E-AIMS
Euro-Argo Improvements for the GMES Marine Service

Biogeochemical float experiment
Final evaluation
D2.3.2

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Authors: Kjell Arne Mork (Institute of Marine Research), Giorgio Dall'Olmo (Plymouth Marine Laboratory), Violeta Slabakova (Institute of Oceanology), Emil Stanev (University of Sofia)

Lead:

Institute of Marine Research, Norway

Co-ordinator:

Institut Français de Recherche pour l'Exploitation de la Mer - France
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1. Summary

The biogeochemical float experiment was carried on by deploying six Argo floats with biogeochemical sensors (PROVOR BIO-Argo) in three different regions with different physical, chemical and biological conditions; two floats in the Nordic Seas, two floats in the Atlantic Ocean, and two floats in the Black Sea. Of the six floats one float was lost after one profile while two floats transmitted intermittent GPS data. Also, one of the latter stopped transmission after 78 profiles. Another float stopped transmitting in August 2015, after nearly two years operation. Thus, by September 2015 three floats, one in each region, are still active.

Despite some GPS problems with some of the floats, this experiment showed that the biogeochemical floats deliver novel data that improve our understanding of the biogeochemical ocean. For instance, in this study the seasonal dynamics of the particle size distribution in two regions was determined by the optical backscattering sensors on these floats. The data from these floats have also already been used in several other studies which also have resulted into submitted peer-review manuscripts.

The biogeochemical measurements acquired in this experiment also raised some new questions about the performance of some of the sensors. For instance, some interesting peaks from one of the fluorescence/backscattering sensors at 850-1000 dbar were observed after four months of operation. The reason is not clear, but a hypothesis exist that small organisms (e.g., plankton/small fish) were attracted by the light from the sensor. In addition, in the Black Sea the calculated chl-a showed maximum concentration in the upper layer, thereafter it decreased to minimum at ~100 m depth, and then increased slightly in the deep layers (~0.02 mg/m^3/100m). The reason for this chl-a increase in the deep sea is still not well understood, but need further investigations.

This study also revealed that in oligotrophic regions the particulate optical backscattering sensors should have higher instrumental sensitivity. As shown in this report, the spectral differences in the particulate optical backscattering spanned over a very restricted range in the North Atlantic sub-tropical gyre due to a combination of low instrument sensitivity and lack of significant changes in signals in this oligotrophic region of the ocean.

The ECO-Triplets on the two floats in the Atlantic Ocean were affected by significant instrumental drift and/or biofouling after less than one year of operation. In addition, one of the sensors malfunctioning when it was exposed to pressures greater than 1000 dbars.

In the section “Recommendation” in this report some recommendations are given on how to handle the biogeochemical floats and sensors to get optimal quality of the biogeochemical data.
2. Introduction

2.1. General presentation

This document contains the description of the Biogeochemical float experiment final evaluation. It is the deliverable D2.232 identified in the description of work DA-1, in the table WT 2, page 2, which is due by the end of June 2015 (T0+30), T0 being the 1st of January 2013.

2.2. Applicable documents

DA-1: Annex 1 to the grant agreement N0 312642: “Description of work”, date 24 April 2012.

2.3. Biogeochemical floats

The observation of biogeochemical cycles and ecosystems has traditionally been based on ship-based platforms with the obvious consequence that measured properties have always been under sampled. Recent technological advances in miniature biogeochemical sensors and autonomous platforms now open remarkable perspectives for observing the “biological” ocean, notably at critical spatio-temporal scales which have been out of reach until recently (Claustre et al., 2010). Use of biogeochemical sensors on Argo floats can revolution our understanding of the coupling between ocean physics and biology (e.g. Claustre et al., 2010). Additionally this is the only way to start the acquisition of global long term time series of biogeochemical variables in the ocean interior from which climatic trend could be eventually detected in the future. Developing biogeochemical observations is also a strong requirement from GMES Marine Service (see EEA GISC report).

2.4. Bio-Argo array

The rationale for the development of a BIO-Argo float array is to enable a cost effective global observation system that would greatly reduce the uncertainties in our estimation of elemental (C, N, O) fluxes at the global scale and our ability to detect change in these processes. This objective will be achieved by developing a generic, low cost, low consumption bio-optical/biogeochemical payload that would be disseminated through the Argo network and would take advantage of the existing infrastructure. Rather than a global network, it might be more efficient to first implement regional approaches. It has thus been proposed (Johnson et al., 2009; Claustre et al., 2010) that pilot studies could be conducted at regional scales in some biogeochemically-relevant "hotspots". There are indeed regional "hot-spots" that are natural laboratories for addressing key scientific questions of global relevance, and which would benefit from being tackled in a highly integrated way. These pilot studies could serve as test cases for evaluating the design and efficiency of a BIO-Argo array, in particular with respect to data management and dissemination. For all these areas, the potential link and synergy with ocean color products is obvious. Dissolved oxygen is
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one of the most important biological parameters that can be monitored in the ocean, and there are now over 260 Argo floats carrying oxygen sensors (Fig. 1.1). There are also now an increasing interest in floats with bio-optical sensors (e.g. Chla fluorescence, backscattering, Nitrate, etc.) and at present there are now over 100 bio-Argo floats with bio-optics (Fig. 1.1).

![Figure 1.1: The distribution of biogeochemical sensors on Argo floats as of June 2015, provided by the Argo Information Centre.](image)

2.5. Application – sensors/parameters

Within this task experiments with Argo floats that include biogeochemial sensors were performed to measure their performance. Tests were conducted in ocean provinces with contrasting biogeochemical properties. The additional biogeochemical sensors include dissolved oxygen, fluorometer (chl-a), backscatter, downwelling irradiance and Photosynthetical Available Radiation (PAR). Below are short description and application of the different biogeochemical sensors.

Dissolved oxygen

Dissolved oxygen concentration is a key quantity for ocean biogeochemistry. It permits study and document of the oceanic impact of global warming on ocean biogeochemistry and circulation, estimates of net community and export production, improved estimates of the oceanic uptake of anthropogenic CO2, improved estimates of ocean ventilation, monitoring of deep convection events and even constraints and the transfer coefficient for air-sea gas exchange.

Fluorescence - Chlorophyll

The fluorescence signal are converted into chlorophyll-a (chl-a) concentration (in mg m-3) using the linear relationship provided by the manufacturer. Chl-a is widely used as a proxy for phytoplankton biomass. The planktonic ecosystems play an important role in the ocean's carbon cycle and the biogeochemical cycles of other important chemical elements. Past studies suggest
that phytoplankton play a critical role in removing greenhouse gases such as CO2 from the atmosphere.

**Backscatter**

The backscatter sensor is an optical sensor that measures the particle concentration by how light is scattered in a backward direction by particles in the water. The backscatter signal can with reasonable accuracy be converted to particulate organic carbon (POC), which is the main source of particles in the open ocean.

**Downwelling irradiance**

The sensor measures the intensity of light penetrating to different depths in the water at specific wavelengths. From these data the diffuse attenuation coefficient of downwelling irradiance (Kd) can be determined. Kd is an important optical properties of seawater as it can be used to quantify the presence of light and the depth of the euphotic zone.

**Photosynthetically available radiation (PAR)**

The PAR sensor measures the intensity of light that are available for photosynthesis, penetrating to different depths in the water. Light diminishes with depth depending on the turbidity of the water. Combined with chlorophyll data this makes it possible to calculate actual phytoplankton production of new organic carbon and relate this to the ocean's uptake of carbon dioxide.
3. **The biogeochemical floats and sensors**

3.1. **The biogeochemical floats**

The French company NKE now provides a float that is designed to be equipped with several different types of biogeochemical sensors, the PROVOR BIO-ARGO CTS4. Six floats of this type were ordered and all six floats had similar equipments. Beside the traditionally CTD the floats were equipped with biogeochemical sensors (oxygen, irradiance, chl-a and backscattering). More specific the sensors on the floats are:

The sensors:

- Pressure, temperature and salinity with the SEABIRD SBE41CP CTD sensor
- Dissolved oxygen with the Oxygen Optode Aanderaa 4330 sensor (multi calibrated)
- Rem A pack – fully integrated (SATLANTIC):
  - OCR503 Irradiance (PAR + 3 wavelengths 380, 412, and 490 nm)
  - ECO Triplet (chl-a + backscattering 532 and 700 nm)

Battery:

The floats use Lithium batteries as energy source and has 66% increased battery capacity compared to the common PROVOR CTS3 used for Argo application.

Communication:

While the float is at the surface, the Iridium transmitter sends stored data to the satellites of the Iridium systems (RUDICS). The communication is two-ways that allow the user to change the mission parameters underway.

Cycle time:

It has been shown from the analysis of BIO-Argo float data (Boss et al., 2008) that the space and time correlation of biological variables are much shorter than that of physical variables. With this respect the cycle time of the six biogeochemical floats is set shorter than the standard 10 days. Within this experiment the cycle time will be 5 days.
3.2. Deployment areas

All the six floats were deployed from October 2013 to January 2014. The biogeochemical float experiment will be carried out in three different areas (Fig. 2.1):

- 2 floats were deployed in the Atlantic Ocean by UKMO/PML
- 2 floats were deployed in the Nordic Seas by IMR
- 2 floats were deployed in the Black Sea by IO-BAS/USOF

Figure 2.1: Schematic view of the deployment of the six biogeochemical floats.
4. The experiments

4.1. The experiment in the Atlantic Ocean (UKMO/PML)

Introduction

Two NKE Provor CST4 floats (metbio001b and metbio002b) were deployed by PML-UKMO during E-AIMS. In addition to the standard CTD, each float mounted the following set of biogeochemical sensors:

- Aanderaa oxygen optode 4330
- Satlantic Rem-A sensor including a WETLabs ECO-Triplet (with three channels to measure chlorophyll-a fluorescence, and optical backscattering at 532 and 700 nm) and a Satlantic OCR540 (with four channels measuring downward irradiance at 380, 412, 490 nm and a channel for photosynthetically available radiation, PAR).

Both floats were deployed during the 23rd Atlantic Meridional Transect on October 13th, 2013 around 30.37°N and 23.16°W.

Metbio001b

![Figure 3.1.1: WETLabs ECO-Triplet data from cycle 4 (max depth 1000 m).]

This float (metbio001b) was initially programmed to collect data over the top 1000 m. Although the physical and biogeochemical data transmitted appeared to be of good quality (Figure 3.1.1),...
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the float had problems with acquiring GPS location. From the 5th cycle, the float was set to
collect data down to 2000 m. However, after descending to 2000 m, the ECO-Triplet data showed
clear signs of instrument/float malfunctioning: step changes in the profiles of chlorophyll-a and
backscattering appeared around 450-500 m (Figure 3.1.2). As of now the causes of this problem
have not been identified and, upon request, WETLabs was not able to provide the data collected
during the pressure test of the instruments. The problem with the ECO-Triplet has persisted since
cycle 5, even though the maximum depth was re-set to 1000 m after cycle 58 (27th Feb 2014).

Data were also collected at the parking depth to monitor instrumental drift, based on the
assumption that the concentration of particles in deep waters does not vary significantly over
time. Figure 3.1.3 shows that two opposite trends are observed in the 532 and 700-nm optical
backscattering channels.

![Figure 3.1.3: Daily averages of data collected by metbio001b during the parking phases of its mission from October 2013 to December 2014.](image)

The parking values from the green channel (532) decreased from May to September 2014 by
about 30 counts. This decline is unlikely caused by bio-fouling, which instead would cause an
increase in the signal. Therefore we speculate that the green channel might have drifted due to
instrument degradation. Interestingly, the decline begins 2.5 months after the maximum depth of
the cycle was re-set to 1000 m. Therefore it is difficult to link this decline to exposure to high
pressure conditions.

The red channel (700 nm) instead showed an opposite trend which began at the same time of the
decline in the parking values of the green channel and reached saturation (>4000 counts) in
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October 2014. In the ECO-Triplet the detector measuring light at 700 nm is shared between the 700-nm backscattering channel (700 nm light source) and the chlorophyll-a fluorescence channel (470 nm light source). However, only a minor deviation from the initial values is visible in the data from chlorophyll channel at the parking depth when the red channel saturated (blue points in Figure 3.1.3). On the other hand, values of chl in the upper water column declined to very low values (not shown). This may indicate that the bio-fouling agent likely covered the 470 and 700 light sources, but not the 700 nm detector.

Metbio002b

Unlike metbio001b, this float was programmed to sample over the upper 1000 m and its GPS worked as expected. Profiles from the ECO-Triplet did not show step changes as for the instrument deployed on metbio001b. Data collected while drifting at the parking depth showed that the green backscattering channel remained stable during the first 11 months of operation (Figure 3.1.4). During the last 3 months, however, its signal at 1000 dbar has begun declining and is currently about 10 counts lower than the deployment value. No drift was instead observed for the red backscattering or for the chlorophyll-a channel.

![Figure 3.1.4: Daily averages of data collected by metbio002b during the parking phases of its mission from October 2013 to December 2014.](image)

Spectral backscattering
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One of the novelties of the biogeochemical instrumentation mounted on the E-AIMS floats funded under WP2 is a 2-channel optical backscattering instrument. These two channels (532 and 700 nm, Figure 3.1.5) should allow us to estimate the spectral dependency of particulate backscattering (b_{bbp}), which is related to the slope of the particle size distribution in the water column. Specifically, as the ratio b_{bbp(532)}:b_{bbp(700)} increases, we expect a relative increase in the concentration of small vs. large particles (Kostadinov et al., 2009).

![Figure 3.1.5: Particulate backscattering coefficients at 532 and 700 nm measured by metbio002b. White lines are estimates of the mixed-layer depth.](image)

Figure 3.1.6 shows that the b_{bbp(532)}:b_{bbp(700)} ratio varied over a restricted range, suggesting that the sensitivity of the ECO-triplet was insufficient for detecting changes in spectral backscattering in the oligotrophic ocean sampled by metbio002b. Further inspection of the instrument scaling factors indicated that the sensitivity of the 532-nm channel was 2.2 times lower than that of the 700-nm channel. Nevertheless, to first order b_{bbp(532)}:b_{bbp(700)} decreases as a function of depth suggesting that small particles become more abundant in the mesopelagic zone.

![Figure 3.1.6: Particle backscattering coefficients at 532 and 700 nm measured by metbio002b. White lines are estimates of the mixed-layer depth.](image)
Spectral downward irradiance measurements

Another novel instrument mounted on the experimental biogeochemical E-AIMS floats is the Satlantic OCR504. This instrument measures planar downward irradiance (Ed) at three separate wavelengths (380, 412, 490 nm) as well as integrated between 400 and 700 nm (PAR, for “photosynthetically available radiation”). Figure 3.1.7 presents the measurements of Ed collected by metbio002b. As expected, Ed declines exponentially with depth and shows a seasonal cycle. High-frequency variations are due to clouds. The data also show that Ed penetrates progressively deeper into the water column as the wavelength shifts from the UV (i.e., 380 nm) to the blue spectral region (i.e., 412, 490 nm).

Figure 3.1.7: Downward irradiance from metbio002b. White lines are the mixed-layer depth.
To further investigate these differences, the spectral vertical diffuse attenuation coefficient for downward irradiance, $K_d(\lambda, z)$, was computed by applying the following equation to smoothed $E_d$ data:

$$K_d(\lambda, z) = -\frac{1}{\Delta z} \ln \left[ \frac{E_d(\lambda, z)}{E_d(\lambda, z_0)} \right]$$  \hspace{1cm} \text{[Eq. 1]}

Although Eq. 1 does not correct $E_d$ profiles for contamination by clouds (Xing et al., 2011), Figure 3.1.8 demonstrates that the derived $K_d$ values provide, nevertheless, a useful view on the spectral attenuation of light in the water column. As expected from the discussion about Figure 3.1.7, $K_d$ was higher in the UV region than in the blue (Figure 3.1.8). Moreover, $K_d$ displayed vertical variability likely related to the different biogeochemical processes affecting the absorption coefficients (e.g., Mobley 1994) of the dissolved and particulate constituents that are optically active at in this spectral region. The most important of these constituents are pure water, coloured dissolved organic matter (CDOM) and phytoplankton cells.

![Figure 3.1.8: Vertical diffuse attenuation coefficient for downward irradiance, $K_d$, at different wavelengths as recorded by methio002b. White lines are estimates of the mixed-layer depth. Values at the bottom of the profiles are anomalous due to increased noise at low light levels.](image-url)
The value of the absorption coefficient of pure water at 380 nm is approximately 0.01 m\(^{-1}\) (Pope and Fry, 1997) and is a constant, thus the variable and relatively high values of Kd(380) reported in Figure 3.1.8 must be due to either CDOM or phytoplankton. The spectral shape of the absorption coefficient by CDOM increases exponentially towards shorter wavelengths. On the other hand, the spectral absorption by phytoplankton peaks around 440 nm (Bricaud et al., 2010). Thus relatively high values of Kd(380) most likely indicate the presence of relatively high concentrations of CDOM. The top plot of Figure 3.1.8 shows that, as the mixed-layer deepens at the beginning of the mission, the concentration of CDOM in the mixed-layer progressively increases likely due to entrainment of CDOM from below the mixed-layer and to production of new CDOM by phytoplankton. When the mixed layer shallows the concentration of CDOM decreases within the mixed layer due to low CDOM production and photo-oxidation caused by relatively high irradiance levels.

Relatively low values of Kd(380):Kd(490): indicate a relative decline in CDOM absorption with respect to the absorption by phytoplankton and pure water (e.g., Figure 3.1.9 near the surface at the end of the mission).

**Conclusions – North Atlantic**

This analysis of the data from the two PML-UKMO floats funded by WP2 of E-AIMS (metbio001b and metbio002b) allowed us to draw the following conclusions:

- The GPS signal was received only intermittently by metbio001b.
- The WETLabs ECO-Triplet mounted on metbio001b failed after it was exposed to pressures greater than 1000 dbars.
- The WETLabs ECO-Triplets installed on both floats were affected by significant instrumental drift and/or biofouling after less than one year of operation.
- Spectral differences in particulate optical backscattering spanned over a very restricted
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range in the North Atlantic sub-tropical gyre due to a combination of low of instrument sensitivity and lack of significant changes in signals in this oligotrophic region of the ocean.

- Downward irradiance data collected in the upper 250 m of the water column decreased, as expected, in an exponential manner with depth and displayed spectral variations that are related to the optically-active constituents that dominate the water column absorption in this spectral region (i.e., CDOM and phytoplankton).
4.2. The experiment in the Nordic Seas (IMR)

The phytoplankton bloom and production is an important factor for the zooplankton production in the Norwegian Sea. Additionally, marine particles produced by photosynthesis sink and consequently carbon is exported from the surface to the deep sea, which contributes to the removing of anthropogenic CO2 from the atmosphere. Data from biogeochemical sensors from Argo floats are used to study the seasonal and interannual variability of the phytoplankton bloom, the primary production and the vertical carbon flux in relation to physical processes such as the mixed layer depth.

The Nordic Seas is characterized by warm, saltier Atlantic Water (AW) in the east deriving from the North Atlantic and cold, fresher Arctic Water in the west. The upper layer of the Norwegian Sea is mainly occupied by the AW (Fig. 3.2.1), except in the southwestern part where it is influenced by Arctic water that is transported from the Iceland Sea.

Both biogeochemical floats were deployed in January 2014 during a cruise with R/V Johan Hjort, when one float was deployed in the Norwegian Basin (64.66ºN, 0.50ºW; float: imrbio001, WMO-id: 6902546,) while the other float was deployed in the Lofoten Basin (69.13ºN, 7.31ºE; float: imrbio002, WMO-id: 6902547). See Figure 3.2.1 for the deployment locations.

Results

**Float imrbio001**: The float passed all tests in advance and deployed without any problem. However, after one cycle there has been no contact with the float and it is considered lost. 

**Float imrbio002**: This float transmitted data and GPS positions as expected and in September 2015 it was still active. The float drifted within a limited area in the Norwegian Sea (see Figure 3.2.2). The cycle time was one day for the first four profiles and five days afterwards. All results are therefore based on this float.
Temperature, salinity and density

The temperature and salinity data revealed the Atlantic Water in the upper 600-700 m. During summer low-salinity water from the Norwegian Coastal Current is observed as a thin fresh surface layer in the upper 40 m (Figure 3.2.3). In mid-November 2014 the float was trapped into an eddy as shown by the change in temperature and salinity. The eddy was also visible in satellite sea level anomaly (not shown). The depth of the mixed layer was the depth when the potential density changed by 0.03 kg/m³ from the surface (the shallowest measurement, ~5-10 m depth).

![Temperature, salinity, and potential density sections from float imrbio002 (from Jan-2015 to Sep-2015). The thick white line is the estimate of the mixed layer depth. The dashed line in the sigma-theta section is the 28 kgm⁻³ isopycnal.](image)

**Dissolved oxygen**
The dissolved oxygen and the apparent oxygen utilisation (AOU) are shown in Fig. 3.2.4. The AOU is the difference between the measured dissolved oxygen concentration ([O2]) and its equilibrium saturation concentration in water ([O2]_{sat}) with the same physical and chemical properties (AOU = [O2]_{sat} - [O2]). Such differences typically occur when biological activity acts to change the ambient concentration of oxygen. Consequently, the AOU of a water sample represents the sum of the biological activity that the sample has experienced since it was last in equilibrium with the atmosphere. The measurements (high values of O2 and low values of AOU) indicate high biological activity during spring and early summer in the upper few tens meters (Fig. 3.2.4).

A drift in the dissolved oxygen and AOU near the parking depth (data are averaged between 950-1000 m depth) and on the isopycnal 28.0 kg m^{-3} (see Fig. 3.2.3, lower figure) is observed during 2014-2015 (Figure 3.2.5). The oxygen concentration decreased with about 4-5 µmol kg^{-1} year^{-1}. In the beginning (February) of the time series this seemed to be caused by changes in the water mass but afterwards this must be due to a drift in the sensor.
Chlorophyll and backscattering (ECO triplet)

The fluorescence signal are converted into chlorophyll-a (chl-a) concentration (in mg m^-3) using the linear relationship provided by the manufacturer. The dark count for the sensor was measured before deployment and was found to be similar to the manufacturer’s value. The measurements detected the spring phytoplankton bloom in early March during a deep mixed layer depth (Fig. 3.2.6, upper figure). Maximum chl-a occured in mid May while during winter (January-February) the chl-a is close to zero (due to absent of phytoplankton). No trend in chl-a at the parking depth is observed but peaks are observed at this depth and depths larger than 850 dbar (Figure 3.2.7). A bias for each profile can often calculated using the deepest measurements, but as shown here the data must be carefully studied in advance. Overall the chl-a concentration seems to have a bias of 0.085 mg m^-3 in the whole water column.

A relatively new biogeochemical sensor mounted on the floats is a 2-channel optical backscattering instrument measuring the backscatter at wavelengths 532 nm and 700 nm. The time series at both wavelengths show no trend at the parking depth but both have a seasonal cycle with maximum during May-September (Figure 3.2.6). Similar to the chl-a measurements peaks are observed near the parking depth which seems to start in late spring/early summer.

These measurements detected the vernal phytoplankton bloom as well as the relative abundance of small versus large particles (i.e., the ratio of bbp(532):bbp(700), Fig. 3.2.8). Small particles peaked in winter when phytoplankton were essentially absent from the water column (spectral bbp ratio is at its maximum, January-February). In March the relative abundance of large particles started to increase within the mixed layer as the bloom started (spectral bbp ratio decreased). The abundance of large particles relative to small particle was largest in the productive layer during spring and summer when the bloom still existed, and increased also in the mesopelagic layer as the summer advanced.
Figure 3.2.6: Sections of chlorophyll-a (CHLA) and particulate optical backscattering (bbp) at 532 and 700 nm. All data are log10. The white line is the mixed layer depth estimate.

Figure 3.2.7: Chlorophyll-a concentration (mg m⁻³) from float imrbio02 during 2014-2015. Left: all profiles of chl-a. Right: time series of chl-a averaged between 950-1000 dbar depth.
Figure 3.2.8: Upper figure: Vertical sum of chlorophyll-a fluorescence in the upper 50 and 800 m during 2014. b) Lower figure: Ratio of green-to-red particulate backscattering (bbp532:bbp700) as a function of depth and time. The data are smoothed. The solid black line is the mixed-layer depth.

Spectral downward irradiance measurements

Another new instrument mounted on the floats is the irradiance sensor that measures the downward irradiance at 380, 412, 490 nm and the photosynthetically available radiation (PAR). Figure 3.2.9 shows the depth reduction of the irradiance. Clouds influence the temporal variability but the time within the day when the measures were taken is also important to take in account. All measurements were taken during noon except for few profiles (in Sep-2014 and Nov-2014) when the measurements were taken during midnight. This explains the low values for these profiles during the two periods.
Figure 3.2.9: Downward irradiance (log10) from float imrbio002 during from Jan-2014 to Sep-2015 at wave length 380 nm, 412 nm, 490 nm, and PAR. All data are log10. The white dashed line is the mixed layer depth estimate.
Conclusions - Nordic Seas

- One of the two biogeochemical floats deployed in the Nordic Seas was lost after one profile.
- A drift in the dissolved oxygen sensor and the AOU is observed at the parking depth and on the isopycnal 28 kg m$^{-3}$.
- There were large peaks in the chlorophyll-a fluorescence sensor on the WETLabs ECO-Triplets at 850 dbar and larger depths after four months of operation (starting in May).
- Both backscattering channels (532 nm and 700 nm) showed a seasonal cycle with maximum during May-September.
3.3 The experiment in the Black Sea (IO-BAS/USOF)

Biogeochemical sensors on Argo floats can extend rapidly our understanding of the spatial and temporal evolution of biological systems (e.g. Claustre et al., 2010). Developing biogeochemical observations is also a strong requirement from Copernicus Marine Service (CMEMS). This is of utmost important for regional basins where processes do not always follow the evolution patterns known for the ocean.

As part of this task, two new biogeochemical floats of the type Provor BIO were deployed and tested in the Black Sea. The first one (Basbio-1, WMO No 7900591) was deployed on 16-Dec-2013 at 43.25 N and 29.25 E. It performed 102 cycles til present day and is still operating. The second one, Basbio2 (WMO No 7900592) was deployed on Dec 15 2013 at 42.24 N and 29.00 E. It did 79 cycles and terminated its mission on 25 October 2014. These profiling floats use Iridium transmission and a sensor suite composed of Pressure, Temperature, Salinity sensors, as well as Aanderaa Optode to measure Dissolved Oxygen, two calibrated fluorimeters for the chlorophyll concentration (CHL), a backscattering sensor for the measurement of particle backscattering coefficient and a sensor measuring downward radiation. The maximum profile depth was set to 1000 m. To explore the usability of the floats to the Black Sea conditions three sampling strategies were analyzed. Until 28/01/2014 the sampling was daily, between 28/01/2014 and 08/04/2014 the profiles were recorded every fifth day, and after the latter date once per 10 days. More technical details of measuring process can be found on http://www.ifremer.fr/coproargoFloats/float?ptfCode=7900591 and http://www.ifremer.fr/coproargoFloats/float?ptfCode=79005912.

The trajectories of both floats are shown in Fig. 3.3.1.

![Figure 3.3.1 Trajectories of float WMO No 7900591 (a) and 7900592 (b).](image_url)
As seen from the trajectory plots (Fig. 3.3.1) WMO No 7900591 was operating in the deeper part of Black Sea, while WMO No 7900592 first moved into the area of Bosporus Straits, and then followed the coast recording thus properties of the water in the area of coastal anticyclonic eddies. This separation of two floats gives a good basis to analyze differences between deep ocean and coastal biogeochemistry (similar exercise but just for oxygen was previously documented by Stanev et al. [2013; 2014]).

The physical variables (temperature, salinity and density) observed by Basbio-1, 2 reveal features of the vertical stratification, which are well known from earlier observations (including Argo, Stanev, 2013). The three profiles of biogeochemistry parameters (bottom plots of Fig. 3.3.2) illustrated by the concentrations of chlorophyll-A and backscatter for two wave lengths (CHL-A, bbp-532 and bbp-700), seem not well known, in particular as far as continuous basin-wide observations are concerned.

The calculated CHL-A shows maximum concentrations in the upper layer, decreases to a minimum at ~100 m and increases slightly in deep layers (~0.02 mg/m³/100m). The reason for this increase in the deep sea is still not well understood: the explanations could be either insufficient calibration of the sensor; or its malfunction in the H₂S environment. Another hypothesis could suggest that the CHL-A sensor reacts to other substances (for example yellow substances or bacteria). This issue requires further investigation which is beyond the scope of this report. Deep layer samples from euphotic layer, thermocline, 200, 500, 750 and 1000 m were taken during 3 expeditions of RV Akademik in May, June and July 2015. The samples were sent to the laboratory of Aquatic Microbial Ecology in the Institute of Ecosystem Study, Italy for further processing and analysis.
Very interesting specificity in the backscattering is the pronounced maximum at about 200 m for the two floats. This layer does not well correlate with the physical variables. It is identified in the lower part of pycnocline, approximately where, as known from previous studies, the light transmission increases dramatically due to abundant bacterial communities and perhaps with particulate manganese.

![Figure 3.3.3](image)

**Figure 3.3.3** Vertical profiles (all data plotted against depth) of temperature (top), salinity (middle) and density (bottom).

In order to give an idea about the temporal variability recorded by BIO-Argo we present in Fig. 3.3.3 the temporal variability of physical variables; the one of oxygen and CHL-a is presented in Fig. 3.3.4. The cold intermediate layer (CIL, Fig. 3-top) shows a good persistence over most of times and areas. Noteworthy is that (1) it forms in the southern and central parts of sea, which disagree with some classical concepts and supports the results of Stanev et al. (2013), (2) it is eroded in some locations (see the event around day 580), (3) it is warmer that what it used to be for several decades.
The temporal evolution of salinity explains the major events controlling the evolution of density (stability of stratification). Two of them are very important: the one at about day 90 and the one by about day 580. The first one happened during the period of cold water formation, thus it contributed to “pumping cold” into the CIL. However the one around day 580 was the reason of the mentioned above erosion of CIL.

Biological system responds actively to these changes. Oxygen concentration increased substantially by day 80 and day 580. Unlike to the case addressed by Stanev (2013; 2014) the intermediate oxygen maximum is less pronounced. However, the stratification of CHL-a shows a clear sub-surface maximum at ~30 m depth. During the second year, at about day 440, which was just after the formation of CIL, that is a period of restratification, there was a clear maximum of CHL-a from the surface layers indicating propagation of the signal from the spring bloom into the deeper layers. Soon after this event, the concentration of CHL-a in the surface layer decreased, this CHLA-a maximum was build.

As explained above the increasing trend of CHL-a below 120 m is probably due to anaerobic processes (still under investigation).

The changing frequency of sampling appeared instructive in order to identify the most appropriate interval of profiling. One-day sampling seems appropriate to resolve temporal and spatial variability. 10-days interval seems too coarse. Perhaps a good compromise, if one wants to extend the life-time of floats, is to sample once every five days.

The costs of sensors made impossible to install nitrate (NO3) sensor on the two floats considered in this report. However in a parallel activity the partner OGS deployed in May 2015 a float BLA_SEA_NOA ogsbio007c. After some initial problems of decoding data the first NO3 and H2S profiles became available (personal communication, P.-M. Poulain). Because these data
Recommendations

- The floats and sensors should be calibrated and tested before deployment. For instance, the dark counts for the optical sensors should be measured and compared with that from the manufacturer.
- If possible, relevant in-situ (ship) measurements during deployment should be taken for comparison with data from the float profiles.
- If no air measurements of oxygen exist deep measurements from the sensor, below the seasonal thermocline, of dissolved oxygen and the calculated apparent oxygen utilization (AOU) can help to detect drift in the oxygen sensor.
- Due to possible peaks in the fluorescence near the parking depth care should be taken if the deepest measurement is used as a bias for each profile. Some analysis in advance is consequently needed.
- In oligotrophic regions the particulate optical backscattering (bbp) sensors should have higher instrumental sensitivity. As demonstrated, in the oligotrophic North Atlantic sub-tropical gyre the sensitivity of the sensor was insufficient to detect significant bbp changes.
- Deep bbp measurements are affected by bbp of “pure” sea water. Drift in deep bbp could reflect both instrumental changes in offset (dark counts) or gain (scaling factor). This needs to be considered when using deep bbp data for drift corrections.
- Further investigations are needed to explain the slightly increase in the calculated chl-a in the deep layers of the Black Sea (~0.02 mg/m³/100m). Suggested explanations are either insufficient calibration of the sensor, its malfunction in the H₂S environment, or that the chl-a sensor reacts to other substances (for example yellow substances or bacteria).
References


