



GROOM

Gliders for Research, Ocean Observation and Management

FP7-Infra-2011-2.1.1 "Design Studies"

Deliverable D3.5

Scientific report on existing sensors to be integrated on gliders for biogeochemical and biological applications and underwater data transmission

Due date of deliverable: 30/09/2013

Actual submission date: 20/02/2014

Partner responsible: UPMC

Classification: PU

Grant Agreement Number: 284321

Contract Start Date: October 1st, 2011

Duration: 36 Months

Project Coordinator: UPMC

Partners: UPMC, OC-UCY, GEOMAR, HZG, AWI, UT, FMI, CNRS, IFREMER, HCMR, CMRE, OGS, UIB, NERSC, CSIC, PLOCAN, SAMS, UEA, NERC.

Project website address <http://www.groom-fp7.eu>

Table of contents

| | |
|---|-----------|
| INTRODUCTION | 5 |
| I.A. Objectives | 5 |
| I.B. General overview..... | 5 |
| I.C. Gathering information | 6 |
| I.D. Organizing the information | 7 |
| PARAMETERS/ VARIABLES | 8 |
| I.E. Sensors already implemented | 9 |
| I.E.1. Chlorophyll-a concentration | 10 |
| I.E.2. Animal biomass and presence..... | 11 |
| I.E.3. CDOM (Chromophoric Dissolved Organic Matter)..... | 12 |
| I.E.4. Current..... | 14 |
| I.E.5. Nitrate (NO ₃ ⁻) | 16 |
| I.E.6. Oxygen (O ₂) (Partial Pressure) | 17 |
| I.E.7. Phycobilins (Phycocyanin, Phycoerythrin) | 19 |
| I.E.8. Turbidity backscatter..... | 20 |
| I.E.9. CTD (conductivity, Temperature, Depth)..... | 22 |
| I.E.10. Radiance-Irradiance | 24 |
| I.E.11. Turbulence | 25 |
| I.F. Sensors with easy implementation on gliders | 27 |
| I.F.1. Actinides | 28 |
| I.F.2. Bioluminescence | 29 |
| I.F.3. Biological Oxygen Demand (BOD)..... | 31 |
| I.F.4. Bromide Concentration (Br ⁻) | 32 |
| I.F.5. Carbon Dioxide (Partial Pressure of CO ₂) | 33 |
| I.F.6. Chlorinated hydrocarbons (CHCs) | 34 |
| I.F.7. Chrome (Chromate CrO ₄ ²⁻ , dichromate Cr ₂ O ₇ ²⁻)..... | 35 |
| I.F.8. Copper (Cu) | 36 |
| I.F.9. Cyanide | 37 |
| I.F.10. Hydrogen (H ₂) | 38 |
| I.F.11. Dinoflagellates..... | 39 |
| I.F.12. Explosives (TNT, RDX)..... | 40 |
| I.F.13. Sulphur (H ₂ S/HS ⁻)..... | 41 |
| I.F.14. Heavy Metals: Lead (Pb), Mercury (Hg), Copper (Cu) and Cadmium (Cd)..... | 42 |
| I.F.15. Hydrocarbons | 43 |
| I.F.16. Hydrogen Peroxide (H ₂ O ₂)..... | 44 |
| I.F.17. Manganese (Mn) | 45 |
| I.F.18. Mapping marine communities | 46 |
| I.F.19. Marine mammals (MM)..... | 47 |
| I.F.20. Methane (CH ₄) | 49 |
| I.F.21. Nutrients | 50 |
| I.F.22. Ozone (O ₃) | 52 |
| I.F.23. Particle and plankton size distributions (PSDs) | 53 |
| I.F.24. Polycyclic aromatic hydrocarbons (PAHs) - Polychlorinated biphenyls (PCBs)..... | 55 |
| I.F.25. pH | 57 |
| I.F.26. Radioactivity | 59 |
| I.F.27. Redox-potential | 60 |

| | |
|---|-----------|
| I.F.28. Rhodamine / Amido-Rhodamine / Fluorescein..... | 61 |
| I.F.29. Deep-sea low-frequency sub-bottom profiler (SBP)..... | 62 |
| I.F.30. Seismic waves..... | 63 |
| I.F.31. Virus (enteroviruses + noroviruses)..... | 64 |
| I.G. Sensors with potential implementation on gliders..... | 65 |
| I.G.1. Alkalinity..... | 66 |
| I.G.2. Bacteria, cells..... | 67 |
| I.G.3. Domoic Acid..... | 68 |
| I.G.4. Perchlorate (ClO ₄ ⁻)..... | 69 |
| I.G.5. Plankton sampler..... | 70 |
| I.G.6. VOCs (Volatile Organics Compounds)..... | 71 |
| I.G.7. Micro-pump (microfluidic pump using conductive polymer for low power consumption)..... | 72 |
| GLIDERS AS DATA MESSENGERS..... | 73 |
| BIBLIOGRAPHY..... | 74 |

D3.5

INTRODUCTION

I.A. Objectives

This document represents the Deliverable D3.5 of the GROOM FP-7 Infra 2011-2.1.1 project.

The deliverable is devoted to a presentation of the existing sensors, already (or potentially) used for biological and biogeochemical applications. This is addressed from the scientific point of view and the "new contributions of gliders to marine research" that these sensors installed on gliders will allow addressing. In addition, the utilization of gliders as data messengers for other oceanographic platforms is discussed.

The deliverable is organized into 3 main sections:

1. Section 1 (present section), which provides a general introduction to the deliverable.
2. Section 2 presents all the inventoried variables and sensors. It is divided into 3 categories: sensors already implemented, sensors that are mature for an implementation and more prospective ones.
3. Section 3 is dedicated to the use of gliders as data messengers.

I.B. General overview

The concept of oceanographic underwater gliders emerged from the need for an enhanced oceanographic sampling of the core parameters in the oceans and for easier and cheaper observations. Gliders, as platforms providing observations at high resolution and in real time, can fill the gaps on the spatio-temporal scales covered by the existing oceanographic platforms. Gliders not only enhance the spatio-temporal sampling of the core parameters, but they also offer a unique possibility to carry any kind of sensors provided these can be miniaturized. As often argued (i.e. Testor et al, 2010), the gliders component will certainly occupy (and already occupies) a critical position in the future ocean observing systems.

The concept of underwater gliders was first explored in 1960's. The first prototypes were powered by a swimmer passenger, with no buoyancy control and only one glide cycle. Only at the end of the 1980's, however, a glider with a buoyancy engine was developed, and, by the middle of the first decade of this century, this type of propulsion has become the most common, and glider technology became mature enough to be even more widely used. This ballast-based propulsion system results in lower speed, though higher endurance than conventional autonomous underwater vehicles (AUV). Today, long endurance enables gliders to explore the oceans, acquiring a wide variety of data over large areas and long durations, up to 6000 meters depth.

From the beginning, gliders were conceived to be multi-function, multi-parameter platforms. All the present-day commercially available gliders enable the integration of sensors measuring physical, chemical and biological parameters of seawater. Additionally, the possibility to pilot gliders in real-time during a specific mission makes gliders today's "perfect" tool for multi-disciplinary process studies, which often require rapid adaptation of sampling to environmental conditions.

Gliders were initially restricted to physical parameters (Temperature and Salinity), but soon started to be equipped with optical sensors delivering biogeochemical proxies. Fluorescence and oxygen sensors were the first to be implemented (Fiorelli et al., 2003 ; Perry et al., 2003; Körtzinger et al., 2005 ; Riser and Johnson, 2008;), and now a large set of other sensors are already successfully tested (among others, Johnson and Coletti, 2002; Siegel and Rusello, 2011, Cf. GROOM D5.2). Miniaturization and energy cost were and are still (and will probably remain) the main limiting factors for implementation of new sensors, in particular biological and chemical. A less important factor, although crucial for long deployments, is the volume of collected data, which could prevent massive on board computation and, consequently, critically affects transmission time and costs. Last but not least, sensor price and the cost for implementation, which could rapidly grow if only few prototypes are developed. However, most of these factors are counter-balanced by the good performances of the technology and its high potential for "new science" (extreme environments, "new vision" of the marine system, etc.). Although some biological and chemical sensors could be expensive (and this is not the

D3.5

case for "basic" sensors as fluorometer or optodes), the total cost of the single observation is however comparable to or less than those of traditional methods (see cost discussion in Testor et al. 2010). One must also consider that miniaturization of sensors (i.e. the other limiting factor for gliders) is strongly progressing in environmental studies, as this is also required for other platforms such as buoys or floats.

Consequently, recent years have seen an exponentially growing interest in new sensors for biological and biogeochemical applications on gliders. At the same time, "basic" sensors (as fluorometers and optodes) are now routinely used on gliders, which has resulted in significant progress in quality control of data methodologies and, consequently, in a much better quality and scientific exploitation of the observations (Janzen, 2008, 2011; Murphy et al., 2008; Slade et al., 2010).

In this GROOM deliverable, a thorough analysis on the potential of the biological and chemical sensors on gliders is presented. A review of sensors already implemented and used on gliders for biogeochemical studies is discussed, considering also (though briefly) data processing issues such as Quality Control. The largest part of the deliverable is, however, devoted to the sensors that could potentially equip gliders, to increase our capability to observe and study marine ecosystems dynamics. Finally, a discussion of the recent advancements of the use of gliders as data messengers for other platforms is presented as an important approach to allow new contributions of gliders to marine research, which is the scope of this deliverable.

The deliverable presented here has strong complementarities with the deliverable D5.2 ("Sensors for gliders: existing, under development, and future sensors"). The D5.2 is more focused on the hardware characteristics of the sensors and concerns all the oceanic parameters including atmospheric ones, while here the focus is on the parameters and sensors useful chemical and biological advanced studies. As will be described later, the document is then organized "by parameter", one form for each parameter, emphasizing more the scientific aspects than the technological ones.

I.C. Gathering information

The collection of information for the deliverable, was first based on reviews on sensors published in recent years,

The already cited "twin" GROOM deliverable D5.2 was extensively used to retrieve information.

The marinERA Publication N°9 (New Developments in Marine Sensor Technologies: Opportunities and Challenges), also provides useful information (at least at European level) despite not being sufficiently detailed on the scientific aspects.

"Le tecnologie del CNR per il mare" (Consiglio Nazionale delle Ricerche), recently published in the frame of the new RITMARE national program (funded by the Italian Ministry of university and Research and coordinated by CNR), is a catalogue of the on going projects for marines technologies in Italy made available to us by the OGS partner.

The collection of information was then continued with thorough web searches.

Firstly, public and private institutes/companies, involved in environmental studies and monitoring, were inventoried. As pertinent sensors for ocean study could be developed for other domains than academic or "industrial" oceanography (for example limnology, soil research or even the medical sector), this initial step provided a first useful overview of the possible sources of information. Oceanographic centers have then been more specifically targeted (SCRIPS, NOCS, IFREMER...) via their « R&D, » « products » or « sensors » departments. Every link referring to projects, conferences, documents or person in charge, have been collected to derive pertinent information. Written reports from workshops, mentioning industry collaboration, which might have played a role in sensor commercialization, have also been used and have led to company websites. When not enough information was available about a sensor or a project, the person in charge was contacted by email or telephone. Direct contacts have often allowed access to unpublished documents and information. ..

The method used to gather information is sketched out in figure 1.

D3.5

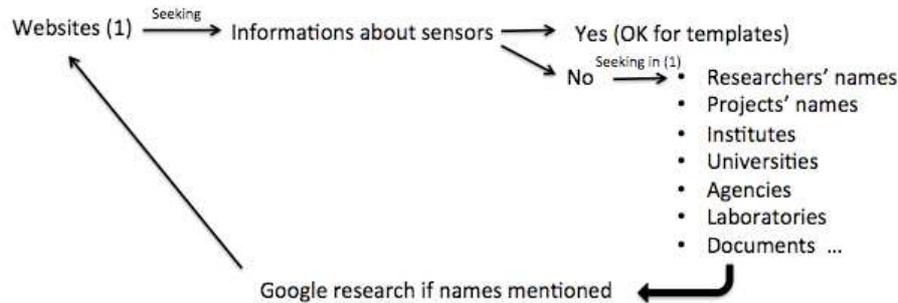


Figure 1. Method to collect information.

I.D. Organizing the information

On the basis of the collected information, we first grouped the sensors on the basis of the observed parameter. For most of the cases, a parameter is available from a unique sensor, often in a prototype phase. However, for “basic” parameter, as chlorophyll-a for example, multiple sensors giving the same parameter exist. In this case, the main differences are on the measuring methods or in the accuracy.

For each parameter, we then compiled a form summarizing the relevant information. The form is organized in four sections:

1. **Scientific rational:** A (brief) explanation of the relevance of the parameter for ocean science. Whenever available, the corresponding scientific publications are cited.
2. **Existing methods:** A description of the different methods available to measure the parameter is given. Some technical characteristics (as for example accuracy) are also provided, if available. Existing sensors’ names are cited when provided by the manufacturer or the laboratory.
3. **Implementation on glider:** the actual implementation or not of the sensor on a glider. When not already implemented, we briefly discuss the possibility of an implementation on a glider of the existing sensors, and the needed modifications of the sensors. We used as main criteria the size of the sensor, and when relevant, the energy consumption.
4. **Data quality control:** A description of the quality control of the data already available, and of “good practices”.

Of course, some forms are not fully filled, in particular the “Data quality control” section. Owing to the rapid technological evolution in that sector, some of these templates should be soon updated.

Finally, the forms (i.e. the parameters) were grouped according to their status of implementation on a glider. Three categories of parameters/sensors have been defined:

1. **Already implemented.** Parameters/sensors already tested and scientifically exploited.
2. **Easy implementation.** Parameters from sensors having suitable characteristics to equip a glider, but that are not yet used on gliders. We also listed here parameters from sensors requiring simple modifications for implementation on a glider.
3. **Potential implementation.** Parameters available from entirely new sensors, needing significant modifications to be mounted on a glider (> 1 year of development).

D3.5

PARAMETERS/ VARIABLES

In our forms, we consider "parameters" and "variables". A parameter is a measurable factor that can help define and characterize a particular system; it could be physical, chemical or biological. A variable is all the numerical values that the parameter can take when it is measured. Thus, the listed parameters are important elements to consider for the comprehension of modifications, or situations, which occur in the ocean.

In oceanography, the "parameter" is either a chemical or biological element (e.g. nitrate, bacteria concentration etc.) with a certain occurrence in seawater that can be identified, or a physical characteristic of the ocean (e.g. temperature, currents etc.). It is considered as a "variable" because, it is quantitatively measurable. More generally, the following scheme is: One "variable" is associated to one 'parameter'; then a sensor measures this variable. In this Deliverable, for some of the variables listed, principally for the *sensors already implemented* and the most commonly studied parameters of seawater (e.g. pH, pCO₂, nutrients etc.) several methods exist. Thus, the scheme becomes; one "variable" is associated to one "parameter", then different techniques exist and therefore different types of sensors are available for the same parameter. For the more "exotic" variable, the scheme is simpler and has the shape of: one 'variable' → one 'parameter' → one sensor.

D3.5

I.E. Sensors already implemented

- I.E.1 – Chlophyll-a concentration
- I.E.2 – Animal Biomass and presence
- I.E.3 – CDOM (Chromophoric dissolved organic matter)
- I.E.4 – Current
- I.E.5 – Nitrate (NO_3^-)
- I.E.6 – Oxygen (O_2)
- I.E.7 – Phycobilin
- I.E.8 – Turbidity
- I.E.9 – CTD (Conductivity, Temperature, Depth)
- I.E.10 – Radiance, Irradiance
- I.E.11 – Turbulence

D3.5

I.E.1. Chlorophyll-a concentration

Scientific rational

Chlorophyll-a (Chla) 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). The spatio-temporal variability of chla concentration is then a proxy for the autotrophs distribution, and consequently is routinely measured in the ocean.

Existing Methods

Two methods to estimate chla concentration could be presently implemented on gliders: the fluorescence-based methods and the radiometric inversion of light measurements. The fluorescence is the most widely used, although fluorometers need external calibration (for the most obtained via simultaneous water samples analysis with laboratories methods, i.e. HPLC). Fluorescence is also affected by Non Photochemical Quenching (NPQ), a photochemical mechanism inducing an artifactual decrease of fluorescence under high levels of solar light. The radiometric inversion method requires at least two wavelengths of irradiance measurements, which have to be checked for QC. Derived chlorophyll is generally accurate and not affected by NPQ.

Implementation on gliders

Approximately one half of the present day fleet of gliders is currently equipped with fluorescence sensors, while very few have irradiance meters. (WP 5, survey).

Fluorescence estimation needs an evaluation of the accuracy and of the stability of the manufacturer calibration, which have to be carried out, possibly, before and after each glider deployment. Ocean colour satellite observations could furnish an alternative method to assess the accuracy of the chlorophyll estimation, for both the irradiance and the fluorometric methods. Existing methods for profiling floats (Lavigne et al., 2012, Boss et al. 2012) have been tested on glider data, although some adjustments are required to account for the increased spatial variability.

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 position of the sensor relatively to the sun and to the air-sea interface) could induce some bias in the irradiance measurements. Accurate estimations of the glider position in the space should be required.

Quality Control

Chla estimations from gliders could be checked using the same QC protocols proposed for Bio-Argo (PABIM white book, D'Ortenzio et al. 2008). Additionally, gliders should be quality controlled at the end of the mission, by verifying sensors performances.

References

- Boss, E., D. Swift, L. Taylor, P. Brickley, R. Zaneveld, S. Riser, M. J. Perry, and S. P.G (2008), Observations of pigment and particle distributions in the western North Atlantic from an autonomous float and ocean color satellite. , *Limnology and Oceanography*, 52(2), 112-122. .
- D'Ortenzio, F., V. Thierry, G. Eldin, H. Claustre, P. Testor, C. Coatanoan, M. Tedetti, C. Guinet, A. Poteau, and L. Prieur (2010), White Book on Oceanic Autonomous Platforms for Biogeochemical Studies: Instrumentation and Measure (PABIM), Version.
- Kirk (1984), Dependence of relationship between IOP of water on solar altitude, *Limnology and oceanography*, 29(2), 350.
- Lavigne, H., F. D'Ortenzio, H. Claustre, and A. Poteau (2012), Towards a merged satellite and in situ fluorescence ocean chlorophyll product, *Biogeosciences* 9, 2111–2125.

D3.5

I.E.2. Animal biomass and presence

Scientific rational

For "Animal biomass and presence", we intend consider observations regarding higher trophic level animals species (i.e. fish, crustaceans, mammals, etc) and how they behave. These observations are primarily used to study animal migrations or determining predator/prey interaction and inter-species association; they are also used to analyze oceanic biogeochemical reactions, which occur in the sea, and that are based on the presence of high trophic level animals. Indeed, animals produce organic matter, which interacts with seawater or others animals, such as biological secretions (mucus, sperm, eggs...) or detritic matter from feeding, fecal material, and dead animals.

Existing Methods

1. **Echosounder 853** – (receiver) - Frequency: 120 kHz ; max detection range: 100m ; max operating range: 1000 m - Manufacturer : Imagenex - (1)
2. **VEMCO Mobile Transceiver (VMT)** : It is a hybrid between a 69 kHz coded transmitter and a 69 kHz monitoring receiver. The VMT also behaves as a VEMCO coded transmitter and can be detected by other VEMCO receivers. The VMT can also detect other tagged fish in its presence.- Depth rating of up to 1000m - Manufacturer: VMT - (2)
3. **Hydrophone** (receiver) for high frequency up to 150 kHz; Sensitivity: without preamp :-204 dB; capacitance: 3,6 nF; max depth : 2000m ; size 2,54cm Ø x 7,6cm – Manufacturer: High Tech Inc. - (3)

A transceiver (transmitter + receiver) is based on the piezoelectric principle. Compressive forces are transmitted to sensitive elements, via pre-stressed mounting bases, which separate the electrical charges in proportion to the force displacement. A charge amplifier then converts these electrical charges to an analog voltage signal.

Implementation on gliders

Mission-proved for the VEMCO (Oliver et al., 2013) and HighTech Inc Hydrophone (Klinck et al., 2012). For the Echosounder 853, according to the website, it is designed for glider uses.

Quality Control

NA

References

- Matthew J. Oliver, Andrew Irwin, Mark A. Moline, William Fraser, Donna Patterson, Oscar Schofield, and Josh Kohut, 2013. Adélie Penguin Foraging Location Predicted by Tidal Regime Switching. PLoS One. 2013; 8(1): e55163
- Klinck, Holger; Mellinger, David K.; Klinck, Karolin; Bogue, Neil M.; Luby, James C.; Jump, William A.; Shilling, Geoffrey B.; Litchendorf, Trina; Wood, Angela S.; Schorr, Gregory S.; Baird, Robin W, 2012. Near-Real-Time Acoustic Monitoring of Beaked Whales and Other Cetaceans Using a Seaglider. PLoS ONE . May2012, Vol. 7 Issue 5, p1-8. 8p.

http://www.imagenex.com/html/853_echo_souder.html (1)

<http://vemco.com/products/vemco-mobile-transceiver-vmt/> (2)

http://www.hightechincusa.com/99_HF.html (3)

D3.5

I.E.3. CDOM (Chromophoric Dissolved Organic Matter)

Scientific rational

CDOM may be produced *in situ* by marine biological activity or derived from terrestrial material. It has a major role in the ocean: it affects the spectral quality of the underwater light field and its photodegradation influences the marine biogeochemistry through the production of labile organic compounds and changes in the bioavailability of metals and nutrients. In coastal areas, CDOM has been successfully used as a tracer of water mass mixing and as a proxy for dissolved organic carbon (DOC) concentration (Andrew et al., 2013 and references therein).

Existing Methods

The main method used to estimate CDOM from gliders is the one based on fluorescence: a fluorometer allows measuring the CDOM fluorescence at an excitation wavelength of ~360 nm and an emission wavelength of ~470 nm, which corresponds to the fluorescence of humic-like material (humic-like material "C" in the Coble's 1996 classification). Because the molecular composition of this humic-like material remains little known, the CDOM fluorometers are externally calibrated using quinine sulphate (QS). QS is highly fluorescent at excitation/emission wavelengths of 350/450 nm when diluted in weak acids (fluorescence domain very close to that of humic-like material C).

The raw signal output of the CDOM fluorometer (in digital counts) is first corrected by subtracting the nominal offset (dark) counts. Then, the offset-corrected signal is multiplied by a linear scale factor to obtain an equivalent concentration (in $\mu\text{g l}^{-1}$ or ppb) of the QS solution used for the calibration (QS diluted in 0.05 M of hydrosulfuric acid). The offset counts and scale factor, which are specific of the fluorometer, are provided by the manufacturer.

The most widespread CDOM fluorometer on gliders is the WETLabs ECO Puck (Niewiadomska et al., 2008; PABIM white Book, D'Ortenzio et al. 2010). In 2012, the Cyclops Integrator fluorometer (Turner Designs) has been proposed in Puck™ format to be also mounted on gliders. These two fluorometers have been used on the "Darwin glider" and a comparison of their performances is currently in progress (Institute of Marine and Coastal Sciences, Rutgers University).

Sensor ECO CDOM fluorometer. It is available for glider uses. It measures optical scattering at 117 degrees of 470, 532 and 650 nm. - Maximum depth: 600m - Manufacturer : WET labs. – (1)

Implementation on gliders

The calibration of CDOM fluorometers should be performed, possibly, before and after each glider deployment. These calibrations are essential to ensure the accuracy and the stability of the instrument parameters (i.e. offset counts and scale factor) and thus to track any drift due to biofouling or aging of the optics (LED etc.). However, the laboratory calibrations are complicated due to the placement of fluorometers within the body of the glider. Because the removal of sensors is generally not possible, the whole vehicle, or a section of it has to be shipped to the manufacturer (for an extended period of time) to carry out calibration. Hence, Cetinić et al. (2009) have proposed a laboratory calibration procedure using a small chamber that can be easily conducted by the user himself. This procedure includes the offset and standard solution measurements. Because the low pH of the QS solutions can potentially damage the fluorometer and the glider, the QS solutions may be replaced by another standard. It has been shown that Sprite Zero® diluted in MilliQ water was a pertinent alternative to QS for CDOM sensor calibration (Cetinić et al., 2009).

To retrieve CDOM absorption [$a_v(412)$] according to Xing et al. (2012), a downward irradiance sensor at 412 nm has to be implemented on gliders. Ideally, the (narrowband) irradiance sensor has to be calibrated regularly in laboratory using a calibrated visible lamp. At sea, deep observations may be used as "black" reference (measurement of the noise value). It is worth noting that the geometry of the measurement (i.e. the position of the sensor relatively to the sun and to the air-sea interface) is quite critical on the glider and could induce some errors. Thus, accurate estimations of the glider position in the water column are required.

D3.5

CDOM data acquired from glider deployments may be compared to those issued from other *in situ* calibrated instruments (fluorometers and irradiance sensors on CTD profiler for instance) or to those derived from measurements on discrete water samples (laboratory fluorescence and absorbance measurements) deployed/collected in the proximity of the glider. In addition, $a_y(412)$ values retrieved from gliders could be compared (at least in the surface waters) to those obtained from ocean color satellite observations.

Quality Control

CDOM estimations from gliders could be checked using the same kind of QC protocols as those proposed for Chla in the framework of Bio-Argo (PABIM white book, D'Ortenzio et al. 2010). Additionally, gliders should be quality controlled at the end of the mission, by verifying sensor performances.

References

- Andrew, A.A., R. Del Vecchio, A. Subramaniam, and N.V. Blough (2013), Chromophoric dissolved organic matter (CDOM) in the Equatorial Atlantic Ocean: Optical properties and their relation to CDOM structure and source, *Marine Chemistry*, 148, 33-43.
- Coble, P.G. (1996), Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, *Marine Chemistry*, 51, 325–346.
- Cetinić, I., G. Toro-Farmer, M. Ragan, C. Oberg, and B.H. Jones (2009), Calibration procedure for Slocum glider deployed optical instruments, *Optics Express*, 17, 15420-15430.
- D'Ortenzio, F., V. Thierry, G. Eldin, H. Claustre, P. Testor, C. Coatanoan, M. Tedetti, C. Guinet, A. Poteau, L. Prieur, D. Lefevre, F. Bourrin, T. Carval, M. Goutx, V. Garçon, D. Thouron, M. Lacombe, P. Lherminier, H. Loisiel, L. Mortier, and D. Antoine (2010), White Book on Oceanic Autonomous Platforms for Biogeochemical Studies: Instrumentation and Measure (PABIM), pp. 55.
- Niewiadomska, K., H. Claustre, L. Prieur, and F. D'Ortenzio (2008), Submesoscale physical–biogeochemical coupling across the Ligurian current (northwestern Mediterranean) using a bio-optical glider, *Limnology and Oceanography*, 53, 2210–2225.
- Xing, X., A. Morel, H. Claustre, F. D'Ortenzio, and A. Poteau (2012), Combined processing and mutual interpretation of radiometry and fluorometry from autonomous profiling Bio-Argo floats: 2. Colored dissolved organic matter absorption retrieval, *Journal of Geophysical Research*, 117, C04022, doi:10.1029/2011JC007632.
- <http://www.wetlabs.com/sites/default/files/documents/ECO-PUCK-2Dec2009.pdf> - (1)

D3.5

I.E.4. Current

Scientific rational

Oceanic currents and climate on earth are closely related. Indeed, currents transfer energy (heat received from the sunlight) from tropical regions to polar areas and play a considerable role in earth temperature regulation (Ganachaud and Wunsch., 2000; Wunsch and Ferrari, 2004). Also, current analysis allows the display and quantification of the biological/ecological conditions of coasts and estuaries (Castelle et al., 2009). It is fully integrated in Ocean Observation Systems (IOOS) and Ocean Observatory Initiatives (OOI) by predicting and modeling of ocean environments (U.S report, 2013).

Existing Methods

An Acoustic Doppler Current Profiler (ADCP) is a type of sonar that measures and records water current velocities over a range of depths. The ADCP is considered as an essential instrument for open ocean and estuary flow current measurements.

An ADCP transmits sound bursts into the water column. Suspended particles carried by water currents produce echoes (from these sound bursts), which are collected by the ADCP. Echoes arriving later are assigned to greater depths in the echo record. This allows the ADCP to form vertical profiles of current velocity. The ADCP measures four different directions simultaneously. The use of Doppler shift (particles within the current flow moving towards the instrument exhibit different frequencies from those moving away) enables precise measurement of direction.

For gliders applications, three instruments are commercially available:

1. **Aquadopp** current meter: The system electronics integrates accurate Doppler velocity measurements with standard sensors such as temperature, pressure, tilt, and compass.- Manufacturer: Nortek - (1)
2. **Signature 75** is based on the ADCP hardware platform. This new platform allows more flexibility than traditional ADCPs. Some of the possibilities include more transducers (Cf. Template *Animal biomass and presence*) than the classical 3 or 4, transducers operating at multiple frequencies, and multiple measurement modes operating simultaneously.- Manufacturer: Nortek - (2)
3. **Explorer Doppler Velocity Log (DVL)** is a compact and versatile sensor designed for small littoral vessels. It has been designed specifically for this next generation of shallow water platforms (gliders).- Manufacturer: Teledyne RD instruments - (3)

Implementation on gliders

Mission-proved for all of them: the *Signature 75* sensor (Russello et al., 2012), Aquadopp current meter (T. Miles et al., 2012) and The explorer Doppler Velocity Log (Ordonez et al., 2012)

Quality Control

It is low maintenance, has no moving parts, requires no recalibration, and has no zero-point drift over time (1). The start and the end periods are problematic in dead reckoning. At the surface, a reasonable estimate of the glider's drift velocity is obtained from GPS position (Russello et al., 2012).

References

- B. Castelle, P. Bretel, S. Morisset, N. Bonneton, P. Bonneton, M. Tissier, C. Sotin, A. Nahon, N. Bruneau, J.-P. Parisot, S. Capo, S. Bujan, and V. Marieu, 2009. *Rip Current System Over Strong Alongshore Non-uniformities: On The Use Of HADCP For Model Validation*; Journal of Coastal Research, Special Issue 56.
- U.S. Integrated Ocean Observing System (U.S. IOOS) 2013 Report to Congress
- Alexandre Ganachaud and Carl Wunsch, 2000. *Improved estimates of global ocean circulation, heat transport and mixing from hydrographic data*. Nature 408, 453-457.

D3.5

Carl Wunsch and Raffaele Ferrari, 2004. Vertical mixing, energy and the general circulation of the oceans. *Fluid Mech*, 36:281–314.

Peter.J.Rusello, Christopher Yahnker and Mark Morris, 2012. Improving Depth Averaged Velocity Measurements from Seaglider with AD2CP. *Oceans*, Virginia Beach VA

Travis Miles, Scott Glenn, Josh Kohut, Greg Seroka, Yi Xuk, 2012. *Observations of Hurricane Sandy from a Glider Mounted Aquadopp*. Not published yet.

Ordonez, C.E., Shearman, R.K. ; Barth, J.A. ; Welch, P. *Obtaining absolute water velocity profiles from glider-mounted Acoustic Doppler Current Profilers*. OCEANS.

<http://www.nortek-as.com/lib/brochures/aquadopp-current-meter> (1)

<http://www.nortek-as.com/en/products/current-profilers/signature75> (2)

http://www.rdinstruments.com/pdfs/explorer_pa_ds_lr.pdf (3)

D3.5

I.E.5. Nitrate (NO₃-)

Scientific rational

Nitrate (NO₃-) is the most relevant nutrient for phytoplankton growth in the ocean. NO₃- concentration is a key parameter to characterize ocean phytoplankton dynamic and, more generally, marine ecosystem functioning. Nutrients are also a critical variable of present-day biogeochemical models (Lequere et al, 2010) as most of the biogeochemical models are based on "NO₃-".

Existing Methods

The absorbance spectrum in the UV (200-400nm) can be directly related to NO₃- concentration of water. A NO₃ sensor is composed by an UV lamp and by a hyperspectral receptor. Water samples are lighted with the UV lamp and the consequent absorption spectra are obtained by the sensor receptor. A direct relationship between the optically active compounds (i.e. NO₃) present in the water sample and the absorption peaks of the spectra allows a direct estimation of the absorbing species concentrations.

1. **SUNA** spectrofotometer is a commercially available NO₃ sensor based on UV absorption technique. Accuracy is relatively low compared with standard method (+/- 0.5 µM/L), though use of SUNA on profiling floats has been already successfully tested (Johnson et al. 2010).- Manufacturer: Satlantic – (1)

Implementation on gliders

SUNA has been implemented on a SLOCUM glider, in the framework of the French monitoring of the Mediterranean coast (MOOSE project). The glider version is now commercially available, as well as the up-to-date software, which comprises the last processing algorithms.

Quality Control

Quality control is essentially based on the reprocessing on land of the measured absorption spectrum (Johnson et al. 2013). Sensor offset and bias are evaluated by comparing in situ samples at deployment. Main issues still exist at very low (around 0µM/L) NO₃ concentrations and/or at high (> 20°C) temperature.

References

- KS Johnson, SC Riser, DM Karl, (2010), Nitrate supply from deep to near-surface waters of the North Pacific subtropical gyre, Nature 465 (7301), 1062-1065
- Johnson, K. S., Coletti, L. J., Jannasch, H. W., Sakamoto, C. M., Swift, D. D., & Riser, S. C. (2013). Long-term nitrate measurements in the ocean using the In Situ Ultraviolet Spectrophotometer: sensor integration into the Apex profiling float. Journal of Atmospheric and Oceanic Technology, (2013).
- Lequéré et al, (2010). Observational Needs of Dynamic Green Ocean Models. Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 2), Venice, Italy, 21-25 September 2009, Hall, J., Harrison D.E. and Stammer, D., Eds., ESA Publication WPP-306, 2010.56-3561.
- <http://satlantic.com/sites/default/files/documents/SUNAV2-July10-2013.pdf> - (1)

D3.5

I.E.6. Oxygen (O₂) (Partial Pressure)

Scientific rationale

Composing partially the planet atmosphere (21%), dioxygen is also present in the oceans. Its concentration can go from almost 0 (anaerobic condition) to 200 µg/L around Polar Regions at the surface (Keeling et al., 2010). Oxygen distribution in the ocean depends on both biological processes, like the respiration of organisms, and on physical processes such as current flow. Changes in either of these processes should therefore lead to changes in the oxygen distribution. Oxygen levels affect geochemical processes in the sediment but also, above all, bacterial metabolism processes, which, under altered oxygen conditions, can be changed dramatically. In oceanography, dissolved oxygen has been an important measurement parameter for over a hundred years.

Existing Methods

For several years already, many sensors are available to measure dissolved oxygen in seawater.

1. The oxygen **Optode** works on an optical measurement principle. It is designed to measure absolute oxygen concentration and % saturation. The optode can be used from surface to deep sea and from polar ice areas to hydrothermal vents. The lifetime-based luminescence quenching principle offers large benefits ; (more than one year without recalibration, maximum depth : 6000m ; small size and weight etc) – Manufacturer: Aanderra (AADI) -(1)
2. The **SBE 43** is a dissolved oxygen sensor. It sets the oxygen measurement standard for oceanographic research. The sensor is a complete redesign of the 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. Range measurement : 120% of surface saturation; maximum depth : 7000m – Manufacturer: SeaBird Electronics - (2)
3. The **Rinko** sensor is an optode model. It provides profiling of oxygen concentration gradients with the sub-meter resolution to the full ocean depth (7000m rated). Range detection : 0 to 200% - Manufacturer: JFE ALEC Co. Ltd (RINKO) - (3)

Implementation on gliders

Mission-proved for all of them: Oxygen optode (KS. Johnson et al., 2009) and SBE 43 (S. Emerson et al, 2008) and Rinko sensor (Perry et al. submitted).

Quality Control

For SBE 43, the calibration drift is caused primarily by membrane fouling from ocean contaminants, and less so by chemical processes inside the sensor. If the membrane is kept clean, the sensor's improved chemical stability yields demonstrated calibration drift rates of less than 0.5% over 1000 hours of operation. Rinko sensor needs an *in-situ* calibration using Winkler-titration samples to provide accurate O₂ data. (4)

For oxygen optode, it is assumed that sensor drift occurs due to the oxygen sensitivity of the sensors, not the temperature compensation. It has significant long-term drift in output when sampling anoxic water. Sensor output at 100% saturation differs from the factory calibrations by up to ±6% up to -12.6% for the optodes (D'asaro et al., 2013). But it displays an accuracy of ±0.4% over a 4-yr period (D'Asaro, Eric, McNeil, 2013)

References

- Ralph F. Keeling, Arne Kortzinger, and Nicolas Gruber. Ocean Deoxygenation in a Warming World. *Marine. Sci.* 2010. 2:199–229
- Johnson, Kenneth S.; Berelson, William M.; Boss, Emmanuel S.; Chase, Zanna; Claustre, Herve; Emerson, Steven R.; Gruber, Nicolas; Kortzinger, Arne; Perry, Mary Jane; Riser, Stephen C. 2009. *Observing biogeochemical cycles at*

D3.5

global scales with profiling floats and gliders: Prospects for a global array. Oceanography vol 22 n°1.

Steven Emerson, Charles Stump, David Nicholson, 2008. *Net biological oxygen production in the ocean: Remote in situ measurements of O₂ and N₂ in surface waters.* Global Biogeochemical Cycles Volume 22, Issue 3.

D'Asaro, Eric A., Craig McNeil, 2013. *Calibration and Stability of Oxygen Sensors on Autonomous Floats.* *J. Atmos. Oceanic Technol.*, **30**, 1896–1906.

RL Perry, SF DiMarco, J Walpert, NL Guinasso Jr., A. Knap. *Glider Operations in the Northwestern Gulf of Mexico.* *Not published.*

http://www.aanderaa.com/media/pdfs/Oxygen-Optode-4831_4831F.pdf (1)

http://www.seabird.com/pdf_documents/Datasheets/43brochureSep13.pdf (2)

<http://www.rocklandocean.com/resources/RINKOsepc.pdf> (3)

http://www.go-ship.org/Manual/Langdon_Amperometric_oxygen.pdf (4)

D3.5

I.E.7. Phycobilins (Phycocyanin, Phycoerythrin)

Scientific rationale

Among the thousands of species of microscopic algae at the base of the food chain, a few dozen produce toxins (Horner et al., 1997). These algae are mainly responsible for the so called "harmful algal blooms," or HAB. Other species bloom in dilute, inconspicuous concentrations but are noticed because they produce potent toxins that kill marine organisms, or transfer through the food chain (Gilbert et al., 2006), harming organisms at multiple levels. The causes of HAB events are poorly understood, but possible explanations range from natural mechanisms of species dispersal to anthropogenic actions such as nutrient loading, climatic shifts, or transport of algal species via ship ballast water (Glibert and Burkholder, 2006). As the impacts of mass mortalities of wild and farmed fish, marine mammals, seabirds, and illness and death in humans from contaminated fish or shellfish increase, research about the mechanisms of HAB events is urgently needed.

Existing Methods

ECO phycobilin fluorometers (Single-wavelength measurement) have the high resolution necessary for early detection of either blue-green (phycocyanin) or brown (phycoerythrin) algae. Range detection: 0-230 ppb; sensitivity: 0,03 ppb; wavelengths measurement : 540/570 nm (phycoerythrin), 630/680 (phycocyanin), maximum depth: 6000m. - Manufacturer : WetLabs. – (1)

Implementation on gliders

Mission-proved (English et al., 2009)

Quality Control

This fluorometer is a relative measurement instrument and should be calibrated by cell counts for a particular water mass.

References

- RA Horner, DL Garrison, FG Plumley, 1997. *Harmful algal blooms and red tide problems on the US west coast. Limnology and Oceanography.* Vol. 42, No. 5 . pp. 1076-1088
- PM Glibert, JM Burkholder, 2006. *The complex relationships between increases in fertilization of the earth, coastal eutrophication and proliferation of harmful algal blooms.* Ecology of harmful algae, vol 189, pp341-354
- D English, C Hu, C Lembke, R Weisberg, 2009. Observing the 3-dimensional distribution of bio-optical properties of West Florida Shelf waters using gliders and autonomous platforms. *Ocean.*
- <http://www.wetlabs.com/sites/default/files/documents/ECO-FL-5Sep2011.pdf> - (1)
- <http://www.wetlabs.com/sites/default/files/documents/ECO-PUCK-2Dec2009.pdf> - (1)

D3.5

I.E.8. Turbidity backscatter

Scientific rationale

Turbidity is the measurement of water clarity. The more turbid the water, the murkier it is. Turbidity can be caused by soil erosion, waste discharge, urban runoff, bottom feeders that stir up sediments and algal growth (Ingwersen et al., 1999). Turbid waters become warmer as suspended particles absorb heat from sunlight, causing oxygen levels to fall. Photosynthesis decreases with lesser light, resulting in even lower oxygen levels. Thus, it is a fundamental parameter for water monitoring.

Existing Methods

1. The **ECO BB** measures scattering at 117 degrees, the angle determined as a minimum convergence point for variations in the volume scattering function (VSF) induced by suspended materials and water itself. As a result, the signal measured by this meter is less determined by the type and size of the materials in the water and is more directly correlated to the concentration of the materials. Wavelength : 470, 532, 650 nm ;Sensitivity = 0,003 m⁻¹ ;Range ~ 0–5 m⁻¹ ; maximum depth : 6000 m – Manufacturer : WETLabs. – (1)
2. **WET Labs' Beam Attenuation Meter (BAM)** is the next generation of transmissometer. The principle is a collimated source, reflective sample cell with diffuser in front of wide area detector. It has been specifically designed for Autonomous Underwater Vehicles (AUVs) and gliders, where size and drag are primary considerations. Wavelengths 470, 532, or 650 nm ; Optical pathlength 10 cm ; Acceptance angle ~ 1 deg ; precision : 532 and 650 nm 0.003 m⁻¹ at 1 Hz - ; maximum depth : 1000 m – Manufacturer : WETLabs.- (2)
3. The **Seapoint Turbidity Meter** detects light scattered by particles suspended in water, generating an output voltage proportional to turbidity or suspended solids. Sensitivity is selected by two digital lines that can be hardwired or microprocessor controlled, thereby choosing the appropriate range and resolution for measurement of extremely clean to very turbid waters. The unique optical design confines the sensing volume to within 5 cm of the sensor allowing near-bottom measurements and minimizing errant reflections in restricted spaces. Light source wavelength: 800nm; Maximum depth : 6000m – Manufacturer : Seapoint Sensors.- (3)

Implementation on gliders

Mission-proved for ECO BB (Mahoney et al., 2009), BAM (Ladner et al., 2012) and the Seapoint turbidity meter (Twardowski et al., 2005).

Quality Control

Since the size of these sensors is small, two of them could be set up on the same glider to compare their data.

References

- S Ingwersen, G Mewett, M Wilton, 1999. Algonquin Ecosystem Headwater Study: Tyne Lake Watershed. PRFO proceedings. .
- Kevin L. Mahoney; Ken Grembowicz; Bruce Bricker; Steve Crossland; Danielle Bryant; Marc Torres; Tom Giddings, 2009. RIMPAC 08: Naval Oceanographic Office glider operations. Ocean Sensing and Monitoring. Edited by (Will) Hou, Weilin. Proceedings of the SPIE, Volume 7317 (2009)., article id. 731706, 11 pp.
- S. D. Ladner ; R. Arnone ; J. Jolliff ; B. Casey ; K. Matulewski, 2012. Forecasting the ocean optical environment in support of Navy mine warfare operations. Ocean Sensing and Monitoring IV,. Edited by Hou, Weilin W.; Arnone, Robert. Proceedings of the SPIE, Volume 8372, article id. 83720Z, 10 pp.
- Michael S. Twardowski ; J. Ronald V. Zaneveld ; Casey M. Moore ; James Mueller ; Charles Trees ; Oscar Schofield ; Scott Freeman ; Tyler Helble ; Gerry Hong, 2005. Diver visibility measured with a compact scattering-attenuation meter (SAM) compatible with AUVs and other small deployment platforms. Photonics for Port and Harbor Security, Volume 5780, pp. 71-80

<http://www.wetlabs.com/sites/default/files/documents/ECO-BB-21Sep2010.pdf> (1)



GROOM Sensors for gliders

Grant Agreement Number: 284321
FP7-Infra-2011-2.1.1 "Design
Studies"



D3.5

<http://www.wetlabs.com/sites/default/files/documents/BAM-8Jul2009.pdf> (2)

http://www.seapoint.com/pdf/stm_ds.pdf (3)

D3.5

1.E.9. CTD (conductivity, Temperature, Depth)

Scientific rational

The CTD is the primary tool for determining essential physical properties of sea water. It gives scientists a precise and comprehensive charting of the distribution and variation of water temperature, salinity, and density that helps to understand how the oceans affect life and climate (Dore et al., 2003). Indeed in oceans, almost all the biogeochemical reactions depend on these three parameters (Windom et al., 2003).

Existing Methods

1- The GPCTD (Glider payload CTD) : It evolved from sensors and measurement circuits used in Argo float CTDs. It measures conductivity, temperature, and pressure (described below). The pressure-proof module allows glider users to exchange CTDs in the field without opening the glider pressure hull. The pump pulls water into the duct at top of the intake sail and immediately past a temperature sensor. Water then flows through an anti-foulant cylinder, through the conductivity cell, and out the top of the exhaust sail to prevent exhaust re-circulation and Bernoulli pressure differences from changing the flow - Manufacturer: Sea-Bird Electronics. The temperature sensor is a compact module containing a pressure-protected, high-speed thermistor and Wien-bridge-oscillator interface electronics. The thermistor is the variable element in the Wien Bridge, while a precision Vishay resistor and two ultra-stable capacitors form the fixed components. The conductivity sensor is similar in operation and configuration to the temperature sensor, except that the Wien-bridge variable element is the cell resistance (cell resistance is the reciprocal of cell conductivity). The Digiquartz® pressure sensor also provides a variable frequency output. Embedded in the pressure sensor is a semiconductor temperature sensor used to compensate the small ambient temperature sensitivity of the Digiquartz. The calibration information for each sensor (C, T, and P) is contained in a series of numeric coefficients used in equations relating frequency to the measured parameter – Manufacturer: Seabird - (1)

| | Measurement Range | Calibration Range | Accuracy (within calibration range) | Accuracy (outside calibration range) | Typical Stability | Resolution |
|-------------------------|--|-------------------|-------------------------------------|--------------------------------------|--------------------|----------------------------|
| Conductivity | 0 to 9 S/m | 0 to 6 S/m | ± 0.0003 S/m | better than ± 0.0010 S/m | 0.0003/month | 0.00001 S/m |
| Temperature C° | -5 to +42 | +1 to +32 | ± 0.002 | better than ± 0.004 | 0.0002/month | 0.001 |
| Pressure (depth) (dbar) | 0 to 100, 0 to 350, 0 to 1000, 0 to 2000 | full scale | ± 0.1% of full scale range | -- | 0.05% of F.S./year | 0.002% of full scale range |

2- The Fin-cell GCTD: It is a new CTD method, which has been designed for gliders. It uses a four-electrode conductivity cell with internal temperature sensor to achieve excellent dynamic response and high spatial resolution. The design is rugged, has low drag and is resistant to fouling. No pump is required and the electronics are self-calibrating and free of thermal drifts – Manufacturer: WHOI - (2)

Implementation on gliders

Mission-proved for both of them: GPCTD (Janzen and Creed, 2011) and Fin-cell GCTD (Schmitt and Petitt, 2006)

D3.5

Quality Control

A methodology is proposed to correct the thermal lag error in data from unpumped CTD sensors installed on Slocum gliders. The advantage of the new approach is twofold: first, it takes into account the variable speed of the glider; and second, it can be applied to CTD profiles from an autonomous platform either with or without a reference cast. The proposed methodology finds values for four correction parameters that minimize the area between two temperature–salinity curves given by two CTD profiles. (Garau et al., 2011)

References

- JE Dore, R Lukas, DW Sadler, DM Karl, 2003. Climate-driven changes to the atmospheric CO₂ sink in the subtropical North Pacific Ocean. *Nature* 424, 754-757.
- H Windom, F Nienches, 2003. Biogeochemical processes in a freshwater–seawater mixing zone in permeable sediments along the coast of Southern Brazil. *Marine Chemistry*, vol 83, issue 3-4.
- CD Janzen, EL Creed, 2011. Physical oceanographic data from Seaglider trials in stratified coastal waters using a new pumped payload CTD. OCEANS.
- Raymond W. Schmitt and Robert A. Petitt, 2006. A fast response, stable CTD for gliders and AUVs. OCEANS-(2)
- Bartolomé Garau, Simón Ruiz, Weifeng G. Zhang, Ananda Pascual, Emma Heslop, John Kerfoot, and Joaquín Tintoré, 2011. *Thermal Lag Correction on Slocum CTD Glider Data*. *J. Atmos. Oceanic Technol.*, 28, 1065–1071.
- http://www.seabird.com/products/spec_sheets/GliderPayloadCTDdata.html (1)

D3.5

I.E.10. Radiance-Irradiance

Scientific rationale

Radiance is a radiometric measure that describes the amount of light emitted from the ocean whereas irradiance is the power of the electromagnetic radiation of the ocean. The radiance distribution is an important input for the study of the interaction of electromagnetic radiation with the sea. From the distribution of radiance in the natural light fields in the ocean, many of the important optical properties, which relate to radiative transfer processes in the ocean can be calculated (Key et al. 1998). Finally, since radiant energy is critical to the beginning of the marine food chain through photosynthetic plankton, (Bancroft et al., 2007) radiance distribution measurements will provide information of fundamental importance to the problem of primary productivity in oceans.

Existing Methods

1. **OCR 500 Multispectral Radiometer** (for radiance and irradiance): A combination of precision optics and high performance microelectronics which can be operated as a stand-alone device or in a networked environment as a part of a larger system- The OCR-500 utilizes four customer-defined discrete optical wavelengths. Two standard, non-isolated, telemetry (data) interfaces are provided. Each interface uses a different transmission medium. Standard wavelengths from 400 - 865 nm ; UV wavelengths available 305, 325, 340 & 380 nm - Manufacturer : Satlantic. (1)
2. **QSP-2000 series (Quantum Scalar Sensor)** is a PAR sensor (Photosynthetically Active Radiation) with a spherical receiver that is equally sensitive to photons from all directions. Measures Quantum Scalar Irradiance. Quantum response: 400 to 700 nm, maximum depth : 2000 m- Manufacturer : Biospherical instruments. (2)

Implementation on gliders

Mission-proved for OCR 500 (Niewiadomska et al., 2008). Regarding QSP-2000, according to the GROOM Deliverable 5.2, it has been field-tested (Jan Kaiser, personal communication) but no report has been published yet. A Biospherical instruments PAR sensor (Biospherical instruments 2011) was deployed on a seaglider operated by the university of East Anglia (Jan Kaiser, personal communication). An implementation seems very easy with a size of 15cm x 5 cm Ø.

Quality Control

Quality control algorithms are available for optical properties measurements. Visual inspection by experts validates the performance, with errors less than half a percentage point (Hou et al., 2010).

References

- JR Key, AJ Schweiger, 1998. *Tools for atmospheric radiative transfer: streamer and fluxnet*. Computer and Geoscience, vol 24, issue 5. Pages 443–451
- BA Bancroft, NJ Baker, AR Blaustein, 2007. *Effects of UVB radiation on marine and freshwater organisms: a synthesis through meta-analysis*. Ecology Letters, Volume 10, Issue 4, pages 332–345.
- Katarzyna Niewiadomska, Herve Claustre, Louis Prieur, and Fabrizio d'Ortenzio, 2008. *Submesoscale physical-biogeochemical coupling across the Ligurian Current (northwestern Mediterranean) using a bio-optical glider*. Limnol. Oceanogr., 53 (5, part 2) 2210–2225.
- Weilin Hou, Derek Burrage, Michael Carnes, Robert Arnone, 2010. *Development and Testing of Local Automated Glider Editing Routine for Optical Data Quality Control*. Naval Research LAB Stennis Space Center MS oceanography Div.
- <http://satlantic.com/sites/default/files/documents/OCR-500-09Jan2008.pdf> (1)
- <http://www.biospherical.com/images/pdf/qsp-2000-erf.pdf> (2)

D3.5

I.E.11. Turbulence

Scientific rational

Turbulence measurement in the oceans is a proxy of energy dissipation (Moum et al., 1995). Most of turbulence measurements at dissipation length scales are carried out using "single-use" vertical profilers. Turbulence observations in the oceans remain sparse, despite half-a-century's worth of measurements. Gliders provide a nearly ideal platform for turbulence measurements, because their propulsion does not rely on moving parts, such as propellers, whose vibrations could introduce noise into the measured turbulent velocity fluctuation.

Existing Methods

The **MicroRider** is a small instrument package for turbulence measurements, designed to integrate with a variety of instrument carriers, especially ocean gliders. The MicroRider carries the following sensors:

- Velocity shear probes (SPM-38-1), Range: $3.10 \cdot 10^{-10} - 4W.Kg^{-1}$; accuracy : 5% ;resolution: $2,5.10^{-3} s^{-1}$
- Fast response thermistors (FP07-38-1), Range: -5 – 35 °C; accuracy: $1.10^{-3} °C$; resolution: $1.10^{-4} °C$
- Micro conductivity probe (SBE7-38-1), Range: 0-7 S/m; accuracy: 0,0003 S/m; resolution: 0,00004 S/m
- High-resolution pressure sensor; Range: 0- 1000 dbar; accuracy: 1% ; resolution: 0,0005 dbar
- High-resolution acceleration sensors; Range: $\pm 2g$; accuracy: 0,5%; resolution: $3.10^{-5} g$; stability: $\pm 0,5\%$
- Tilt sensor: Range: dual axis $\pm 90^\circ$; accuracy: $0,1^\circ$; resolution: $0,025^\circ$

Internal accelerometers provide vibration information. Since the MicroRider is designed to ride on a wide range of instrumentation platforms, the vibration data are of vital importance to the measurement. Maximum depth: 6000 m – Manufacturer: Rockland Scientific – (1)

Implementation on gliders

Mission-proved for MicroRider (Balfour et al., 2011).

Quality Control

NA

References

Balfour, C., Knight, P. and McLaughlin, D. (2011) *NOC turbulence glider deployment report for the OSMOSIS Project*. Southampton, UK, National Oceanography Centre, 25pp. (National Oceanography Centre Research and Consultancy Report, 06).

JN Moum, MC Gregg, RC Lien, ME Car, 1995. *Comparison of turbulence kinetic energy dissipation rate estimates from two ocean microstructure profilers*. Journal of Atmospheric and oceanic technology, vol 12, pp 346-366.

<http://www.rocklandscientific.com/LinkClick.aspx?fileticket=2QpE2AQoUco%3d&tabid=133> - (1)



GROOM Sensors for gliders

Grant Agreement Number: 284321
FP7-Infra-2011-2.1.1 "Design
Studies"



D3.5

D3.5

I.F. Sensors with easy implementation on gliders

- I.F.1- Actinides
- I.F.2- Bioluminescence
- I.F.3- BOD (Biological Oxygen Demand)
- I.F.4- Bromide concentration (Br^-)
- I.F.5- Carbon Dioxide (CO_2)
- I.F.6- Chlorinated hydrocarbons (CHCs)
- I.F.7- Chrome (Cr)
- I.F.8- Copper (Cu)
- I.F.9- Cyanide
- I.F.10- Dihydrogen (H_2)
- I.F.11- Dinoflagellate
- I.F.12- Explosives
- I.F.13- Sulphur ($\text{H}_2\text{S}/ \text{HS}^-$)
- I.F.14- Heavy Metal (Pb, Hg, Cd, Cu)
- I.F.15- Hydrocarbons
- I.F.16- Hydrogen Peroxide (H_2O_2)
- I.F.17- Manganese (Mn)
- I.F.18- Mapping communities
- I.F.19- Methane (CH_4)
- I.F.20- Nutrients
- I.F.21- Ozone (O_3)
- I.F.22- Polycyclic aromatic hydrocarbons (PAHs) - polychlorinated biphenyls (PCBs)
- I.F.23- pH
- I.F.24- Radioactivity
- I.F.25- Redox potential
- I.F.26- Rhodamine / Amido-Rhodamine / Fluorescein
- I.F.27- deep-sea low-frequency sub-bottom profiler (SBP)
- I.F.28- Seismic waves
- I.F.29- Virus

D3.5

I.F.1. Actinides

Scientific rational

The actinide series encompasses the 15 metallic chemical elements with atomic numbers from 89 to 103. They are all radioactive and then carcinogenic. The best known are uranium, plutonium and thorium. In surface seawater, uranium and thorium concentrations were measured at 13 nmol/kg at 430 femtomol/kg, respectively (Chen et al. 1986). In India, for example, a large amount of thorium was measured in placer deposits of the Western and Eastern coastal dune sands, particularly in the Tamil Nadu coastal areas. The residents of this area are exposed to a naturally occurring radiation dose ten times higher than the worldwide average (Mohanty et al., 2004).

Existing Methods

The sensor is based on a cationic-coated Surface Enhanced Raman Spectroscopy (SERS) substrates. The coating attracts the anions to the SERS substrate where they are identified and quantified by their characteristic Raman emission. The cationic coating stabilizes the SERS substrate, thereby extending its lifetime and has a characteristic SERS spectrum, which can be used as an internal calibration standard. The advantages of this approach over conventional techniques are (1) the required information is obtained in real-time, (2) it doesn't require the additional cost of an outside laboratory, and (3) decisions can be made in a timely fashion as to whether or not additional sampling is required and where that sampling is needed. In this effort, methods of improving selectivity and sensitivity are addressed as well as sensor design. - Manufacturer: SERDP. – (1)

Implementation on gliders

The sensor has not been tested in seawater, therefore some work needs to be done to adapt it for oceanography studies. Nevertheless, its size should permit a glider implementation.

Quality Control

NA

References

A.K. Mohanty, D. Sengupta, S.K. Das, S.K. Saha, K.V. Van, 2004. *Natural radioactivity and radiation exposure in the high background area at Chhatrapur beach placer deposit of Orissa, India. Journal of Environmental Radioactivity Volume 75, Issue 1, 2004, Pages 15–33*

Chen, J.H., Edwards, R.L. and Wasserburg, G.J., 1986. 235U, 234U and 232Th in seawater. *Earth Planet. Sci. Lett.*,80: 241-251.

<http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER-1267> - (1)

D3.5

I.F.2. Bioluminescence

Scientific rationale

Bioluminescence is a major and often underappreciated feature of the dysphotic and aphotic oceanic realm (Widder 2002). Bioluminescence-capable taxa range from unicellular aggregation-forming microbes to fast-swimming predators such as cephalopods and fish, most commonly emitting in the blue, with peak intensities between 450-500 nm. Activity is usually mechanically stimulated (by an external force), but can also be generated voluntarily. Consequently, bioluminescence has attracted interest not only because of its ecological repercussions but also because of potential military applications.

Existing Methods

In principle, the detection of bioluminescence is achieved by imaging detection systems that can record ambient visible light wavelengths, with various improvements or additions (e.g., cross-polarizers, fluorescence detection, etc.) to detect a broader range of physiological adaptations to vision in the deep ocean (see Widder 2007 for further details).

However, stimulated bioluminescence poses a methodological conundrum: most of these detection systems generate some sort of motion which stimulates a response, but whose intensity is unknown. Therefore, systems have evolved to allow careful control of the stimulation. Typically, they consist of a light detector viewing a light-tight chamber in which ambient water is sampled and subjected to mechanically generated turbulence (Widder 2002). One example of such an instrument is the Multipurpose Bioluminescence Bathypotometer (MBBP, Herren et al. 2005).

Undisturbed (background) bioluminescence is much more difficult to achieve, but not impossible. Untethered submersibles have documented decreases and even cessation of bioluminescence moments after the vehicles achieved neutral buoyancy in mid-water (Widder 2002).

Implementation on glider

WETLabs has designed a sensor dubbed the Underwater Bioluminescence Assessment Tool (**UBAT**) for deployment on ship-board profilers, AUVs and moorings (WETLabs 2010). The UBAT is a controlled-stimulation sensor, based on the MBBP mentioned above, that uses a pump impeller to generate a highly turbulent passage of the sampled organisms through a 0.44-L detection chamber. The UBAT measures 34.93 × 10.80 × 16.83 cm, weighs 1.64 kg in water, and draws 600 mA, which render its adaptation for glider use promising – Manufacturer: Wetlabs – (1).

Quality Control

Calibration for bioluminescence sensors typically involves the measurement of stimulation efficiency (the fraction of total mechanically stimutable light) using live cultures of bioluminescent unicellular organisms and comparing the sensor performance with that of an independent photometer on the same cultures. Details of such a calibration using two dinoflagellate species are given in Herren et al. (2005). Intercomparison in the field would require the deployment of a separate sensor on a mooring or from a ship. Clearly, the calibration procedure may require access to infrastructure and know-how not typically available within a glider group, but perhaps within a closely collaborating or parent-institution.

References

- Herren, C. M., Haddock, S. H. D., Johnson, C., Orrico, C. M., Moline, M. A., Case, J. F. (2005) A multi-platform bathypotometer for fine-scale, coastal bioluminescence research. *Limnol. Ocean. Methods*, 3: 247–262.
- WETLabs. (2010) Underwater Bioluminescence Assessment Tool (UBAT) Hardware User's Guide, WETLabs. Retrieved from <http://www.wetlabs.com/sites/default/files/documents/ubathwb.pdf> - (1)
- Widder, E. (2002) Bioluminescence and the pelagic visual environment. *Mar. Freshw. Behav. Physiol.*, 35 (1-2): 1–26.



GROOM Sensors for gliders

Grant Agreement Number: 284321
FP7-Infra-2011-2.1.1 "Design
Studies"



D3.5

Widder, E. (2007) Sly eye for the shy guy: Peering into the depths with new sensors. *Oceanography*, 20 (4): 46–51.

D3.5

I.F.3. Biological Oxygen Demand (BOD)

Scientific rationale

Dead zones are hypoxic (low-oxygen: <2mg/L) areas in the world's oceans. They are generally formed by excessive nutrient pollution from human activities (Doney, 2010). Very often, coupled with other factors (nutrients, light, currents etc) oxygen is required to support most marine life in bottom and near-bottom water. In the 1970's, oceanographers began noting increased instances of dead zones, in particular near inhabited coastlines, where aquatic life is most concentrated. Global Environment Outlook Year Book (*GEO Year Book 2003*) reported, in 2004, 146 dead zones in the world's oceans where marine life could not be supported due to depleted oxygen levels. A 2008 study counted 405 dead zones worldwide (Diaz, 2008). Because most marine life either dies, or, if they are mobile such as fish, leave the area, the study and the comprehension of these zones is crucial, as well as the biological aspect that the economic aspect.

Existing Methods

The sensor **Uvilux BOD** detects fluorescent proteins that are inherent within sewage and slurry and provides an output in BOD equivalent units. The principle behind the measurement is the excitation of Tryptophan-like UV fluorescence, which correlates with both bacterial loading and BOD. An internal calibration factor is used to convert the Tryptophan-like fluorescence measured to the reported BOD equivalent value in units of mg/L. The use of fluorescence provides signal detection sensitivity far superior to optical absorption methods. - Manufacturer : Chelsea Technologies Group Ltd – (1).

| Excitation | Emission | Sensitivity | Calibrated Range | Depth Rating |
|------------|----------|-------------|------------------|--------------|
| 280nm | 360nm | 0.001 mg/l | 0.001 - 50mg/l | >50m |

Implementation on gliders

With a size of Ø70mm x 149mm, the Uvilux BOD sensor is a good candidate for gliders. However, on the manufacturer website (<http://chelsea.co.uk>), it is mentioned that it can be used in natural water system and presented in the "marine application" tab, although the sensor's technical sheet is listed in "freshwater". So, its use for seawater needs to be verified.

Quality Control

NA

References

SC Doney,,2010. *The growing human footprint on coastal and open-ocean biogeochemistry*. Science, vol 328 no. 5891, pp. 1512-1516

Robert J. Diaz, Rutger Rosenberg, 2008. Spreading Dead Zones and Consequences for Marine Ecosystem. Science Vol. 321 no. 5891 pp. 926-929

<http://chelsea.co.uk/marineapps/sewage-outflow-monitoring> - (1)

<http://chelsea.co.uk/allproduct/environmentalfresh-water/fluorometers/uvilux-bod-indicator> - (1)

D3.5

I.F.4. Bromide Concentration (Br⁻)

Scientific rationale

Bromide occurs naturally in the ocean. It is observed in typical seawater (salinity: 35g/L) with a concentration of around 65 mg/L (Haag and Holgn, 1983), which is around 0.2% of all dissolved salts. Seafoods and deep sea plants generally have high levels of Br⁻ (Boon et al., 2002), while foods derived from land have variable amounts. Chronic toxicity from Br⁻ can result in bromism, a syndrome with multiple neurological symptoms (Carney, 1971).

Existing Methods

The **ISUS** is a sensor used to measure concentrations of dissolved chemical elements directly from their ultraviolet absorption. Br⁻ absorbs light in the UV and it has a unique absorption spectrum. Br⁻ concentration could be then evaluated without chemical manipulation, by measuring the absorption spectrum of seawater in the UV and then deconvolving the spectra. The detection limit is 0.5 to 2000 µM and the sample rate is 1 Hz. – (1)

Implementation on gliders

Although it has already been tested on a mooring (personal communication), a deployment on a glider has not been done or published yet. Nevertheless, its length of 608 mm and diameter of 114 mm, make more than possible an implementation. In water, its weight is 0,7 kg and the lamp lifetime of the spectrophotometer is 900 hours. It can go up to 2000 meters depth. – Manufacturer : MBARI.

Quality Control

NA

References

- M. W. P. Carney, 1971. *Five cases of bromism*. The Lancet
- Jan P. Boon, Wilma E. Lewis, Michael R. Tjoen-A-Choy, Colin R. Allchin, Robin J. Law, Jacob de Boer, Cato C. ten Hallers-Tjabbes, and Bart N. Zegers, 2002. *Levels of Polybrominated Diphenyl Ether (PBDE) Flame Retardants in Animals Representing Different Trophic Levels of the North Sea Food Web*. *Environ. Sci. Technol.*, 36 (19), pp 4025–4032
- Werner R. Haag and Jurg Holgn, 1983. *Ozonation of Bromide-Containing Waters: Kinetics of Formation of Hypobromous Acid and Bromate*. *Environ. Sci. Technol.*, Vol. 17, No. 5, 267
- Johnson, K.S., Coletti, L.J. (2002) *In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean*. *Deep Sea Research* 49 1291-1305
- <http://www.mbari.org/chemsensor/ISUSHome.htm> - (1)

D3.5

I.F.5. Carbon Dioxide (Partial Pressure of CO₂)

Scientific rationale

The ocean plays a critical role in mitigating climate change taking up nearly 30 per cent of anthropogenic CO₂ emissions (Le Quéré et al., 2009). Since the industrial revolution (~1800's), the anthropogenic CO₂ concentration into the atmosphere has increased exponentially from 280 to 400 ppm (part per million) in 2013 (IPCC, 2007). CO₂ diffuses into the seawater and dissolves, inducing an increase of the partial pressure (pCO₂) (Feng et al., 2008). pCO₂ ranges presently between ~180 and ~1420 µAtm (de Kluijver et al., 2012). The first consequence of the increase is decrease of the seawater pH and a disturbance in marine ecosystems, referred to as acidification (Feely et al., 2009).

Existing Methods

1. **CONTROS HydroC™** CO₂ sensor is an underwater sensor for *in-situ* and online measurements of dissolved CO₂. Dissolved CO₂ molecules diffuse through a patented thin-film composite membrane into the detector chamber, where their volume is determined by means of IR absorption spectrometry. Concentration-dependent IR light intensities are converted into output signals. – Sensor characteristics: Measuring range : from 200 to 1000 ppm* (other ranges available according to the manufacturer), Resolution: < 1 ppm, Accuracy : ±1 % reading, Max depth : 6000m. Manufacturer : Contros.
2. The **SAMI-CO₂** measures the partial pressure of CO₂ in water (pCO₂) using a highly precise and stable colorimetric reagent method. It is designed to provide researchers with valuable *in-situ* time series. The SAMI-CO₂ can run for over a year taking hourly measurements. Sensors characteristics: Measuring range : from 150 to 700 µatm (other ranges available by request) ; Accuracy : ± 3ppm ; Precision : <3 µatm; Max depth : 600m. (*) µatm=ppm. Manufacturer: Sunburst Sensor.

Implementation on gliders

For both of them an implementation seems possible inside or on the glider's hull: CONTROS' Size : 9cm Ø x 37,6cm: SAMI's size : 55cm x 15,2 cm Ø

Quality Control

The measure of alkalinity and of Dissolved Inorganic Carbon (DIC) allows, via the carbonate system equations to recalculate the pCO₂ value. Although pH is also integrated into this system, the measurement of this parameter is not precise enough for the seawater and would bring an uncertainty on the recalculated pCO₂ value

References

- De Kluijver, K. Soetaert, J. Czerny, K. G. Schulz, T. Boxhammer, U. Riebesell, and J. J. Middelburg, 2012. *CO₂ effect on pelagic carbon flows. Biogeosciences, Discuss., 9, 8571–8610*
- Le Quéré, C. et al. 2009 Trends in the sources and sinks of carbon dioxide. *Nat. Geosci.* 2, 831–836.
- RA Feely, SC Doney, SR Cooley., 2009. *Ocean acidification: present conditions and future changes in a high-CO₂ world. Oceanography 22 no. 4: 36-47.*
- RA Houghton, 2003. Revised estimates of the annual net flux of carbon to the atmosphere from changes in land use and land management 1850–2000. *Tellus B Volume 55, Issue 2, pages 378–390*
- Yuanyuan Feng, Mark E. Warner, Yaohong Zhang, Jun Sun, Fei-Xue Fu, Julie M. Rose, David A. Hutchins, 2008. *Interactive effects of increased pCO₂, temperature and irradiance on the marine coccolithophore *Emiliania huxleyi* (Prymnesiophyceae).* *European Journal of Phycology Volume 43, Issue 1, 2008*
- <http://www.contros.eu/hydroc-co2-carbondioxide-sensor.html> - (1)
- <http://www.sunburstsensors.com/products/sami-co2.html> - (2)

D3.5

I.F.6. Chlorinated hydrocarbons (CHCs)

Scientific rationale

Chlorinated hydrocarbons are organic molecules. During the last decade there has been growing evidence that the distribution of chlorinated hydrocarbon pesticides in the open ocean air and water is global in extent (Tanabe et al., 1983; Carvalho et al., 2010). The increasing number of environmentally relevant pollutants, such as CHCs, create a considerable demand for rapid, specific and inexpensive analytical methods. Key requirements on such systems are reliability, substance specificity, facile usability, low cost and no sampling. The devices must be able to perform measurements in real time under in-situ conditions over a long period of time. The ultimate aim is to install autonomous sensor networks, complementing conventional analytical techniques. This clearly requires the application of chemical sensor systems.

Existing Methods

The **SOFIE** (Spectroscopy using Optical Fibres in the Marine Environment) underwater system consists of two aluminium pressure vessels containing the instrumental components, such as spectrometers, light sources, detectors and electronics. The actual fiber optic sensor heads provide contact to the marine environment. The core elements of SOFIE are two robust, miniaturized spectrometers. The sensing system operates in the MIR, based on mid-infrared fiber evanescent wave spectroscopy (FEWS). Fourier-transformed mid-infrared radiation is coupled into an IR transmitting waveguide, in this case a silver halide fiber, acting simultaneously as waveguide and as active sensor element capable of detecting Chlorinated hydrocarbons. Sensor characteristics: Max depth : 300m ; Salinity range : 0-40 ; Turbidity range : ≤ 400 NTU ; Temperature : 0-18°C. Manufacturer : IFREMER (Mizaikoff et al., 2001).

Implementation on glider

The manufacturer specifies no size. Since the sensor has been designed to be towed and according to the available pictures (Mizaikoff et al., 2001) it could be adaptable to gliders.

Quality Control

NA

References

- Boris Mizaikoff, Manfred Karlowatz and Martin Kraft, 2001. *Mid-infrared sensors for marine monitoring*. Proceedings of SPIE. vol 4204. pp 11.
- Fernando P. Carvalho, Jean-Pierre Villeneuve, Chantal Cattini, Cristina M. Bajetb & Mariafe Navarro-Calingacionbc., 2010. *Chlorinated hydrocarbons in sediments from Manila Bay, the Philippines*. International Journal of Environmental Studies, Volume 67, Issue 4. pages 493-504.
- S Tanabe, R Tatsukawa, 1983. *Vertical transport and residence time of chlorinated hydrocarbons in the open ocean water column*. Journal of the Oceanographical Society of Japan, Volume 39, Issue 2, pp 53-62

D3.5

1.F.7. Chrome (Chromate CrO_4^{2-} , dichromate $\text{Cr}_2\text{O}_7^{2-}$)

Scientific rationale

Chromate and dichromate are Cr(VI) species that have been used in metal finishing and in metal plating operations could be observed in the oceans. Cr(VI) is a strong oxidizer and is both highly toxic and carcinogenic. Chromate and dichromate are very water soluble and have little interaction with the soil (Rowbotham et al., 2000). Consequently, these pollutants are mobile, resulting in widespread groundwater contamination and finally in coastal areas (Olsen et al., 1982).

Existing Methods

The sensor is a cationic-coated surface enhanced Raman spectroscopy (SERS) substrates. The coating attracts the anions to the SERS substrate where they are identified and quantified by their characteristic Raman emission. The cationic coating stabilizes the SERS substrate, thereby extending its lifetime and has a characteristic SERS spectrum, which can be used as an internal calibration standard. The advantages of this approach over conventional techniques are - (1) the required information is obtained in real-time, - (2) it doesn't require the additional cost of an outside laboratory, and - (3) decisions can be made in a timely fashion as to whether or not additional sampling is required and where that sampling is needed. In this effort, methods of improving selectivity and sensitivity are addressed as well as sensor design. – Manufacturer : SERDP. – (1)

Implementation on gliders

The sensor has not been tested in seawater, nevertheless it is small enough to be stored in a shoe box, therefore the implementation on a glider seems possible.

Quality Control

NA

References

- AL Rowbotham, LS Levy, LK Shuker, 2000. *Chromium in the environment: an evaluation of exposure of the UK general population and possible adverse health effects*. Journal of Toxicology and Environmental Health, Part B: Critical Reviews Volume 3, Issue 3
- CR Olsen, NH Cutshall, IL Larsen, 1982. *Pollutant—particle associations and dynamics in coastal marine environments: a review*. Marine Chemistry Volume 11, Issue 6, Pages 501–533.
- <http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER-1296> - (1)

D3.5

I.F.8. Copper (Cu)

Scientific rational

Sources of copper (Cu) from Navy activities, such as antifouling agents on ship bottoms and dredging operations, require active monitoring and sensing of Cu(I) and Cu(II) individually to ensure environmental compliance and protection. Because of the toxicity of Cu, especially in estuary environments, all sources of Cu must be monitored to account for the relative impacts of the various sources (Zwolsman et al., 1997). Total Cu in seawater varies widely depending on the sources and water exchange with the ocean reservoir. It can sometimes exceed 3 ppb ($4,7 \cdot 10^{-8}$ M). Most of this Cu is bound to organic and inorganic ligands and is not available for interaction with biorganisms. The free Cu in seawater is typically 10^{-11} to 10^{-12} M (Zirino et al., 1998).

Existing Methods

The direct detection of Cu with ion-selective electrodes is unlikely to be possible due to the low levels of uncomplexed Cu present. Instead, it is proposed that the ion selective electrodes are measuring the activity of naturally occurring binding ligands for Cu and thereby an indirect measurement of uncomplexed Cu. Copper ion-selective electrodes are based on the jalpaite membrane structure (nominally $\text{Cu}_2\text{S} \cdot 3\text{Ag}_2\text{S}$). This is a solid state (pressed pellet) type of ion-selective electrode and can detect Cu(II) down to 10^{-10} M (0.006ppb). – Manufacturer: SERDP – (1).

(Also Cf. template I.F.14)

Implementation on gliders

Being just an electrode the sensor is easily adaptable on a glider. But since the detection limit is 10^{-10} M, it can be used only in enriched areas by human activities, as coastal areas, estuaries, fishing zones or harbors.

Quality Control

NA

References

John J.G. Zwolsman Bert T.M. Van Eck, Cornelis H. Van Der Weijden, 1997. Geochemistry of dissolved trace metals (cadmium, copper, zinc) in the Scheldt estuary, southwestern Netherlands: impact of seasonal variability

Zirino, S.L. Belli, and D.A. Van der Weele, "Copper concentration and Cu(II) activity in San Diego Bay", *Electroanalysis*, 10 (1998) 423-427.

<http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER-1266> - (1).

D3.5

I.F.9. Cyanide

Scientific rationale

Most cyanide is released into the environment as a result of mining operations. Coastal areas directly in contact with mines are threatened by this pollutant. With precipitation, cyanide is liberated by run off and reaches the ocean (McKinnon, 2002). Also, in military and industrial sites, cyanide is used in electroplating processes for silver, cadmium, gold, and copper (Brennan et al., 1999). Cyanide is highly toxic. Exposure by eye or skin contact or ingestion can be rapidly fatal.

Existing Methods

The sensor is a cationic-coated surface enhanced Raman spectroscopy (SERS) substrate. The coating attracts the anions to the SERS substrate where they are identified and quantified by their characteristic Raman emission. The cationic coating stabilizes the SERS substrate, thereby extending its lifetime and has a characteristic SERS spectrum, which can be used as an internal calibration standard. The advantages of this approach over conventional techniques are (1) the required information is obtained in real-time, (2) it doesn't require the additional cost of an outside laboratory, and (3) decisions can be made in a timely fashion as to whether or not additional sampling is required and where that sampling is needed. In this effort, methods of improving selectivity and sensitivity are addressed as well as sensor design. – Manufacturer: SERDP – (1).

Implementation on gliders

The sensor has not been tested in seawater, nevertheless it is small enough to be stored in a shoe box, and therefore the implementation on a glider seems possible.

Quality Control

NA

References

Elisabeth.McKinnon, 2002. The environmental effects of mining waste disposal at Lihir Gold Mine, Papua New Guinea. *Journal of Rural and Remote Environmental Health* 1(2): 40-5

Richard J Brennan, Joseph F Waeckerle, Trueman W Sharp, Scott R Lillibridge, 1999. Chemical Warfare Agents: Emergency Medical and Emergency Public Health Issues. *Annals of Emergency Medicine* Volume 34, Issue 2, August 1999, Pages 191–204.

<http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated Groundwater/Monitoring/ER-1296> - (1).

D3.5

I.F.10. Hydrogen (H₂)

Scientific rational

Fixed nitrogen is a key nutrient involved in regulating global marine productivity and hence the global oceanic carbon cycle. It is well established that N₂ fixation, mediated by the enzyme nitrogenase, is a source of hydrogen H₂ (Scranton, 1983), but the extent to which it leads to supersaturation of H₂ in oceanic waters is unresolved. There is a significant correlation between dissolved H₂ and rates of N₂ fixation (Moore et al., 2009).

Existing Methods

The shallow water sensor of AMT for depths of up to 10 bar (100m) consists of a pre-amplifier covered by titanium housing, a sensitive tip covered by a titanium protection cage and a connector.

Because of the partial pressure of the gaseous H₂ dissolved in the sample, the sample is separated from the inner electrolyte by the membrane. The membrane is only impervious to gases, so that liquids, ions and solids are not able to reach the inner electrolyte or the electrodes of the sensor. The sensor contains inside a special electrolyte and 3 electrodes. If the H₂ has passed through the membrane, it is transported by diffusion to the working electrode followed by the electrochemical oxidation of H₂. This causes a current depending on the H₂ partial pressure/ H₂ concentration of the sample. Besides, in contrast to other measuring principles, the current flow in the amperometric sensor leads to a rapid decrease of the analyte inside the sensor resulting in very fast response times even though there is a concentration jump from high to low concentrations. – Sensor characteristics: measuring ranges: 0,0002 to 3 mg/l H₂; response times: t_{90%}: below 2 seconds; may be influenced by the samples matrix - Manufacturer : AMT Analysenmesstechnik GmbH – (1)

Implementation on gliders

With a 48 mm diameter, and a 440 mm total length, this probe is an excellent candidate for glider implementation.

Quality Control

NA

References

Moore, Robert M.; Punshon, Stephen; Mahaffey, Claire; Karl, David, 2009. *The relationship between dissolved hydrogen and nitrogen fixation in ocean waters*. Deep-Sea Research Part I-Oceanographic Research Papers 56(9): 1449-1458.

Scranton, M.I., 1983. *The role of the cyanobacterium Oscillatoria (Trichodesmium) thiebautii in the marine hydrogen cycle*. Marine Ecology-Progress Series 11, 79–87

[http://www.amt-gmbh.com/pdf/H2 Microsensor.pdf](http://www.amt-gmbh.com/pdf/H2%20Microsensor.pdf) – (1)

D3.5

I.F.11. Dinoflagellates

Scientific rationale

Among the thousands of species of microscopic algae at the base of the food chain, a few dozen produce toxins (Horner et al., 1997). These algae make their presence known during what is referred to as a "harmful algal bloom," or HAB. One of phytoplankton groups inducing HAB is dinoflagellates. Dinoflagellates sometimes bloom in concentrations of more than a million cells per millilitre. Under such circumstances, they can produce toxins (generally called dinotoxins) in quantities capable of killing fishes and, accumulated in filter feeders such as shellfish, may be ingested by humans (Cembella, et al., 1987), leading to major financial losses for fisheries and tourism.

Existing Methods

Studies have already shown that RNA (Ribonucleic Acid) amplification with nucleic-acid-sequence-based amplification (NASBA) is particularly suitable for early detection of the marine dinoflagellate *Karenia brevis*.

AMG: The Autonomous Microbial Genosensor is designed to sample ambient seawater with a syringe pump, filter and extract RNA, partially purify the RNA, and perform NASBA using RNA. NASBA Detection of Microbial Targets Nucleic acid sequence-based amplification is an isothermal-based method of RNA amplification. Using this method, RNA is amplified by the action of an enzyme cocktail that includes AMV Reverse Transcriptase, T7 RNA polymerase and RNase H at a fixed temperature (41°C). By pairing this technique with the ability to monitor the fluorescence signal produced from Molecular Beacon probes in real time as they hybridize to the amplicon, it is possible to perform real time analysis of samples and obtain data in a matter of minutes (Casper et al., 2004) – Manufacturer: NOC, UK. – (1), (2).

Implementation on gliders

The AMG is housed in a 22cm Ø x 122cm (anodised aluminium pressure vessel. It could be easily set up on a glider.

Quality Control

NA

References

- Allan D. Cembella*, John J. Sullivan, Gregory L. Boyer, F.J.R. Taylor, Raymond J. Andersen: 1987. *Variation in paralytic shellfish toxin composition within the Protogonyaulax tamaronis/catenella species complex; red tide dinoflagellates*. Biochemical Systematics and Ecology Volume 15, Issue 2, Pages 171–186
- Erica T. Casper, John H. Paul, Matthew C. Smith, and Michael Gray. 2004. *The detection and quantification of the red tide Dinoflagellate Karenia brevis by real-time NASBA*. Appl. Environ. Microbiol.
- RA Horner, DL Garrison, FG Plumley, 1997. *Harmful algal blooms and red tide problems on the US west coast*. Limnology and Oceanography. Vol. 42, No. 5, pp. 1076-1088.
- Casper, E. T., J. H. Paul, M. C. Smith, and M. Gray (2004). *Detection and quantification of the red tide dinoflagellate Karenia brevis by real-time nucleic acid sequence-based amplification*. Applied and Environmental Microbiology. Vol. 70, No. 8, pp. 4727-4732.
- <http://noc.ac.uk/science-technology/research-groups/ote/instruments-sensors/biological-microsensors> - (1).
- <http://www.marine.usf.edu/microbiology/genosensor.shtml> - (2).

D3.5

I.F.12. Explosives (TNT, RDX)

Scientific rationale

TNT (trinitrotoluene) and RDX (cyclotrimethylenetrinitramine) are among the most commonly used explosives, and they are both frequently detected near military installations due to their persistence and high mobility (Clausen et al., 2009). Besides, at the end of the World War II, large amounts of munitions were disposed in marine dumping sites or buried underground. Thus, reliable pollution assessment and monitoring of soil and water contaminated with these explosives are a major priority. They are proven toxins in marine systems (Nipper et al., 2001).

Existing Methods

The sensor is a sensitive gold nanoparticle-based SERS (Surface Enhanced Raman Spectroscopy) substrate. It is coupled with a 300-mW near infrared laser and a fiber-optic probe. The detection limit is 2,3 µg/L and 0,12 mg/L for TNT and RDX respectively. – Manufacturer: SERDP. – (1).

Implementation on gliders

It has never been tested on seawater and some works need to be done to make it completely autonomous. No size is indicated by the manufacturer, but as a portable sensor, it should be adaptable to a glider.

Quality Control

NA

References

- Clausen, J., Cramer, R., Clough, S., Gray, M., and Gwinn, P., 2009. Assessing the sensitivity of quantitative structural activity analysis models for evaluating new military compounds. *Water Air Soil Poll.*202, 141-147.
- Nipper et al., 2001, M. Nipper, R.S. Carr, J.M. Biedenbach, R.L. Hooten, K. Miller, S. Saepoff. Development of marine toxicity data for ordnance compounds Arch. Environ. Contam. Toxicol., 41 (2001), pp. 308–318
- <http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER-1602#factsheet-6189-result> - (1)

D3.5

I.F.13. Sulphur (H_2S/HS^-)

Scientific rationale

Deep-sea hydrothermal vents are complex systems with total absence of light and huge pressure. In such extreme conditions, life exists, with chemolithotrophic bacteria at the base of the food chain (Laubier 1990). The presence of these bacteria allows bigger organisms to develop and to prosper. The sulphur flux appears to be one of the keys of these deep-sea communities, regulating community structure (Plant et al., 2010). Bisulfide concentration ranges measured at hydrothermal vents span between 75 μ M and 4500 μ M (Plant et al., 2010).

Existing Methods

1. The **ISUS** is a sensor used to measure concentrations of dissolved chemicals directly from their Ultraviolet Absorption. Bisulfide (HS^-) absorbs light in the UV and it has a unique absorption spectrum (see also Bromide). We can determine the Bisulfide concentration by measuring the absorption spectrum of seawater in the UV and then deconvolving the spectra to yield the concentration. The range detection is 2,5 to 400 μ M and its sample rate is 1 Hz. –Manufacturer: MBARI - (1)
2. The other existing sensor measures H_2S . Because of the partial pressure of gaseous H_2S dissolved in the sample the sample is separated by permeation through the membrane. The sensor contains a buffer solution with a redox catalyst and 3 electrodes. At the electrodes a special polarization voltage is adjusted to realize a well-defined concentration ratio of the oxidized and of the reduced form of the redox catalyst. If the H_2S passes through the membrane, the hydrogen sulphide reacts first chemically with the redox catalyst to form a reaction product followed by the electrochemically oxidation of the reaction product at the working electrode. The polarization voltage causes the system to adjust the former concentration ratio. The amperometric sensor determines H_2S concentration. There are 3 models of this sensor which allow a range detection from 0,01 to 50 mg/L. (the probe is also measuring pH and $T^\circ C$) – Manufacturer: AMT Analysenmeßtechnik GmbH - (2)

Implementation on gliders

ISUS has never been tested on a glider, but with a length of 608 mm and a diameter of 114 mm, the implementation seems more than possible. In water, its weight is 0,7 kg. The lamp lifetime of the spectrophotometer is 900 hours and it can go down to 2000 meters depth.

The electrode is easily adaptable to a glider with a size of a basic electrode used in laboratory (48 mm x 450 mm), nevertheless its detection limit appears to be lower than natural concentration near hydrothermal vents.

Quality Control

NA

References

- Laubier Lucien, 1990. Benthic ecosystems and bacterial chemosynthesis: Hydrothermal springs, hydrothermal vents, hydrothermal communities and cold seeps. Actes de colloques. Ifremer. Brest
- Plant, J., Johnson, K.S., Fitzwater, S.E., Sakamoto, C.M., Coletti, L.J., Jannasch, H.W. (2010) Tidally oscillating bisulfide fluxes and fluid flow rates observed with in situ chemical sensors at a warm spring in Monterey Bay, California *Deep Sea Research* 57(12) 1585-1595
- Johnson, K.S., Coletti, L.J. (2002) In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean. *Deep Sea Research* 49 1291-1305
- <http://www.mbari.org/chemsensor/ISUSHome.htm> (1)
- <http://www.amt-gmbh.com/> (2)

D3.5

I.F.14. Heavy Metals: Lead (Pb), Mercury (Hg), Copper (Cu) and Cadmium (Cd)

Scientific rationale

Major controls influencing trace metal distributions in natural waters include inputs from various external sources (e.g. gasoline leak), in-situ scavenging and recycling, and the physical mixing processes within the water mass. Important external inputs of both naturally and anthropogenically mobilized trace metals are atmospheric input consisting of wet and dry deposition, and riverine input of dissolved and particulate phases (Mart et al., 1982). Cadmium and mercury are generally considered to be the metals most likely to give rise to pollution problems in marine ecosystems (Bryan, 1984). Mercury, unlike other metals, shows biomagnification, because the organic form methylmercury is lipid-soluble. Cadmium is stored long-term in the kidney of marine vertebrates, and levels increase with age in some marine mammals (Bryan, 1984), while physiological functions of phytoplankton can be disturbed when lead interferes (Shakya et al., 2006).

Existing Methods

The sensor for heavy metal ions, e.g. Pb^{2+} , Cu^{2+} , Hg^{2+} or Cd^{2+} is based on absorption/fluorescence measurements by reversible complex formation of the metal ions with immobilized chelating agent –Manufacturer: IFREMER (Mizaikoff et al., 2001)

Implementation on gliders

No size is specified by the manufacturer. Since the sensor has been designed to be towed and according to the available pictures (Mizaikoff et al., 2001) it could be adaptable to gliders.

Quality Control

NA

References

- Boris Mizaikoff, Manfred Karlowatz and Martin Kraft, 2001. *Mid-infrared sensors for marine monitoring*. Proceedings of SPIE. vol 4204.
- Bryan, G. W. (1984). *Pollution due to heavy metals and their compounds*. In Marine Ecology. (O. Kinne, Ed.), pp. 1289-1431.
- L. Mart, H. Rützel, P. Klahre, L. Sipos, U. Platzek, P. Valenta, H.W. Nürnberg, 1982. *Comparative studies on the distribution of heavy metals in the oceans and coastal waters*. Science of The Total Environment, Volume 26, Issue 1, Pages 1–17
- PAWAN RAJ SHAKYA, PRATIMA SHRESTHA, CHIRIKA SHOVA TAMRAKAR AND PRADEEP K. BHATTARAI, 2006. *Studies and Determination of Heavy Metals in Waste Tyres and their Impacts on the Environment*. Pak. J. Anal. & Envir. Chem. Vol. 7, No. 2, 70 n° 76

D3.5

I.F.15. Hydrocarbons

Scientific rationale

As the main source of our energy, as well as for transport, heating or plastic fabrication hydrocarbons are widely used. They are widely present in the oceans because of pollution, either from boat dumping or coastal run off. For preservation marine ecosystem, they need to be monitored.

Existing Methods

The presence of both scattering and fluorescence is an excellent indicator of the existence of an oil emulsion. Crude oil has extremely broad absorption and emission spectra and the emission wavelength of the CDOM fluorometers is centered at the primary crude emission peak. The Triplet sensor is a special-order, three-optical-sensor instrument available in a user-defined configuration. The Triplet addresses the need for multiple simultaneous scattering and fluorescence sensors for autonomous platforms – Depth rating: 600m – Manufacturer: Wet Labs. – (1), (2).

| | Wavelengths | Sensitivity | Ranges |
|---------------------|-----------------------|-----------------------|---------------------|
| Scattering | 470, 532, 650, 700 nm | 0,003 m ⁻¹ | 0-5 m ⁻¹ |
| Fluorescence (CDOM) | 370, 460 nm | 0,28 ppb | 0-375 ppb |

Implementation on gliders

With its dimensions (12,7cm x 6,3cm Ø), the triplet sensor is an excellent candidate for glider applications.

Quality Control

Because the CDOM fluorometer will respond to a wide range of fluorophores other than crude oil, ancillary measurements are useful to decrease false positive results.

References

<http://www.wetlabs.com/applications/oil-water> - (1)

<http://www.wetlabs.com/eco-triplet> - (2)

D3.5

I.F.16. Hydrogen Peroxide (H₂O₂)

Scientific rationale

Hydrogen peroxide is ubiquitous in seawater where it is one of the major products formed photochemically from dissolved organic matter (Naffrechoux et al., 2000). H₂O₂ has been studied by numerous investigators because of its high concentration relative to other reactive oxygen species and because of its potential chemical and biological reactivity (Kieber et al., 2003). Traces of dissolved substances, of the order of 10⁻⁷ M have been measured in oceans (Van Baalen and Marler, 1966, Resing et al., 1993).

Existing Methods

The AMT sensor is essentially an amperometric membrane covered micro-sensor. Because of the partial pressure of the gaseous H₂O₂ dissolved in the sample, the analyte is separated from the inner electrolyte by means of the membrane. The membrane is only pervious to gases, so that liquids, ions and solids are not able to reach the inner electrolyte or the electrodes of the sensor. If H₂O₂ passes through the membrane, it reacts chemically with the redox catalyst and forms a new compound. After this, H₂O₂ is transported by diffusion to the working electrode where the electrochemical reaction takes place. This causes a current proportional to the H₂O₂ partial pressure/ H₂O₂ concentration of the sample. – Sensor characteristics: Measuring ranges: 0,02 to 10% of H₂O₂; accuracy: 2% of reading; resolution: 0,02 % H₂O₂; response time : <2s - Manufacturer : AMT Analysentechnik GmbH. – (1), (2).

Implementation on gliders

With a 48 mm diameter, and a 440 mm total length, this probe is an excellent candidate for gliders.

Quality Control

NA

References

- E Naffrechoux, S Chanoux, C Petrier, J Suptil, 2000. Sonochemical and photochemical oxidation of organic matter. Ultrasonics photochemistry, Volume 7, Issue 4,*
- J. RESING, G. Tien, R. LETELIER, and D.M. Karl, Palmer LTER: Hydrogen peroxide in the Palmer LTER region: II. Water column distribution, 1993. Antarctic journal.
- Kieber, D.J., Peake, B.M., Scully, N.M., 2003. Reactive oxygen species in aquatic ecosystems. The royal Society London, Cambridge, UK, pp. 251-288.
- Van Baalen, C., Marler, J.E., 1966. Occurrence of hydrogen peroxide in seawater. Nature 211, 951;
- <http://www.amt-gmbh.com/pdf/Microsensor H2O2.pdf> – (1)
- <http://www.amt-gmbh.com/pdf/pdfs12082013/Hydrogen Peroxide Probe System.pdf> – (2)

D3.5

I.F.17. Manganese (Mn)

Scientific rationale

Oceanic phytoplankton plays a key role in controlling the atmospheric concentrations of climatic active gases like carbon dioxide (CO₂). Mn is an essential element for algal growth, being a key component of carbon fixation processes (Landing and Bruland, 1987). Although, the average concentration in ocean is 360 pmol/kg (Chapin, et al. 1991; Statham, et al., 1998), in some areas, where anoxic conditions are observed (e.g. the Baltic sea) the concentration of Mn(II) can reach more than 8µM (Meyer et al., 2012).

Existing Methods

METIS: The METal In Situ analysers are compact wet-chemical analysers that are designed to determine the presence and concentration of dissolved Mn(II) in the water column. The analyzers employ a method of unsegmented continuous flow analysis. The sample stream is inoculated with a reagent, the combined solutions are mixed and pass into a cell where the intensity of colour is determined using an LED as light source and a photodiode with light to frequency converter (TAOS) as detector. – Manufacturer : Leibniz Institute for Baltic Sea Research and NOCS.uk – (1)

Implementation on gliders

METIS is already used in the nose cone of AUVs (Personal communication). Technically, an implementation is possible on a glider. But some amelioration is needed for the typical time's glider deployment, as the METIS deployment period is limited by the shelf life of the standard (few days). Also, solenoid pumps for the reagent and sample, kit out the sensor, which consume the average power of 2 to 3 Watts.

Quality Control

NA

References

- Chapin, T. P., K. S. Johnson and K. H. Coale. 1991. Rapid determination of manganese in seawater by flow injection analysis with chemiluminescence detection. *Analytica Chimica Acta*, 249, 469-478
- Statham, P. J., Yeats, P. A., and Landing, W. M., 1998. Manganese in the eastern Atlantic Ocean: processes influencing deep and surface water distributions. *Mar. Chem.* 61: 55-68
- Landing W.M., Bruland K.W., 1987. The contrasting biogeochemistry of iron and manganese in the Pacific Ocean. *Geochim. Cosmochim. Acta.* 51: 29-43.
- Meyer, D., Prien, R.D., Dellwig, O., and Schulz-Bull, D.E. (2012) *High resolution data for dissolved manganese(II) in the water column of the central Baltic sea using a new wet chemical analyzer.* Ocean Science Meeting 2012, Conference, Salt Palace Convention Center, Salt Lake City, Utah, USA, 20.-24.02.2012, poster
- <http://www.io-warnemuende.de/che-ag-in-situ-sensors-iron-and-manganese-analysers.html> - (1)

D3.5

I.F.18. Mapping marine communities

Scientific rational

The knowledge of the occurrence, extension and limits of submerged marine ecosystems has a primary importance both for scientific and coastal management purposes. Large scale mapping programs have focused on major coastal biological indicators as mangroves, coral reefs, macroalgae and seagrass beds (Chauvaud et al., 1998).

Existing Methods

GIB: The GPS intelligent buoy is a portable tracking system that consists of one underwater pinger, four buoys and a receiving (deck) unit. The pinger is mounted on an underwater vehicle driven by a scuba diver. The system works on the principle of 'long baseline' system with the GPS differential correction (Thomas, 1994) The pinger emits a signal at 32 kHz, one pulse per second, that is detected by the four buoys that, by turn, transmit their distances from the pinger to the deck unit (Sgorbini et al., 2002).

Implementation on gliders

The implementation on gliders seems possible since the system has been used on towed sonar (by boats) or placed on driven underwater vehicles. The only difference would be on the mapping speed. Indeed, the first method depends on the speed of the boat, whereas the second one depends on the scuba divers who directly follow the contours of marine communities.

Quality Control

When used in shallow water, scuba divers can control the precision.

References

- Sergio Sgorbini, Andrea Peirano, Silvia Cocito, Massimo Morgigni, 2002. An underwater tracking system for mapping marine communities : an application to Posidonia oceanica. *Oceanologica Acta* 135-138.
- S Chauvaud, C.Bouchon, R.Maniere, 1998. Remote sensing techniques adapted to high resolution mapping of tropical coastal marine ecosystems (coral reefs, seagrass beds and mangrove). *International Journal of Remote Sensing* Volume 19, Issue 18, pp. 3625-3639.
- Thomas, H., 1994. New Advanced Underwater Navigation Techniques Based on Surface Relay Buoys, OCEAN 94 Osates, Brest.

D3.5

I.F.19. Marine mammals (MM)

Scientific rationale

MM produce a variety of sounds and use hearing for different types of communications such as individual recognition, predator avoidance, prey detection/capture, orientation and navigation. Mammal monitoring is relevant to study MM distribution and migration, and to relate the MM presence and activity to oceanography. The detection of MM is also important prior and during sonar operations (e.g. to avoid collisions with vessels or disorientation). Passive acoustic monitoring (PAM) represents an essential component to a comprehensive MM monitoring solution and gliders are promising vehicles for towing short acoustic arrays. Because of their long-duration on-station time and acoustically silent operation, gliders provide attractive platforms that can operate over extended periods of time, with significant processing capabilities for detection, classification and localization of MM calls.

Existing Methods

Mammals vocalize with some form of exploitable calls/songs, clicks and whistles. These vocalizations are extremely varied in character and frequency: e.g. blue whales vocalize with a very low frequency (~20Hz) while dolphins use very high frequency whistles and foraging clicks (>100 kHz). There are a variety of methods used to remotely monitor MM using PAM over long periods: some provide real-time acoustics via radio-linked hydrophones [1] while other systems are autonomous and record sounds internally. These autonomous acoustic recorders are more practical for gliders because they have lower costs, larger data and power storage capacities which allow them to monitor for longer periods (months – year). These autonomous acoustic recorders can be configured into different ways for tracking individuals or groups of animals. One of the most capable autonomous systems currently available for gliders is a miniaturization of the High-frequency Acoustic Recording Package (HARP) that is an autonomous data logging system optimized for long-term, broad-band marine mammal monitoring. The HARP system includes low-power electronics, high-speed data sampling, large capacity data storage, and batteries for self-contained power. As an efficient alternative to HARP, a new self-contained, low-power digital acoustic monitoring device (DMON) has been recently (April 2012) created specifically for passive acoustic detection by the Woods Hole Oceanographic Institution (WHOI), [3]. DMON has the necessary broadband, low-noise signal acquisition capabilities. DMON records sound to solid state memory either continuously or when a detection is made. Compared to a HARP implementation DMON method is much smaller as it offers low power consumption (longer deployment lifetime). – Manufacturer: WHOI

Implementation on gliders

Due to the Slocum glider limitations in payload and battery capabilities, the main characteristics of the implementation of methods for MM analyses into gliders must be the low-power consumption and the compact hardware requirements, reducing the demands on the glider platform. Usually, acoustic data are measured as time series of pressure which then can be transformed into the frequency domain via Fourier transforms and displayed as time-frequency plots (spectrograms) that are used to evaluate acoustic data for animal and anthropogenic sounds. Unfortunately, due to the wide frequency band data, the spectrogram evaluation can be conducted only near real-time (computational limitations). To allow real-time processing the alternative is to compute Long-Term Spectral Averages (LTSAs) to provide an overall view of a large data set along with providing a means to search for and evaluate events of interest. LTSAs are essentially spectrograms with each time pixel representing many spectra (e.g. 5 sec) instead of just one (e.g. 5 milliseconds as with spectrograms).

For a more complete analysis, automated detection/tracing algorithms can be implemented to find specific sounds with known characteristics. Due to the different types of MM vocalizations, the general idea is to implement at least two different detection algorithms allowing the identification two critical classes of marine mammals: low-frequency baleen whales (e.g. right, fin, humpback

D3.5

whales) and high-frequency beaked whales (e.g. dolphin). There are several available tools that have been developed at CMRE throughout 10 years of SIRENA research cruises [4,5] and that can be adapted for glider deployments.

Quality Control

The passive acoustic glider data may be verified by applying two different procedures for data quality control:

1. Signals from known species recorded in the field may be used for bench verification of the detection algorithms;
2. Complete autonomous systems can then be tested in the field to simultaneously detect and record sound.

Additionally, after each mission, gliders should be quality controlled by verifying sensors performances and missed detects.

References

- McDonald, M., (2004), DIFAR Hydrophone Usage In Whale Research, Canadian Acoustics Vol. 32, No. 2. 155-160.
- [Wiggins, S. M. and J. A. Hildebrand, (2007), High-frequency Acoustic Recording Package (HARP) for broad-band, long-term marine mammal monitoring, International Symposium on Underwater Technology 2007, pp. 551-557.
- Johnson, M., Fratantoni, D., Baumgartner, M. and Hurst, T., Beta Testing of Persistent Passive Acoustic Monitors, Award Number: N000141010381.
- Cross, P., (2009), Using Ocean Gliders for Passive Acoustic Monitoring of Marine Mammals, Ocean Acoustical Services and Instrumentation System, Inc., Approved for Public Release.
- Gerard, O., Carthel C. and Coraluppi, S., (2009), Algorithms for the detection and classification of marine mammals, Technical Report, NURC-SWP-006, NATO UNCLASSIFIED.

D3.5

I.F.20. Methane (CH₄)

Scientific rationale

Huge volumes of CH₄ lie locked up in deposits deep under the ocean (Pecher, 2002). This CH₄ is contained in structures formed in methane hydrate, an ice-like form of water, which has voids filled with CH₄ from decayed biological material. This presents a possible new source of energy and also a possible concern for climate change, if these stable structures destabilize and release large amounts of CH₄ to the atmosphere (Wood et al., 2002). Close to oceanic ridges, CH₄ concentration has been measured in hydrothermal fluids, ranging from 50 to 120 μM (Lilley et al., 1993). Thus, we would need to be able to detect dissolved CH₄ from the bottom of ocean to integrate it in climate modeling.

Existing Methods

HydroCTM CH₄ sensor is an underwater methane sensor for *in-situ* and online measurements of dissolved CH₄. Dissolved CH₄ molecules diffuse through a patented thin-film composite membrane into the detector chamber, where their concentration is determined by means of IR absorption spectrometry. Concentration-dependent IR light intensities are converted into output signals. – Manufacturer: CONTROS. – (1).

Implementation on gliders

The adaptation of this sensor on a glider's hull seems possible. The size is: 90mm Ø x 376 mm. However, the upper limit of the range of detection of the sensor is under the concentration measured at oceanic ridges. Some work need to be done to modify and improve the sensor range (except if the other range mentioned by the manufacturer allows detecting higher concentration – numeric values are not given).

Quality Control

NA

References

Ingo A. Pecher, 2002. *Oceanography: Gas hydrates on the brink*. *Nature*, *Nature* 420, 622-623

MD Lilley, DA Butterfield, EJ Olson, JE Lupton, 1993. Anomalous CH₄ and NH₄⁺ concentrations at an unsedimented mid-ocean-ridge hydrothermal system. *Nature*, 364, 45 - 47

Wood, W. T., J. F. Gettrust, N. R. Chapman, G. D. Spence, and R. D. Hyndman, 2002: Decreased stability of methane hydrates in marine sediments owing to phase-boundary roughness. *Nature* 420, 656-660.

<http://www.contros.eu/hydroc-ch4-hydrocarbon-methane-sensor.html> -(1).

D3.5

I.F.21. Nutrients

Scientific rationale

Nutrient data are required for a wide range of applications such as environmental monitoring, risk assessment and ecosystem zone modelling studies; elements such as nitrogen and phosphorus are essential to life in the oceans. They have high concentrations in deep water, while the concentration close to the surface is often below the detection limit. The gradient of nutrient concentrations between these two regions encompasses the euphotic zone and can be very dynamic in response to both physical and biological processes. Because the global coverage of nutrients is currently inadequate, it is desirable to install nutrient sensors on long range autonomous vehicles such as gliders.

Note that NO₃⁻ is discussed in a separate section (I.E.5).

Existing Methods

Wet chemical techniques (with reagents and micro-fluidics). A technology with the potential to satisfy glider requirements (low consumption and high sampling rate) is micro-fluidics, consisting in microelectromechanical systems (MEMS) based on silicon or polymers or printed circuit boards. There are two Sub-Chem System Inc.^[3] solutions actually available for gliders: the Autonomous Profiling Nutrient Analyzer-APNA (four-channel) and ChemFIN (single channel). APNA is an autonomous, submersible chemical analyzer utilizing spectrophotometric and fluorometric analytical methods for continuous or intermittent *in situ* measurements of nutrients. It is user-programmable for either continuous operation (i.e. 1 reading per second when profiling) or intermittent measurements (10-15 minutes per measurement cycle). ChemFIN is a single channel analyzer that was specifically designed for low-power underwater measurements. Both analyzers use wet chemical techniques and micro-fluidics based on laboratory method. They include a reagent set, a reagent reservoir kit, test cable, deck box, operating manual and software.

1. **APNA:** An autonomous, multi-channel submersible chemical analyzer utilizing spectrophotometric and fluorometric analytical methods for continuous or intermittent *in-situ* measurements of nutrients in marine waters. (Nitrite, nitrate, phosphate, silicate, iron(II), ammonium) - Depth capacity : 200m ; Analysis : 28W – (1)
2. **ChemFIN:** A compact, low-power autonomous single or dual-channel submersible chemical analyzer utilizing spectrophotometric and fluorometric analytical methods for continuous or intermittent *in situ* measurements of nutrients in marine waters. (same as APNA except iron) - Depth capacity : 600m, Analysis : 3W – (2)
3. **MarChem:** A compact, low-power autonomous single or multi-channel submersible chemical analyzer, which utilizes spectrophotometric and fluorometric analytical methods for continuous or intermittent *in-situ* measurements of nutrients in marine waters. MarChem was specifically designed as a payload for Autonomous Underwater Vehicles (AUVs). (ammonium , chlorophyll) – (3)

Manufacturer for all : SubChem Syst. Inc

Implementation on gliders

The levels of nutrient concentration are highly variable from coastal to open ocean, as well as between surface and deep ocean waters. Monitoring nutrient changes in oligotrophic surface waters requires instrumentation with very high sensitivity, while measuring over full ocean depth does not. For that reason, there is the need to define automatic procedures to sampling with enough frequency to avoid aliasing that confound analysis of short-term variability. **An adaptive sampling strategy** may be useful to capture short-term variability when such type of changes are expected (e.g. in a known environment or during the spring bloom) (Grasshoff et al., 1999). For example, rapid change in temperature or fluorescence may be used to trigger a change in the



GROOM Sensors for gliders

Grant Agreement Number: 284321
FP7-Infra-2011-2.1.1 "Design
Studies"



D3.5

glider sampling frequency.

Quality Control

NA

References

Johnson, K.S, and Coletti, L.J., (2002), In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean. Deep Sea Research Part I: Oceanographic Research Papers 49(7), 1291-1305.

Plant, J.N, Johnson, K.S., Needoba, J.A. and Coletti, L.J., (2009), NH₄-Digiscan: An in situ and laboratory ammonium analyzer for estuarine, coastal and shelf waters. Limnol. Oceanogr. Methods 7, 144-156.

Sub-Chem System Inc., 65 Pier Rd, Narragansett, RI 02882, phone: 4017834744, www.subchem.com, e-mail info@subchem.com.

Grasshoff, K., Kremling, K., Ehrhardt, M., (1999), Methods of Seawater Analysis, 3rd ed. Wiley 632 pp.

[http://www.subchem.com/Autonomous%20Profiling%20Nutrient%20Analyzer%20\(APNA\).pdf](http://www.subchem.com/Autonomous%20Profiling%20Nutrient%20Analyzer%20(APNA).pdf) - (1)

<http://www.subchem.com/ChemFin%20Analyzer.pdf> - (2)

<http://www.subchem.com/MarChem%20%20Analyzer.pdf> - (3)

D3.5

I.F.22. Ozone (O₃)

Scientific rational

Ozone is increasingly being used as a disinfectant in aquaculture. It destroys viruses, bacteria, fungi and protozoa (Kim et al., 1999). It can be found in the ocean due to dumping of hatchery wastewater (Conrad et al., 1975). Direct exposure of fish and other organisms to O₃ and the oxidants formed in ozoned seawater can be lethal (Wedemeyer et al., 1979; Fisher et al., 1999).

Existing Methods

Amperometric ozone micro-sensor: because of the partial pressure of gaseous O₃ dissolved in the sample, the analyte is separated by permeation through the membrane. The membrane is only pervious for gases, so that liquids, ions and solids are not able to reach the inner electrolyte of the sensor. The sensor contains inside an electrolyte with a redox catalyst (= redox mediator) and 3 electrodes. A special polarization voltage is applied at the electrodes to measure a well-defined concentration ratio of the oxidized and of the reduced form of the redox catalyst. If the O₃ passes through the membrane, first it reacts chemically with the redox catalyst to form a reaction product followed by the electrochemically reduction of the reaction product at the working electrode. Caused by the polarization voltage the system adjusts the former concentration ratio. This causes a current similar to the dissolved O₃ amount of the sample. Moreover, the current flow in the amperometric sensor leads to a rapid decrease of the analyte inside the sensor resulting in very fast response times as well, if a rapid change from high to very low concentration levels is necessary. All electrochemical sensors, including the amperometric O₃ sensor, have to be combined with a temperature measurement. – Manufacturer: AMT Analysentechnik GmbH. – (1), (2).

Implementation on gliders

The amperometric O₃ micro-sensor has been developed for the *in-situ* determination of O₃ containing aqueous solutions. Therefore the sensor is suitable for direct measurements in coloured, turbid and solid containing solutions. This amperometric O₃ micro-sensor contains a redox catalyst, which works with a very low analyte consumption. With a size of 440mmx 48mm (diameter) and a maximum depth deployment of 100 meters, the probe can be set up on a glider.

Quality Control

NA

References

- Conrad, J.F., Holt, R.A., Kreps, TD., 1975. Ozone disinfection of flowing water. Prog. Fish Cult. 37, 134-136
- Fisher, D.J., Burton, D.T., Yonkos, L.T., Turley, S.D., Ziegler, G.P., 1999. The relative acute toxicity of continuous and intermittent exposures of chlorine and bromine to aquatic organisms in the presence and absence of ammonia. Water Res. 760-768
- JG Kim, AE Yousef, S Dave, 1999. Application of ozone for enhancing the microbiological safety and quality of foods: a review. Journal of Food Protection, Number 9pp. 975-1096, pp. 1071-1087(17)
- Wedemeyer, G.A, N.C., Yasutake, W.M., 1979. Potentials and limits for the use of ozone as a fish disease control agent. Ozone, Sci. Eng. 1, 295-318.
- <http://www.amt-gmbh.com/pdf/pdfs12082013/Dissolved O3 Probe System.pdf> – (1)
- <http://www.amt-gmbh.com/pdf/pdfs12082013/O3 Microsensor.pdf> – (2).

D3.5

1.F.23. Particle and plankton size distributions (PSDs)

Scientific rationale

A comprehensive understanding of the distribution, abundance, and dynamics of particulate matter and organisms in pelagic environments is crucial to predicting the export and sequestration of biogenic carbon. The existence of thin (cm to m) layers of marine snow aggregates, phytoplankton, and zooplankton indicates that the pelagic ecosystem is very structured. Therefore, measurements of particles and plankton size distributions (PSDs) made at sampling frequencies that are compatible with other standard oceanographic instruments hold enormous potential for revealing factors that regulate distribution and abundance patterns.

Existing Methods

Different methods to estimate PSD exist. They are or could be implemented on gliders: Optical methods are currently used. Light absorption depends on the properties of the particles (e.g., size, shape, pigment concentration) as well as the nature and quantity of the available subsurface light. Underwater visibility depends on the underwater light distribution, which is determined by the underwater optical properties (absorption, polarized scattering, and fluorescence), which are themselves determined by the concentration, size, shape, packaging, and composition of particulate and dissolved materials in the water. Such backscatter or transmissionmeter have been implemented (Johnson et al 2009) and will not be discussed in details. In the future, imaging instruments triggered by optical properties will take pictures of particles directed at a camera's focal plane. Silhouette cameras measuring light absorbance in different beams, such as the Laser Optical Particle Counter (LOPC, Brooke Ocean), are deployed on a variety of platforms to study zooplankton and particles, having $100 \mu\text{m} < d < 1.5 \text{ mm}$ (Checkley et al 2008, Finlay et al 2007, Herman et al 2004, Vanderploeg & Roman 2006). Photographic and, more recently, CCD (charge-coupled device) cameras have been used to study aggregates and plankton, with sizes ranging from a few tens of micrometers to a few millimeters (Benfield et al 2007, Picheral et al 2010). Several of these cameras are commercially available, and most recently the holographic ones, but have yet to be miniaturized enough to fit in/on gliders (Stemmann & Boss 2012).

Implementation on gliders

The following description focuses on instruments based on camera systems that are in development. Typically, such instrument package contains an intelligent camera, lens, pressure and angle sensors, acquisition and piloting board, Internet switch, hard drive, and dedicated electronic power boards. A collimated illumination should deliver a structured light beam (ideally red light-emitting diodes (LEDs) to avoid solar interference in the upper layers). Particles or plankton size range will depend on the camera and the illuminated volume. Current systems tethered to the ships have volume ranging from few ml to L, but they are not available for gliders. Here we describe what imaging sensors should be implemented on gliders

Such a imaging system should be able to operate in real time image processing and data transmission or delayed mode in which data are not transmitted but stored until the recovery of the glider. The software should acquire and process images in real time and several modes of operation should be provided to adapt the system to users' needs. In the UVP5 sensor system, 4 modes are proposed (Picheral et al., 2010). These modes are (1) full process, (2) image acquisition only, (3) mixed process, and (4) process only. In the full process mode, all images are saved and processed in real time, generally limiting the acquisition frequency. In the image acquisition only mode, the images are recorded. In the mixed process mode, the images are acquired and processed to get size and gray level for each object. Vignette images or full images of objects above a preset size limit are saved. This mode saves memory, keeps images of "interesting targets" to be identified later, and allows an increase in the rate. Finally, in process only mode, the images are processed, and only the size and mean gray value of each of the detected objects is saved in a text file. This latter mode is the fastest. Depending of the setting, binary files of particles

D3.5

counts and/or images can be transmitted in real time if the bandwidth allow it.

Quality Control

An idealized imaging sensor should observe both the very small living or dead particles and the large particles to provide a large range of particle and plankton size. Currently, optical instruments measure bulk signal and can provide only basic information for small particles in the water column based on bulk measurements at different wavelengths). For larger objects, imaging systems provide information on individual objects which can be further sorted and abundance estimated providing the knowledge of the sampled volume, the matching between the light beam and the field of view of the camera, the pixel to millimeter conversion and a detailed cross calibration between sensors in order to make sure that you can reproduce the measurements (Benfield et al. 2007; Stemmann et al., 2012). All those steps are described in details for the UVP5 (Picheral et al., 2010) which give guidelines for QC protocols. All sensors should be controlled using the same standard object to ensure homeogenous measurements before all deployments. Additionally, gliders should be quality controlled at the end of the mission, by verifying sensor performances.

References

- Benfield MC, Grosjean P, Culverhouse PF, Irigoien X, Sieracki ME, et al. 2007. RAPID: Research on Automated Plankton Identification Oceanography 20
- Checkley DM, Davis RE, Herman AW, Jackson GA, Beanlands B, Regier LA. 2008. Assessing plankton and other particles in situ with the SOLOPC. Limnology and Oceanography 53: 2123-36
- Finlay K, Beisner BE, Barnett AJD. 2007. The use of the Laser Optical Plankton Counter to measure zooplankton size, abundance, and biomass in small freshwater lakes. Limnology and Oceanography-Methods 5: 41-49
- Herman AW, Beanlands B, Phillips EF. 2004. The next generation of Optical Plankton Counter: the Laser-OPC. Journal of Plankton Research 26: 1135-45
- Johnson KS, Berelson WM, Boss ES, Chase Z, Claustre H, et al. 2009. OBSERVING BIOGEOCHEMICAL CYCLES AT GLOBAL SCALES WITH PROFILING FLOATS AND GLIDERS PROSPECTS FOR A GLOBAL ARRAY. Oceanography 22: 216-25
- Picheral M, Guidi L, Stemmann L, Karl DM, Iddaoud G, Gorsky G. 2010. The Underwater Vision Profiler 5: An advanced instrument for high spatial resolution studies of particle size spectra and zooplankton. Limnology and Oceanography-Methods 8: 462-73
- Stemmann L, Boss E. 2012. Plankton and Particle Size and Packaging: From Determining Optical Properties to Driving the Biological Pump. In Annual Review of Marine Science, Vol 4, ed. CAGSJ Carlson, pp. 263-90
- Vanderploeg HA, Roman MR. 2006. Introduction to special section on Analysis of Zooplankton Distributions Using the Optical Plankton Counter. Journal of Geophysical Research-Oceans 111: -

D3.5

I.F.24. Polycyclic aromatic hydrocarbons (PAHs) - Polychlorinated biphenyls (PCBs)

Scientific rationale

Among the most impacting contaminants, the hydrophobic organic contaminants (HOCs), which include PAHs and PCBs, have been detected at high levels in many North-Atlantic estuaries (Ko and Baker, 1995, Fernandez et al., 1997 and Minier et al., 2006). Since the 1980's, traces of these molecules have been found in marine sediments and in the water column on the ocean (Garrigues P. et al., 1987; G Witt, 1995; K Cailleaud et al., 2007). Coastal run off and dumping in rivers are the main source of HOCs occurrence in the ocean (Merrill and Wade, 1985).

Existing Methods

The **SOFIE** (Spectroscopy using Optical Fibres in the Marine Environment) underwater system consists of two aluminum pressure vessels containing the instrumental components, such as spectrometers, light sources, detectors and electronics. The actual fiber optic sensor heads provide contact to the marine environment. The core elements of SOFIE are two robust, miniaturized spectrometers. One of them is a surface enhanced Raman scattering (SERS) sensor for environmentally relevant hydrocarbons, such as polycyclic aromatic hydrocarbons (PAH's) and polychlorinated biphenyls (PCB's). – Manufacturer : IFREMER (Mizaikoff et al., 2001)

Raman Spectroscopy consists of light beam excitation of molecules of the target compound to be identified. The photon energy is then absorbed providing a vibration that gives a secondary photon emission at a typical wavelength shift from the excitation representing the signature of the different atomic bonds. The obtained spectrum provides a true image of the molecules present in the light beam

Implementation on glider

Sensor has been designed to be towed, and according to the available pictures (Mizaikoff et al., 2001) it could be adaptable to gliders.

Quality Control

NA

References

- E.G. Merrill, T.L. Wade, 1985. Carbonized coal products as a source of aromatic hydrocarbons to sediments from a highly industrialized estuary. *Environ. Sci. Technol.*, 19, pp. 597–603
- C. Minier, A. Abarnou, A. Jaouen-Madoulet, A.M. Le Guellec, R. Tutundjan, G. Bocquené, F. Le Boulenger. A pollution-monitoring pilot study involving contaminant and biomarker measurements in the Seine estuary, France, using Zebra Mussels (*Dreissena polymorpha*). *Environ. Toxicol. Chem.*, 25, pp. 112–119
- Boris Mizaikoff, Manfred Karlowatz and Martin Kraft, 2001. Mid-infrared sensors for marine monitoring. *Proceedings of SPIE*. vol 4204.
- M.B. Fernandez, M.A. Sicre, A. Boireau, J. Tronczynski, 1997. Polyaromatic Hydrocarbons (PAH) distributions in the Seine River and its estuary. *Mar. Pollut. Bull.*, 34 (11) pp. 857–867
- F.C. Ko, J.E. Baker, 1995. Partitioning of hydrophobic organic contaminants to resuspended sediments and plankton in the mesohaline Chesapeake Bay. *Mar. Chem.*, 49, pp. 171–188
- K. Cailleaud b, c, J. Forget-Leray S. Souissib, D. Hildeb, K. LeMenacha, H. Budzinski, 2007. Seasonal variations of hydrophobic organic contaminant concentrations in the water-column of the Seine Estuary and their transfer to a planktonic species *Eurytemora affinis* (Calanoida, copepoda). Part 1: PCBs and PAHs. *Chemosphere Volume 70, Issue 2, Pages 270–280*.
- P Garrigues, HH Soclo, MP Marniesse, 1987. Origin of polycyclic aromatic hydrocarbons (PAH) in recent sediments from the continental shelf of the «Golfe de Gascogne» (Atlantic Ocean) and in the Gironde Estuary. *International journal of environmental analytical chemistry*, vol. 28, no1-2, pp. 121-131.



GROOM Sensors for gliders

Grant Agreement Number: 284321
FP7-Infra-2011-2.1.1 "Design
Studies"



D3.5

G Witt, 1995. Polycyclic aromatic hydrocarbons in water and sediment of the Baltic Sea. Marine Pollution Bulletin, Volume 31, Issues 4–12, , Pages 237–248

D3.5

I.F.25. pH

Scientific rationale

The *power of Hydrogen (pH)* is a water parameter which represents the acidity of the solution. pH is the negative logarithm of hydrogen ion concentration (more precisely its activity) in a water-based solution. It is a basic parameter of seawater and might have been a key in life emergence in the ocean (Macleod et al., 1994). Nevertheless, its value in different regions of the ocean is nowadays known only by calculation. Indeed, via the measurable carbonate system parameters (Alkalinity, Dissolved Inorganic Carbon and Partial pressure of CO₂) and the relevant equations, the pH value can be deduced. That is why very few *In-situ* measurements have been conducted in the ocean. The only local (references times series: BATS and HOTS, Tortell et al., 2012) measurements performed haven't been done with a precise method (Potentiometry).

Existing Methods

Two methods to estimate the pH of seawater are presently available: potentiometry and colorimetry. Potentiometry with electrodes is the most common method used in marine environment, although precision and accuracy are better for the colorimetry method. Potentiometric pH measurement is based on the NERNST equation, which describes in a relatively simple form the relationship between the potential of a defined electrode assembly and the chemical activity of the measured ion concentration. An electrodes assembly consists of a measuring electrode, which is sensitive to the ion activity to be measured, and a reference electrode. Potentiometry requires calibrations at a given salinity and presents drift with time. It is relatively less suitable for oceanic measurements

The colorimetric method is based on a spectrophotometer and on a dye. The pH of an unknown solution is determined by addition of a small amount of a pH indicator (dye) and determination of the extent of dissociation of the indicator. Spectra of the dye are then measured by the spectrophotometer. Because of overlap exists between the spectra for the acid form (generically represented as HIn) and base form (In⁻), individual molar absorptivities for each form at two wavelengths (λ_1 and λ_2) are required. Usually these are the wavelength peaks (absorption maxima) of HIn and In⁻. Assuming that the absorbances of the two forms are additive (independent of one another), we obtain two simultaneous linear equations for the absorption at the two wavelengths measured. From the sample absorbance, the pH is then determined.

A third method to measure pH is the Ion Sensitive Field Effect Transistor (ISFET). The pH is determined potentiometrically in two different ways. The ISFET potential is measured against a reference electrode bearing a liquid junction (internal reference) and against a solid state reference electrode without a liquid junction (external reference).

Existing sensors are based on the colorimetric and on the ISFET method:

1. **SAMI-pH** measures pH_T (total hydrogen scale) in the range of 7-9, using the colorimetric reagent method. It does not suffer from the drift that plagues most electrode based pH probes. The SAMI-pH is designed to provide researchers with valuable *in-situ* time series data at depths up to 600 m. – Sensor characteristics: Salinity range: 25 -40; response time: 3 min; accuracy: $\pm 0,003$ pH units; precision: $< 0,001$ pH units; long term drift: $< 0,001$ pH units over 6 months; thermistor accuracy, Precision: 0,1°C, $\pm 0,01$ °C- Manufacturer : Sunburnst Sensor - (1)
2. The **SeaFET™** Ocean pH sensor is an ion selective field effect transistor (ISFET) type sensor for accurate long-term pH measurements in salt water.- Max depth : 50m – Sensor characteristics: pH range : 6,5 -9,0 ; Response time: 3 min; accuracy: 0,05 pH units ; precision: $\pm 0,001$ pH units; Long term drift: 0,005 pH per month ; thermistor accuracy, Precision: 0,1°C, $\pm 0,01$ °C- Manufacturer : Satlantic - (2)

D3.5

Implementation on gliders

According to the existing sensor size, the implementation on gliders seems possible for both :
SAMI-pH : 55cm x 15,2cm Ø and SeaFet: 11,4cm Ø x 40,6cm.

Quality Control

The measure of two parameters of the carbonate system (Alk, DIC, pCO₂) provides a method to estimate independently pH to recalculate the pH value.

References

Gordon Macleod, Christopher McKeown, Allan J. Hall, Michael J. Russell. 1994. Hydrothermal and oceanic pH conditions of possible relevance to the origin of life. *Origins of life and evolution of the biosphere, Volume 24, Issue 1, pp 19-41*

X.Liu and al., 2006. Spectrophotometric measurements of pH-in situ : laboratory and field evaluations of instrumental performance. *Aquatic chemistry. Vol22,p42*

Philippe D. Tortell, Matthew C. Long, Christopher D. Payne, Anne-Carlijn Alderkamp, Pierre Dutrieux, Kevin R. Arrigo, 2012.: *Topical Studies in Oceanography, Deep Sea Research Part II Volumes 71-76, 15 September 2012, Pages 77-93*

<http://www.sunburstensors.com/products/sami-ph.html> (1)

<http://satlantic.com/seafet> (2)

D3.5

I.F.26. Radioactivity

Scientific rational

Since nuclear tests in the Pacific Ocean in the 1950's, and more recently the Fukushima disaster, radioactivity is undeniably a parameter to monitor in the ocean. The aim would be to localize contaminated water and to predict the spread (according to currents and winds). Fisheries closures in these areas would be the next step to protect the population.

Existing Methods

The **GAMMA-RAD5** is a complete, integrated γ -ray spectrometer. It includes a scintillator and PMT (Photo-Multiplier Tube), a charge sensitive preamplifier, a digital pulse processor and MCA (Multi-Channel Analyzer), all the hardware and software necessary to control and communicate to a PC, and all power supplies. It is a single, integrated, portable module. Several key innovations make this system ideal for field use. First, the scintillator and PMT are ruggedized to protect against mechanical shock and vibration. Second, the Ethernet interface permits operation over long distances: 100 m via Ethernet or, with Internet software, globally while the USB interface permits a single connection (power and data) to virtually any computer. Third, it has a flexible digital architecture so it can be easily tailored for specific applications. The GAMMA-RAD5 is ideally suited for a wide range of γ -ray spectroscopy measurements. – Sensor Characteristics: Dynamic range : 10 to 3000 ke; resolution: <7% FWHM at 662; count rates: to 200000 cps; power: 750 mW typical. - Manufacturer: AMPTEK Inc – (1)

Implementation on gliders

The size (31,5cm x 9,2cm \varnothing) and the cylindrical shape make possible a glider implementation.

Quality Control

NA

References

<http://www.amptek.com/grad.html> - (1)

D3.5

I.F.27. Redox-potential

Scientific rationale

In the field of environmental chemistry, the *reduction potential* is used to determine if oxidizing or reducing conditions are prevalent in water and to predict the states of different chemical species in the water, such as dissolved metals (Ussher et al., 2004 ; Fitzgerald et al., 2007). In marine biogeochemistry, the redox potential is a key parameter to characterize the chemical conditions of seawater.

Existing Methods

1. **ORP.** The ORP (Oxidation Reduction Potential) sensor (which was developed to be fully integrated with a CTD probe) consists of a pressure-balanced platinum electrode and a reference electrode (Ag/AgCl) in a plastic rod. It is equipped with a ceramic diaphragm containing a high number of pores. The electrolyte is a KCl containing gel without silver ions. However, using ORP at depth could induce errors (high and variable junction potentials could develop at pressure). Therefore, redox potential-measuring systems have been commercialized only for depths of up to 1200 m. Besides, it is inconvenient to use 2 free channels for redox measurements - one for the noble metal electrode and another one for the reference electrode. Sensor characteristics: for depths < 1200 m ; measuring range: +/- 2000 mV ; accuracy: +/- 1 mV. Manufacturer : AMT Analysentechnik GmbH. – (1).

When measuring the ORP in sea water troubles may occur, if conventionally reference electrodes with ceramic diaphragms are used because high and variable junction potentials are developed at pressures. Therefore, until now redox potential measuring systems have been offered only for depths of up to 1200 m. Besides, it was a little bit inconvenient to use 2 free channels for redox measurements - one for the noble metal electrode and another one for the reference electrode.

The solution - a new combined electrode for submersible probe systems

2. **Special double diaphragm.** To allow measurements at depths (> 1200 m) a new method has been developed, which consists of a reference electrode and a noble metal electrode, in one housing to save one free channel of the probe system. For accurate measurements at depth, a special double diaphragm for the reference electrode is used, providing a better signal stability when pressure increases.- For depths of up to 6000 m ; accuracy/resolution: 2 mV/0,1 mV – Manufacturer : AMT Analysentechnik GmbH – (2)

Implementation on gliders

Both of the sensors can be set up on a glider's hull:

ORP-combined shallow water sensor: 240mm x 37mmØ

Special double diaphragm: 250mm x 30mmØ

Quality Control

As with all electrodes, a calibration is required before and after the deployment, in order to determine the drift.

References

SJ Ussher, EP Achterberg, PJ Worsfold, 2004. *Marine biogeochemistry of iron*. Environmental Chemistry, Volume 1 (Issue 2) Pages 67-80.

William F. Fitzgerald , Carl H. Lamborg , and Chad R. Hammerschmidt, 2007. *Marine Biogeochemical Cycling of Mercury*. *Chem. Rev.*, 107 (2), pp 641–662

<http://www.amt-gmbh.com/> → "sensors" → "redox" (1) (2)

D3.5

I.F.28. Rhodamine / Amido-Rhodamine / Fluorescein

Scientific rational

Transport of tracers (such as Rhodamine, Amido- Rhodamine and Fluorescein) in complex marine environments and in near-shore could be relevant to chemically detecting mines (Corbau et al., 1994; Field, 2005), preventing contact with dangerous substances, and predicting where optical clarity will be clouded by fine sediments and silt.

Existing Methods

MiniPack is a low-cost, compact, robust and fully integrated CTD-F sensor suite incorporating a 24 channel data logger and designed to meet the demands of open ocean, estuarine waters, environmental monitoring,. This instrument contains a fluorometer to detect Rhodamine, Amido-Rhodamine, Fluorescein and incidentally conductivity, temperature and depth. Sensor characteristics: for rhodamine: detection range: 0,03-100 µg/l ; resolution : 0,01 µg/l; for amido-rhodamine: detection range: 0,04-200 µg/l; resolution: 0,025 µg/l; for fluorescein: detection range: 0,03-100 µg/l ; resolution : 0,01 µg/l. Depth rating: 600m - Manufacturer : Chelsea Technologies Group Ltd. – (1)

Implementation on gliders

Since the sensor has been designed to be towed from an AUV and according to its size (114 mm Ø x 200 mm), it could be easily set up on a glider.

Quality Control

NA

References

- Malcom S Field, 2005. *Assessing Aquatic Ecotoxicological Risks Associated with Fluorescent Dyes Used for Water-Tracing Studies*. Environmental & Engineering Geoscience v. 11 no. 4 p. 295-308
- Corbau C, HowaH, Tessier B, De Resseguier A, Chamley H, 1994; *Evaluation of the sediment transport on a macrotidal beach using fluorescent tracers, Dunkerque Est, France*. vol. 319, n°12, pp. 1503-1509.
- <http://chelsea.co.uk/marine/sensors/minipack-ctd-f> - (1)

D3.5

I.F.29. Deep-sea low-frequency sub-bottom profiler (SBP)

Scientific rational

In the context of archaeological research, natural resources assessment, or geological surveys, deep-sea bottom analysis is often used. Most of the seafloor consists of sediments and loose rocks, more or less compacted, that are transparent to low-frequency waves, penetrating several dozens of meters (Frappa et al., 1983).

Existing Methods

SBP. Sub-Bottom Profiling (SBP) systems identify and measure various sediment layers by acoustic methods. The acoustic emission is based on the use of a Janus-Helmholtz transducer. The frequency band extends from 1800 to 6200 Hz. Power electronics and impedance matching unit have been specifically optimized to deliver a sound level of 190 dB, compatible with a 50 m penetration depth. The vertical resolution is better than 20 cm. The receiver is a three-hydrophone array. Data acquisition is performed with the acquisition system SUBOP. Working depth: up to 6000 m. – Manufacturer: IFREMER – (1)

Implementation on gliders

SBP has been initially developed for AUVs, which are about twice as big as gliders; by removing the metallic structure, the sensor's 2 back cylinders and 2 lateral black tubes could be set up on a glider.

Quality Control

NA

References

M Frappa, M Duprat, 1983. Relations entre la réponse acoustique (5 kHz) et la nature lithologique des fonds marins
english Marine Geophysical Researches, 1983, Volume 5, Number 4, Page 405

<http://flotte.ifremer.fr/Presentation-de-la-flotte/Equipements/Equipements-acoustiques/Les-sondeurs-de-sediments/Le-sondeur-de-sediments-de-l-AUV> - (1)

D3.5

I.F.30. Seismic waves

Scientific rationale

Seismic waves, used in seismic tomography, are generally recorded by seismic stations. The accuracy of the imaging critically depends on the number of recorded arrivals. While a dense network of seismic stations covers the land, the coverage of the oceans remains poor, principally due to high cost of the installation and recovery of the conventionally used instruments, such as Ocean Bottom Seismometers (OBS) and moored hydrophones.

Existing Methods

MERMAID (Mobile Earthquake Recording in Marine Areas by Independent Divers) is an autonomous freely-drifting underwater robot, which, by changing its buoyancy, is able to dive to and remain at a programmed depth. A seismic wave arriving at the ocean bottom refracts into the water and generates an acoustic wave, which propagates almost vertically due to large acoustic impedance mismatch between the water and the Earth crust. To record these acoustic signals, the MERMAID is equipped with a hydrophone and will continuously monitor the pressure variation by calculating the ratio of Short-Term to Long-Term moving averages (STA/LTA algorithm). Once an acoustic signal generated by a teleseismic P-wave is detected, the MERMAID will surface as quickly as possible to transmit via satellite connection the recorded signal and other important information (e.g. time of the signal arrival, robot's depth at the moment of detection and its position at the surface). – Manufacturer: Geoazur – (1).

Implementation on gliders

The complete MERMAID system has more or less the same size as a glider. If we remove the buoyancy system, that already exists on a glider, the system can be set up on a glider.

Quality Control

NA

References

<https://www.geoazur.net/GLOBALSEIS/sukhovich/File1.html> - (1)

<https://geoazur.oca.eu/spip.php?rubrique760> - (1)

D3.5

I.F.31. Virus (enteroviruses + noroviruses)

Scientific rational

Enteroviruses are a group of small RNA viruses responsible for a wide range of symptomatic and asymptomatic infections worldwide (Frankhauser et al., 1998). Norwalk-like viruses, referred as Noroviruses (NV), are a group of small non-enveloped RNA viruses. NVs cause epidemic acute gastrointestinal illness in humans and are thought to be the most common cause of viral gastroenteritis worldwide. Both can be found in recreational waters and therefore in coastal areas (Goldberg, 1995).

Existing Methods

AMG: The Autonomous Microbial Genosensor represents a fully automated system for in situ genetic analysis. Designed for field deployment, the AMG combines systems for sample collection, filtration, cell lysis, RNA extraction/purification/concentration (NASBA), gene amplification and data transmission. Nucleic acid sequence-based amplification (NASBA) is an isothermal-based method of RNA amplification (Davey and Malek, 1989). Using this method, RNA is amplified by the action of an enzyme cocktail that includes AMV Reverse Transcriptase, T7 RNA polymerase and RNase H at a fixed temperature (41°C). By pairing this technique with the ability to monitor the fluorescence signal produced from Molecular Beacon probes in real time as they hybridize to the amplicon, it is possible to perform real time analysis of samples and obtain data in a matter of minutes. (Green et al., 2003; Casper et al., 2004; Moore et al., 2004) – Manufacturer: NOC UK – (1), (2).

Implementation on gliders

The AMG is housed in a 22cm x 122cm (diameter x length) anodised aluminium pressure vessel. It could be easily set up on a glider.

Quality Control

NA

References

- Casper, E.T., S.S Patterson, M.C. Smith, and J.H. Paul. 2004. Developpement and evaluation of a method to detect and quatify enteroviruses using NASBA and internal control RNA (IC-NASBA). *J.Virol. Meth*
- Davey, C. and L.T. Malek. 1989. Nucleic acid amplification process. European Patent No. EP 0329822
- Edward D. Goldberg, 1995. Emerging problems in the coastal zone for the twenty-first century. *Marine Pollution Bulletin*, Volume 31, Issues 4–12, Pages 152–158
- Greene, S. R., C. L. Moe, L. Jaykus, M. Cronin, L. Grosso, and P. van Aarle. 2003. Evaluation of the NuclisensÒ Basic kit assay for detection of Norwalk virus RNA in stool specimens. *J. Vir. Meth.* 108: 123-131.
- Moore, C., E. M. Clark, C. I. Gallimore, S. A. Corden, J. J. Gray and D. Westmoreland. 2004. Evaluation of a broadly reactive nucleic acid sequence based amplification assay for the detection of Noroviruses in faecal material. *J. Clin. Vir.* 29: 290-296.
- Fankhauser R.L., J.S. Noel, S.S. Monroe, T. Ando, and R.I. Glass. 1998. Molecular epidemiology of "Norwalk-like viruses" in outbreaks of gastroenteritis in the United States. *J. Infect. Dis.*178:1571-8.
- <http://www.marine.usf.edu/systems/?q=amg> - (1)
- <http://www.marine.usf.edu/microbiology/nasba.shtml> - (2)

D3.5

I.G. Sensors with potential implementation on gliders

- I.G.1- Alkalinity
- I.G.2- Bacteria, cells
- I.G.3- Domoic Acid (Neurotoxin)
- I.G.4- Micro-pump
- I.G.5- Perchlorate (ClO_4^-)
- I.G.6- Plankton Sampler
- I.G.7- Volatile Organics Compounds (VOCs)

D3.5

I.G.1. Alkalinity

Scientific rationale

Alkalinity is one of the parameters of the carbonate system. Measuring alkalinity is important in determining the ocean's ability to neutralize acidic pollution from rainfall or wastewater. It is a crucial parameter to characterize water quality. In seawater the range of alkalinity is between 2200 and 2450 $\mu\text{mol/kg}$ (Copin-Montégut, 1996).

Existing Methods

The total alkalinity analysis is based on titration, which is the addition of small, precise quantities of strong acid (the reagent) to the sample, to reach a sample pH of 4. The quantity of used acid corresponds to the total alkalinity of the sample. Alkalinity can be measured using a buret, titrator, or digital titrator.

APASCH: (Autonomous pH and Alkalinity Sensor by Colorimetry for fresh water) is a new spectrophotometric method involving a dye indicator that has been developed to determine alkalinity. A weak acid (Formic Acid) mixed with a dye indicator (BBP) is added to the sample. This leads to a pH variation measured by spectrophotometry. The alkalinity (and the pH) is then deducted from this variation (Podda and Michard, 1994. Darmoul, 2012) The range detection is between 1000 and 4000 $\mu\text{mol/kg}$. – Manufacturer: NKE and IPG Paris.

Implementation on gliders

APASCH sensor is still a prototype, although a commercialized version should be developed in the next few months by the manufacturer. The industrial model would have a cylindrical shape.

Quality Control

NA.

References

Copin-Montégut, 1996. *Chimie de l'eau de mer*. OPUS. pp 216

Podda and Michard, 1994 F. Podda and G. Michard, Mesure colorimétrique de l'alcalinité, *Compte Rendus de l'Académie des Sciences — Série II* 319 (1994), pp. 651–657.

Darmoul 2012. La mesure spectrophotométrique du pH et de l'alcalinité dans les eaux continentales. Thèse, université Paris Diderot.

D3.5

I.G.2. Bacteria, cells

Scientific rational

Bacteria are living unicellular and prokaryotic organisms. They are present in most habitats on the planet and in the ocean, throughout the water column and into the sediments (Azam et al., 1983 ; Sahn et al., 1999). They are key players in nutrient cycling, with many steps in nutrient cycles depending on these organisms (Mort et al., 2007), such as the fixation of nitrogen from the atmosphere, or photosynthesis (Zehr et al., 1998). Other species are pathogenic and could cause infectious diseases.

Existing Methods

Cytosub: Microscopic analysis of particles such as bacteria and cells in water is nowadays possible thanks to the Multiwavelength Microfluidic Flow Cytometer. It has been designed for *In Situ* sampling and speciating phytoplankton. The system detects and distinguishes particles coded with two fluorescent dyes. The coded particles are in turn coated with antibodies, which bind specific targets, such as bacteria and cells. After exposing the sample, tracer antibodies carrying a dye fluoresces at a third wavelength bind to any target captured on the coded particles. In other words, the particles are identified, while fluorescence at a third wavelength is used to determine the presence or absence of each target. The microflow cytometer measures the levels of the third fluorescent dye to detect and quantify the amount of the target present in the sample.– Detection limit: 103 cells/ml for E. coli, 104 cells/ml for Listeria, 105 cells/ml for Salmonella, 1.6 ng/ml for cholera toxin, 0.3 ng/ml for Staphylococcal enterotoxin B, and 8 ng/ml for ricin. - Manufacturer: Cytobuoy – (1), (2), (3).

Implementation on gliders

The flow cytometer' size (Cytosub) is 31cmØ x 55cm. The diameter seems relatively too large for a glider. It would need modification, especially in diameter dimension for an implementation. An other issue is the max depth: up to 200 meters depth.

Quality Control

NA

References

- Kerstin Sahn, Barbara J. MacGregor, Bo B. Jørgensen, David A. Stahl, 1999. Sulphate reduction and vertical distribution of sulphate-reducing bacteria quantified by rRNA slot-blot hybridization in a coastal marine sediment. Environmental Microbiology, Volume 1, Issue 1, pages 65–74
- F Azam, T Fenchel, JG Field, JS Gray, 1983. The ecological role of water-column microbes in the sea. Marine ecology, Vol 10, pp 257-262.
- Haydon P. Mort, Thierry Adatte, Karl B. Föllmi, Gerta Keller, Philipp Steinmann, Virginie Matera, Zsolt Berner and Doris Stüben, Phosphorus and the roles of productivity and nutrient recycling during oceanic anoxic event 2. Geology, vol. 35 no. 6 p. 483-486
- JP Zehr, MT Mellon, S Zani, 1998. New nitrogen-fixing microorganisms detected in oligotrophic oceans by amplification of nitrogenase (nifH) genes. Appl. Environ. Microbiol. vol. 64 no. 9 3444-3450
- http://www.nrl.navy.mil/content_images/09_Chemical_Ligler.pdf - (1)
- <http://noc.ac.uk/science-technology/research-groups/ote/instruments-sensors/biological-microsensors> - (2)
- <http://www.cytobuoy.com/products/submersible/> - (3)

D3.5

I.G.3.Domoic Acid

Scientific rational

Domoic acid (DA) is a neurotoxin that causes amnesic shellfish poisoning. Although multiple macroalgal and diatom sources of DA have been identified, toxigenic diatoms pose the biggest threat to human health through the accumulation of DA in filter-feeding marine organisms (Lefebvre et al., 2010). Toxic blooms of DA-producing diatoms are a global issue (Trainer et al., 2008) and appear to be increasing in frequency and toxicity, thereby presenting a continued threat to human health and seafood safety.

Existing Methods

SPR (Surface Plasmon Resonance) is an optical technique to detect a immobilized ligand bound to a receiver on a surface. It measures the adsorption of material onto planar metal (typically gold and silver) surfaces. In the context of harmful algal blooms, the SPR sensor has been implemented for the determination of domoic acid. (Qiuming et al., 2005 ; F.Colas et al., 2010a 2010b) – Manufacturer : IFREMER – (1)

Implementation on gliders

There is no size indicated by the manufacturer. There is a submarine version of the sensor towed from a ship, so we can suppose that the dimension is relatively small.

Quality Control

NA

References

- Kathi A. Lefebvre, Alison Robertson, 2010. *Domoic acid and human exposure risks: A review*. *Toxicon*, Volume 56, Issue 2, Pages 218–230
- V.L. Trainer, B.M. Hickey, S.S. Bates, 2008. *Toxic diatoms*. P.J. Walsh, S.L. Smith, L.E. Fleming, H. Solo-Gabriele, W.H. Gerwick (Eds.), *Oceans and Human Health: Risks and Remedies from the Sea*, Elsevier Science Publishers, New York, pp. 219–238
- F. Colas, M.-P. Crassous, W. Litaker, S. Laurent, E. Rinnert, C. Compère, P. Gentien. New approach for underwater detection of domoic acid, HAB 2010a, 1-5 novembre, Hersonissos, Grèce.
- Y. Qiuming, S. Chen, A.D. Taylor, J. Homola, B. Hock, S. Jiang. Detection of low-molecular-weight domoic acid using surface plasmon resonance sensor. *Sensors and Actuators B: Chemical* 107(1), 193-201, 2005.
- F. Colas, S. Laurent, M.-P. Crassous, C. Dreanno, O. Péron, E. Rinnert, C. Compère. New approach for in situ algae detection, *Biosensors* 2010, 26-28 mai 2010b, Glasgow, RU.
- <http://www.ifremer.fr/ic/fr/spr.htm> - (1)

D3.5

1.G.4. Perchlorate (ClO_4^-)

Scientific rationale

Perchlorate is a widely known inorganic endocrine disruptor. It affects the thyroid gland by competitively inhibiting iodide transport (Snyder et al. 2003). ClO_4^- is used as an oxidizer and explosive for military and civilian applications. It is attracting increasing attention as an inorganic contaminant in drinking water, groundwater, and surface water, it can also be found in seawater through coastal-runoff. In the coastal ocean the concentrations could be greater than 1 $\mu\text{g/L}$ (Namguk et al., 2011).

Existing Methods

Novel selective and controllable surfactant-based extraction chemistry that can segregate and concentrate ClO_4^- from complex environmental waters was studied (Gertsch et al., 2012). This affinity chemistry was combined with the current LOC (Lab-On-a-Chip)* sensor design to test the ability to embed this extraction scheme within sensitive and powerful microchip electrophoretic separations coupled to electrochemical detection. The device is capable of analyzing ClO_4^- over a relatively large linear range, with a detection limit of 5 ppb. – Manufacturer: SERDP. – (1).

(*A lab-on-a-chip (LOC) is a device that integrates one or several laboratory functions on a single chip of only millimeters to a few square centimeters in size.

Implementation on glider

The sensor has not been tested on seawater and is not ready yet as a "real" sensor. No size is given by the manufacturer, though pictures available (Cf. website) display a size small enough for use on a glider.

Quality Control

NA

References

Jana C. Gertsch, Imee G. Arcibal, Charles S. Henry and Donald M. Cropek, 2012. Lab-on-a-Chip Sensor for Monitoring Perchlorate in Ground and Surface Water. Strategic Environmental Research and Development Program ER-1706. US army corps of engineers . Engineers Research and Development Center.

Namguk Her, Hyunchan Jeong, Jongsung Kim, Yeomin Yoon, 2011. Occurrence of Perchlorate in Drinking Water and Seawater in South Korea. Arch Environ Contam Toxicol 61:166–172

Snyder SA, Westerhoff P, Yoon Y, Sedlak DL (2003) Pharmaceuticals, personal care products, and endocrine disruptors in water: Implications for the water industry. Environ Eng Sci 20:449–469

[http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER-1706 - \(1\).](http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER-1706 - (1).)

D3.5

I.G.5. Plankton sampler

Scientific rational

Plankton sampling provides invaluable insights for numerous aspects of plankton dynamics and ecology including: climate change, biodiversity and biogeography, eutrophication, harmful algal blooms, fisheries investigations, plankton ecology, taxonomy, regime shifts and non-indigenous species (Larsson et al., 1982 ; Horner, 1997 ; Hays et al., 2005).

Existing Methods

The Autonomous Plankton Sampler is a sensor constructed in stainless steel with two spools of silk or nylon gauze, integral microcontroller, motor, batteries and flow meter. The water passes through the intake aperture and zooplankton is captured upon a filtration gauze, which is then covered by a second gauze. Finally, the sample is wound on to a collection spool immersed in preservative. Plankton concentration is finally obtained at post-deployment, when analyses are undertaken, either on the gauze or the wash-off. – Manufacturer: Chelsea – (1).

Implementation on glider

With a cubic shape, the sampler is not adapted for a glider. However, the size (140mm x 235mm x 291mm) could allow glider implementation, with a few modifications. The sampler has proven itself and is already used towed from boats.

Quality Control

NA

References

GC Hays, AJ Richardson, C Robinson, 2005. *Climate change and marine plankton*. Trends in Ecology & Evolution, Vol 20, issue 6, pp 337-344.

U Larsson, Å Hagström, 1982. Fractionated phytoplankton primary production, exudate release and bacterial production in a Baltic eutrophication gradient. Marine Biology, Volume 67, Issue 1, pp 57-70

RA Horner, DL Garrison, FG Plumley, 1997. *Harmful algal blooms and red tide problems on the US west coast*. Limnology and Oceanography.

<http://chelsea.co.uk/marine/sensors/plankton-sampler> - (1)

D3.5

I.G.6. VOCs (Volatile Organics Compounds)

Scientific rationale

The VOCs are molecules with a wide range of uses, from making cookware to creating industrial solvents. VOCs are a threat to human and environmental health. If released into the environment, they can cause sickness, birth defects, and other problems (Brown, 2002). In some cases, these problems may not be readily apparent. The types and concentrations of the compounds found depends upon the extent of anthropogenic and terrestrial influences. Open ocean samples consist mostly of aromatic hydrocarbons, whereas coastal samples included alkanes, cycloalkanes, cycloalkenes, aromatic hydrocarbons, aldehydes and chlorinated hydrocarbons. The concentration measured from unpolluted water is 5ng/Kg and can reach 1000 ng/Kg. (Sauer, 1981).

Existing Methods

The prototype sensor **ME-IMS** (Membrane Extraction Ion-Mobility Spectrometry) is capable of uniquely identifying 32 VOCs, including the most common, TCE (tetrachloroethylene). The limit of detection is 0,37 ppbv.

It converts contaminants from liquid phase into vapour phase using a novel membrane separation and can achieve sensitive identification by combining linear and nonlinear IMS. In other words, the sensor is a combination of membrane extraction with miniature linear and non-linear IMS analyzers. – Manufacturer: SERDP – (1)

Implementation on gliders

No test has been conducted on seawater, and the sensor is still a prototype. Some work is needed to adapt it for use in the ocean. As a portable sensor the size should make possible its implementation on a glider.

Quality Control

NA

References

- Theodor C. Sauer Jr. 1981 Volatile organic compounds in open ocean and coastal surface waters. Organic Geochemistry Volume 3, Issue 3, Pages 91–101.
- V Brown. 2002. World's children threatened. Environ Health Perspect, 110(6)
- <http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER-1603> - (1)

D3.5

I.G.7. Micro-pump (microfluidic pump using conductive polymer for low power consumption)

Scientific rationale

Fluid transport is crucial in the development of micro-analytical devices. While there are many micro-pump designs available for micro-nano scale liquid delivery, they generally require high operation voltages and high running current and therefore are very power hungry.

Existing Methods

The micro-pump consists of two functional PMMA (polymethylmetacrylate) layers; a bottom layer incorporating two push-button type PDMS (poly dimethylsiloxane) check-valves and fluidic channels, and a top layer holding a PPy (polypyrrole) membrane and PDMS diaphragm used for actuation. The PPy membrane deforms from convex to concave shape depending on the polarity of the applied voltage. The movement of this PPy membrane induces a push-pull action in the PDMS diaphragm. This design employs PPy as the electrochemical actuator to give the mechanical movements required for the pumping action. – Manufacturer: Dublin university.- (1)

Implementation on glider

It is small in size, has low power demand and can be easily integrated into microfluidic devices to reduce any sensors size. This PPy actuator can operate below 1V and is extremely energy-efficient, it can be operated using a 1.5 volt AA battery and is particularly suitable for microfluidic devices that will be used for long-term field deployments. Therefore, it is particularly suitable for gliders.

Quality Control

NA

References

<http://www4.dcu.ie/chemistry/asg/danielKim.shtml> - (1)

D3.5

GLIDERS AS DATA MESSENGERS

The increasing need for oceanographic data imposes high technical requirements on data acquisition and data storage capacities. Many oceanographic data acquired today are measured with subsurface platforms, such as moorings or bottom-mounted installations. As the recovery and redeployment of such platforms by ships is very expensive, the instruments are designed to remain in the water for two years or more. However, ship-time is still a major cost factor in observational oceanography. The idea of employing gliders as data messengers is therefore a promising way for cost-effective acquisition of data from oceanographic long-term observations. The glider as a data messenger is supposed to autonomously retrieve information from moored subsurface instruments by acoustical communication and to transmit them to the data centre via the Iridium satellite system. In this way, time-consuming and expensive efforts of instrument recovery by ships could be reduced to a practical minimum and data might become available sooner, possibly allowing near-real-time usage.

The technical design of acoustical communication requires that both the mooring and the glider are equipped with acoustic modems. Such a system has been successfully operated by the Scripps Institution of Oceanography in the framework of the Consortium on the Ocean's Role in Climate (CORC) project [Send et al., 2013]. This glider mission, however, also demonstrated the technical challenges of acoustical communication.

One problem is the quality of the sound signals transmitted in the ocean. Once it has left the sound source, sound energy is absorbed and dissipated in the water. This effect reduces the transmitting distance between the moored modem and the glider. The problem can be reduced by selecting low communication frequencies (9-14 kHz). Another problem is multiple reflections of the sound signal by the ocean bottom and the sea surface, which disturb the signal detection and lower the quality of the received signal. To reduce the multipath delay the acoustic communication between mooring and glider is performed when the glider is at the surface. In this way, data have been successfully transmitted over distances of up to 8 km between the glider and the moored modem at 3700 m depth.

The main problem is energy consumption together with a low data transmission rate. A typical amount of available battery energy for a modem installed on a glider is 1260 kJ at 28 V. To save energy, the glider modem is turned on only during communication with the moored modem. The amount of energy consumed depends on the acoustic baud rate (baud: transmitted symbols per second) and the size of the transmitted data. The average data throughput in the study of Send et al. [2013] was about 3 byte/s with the modem operating at 140-600 baud. On average only 60 kb of data were transferred per day between mooring and glider. In one glider mission (31 days long), 2 Mb of error-free data could be obtained. 17% of the consumed energy was spent establishing an acoustic link with the mooring, and the remaining 83% were used for listening to the data signals. It was shown that it needs approximately 0.5 J to transmit one byte of oceanographic data.

Typical data file sizes for a one-year measuring period from moored CTD (conductivity/temperature/depth) instruments, current meters or ADCPs (Acoustic Doppler Current Profiler) range between 200 kb and 7.5 Mb, which demonstrates that the data throughput for acoustical communication needs to be improved. One future perspective could be short-range modems. If the glider were able to stably float close to the moored modem, data could be transferred with higher efficiency. Enhancements of the glider systems with loitering (to be able to approximately stay in one location underwater) functions are already planned (Send et al., 2013). Over very short distances (less than 1 m) data could possibly be transferred via optical links. Despite technical problems, the first steps in acoustical communication with gliders have been made, and it was shown that this technique can provide a very useful means for oceanographic data retrieval..

D3.5

BIBLIOGRAPHY

- Edward Fiorelli, Pradeep Bhatta, Naomi Ehrich Leonard, 2003. Adaptive Sampling Using Feedback Control of an Autonomous Underwater Glider Fleet. Proc. 13th Int. Symp. on Unmanned Untethered Submersible Technology (UUST)
- Carol Janzen, 2011. Improving CTD Data from Gliders by Optimizing Sample Rate and Flow Past Sensors. Ocean News and technology, Volume 17, Issue 7. pp. 22-23
- Carol Janzer, Nordeen Larson, and David Murphy, 2008. Long-Term Oxygen Measurements. International Ocean Systems, Volume 12, Number 2.
- Consiglio Nazionale delle Ricerche, 150 pages, publication of the catalogue for the scientific and technological research for the sea, funded by the Italian Ministry of university and Research and coordinated by CNR.
- David Murphy, Nordeen Larson, and Brad Edwards, 2008. Improvements to the SBE 43 Oxygen Calibration Algorithm. From Poster Presentation, 2008 Ocean Sciences Meeting, Orlando Florida, 2 - 7 March 2008.
- Kenneth S. Johnson, Luke J. Coletti, 2002. In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean. Deep-Sea Research I 49 (2002) 1291–1305.
- Körtzinger, A., J.Schimanski, and U.Send.2005. High quality oxygen measurement from profiling floats: A promising new technique. Journal of Atmospheric and Oceanic Technology 22:302-308
- New Developments in Marine Sensor Technologies: Opportunities and Challenges, workshop report, held in Dublin the 26th of march 2009
- Perry, Mary Jane ; Eriksen, Charles C, 2003. Incorporation of Sensors into Autonomous Gliders for 4-D Measurement of Bio-optical and Chemical DTIC Document
- Peter J Russelo, Eric Siegel, 2011. High resolution doppler profiler measurements of turbulence from a profiling body. Current, Wave & Turbulence Measurement Workshop, Monterey, CA.
- Riser, S.C., and K.S Johnson. 2008. Net production of oxygen in the subtropical ocean. Nature 451:323-326
- Schmitt, R. W., R. Petitt, 2006. A fast-response, stable CTD for gliders and AUVs. Proceedings:IEEE/MTS Oceans 2006 Meeting, Boston, MA. September 18-21. 4 pp.
- Send, U., Davis, R., Fischer, J., Imawaki, S., Kessler, W., Meinen, C., ... & Beal, L. (2009). A global boundary current circulation observing network. OceanObs09 Community White Paper.
- Testor, P., Meyers, G., Pattiaratchi, C., Bachmayer, R., Hayes, D., Pouliquen, S., Petit de la Villeon, L., Carval, T., Ganachaud, A., Gourdeau, L., Mortier, L., Claustre, H., Taillandier, V., Lherminier, P., Terre, T., Visbeck, M., Krahman, G., Karstensen, J., Alvarez, A., Rixen, M., Poulain, P.M., Osterhus, S., Tintore, J., Ruiz, S., Garau, B., Smeed, D., Griffiths, G., Merkelbach, L., Sherwin, T., Schmid, C., Barth, J.A., Schofield, O., Glenn, S., Kohut, J., Perry, M.J., Eriksen, C., Send, U., Davis, R., Rudnick, D., Sherman, J., Jones, C., Webb, D., Lee, C., Owens, B., Fratantoni, D., 2010: Gliders as a component of future observing systems, in Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 2), Venice, Italy, 21-25 September 2009, Hall, J., Harrison D.E. and Stammer, D., Eds., ESA Publication WPP-306.
- Wayne H. Slade, Emmanuel Boss, Giorgio Dall'Olmo, M. Rois Langner, James Loftin, Michael J. Behrenfeld, Collin Roesler, and Toby K. Westberry, 2010. Underway and moored methods for improving accuracy in measurement of spectral particulate absorption and attenuation. Journal of Atmospheric and Oceanic Technology. Volume 27, issue 10, pp. 1733-1746.