousands of kilometers. Furthermore, they have been shown to operate correctly during severe storms/hurricanes and strong currents.

At the moment, there are 3 groups in the USA who have developed operational gliders: the Seaglider by APL-University of Washington; the Slocum by Webb Research Corp; the Spray by Scripps Institution of Oceanography. Although the designs are different they have many features in common. They all have a small size (weighing around 50kg in air and +/-200g in water), with comparable horizontal and vertical speeds. During each surfacing, a two-way communication system via satellite allows us to download data in near real time and to send commands to the glider in order to change the mission parameters (heading, angle of ascent/dive, max depth,...). In this way gliders can be steered remotely. Data are telemetered via iridium either via a point-to-point link (Seaglider, Slocum) or via short burst messages "sbd" (Spray). The data transmission rate is about 120 bps and allows to download a number of parameters (measured about every 3m along the vertical) in about 10 minutes. A glider needs to stay the shortest period of time at surface to avoid long drifts or collisions with ships when at surface. There is usually only one downcast (dive), but the upcast (climb) could also be available and in some cases, several yos (dive+climb) are made between two surfacings.

Biogeochemical parameters on gliders comprise presently dissolved oxygen, fluorescence (e.g. Chla, CDOM, phycoerythrin), turbidity and optical backscattering (Davis et al, 2008; Niewiadomska et al, 2008, Perry et al, 2008). Moreover, the present development of various, smaller, and smarter sensors for gliders is very promising. Direct current measurements (small ADCP) or nutrient (e.g. nitrates) sensors will be available soon. Optical particle counters and active/passive acoustic sampling for higher trophic levels have already been tested.

As they have a relatively small size, gliders can be deployed from small boats (or even rubber boats) in the coastal environment. From larger vessels, a crane allowing a good distance from the hull and deployment tool is needed in order to put smoothly the glider in the water and to release it a bit away from the hull of the ship. Recovery is still an issue. Various recovery tools have been tested so far but at the moment none is really satisfactory.

4.3 THE ANIMALS

Specially developed data relayed satellite tags were developed by the Sea Mammal Research unit and deployed on a number of seal species foraging in high latitude waters. While diving (up

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to 2000 meters) these animals are collecting accurate temperature and salinity data, which are transferred in near real-time by the ARGOS system along the foraging track of these animals (Charassin et al, 2010).

Depending on the species, sex and age classes, we can target different high latitude water masses. For instance, equipped southern elephant seals allowed to sample the main Circum Antarctic Current frontal structures crossed by these animals when travelling to their Antarctic foraging ground. These custom-built satellite linked recorders mounted on seals provide CTD profiles from key areas within the Arctic and the Southern Ocean. This is a cost-effective means of adding to existing global oceanographic data archives. It has the potential to complement existing sampling methods, especially for regions and times from which data are scarce and where these alternative methods may be difficult or prohibitively expensive to implement. Near real-time data obtained allow to explore the links between seal behaviour, foraging activity, and oceanographic features, such as frontal systems, local eddies and thermoclines. The data are directly transferred to global ocean data base and assimilated in the numerical systems to ocean prevision. Such approach is extremely efficient to investigate oceanographic conditions in high latitude regions.

Most of the animals are accessible only at specific period of the year (i.e. during reproduction and moult). As tags have an expectancy life of about 6 to 8 month, deployment should be spread out through the year, to optimize the coverage of oceanographic conditions.

Strong constraints exist on the data transmission, due to the short period of time spent at the surface to breathe between dives and to the intrinsic limits of the ARGOS system. In his present form, the ARGOS system provides only a very limited transfer of data, and then only reduced data packets may be sent. Acquisition system should account for the transmission constraints, which results in specific acquisition protocols.

Generally, a certain proportion of tags can be recovered depending on the location and species and the deployment season (recovery rate varies from 0 % to 90 %). For example, elephant seals recovery rate at Kerguelen is about 30 %. Recovered tags can be rebatteried, and the full resolution data set can also be recovered.

An important point needs, however, to be stressed. As tags require to be deployed in the animal habitat, people studying the foraging ecology of these animals need to be present. Other than for technical and operational reasons, it is, however, mandatory to involve scientists interested in the animal ecology, as it will be ethically questionable to equip living individuals only to collect oceanographic data.

5. CHLOROPHYLL-A CONCENTRATION

5.1 SCIENTIFIC RATIONALE

Chlorophyll-a is a pigment found in most plants, algae and cyanobacteria. It serves the primary function of photosynthesis by absorbing and transferring solar energy to chemical energy, allowing plants to obtain energy from sun radiation (Kirk, 1994). During photosynthesis, photosynthetic organisms (i.e. primary producers or autotrophs) consume the CO2 present in the water, which derives primarily by exchange with the atmospheric CO2. Included in organic molecules, carbon is partially removed by surface layers when dead organisms fall on deep and bottom layers. With this mechanism (the "CO2 biological pump"), oceanic primary producers act as regulators of the global CO2 concentration on the Earth (Takahashi et al. 2002). Marine primary producers play than a key role in the global climate mechanism. Understanding the spatio-temporal variability of the autotrophs distribution, using as a proxy the chlorophyll-a concentration, is then a primary goal of the present day oceanography.

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The climate, and his forcing factors, does not represent the only issue requiring more information on the chlorophyll-a concentration. Several studies addressed on the biological mechanisms used by autotrophs to growth (i.e. Geider et al. 2001), on the phytoplankton control of the chemical elements in the ocean (i.e. Rixen et al. 2005), or on the role played by phytoplankton organisms in the food web, and his final impact on fisheries resources (i.e. Platt et al. 2003).

Consequently, chlorophyll-a concentration is routinely measured in the ocean, as well as is a "core" parameter of the global physical-biological oceanic models.

However, despite of this widely acknowledged importance (or maybe as a consequence), several experimental methods exist to determine the oceanic chlorophyll-a concentration: radiometric (in-situ and from space), chemical (HPLC on discrete samples) or using specifically calibrated sensors based on fluorescence or light absorption. Compared with the standard physical measures, as temperature and salinity, the number of observations remains, however, low. Satellites allow a global, synoptic and high-resolution coverage, but they observe only a relatively small surface layer of the ocean. Concerning the others methods, only the HPLC allows a precise and accurate determination of the chlorophyll-a concentration, though it is a sophisticated technique requiring in situ samples. The others methods, as the fluorescence, need calibration, which is generally performed *via* concurrent HPLC estimations. However, they could be used in a continuous way, coupled, for example, to a CTD or to a peristaltic pump.

5.2 MEASUREMENT THEORIES

Only two of the available methods to estimate chlorophyll-a concentration could be presently implemented on autonomous platforms: the fluorescence-based methods and the radiometric inversion of light measurements (HPLC estimation needs collecting in situ samples, while instruments based on absorption are still far to be miniaturised).

5.2.1 Fluorescence

Part of the photons absorbed by a chlorophyll-a molecule in the blue part of the spectrum is re-emitted as less energetic photons in the red part. This rapid (~ns) process is known as fluorescence and actually corresponds to the relaxation of the excited chlorophyll-a molecule to its ground state. The light emitted through chlorophyll-a fluorescence, F (mole quanta m^{-3} s^{-1}), can be roughly expressed through:

$$F = E\,[Chla]\,a^*\,\Phi f \qquad (1)$$

E is the excitation irradiance (mole quanta m^{-2} s^{-1}). It corresponds to either sun irradiance (and the subsequent process is the so-called sun-induced fluorescence) or to irradiance provided by a light source; only the later is considered here. [Chla] corresponds to the concentration in chlorophyll-a (mg m^{-3}), a* to the chlorophyll-a specific absorption coefficient (m^2 mg $Chla^{-1}$) and $\mathbf{\Phi}_f$, the fluorescence yield (mole emitted quanta mole absorbed $quanta^{-1}$). The retrieval of [Chla] from the measurement of F depends, then, on the excitation irradiance, which is relevant to the instrumentation, and on an absorption term (product [Chla] a*) and a fluorescence efficiency term ($\mathbf{\Phi}_f$), both of which being relevant to phytoplankton photo-physiology.

The fluorescence emission of chlorophyll-a is centered at 685 nm. The excitation of the chlorophyll-a molecule is triggered by the blue photons not only absorbed by the chlorophyll-a molecule itself but, also, by other photosynthetic pigments (mostly carotenoids but also phycobiliproteins for some phytoplankton groups), which subsequently transfer their absorbed energy to the chlorophyll-a.

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5.2.2 Radiometric Inversion

In the ocean, the solar radiation is attenuated and scattered by the water and by the optically active compounds presents in the water, which comprise essentially chlorophyll-a, CDOM and detritus (Morel, 1988). Measuring the light attenuation in the ocean allows then an evaluation of the concentration of optically active compounds present in the water.

For a wavelength λ and for a depth z:

$$Ed(\lambda,z)=Ed(\lambda,0) * \exp(-Kd*z) \quad (2)$$

where $Ed(\lambda,z)$ is the downwards planar irradiance (i.e. the quantity of light radiation integrated over the upper hemisphere) and $Kd(\lambda)$ is the diffuse attenuation coefficient .

Kd depends of the concentration of optically substances, but in the open ocean, their concentrations generally co-vary, and only chlorophyll concentration is considered. Following Morel and Maritorena (2001):

$$K_d(\lambda)= \chi(\lambda) [Chl]^{e(\lambda)} \quad (3)$$

Where [Chl] is the chlorophyll-a concentration and χ and e are coefficient empirically determined. Measures of Ed on the water column can be then used to retrieve Kd, and then, inverting equation 3, to obtain the chlorophyll concentration. Generally, Kd is calculated at different wavelengths (i.e. 412, 443, 490 or 555 nm), and the chlorophyll-a concentration profile is obtained averaging the different estimations.

Irradiance meters to obtain Ed consist essentially in submersible light sensors, which use spherical devices to diffuse the light (i.e. to have an integrated observation on the upper hemisphere). They generally use individual photodiode and filter combinations for each channel, and typically have bandwidths of the order of 10 nm.

5.3 MEASURING CHLOROPHYLL WITH PROFILING FLOATS

Presently (June 2009), a reduced number of profiling floats are equipped with chlorophyll sensors. In the CORIOLIS database, more than 400 profiles of fluorescence are stored. These data are collected using the Argo strategy (i.e. 10 days cycle, 10 and 25 meters vertical resolution). Additionally, Boss and co-workers (2008) published chlorophyll 2 years data obtained with an APEX float equipped with a fluorometer. Finally, the LOV PROVBIOs collected more than 200 fluorescence and irradiance profiles in different regions of the world.

Concerning the irradiance approach, sensor should be located on the top of the platform, to avoid any shade contamination of the data. At least three wavelengths should be required, as a single wavelength inversion could bias the chlorophyll estimation (i.e. influence of other then chlorophyll optical active substances affecting the radiance at a specific wavelength).

For the fluorescence method, sensor could be affected by bio-fouling. On the floats, the impact on the data should be probably weak, as float spent most of time on deep layers (Boss et al. 2008). To definitively prevent any bio-fouling influence, parking depth should be selected adequately high (i.e. greater than 200 m). Additionally, surface time should be short, using, for instance, more performing transmission systems. Vertical resolution of acquisition is a crucial issue. The accuracy of the radiance estimation method is obviously enhanced if the number of radiance points on the vertical is elevated. Surface layers should be more intensively sampled, as chlorophyll disappears below 200 meters. Deep observations are, however, crucial, because they could furnish a "black" for the sensors.

As indicated in paragraph 3.1, both methods to obtain chlorophyll concentration on autonomous platforms need to be calibrated.

Irradiance inversion depends on the accuracy of the radiometric data, which could be assessed using deep observations as "black" reference. Furthermore, the geometry of the measure (i.e. the

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position of the sensor relatively to the sun and to the air-sea interface) could induce some bias in the irradiance measurements. Preliminary test on the LOV PROVBIOs show than profiling floats are enough stable to maintain an adequate relative position during the acquisition phase. More tests are, however, required.

Fluorescence estimation needs an evaluation of the accuracy and of the stability of the manufacturer calibration. The "scale factor" and the "dark counts" of a generic fluorimeter could be assessed independently using, for instance, chlorophyll data collected just before the deployment (using, by preference, HPLC estimation on water samples). Alternatively, a chlorophyll calibrated fluorescence profile, obtained with a fluorometer mounted on a rosette and deployed by a ship (i.e. a reference profile), should be acquired at the autonomous platform deployment time. As the "reference profile" could be more easily calibrated, it should be used to assess the manufacturer calibration of the autonomous fluorometer. For the not recoverable profiling floats, the acquisition of a "reference profile" should strongly improve the accuracy of the obtained data and should assure an improved characterisation of the fluorometer data.

If water samples and reference profiles cannot be acquired at the float deployment time, satellite observations could furnish an alternative method to assess the accuracy of the chlorophyll estimation, for both the irradiance and the fluorometric methods.

5.4 MEASURING CHLOROPHYLL WITH GLIDERS

Approximately one half of the present day fleet of gliders is currently equipped with fluorescence sensors, while very few have irradiance meters. Most of the recommendations indicated in the previous paragraph for the profiling floats are applicable to chlorophyll estimation from gliders. More importantly, all the issues related to the profiling floats sensor degradation and calibration are irrelevant for the recoverable gliders.

5.5 MEASURING CHLOROPHYLL WITH ANIMALS

On animals, only fluorescence sensor have be implemented, and in a very limited number. The program lead by the CEBC-CNRS (8 Argos CTD tags equipped with a fluorometer, deployed on southern elephant sea at Kerguelen Island in 2008) is the only example at our knowledge.

Again, the main features of the profiling floats chlorophyll estimation are applicable also to the animal based observations, although additional issues are present.

In particular, the limitations in the ARGOS transmission system require a data compressing procedure in the acquisition protocol. In the CEBC elephant seals tags, the temperature, salinity and fluorescence profiles are averaged on a 10 meter resolution (1 Hz sampling frequency) in the layer between 0 to 180 meters (approximately the euphotic depth). Six additional measures of only temperature and salinity, selected between 180 meters and the maximum diving depth, are then included into the message and transmitted. Full resolution data are, however, stocked in the tag and can be eventually obtained, if the tag is recovered.

5.6 QUALITY CONTROL

A Quality Control for chlorophyll fluorescence data is presented in the Appendix C.

6. DISSOLVED OXYGEN CONCENTRATION

6.1 SCIENTIFIC RATIONALE

Dissolved oxygen concentration (O_2 hereafter) is a key parameter to understand both dynamics and biogeochemistry of the world oceans: it has been used for a long time as a tracer to

follow water masses pathways and quantify mixing rates; on the other hand, O_2 variability is associated with many biological processes, production, respiration, remineralization.

One important scientific question is to understand how the current global climatic change could affect these dynamic and biological processes on the long run. Several studies, based on cruise O_2 measurements or on the sparse existing repeat sampling locations have already provided some indications, and stress the importance of obtaining long term, global O_2 data. Firstly, O_2 responds very quickly to changes in general circulation (e.g. Shaffer et al., 2000), and a pilot study (Körtzinger at al., 2004) has shown that deep convection in the North Atlantic could be efficiently monitored through long-term O_2 measurements. Observations in several parts of the world ocean show a general decrease in O_2 (Johnson & Gruber, 2007; Deutsch et al., 2005; Ono et al, 2001; Schaffer et al., 2000).

Models have indeed predicted an overall decline in O_2 under global warming (Matear & Hirst, 2003; Bopp et al., 2002), mostly in extra-tropical regions. That decline should be associated with an expansion of tropical Oxygen Minimum Zones (OMZ), with far reaching consequences on coastal ecosystems, and this appears to be confirmed by observations (Stramma et al., 2008). The ocean's "carbon pump" has an important effect on atmospheric CO_2 and thus on global climate. Biological mechanisms govern that system, and the strength of that pump can be measured through variability of O_2 (Jenkins & Doney, 2003); if global O_2 data were available, the net biological carbon export could be estimated.

Asides from the global change problem, an increase in O_2 data is needed in several respects, of which a few can be cited here. Ocean biogeochemistry models generally do not properly represent oxygen in the ocean interior (Najjar et al., 2007), and availability of global O_2 data would help constrain these models, with even a future perspective of data assimilation. Air-sea fluxes of oxygen cannot be determined only from oceanic measurements, but can be estimated from inversion techniques (e.g. Ganachaud & Wunsch, 2002). Currently, with sparse O_2 data, these methods can only provide steady-state estimates. Here again, multiplication of O_2 data in the world ocean will allow time varying estimates of these fluxes.

6.2 MEASUREMENT THEORIES

Historically, O_2 has been first measured through a chemical titration method (Winkler, 1888), which cannot be practically used on an autonomous platform. Nowadays, sensors are based on two techniques, an electrochemical method and an optical method.

6.2.1 The electrochemical method.

It is based on a technique described by Clark et al. (1953), originally devised for medical applications (Figure 1). The Clark cell works on the principle of reduction of molecular oxygen at a cathode.

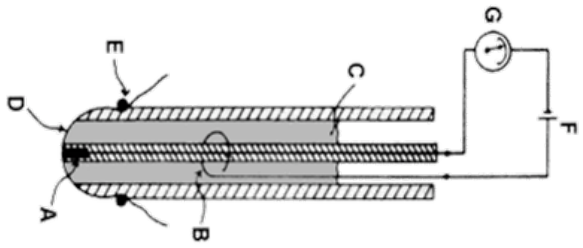

Figure 1: The basics of the Clark cell. A: Au or Pt cathode; B:anode; C: electrolyte; D: membrane; E: O-ring; F: battery; G: measured current.

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Under a constant voltage, the current flow from cathode to anode is proportional to oxygen partial pressure in the surrounding fluid. The electrodes are covered with an oxygen permeable membrane to prevent fouling and to maintain a well-defined chemical medium at the electrode surface. O_2 must diffuse through this membrane in order to reach the cathode and initiate a current flow. The Clark cell principle has been used in shipboard CTD systems since the 1970s. In a marine environment sensors based on that principle were affected by drift problems due to changes in membrane tension, fouling, depletion of electrolyte, impairment of the anode, plating of anode metal on the cathode, the presence of chemical contaminants in the sensor's plastic body, etc. In recent years, the basic arrangement has been largely improved, mainly by improving the technical design of the sensors. Simultaneous measurements of temperature, salinity and pressure are necessary to compute O_2 values from the partial pressure measurement.

6.2.2 The optical method

An optical method was recently developped, operating on the principle of fluorescence quenching (Tengberg et al., 2006). Blue light excites molecules of a fluorescent dye that are included in a foil on the sensor optical surface. The excited dye molecules emit photons with a lower energy state (red light).

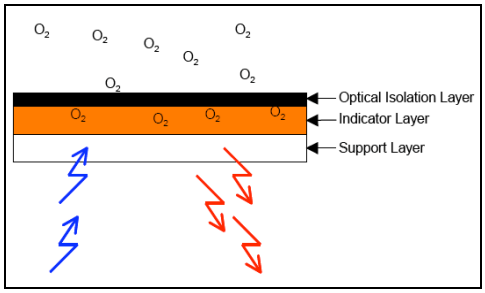

Figure 2 : Principle of the fluorescence quenching method.

When oxygen molecules diffuse into the film, they collide with excited dye molecules before they emit their photons, and energy is transferred to O_2 rather than lost by fluorescence emission (figure 2). This reduces the time period (of order 10s of µs) over which the fluorescence is emitted by the dye. The sensor operates by detecting the decrease in fluorescence lifetime that is produced by interaction of the dye molecules with oxygen. Detecting changes in fluorescence lifetime, rather than fluorescence intensity, have significant advantages for sensor stability. If some of the fluorescent dye is lost due to bleaching, fouling or diffusion from the film, fluorescence intensity will decrease, but the fluorescence lifetime is unchanged. Besides, time delays are one of the physical parameters that can be measured with the best accuracy. The sensor response is here also proportional to oxygen partial pressure in water, so environmental conditions (pressure, temperature, salinity) must be known to compute O_2.

6.3 MEASURING DISSOLVED OXYGEN WITH PROFILING FLOATS

Two different types of O_2 sensors are presently operational on profiling floats: the SBE 43 sensor based on an electrochemical method and the optode sensor based on an optical method. There are also different types of transmission systems that allow transmitting profiles at high (IRIDIUM system) or low (ARGOS system) vertical sampling rate. Finally, there are different types of float with different sampling strategies: spot sampling (APEX float for instance) or bin averaging (PROVOR float for instance). The different available configurations are summarized in Table A.2.3, in the appendix A. Energy issues relative to the various configurations of the APEX floats were addressed in the Argo-O_2 white paper (Gruber et al, 2007).

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For the optode method, an important issue concerns the present algorithm to compute oxygen concentration (see appendix A.2.2). In presence of strong vertical temperature gradients, the very low time response of the current optode temperature sensor could induce errors in the final O_2 estimation. It is then recommended to transmit BPHASE or DPHASE (i.e. the uncalibrated or calibrated phase data measured by the optode), and perform O_2 calculation on land. Furthermore, it is recommended to estimate the O_2 from the CTD temperature, instead of the internal temperature sensor of the optode. This recommendation remains valid for float transmitting bin-averaged values. When considering 50 dbar-bin for instance, the difference between the bin-averaged value of the dissolved oxygen concentration and the dissolved oxygen concentration estimated from bin-averaged value of pressure, temperature and salinity is less than 1 µmol/l through strong temperature and oxygen gradient (Figure 3).

It is worth mentioning that those recommendations may changes in the future as Aanderaa Data Instruments is currently working to improve many aspects of this sensor (foil, electronics, temperature sensor time response, etc…). An O_2 sensor with a faster temperature sensor is already available but it needs to be tested on the long term to verify its stability.

There is no specific recommendation concerning the SBE 43 sensor.

Another important point concerns the position of the O_2 sensor on the float. Environmental conditions (pressure, temperature, salinity) are necessary to convert output from the SBE43 (voltage) and the optode (phase) into O_2. We thus recommend placing the oxygen sensor nearby the CTD sensor, on top of the float. The SBE43 being connected to a SBE CTD, it is automatically at the right position. The optode sensor is not connected to a SBE CTD and can be placed anywhere on a float. On APEX floats, the optode is located on top of the float nearby the CTD. The initial position was not optimal on PROVOR float as it was initially located at the bottom of the float (Figure 3). This has been changed and DO sensors on PROVOR floats are now located nearby the CTD.

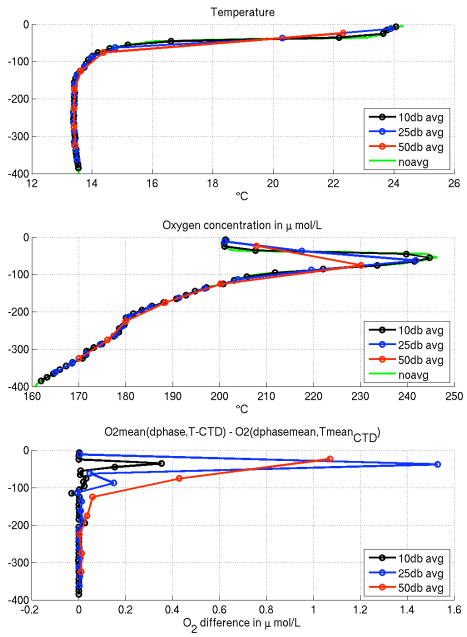

Figure 3: (Upper panel) Comparison between a temperature profile as measured by a glider at 1-db sampling and those estimated in bin averaging the initial profile. (Middle panel) Same as upper panel but for the dissolved oxygen concentration. (Lower panel) Difference between oxygen profiles estimated in bin-averaging the dissolved oxygen concentration or estimated from bin-averaged values of DPHASE, T, S and P.

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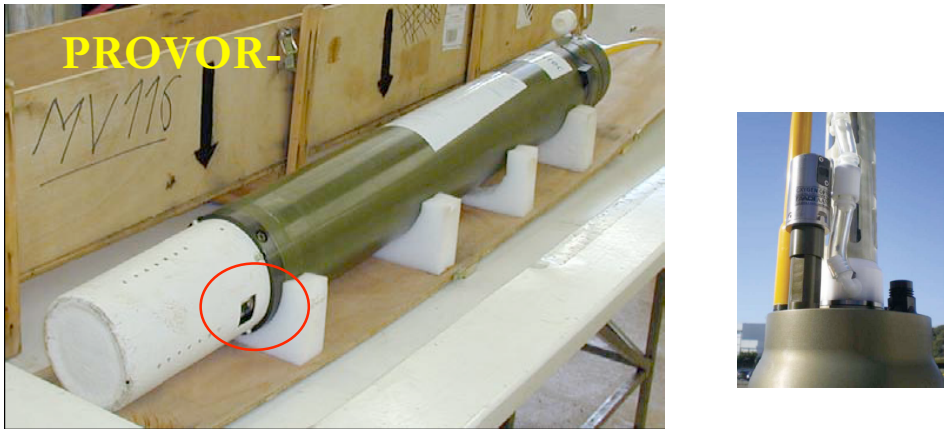
Beside the proximity of the CTD, the position of the O_2 sensor on top of the float has many advantages. It ensures that the sensor is located in the main flow and not in shadow or turbulent zone where the oxygen concentration might not be representative of the concentration of the surrounding water mass. The optode Aandera is also able to measure in (moist) air and could be coupled to a high resolution pressure sensor (such sensor exists but still needs to be tested) to detect any drift or bias in the optode sensor (Gruber et al, 2007). Finally, the optode was initially located in the float's lower end cap (Figure 4a) on the PROVOR-DO float. We suspect that the temperature measurement done by the optode temperature sensor is influenced by the temperature of the float itself, and, then, it might be biased, especially when the float goes through a strong temperature gradient. On the latest PROVOR CTS3-DO floats, the optode is now located at the top of the float (Figure 4b)



(a) (b)

Figure 4: a) First model of PROVOR-DO, equipped with an Aandera optode at the bottom of the float; b) on recent PROVOR-CTS3-DO floats, the optode is located on top, near the CTD.

6.4 DATA MANAGEMENT[1]

The official Argo unit for O_2 is µmol/kg, as in JGOFS and CLIVAR, but none of the existing sensors provides O_2 data in native units of µmol/kg. As mentioned in the appendix (A2) the O_2 unit converted from the outputs of the SBE DO sensor is ml/L, while that of the Aanderaa Optode is µmol/L.

Depending on the sensor, additional conversions must also be done to correct for pressure or salinity effects for example. As a consequence, whatever the sensor considered, sensor output must be transformed and converted in O_2, to take into account temperature, salinity and pressure effects or to convert the data in µmol/kg. We suggest to report O2 related data as follow [1]:

1. Store any transmitted data by the oxygen sensor with meaningful names, whatever the unit of the sensor output is. It is important to store those data if changes occur in the calibration/conversion equations used to convert the sensor output in DOXY. The proposed names are:
   1. VOLTAGE_DOXY when SBE43 sensor output is a voltage (Unit = V)

[1] All those recommendations are included in a proposal entitled "**Processing Argo oxygen data at the DAC level** " that has been submitted for endorsement at the last Argo Data Management Meeting in September 2009 in Toulouse. The proposition has been agreed and DACs are going to manage oxygen data accordingly.

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2. FREQUENCY_DOXY when SBE43 sensor output is a frequency (Unit = Hz)
3. COUNTS_DOXY when SBE43 sensor output are counts (no Unit ?)
4. BPHASE_DOXY when Aanderaa optode output is BPHASE (Unit = degree)
5. DPHASE_DOXY when Aanderaa optode output is DPHASE (Unit = degree)
6. DOXY_ORI when Aanderaa optode output is DO concentration at zero pressure and in fresh water or at a reference salinity (Unit = degree)
7. TEMP_DOXY when the Aaandera optode transmits its temperature measurement (Unit =degree Celsius)
8. XXX_DOXY for any new variables

2. Store in DOXY the dissolved oxygen value in μmol/kg estimated from the telemetered variables and corrected for any pressure, salinity or temperature effects.

3. Fill properly the metadata to document the calibration and conversions equations

4. Add the PRES_DOXY variable when the Optode reports in low resolution mode while the CTD reports in high resolution mode (vertical sampling)

The official Argo unit for dissolved oxygen concentration is μmol/kg. *T*he conversion of μmol/l *or* ml/l in μmol/kg requires a division by the potential density ρ. Such operation being a source of errors, a discussion is necessary to decide whether μmol/kg is the more appropriate unit for Argo-oxygen dataset.

The knowledge of the reference salinity that is internally set in the optode is necessary to estimate the salinity compensation when $DOXY_{T,S=0,P=0}$ is computed on board the platform. By default, the reference salinity is set to 0 (freshwater) but it is possible to change this default value to 35 for instance or to any other value. The knowledge of the reference salinity is mandatory because the dissolved oxygen concentration can be overestimated by 25% when the reference salinity is set to 0.

There is currently no recommendation on best practice concerning this parameter (when $DOXY_{T,S=0,P=0}$ is transmitted) : what reference salinity should we set ? Where to keep the data? We could think that it is better to set the reference salinity to 35 in order to minimize the error on DOXY if the salinity compensation is not taken into account. However, if the information is not available, a user will never know whether the salinity compensation has been applied or not. If the salinity is set to 0, a simple comparison to historical data will show an overestimation of the dissolved oxygen concentration and will warn the user that salinity compensation must be applied. In addition, the optode is delivered with the reference salinity set to 0. Modifying this value is not straightforward, especially for non-expert user. It is thus simpler to leave this value unchanged, especially if a growing number of oxygen profiling floats is deployed in a more operational way. We thus recommend setting the reference salinity of the optode to 0 and storing this crucial information for the post-treatment of the data in the metadata file.

When DPHASE is transmitted instead of $DOXY_{T,S=0,P=0}$, it is mandatory to know the 20 calibration coefficient Cij to calculate the dissolved oxygen concentration from DPHASE. Again, we recommend storing those coefficients in the metadata file.

Similar considerations could be done for the SBE43 sensor. The voltage or frequency signal measured by the SBE43 sensor is converted in O_2 on shore. The conversion uses a set of sensor-dependant coefficients with temperature, salinity, and pressure measured by the floats. As for the Aanderaa Optode, we recommend storing those coefficients in the metadata file.

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6.5 QUALITY CONTROL

To facilitate the control of the data in delayed mode, we recommend the acquisition of a ship-based calibrated reference profile at the float deployment.

The Aanderaa Optode sensor is expected to be stable over time. However, past experiences have shown that some sensors need to be calibrated before deployment. We recommend checking the calibration of the optode sensor before its implementation in a float and to perform a two points calibration (see the Aandera optode manual) when necessary.

Concerning the quality control of the data in delayed mode, three procedures are currently envisioned. The first one is based on comparison with reference data as it is done for the salinity (Wong et al., 2003, Böhme and Send, 2005). The main problems are the amount of data available in historical oxygen databases and their quality. Those databases have been less used than the temperature and salinity databases and lots of works are needed to check the quality of the available oxygen profiles.

The second one is based on the oxygen saturation in the uppers layers estimated form the float measurements. The oxygen saturation is expected to oscillate around 100% over the float life –time. Any deviations from this expectation should be a sign of a sensor drift or bias (D. Gilbert, 2009, presentation at the 3rd Argo Science Workshop).

The third procedure is based on the combination of oxygen measurements in the air and surface pressure measurements that require the implementation of an additional pressure sensor. Although the method is promising, it must be tested, his efficiency must be proven and the extra-cost must be evaluated.

7. IMPLEMENTATION

Here, some example of the possible implementation of network of biogeochemical autonomous platforms is reported.

7.1 PROFILING FLOATS

Biogeochemical profiling floats could be used in two principal types of mission. An additional, more specific, mission is also described.

7.1.1 Biogeochemical ARGO-like missions

A sufficient number of profiling floats could be used to characterise a large oceanic region and his spatio-temporal variability. Integrated with satellite surface observations, the acquired profiles could provide a 3-dimensional picture and a long term monitoring of large oceanic regions.

This is what is presently done for the physical state of the ocean by the Argo network, integrating Argo profiles with satellite SST and SLA observations. To ensure a long-term global coverage and to keep favourable the ratio between costs and benefits, the profiling frequency cannot be excessively high (i.e. for Argo is 10/5 days).

Existing biogeochemical floats could be used in a similar manner, because:

1. satellites provide surface observations of most of the parameters measured by biogeochemical floats (chlorophyll-a, CDOM, POC), with the notable exception of the oxygen;
2. new communication systems and advanced energy batteries can sustain, on a single float, the several different sensors required to characterize the ocean biogeochemistry. Additionally, they can support an increased vertical resolution, which is crucial for upper layers biogeochemistry;

An example of a large scale biogeochemical monitoring is represented by the operation conducted in the Mediterranean by the LOV PROVBIO in the 2008 (LeReste et al, 2009). Two biogeochemical profiling floats and 8 Argo like buoys are presently (i.e. September 2009)

operational in the basin, with an automatic and real time acquisition of the correspondent satellite imageries, furnished by the GLOBCOLOUR project (http://www.globcolour.info) via the private company ACRI.

Large scale missions should ensure a long-term monitoring of the sensors accuracies, to prevent the risks of artificial drift in the scientific results. In the framework of Argo project, a unique, semi-automatic and centralized data processing system was build-up, applying an automated and a human driven quality control on the acquired T and S data.

7.1.2 Process studies missions

More specific and focused missions could be realized with a limited number of profiling floats. These kind of missions are not envisaged by the present Argo programme, more focused on the large scale oceanic circulation. For biogeochemical studies, however, this kind of missions could be extremely attracting. A process studies mission should dedicate to a high spatial resolution, short or middle-term monitoring of a particular oceanic regions or to the characterisation of a restricted oceanic layer, where specific process take place. In fact, during a process studies mission, the float's cycle parameters are not rigidly constrained, as is the case for a large scale mission. Conversely, the two-way transmission systems should permit to adapt in real-time the sampling strategy of the floats, in response to particular situations or to some relevant unexpected phenomena.

A process studies mission should also be dedicated to test new sensors and their potentialities when mounted on autonomous platform.

An example of a process studies missions involving biogeochemical floats is the operation conducted by Bishop and co-workers, who adapted an APEX profiling float to carry out sensors calibrated to retrieve vertical carbon fluxes during an iron-enrichment experiment (Bishop et al. 2004). Similarly, Kenneth Johnson and collaborators have tested an ISUS nitrate-meter on an APEX profiling float in the Pacific Ocean, to characterize the episodic injection of nutrients in the upper layers (Johnson et al. 2006).

7.1.3 Satellite CAL/VAL missions

Argo data have been extensively used to validate existing (SST and SLA) and future (SMOS) satellite sensors (Boutin and Marint, 2006).

Similarly, biogeochemical floats should be used to calibrate and validate satellite ocean color sensors. Calibration and validation protocols for ocean color sensors are generally fixed by space agencies, which stimulate, by funding and endorsing, the collection of level-2 (i.e. radiometric) and level 3 (i.e. derived parameters, as chlorophyll) in situ observations.

For the level 3 parameters, surface data obtained during large scale or process studies missions could be employed, for CAL/VAL analysis, without additional requirements.

For the level-2 radiometric data, which are the most required data as they allow a direct validation of the primary satellite parameter, the spectral water leaving radiance, protocols for ocean color calibration are more severe, as only high-quality observations, collected in specific conditions, can provide useful sea-truth data for ocean color validation. For the CAL/VAL missions, then, standard profiling floats should be specifically adapted. In particular, accurate sensor for the geometry (i.e. tilting), should be provided.

It is important to remember here, that the space agencies, via the International Ocean Color Coordination Group (IOCGG) promoted a specific and dedicated working group (BIO-ARGO) to define the strategies of the use of biogeochemical profiling floats as support of the space biogeochemical observations (http://www.ioccg.org/groups/argo.html).

7.2 BIOGEOCHEMICAL GLIDERS

Gliders could cover a wide range of missions and complex sampling strategies. Among the others: virtual mooring (quasi-Eulerian sampling by collecting profiles at the same location),

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quasi-Lagrangian (profiling following the currents, i.e., behave like a profiling float until maneuverability is necessary), flying perpendicular to the oceanic depth average currents they measure. Additional configurations are possible, which comprise several gliders working simultaneously: persistence in a specific region (around, for instance, a mooring array), the tracking of an oceanic feature (i.e. eddy) or of a living creatures (i.e. foraging penguins). Robust algorithms to perform such complex piloting have already been tested in real oceanic conditions (Leonard et al, 2004; Lekien et al, 2008). Furthermore, numeric tools to optimize the glider path and to adapt waypoints on the basis of satellites imageries or on outputs of operational forecasting models have been also developed.

The endurance of 3-7 months limits deployments and, despite current technological developments, an increase of endurance by an order of magnitude in the coming decade is not foreseen. Constraints are due to not only endurance but also to the need for local support expertise and logistics. Gliders are complex systems that can be in operation for several years but they need to be serviced regularly by highly proficient marine engineers and technicians. Periodic maintenances include exchange of primary batteries, calibration of sensors and updating the hardware and software. These tasks are technologically demanding and require expertise and dedicated devices (e.g. calibration tanks) that are available only in a few places.

As they are relatively slow, some issues raise about whether the observations can be treated as synoptic and about the degree of representativeness of the ocean state obtained by the collected profiles. This problem is a major one but it can be solved by increasing the number of instruments at sea (point measurements) at the same time. As such, this is the float/glider philosophy but it demands a collective coordinated approach. But above all, the problem of synopticity can be solved because operational models are now mature and 4D evaluations of the state of the ocean can be performed with suitable data and data assimilation techniques.

In terms of scientific payload, a glider will not be able to carry all possible sensors, as its capacity is limited in size, weight and power. Several gliders, simultaneously deployed with different payloads, could overcome this problem. The concept of "heterogeneous cluster" has been introduced for a glider swarm able to collect a large number of ecosystem parameters, each glider being equipped with a dedicated payload having specific capabilities. Such an approach will enable to study, in a precise geo-localized frame, the dynamical interaction between e.g. the atmospheric forcing, the physical mixing and transport, and the phytoplankton concentration, metabolism and diversity.

In terms of possible scientific missions that fleets of coordinated gliders can carry, it is worth to distinguish (Testor et al, 2010) :

- Process studies. Because of the high spatial resolution and the wide range of parameters that gliders can collect simultaneously, they are appealing for fine scale (sub-mesoscale) process studies, in particular those where physics, biogeochemistry and biology are strongly coupled.
- Assessing the variability around long-term time series sites. Gliders will be used between the moorings of the existing trans-oceanic arrays, to enhance their observing capabilities. The objective is to evaluate the scales of correlation of these fixed-point measurements and to assess the significance of the signals at these locations/dates with respect to a whole region.
- Gliders and profiling floats arrays. Gliders are presently the sole platforms acquiring routine data with a controlled sampling and ability which are able to fill gaps left by a future array of biogeochemical floats which does not properly cover the coastal zone, any marginal sea, and divergence areas (from which floats simply drift away due to currents) Since glider are 'reusable' and usually recovered at the end of their missions, all sensors on-board can be (re)calibrated regularly. In addition, gliders could be steered to provide unique cross-calibration opportunities for the sensors on-board profiling floats which are expandable platforms.
- Gliders and remote sensing. Similar to what has successfully been achieved by the complementarities between the JASON altimetry program and ARGO for the large scale,

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synergies between gliders and satellite measurements at high resolution represents a potential benefit for a better understanding of the dynamics in the upper ocean.

7.3 ANIMALS

A sufficient number of tags could be used to characterise a large oceanic region and his spatio-temporal variability. Integrated with satellite surface observations, the acquired profiles could provide a 3-dimensional picture and a long term monitoring of large oceanic regions. In this sense, tags could be used in a "profiling floats" like missions.

Respect to the profiling floats, however, the possibilities of the animals to cross water masses and fronts give an additional capability to the animal tags. In this sense, they could be seen as an "intermediate" platform between the purely passive lagrangian floats and the more active gliders. Moreover, respect to the gliders, they have a more important autonomy, allowing missions in very difficult regions. The capability of the animals to collect data in regions inaccessible to the others autonomous platforms was demonstrated, for instance, by the number of T/S data presented in the CORIOLIS data base south of 60°S and within sea-ice, which are for the 95% and 98%, respectively, collected by elephant seals.

7.3.1 Process studies

More specific and focused missions could be realized with a limited number of equipped male elephant seals who tend to adopt over extended period of time a restricted foraging range on a the Antarctic or the Kerguelen-Heard shelf. So, in these situations, they act like a mooring system allowing to detect change in the fluorescence profiles according to physical processes such as internal tide and/or seasonal change. Preliminary results were obtained on the deployment conducted in 2009.

7.3.2 Satellite CAL/VAL missions

Data obtained from the Argos CTD-Fluo tags could be useful to validate satellite ocean colour sensors. Due to the scarcity of data available for the southern ocean the data obtained via the Argos CTD-Fluo tags might be particularly useful, mostly when investigating change in the fluorescence-Chlorophyll-a ratio in relation to the different water masses visited and in particular north and south of the sub-antarctic front.

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APPENDIX A: PRESENTLY AVAILABLE SENSORS

A.1 CHLOROPHYLL-A CONCENTRATION

A.1.1 FLUORESCENCE

For the available fluorometers, the calibration methods are very similar. A general overview is presented, with the details for each sensors furnished in the dedicated paragraph.

A.1.1.1 Calibration

Calibrations consist in

(i) A pre-calibration procedure with tests of pressure, mechanical and electronically stability, and precision.

(ii) Signal output calibration to measure the dark and maximal counts. Dark count is the measured signal output of meter in pure water with black tape over the detector. Maximal count is assessed by placing a fluorescent stick at approximately 1 cm from the detector. This produces a signal output close to saturation. These signal outputs are found in the instrument's device file.

(iii) An internal temperature calibration to take into consideration the effect of instrument internal temperature on some optical components. This calibration is performed by placing the fluorometer in a water bath.

(iv) A water calibration to determine the offset values of pure water (for a given temperature). Once the final offsets are collected, they are recorded in instrument's device file. Temperature has to be recorded since fluorescence is temperature sensitive (as the temperature of the sample increases, the fluorescence decreases).

(v) Manufacturer Calibration. The scale factor is factory-calculated by obtaining a consistent output of a solution with a known concentration, then subtracting the meter's dark counts. The scale factor, dark counts, and other characterization values are on the instrument's characterization sheet. Because of the varied environments in which each user will work, it is important to perform characterizations using similar seawater as you expect to encounter in situ. This will provide an accurate dark count value, equivalent phytoplankton types and similar physiological conditions for calculating the scale factor, thereby providing an accurate and meaningful calibration. Once a zero point has been determined and a scale factor established, obtaining a "calibrated" output simply involves subtracting the digital dark counts value from output when measuring a sample of interest and multiplying the difference by the instrument scaling factor:

$$[XX]sample = (Coutput - Cdc) * Scale\ Factor \quad (1a)$$

Where
[XX]sample = concentration of a sample of interest (μg/l)
Coutput = raw counts output when measuring a sample of interest
Cdc = dark counts, the measured signal output of meter in clean water with black tape, over the detector
Scale factor = multiplier in μg/l/counts.

To calibrate the instruments, manufacturers use samples obtained from different phytoplankton monospecific cultures (see table A1).

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A.1.1.2 WET Labs ECO Fluorometer for Chlorophyll-a

A sensor based on fluorescence method for chlorophyll-a is available from Wet Labs manufacturer. The Environmental Characterization Optics (ECO) miniature fluorometer (figure A1) is an open-face sensor, using a LED to provide the excitation source combined with an interference filter to reject the small amount of out-of-band light emitted by the LED. The light from the source enters the water volume at an angle of approximately 55–60 degrees with respect to the end face of the unit. Fluoresced light is received by a detector, which is positioned where the acceptance angle forms a 140-degree intersection with the source beam. An interference filter is used to discriminate against the scattered excitation light.

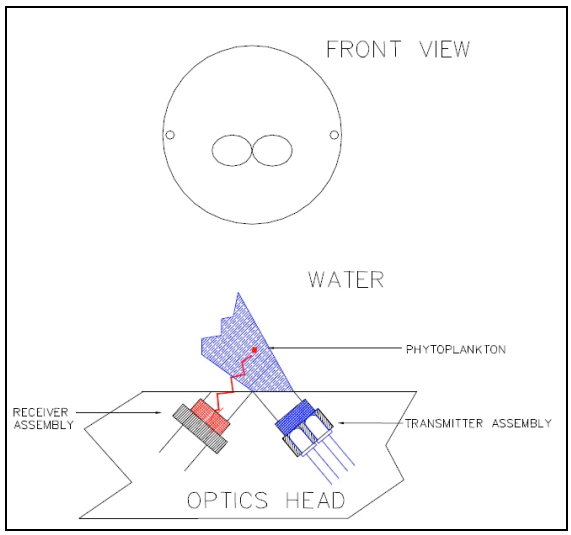

Figure A1: Optical configuration of ECO fluorometer.

To integrate ECO fluorometer on autonomous platform, the Wet Labs company designed and developed a specific instrumental system, the Triplet Pucks, which is easily adapted to most of the commercially available profiling floats and gliders. On the Triplet Pucks system, several devices (up to three) could be combined within a single basic design, greatly reducing the problems related to the connectivity and to the interfacing with the platform

A.1.1.3 Seapoint fluorometer for chlorophyll-a

The Seapoint manufacturer distributes the SFC, a chlorophyll-a calibrated fluorometer (figure A2), which uses a modulated blue LED lamps and a blue excitation filter to excite samples, and detects fluorescent light by a silicon photodiode and a red filter. The SCF may be operated with or without a pump. The resolution and the range of measurements can be controlled by changing control lines, which may be hardwired or microprocessor controlled.

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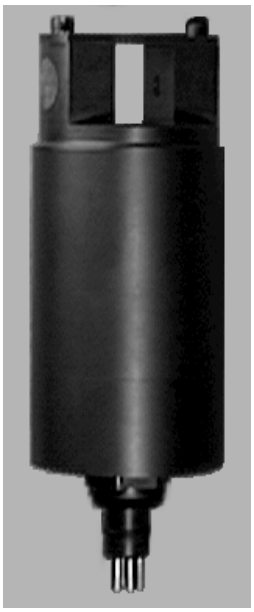

Figure A2 : Seapoint Chlorophyll-a Fluorometer (SCF).

A.1.1.4 Chelsea Mini Tracka II

Mini Tracka from Chlesea is a fluorometer for chlorophyll-a concentration, which uses a blue LED combined with optical filtering for sample excitation, and a low temperature coefficient photodiode, feeding a low noise preamp, to detect optical emissions. Using MINItracka II means there is generally no requirement to pump seawater through a dark observing chamber, thus obviating the need for water flow corrections - not to mention the cost, inconvenience and power drain of a pump.

A.1.1.5 Trios MicroFlu

MicroFlu from Trios (figure A3) is a miniaturized submergible fluorometer for chlorophyll-a fluorescence measurements. Internal reference measurement of the emitted light compensates aging and temperature dependences of the LEDs, used for fluorescence excitation. The TRIOS MicroFlu fluorometer is fully RS232 controllable and auto-ranging between -10 µg/l and 0-100µg/l. Internal reference measurement of the emitted light compensates aging and temperature dependences of the high-efficient LEDs, used for fluorescence excitation.

Figure A3: TRIOS MicroFlu sensor.

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A.1.1.6 Micromodule FL

The Micromudule FL mini, still under testing, has been especially designed to be integrated to the Argos CTD tags conceived by the Sea Mammals Research Units and which is deployed on pinipeds. It could also be integrated to autonomous platform such as profiling floats and gliders.). The main advantages of Micromodule FL are small size (20x30 x30 mm), light weight (i.e. 20 g), low energy consumption and pressure up to 2000 meters. Detection range of the current version: 0.5 à 30 µg/l and we are targeting a detection range of 0 to 30 µg/l with a sensitivity of 0.05 µg/l. The energy consumption is lower than 300mW, with a stand by position and a start up time <250ms.

A.1.1.7 Resuming tables

	WetLabs ECO FL	Seapoint Fl	Chelsea Mini Tracka II	TRIOS MicroFlu	Micromodule FL
Diameter (cm)	6.3	6.4	7	4.8	2.3
Length (cm)	12.7	16.8	14.9	20	4.4
Weight in air (g)	400	850	700	500	20
Weight in water (g)	20		150		
Pressure housing	titanium	ABS plastic	Acetal C	Seawater resistant plastic, stainless steel	Seawater resistant plastic
Depth rating (m)	6000	6000	600	500	2000
Connector	Subconn MCBH6M	Impulse AG-306/206	Subcon MCBH4M	SUBCONN Micro 5 pin, male	5 wire

Table A1: Sensors mechanical characteristics.

	WetLabs ECO FL	Seapoint Fl	Chelsea Mini Tracka II	TRIOS MicroFlu	Micromodule FL
Sample rate (Hz)	up to 8				up to 10
Input (VDC)	7-15	8-20	7-40	7-14.5	3.3-6
Current, typical (mA)	80	15 (avg) 27 (pk)	58	25	80 (avg) 110(pk)
Current, sleep (µA)	85				0
Interface	RS-232			RS-232	10

Table A2: Sensors electrical characteristics.

	WetLabs ECO FL	Seapoint Fl	Chelsea Mini Tracka II	TRIOS MicroFlu	Micromodule FL
Ex (nm) **Em (nm)**	470 695	470 (30) 685 (30)	470 (30) 685 (30)	470 (20) 685 (20)	430(20) 650 (100)
Sensitivity (µg/L)	0.01	0.033	0.01	0.1	0.5
Linearity	99% R2				99% R2
Range (µg/L)	0.01-125	0.02-150	0.03-100	0-10 or 0-100	0.5-300

Table A3: Sensors optical characteristics.

	WetLabs ECO FL	Seapoint Fl	Chelsea Mini Tracka II	TRIOS MicroFlu	Micromodule FL
Chlorophyll equivalent concentration (CEC)	Talassiosira weissflogii	Isochrysis galbana	Isochrysis	Cryst. Chl-a dissolved in aceton.	Cryst. Chl-a dissolved in propanol

Table A4: Factory calibration characteristics.

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A.1.2 RADIOMETRIC INVERSION

A.1.2.1 Calibration

The absolute calibration of a radiometer is generally performed using sources traceable to radiometric standards. Emitting a uniform light at different wavelengths, the calibration sources allow an absolute calibration of the photodiodes outputs in irradiance (W/m^2). The response of a radiometer submitted to the lamp's light is recorded, and the instrument is calibrated consequently. Temperature effects are also considered, as they could affect the photodiodes response. Finally, immersion factors are applied to account for the different index of refraction of the light path (i.e. water, glass of the instrument window, air).

A.1.2.2 Satlantic OCR-500

Satlantic Inc. produces and commercializes a large series of radiometers, expressly adapted to in situ radiometric measurements. The OCR-500 series radiometer (figure A4) is a passive radiometric systems equipped of silicon photodiodes detectors, which is specifically designed to be mounted on real-time profilers, moored, and autonomous deepwater buoys and autonomous underwater vehicles. Instruments with 4 or 7 channels are available: the measurement wavelengths can be selected by the user in a spectral range from 400 to 868 nm, though they cannot be changed dynamically. The filters used to select wavelengths integrated in the instrument and consist in a custom low-fluorescence interference of 10nm or 20nm bandwidth.

Figure A4: Satlantic OCR-500 Irradiance sensor.

A.1.2.3 TRIOS RAMSES Hyperspectral Irradiance Sensor

The RAMSES radiometer (figure A5) family is a combined system, consisting in modular instruments, with different detection characteristics and spectral ranges, and a modular acquisition/data logging unit. The modular system allows several individual sensor configurations and it was specifically designed for profiling floats. Two Irradiance sensors are commercially available: the ACC cosine collector (with 2 wavelength options, 280-500 nm or 320-950nm) and the ASC 2PI sensor (available for 320-950nm spectral range).

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Figure A5: TRIOS RAMSES-ACC-UV Hyperspectral UVA/UVB Irradiance Sensor (left) and modular docking unit for NEMO float.

A.1.2.4 BIC Multichannel Radiometers

Biospherical Inc. produces the BIC Multichannel radiometer (figure A6), which is the version of the Biospherical profiling radiometers, specifically adapted to autonomous platforms. The standard BIC measures downwelling (cosine) irradiance in three monochromatic wavebands as well as PAR (400-700nm). Wavelengths are available ranging from 305 nm in the UVB to 875 nm in the near infrared. BIC photodetectors share a common Teflon® collector. In addition to measuring cosine irradiance and PAR, the instruments can be optionally equipped with sensors for water temperature and pressure/depth.

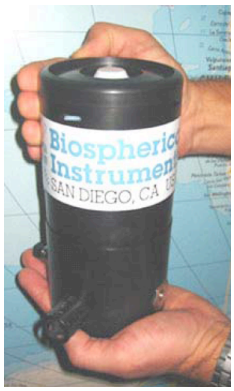

Figure A6: Aquatic BIC Radiometer with optional temperature and pressure sensors

A.1.2.5 Resuming tables

	Satlantic OCR500-AUV	**Trios RAMSES**	**Biospherical BIC**
Diameter (cm)	4.6/6.5	4.7	10.2
Length (cm)	11.0/12.5	26	20
Weight in air (g)	260/420	< 1000	2000
Weight in water (g)			
Pressure housing	Anodized aluminium	Stainless steel / POM housing	PET plastic housing
Depth rating (m)	1000	300	
Telemetry Interface Data		RS-232 (1200-19200 baud)	RS-232

Table A5: Sensors mechanical characteristics.

	Satlantic OCR500-AUV	**Trios RAMSES**	**Biospherical BIC**
Sample rate (Hz)	7Hz / 24Hz		
Input (VDC)	6 – 22 VDC	5 – 11 VDC	
Current (mA)	25	85	12 (2mA per channel)
Current, sleep (µA)		0.05	

Table A6: Sensors electrical characteristics.

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	Satlantic OCR500-AUV	TRIOS RAMSES	Biospherical BIC
Detectors	17 mm2 Silicon photodiodes	Channel silicon photodiode array	Teflon-covered quartz
Bandwidth range	400-865 (nm)	320-950 (nm)	305-875 (nm)
Number of channels	4 or 7	190	3
Spectral bandwidth	10 or 20 nm		10 nm
Typical saturation	300 $\mu Wcm^{-2}mm^{-1}$	800 $\mu Wcm^{-2}nm^{-1}$	
System time constant	0.011 sec.	4 ms – 8 sec.	

Table A7: Sensors optical characteristics.

A.1.3 AVAILABLE CONFIGURATIONS FOR PROFILING FLOAT

Float	Chlorophyll	Irradiance	Sensors position	Transmission system	Extra energy cost due to sensors
PROVBIO	Wetlabs	Satlantic	On the side of the float	Argos/Iridium	40%
APEX	Seapoint Wetlabs		At the base of the float	Argos/Iridium	4%
NEMO Optimare	Trios	Trios	Modular docking unit (3 sensors) at the bottom cap (fluo, radiance) or top cap (irradiance)	Argos/Iridium	NP
SOLO	NP	Biospherical	On the side of the float	Argos/Iridium	NP

Table A8: Available configurations for profiling float.

A.2 DISSOLVED OXYGEN CONCENTRATION

A.2.1 SEA-BIRD SBE-43

Produced by SEA-Bird Electronics, Inc., the SBE 43 sensor (figure A7) is, according to SEA-Bird literature, "a Clark polarographic membrane type in which careful choices of materials, geometry, and sensor chemistry are combined with superior electronics interfacing and calibration methodology to yield major gains in performance." Compared with previous designs, calibration stability, temperature response and pressure hysteresis have been much improved. Some people refer to the SBE 43 as the SBE IDO.

The SBE43 sensor determines dissolved oxygen concentration by counting the number of oxygen molecules per second (flux) that diffuse though the membrane from the ocean environment to the working electrode. At the working electrode (cathode), oxygen gas molecules are converted to hydroxyl ions (OH-) in a series of reaction steps where the electrode supplies four electrons per molecule to complete the reaction. The sensor counts oxygen molecules by measuring the electrons per second (amperes) delivered to the reaction. (from Application note No. 64, revised in April 2008; prepared by Sea-Bird Electronics, Inc.)

The measurable electrical current is converted to a voltage by the sensor electronics. The voltage signal varies linearly with partial pressure of oxygen. Among the SBE sensors, the SBE43 outputs the voltage itself, whereas the SBE 43F (SBE 43I) converts it to a frequency signal, which is proportional to the voltage. The conversion in oxygen concentration needsa set of

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sensor-dependant coefficients with temperature, salinity, and pressure. The dissolved oxygen concentration unit converted from the outputs of the SBE sensor is ml/L.

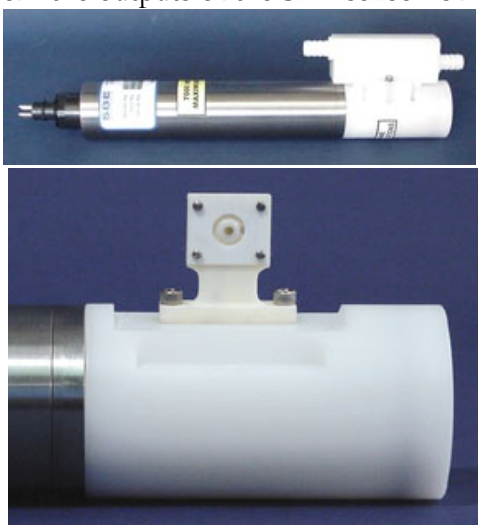

Figure A7: SBE-43 sensor, with pump adaptor (upper frame), and close-up on cathode and membrane (lower frame).

Mechanical characteristics

Two versions exist, one with data output as voltage, the other with frequency output. The voltage output version is by far the most widespread. Mechanical characteristics are given in figure A8. Cost of the VO version with Ti housing was about US$ 5000 at end 2007.

Electrical characteristics

Necessary power is 6.5-24 VDC, 60 mW. To provide useful measurements, the sensor must be associated with a CTD package including a pumping system to insure a regular water flow over the sensor membrane, as provided by SEA-BIRD.

Sensor characteristics

Measurement range: 120% of surface saturation in all fresh or salt waters
Initial accuracy: 2% of saturation
Typical stability: 0.5% per 1000 hours (clean membrane)
Response time: varies upon temperature and sensor membrane. Typically between 7 and 28 seconds (http://www.seabird.com/application_notes/AN64.htm).

Manufacturer's calibration

Sensors are factory calibrated using oxygen and temperature controlled baths. For profiling applications, it is recommended to obtain water samples for Winkler titration, to correct for residual drift and hysteresis. The method is deduced from Owens & Millard (1985). For long-term deployments with sparse water sample titrations available, a variant of the method is provided by SEA-BIRD

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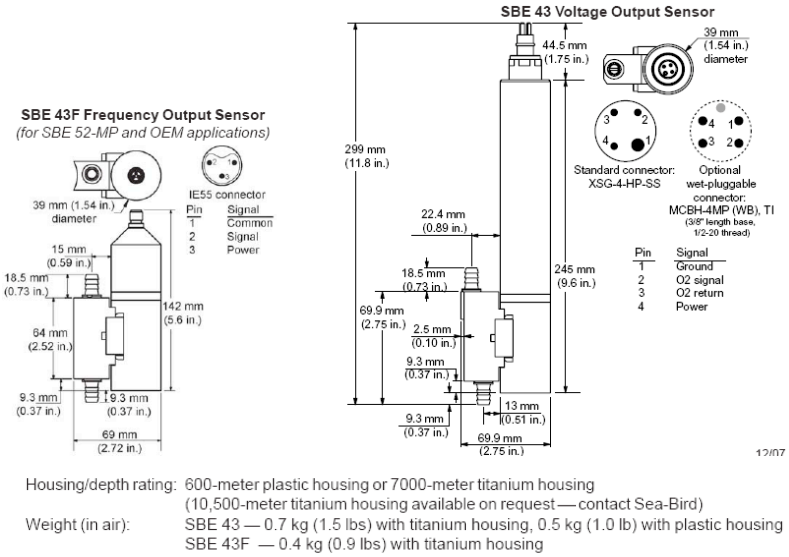

Figure A8. Mechanical and electrical characteristics of the SBE 43 O2 sensor

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A.2.2 AANDERAA OPTODE

A sensor based on the fluorescence quenching method is manufactured and sold by AAnderaa Data Instruments (AADI), under different configurations. The sensing foil (platinum-porphyrine complex) is mounted outside the optical window and is exposed to the surrounding water. The foil is held in place by a screw fixed PVC plate. Two light emitting diodes (LEDs) and one photodiode are placed on the inside of the window. A blue-green LED is used for excitation of the foil. The photodiode is used for sensing the fluorescent light. The photo diode is equipped with a colour filter that stops light with short wavelengths to minimize the influence of the reflected light. Further, the blue-green LED is equipped with a filter that stops light with long wavelengths. In addition, a red 'reference' LED was included to compensate for potential drift in the electronics of the transmitter and receiver circuit. As of today the red LED does not improve the sensor characteristics and is consequently not connected. In order to measure this luminescence decay time, the exciting light modulated at 5 kHz. The fluorescence decay time is a function of the phase of the received signal.

The Aandera optode measures a time delay (BPHASE in degree) that is proportional to oxygen partial pressure in sea water. This uncalibrated pahse measurement is then calibrated (DPHASE) and then converted in dissolved oxygen concentration ($DOXY_{T,S=0,P=0}$) from a 4th degree polynomial. DOXY unit is µmol/L. The five coefficients C_x of this polynomial are temperature dependant and are deduced from a 3rd degree polynomial. The calculation of $DOXY_{T,S=0,P=0}$ thus requires the knowledge of 20 coefficients C_{ij} (4 for each C_x coefficient) that are provided by the manufacturer. It can be done on board the instrument using the temperature (TEMP_DOXY) measured by the optode temperature sensor. If DPHASE is transmitted, $DOXY_{T,S=0,P=0}$ can be computed either from TEMP_DOXY or from the CTD temperature measurement. The optode always measures as if immersed in fresh water (salinity = 0) and at atmospheric pressure. The sensing foil that equips each optode is sensitive to the ambient pressure. It is thus necessary to compensate the estimated dissolved oxygen concentration ($DOXY_{T,S=0,P=0}$) from the salinity and pressure effects. The compensation is done on shore with salinity and pressure measured by the CTD.

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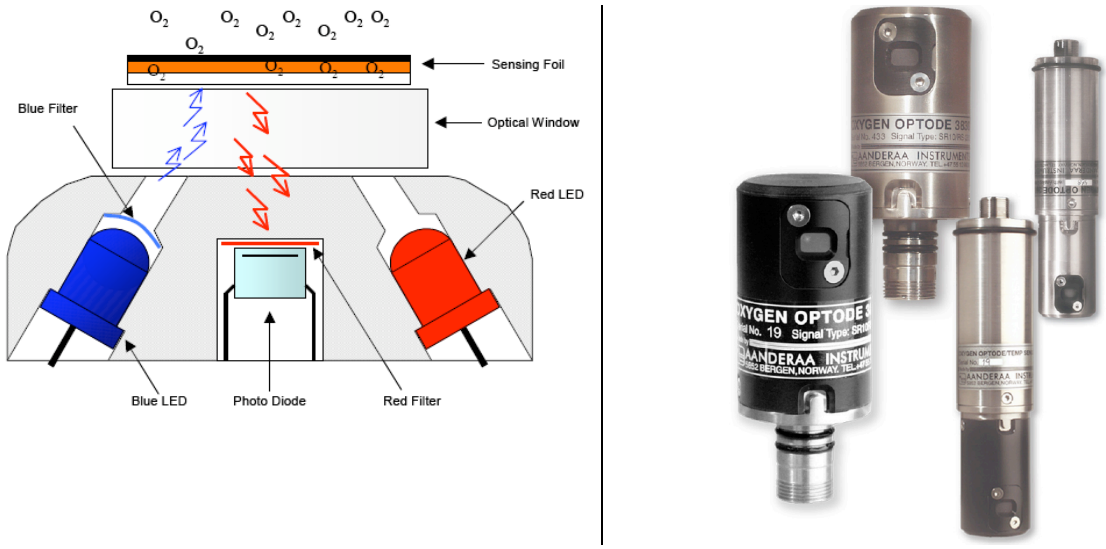

Figure A9: Optical design of the AADI Optode sensor, and photograph of different versions of the Optode.

Mechanical characteristics

The sensor is sold in several configurations. For the sake of simplicity we present only one of them here, the Optode 3830, which is designed to be adapted to owner's equipment. Cost of the sensor was about € 4500 at the end of 2009.

Operating depth: 6000 m
Weight in air: 238 g.

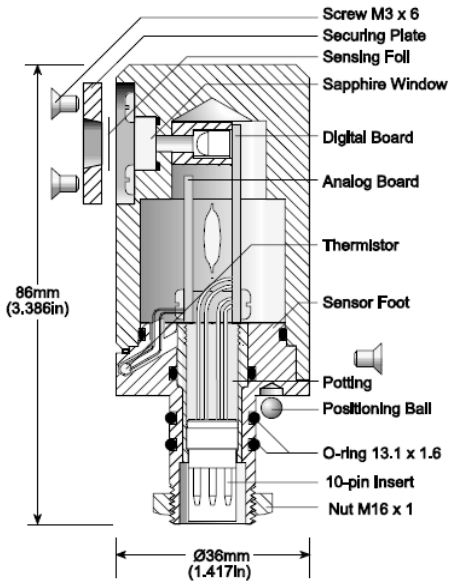

Figure A10. Internal view of the AADI Optode sensor

Electrical characteristics

Power need depends on the communication protocol chosen, either AADI SR10 proprietary protocol or RS232: voltage range is -14 - +14 VDC, and current consumption is either 10mA/T where T is recording interval in min for SR10), or 80mA/s +0.3mA where s is recording interval in sec (for RS232).

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A temperature sensor is included in the Optode to compute O_2 values. Although the role of salinity and pressure is less important than for electrochemical devices, a corresponding compensation must be applied afterwards, or a fixed salinity value introduced in the configuration of the sensor.

Sensor characteristics

Measurement range: 120% of surface saturation in all fresh or salt waters
Initial accuracy: <5% or 8 μM, whichever is larger.
Typical stability: no drift.
Response time: 8 s, the optode temperature sensor has a much slower response time (40 s for a 3°C temperature variation)

Manufacturer's calibration

The sensing foils are cut from slabs of platinum-porphyrine complex, which are calibrated by AADI. This means that individual calibration of each sensor is not carried out. AADI is currently checking the possibility that each sensor be calibrated (with extra cost). Because the foil response is very linear a 2-point calibration (zero-oxygen, and air-saturated water) is only necessary, and performed only when the foil is changed. The characteristic of no-time-drift claimed by AADI is very seductive, but longer data time-series from these sensors are needed to check the validity of that property on the long run and to determine the associated errors.

Note also that to attain the accuracy given by Aanderaa, pressure and salinity compensation must be carried out. A typical order of magnitude of the correction for 35 salinity and at 1000 db pressure is 15% of the measurement at p=patm and salinity=0, which is not negligible.

A.2.3 AVAILABLE CONFIGURATIONS FOR PROFILING FLOAT

Float	Sensor	CTD sensor	Unit	Sensor position	Transmission system	Sampling mode	Extra energy cost due to the oxygen sensor
PROVOR	Optode	SBE-41CP	μmol/l	Bottom of the float	Argos	Bin-average	
PROVOR	Optode	SBE-41CP	μmol/l	Top of the float	Argos	Bin-average	
APEX	Optode	SBE-41	μmol/l	Top of the float nearby the CTD	Argos	Spot sampling	low
APEX	Optode	SBE-41CP	μmol/l	Top of the float nearby the CTD	Iridium	Spot sampling	high, unless the oxygen sampling is done at low resolution
APEX	SBE43	SBE-41	ml/l	Top of the float coupled to the CTD	Argos	Spot sampling	high
APEX	SBE43	SBE-41CP	ml/l	Top of the float coupled to the CTD	Iridium	Spot samplig	low

Table A9: Characteristics of each couple platform/sensor for different transmission systems or sampling strategy. To convert ml/l in μmol/l, one has to multiply by 44.66.

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APPENDIX B: ADDITIONAL PARAMETERS

B.1 COLORED DISSOLVED ORGANIC MATTER

B.1.1 SCIENTIFIC RATIONALE

Colored (or chromophoric) dissolved organic matter (CDOM), also known as gelbstoff, gilvin and yellow substances, is operationally defined as the component of dissolved organic matter (DOM, <0.2 μm) that absorbs light over a broad range of ultraviolet (UV) and visible wavelengths. Abundance and distribution of CDOM in the ocean is essentially controlled by *in situ* biological production, terrestrial inputs (sources), photochemical degradation, microbial consumption (sinks), as well as deep ocean circulation (Siegel et al., 2002; Nelson et al., 2007; Coble, 2007).

CDOM comprises a significant fraction (from 20 to 70%) of dissolved organic carbon (DOC) with the highest contributions observed in coastal areas, where river inputs are dominant, and the lowest percentages found in open oceans (Coble, 2007). In most coastal waters and below the euphotic zone, CDOM displays a conservative behavior on the time scale of physical mixing. Therefore, it has been used to trace river inputs (Coble, 1996), polluted waters (Clark et al., 2007) and water masse incursions (i.e. convergences/divergences; Niewiadomska et al., 2008). Positive correlations between CDOM and DOC can be observed in areas where mixing between rivers and seawater control the distribution of these two parameters (Blough and Del Vecchio, 2002). However, in open ocean or coastal areas away from terrestrial influence, these correlations tend to disappear, or even, to be negative (Nelson and Siegel, 2002). Indeed, depth profiles usually exhibit high DOC concentrations (due to phytoplankton activity) and low CDOM amounts (due to photochemical degradation) in the surface layer, whereas below the euphotic zone, DOC concentrations decrease and CDOM amounts increase (Hansell, 2002).

CDOM is the major factor controlling the attenuation of UV radiation in the ocean (Kirk, 1994; Diaz et al., 2000). Recently, it has been shown that CDOM, combined to non algal particulate (NAP), could be more important than Chlorophyll-a in the attenuation of visible radiation at 440 nm (Siegel et al., 2005). CDOM is highly photoreactive and efficiently destroyed upon exposure to solar radiation. The photochemical degradation of CDOM in the surface waters leads to its bleaching (loss of absorption and fluorescence), to the reduction of some trace metals (Fe), and to the production of different species such as free radicals ($^{\bullet}OH$, $R^{\bullet}$), dissolved inorganic carbon (DIC), carbon monoxide (CO), carbonyl sulfide (OCS), low molecular weight organic compounds (carbonyls and monocarboxylic acids) and nutrients (PO_4^{3-}, NH_4^{+}) (Mopper and Kieber, 2000; 2002). The photochemical degradation of CDOM modifies the DOM bioavailability to heterotrophic bacteria and plays a significant role on the oceanic carbon cycle.

Consequently, the study of CDOM covers a broad spectrum of disciplinary fields including ocean circulation, biogeochemistry of carbon, trace elements and gases, ocean optics and remote sensing, photochemistry and photobiology. There is thus a substantial interest in getting accurate CDOM estimates in the global ocean. Since its exact chemical composition is (still) unknown, it is not currently possible to quantify CDOM in terms of mass or carbon equivalents separately from the total DOM pool. So, CDOM is generally characterized and quantified by using spectroscopic methods, in particular UV-visible absorption and fluorescence. In this chapter, only method and sensors regarding fluorescence are addressed. Indeed, absorption method for CDOM refers to instruments (WET Labs ac-9, ac-s) that cannot be presently integrated onto autonomous platforms such as gliders and profiling floats because of their too high energy consumptions.

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B.1.2 MEASUREMENT THEORIES

B.1.2.1 Fluorescence

Fluorescence is a photoluminescence phenomenon in which the molecular absorption of a photon generates the emission of another photon with a longer wavelength. Fluorescent compounds are called fluorophores. When of photon is absorbed by a fluorophore, the latter is electronically excited passing from its ground state to an excited state. The return to ground state conducted by emitting of a photon. Because some energy is lost from the excited electron by collision, non-radiative decay and other processes, the energy of the emitted photon is lower than the excitation energy. The wavelength at which absorption (excitation) and emission occur is specific to the fluorophore. Since absorption of photons is the first step in fluorescence, one may say that fluorescent DOM is CDOM (fluorophores are chromophores) but not all CDOM is fluorescent (chromophores are not all fluorophores). Actually, while CDOM absorption spectra display a featureless increase in intensity with decreasing wavelength between 200 and 700 nm, CDOM fluorescence excitation spectra show discrete peaks, most of them around 250 and 350 nm.

Fluorescence of CDOM is directly proportional to its concentration for DOM absorption coefficients lower than ~10 m^{-1}. For samples and wavelengths where absorption coefficients are above 10 m^{-1} (corresponding to an absorbance of 0.04 in a 1 cm cuvette), significant reductions in the fluorescence signal are expected due to inner filtering effects (Zepp et al., 2004; Stemon and Bro, 2008). The fluorescence intensity of CDOM, F (mole quanta m^{-3} s^{-1}), can be theoretically expressed as follow:

$$F = E\,[CDOM]\,e_{CDOM}\,\boldsymbol{\Phi}_{CDOM} \qquad \text{(B1)}$$

where E is the excitation irradiance (mole quanta m^{-2} s^{-1}) provided by a light source, $[CDOM]$ is the CDOM concentration (μg l^{-1}), e_{CDOM} is the CDOM extinction coefficient (m^{-1} (μg l^{-1})$^{-1}$) and $\boldsymbol{\Phi}_{CDOM}$ is the CDOM fluorescence quantum yield (ratio between the number of photons emitted and the number of photons absorbed by the molecule). CDOM, whose molecular composition remains largely unknown, is typically quantified using quinine sulfate (QS). Owing to its relatively high fluorescence quantum yield, QS has often been employed as standard in spectrofluorometric analyses. QS has excitation and emission wavelengths of 350 and 450 nm, respectively, which is similar to many CDOM components. Its fluorescence intensity substantially increases when diluted in weak acids. Therefore, the fluorescence of 1 μg l^{-1} QS in 0.05 M H_2SO_4 (equivalent to 0.1 N H_2SO_4) has been chosen as the quinine sulfate unit (QSU).

Fluorometers used to assess the *in situ* CDOM concentration have a single excitation/emission wavelength pair, generally 350/450 nm. A typical CDOM fluorometer is composed by a light source (lamp, LED) that supplies the excitation signal, a detector (photodiode, photomultiplier) that measures the intensity of the emission (fluorescence) light, and interference filters for selecting the excitation/emission bandwidths. Interestingly, Belzile et al. (2006) compared the *in situ* signal of the WETStar CDOM fluorometer (WET Labs), with the fluorescence signal of 0.2 nm filtered discrete samples provided by two laboratory spectrofluorometers. They obtained a strong linear correlation ($r^2 > 0.96$) and found furthermore that particles had negligible impact on the WETStar signal with decreases by 0-4% after filtration onto 0.2 nm. This shows that solely the "true" (< 0.2 μm) dissolved fraction accounts for the *in situ* fluorescence signal measured by CDOM fluorometers.

B.1.3 PRESENTLY AVAILABLE SENSORS

For the available fluorometers, the calibration methods are very similar. A general overview is presented, with the details for each sensors furnished in the dedicated paragraph.

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B.1.3.1 Calibration

Calibrations consist in:

(i) A pre-calibration procedure with tests of pressure, mechanical and electronical stability, and precision.

(ii) Signal output calibration to measure the dark and maximal counts. Dark count is the measured signal output of meter in pure water with black tape over the detector. Maximal count is assessed by placing a fluorescent stick at approximately 1 cm from the detector. This produces a signal output close to saturation. These signal outputs are found in the instrument's device file.

(iii) An internal temperature calibration to take into consideration the effect of instrument internal temperature on some optical components. This calibration is performed by placing the fluorometer in a water bath.

(iv) A water calibration to determine the offset values of pure water for a given temperature. Once the final offsets are collected, they are recorded in instrument's device file. Temperature has to be recorded since fluorescence is temperature sensitive (as the temperature of the sample increases, the fluorescence decreases).

(v) Absolute calibration. As molecular composition of CDOM is unknown, quinine sulfate (QS), has been the most commonly fluorescent compound used for CDOM calibration. The fluorescence of 1 $\mu g\ l^{-1}$ QS in 0.05 M H_2SO_4 has been chosen as the quinine sulfate unit (QSU). CDOM concentration in $\mu g\ l^{-1}$ QS (or QSU) is derived from the following equation:

$$[CDOM]_{sample} = Scale\ factor * (C_{output} - C_{dark}) \quad \text{(B2)}$$

where C_{output} is raw counts of sample, C_{dark} is dark counts, the measured signal output of meter in clean water with black tape over the detector, and scale factor is multiplier in $(\mu g\ l^{-1})\ count^{-1}$ determined from the measurement of raw count signal of a QS standard solution. Scale factor and dark counts are recorded in the instrument's device file.

(vi) User's calibration. Calibrations should be performed by the user before and/or after deployments of the instrument mounted on the autonomous platform, in order to track any drift due to fouling or instrument changes. These calibrations are done by measuring dark (black tape) and maximal (fluorescent stick) counts, and if possible counts of different QS standard solutions to determine scale factor and offset parameters. The fluorescent stick provided by WET Labs has to be held 1-4 cm above the optical paths in an orientation that maximizes exposure of the stick (parallel with the beams, not intersecting them). The signal will increase toward saturation (the maximum value is given on characterization sheet). To measure the fluorescence intensity of QS solutions, it is recommended to use glass material (not plastic which interfere with fluorescence signal). It is important to be sure that the sensor can be in contact with QS solutions made in hydrosulfuric acid (0.05 M H_2SO_4), otherwise QS solutions have to be prepared in pure water.

B.1.3.2 WET Labs ECO Triplet Puck (fluorometer calibrated for CDOM)

The WET Labs ECO Triplet Puck can be used to measure CDOM concentration, by fluorescence, providing a specific calibration for CDOM. See paragraph A.1.1.2 for the instrument description.

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B.1.3.3 Seapoint Ultraviolet Fluorometer

The SeaPoint Fluorometer could be used to measure CDOM concentration, by florescence, providing a specific calibration for the CDOM. See chapter A.1.1.3 for the instrument description.

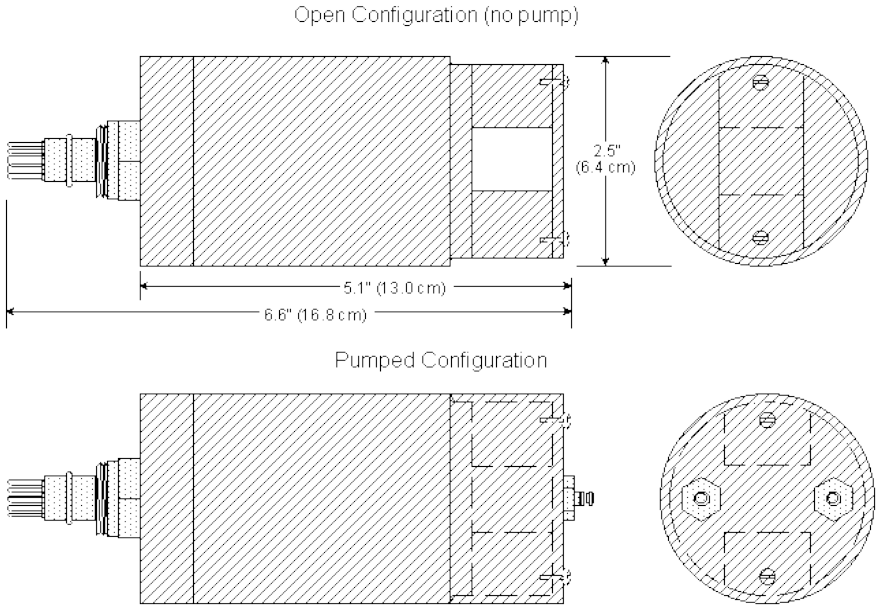

Figure B1: Seapoint Ultraviolet Fluorometer (SUVF) for CDOM quantification available either in open or pumped configuration.

B.1.3.4 Chelsea UV MINI^{Tracka}

The Chelsea UV Mini^{Tracka} is a submersible fluorometer dedicated to the monitoring of CDOM in a wide range of oceanographic applications. It has been designed to be deployed from submersible vehicles, moored or profiling systems. The UV Mini^{Tracka} 's pressure housing is manufactured in acetal for long life. It utilizes a high power LED light source and a low temperature coefficient photodiode which feeds a low noise preamp that, together with phase sensitive detection, gives an overall electronic noise figure close to the theoretical minimum possible. Data output is factory set as linear analogue. The UV Mini^{Tracka} has a high degree of insensitivity to water temperature changes due to the low temperature coefficient of the new generation SQW LEDs, the selected photodiode used and the careful circuit design. It is operated as an open system (no pump). Due to its shorter excitation wavelength (255 nm instead of 350 nm for other CDOM fluorometers), the sensor used perylene for absolute calibration in place of QS. Perylene is a polycyclic aromatic hydrocarbon whose chemical formula is $C_{20}H_{12}$.

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B.1.3.5 Resuming Tables

	WET Labs Triplet Puck	Seapoint Ultraviolet	Chelsea UV Mini^{Tracka}
Size (Ø x L)	63 x 127 mm	64 x 168 mm	70 x 149 mm
Weight (air/water)	400/20 g	1000/? g	800/150 g
Temperature range	0-30 °C	0-65 °C	-2-40 °C
Depth rating	600 m	6000 m	600 m
Housing	Acetal copolymer	ABS plastic	Acetal copolymer
Connector	MCBH6M	Impulse AG-306/206	MCBH-6-MP-SS
Integration to autonomous platform	WRC Slocum gliders PROVOR	Spray gliders	No
Cost	6500 €	4300 €	5200 €

Table B1. Mechanical characteristics of CDOM sensors

	WET Labs Triplet Puck	Seapoint Ultraviolet	Chelsea UV Mini^{Tracka}
Input	7-15 VDC	8.5-20 VDC	7-40 VDC
Energy	90 mA at 12 VDC (1080 mW)	27 mA at 12 VDC (324 mW)	58 mA at 12 VDC (700 mW)
Data output	Digital (RS-232) and analogue (0-5 VDC)	Analogue (0-5 VDC)	Digital (RS-232) and analogue (0-5 VDC)
Data memory	50000 measurements	No	No

Table B2. Electrical characteristics of CDOM sensors

	WET Labs Triplet Puck	Seapoint Ultraviolet	Chelsea UV Mini^{Tracka}
Principle	Fluorescence	Fluorescence	Fluorescence
Excitation/Emission	370/460 nm	370/440 nm	255/430 nm
FWHM (bandwidths)	10/120 nm	12/40 nm	12/50 nm
Frequency of acquisition	4-8 Hz	1 Hz	0.1-3 Hz

Table B3: Optical characteristics of the CDOM sensors.

	WET Labs Triplet Puck	Seapoint Ultraviolet	Chelsea UV Mini^{Tracka}
CDOM equivalent	Quinine sulfate (QS)	Quinine sulfate (QS)	Perylene
Range	0.18-375 $\mu g\ l^{-1}$ QS	0-50, 0-150, 0-500 or 0-1500 $\mu g\ l^{-1}$ QS	0-10 $\mu g\ l^{-1}$ perylene
Limit of detection	0.18-0.30 $\mu g\ l^{-1}$ QS	0.10 $\mu g\ l^{-1}$ QS	0.02 $\mu g\ l^{-1}$ perylene

Table B4: Factory calibration characteristics of the CDOM sensors.

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B.2 PARTICULATE ORGANIC CARBON

B.2.1 SCIENTIFIC RATIONALE

The Particulate Organic Carbon (POC) represents one of the main pools of organic carbon observed in the ocean. It composed by a mix of living and non living materials (phytoplankton, zooplankton and bacteria in the first case; aggregates, pellets and detritus for the second).

The POC is considered a key parameter for the global carbon cycle (Longhurst and Harrison, 1989), since it contributes relevantly to the so-called biological pump (i.e. the biological driven export of carbon from the ocean surface to depths). Consequently, several attempts are historically attempted to determine his global distribution and temporal evolution (Gardner et al 2006 and references therein).

The POC concentration standard samples collection was definitively fixed during the JGOFS program (JGOFS, 1996, but see also Gardner et al. 2003), which dedicated a specific observational effort to POC parameter. Water samples, collected with a rosette bottle, are initially filtered (typically at 0.7 μm); filter is then dried, and later analyzed with an elemental analyzer to determine carbon mass (Gardner et al. 2003)

More recently, some bio-optical techniques based on c_p *vs* POC and b_b *vs* POC relationships were developed (see next paragraphs). Additionally, these new methods allowed the exploitation of remote sensed data to assess the POC concentration on surface layers (see Loisel et al. 2006, and reference therein).

Space algorithms, and the consequent huge amount of data available, have dramatically increase the modelling effort dedicated to the POC dynamic, as, finally, a direct estimation of the carbon pool becomes available for numerical simulations validation and initialization.

However, the homogenisation of data from different methods would require a more dedicated effort to ameliorate the "consensual" protocols and algorithms, as well as to better integrate the different data sources (see for example Gardner et al. 2003).

B.2.2 MEASUREMENTS THEORIES

B.2.2.1 Attenuation Coefficient

The beam attenuation coefficient c [m-1] is defined as the percentage of the intensity of a plane parallel light beam, which is loss when a medium is penetrated. It is decoupled in absorption (a) and scattering (b) coefficients, to separate the effects of the two different physical processes accounting for the decrease of beam intensity:

$$c = a + b \tag{B3}$$

According to the above definition, c depends of the light path of the beam, and is then practically estimated by measuring the beam loss intensity in a know path length of a specific medium.

The attenuation coefficient is wavelength dependent, though the most widely used wavelength for such type of measurements in the seawater is the 660 nm (related to the large availability of REDs leds in the past).

Corrected for absorption of pure water, $c(660)$ gives the attenuation coefficient by particles (c_p), since the contribution of dissolved material could be considered negligible at this wavelength (Loisiel and Morel, 1998). Finally, $c_p(660)$ could be linearly related to POC concentration (Gardner et al., 1993 ; Loisel and Morel, 1998; Claustre et al., 1999), allowing the definition of empirical global (i.e. Siegel et al. 1989) and regional (i.e. Claustre et al. 1999) POC algorithms.

An instrument measuring c is generally denoted as a transmissiometer. The collimated bean, emitted from a light source at fixed, known and stable intensity, cross the medium (i.e. seawater)

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and is measured by a receiver. The measured variable, the loss of intensity across the path (i.e. the transmittance, *Tr*), is related to *c* following:

$$Tr = e^{-cx} \tag{B4}$$

where *x* is the distance between source and receiver.

Although the method is relatively simple and accurate, recent comparisons of commercial available transmissiometers highlighted differences between the estimations (about tens of percents). The problem was identified in the difference in the acceptance angle of the various instruments.

B.2.3 BACKSCATTERING COEFFICIENT

Scattering coefficient (*b*) of a medium is the scattered fractions of incident light flux, divided by the infinitesimal thin layer of the medium (see eq. 7). It is usual, for the bio-optical purposes, to decompose the scattering coefficient in two components depending on the direction of the scattered flux. The forward scattering coefficient (b_f), indicating the flux scattered from the beam in the forward direction, and the backscattering coefficient (b_b), relating to light scattered from the beam in the backward direction. More specifically, if $\beta(\Theta)$ is the volume scattering function ([m-1 sr-1], the angular distribution of scattering relative to the direction of light propagation, Θ), b_b [m-1] could is defined as:

$$b_b = 2\pi \int_{\pi/2}^{\pi} \beta(\theta) \sin\theta d\theta \tag{B5}$$

Measurements at a single plane (i.e. assuming azymuthal symmetry) and at a single angle have been found to provide b_b with an uncertainty smaller than about 10% (Boss and Pegau, 2001)

Optical theory (Preisedendorfer, 1961, Morel and Prieur 1977) relates b_b to the spectral reflectance of the ocean (i.e. ocean colour), though it represents only 3-5% of the total scattering coefficient *b*.

According to the above definition, b_b is directly related to the density and size of particles, but also to their composition (i.e. organic vs inorganic).

More importantly in this context is that recent derived empirical relationships have found, correlating b_b to POC concentration (see Stramski et al., 2008, and reference therein). Algorithms have different functional forms, as can be derived from direct measurements of b_b or from b_b estimations using reflectance ratios (more suitable for remote sensing applications, i.e. see Gardner et al. 2006 for a review).

B.2.4 PRESENTLY AVAILABLE SENSORS – TRANSMISSIOMETERS

B.2.4.1 WETLabs C-Star

The C-Star transmissometer, produced by the WETLabs Company, measures the beam transmittance at one specific wavelength among the 4 available (370, 470, 530 or 660 nm). The instrument can be used to measure beam transmittance in free space measurements, or through the use of an optical flow tube, flow-through sampling with a pump. The C-Star can be easily interfaced to a wide variety of small battery-powered CTDs and loggers.

The light (LED with appropriate wavelength) passes through a beam splitter so that a portion of the transmitted light can be monitored by the reference detector and used in a feedback circuit to account for variations in the LED source over time as well as changes in the instrument's internal temperature. The light enters the sample volume after passing through the first pressure window, transits the sample volume and enters the receiver optics after passing through the other

pressure window. The light passes through additional focusing optics and finally strikes a silicon photodiode detector which converts the amount of received light to a corresponding 0–5 V analog output signal which represents the amount of light received.

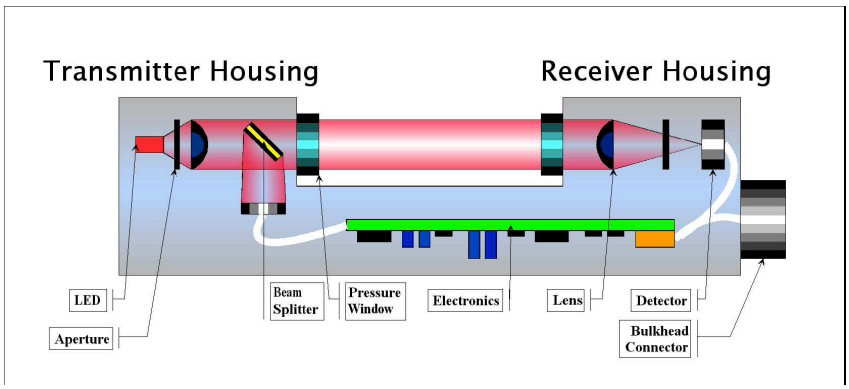

Figure B2: Configuration description of the C-Star transmissiometer (from the C-Star WETLabs User Manual)

B.2.5 PRESENTLY AVAILABLE SENSORS – BACKSCATTER METERS

B.2.5.1 WET Labs ECO backscatterometer

The ECO backscatterometer from WETLabs measures (figure B3) optical backscattering at one wavelength, among the nine available (412, 440, 488, 510, 532, 595, 650, 676, 715 nm). The instrument uses a centroid angle of 117 degrees, which minimizes the error in extrapolating to the total backscattering coefficient.

Following the user manual, voltage counts are transformed in total volume scattering coefficient, corrected for the absorption (about 4% of the signal) and pure sea water (tabulated) influence, to obtain the particle volume scattering coefficient, which is finally transformed in backscattering coefficient using the formula of Boss, E., and S. Pegau (2001).

The ECO backscatterometer is one of the possible options in the ECO-Triplet and is totally integrated to be used on profiling floats and gliders (see paragraphe A.1.1.2 for the description of the ECO triplet puck).

Figure B3: the ECO backscatterometer sensor

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B.2.6 RESUMING TABLES

	C-Star	ECO BB
Size (Ø x L)	470x64x93mm (25cm pathlength) 292x64x93mm (10cm pathlength)	146 x 305 mm
Weight (air/water)	3600(900 plastic)/2700 g	3100/1800 g
Temperature range	0-30°C	0-30 °C
Depth rating	600/6000m	600 m
Housing	Plastic/Aluminium	Plastic
Integration to autonomous platform	ProvBio	Webb and Sea gliders
Cost		

Table B5. Mechanical characteristics of all the sensors

	C-Star	BB9
Input	7-15 VDC	7-15 VDC
Energy	40 mA at 12 VDC (480 mW)	300 mA at 12 VDC (3600 mW)
Data transmission		RS-232 or 485

Table B6. Electrical characteristics of all the sensors

	C-Star	BB9
Principle	Beam transmittance	Backscattering
Wavelength	370, 470, 530, 660	412, 440, 488, 510, 532, 595, 660, 676, 715 nm
Bandwidth	10-12 nm for 370 nm ~20 nm for 470, 530 and 660 nm	
Sensitivity	1.25 mV	$2.44x10^{-5}$, $2.60x10^{-5}$, $2.14x10^{-5}$, $1.81x10^{-5}$, $7.70x10^{-6}$, $1.02x10^{-5}$, $3.79x10^{-6}$, $3.60x10^{-6}$, $3.20x10^{-6}$
Range	0-5V (analog) 0-4095 counts (digital)	~0.0024-5 m^{-1}
Frequency of acquisition		1Hz

Table B7. Sensors characteristics of all the sensors

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B.3 NUTRIENTS

B.3.1 SCIENTIFIC RATIONALE

Nutrients concentration is a key parameter to characterize ocean phytoplankton dynamic and, more generally, the marine ecosystem functioning. Nutrients are also a critical variable of the present day biogeochemical models (Lequere et al, 2010). With light, nutrients are considered the main limiting factor for phytoplankton, and then macro (i.e. nitrates, silicate, phosphate) and micro (i.e. iron) nutrients distribution determine the oceanic areas where phytoplankton could growth.

Nutrients concentrations are generally obtained by laboratory analysis on water samples collected with classical shipboard techniques. Recently, a new series of automatic sensors based on UV absorbance allowed the determination of nitrates (NO_3) concentration (Johnson and Coletti, 2002). Though characterized by low sensitivity compared with the classical laboratory method, the UV based sensors are extremely promising to be used on autonomous platform as they match the necessary requirements of miniaturization.

A UV based nitrate sensor (i.e. ISUS) has been successfully implemented on a profiling float (Johnson et al, 2006), collecting more than 500 days of data.

B.3.2 MEASUREMENTS THEORIES

B.3.2.1 UV absorption

Absorbing spectrum in the UV (200-400nm) can be directly related to nitrates (NO_3) concentration of water (figure B4). A NO_3 sensor is composed by an UV lamp and by a hyperspectral receptor. Water samples are lightened with the UV lamp and the consequent absorption spectra are obtained by the sensor receptor. Using a direct relationship between the optically active compounds (i.e. NO_3) present in the water sample and the absorption peaks of the spectra, allow a direct estimation of the absorbing species concentrations.

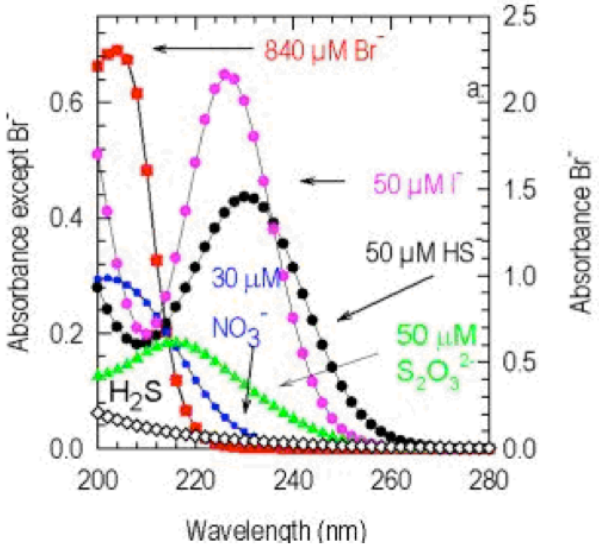

Figure B4. Primary absorbing UV species in seawater. Green line indicates NO_3 absorption (from SUNA Technical manual, Satlantic Inc.)

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B.3.2.2 Electrochemistry

Electrochemical detection opens very promising future avenues to go forward into miniaturization, versatility, response time reduction, energy consumption decrease without the use of chemical reagents (Lacombe et al., 2007; 2008). Microfabrication offers tremendous opportunities for *in situ* marine sensor research as multiple order of magnitude changes in size, cost, resource consumption and performance can be achieved. The LEGOS/DYNBIO team is moving towards integrated silicon technology microelectrodes, which allows a low cost collective fabrication.

B.3.3 PRESENTLY AVAILABLE SENSORS

B.3.3.1 The Satlantic ISUS and SUNA, UV spectrofotometers

The Satlantic ISUS and SUNA spectrofotometers (figure B5 and B6) are the first commercially available NO_3 sensors based on UV absorption technique. They are based on the same conceptual approach (absorption in the UV region of the spectrum). The main differences concern the software interfaces, the acquisition methods, which are more flexible in the SUNA model, and the size, which is more reduced for the SUNA more recent sensor. Though accuracy is relatively low compared with standard method (+/- 0.5 μM/L), the main concern about the SUNA/ISUS implementation on autonomous platforms is related to the energetic consumption, as UV lamp is extremely demanding in energy. The protocol used by Johnson et al. (2006) to save energy of an APEX profiling float was consequently based on a discrete sampling strategies. The sensor is then switch on/off at 30 fixed depths.

Figure B5. The ISUS Satlantic NO_3 sensor

Figure B6. The SUNA Satlantic NO_3 sensor

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APPENDIX C: QC FOR CHLOROPHYLL

C.1 SYNOPSIS

The Chlorophyll-a concentration parameter is presently measured on profiling floats, gliders and animals. As already indicated, two measuring methods are mostly used: the first, based on the fluorescence, the second, based on the radiometric inversion of irradiance data.

Fluorescence is historically the most widely used approach, and it will be then considered as the reference method to evaluate the chlorophyll-a concentration. Radiometric inversion based estimations of chlorophyll-a are, however, more accurate when compared with classical HPLC samples. When data are available, then, they will be used to ameliorate, to confirm, and to correct the fluorescence based observations.

For the Chlorophyll-a QC proposed in the follow, the provenance of the data is not considered. In the follow, the only hypothesis for the proposed QC process is that the incoming data have a "profile-like" format: the observations should be vertically organized from surface to the maximum depth reached during the sampling. In this context, "vertical" means the direction orthogonal to the sea surface.

Gliders and animal data require then a pre-processing step, as they are collected along trajectories, which could deviate from the strict profile-like data structure. Data are then initially decoupled in sections, separating the trajectories comprised between the surface and the maximum depth (or *viceversa* depending on the acquisition protocol). Data from each section are then treated as a profile, although they are generally collected along a direction not strictly orthogonal to the sea surface. The position and timing of the final profile are generally assumed as the mean of the correspondent raw data.

In some cases (i.e. for gliders acquiring data in both the ascending and descending phases), two subsequent sections could be averaged in a single profile or keep separated as two distinct profiles. The pre-processing of gliders and animals data is then independent of the QC, and is generally performed before the QC.

Measure unit for chlorophyll-a concentration is the mg/m^3. If a different unit is used, data should be transformed before performing the QC, as threshold values for most of the proposed tests are calibrated for concentrations expressed in mg/m^3.

In the next, we then assumed that the input data is a profile, with a unique lat/lon position and acquisition GMT time, and with chlorophyll-a concentrations expressed in mg/m^3.

Chlorophyll-a concentration Quality Control (ChlQC) will follow the same strategy of the ARGO QC for temperature and salinity. It is then performed using a three levels approach: "Real time" (RT), "Adjusted" (A) and "Delayed" modes (DM).

In the next, only the RT mode adaptation of Argo QC to the Chlorophyll-a parameter will be detailed, as the number of observations is still too low to clearly determine the correct procedures for the Adjusted and the Delayed modes. However, some hints will be proposed, mainly derived by the scientific activities on the fields and by similar methods already existing for T and S.

C.2 THE "REAL TIME" MODE

The ARGO QC RT mode is based on 19 successive tests, which assess, in an automatic way, the quality of the observations. The results of the tests are summarized assigning a QC flag, which ranges from 1 (good data) to 4 (bad data). A 0 value is assigned if QC is not performed.

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Most of the ARGO QC RT tests are performed to identify problems related to bad geo-localisation, erroneous timing, wrong platform identification, pressure errors etc. For these tests, the ARGO procedure is strictly adopted also for the RT ChlQC. More specifically:

Test 1. Platform Identification

Test 2. Impossible date test

Test 3. Impossible location test

Test 4. Position on land test

Test 5. Impossible speed test

Test 8. Pressure increasing test

Test 13. Stuck value test

Test 15. Grey List

Test 17. Visual QC

Test 19. Deepest pressure test

For a detailed description of these tests, the reader is referred to the latest version of the Argo quality control manual.

Another set of tests is not applicable to the Chlorophyll-a parameter. Specifically:

Test 7. Regional Test.

Chlorophyll-a concentration is much more variable than Temperature and Salinity. This variability is observed on the vertical, on the horizontal and on the temporal scales, and it can spawn between 2-3 orders of magnitude. A regional test, which should check the quality of data in sea regions having specific (and identified) characteristics, appears presently not applicable to Chlorophyll-a concentration. In the future, however, the test could be implemented, if the increased data collection will allow the identification of anomalous regions, requiring a specific treatment.

Test 12. Digit Rollover test.

At present day, no problems related to the storage of data on autonomous platforms are identified for the Chlorophyll-a Concentration parameter. The platforms dedicated to the autonomous observation of Chlorophyll-a are developed recently, allowing the exploitation of data storage medium of increased capacity.

Test 14. Density inversion.

Inapplicable.

Test 16. Gross Salinity or Temperature sensor drift.

In principle, this test could be used to check the stability of the fluorescence sensors, exactly in the same way as it was implemented for Temperature and Salinity in the Argo RT QC. However, in this first version of the RT ChlQC, we suggest to don't implement this test. The

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main reason is that deepest fluorescence values could be used to verify the pertinence and the validity of the correspondence fluorescence = chlorophyll-a.

Four tests of the Argo RT QC systems required modifications to be adapted to the Chlorophyll-a parameter. In some cases, the modification concerned only a simple re-adjustment of the test's parameters (i.e. Global range test), to fitting the specificity of the chlorophyll-a parameter.

Test 6. Global range.

Global test range is a first, rough, test to identify spurious or strongly erroneous data. The rationale is that, outside a specific range, data cannot be considered good, as never observed in natural conditions.

The application of a global range test to the Chlorophyll-a concentration is, however, complicated by the extremely high degree of variability of the chlorophyll-a parameter. Satellite derived statistics on the frequency distribution of the surface layers show that chlorophyll-a concentration follows a log normal distribution, with extreme's range spanning between 2-3 orders of magnitude. Additionally, vertical distribution is intricate, as chlorophyll-a concentration is not monotonic with depth. "Standard" profile is characterized by a sub-surface maximum, which could be 10-20 times greater than surface values, and by deep concentrations close to zero. This "standard" picture, already puzzling, is, however, still more complicated by the variability of biogeochemical and physical dynamic of the oceans (i.e. deep mixing events homogenizing the chlorophyll-a concentration for hundreds of meters, photoprotection or photobleeaching mechanisms producing daily variability on surface layers, two or three sub surface maxima resulting by lateral intrusion of surface water, etc).

Negative values could also occur, ascribed mainly to instrumental and electronic noise of the fluorescence sensors. At depth (i.e. no natural light, no chlorophyll-a), negative values, generally very low in absolute, could be obtained. The main responsible in this case is the fluorometer calibration (and in particular the "dark" parameter of the calibration equation), which could retrieve negative values, when in water concentrations approx to zero.

A statistical analysis performed on the LOV-PROVBIO fluorometer data demonstrated that negative values are generally of two different types: large negative values (i.e. -1,-2 mg/m^3), which could be obtained everywhere along a profile (i.e. no dependence with depth) and very low negative values, which result quite exclusively at depth (i.e. more than 300 meters). The firsts should be flagged as bad data. For the seconds, we propose to fix as a lower limit for the global range test the value of -0.1 mg/m^3, as observations in the interval -0.1-0.0 mg/m^3 should be corrected in a second phase (i.e. Adjusted or Delayed modes).

The value of -0.1 mg/m^3 corresponds approximately to 4 bin counts of a standard fluorometer.

Global range for chlorophyll-a concentration is then fixed to 0.00 – 50.00 mg/m^3. Negative values are flagged as bad data if they exceed -0.1 mg/m^3. Otherwise, they are flagged with flag "3", as they are potentially correctable.

Test 9. Spike test

Argo test number 9 is primarily devoted to the identification of spike, defined as "measurement quite different than adjacent ones" (Argo QC manual, version of February 2009). The spike test is implemented by computing a "test value" defined as:

$$Test\_Value = |V2 - (V3 + V1)/2| - |(V3 - V1)/2|$$

-

where V2 is the measurement being tested as a spike, and V1 and V3 are the values above and below. Measurements are identified as a spike when Test_Value exceeds a fixed threshold value. Test_Value is independent of the depth and of the vertical resolution, though threshold values are different for the two main layers of Argo protocol (upper layer 0-500 m at 10 m resolution, deep layer, 500-2000 m at 25 m resolution).

The simple adaptation of the Argo Spike test to the chlorophyll-a parameter is complicated by the important differences between T and S and chlorophyll-a vertical distributions:

1. chlorophyll-a concentration is not uniformly increasing or decreasing with depth;
2. the sub surface chlorophyll-a maxima could be extremely sharp, as chlorophyll concentration values could increase (and decrease) of one or two orders of magnitude in few teens of meters;
3. chlorophyll vertical distribution could be highly noisy, especially at depth, where concentrations are (or should be) close to zero .

For the ChlQC, we propose then to maintain unchanged the functional form of the spike test algorithm, introducing, however a threshold value depending of the data. The proposed form for the threshold is:

$$\textbf{Threshold\_Value} = |\textbf{median}(V0,V1,V2,V3,V4)| + |\sigma\,(V0,V1,V2,V3,V4)|$$

where, V1,V2 and V3 are as in the previous formulation, V0 and V4 are, respectively, the values above V1 and below V3, and σ is the standard deviation operator.

The proposed formulation has the advantage to identify as a spike, observations that are locally different of the surrounding data. The use of 5 points for the median and standard deviation computation allow to better account for the high local variability of the chlorophyll-a field, without dramatically change the functional form of the test.

Test 11. Gradient Test

Argo gradient test is introduced to identify data points having difference between vertically adjacent observations too sharp. Similarly to the spike test, it is implemented in the Argo QC, by calculating a test value defined as:

$$\text{Test\_value} = |V2 - (V3 + V1)/2|$$

where V1, V2 and V3 are as in the spike test. Observations with test_value exceeding a fixed threshold value are flagged as bad data.

Although relevant for Temperature and Salinity that change relatively slow with depth, this test is less appropriate for the Chlorophyll-a parameter, which could rapidly increase or decrease in few meters (see discussion in the Spike test).

We decided to maintain the test for the ChlQC in his present form, fixing however an elevated threshold value. The declared (and limited) objective of this test is to flag points really bad, which, for some reasons, have pass the spike test.

For the ChlQC, we propose then to maintain unchanged the functional form of the gradient test algorithm. The proposed threshold value is fixed at 3 mg/m^3.

Test 18. Frozen Profile Test

To be implemented

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C.3 THE "ADJUSTED" AND THE "DELAYED" MODES

The real time ChlQC assumes that transmitted fluorescence data are well calibrated. Then, the RT checked data are stocked in the data base as measurements of Chlorophyll-a Concentration. Although in a first approximation (i.e. RT) this assumption could be considered realistic, it could not be exact, and needs to be verified.

Fluorescence could give an erroneous estimation of the Chlorophyll-a content. Two main situations can be defined: the relationship Fluorescence/Chlorophyll-a is:

1. erroneously determined by the fluorometer manufacturer
2. correctly characterized by manufacturer but temporarily or permanently degraded

The two situations required a different processing of the data.

In the first case, data are affected by a calibration problem, which concerns all the data of a specific instrument, and which could be, at least in theory, corrected by a re-calibration of the fluorescence observations.

In the second case, the error could affect only a limited portion of the fluorescence data obtained by a specific instrument, even if the initial calibration should be considered correct. This should be the case, for example, for profiles affected by important biofuling. Again, following the strategy of the Argo QC system, we proposed to address the issue of the calibration fluorescence/chlorophyll-a in the "Adjusted" mode and the issue of stability of the chlorophyll-a estimations in the "Delayed" mode.

C.3.1 THE "ADJUSTED" MODE

Chlorophyll-a data stored as "Adjusted" differs from the RT data as their fluorescence/chlorophyll-a relationship has been checked.

Adjusted Chlorophyll-a data could be recalibrated, if biases on the RT data are identified, on the basis of information derived by external or ancillary method. Although methods are still in progress, some hints are given in the follow.

C.3.1.1 HPLC calibration

The best way to check the validity of the relationship fluorescence/chlorophyll is to compare fluorescence data to concurrent chlorophyll estimations obtained with standard methods, as HPLC or equivalent.

A water column HPLC determination of the chlorophyll concentration should be considered mandatory every time an autonomous mission starts.

HPLC estimations should be performed as close as possible in time and in space to the deployment of the autonomous platform. HPLC data should be stored in the meta-data of the missions and a re-calibration of the RT data should be performed, if biases are detected. The corrected data should be stored as "Adjusted" data.

In the case of recoverable platforms (i.e. gliders and, in some case, animals), an HPLC profile should be also performed at the end of the mission, when platform is recovered.

If the collection of concurrent HPLC samples is impracticable, fluorometers should be calibrated in laboratory, before and after the sea operations.

For recoverable platforms, the HPLC calibration of the fluorometer data should be considered the primary method to verify the consistency and the accuracy of the Chlorophyll-a estimations.

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C.3.1.2 Radiometric Data

As already introduced before, the inversion of radiometric data and the further application of bio-optical algorithms could allow an independent and alternative estimation of chlorophyll-a concentration, which could be then used to verify the precision of the fluorimetric data.

Before their introduction as input for bio-optical algorithms, the autonomously collected irradiance data should be submitted to a specific RT QC, which is, presently, not still implemented.

When radiometric data are available (i.e. PROVBIO-A/B), chlorophyll-a concentrations derived by radiometric inversion could be used to verify the accuracy of the fluorimetric based estimations.

C.3.1.3 The shape of the chlorophyll-a profile

More than 20 years ago, Morel and Berthon (1989) demonstrated that, at the first order, a statistically relevant relationship exists between the vertical distribution of the chlorophyll-a concentration and his surface signature (see also UItz et al. 2005 for a recent confirmation). Implicitly, the Morel and Berthon (1989) results indicated that the adimensional shape of the vertical distribution of chlorophyll-a cannot be considered totally independent to the surface and sub-surface concentrations.

In the context of the calibration of a remote fluorimeter, statistical relationships inferred from a CTD and HPLC database regrouping 18 cruises over the global ocean are used to determine key shape parameters of fluorimetric profiles. The obtained empirical relationships are then used to recalibrate the entire vertical fluorescence profile on chlorophyll-a concentration.

C.3.2 THE "DELAYED" MODE

The delayed mode allows a more precise assessment of the data set accuracy, as statistics and tests can be applied to a long time series. During the delayed mode process, visual inspection of the profiles is also required, and generally performed by the scientists involved in the scientific exploitation of the data (and, then, not by the data center). This approach allows the identification of data problems that passed all the automatic tests.

For the ChlQC, the delayed mode should check the occurrence of important deviations in the time series, which should concern a single profile or a series of profiles.

This type of deviations could be ascribed to

1. a temporary failure of the fluorescence calibration; the relationship chlorophyll-a/fluorescence is dependent of the phytoplanktonic species and on the trophic and light regime of the phytoplankton communities; even then a well calibrated fluorimeter could retrieve erroneous data if it is sampling a region where a specific and located pytoplankton event take place
2. a strong degradation of the sensor accuracy; in this case, observations of an autonomous platform, initially of a good quality, could become less and less truthful; for evident reasons, the recognition of this situation is particularly crucial for not recoverable platforms (as profiling floats and animals);

Additionally to the visual check performed by experts on the field, we suggest, for the Delayed mode ChlQC two semi-automatic methods, which aim principally to identify temporary or permanent bias in the time series.

C.3.2.1 Using Satellite data

Satellite ocean color sensors collected routinely surface chlorophyll-a concentration from the space. Presently (July 2009), 4 ocean color satellites are operational, and even if data from different satellites are not entirely coherent, the spatial and temporal coverage of the global ocean

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is now extremely elevated. Satellite observations could be used to routinely (i.e. 6 months) check the stability of the in situ platforms data

C.3.2.2 The chlorophyll-a climatologies

Existing climatologies for chlorophyll concentration (i.e. Conkright et al, 2001) are presently not suitable to check the quality of autonomous platform observations. Developed with the primary aim of producing "gap free" arrays, climatologies are computed by intensively interpolating (horizontally and on the vertical) the scarce available data (only discrete chlorophyll estimation are used).

An additional effort is then required to produce a new type of climatology, without, or with a slight use, of any interpolation procedures. They should be also merged with surface satellite observations to increment, at least on surface, the spatial coverage.

A delayed mode procedure, based on the consistence between the autonomously acquired data and the climatology, could be then implemented, although, initially, it could be effective only in some regions (i.e. where climatology "without interpolation" are available).

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