AUTONOMOUSLY PROFILING THE NITRATE CONCENTRATIONS IN THE OCEAN: THE PRONUTS PROJECT.

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Introduction

In the 2000's, a new optical sensor to evaluate nitrate (NO_3) concentration in seawater was realized (Johnson *et al.*, 2002) and then commercialized. Few years later, a first prototype of an APEX profiling float equipped with a NO_3 sensor was achieved and deployed in the Pacific Ocean, acquiring NO_3 profiles for about two years(Johnson *et al.*, 2010). The experiment with the APEX prototype indicated the huge potential of the duo "profiling float- NO_3 sensor" for a wide range of scientific applications, spanning from a better understanding of the physical biological interactions in the oceans (Claustre *et al.*, 2010) to a potential strongly enhancement of the performance of ecosystem models, via assimilation (Brasseur *et al.*, 2009).

In 2008, a large consortium of French laboratories dedicated a scientific and technological effort (PRONUTS project, GMMC + PACA region) to verify the feasibility of a PROVOR CTS03-based profiling float equipped with a NO_3 sensor (PRONUTS profiling float). The main aim was to develop two prototypes of PRONUTS, and to test their performances, in terms of sensor integration, of reliability of the couple profiling float+NO_3 sensor and of the quality of the collected data.

The PROVOR CTSO3 series provides some unquestionable advantages. Its high reserve of floatability and large energetic autonomy could enable a large number of sensors, longer missions and improved cycling frequency. Moreover, a biogeochemical version (but without NO_3 sensor) of a PROVOR-based profiling float (PROVBIO) was already tested and scientifically exploited (Xing *et al.*, 2011);a new PROVBIO model, integrating an additional NO_3 sensor, could be then developed with few hardware and software modifications. This new PROVBIO model could provide simultaneous observations on the physical state of the water column (Temperature and Salinity profiles), on the chemical/ resources distribution (NO_3 profiles) and on biological dynamics (Chlorophyll and Colored Dissolved Organic Matter profiles). This motivated to the PRONUTS project, which was strongly coordinated with the American and Canadian laboratories involved in the development of the APEX NO3 profiling float (http://www.mbari.org/chemsensor/APEXISUS.htm).

In this note, we rapidly describe the technical characteristics of the two prototypes of PRONUTS that we developed. A short overview of the acquired profiles and of the (preliminary) data processing system will be done. Finally, some perspectives, in the framework of the NAOS-EQUIPEX and remOcean-ERC projects will be discussed.

The PRONUTS: a PROVOR-based NO_3 profiling float

Two NO_3 sensors were commercially available at the beginning of the project, both developed by Satlantic Inc: the SUNA and the ISUS sensors. The two instruments are based on the same principle: the measured absorption on the UV part of the spectrum permits to evaluate the NO_3 concentration, using the Beer-Lambert law. The SUNA sensor is the most recently developed device and the manufacturer suggested it as our primary choice. It is smaller and more compact than the ISUS, and, consequently, could be more easily integrated on a PROVOR. For the ISUS integration on an APEX, important hardware modifications were required (the instrument was squeezed and recombined in the interior of the APEX). A similar operation was required to mount an ISUS on a PROVOR, inevitably increasing technical difficulties and final costs. But since the ISUS has already been mounted on a profiling float (Johnson *et al.*, 2010), collecting data of very high quality, while no similar experiences existed on the SUNA, its development seemed important.

Both sensors are easily integrated with the PROVOR software, more specifically the version implemented on the PROVBIO. However, only the NO_3 concentration was transmitted on land, instead of the complete acquired absorption spectrum. This was the main difference with the APEX technical solution and the one having the greatest impact on the data quality. We will deserve a specific discussion in the next paragraphs.

After exchanges with our American and Canadian colleagues, and after some, preliminary tests, we decided to implement two versions of PRONUTS, the one equipped with a SUNA (PRONUTS-SUNA), the other with an ISUS (PRONUTS-ISUS). In the first case, the sensor was simply connected to the PROVOR motherboard and externally installed on the side of the PROVOR tube (Figure 1, right). In the second case, the ISUS was entirely dismantled and then reassembled into the PROVOR chassis, similarly to the APEX version (Figure 1, left).

All the preliminary tests (i.e. floatability, transmission, energy, on-board data processing) carried out on land or during some short deployments were successful for both versions. The two prototypes were ready to be deployed in May 2011.

Figure 1 : The two PRONUTS prototypes: right the PRONUTS-SUNA, on the left the PRONUTS-ISUS

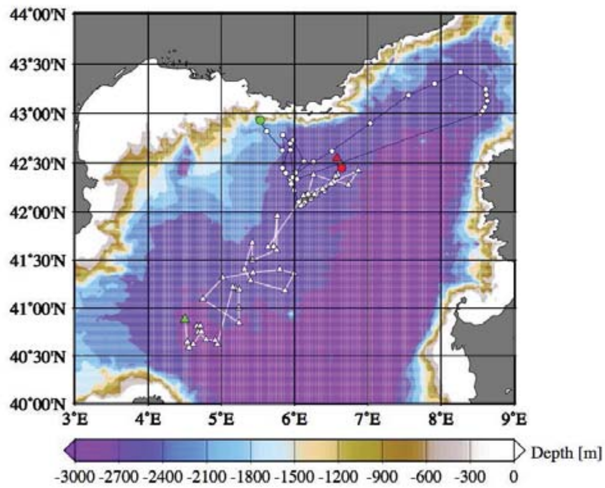

Figure 2 :Trajectories and positions of the profiles for the two PRONUTS in the North Western Mediterranean Sea. Triangles: PRONUTS-SUNA; Circles: PRONUTS-ISUS. Red dots indicate the deployement points (28 June 2011). Green dots indicate the last position at the moment of the writing of this note (end of February 2012).

The North Western Mediterranean Deployment

During the summer 2011, the two PRONUTS were deployed in the open North Western Mediterranean(Figure 2), in the framework of the Mediterranen Ocean Observing System for the Environment observing system (MOOSE) during the MOOSE-GE cruise (PI P. Testor). The area was selected for two main reasons:

- in a strong oligotrophic environment lasting for most of the year, winter deep water convection events, followed by huge phytoplankton blooms, are recurrently observed in the area (D'Ortenzio *et al.*, 2009); the range of variability of the NO_3 concentrations was supposed to be high, giving an ideal site to test the PRONUTS performance(Marty *et al.*, 2002);
- in the framework of the French MOOSE Mediterranean observing system (http://www.allenvi.fr/?page_id=777) the area is recurrently monitored by research vessels, which strongly facilitates any logistic issues during the PRONUTS tests (in case of failure, for example, a recover of the profiling floats could be easily planned).

The sampling strategy was strictly the same for the two PRONUTS, and it was fixed to be as close as possible to the strategy of the APEX NO_3 float. At 100 levels from 1000m depth (at 10 m resolution) to surface seven measurements were acquired in a very rapid sequence, and transmitted to land at the profiling float surfacing. Initial cycling frequency was based on the standard ARGO protocol (10 days), although sensor restrictions limited the maximum profiling depth to 1000m. Parking depth was set at 1000m.

Data processing was different from the APEX-NO_3 protocol (K. Johnson, personal com). For the APEX-NO3 profiling float, the whole acquired spectrum (from 200 to 400 nm) was transmitted on land. The NO_3 concentrations were then derived by specific algorithms, which corrected eventual sensor bias or any interference in the UV absorption due to salinity and temperature effects (Sakamoto *et al.*, 2009). For the PRONUTS, the estimation of the NO_3 concentrations was carried out directly by the sensors, and no information on the spectrum were available on land. Consequently, the PRONUTS data could be likely affected by erroneous NO_3 estimations, which could not be corrected.

For this reason, a high-resolution profile of NO_3 concentrations by water samples analysis was carried out during the deployment, and a calibration of the first profiles was performed (Figure 3). For the following profiles, a preliminary calibration procedure was applied, based on two main hypotheses derived during the tests on land (Lavigne et al. in preparation). According to the first hypothesis, NO_3 concentration at depth is relatively stable all along an annual cycle. More specifically, we assume that the possible variations of the NO_3 concentration at depth are about the sensors accuracy (+/- 2 µmole). For each profile, and for the whole lifetime of the PRONUTS, a calibration factor was calculated by difference between the average of the PRONUTS data in the 800-1000 m layer and the deep values obtained at the deployment by water sample analysis. The second hypothesis is that the calibration factor could be linearly applied to the whole profile (i.e. possible bias of the sensors is linear).

Presently (February 2012) 43 NO_3 profiles of the PRONUTS-SUNA and 46 profiles of the PRONUTS-ISUS were collected (Figure 4) and validated (i.e. correct lat/lon position, complete profile). The PRONUTS-ISUS experienced a serious transmission failure in September, with a total loss of contact. Fortunately, the contact was re-established in November and, up to now, no other severe malfunctions were detected. The data of the PRONUTS-SUNA were generally more noisy than the data of the PRONUTS-ISUS (compare error bars on Figure 3).

For both sensors, the calibration method appears promising. After the application of the calibration factors, the surface values during the oligotrophic period (i.e. August to October) are close to zero, as expected in the area. NO_3 surface concentrations start to be significant when important events of mixed layer deepening bring nitrates from the deep reservoir to the surface through mixing (i.e. in December 2011, for the PRONUTS-SUNA, Figure 4). The event of mixed layer deepening observed by the PRONUTS-ISUS (> 1000m), which induced a complete homogenization of the NO_3 concentrations (Figure 4) is particularly spectacular. In order to better monitor the sequence of the mixed layer deepening and the modifications of the NO_3 concentration vertical structure, the frequency of cycling from both prototypes was switched to 2 days, starting from the 15^{th} of January.

This mechanism of re-distribution of NO3 along the water column after a deep mixing event is relatively a well known process, but was never quantified in-situ like that before to our knowledge.

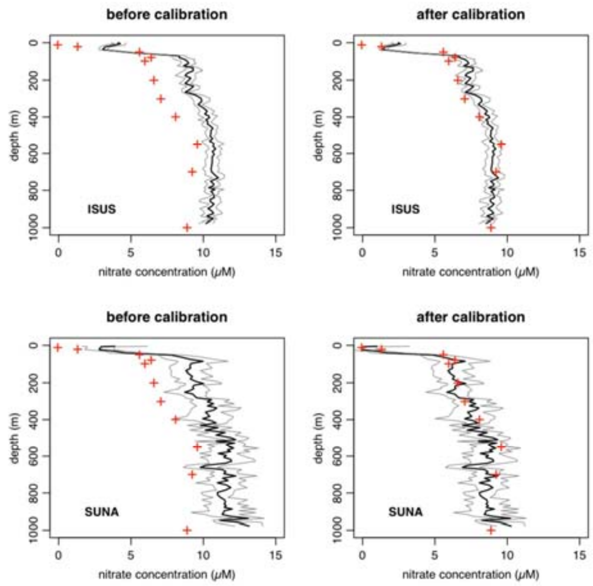

Figure 3 : First profiles of NO3 concentration from the two PRONUTS prototypes (black lines) and the corresponding standard deviation (grey lines). Red crosses indicate the NO_3 estimations by water samples carried out at the deployement (28 June 2011). Upper panels: PRONUTS-ISUS ; lower panels : PRONUTS-SUNA. On the left : not calibrated NO_3 profiles ; right: calibrated profiles.

Conclusions and Perspectives

At the present day (February 2012), the two PRONUTS are still operational, and the acquired data are visible in real-time on the web (http://www.oao.obs-vlfr.fr/pronuts/pronuts.html). Despite some technical problems (in particular on the PRONUTS-ISUS), both prototypes successfully carried out their mission. The calibration procedure, although not perfect, seems to accomplish the first-order ous scientific requirements (i.e. depths of nitraclines), and appears as a promising method when absorption spectrum data are not available. However, the strong mixing event observed by the PRONUTS-ISUS, modifying the NO_3 concentrations over the whole water column, could overrule our first calibration hypothesis. A first check of the quality of the method will be possible at the coming back of oligotrophic conditions (i.e. June, July), when surface NO_3 concentration values should be close to zero again. Alternatively, the recovery of the prototypes is considered. This operation, although always potentially risky, could allow to evaluate the degree of degradation of the two prototypes and of the sensors.

The experience and the know-how acquired during the PRONUTS project will be strongly capitalized in the next years. Two important funded projects (the NAOS EQUIPEX, PI PY LeTraon, http://www.naos-equipex.fr/Le-Projet, and the remOcean ERC Advanced Grant, PI H. Claustre, http://www.oao.obs-vlfr.fr/projectssm/ongoing-large-projectssm) plan to deploy more than 60 biogeochemical profiling floats in key areas of the world ocean (North Atlantic, Mediterranean, Arctic) during the period 2012-2015. The pool of the NAOS and remOcean biogeochemical profiling floats will partially include a new version of PROVBIO. This new version will be equipped with the “standard” PROVBIO sensors suite (CTD, backscatterometers, irradiance sensors, fluorometers for Chl and CDOM, optodes for oxygen) plus a NO_3 concentration sensor (most likely a SUNA).

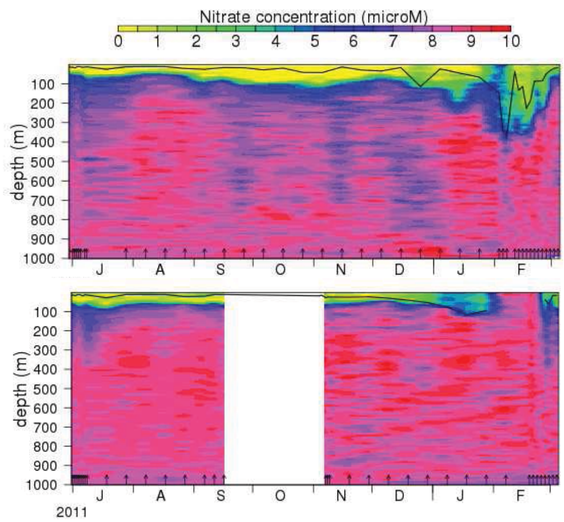

Figure 4 : Times series of the NO3 concentration as a function of time and depth. Upper panel PRONUTS-SUNA ; lower panel PRONUTS-ISUS. The black lines indicate the mixed layer depth, estimated from T and S profiles of the floats. The arrows indicate the time of the profiles.

No more PRONUTS will be produced. The two prototypes demonstrated the feasibility of the PROVOR based observations of NO3 concentrations and the next step is now to couple such physical and chemical observations with biological ones.

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