UNIVERSITÀ DEGLI STUDI DELLA Tuscia

UNIVERSITÀ DEGLI STUDI DELLA TUSCIA DI VITERBO

DIPARTIMENTO DI SCIENZE ECOLOGICHE E BIOLOGICHE

Corso di Dottorato di Ricerca in

ECOLOGIA E GESTIONE SOSTENIBILE DELLE RISORSE AMBIENTALI - XXIX Ciclo

IMPLEMENTATION AND APPLICATION OF NEW TECHNOLOGIES FOR MARINE ENVIRONMENTAL RESEARCH

(s.s.d. BIO/07)

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A.A. 2016/17

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ABSTRACT

Oceans play a fundamental role in the climate balance and change both physically, through heat transport and water masses exchanges, and chemically, interacting in the carbon cycle through the photosynthesis and the biological pump. Knowledge and understanding are the keys to sustainable development and good ocean governance, as required by international organizations and european maritime policy. Everyday new technologies emerges in all marine science sectors to facilitate the understanding of marine life, to promote traditional maritime sectors and to provide solutions to prevent and forecast climate change and marine pollution. Unfortunately there is a structural lack of observational networks for open oceans and coastal seas and a limit to physical domain. The knowledge of the oceans is stringly limited by the observational capacity, consequently the development of new sensors and platforms contributes to the extension of measuring capacity of marine phenomena. My research work shows new low-cost sensors and probes developed to measure marine temperature, conductivity, chlorophyll *a* and CDOM fluorescences, turbidity, focusing both on sensing strategies, general architecture and laboratory trials and on the different application during several oceanographic surveys in the Mediterranean Sea. These technological solutions were designed for the implementation of oceanographic monitoring networks to contribute to the understanding of physical and biological marine processes.

1. SYNOPSIS

The ocean covers 71% of the Earth's surface, and is linked to human living in many ways. From its role in influencing the climate to how it provides a variety of socio-economical, cultural and environmental benefits, the ocean contributes greatly to human wellbeing.

In a context of growing demand for resources and maritime services, demonstrating the potential of seas and oceans, is critical to turning this potential into an asset with long-lasting economic, social and environmental benefits.

For this reason the EU defined her Integrated Maritime Policy based on these cross-cutting policies: blue growth; marine data and knowledge; maritime spatial planning; integrated maritime surveillance and sea basin strategies.

Identifying seas and oceans as the main drivers for the European economy, the Blue Growth is the long-term strategy to support sustainable progress in the marine and maritime sectors as a whole, achieving the goals of the Europe 2020 strategy for smart, sustainable and inclusive growth.

Oceans play a fundamental role in the climate balance and consequently in the climate change, both physically, through the heat transport and through the water masses exchanges, and chemically, interacting in a decisive way in the carbon cycle through the photosynthesis and the 'biological pump'.

For this reason a detailed understanding of ocean climate and ecosystems, as well as human impacts and vulnerabilities, requires the coordination of a continuous and long-term system of ocean observations. Unfortunately there is a structural lack of observational networks for open oceans and coastal seas, the opposite of what yalready exists for atmosphere and terrestrial systems.

For the study and the monitoring of the oceans physical features, low-cost measurement technologies have been developed to measure temperature, currents and partially salinity.

Integrating satellite observations and mathematical models, the new low-cost technologies have allowed the IOC (Intergovernmental Oceanographic Commission) to launch some observational programs in worldwide oceans (GOOS) such as the Global Drifter Program (GDP) and ARGO.

With regard to the measures of fundamental biological variables to study the carbon cycle, as the photosynthetic pigments and CDOM, the available tools are still too expensive. This fact inhibits the capability to integrate the long-term global scale observational programs by measuring also biological varibles such as chlorophyll a and CDOM in order to calibrate and integrate satellite measurements and mathematical climate models.

Indeed the knowledge of the oceans is stringly limited by our observational capacity, consequently on the development of new sensors and platforms, which provide multi-disciplinary datasets, advanced sampling strategies and contribute to the expansion of temporal and spatial coverage of our measuring capacity of marine phenomena.

These devices must be able to be used for several applications, ranging from vertical profilers to stand-alone systems, and can be installed on different platforms (buoys, Voluntary Observing Ships, underwater vehicles, etc.). In this way the availability of low-cost biological instruments will enable the implamantation of extended observatory networks for the study of marine physical and biological processes carrying out an important step forward an integrated approach for in situ observations, forecasting models and remotely sensed data.

My research work shows new low-cost sensors and probes developed to measure marine temperature, conductivity, chlorophyll *a* and Chromophoric Dissolved Organic Matter fluorescence, turbidity, focusing both on sensing strategies, general architecture and laboratory trials and on the different application during several oceanographic surveys in the Mediterranean Sea.

2. THE NECESSITY OF GLOBAL BIO-OPTICAL MEASURES

'Ecological monitoring aims at inferring causes of ecosystem changes, by measuring ecosystem state variables in space and time' (Yoccoz 2012).

In a context of growing demand for marine resources and maritime services the study of ecological and environmental characteristics of marine ecosystems is fundamental to understand and forecast natural and non-natural variations.

Along these lines, the Ecosystem-based Management method proposed by the Marine Strategy Framework Directive (MSFD) (2008/56/EC) requires an integrated approach composed of in situ observations, forecasting models and remotely sensed data for the monitoring and assessment of the environmental status of marine ecosystems. The Marine Strategy Directive constitutes the environmental pillar of the European maritime policy, which puts greater emphasis on the need to collect large amounts of in situ data during observational monitoring programmes for the correct management of marine ecosystems.

A significant amount of effort has been invested studying marine dynamics and processes, and there are different scientific programs focused on measuring physical, chemical and biological variables. But the knowledge of the oceans is stringly limited by our observational capacity (Petersen 2014), consequently on the development of new sensors and platforms, which provide multi-disciplinary datasets, advanced sampling strategies and contribute to the expansion of temporal and spatial coverage of our measuring capacity of marine phenomena.

Marine measurements provide a long story of improvement in instrumentation capacity, and the different technological advances obtained in the course of time have produced new ways to observe and monitor the ocean.

Operational oceanography and remote sensing studies currently represent the biggest part of the ocean sciences that provide high-quality models and observational data for research and practical applications, but critically depends on the near-real-time availability of a large amount of in situ data collected with sufficiently dense spatial and temporal sampling. This issue directly influences the robustness of ocean forecasting models and remote sensing observations through data assimilation and validation processes (Pinardi et al. 2003, 2010).

Like physical models and remote data, ecological once must be developed and validated. Examples of such ecological uses could be the description of the distribution and abundance of the phytoplankton community and the advancement to the study of the ocean carbon cycle and assimilation (Irwin & Finkel 2008). The ocean carbon cycle and ecosystem research relating to climate change are strictly connected to the estimation of phytoplankton biomass and to those factors which influence the rates of primary production and the export of organic carbon to the deep ocean. In particular, the chromophore-containing components of dissolved organic matter (CDOM) can reduce the photosynthetically active radiation available to phytoplankton, as well as degrade the accuracy of chlorophyll measurements by satellite colour sensors (Carder et al. 1989, 1991) due to their strong absorption of ultraviolet light and the blue region of the light spectrum. In addition the study and the prediction of phytoplankton response to climate changes are fundamental to forecast the potential variation of the capacity of oceans to act as a carbon sink. With regard to phytoplankton biomass distribution, the main investigation tools are both traditional oceanographic methods, which are expensive and spatially and temporally limited, and the ocean-colour satellite observations, which lack information about the deep chlorophyll maximum (DCM).

Chlorophyll *a* fluorometry remains the principal method to study phytoplankton biomass along the water column and on the marine surface, because together with CDOM is one of the most optically active components of the oceans (Roesler et al. 1989, Babin et al. 2003). However, the high costs of commercially instrumentation have made these measures unavailable for extensive use.

To meet these challenges, in the last decades the use of low-cost instrumentations have gained greater attention (Manzella et al. 2003). The scientific community has made much effort towards modelling marine dynamics, and there are now exhaustive scientific programmes and novel technological developments (e.g. the Argo system and gliders) for monitoring physical variables; however, there remains a lack of biological monitoring programmes and technologies. The existing technologies allow to deploy sensors and probes on many kind of platforms, but are too expensive for extensive utilization.

The Ship Of Opportunity Programme and the Voluntary Observing System represent the most important world initiatives based on low cost technologies. These programmes are based on the possibility to use merchant ships that join to the programme, in routinely strategic shipping routes. The basic instrumentation can be divided in two main branch: the expendable probes and the Ferrybox. Since the 1960s, XBTs (eXpendable BathyThermographs) have been successfully adopted as an easy way to collect temperature profiles using commercial ships. Nowadays the XBT remains the most effective method for low-cost and simple acquisitions of temperature profiles, although the quality of the data must be checked (Reseghetti et al 2006). Despite the extensive use of this kind of sensors to provide data of the physical variables of the oceans, a big gap remains in the estimation of biological ones (e.g., phytoplankton biomass, CDOM). For what concerns the Ferrybox concept it has been developed in partnership with scientists and with companies that operate ferries in Europe. From 2003 to 2005, the European-funded FerryBox project was initiated to further develop the use of the FerryBox systems for automated measurements and water sampling by ships of opportunity (Petersen 2014) and the core parameters were temperature, salinity, turbidity, and chlorophyll *a* fluorescence. Non-standard sensors have been additionally tested such as currents, pH, oxygen, nutrients, and algal species. This system has shown a promise in reducing this cost thanks to the use of SOOP or VOS platforms , but the instrumentation is still basically too expensive.

For this reason a significant effort has been undertaken to develop a system that enables both high performance measurements of physical and biological variables and high flexibility despite the low costs of the production compared with traditional instruments, in order to have the possilbility to realize extended observatory networks for the study of marine physical and biological processes.

3. TOPICS AND OBJECTIVES

My research work shows new low-cost sensors and probes developed to measure marine temperature, conductivity, turbidity, chlorophyll *a* and CDOM fluorescences, focusing both on sensing strategies, general architecture and laboratory trials and on the different application during several oceanographic surveys in the Mediterranean Sea.

The general objectives of this research are to meet the specific measurement requirements and lack that the ocean observing international programs identify like priorities.

Even now the demand of new technologies for the measurement of marine biological variables is one of the problems that scientific community has to face as response to the 2015-2019 general objective of the Global Ocean Observing System (GOOS) Biology & Ecosystem Panel. The only possibility to realize global observational networks is to realize new low-cost technologies, which is one the principal requirements of the last and future EU Horizon 2020 research and innovation framework programme. In addition the development of new technologies to implement low cost coastal observational nets including biological variables is a priority of the Marine Strategy Framework Directive.

In this general context the objective of my research was to realize a technology that could be adapted in different measuring platforms, in different observative systems as identified by GOOS and also in coastal monitoring systems to provide continuous data collection on both physical and biological characteristics of marine environment. Furthermore I tried to identify, test and verify the potential use of the developed technologies in different operating modes, from different measurement platforms and to apply them in specific research projects to contribute to mathematical models data assimilation and remote sensing data validation.

The original technology T-FLaP (Temperature Fluorescence Launchable Probe) was created as an expendable probe (Marcelli et al. 2007; Marcelli et al. 2008) for profiling vertical temperature and chlorophyll *a* fluorescence from moving ships. Subsequent experimental activities conducted in the last years have led to further improvements, including both an increased sensitivity of the chlorophyll *a* fluorescence sensor and strucure modularity and the realisation of two new low-cost sensors (conductivity and CDOM fluorescence). These improvements allowed to reach the new applications: the recoverable vertical profiler and the Spectra mini-ferrybox system (Marcelli et al. 2014, Marcelli et al. 2016, Fiori et al 2016).

In this work I present the low-cost technology and its applications through different research papers and works, which contains the development phases, the upgrades, the in situ surveys and the data.

4. THE INTERNATIONAL CONTEXT

A sustainable use of marine environment involves a work on long-term basis directed towards a safe and uncorrupted ocean able to maintain resources and a productive habitat.

In this direction the political priorities of the marine environmental policy are based on the main principles of the prevention, the precautionary and of the sustainable management.

The marine environmental policy is principally driven by international agreements, particularly at the level of the European Union, which guarantees a constant in the functioning of the Marine Environment service.

4.1 European environmental policy

The main pillar of the last ten years within the international policy context is represented by the Marine Strategy Framework Directive (MSFD, Directive 2008/56/EC), (Tunesi et al. 2013). The main objective of the MSFD is to achieve or maintain the Good Environmental Status (GES) in the marine environment by the year 2020. The GES is the core of the MSFD and is defined as: "The environmental status of marine waters where these provide ecologically diverse and dynamic oceans and seas which are clean, healthy and productive" Article 3. The GES is achieved using 11 descriptors and using a number of criteria and indicators associated to each descriptor.

In the last decades awareness has raised that "pressure on natural marine resources and the demand for marine ecological services are often too high and that the European Community needs to reduce its impact on marine waters regardless of where their effects occur". On the other hand, "The marine environment is a precious heritage that must be protected, preserved and, where practicable, restored with the ultimate aim of maintaining biodiversity and providing diverse and dynamic oceans and seas which are clean, healthy and productive" (EC, 2013). To meet these needs, the European Parliament and the Council of the European Union, on 17th June 2008, enacted the Marine Strategy Framework Directive 2008/56/EC (MSFD); Italy, as due by all Member States, transposed it in its national legislation through the Legislative Decree n. 190 of 13th October 2010. The Directive promotes the integration of environmental considerations into all relevant policy areas and constitutes the environmental pillar of the future Integrated Maritime Policy (IMP) for the European Union (Casazza et al., 2007; Tunesi et al., 2008). The Directive applies to all marine waters, seabed and subsoil of areas where Member States have and/or exercise jurisdictional rights, which entail an integral part of different marine regions and subregions.

In this context monitoring programme plays a fundamental rule in order to achieve the final goals of environmental policy, including monitoring procedures and methods for data collection. The assessment or the achievement of GES cannot exclude the analysis of ecosystems characteristics, pressures and impacts providing elements for assessing ecological status and the assessment of environmental targets achievement. To do this a medium- or long-term observation system must be implemented to track factors involved in observed changes and to provide long-time series on functioning of complex ecosystems.

Together with the MSFD the European Commission seeks to provide a more coherent approach to maritime issues, with increased coordination between different policy areas, focusing on different issues which do not fall directly under a single sector-based policy. In particular they developed and adopted the Blue Growth which is the long-term strategy to support sustainable growth in the marine and maritime sectors. In a context of growing demand for resources and maritime services including transport, sustainably capturing and demonstrating the potential of seas and oceans is critical to turning this potential into an asset with long-lasting economic, social and environmental benefits for Europe. Targeted innovation in our seas and oceans and an optimal use of research infrastructures available can play a key role in tackling global challenges such as the scarcity and vulnerability of strategic resources, while providing valuable ecosystem services factoring in climate change. However, a risky environment, insufficient knowledge, data, data access are critical barriers to overcome. It is important that European Commision intervenes to create the conditions for mobilising investment in testing and demonstration projects for new technologies, bringing them ‘from lab to market' and avoiding the costly duplication of work. Within Horizon 2020 a focus area is dedicated to the Blue Growth work programme which is pointed to bring technologies to the readiness level needed for commercial applications and to improve current European marine observing, surveyin and monitoring capabilities in order to increase the knowledge of marine environment processes and its interaction with human activities. One the main objective of the Blue Growth strategy is valorising the Mediterranean Sea Basin: the objective is to deepen knowledge on the Mediterranean marine ecosystems and their services and to strengthen the European ocean observing, surveying and monitoring capabilities and related technologies necessary for accelerating the production of high-resolution maps and assessments. The Mediterranean environment is rapidly changing to the natural and non-natural pressures so that it is difficult to establish a suitable situation provide the progress of a blue economy.

In this context many organizations and institutions coordinates observations around the global ocean to support the research and the objectives suggested by the international policy.

From the origin of the climate studies, oceanographic measures has been acquired by ships, the only available platforms to survey the oceans. Although there are now several other platforms (i.e. satellites, drifting buoys, floatings and radar) ships still play a very important role providing sea truth for the calibration of satellite observations and because of they allow measurements not yet obtainable by other means, such as air temperature and dew point (www.bom.gov.au/jcomm/vos/). The World Meteorological Organization (WMO) within Intergovernmental Oceanographic Commission (IOC) of UNESCO, the United Nations Environment Program (UNEP), and the International Council for Science (ICSU) sponsor the Global Ocean Observing System (GOOS) that is the oceanographic component of GEOSS, the Global Earth Observing System of Systems. WMO members directly participate in the GOOS, providing in situ and satellite observations. Since 1999, the marine activities of WMO, as well as those of IOC, have been coordinated by the Joint Technical Commission for Oceanography and Marine Meteorology (JCOMM - www.jcomm.info). The creation of this Joint Technical Commission results from a general recognition that worldwide improvements in coordination and efficiency may be achieved by combining the expertise and technological capabilities of WMO and IOC. The Observations Program Area of JCOMM is primarily responsible for the development, coordination and maintenance of moored buoy, drifting buoy, ship-based and space-based observational networks and related telecommunications facilities. In this framework it was created a Ship Observations Team (SOT) which coordinates two programs: the Voluntary Observing Ship Scheme (VOS) and the Ship of Opportunity Program (SOOP).

4.2 Ocean observatories initiatives

VOS (Voluntary Observing Ships) and SOOP (Ship Of Opportunity Program)

The World Meteorological Organization (WMO) Voluntary Observing Ships' (VOS) scheme is based on ships, which are recruited by National Meteorological Services (NMSs) and ply the various oceans and seas of the world for taking and transmitting meteorological observations. The SOOP is based on the possibility to use merchant ships that join to the programme, in routinely strategic shipping routes for taking oceanographical and hydrological data. The basic instruments used in these programs are the Expendable Bathythermographs (XBTs) and the Ferrybox. At predetermined sampling intervals, Expendable Bathythermographs (XBTs) are launched to acquire temperature profiles in the open ocean in order to be assimilated into operational ocean models. SOOP plays a relevant role as it serves as a platform for other observational programmes, communicating closely with the scientific community. In this way, SOOP assumes a big relevance to seasonal an interannual climate prediction. The programme is managed by the SOOP

Implementation Panel (SOOPIP). Along the strategic shipping routes, SOOPIP identifies and coordinates the measuring necessities in terms of type of instruments, their use modality and deployment. So, thanks to the use of different instruments, it is possible to obtain long measuring series of physical, chemical and biological parameters. Moreover SOOP looks at new instrumental technological development and coordinates the exchange of technical information; in particular: functionality, reliability and accuracy, and recommended practices about relevant oceanographic equipment and expendables.

The main important aspect of VOS and SOOP programs deals with the possibility of collect data in a cost effective way.

Within these programs (VOS and SOOP), many international initiatives are presently carried out in order to develop new observing devices and systems, suitable to be utilized from as many vessels as possible. New expendable probes and devices (low cost and user friendly) represent the ultimate effort of oceanographic technological development in order to collect even more accurate measurements and to enhance the range of variables to be measured in automatic way, particularly for the biological ones.

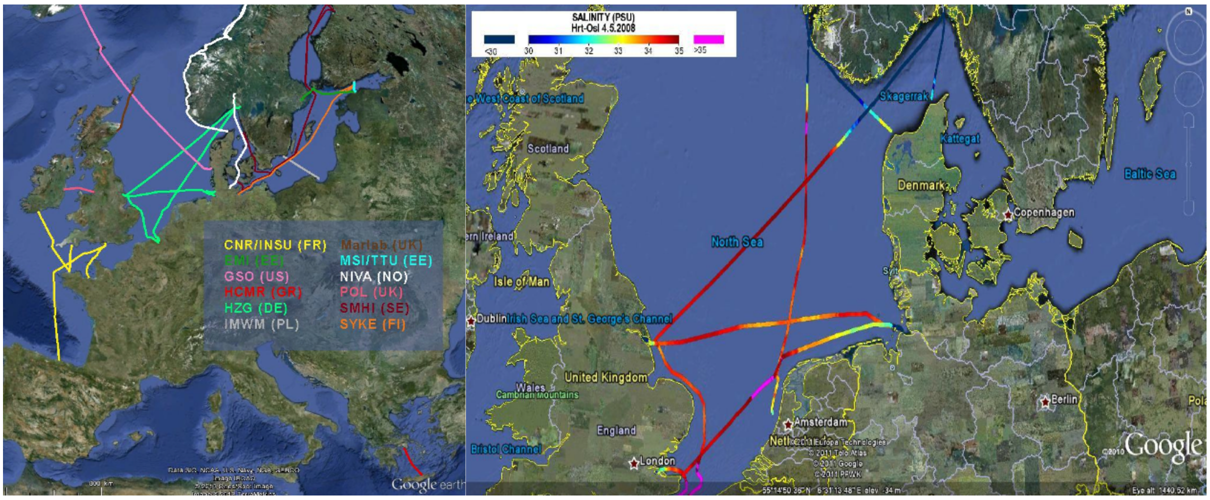

Fig. 1 On the left an example of Ferrybox routes; on the right a map for seasurface salinity obtained by Ferrybox data

The Global Ocean Observing System

(GOOS - http://www.goosocean.org)

One of the main problem is that the information needed by administrations, governments, industry, science and the public to deal with marine related issues, including the effects of the ocean upon climate, needs to be supported by a unified global network that systematically acquires, integrates and distributes oceanic observations, and generates analyses, forecasts and useful products.

For this reason, in response to calls from the Second World Climate Conference (Geneva, 1990) and the United Nations Conference on Environment and Development (Rio de Janeiro, 1992), the Intergovernmental Oceanographic Commission (IOC) created the Global Ocean Observing System (GOOS) in March 1991 (Dexter et al. 2010). GOOS (www.ioc-goos.org) was designed to provide observations of the global ocean, related analysis and modelling, supporting operational oceanography and climate change predictions. Through Regional Alliances and dedicated linked programmes, GOOS allows all data to become accessible to the public and researchers by standard and simple shared methods to produce products useful to a wide range of users. In this way GOOS should sustain the management of marine and coastal ecosystems and resources, supporting human activities like mitigate damage from natural hazards and pollution, protect life and property on coasts and at sea and suggest scientific research activities.

GOOS is:

- a sustained, coordinated international system for gathering data about the oceans and seas;
- a system for processing data to enable the generation of beneficial analytical and prognostic environmental information services;
- the research and development on which such services depend for their improvement.

The GOOS id divided in two main branches: the open ocean and the coastal one.

The open ocean component of the GOOS is designed to:

- monitor, describe and understand the physical and biogeochemical processes that determine ocean circulation and its effects on the carbon cycle and climate variability;
- provide the information needed for ocean and climate prediction, including marine forecasting;
- provide observational requirements;
- ensure that the designs and implementation schedules are consistent and mutually supportive and working as planned; and
- ensure that the system benefits from research and technical advances.

Coastal GOOS has six goals for the public good. These are to:

- improve the capacity to detect and predict the effects of global climate change on coastal ecosystems;
- improve the safety and efficiency of marine operations;
- control and mitigate the effects of natural hazards more effectively;
- reduce public health risks;
- protect and restore healthy ecosystems more effectively; and
- restore and sustain living marine resources more effectively.

The main difficulty of the present observing system is the lack of global coverage, the need for autonomous and remote instruments for the whole variables list, the need for expanded and more effective data and product systems, and the need for long-term continuity of national efforts along with international coordination. For this reason a continued research is needed to improve and develop observing capabilities for some variables and to make systems more robust and cost-effective.

Examples of phenomena of interest from the coastal ocean (Dexter et al. 2010)				
Sea state	Forces on structures	Coastal flooding	Currents	Sea level
Shoreline change	Seabed topography change	Chemical contamination of seafood	Human pathogens in water and shellfish	Habitat modification and loss
Eutrophication, oxygen depletion	Change in species diversity	Biological response to pollution	Harmful algal bloom events	Invasive species
Water clarity	Disease and mass mortality in marine organisms	Chemical contamination of the environment	Harvest of capture fisheries or of aquaculture	Abundance of exploitable living marine resources

Mediterranean Operational Network for the Global Ocean Observing System (MonGOOS - http://www.mongoos.eu)

The Mediterranean Operational Network for the Global Ocean Observing System has been established in 2012 to further develop operational oceanography in the Mediterranean Sea. MONGOOS shall engage in activities related to the production and use of operational oceanography services in furtherance of four principal objectives:

- Improved Fitness for Purpos: continuously advance the scientific understanding and technological development upon which the Services are based.
- Greater Awareness: promote the visibility and recognition of the Services with governmental agencies and private companies, encourage their integration at national, regional, European and global levels.
- Increased Downstreaming: enhance the usability of the Services and their usefulness for policy implementation, societal needs and science.
- Improved Capacity: support the planning and implementation of international initiatives involving

operational oceanography and promote the participation of non-EU Mediterranean countries in producing the Services.

One the main activity is to contribute to the international planning and implementation of the Global Ocean Observing System and to coordinate and harmonize the development of a sustainable Integrated Observing System at the basin and shelf/coastal scales.

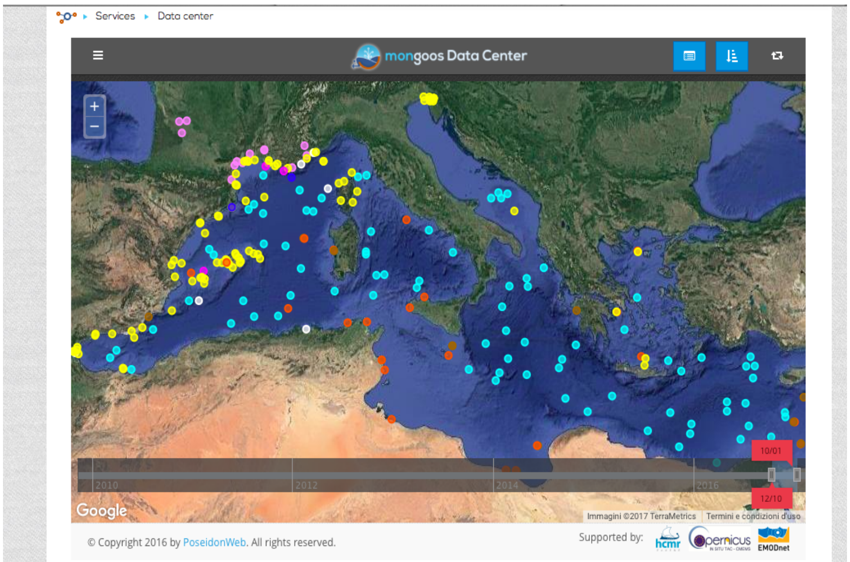

Fig. 2 MonGOOS data center

European Programme for the establishment of a European capacity for Earth Observation (Copernicus - http://www.copernicus.eu)

Copernicus consists of a complex set of systems which collect data from multiple sources: earth observation satellites and in situ sensors such as ground stations, airborne and sea-borne sensors. It processes these data and provides users with reliable and up-to-date information through a set of services related to environmental and security issues.

Copernicus, previously known as GMES (Global Monitoring for Environment and Security), is the European Programme for the establishment of a European capacity for Earth Observation. The services address six thematic areas: land, marine, atmosphere, climate change, emergency management and security. They support a wide range of applications, including environment protection, management of urban areas, regional and local planning, agriculture, forestry, fisheries, health, transport, climate change, sustainable development, civil protection and tourism.

In situ data means observation data from ground-, sea-, or air-borne sensors as well as reference and ancillary data licensed or provided for use in Copernicus. The Copernicus services and the space component need sustainable and reliable access to in situ data to produce, validate, and calibrate products, and to establish reliable information services required by end users. For this reason the Copernicus in situ component is implemented in different tiers, with particular attention to the marine environment monitoring services, which provides regular and systematic information on the physical state, variability and dynamics of the ocean and marine ecosystems for the global ocean and the European regional seas. The service also contributes to the protection and the sustainable management of living marine resources in particular for aquaculture, fishery research or regional fishery organisations. The continuous acquisition of physical and marine biogeochemical components is necessary for water quality monitoring and pollution control, for exampel the sea surface temperature is one of the primary physical impacts of climate change and has direct consequences on marine ecosystems. As a result of this, the service supports a wide range of coastal and marine environment applications.

European Marine Observation and Data Network
(EMODnet - http://www.emodnet.eu)

The European Marine Observation and Data Network (EMODnet) consists of more than 160 organisations assembling marine data, products and metadata to make these fragmented resources more available to public and private users relying on quality-assured, standardised and harmonised marine data which are interoperable and free of restrictions on use. EMODnet is currently in its second development phase with the target to be fully deployed by 2020.

The main purpose of EMODnet is to unlock fragmented and hidden marine data resources and to make these available to individuals and organisations, and to facilitate investment in sustainable coastal and offshore activities through improved access to quality-assured, standardised and harmonised marine data. In particular EMODnet Biology contributes to the knowledge about abundance and diversity of life, from large species to the microscopic marine algae that form the base of the marine food chain. So the data portal allows users to search for datasets by theme such as biomass and pigments.

Citizen Observatories (CO)

As Liu (2014) defined a CO is: “the citizens’ own observations and understanding of environmentally related issues and in particular as reporting and commenting on them within a dedicated ICT platform”.

Citizen observatories aim to involve people into a collective monitoring of the territory, thus contributing to a better appropriation of the territory by users and a better understanding of issues affecting it.

In particular the CO promotes communication and supports the sharing of technological solutions (e.g., sensor and sensor platforms, mobile apps, web portals) and community participatory governance methods (e.g., aided by various social media streams) among citizens. This definition shows three core components that underpin some of its objectives, i.e., raising the citizens' environmental awareness; enabling dialogue among citizens, scientists and policy- and decision-makers; and supporting data exchange among citizens, scientists and other stakeholders. It also promotes a more active role for the community concerning understanding the environment, since citizens are traditionally considered as consumers of information services at the very end of the information chain and not as data providers.

Numerous examples of citizen observatories have been reported in the last years, while I will report some of the most significant in the Mediterranean basin. One is the Jellyfish Spotting platform, which was created within the framework of the PERSEUS Jellyfish Spotting campaign. It aims at improving knowledge about jellyfish distribution patterns by integrating observations from all users. This platform is opened to everybody and anybody can contribute by reporting a sighting. The other one is the MedObs-Sub observatory, which aims to initiate a citizen dynamic by giving stakeholders a key role in monitoring and by raising awareness about environmental issues related to coastal uses. Any diver or fisherman (fishing from the shore, from a boat or spearfishing) can become a watchman and report sightings about: underwater landscapes, alien species, pollutions, biological diversity and uses.

5. DEVELOPMENT AND INNOVATION IN MARINE SCIENCE

One of the most relevant issue in marine sciences concerns the data availability, quality and accessibility. The employment of traditional methods limits data collection because of the high costs of surveys, fixed installations and instruments. Remote sensing only partially meets these difficulties such as it provides information only of the marine surface layer and lacks an adequate spatial and temporal resolution to study coastal seas, and in turn needs to be calibrated and validated by in situ data.

As already described, within the international projects knowledge necessities, it is fundamental the development of innovative technologies according to requirements of high performances, data quality and low-cost. Even if data provided by models, by high resolution remote sensing and by the new autonomous sampling platforms are increasing temporal and spatial sampling capabilities (Dickey & Bidigare, 2005), however, there is still a lack of operational, multidisciplinary, in situ observing systems. This fact is particularly related to the biological variables that need to be observed in situ more than the physical once. Especially in the mid-high latitudes, a complete upper layer observation of the water column is needed, because of the typical distribution of phytoplanktonic biomass (Mann &Lazier, 1991).

Traditional methods (water sampling, storage and laboratory analysis) are too expensive and do not allow to have enough measures to describe variability of marine natural phenomena with sufficient temporal and spatial detail. Therefore, bio-optical measures, used to study the main environmental characteristics, such as phytoplankton biomass, CDOM (Coloured Dissolved Organic matter), turbidity, can be integrated in new technological developments to give continuous measures. In such a context our aim was to answer to all the above issues, developing new user friendly technologies, based on low cost materials and suitable to different configurations (Moored, stand alone, expendable, continuous and towed). In order to face the necessity of the world oceanographic observations, and of the coastal marine observatories, we identified the main development necessities: low cost flexible modular instrument, to be used like profiler, expendable, stand alone and instrumental payload to be integrated in other platforms.

5.1 State of the art

This paragraph points out the state of the art relevant to my contribution and to the specific developments topics, as evidenced by the articles shown below.

Expendable probes

Expendable probes (such as XBT – eXpendable BathyThermograph), represent an approach to ocean measurements in which the high accuracy of measurements may be sacrificed considering lower costs and operational expediency (Thorpe, 2009). Relating to operational oceanography, this kind of technology derives from the needs of adequate spatial sampling on timescales commensurate with temporal variability. These probes can provide measures of temperature quickly as they can be used by a ship moving up to 20-30 knots. This technique also provides standard results and it became the central component of programmes such as the Global Ocean Observing System (GOOS). Current expendable probe capabilities include also the measurements of sound speed, conductivity, ocean current and (most recently) optical irradiance (Thorpe, 2009). Such expendable measurements could be fundamental for satellite data calibrations and for programmes such as Marine Forecasting System (MFS). Despite the development and extensive use of this kind of sensors to provide near real-time analysis of the principal physical variables, gaps remain in the estimation of certain biological variables (e.g., phytoplankton biomass, Chromophoric Dissolved Organic Matter), which instead play a key role, particularly at mid-low latitudes, in the ocean carbon cycle and ecosystem research relating to climate change.

Multiparameter Profilers

One of the most useful instruments developed for determining seawater properties during the last four decades has been the CTD (conductivity, temperature, depth) (Thorpe 2009). This device has supplanted the traditional hydrocast using Nansen and Niskin bottles and reversing thermometers that was standard physical oceanographic practice from about 1910 to 1970. The computations of properties such as depth, salinity, density, speed of sound, and potential temperature have been greatly facilitated by having the measurements of conductivity, temperature, and pressure in digital format for direct entry into standard formulas. However nowadays the term CTD is often used to describe a package that includes the actual CTD as well as auxiliary sensors to measure other parameters, such as dissolved oxygen, pH, turbidity, fluorescence of pigments.

Traditionally a profiling CTD measures water parameters as it travels through the water, whether lowered over the side of a ship with a winch to take measurements of a vertical column of water, but it can be also integrated with an autonomous vehicle or glider, or in a fixed station.

Today a wide variety of probes are available for sale, but normally these sensors are fabricated using costly components. Current commercially available CTD instruments range in cost from 2000s to 10000s dollars depending on the application, the accuracy and the manufacturer. Instruments that are packaged for deep deployments (1000 + m) are costlier than others due to the housings used, where as the average cost of a coastal water system is 5500 dollars (Broadbent et al. 2007). The costs become higher when the user wants to integrate other sensors to measure chemical and biological variables.

For this reason a multiparameter probe produced with low cost components and which provides accurate, precise and highly resolved measurements comparable to those obtained using commercially available instruments.

FerryBox

Until recently a serious hindrance to understanding and forecasting the state of marine systems has been the lack of monitoring systems that provide on-line data, and observations with sufficient spatial coverage and temporal resolution to give a true view state and change. To overcome this hindrance developments have been pursued in measurement technologies, data logging and ship-shore communications. It is now possible for scientists and governmental (environmental) agencies to work with merchant shipping companies to collect this much needed data autonomously in a cost effective manner (Hydes 2010). FerryBox (http://www.ferrrybox.org) is about a partnership between scientists and the companies operating the large numbers of ferries around the world - 800 in European seas. The name signifies (1) the use of a ferry (or other commercial ship), (2) boxes of autonomous equipment (3) the ability of data collected on regular route not only to provide much needed time series data but also boundary conditions for numerical models boxing in an area of sea or ocean. The coastal carbon system needs to be better monitored in respect to the overall carbon cycle issues and natural carbon sequestration processes. The FerryBox approach is probably the only way that can provide the needed monitoring coverage of carbon import and export in shelf seas and acidification in the coastal zone cost effectively.

5.2 Design and Application of New Low-Cost Instruments for Marine Environmental Research

Adapted from:

Marcelli M., Piermattei V., Madonia A., & Mainardi U. (2014). Design and application of new low-cost instruments for marine environmental research. Sensors, 14(12), 23348-23364.

Sensors **2014**, *14*, 23348-23364; doi:10.3390/s141223348

OPEN ACCESS

sensors

ISSN 1424-8220

www.mdpi.com/journal/sensors

Article

Design and Application of New Low-Cost Instruments for Marine Environmental Research

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External Editor: Stefano Mariani

Received: 7 October 2014; in revised form: 26 November 2014 / Accepted: 27 November 2014 / Published: 5 December 2014

Abstract: The development of low-cost instrumentation plays a key role in marine environmental studies and represents one of the most innovative aspects of current oceanographic research. These kinds of devices can be used for several applications, ranging from vertical profilers to stand-alone systems, and can be installed on different platforms (buoys, Voluntary Observing Ships, underwater vehicles, *etc.*). The availability of low-cost technologies enables the realization of extended observatory networks for the study of marine physical and biological processes through an integrated approach merging *in situ* observations, forecasting models and remotely sensed data. We present new low-cost sensors and probes developed to measure marine temperature, conductivity, chlorophyll *a* and Chromophoric Dissolved Organic Matter fluorescence, focusing on sensing strategies, general architecture, laboratory trials, *in situ* tests and comparison with standard instruments. Furthermore, we report the expendable (*New T-FLaP*), vertical profiler (*T-FLaPpro*) and stand-alone (*Spectra*) applications of these technological developments that were tested during several oceanographic surveys in the Mediterranean Sea.

Keywords: low cost sensors; instrumentation development; chlorophyll *a* and Chromophoric Dissolved Organic Matter fluorescence

Introduction

Marine ecosystem monitoring is nowadays a main concern in the worldwide scientific community (Albaladejo et al. 2012). A significant amount of effort has been invested modelling marine dynamics and processes, and there are exhaustive scientific programs and technological developments, e.g., Argo floats (Roemmich et al. 2009) and Expendable BathyThermograph (XBTs) probes (Hannon 2000), to measure physical and biological variables. Ocean sciences are strictly dependent on the development of new sensors and platforms, providing multi-disciplinary datasets, advanced sampling strategies and the expansion of temporal and spatial coverage of our measuring capacity of natural phenomena. Ocean measurement provides a long story of improvement in instrumentation capacity, from the accuracy, precision and resolution, until quality control and precision manufacture (Steele et al. 2009). Technological advances in oceanographic measurement capabilities have produced new ways to observe and monitor the ocean that improve operational and forecasting oceanography. Operational oceanography currently represents a part of the ocean sciences that provides high-quality observational data and models for research and practical applications (Pinardi et al. 2003, Pinardi et al. 2010), but critically depends on the near-real-time availability of a large amount of in situ data collected with sufficiently dense spatial and temporal sampling. This issue directly influences the robustness of ocean forecasting models and remote sensing observations through data assimilation and validation processes. Extended observatory networks represent an important new field in the study of global phenomena, through the development of cheap, small and integrated smart sensors (Johnstone et al. 2008).

Along these lines, the use of low-cost instrumentation from ships of opportunity, promoted by international research programs, is gaining more and more attention. This instrumentation makes it possible to reduce the costs of oceanographic surveys and, at the same time, to improve data spatial density and coverage and collect relevant data about studied phenomena (Trevathan et al. 2012).

Furthermore, the new emerging Ecosystem-based Management method proposed by the Marine Strategy Framework Directive (MSFD) (2008/56/EC) (European Commission 2008) requires an integrated approach composed of in situ observations, forecasting models and remotely sensed data for the monitoring and assessment of the environmental status of marine ecosystems. Although the existing technology allows to deploy sensors and probes on buoys, mooring and many other kind of platforms (Kröger et al 2009) the MSFD objectives cannot be achieved with current marine measurement technologies, which are too expensive for extensive utilization.

The Ship Of Opportunity Programme and the Voluntary Observing System represent the most important world initiatives that largely rely on (XBTs) (Manzella et al. 2003, Goni et al. 2009).

Since the 1960s, XBTs have been successfully adopted by oceanographers as an easy way to collect temperature profiles using commercial ships. Even now, XBT remains the most effective method for low-cost and simple acquisitions of temperature profiles, although the quality of these data must be checked (Reseghetti et al. 2006). Despite the development and extensive use of this kind of sensors to provide near real-time analysis of the ocean temperature, gaps remain in the estimation of certain biological variables (e.g., phytoplankton biomass, Chromophoric Dissolved Organic Matter). Observation and study of the distribution of biological variables plays a key role, particularly at mid-low latitudes, where a deep observation of the water column is needed because of the typical distribution of phytoplankton biomass (Mann and Lazier 1991). chlorophyll *a* (Chla) fluorometry is the principal method to study phytoplankton biomass in the ocean. However, the high costs of commercially instrumentation have made it unavailable for extensive use (Leeuw et al 2013). Dissolved organic matter (DOM) in the oceans is one of the largest reserves of reactive organic carbon on Earth (Hedges et al. 1992) controlling the concentration of CO2 in the atmosphere and affecting global climate change (Hedges et al. 2002). CDOM, also known as gelbstoff or yellow substance, is that component of DOM that absorbs light over a broad range of visible and UV wavelenghts, having a strong impact on the availability and spectral quality of light in photosynthesis (Kirk 1983). The emission fluorescence of CDOM covers a wide spectral range at blue-green wavelengths, allowing to estimate its concentration in natural waters. Furthermore, together with phytoplankton, CDOM is one of the most optically active components of the oceans (Roesler et al. 1989, Babin et al. 2003), representing a key parameter in primary production estimates with bio-optical models. A significant effort has been undertaken recently to develop a system that enables both high-performance measurements of physical and biological variables and high flexibility and low costs of the production compared with traditional instruments. Our aim was to realize a technology that could be adapted for use in different monitoring systems to provide continuous data collection (Glasgow et al. 2004).
In this paper, we present a new low-cost system for marine temperature, conductivity, Chla and CDOM measurement developed by the University of Tuscia Laboratory of Experimental Oceanology and Marine Ecology, the last upgrades and in situ tests.

Low-cost Technology

With the aim of adding biological profiling measurements to the physical measurements performed by commercial XBTs, in 2003 Temperature-Fluorescence Launchable Probe (T-FLaP) technology was developed and the first 30 prototypes were tested in the frame of the Mediterranean Forecasting

System: Toward Environmental Prediction (MFS-TEP) project (Pinardi et al. 2003, Manzella et al. 2003, Marcelli et al.2010). T-FLaP is an expendable fluorometer designed to obtain vertical temperature and fluorescence of Chla profiles along the water column by moving ships. The probes provided real-time temperature and Chla fluorescence profiles up to a depth of 500 m with an accuracy of 0.1 °C and 0.1 mg/m^3, respectively.

T-FLaP technology has recently been refined and improved. The new advances can be summarized in the following points:

- replacement of Chla fluorescence and temperature sensors with more sensitive devices (temperature accuracy: 0.01 °C; Chla accuracy: 0.01 mg/m^3);
- integration of a miniature 500 dBar pressure transducer, of a triaxial accelerometer and a gyroscope (optional) for the study of the dynamic behavior of the probes following the release;
- development of new sensors for the measurement of conductivity and CDOM fluorescence;
- improvement of miniaturized electronic devices;
- realization of a modular measuring cell;
- reduction of light-reflection phenomena inside the measuring cell by means of an anodic oxidation treatment with a matte black covering on the mechanical components.

Thanks to these innovations, it has been possible to improve the expendable probe and develop two additional new applications usable and adaptable to different scientific and operational needs: the recoverable vertical profiler T-FLaPpro, for use as a CTD (Conductivity Temperature Depth) probe from research vessels, and the stand-alone system Spectra, working as a mini-ferrybox for surface mapping of the bio-physical properties of seawater.

Main Goals

Ease of use, *low cost* and *modularity* are the basic principles of this technology, which is ideal for deployment from voluntary boats, even by non-specialized operators. A significant effort was dedicated to the selection of low-cost components, in order to realize a technology that could be implemented in extended monitoring systems. Despite the *low-cost* philosophy, all of the sensors were made with the aim of identifying, with good accuracy, the physical structures and biological phenomena of the oceans (thermocline, pycnocline, Deep Chlorophyll Maximum (DCM), etc.). The *modularity* of the measuring cell allows us to combine the sensors depending on specific needs: the system has been designed to be *flexible* and *customizable* enough to address heterogeneous operative demands and oceanographic platform installation. Furthermore, much effort has been expended to ensure the *miniaturization* of electronic components and a reduction in packaging, which allows us to increase the internal volume available for the inclusion of new features in the future.

General Architecture

The new expendable, vertical profiler and stand-alone instruments present different external cases with technical characteristics adapted to their operative use (submersible, waterproof, expendable etc.). Nevertheless, they share a standard internal measuring cell (Fig. 3a–c).

The measuring cell is a flow-through tubular cell where the water flows. As discussed above, the measuring cell has a modular structure. The modules are aluminium cubes 40 × 40 × 40 cm, placed in sequence and perforated to allow the water to flow. The design of the measuring cell has been studied in order to ensure that the sensors are in direct contact with the volume of water passing through the probe.

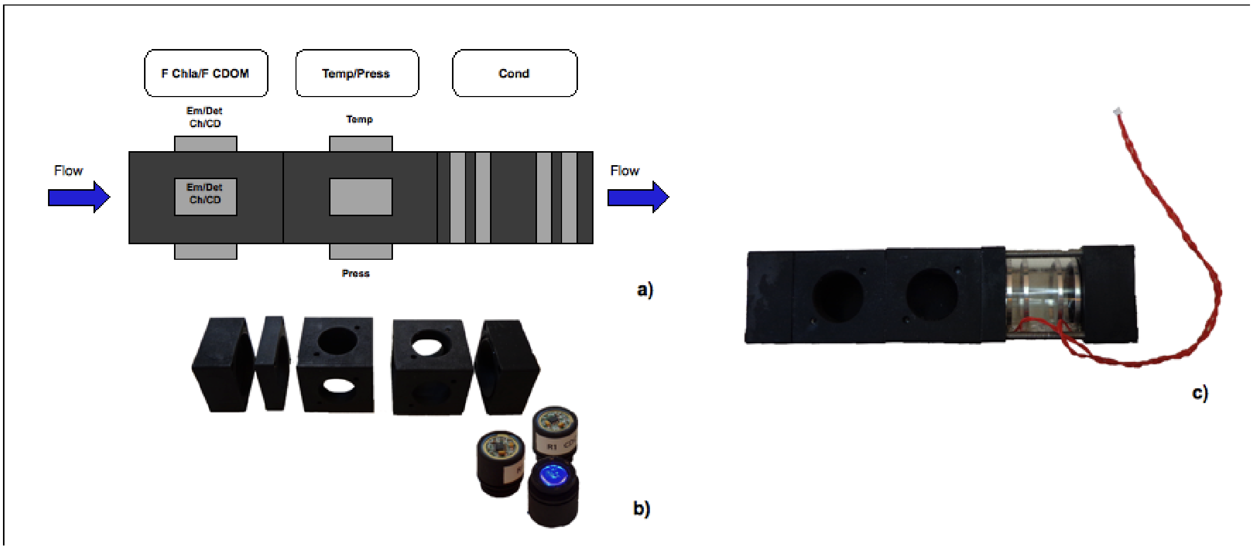

Fig. 3 a) Possible combinations of the sensors inside the measurement cell. b) Modules of the measurement cells. c) A prototype of the measurement cell.

Each of the modules can accommodate up to three cylindrical, interchangeable supports containing all of the possible elements for physical and biological sensing. Each probe can house the following configurations:

- temperature sensor;
- pressure sensor;
- excitation/detection devices of Chla fluorometer;
- excitation/detection devices of CDOM fluorometer.

The probes can be easily taken out of the cell to facilitate optics cleaning or replacement operations in the case of biofouling. All of the mechanical components are completely anodized and covered with a matte black deposit to reduce scattered light emitted within the cell. Batteries and electronic boards are placed on the external part of the measuring cell. A specific battery package makes the instrument totally autonomous, depending on the operative time required for each application. The electronic boards are placed around the measuring cell, allowing for the management of the power supply and the modulation of light sources, and the control of the the sensor signal, the signal conditioning, the digital conversion functions and the data transmission. The firmware of the instrument allows it to communicate in real time with a user through a remote terminal, in order to switch on and configure the instrument with the best measurement conditions. In particular, the program makes it possible to set and control a series of configurations and information, including the operative ranges of the parameters, LED excitation, battery and memory status. An example of the terminal screen before and during acquisition is illustrated in Figure 4.

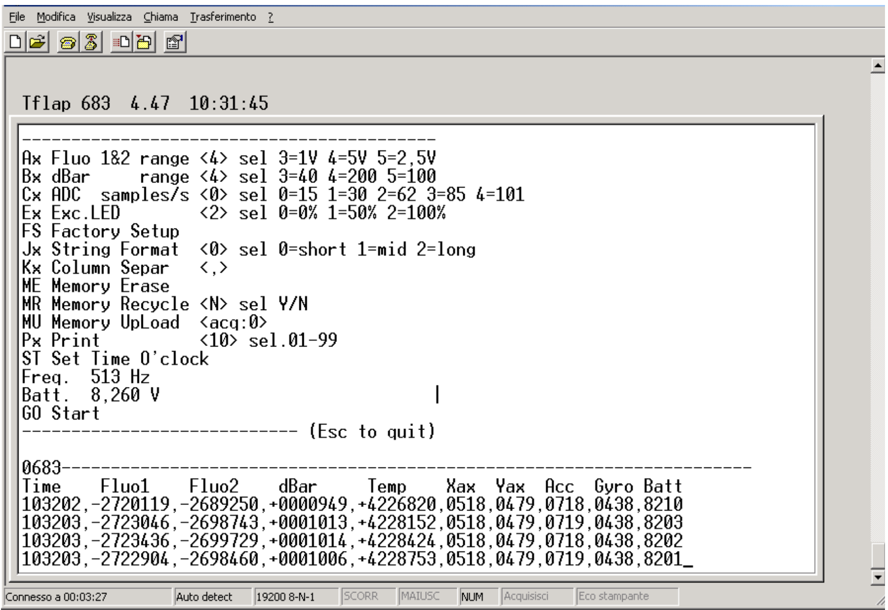

Fig. 4 Terminal screen showing the different instruments and sensor configurations and controls.

Sensors

Temperature and Pressure Sensors

The temperature microsensor consists of a sensitive bulb (1.5 mm in diameter), located on the top of a quartz stem 10 mm in length. The sensitive part is a thermistor inserted into the glass bulb. Given its minimum dimensions, this sensor has the sensitivity to detect temperature variations of 0.01 °C with a response time of 0.05 ms (Marcelli et al. 2007). Depth is measured through a submersible pressure transducer (KELLER AG für Druckmesstechnik).

Chlorophyll a Fluorometer

The Chla fluorometer is composed of an emitter and a detector positioned orthogonally to each other, in order to reduce the amount of excitation light scattered to the detector (Figure 5). The emission module is equipped with a blue high-power LED light source (430–470 nm), an optical short-pass filter and an aspheric lens. Blue light excites Chla pigments of phytoplankton cells passing through the measuring cell. The detection module, composed of a red optical band-pass filter, a plano-convex lens and a silicone photodiode, receives the fluorescent signal produced by the excited cells, and selects, focuses and amplifies the red peak between 682 and 685 nm, as shown in Figure 6. The insertion in the emission/detection modules of optical windows with high transmission to incident radiation constitutes a useful tool for the maintenance of the sensors, particularly for making sure that the optics of the instrument do not become *biofouled*.

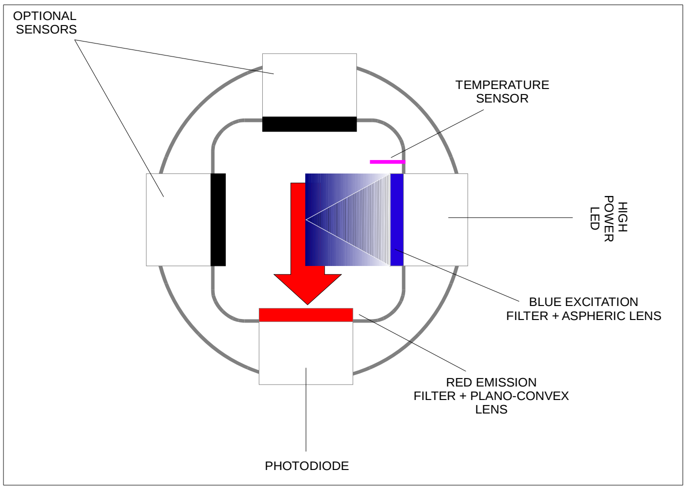

Fig. 5 The new fluorimetric cell

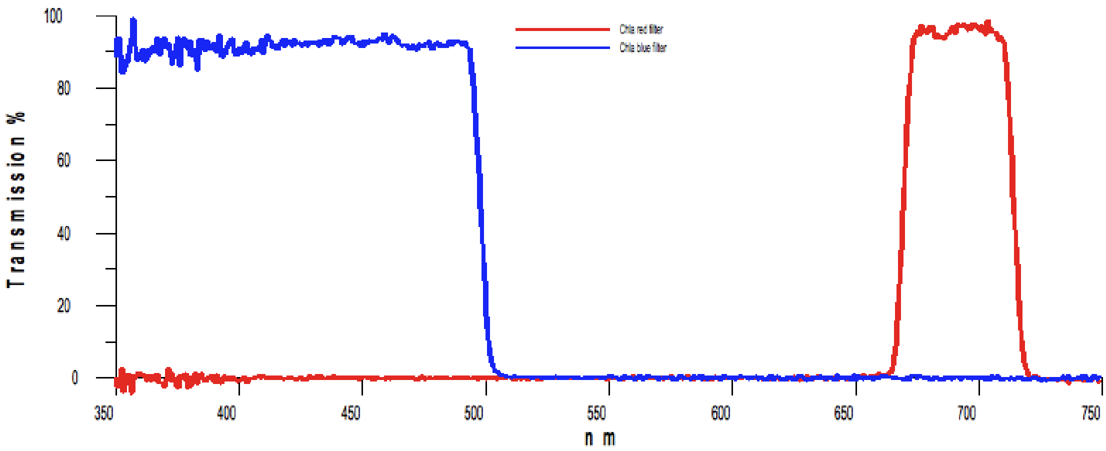

Fig. 6 Transmission spectra of the optical filters in the excitation (blue curve) and in the detection (red curve) modules

obtained by Ocean Optics QE65000 spectrometer.

CDOM Fluorometer

The CDOM fluorometer has the same structure as the Chla fluorometer, with orthogonal emission and detection modules, except for using LED and optical filter wavelengths. The excitation source produces ultraviolet radiation (370 nm) and the receiving device selects the CDOM fluorescent signal (400–500 nm), transmitting it to the photosensitive element, as shown in Figure 7.

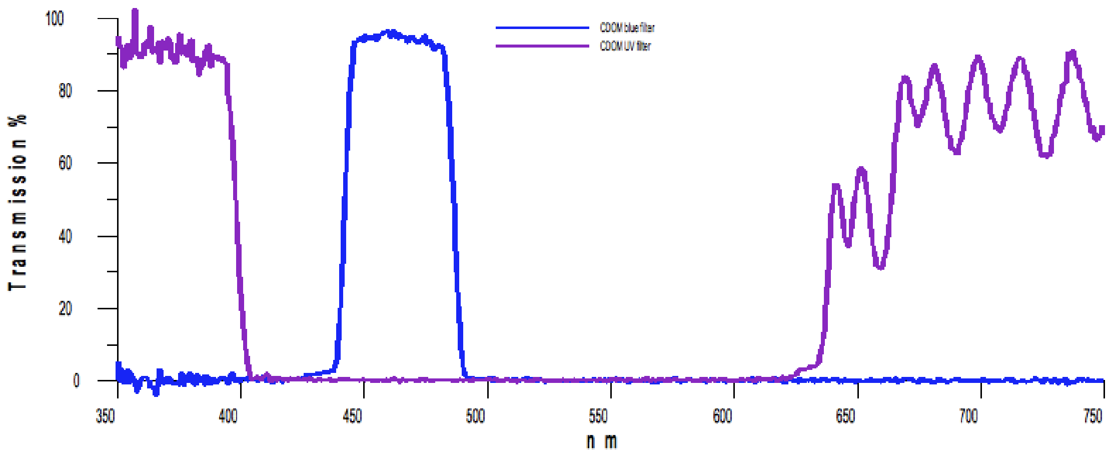

Fig. 7 Transmission spectra of CDOM optical filters in the excitation (violet curve) and detection (blue curve) modules obtained by Ocean Optics QE65000 spectrometer.

Conductivity Sensor

The conductivity sensor consists of a specific cylindrical module containing four platinum rings placed on the flow line. The outer rings generate an electric current and the inner rings measure the potential difference that is determined by the induced current. Using an electronic control circuit, the potential difference is kept constant in time. The current generated by the outer rings is controlled and measured by the electric circuit of the reaction in such a way that it increases and decreases proportionally, depending on variations in the conductivity.

Calibration System

The calibration procedure is a very important step in the development of new technologies. In order to convert the electrical outputs of each sensor to physical values, we designed and realized an automatic calibration system that allows us to calibrate the instruments in the laboratory, before their use. The calibration system is a closed hydraulic circuit composed of a calibration chamber that can house eight probes at a time, a circulation heat exchanger, a pump for the water flow and the control sensors (Figure 8).

The calibration chamber has a modular construction including a manifold, flow distributors and pipelines. All components were realized by subjecting two plexiglass bocks to laser manufacturing to produce the smoothest possible finish and to ensure flow uniformity and a minimum loss of pressure. The manifold was produced to simultaneously distribute both water and pressure inside the system.

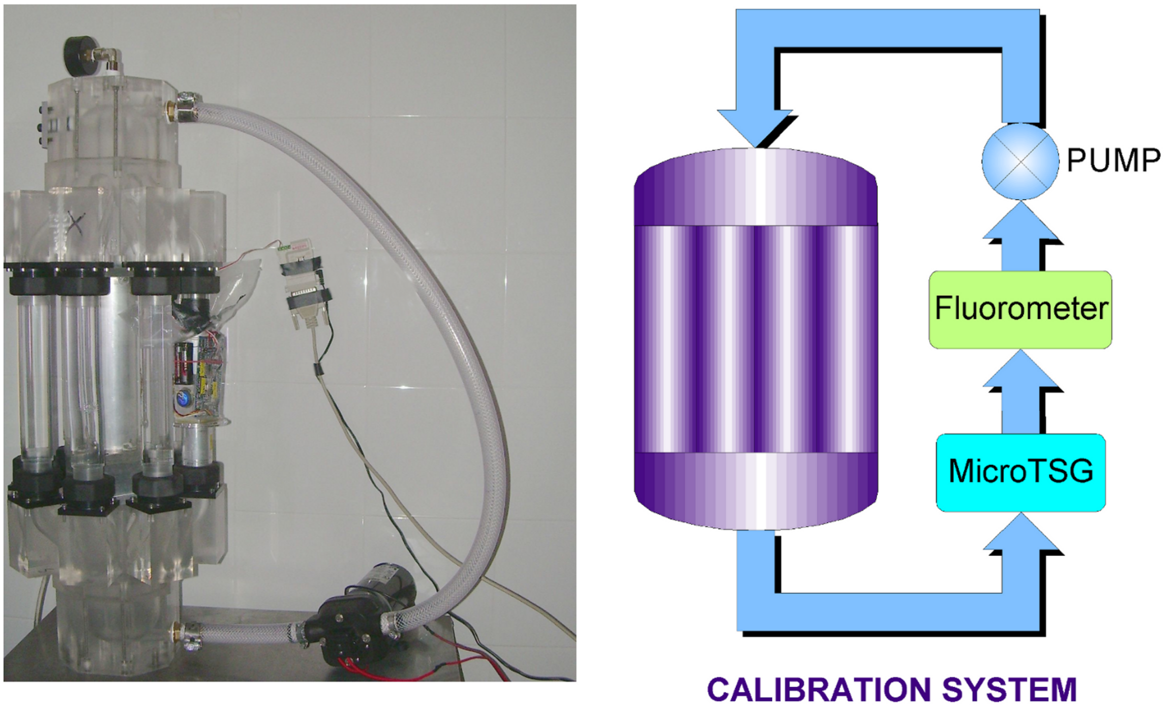

Fig. 8 The calibration system

Above the upper manifold, a Millipore two-way vacuum valve makes it possible to inject the specific standard solutions for the calibration of the Chla and CDOM fluorometers (phytoplankton cultures or Quinine Sulphate dissolved in H2SO4 0.05 M solutions) into the system (Coble 1996). The water flow is regulated by a high-capacity, low-velocity pump located adjacent to the control sensors. The outflow pump goes through the temperature conditioning system and upper manifold via the eight probes and is collected in the lower manifold before the water flows through the control sensors and ultimately returns to the pump. The flow is closed and hermetic.

The control sensors system forms a collateral circuit. Temperature and conductivity were measured by a MicroTSG (MicroThermosalinograph) SBE 45 Sea-Bird Electronics (temperature resolution: 0.0001 °C; conductivity resolution: 0.0001 mS/cm) and fluorescence was controlled by a flow analysis system (FIAlab Instruments by Ocean Optics, spectral range 310–750 nm; photomultiplier based for ultra-low fluorescence). In Figure 9, we show the calibration curves of temperature, conductivity and the Chla and CDOM fluorescence sensors. Concentration abundances of phytoplankton solutions used for the calibration of Chla fluorometers were also analyzed with the standard spectrophotometric method reported in (ISO10260 1992, Jeffrey and Humphrey 1975).

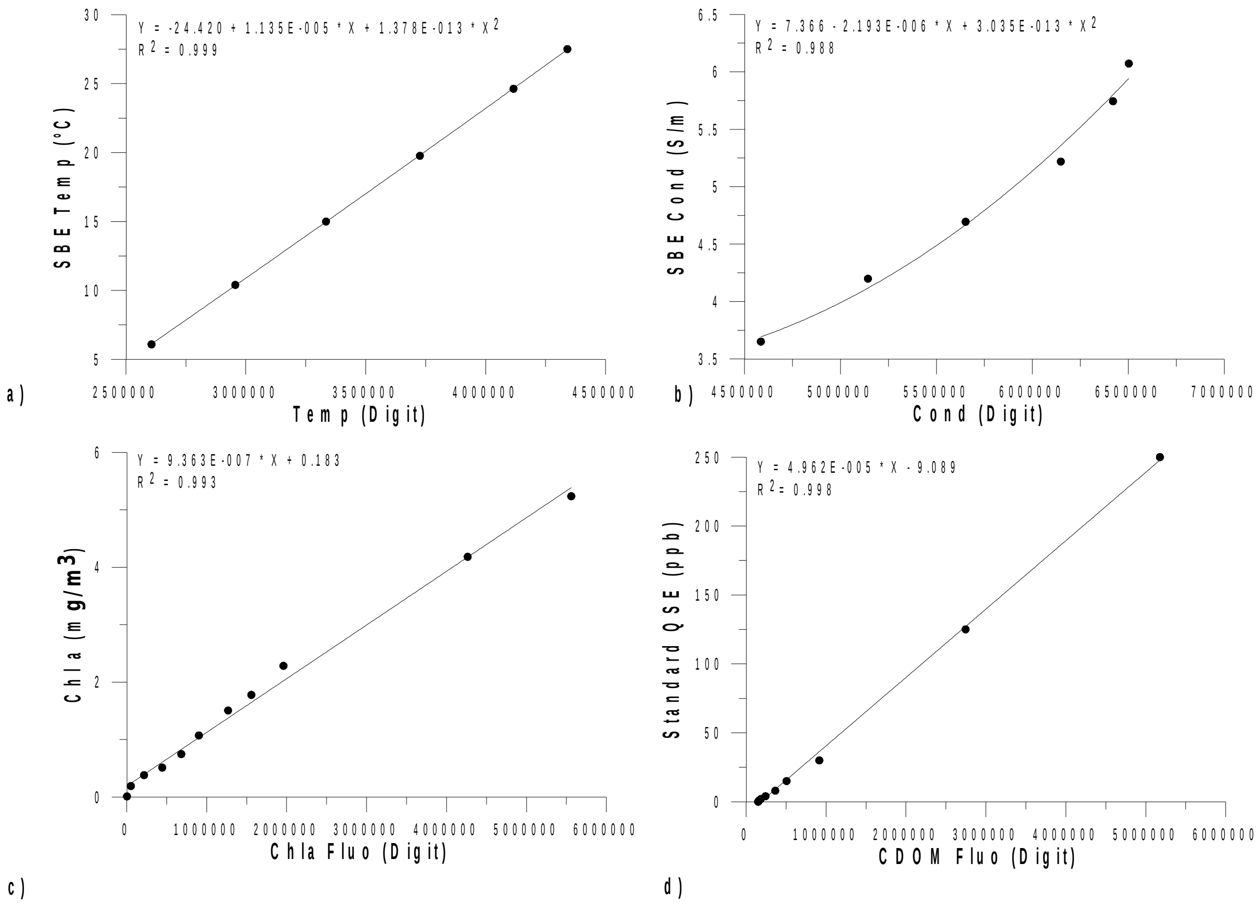

Fig. 9 Calibration curves of a) temperature, b) conductivity, c) Chla fluorescence and d) CDOM fluorescence sensors.

Prototype Applications

New T-FLaP: the Expendable Probe

As discussed previously, the basic application of this technology has been the expendable one. Improvements to the first T-FLaP started with the Adriatic Sea Integrated Coastal Areas and River Basin Management System Pilot Project in 2008 (Castellari et al. 2006). Unlike earlier prototypes, the new T-FLaP has a modular cell that can be used to change the configuration of the sensors.

The probe is equipped by a specific tail designed and realized to spin the probe during a fall; the rotation allows the coil to correctly unroll itself. As shown in Figure 10, digital data transmission is assured by twin copper wires wrapped on two reels: one in the probe tail and the other onboard the ship. This setup ensures a connection with the computer until the signal interrupted by a broken wire. Data transmission is provided by an RS-485 serial interface and the communication rate is 19,200 baud, no parity check, one bit stop and no flow control. Data can be acquired on a pc through a serial converter RS-485/232 and a terminal as Windows® HyperTerminal, following the information transmitted by the connected device.

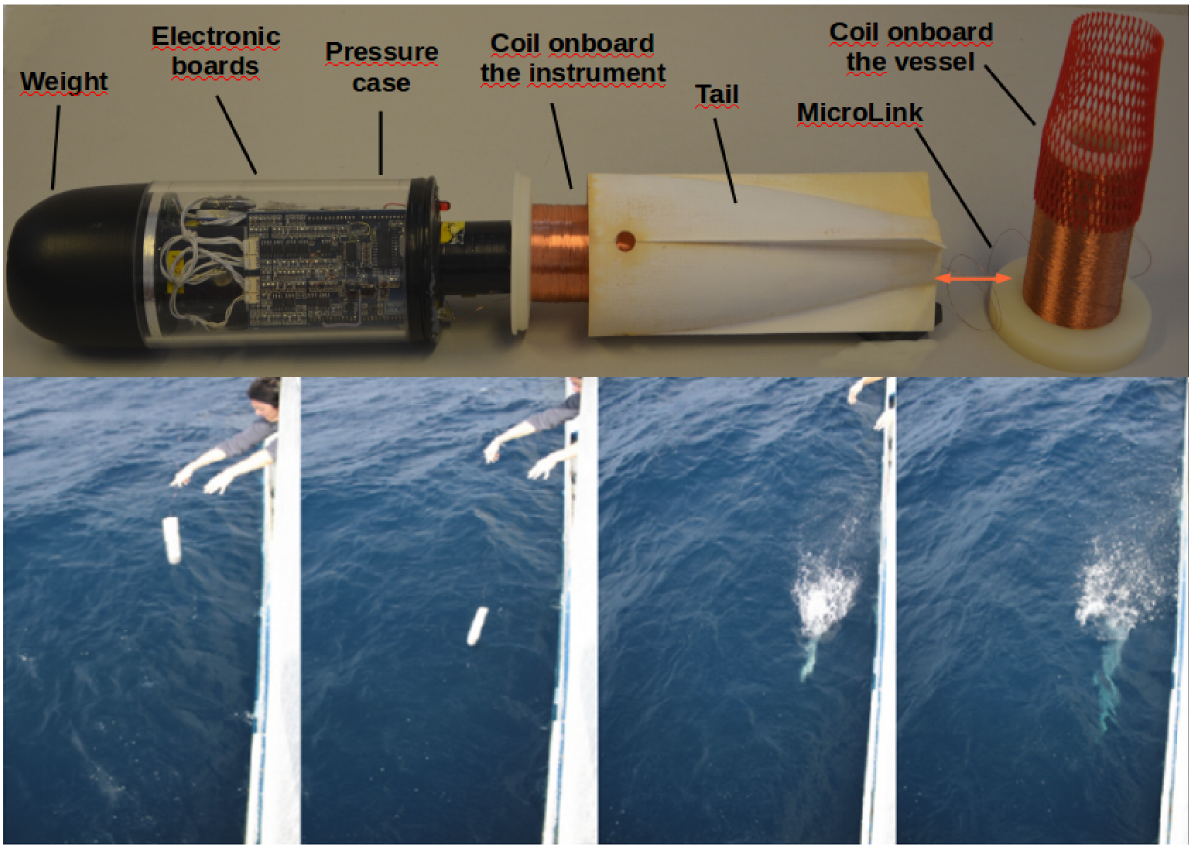

Fig. 10 A new T-FLaP prototype with a transparent case for electronic visualization and the launch during ADR0208 survey

<u>Field Tests</u>

The ADR0208 Oceanographic Cruise coordinated by the Institute of Atmospheric Sciences and Climate of the Italian National Research Council (SAC-CNR) departed on 17 October 2008 from the Port of Bari and ended on 28 October of the same month. The research area consisted of the Southern Adriatic Sea, the Montenegro and Albanian coastal zone and the Boka Kotorska Bay.

The Adriatic Sea is a high productivity area and estimates based on the Coastal Zone Color Scanner (CZCS) confirm that the Adriatic Sea has the highest pigment biomass and primary production of all Mediterranean sub-basins (Bohm et al. 2003, Antoine et al. 1995). This dynamic area was chosen to test the sensors' responses at different trophic conditions. Five new T-FLaPs were launched along the Dubrovnik-Bari transect at the end of the survey. In each T-FLaP station, standard CTD casts and water sampling were performed using a standard SBE 911 CTD probe with a Chelsea Aquatraka III fluorometer and a rosette sampling system. Since we did not use T-FLaP from a moving ship, we were able to compare the T-FLaP fluorescence measurements with in situ Chla, as shown in Figure 11 a.

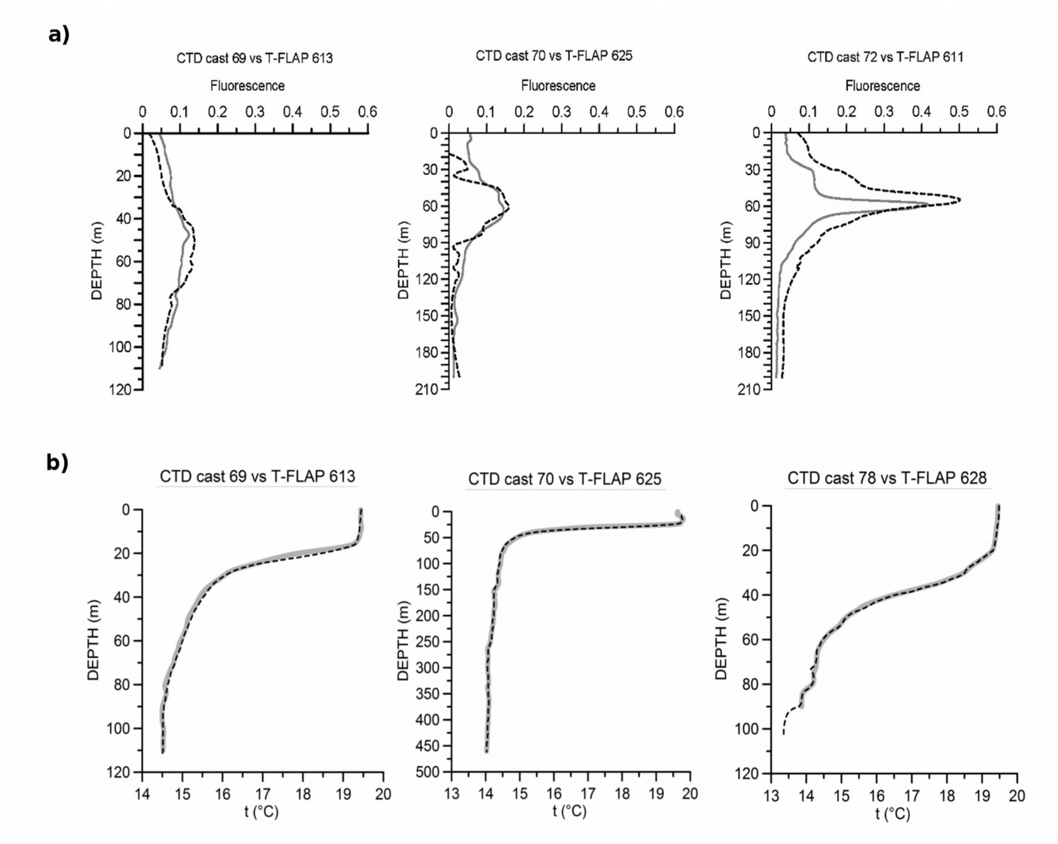

Fig. 11 Comparison between T-FLaP (dashed dark line) and Chelsea Aquatraka III (solid grey line) fluorescence profiles and b) Comparison between T-FLaP (dashed dark line) and SBE911 (solid grey line) temperature profiles.

In the first 5–10 m of the water column, depending on the lighting conditions, the T-FLaP fluorometer response can be unreliable due to the saturation of the photodiode; the response becomes consistent at deeper depths. The vertical temperature profiles show how T-FLaP can resolve the structures detected by the CTD with good resolution (Fig.11 b). Although the T-FLaP temperature sensor has an accuracy of 0.01°C with a dynamic response time of 1.5 ms/°C, the sensor performances are obviously lower than that of SBE (Hedges 2002). The main differences between the two probe profiles are more evident in the zone of rapid temperature changes. In fact, even if the accuracy and the response time of the sensor are sufficient for expendable use, the relation between the falling velocity and data transmission rate is the most important operational aspect, with the T-FLaP now capable of producing data information at every meter of depth.

T-FLaPpro: the Vertical Profiler

Based on previous applications, a non-expendable vertical profiler (*T-FLaPpro*) was realized, in order to create a small and low-cost multiparametric probe that can be easily used onboard coastal and smaller vessels. The largest differences are found between the transmission system and the launching methods. In particular, the probe was provided with an underwater connector and a cable developed *ad hoc* for this application, which allows for real-time data transmission and visualization.

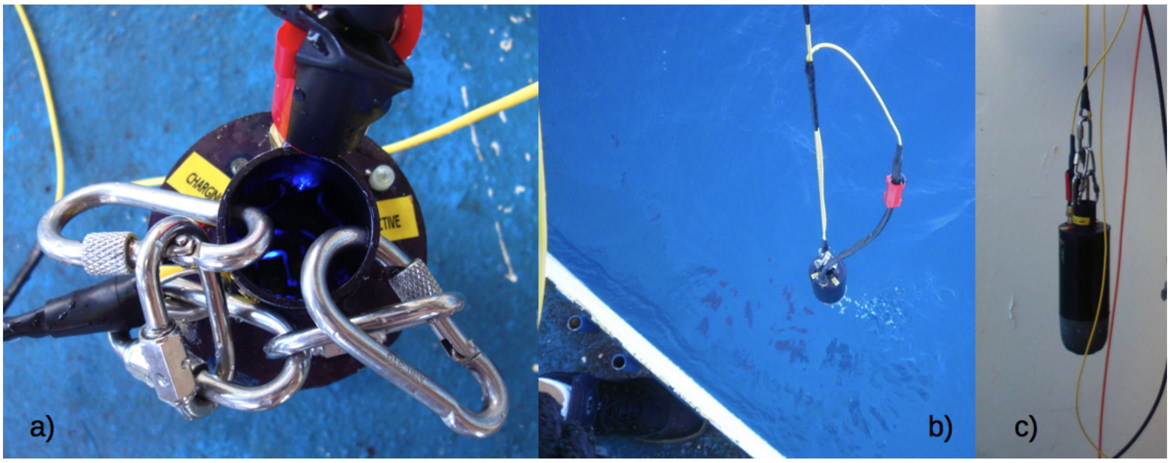

Fig. 12 The T-FLaPpro: a) blue LEDs inside the measure cell, b) the probe during the launching, c) a wide-angle view of the probe.

<u>Field Tests</u>

A series of tests were carried out during the phytoplankton bloom period in order to observe the DCM structure. For this purpose, a survey was conducted off the shore of Civitavecchia (Tyrrhenian Sea, Latium, Italy) coastal area on April 16, 2013.

A vertical profile along the water column was performed by T-FLaPpro and, at the same time, by the IDRONAUT OCEAN SEVEN 316 Plus probe, which was equipped with a temperature sensor and the Seapoint fluorometer. Therefore, it was possible to compare the profiles, as shown in Figure 13 a, and to analyze the capability and sensitivity of T-FLaPpro to detect the DCM structure.

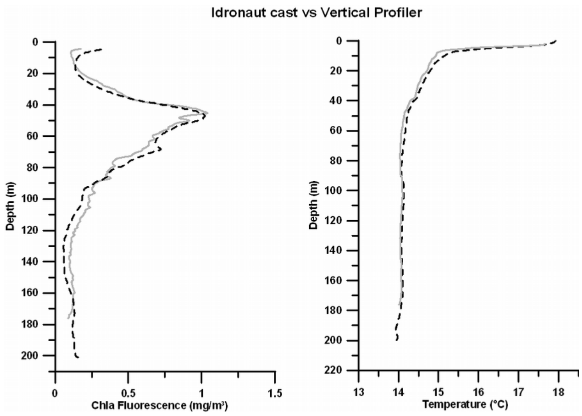

Fig. 13 a) Comparison between T-FLaPpro (dashed dark line) and Seapoint (solid grey line) fluorescence profiles and b) Comparison between T-FLaPpro (dashed dark line) and IDRONAUT OCEAN SEVEN 316Plus (solid grey line) temperature profiles.

An analysis of the distribution of variables along the water column shows an almost-complete overlap between the profiles acquired with the *TFLaPpro* and the probe IDRONAUT OCEAN SEVEN 316Plus. In particular the Chla fluorescence profile shows an intense DCM, reaching concentrations of 1 mg/m^3.

Spectra: the Stand-alone System

The last prototype, derived from the original technology, is an in-line measuring system, which provides continuous real-time information about the physical and biological states of the surface waters through which the vessel passes. It was developed to be used onboard both coastal, smaller vessels and ships of opportunity such as ferries and commercial ships. The philosophy that inspired this instrument is therefore that of Ferrybox, but with miniaturization of components and a considerable reduction in costs.

This system, called *Spectra*, is composed of three main modules:

- the electronic unit dedicated to the data acquisition, transmission and storage (Fig. 14);
- the control unit (Fig. 15);
- the hydraulic and measuring unit (Fig. 16).

The first unit includes the computer, with a waterproof touch-screen display to manage the acquisition and visualization of data via customized software, and the GPS, essential for measuring position.

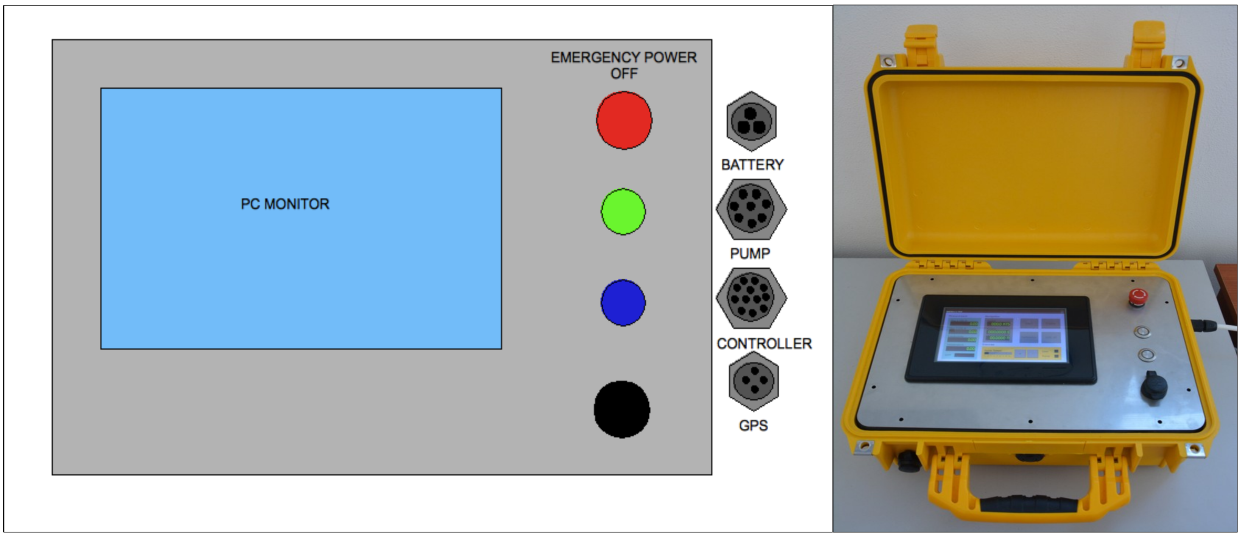

Fig. 14 The electronic unit: the scheme (left) and the realized prototype (right)

The control unit, placed under the electronic unit, manages the turning on and off of the devices and the signals of all the payloads; the control unit also controls the pump velocity. The hydraulic and measuring unit houses the flow through the system composed of the diaphragm pump and the two modular measurement cells, equipped with temperature, conductivity, Chla and CDOM fluorescence sensors.

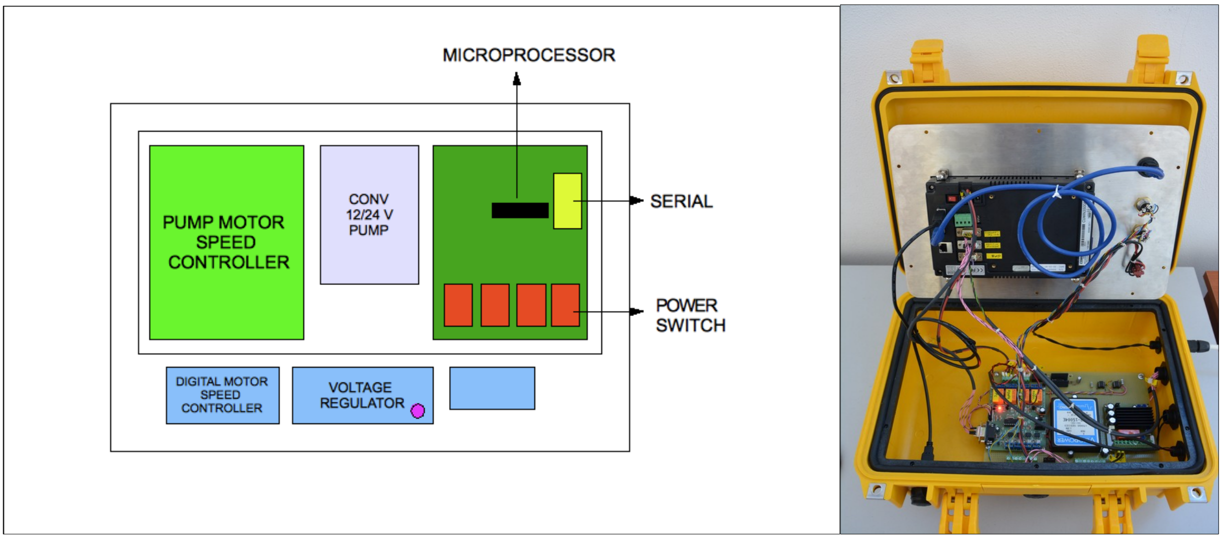

Fig. 15 The control unit: the scheme (left) and the realized prototype (right).

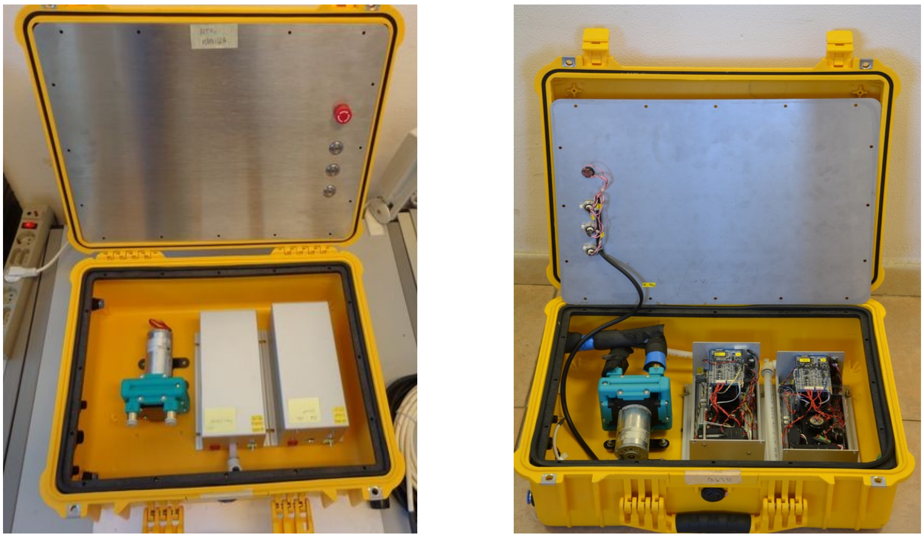

Fig. 16 The hydraulic and measure unit: on the left the scheme the measure units area closed, on the right the same are open

<u>Field Tests</u>

The field tests of the stand-alone application were performed along the Civitavecchia (Central Tyrrhenian Sea, Italy) coast on February 4, 2014. Spectra was fixed on the poop deck of a small coastal vessel and equipped with an input/output pipe system able to transfer water from the sea surface to the internal measuring cells (Fig. 17). The stand-alone application was extremely versatile and the integrated pumping system allowed for installation on different types of vessels.

This area was chosen because of the presence of urban discharges and effluents that can be characterized by a high variability in both physical and biological parameters. Temperature and conductivity isosurface maps, shown in Figure 18, exhibit lower values in the southern area, characterized by the presence of the Scarpatosta River. Chla and CDOM fluorescence results are inversely correlated, with lower Chla abundances and higher CDOM levels in the southern study area, indicating the relevant intake of urban water masses, strongly connected to the heavy precipitations that occurred in the previous days.

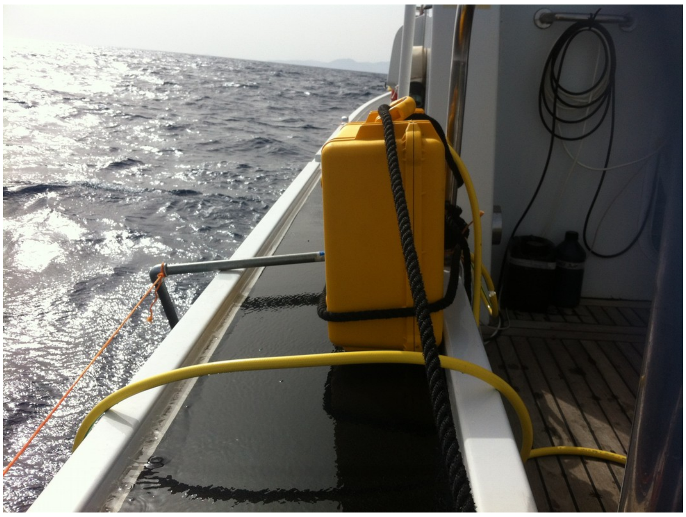

Fig. 17 Spectra system installed on board a coastal vessel

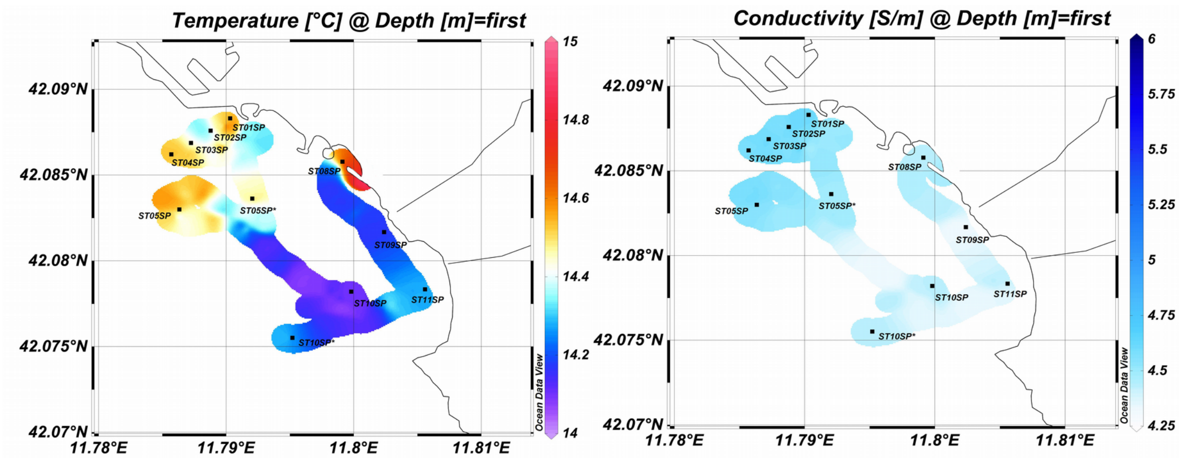

Fig. 18 In situ Spectra acquisitions: a) temperature, b) conductivity, c) Chla and d) CDOM fluorescence isosurface maps.

Conclusion and Future Directions

We have presented an advanced technology for marine bio-physical measurements. The sensors and the probes that we have developed allow integrated and distributed low-cost marine environmental monitoring. The cost of the prototypes (not engineered) ranges from 1200 Euros for the expendable application (a corresponding probe is not available on the market), 2500 Euros for the T-FLaPpro up to 5000 Euros for the Spectra, far below the cost of the equipment that is currently on the market. The typical investment costs of this kind of instrumentations is much higher: a standard oceanographic fluorometer cost approximately between 1900 and 9000 Euros, while a FerryBox starts at 25,000 Euros.

Despite the lower prototype costs, the measurement accuracy of the different variables is very high and comparable with standard commercial instruments. A comparison between the data acquired by the new technological developments and traditional probes yields strong consistency, satisfying the resolution requirements for the description of the physical and biological structures with good accuracy. The expendable and the vertical profiler were shown to be capable of identifying the distribution of phytoplankton populations along the water column both in eutrophic and oligotrophic marine waters. The in situ application of the Spectra prototype confirmed the validity of the measurement system developed for temperature, conductivity, Chla and CDOM fluorescence acquisition on the surface layer of the sea, which can be a useful tool for calibrating and validating remotely sensed data and mathematical models.

These technological solutions were specially designed to be used onboard ships of opportunity and for the implementation of oceanographic monitoring networks, in order to improve the quality of operational oceanography products. The availability of extended datasets is fundamental to our understanding and forecasting of physical and biological marine processes.

In conclusion, we have confirmed progress in technological development and provided important research directions for future work. In particular we are working on different aspects: the development of new sensors (e.g., backscatter) and the integration of this technology on other platforms (e.g., AUVs, buoys and fixed stations). Both these activities are now under testing and we are planning different experimental surveys. The improvement of this technology and its integration in different oceanographic platforms will be an important progress toward a cost-effective extended monitoring network.

5.3 T-FLaP advances: instrumental and operative implementation

Adapted from:

Marcelli M., Piermattei V., Madonia A., Lacava T., & Mainardi U. (2016). T-FLaP advances: instrumental and operative implementation. Journal of Operational Oceanography, 9(sup1), s185-s192.

Journal of Operational Oceanography

ISSN: 1755-876X (Print) 1755-8778 (Online) Journal homepage: http://www.tandfonline.com/loi/tjoo20

T-FLaP advances: instrumental and operative implementation

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To cite this article: M. Marcelli, V. Piermattei, A. Madonia, T. Lacava & U. Mainardi (2016) T-FLaP advances: instrumental and operative implementation, Journal of Operational Oceanography, 9:sup1, s185-s192, DOI: 10.1080/1755876X.2015.1117765

To link to this article: http://dx.doi.org/10.1080/1755876X.2015.1117765

Published online: 10 Jun 2016.

Abstract

The development of new technologies is a fundamental aspect of oceanographic research, a trend driven by the increasingly large data sets required for integrated approaches utilizing *in situ* observations, forecasting models, and remotely sensed data. These requirements cannot be achieved with the current marine measurement technologies, which are too expensive for extensive utilization. The T-FLaP technology provides low cost and user-friendly *in situ* measurements of physical and bio-optical variables of water bodies, representing a useful tool in multi-platform observing system networks. This paper reports the results of the latest research activities on T-FLaP evolution and its various applications.

Introduction

The description of the oceans and the ability to make predictions cannot be separated from the creation of observational networks whose performances and feasibility are closely related to the development of reliable, user-friendly, and low cost technologies.

An operational observing and forecasting system of ocean properties requires effective data collection programs for model data assimilation and satellite calibration. Like physical models, ecological models must be developed and validated. Describing the distribution and abundance of the phytoplankton community and contributing to the study of the ocean carbon assimilation are examples of such oceanographic ecological models (Irwin & Finkel 2008). Ocean carbon cycle and ecosystem research relating to climate change are strictly connected to the estimation of phytoplankton biomass and to those factors which influences the rates of primary production and the export of organic carbon to the deep ocean. In particular, the chromophore-containing components of dissolved organic matter (CDOM) can reduce the photosynthetically active radiation available to phytoplankton, as well as degrade the accuracy of chlorophyll measurements by satellite color sensors (Carder et al. 1989, 1991), due to their strong absorption on UV and blue region of the light spectrum. In addition to temperature, nutrient availability, and ocean circulation, prediction of phytoplankton response to changes in climate is fundamental in the estimation of how global change will modify the capacity of oceans to act as a carbon sink(Irwin & Finkel 2008), (i.e., the oceans ability to act as a biological pump and absorb atmospheric CO_2). Despite its importance, the biological pump has been poorly quantified. This is principally because of a lack of measurements of biological variables (Beatriz et al. 2001). With regard to this variable distribution, the main investigation tools are the ocean color satellite observations, which lacks information about the deep chlorophyll maximum (DCM), and the traditional oceanographic methods, which are expensive and spatially and temporally limited.

Technological advances of sensors and platforms to observe the oceans by *in situ* and remotely sensed measurements have become increasingly useful for operational oceanography, providing near real-time datasets with higher spatial and temporal resolution.

In this direction, the Marine Strategy Directive 2008/ 56/CE (European Commission 2008), which constitutes the environmental pillar of the European maritime policy, puts ever greater emphasis on the need to collect large amounts of *in situ* data during observational monitoring programs for the management of marine ecosystems. In this context, ocean monitoring requires a great technological effort to solve the difficulties posed by the extreme marine environment. Principal challenges include deploying sensitive measurement systems and overcoming the high cost of current oceanographic technologies, which do not allow extensive utilization.

To meet these challenges, in the last decades the use of low cost instrumentations from the ship of opportunity (promoted within VOS and SOOP international research programs) have gained greater attention (Manzella et al. 2003). The scientific community has made much effort towards modelling marine dynamics, and there are now exhaustive scientific programs and novel technological developments (e.g., Argo system and gliders) for monitoring physical variables, however, there remains a dearth of biological monitoring programs and technologies.

Temperature-Fuorescence Launchable Probe (T-FLaP) technology provides low cost and user-friendly *in situ* measurements of physical and bio-optical variables of water bodies. T-FLaP is an expendable instrument (Marcelli et al. 2007), providing rapid vertical profiles of temperature and chlorophyll *a* fluorescence along the water column. T-FLaP was realized with the aim of adding chlorophyll *a* fluorescence profiling measurements to the temperature profiles gathered by commercial XBTs, which have long been successfully adopted by oceanographers as an easy way of collecting data by using commercial ships (Goni et al. 2009). In recent years experimental activities have rapidly evolution, both in terms of technological advances (Marcelli et al. 2008; Marcelli et al. 2014) and field operation.

Here a detailed description of the advances made by the newly developed sensors (conductivity and CDOM fluorescence) and the results their application (e.g., as expendable, recoverable vertical profilers and in the mini-ferrybox system) in various oceanographic surveys are provided.

T-FLaP advances

T-FLaP was created as an expendable probe (Marcelli et al. 2007; Marcelli et al. 2008) for vertical temperature and chlorophyll *a* fluorescence profiling from moving ships. Subsequent experimental activities conducted in the last years have led to further improvements, including increased sensitivity and modularity as well as the realization of two new low cost sensors for the integration of marine conductivity and CDOM fluorescence measures.

These improvements have now made it possible to integrate the expendable probe with two new applications: the recoverable vertical profiler and the mini-ferrybox system, *Spectra* (Marcelli et al. 2014).

Low cost CDOM fluorescence sensor

CDOM sensors typically use UV light to excite the emission of blue light from the chromophores of the organic molecules dissolved in natural waters, allowing investigators to quantify CDOM fluorescence as a proxy for organic carbon concentration (Watras et al. 2014).

The newly developed low-cost CDOM fluorometer presents the same feature of the T-FLaP chlorophyll *a* fluorimetric cell. It is equipped with two orthogonal optical modules containing the emitter and the detector devices, respectively. The excitation source consists of a commercial UV high-power LED (370 nm), an optical UV short-pass filter, and an aspheric lens to collimate and amplify the LED radiation to the center of the cell, where the water flows. The detection module captures the fluorescent light produced by the excited molecules and transmits it to a silicone photodiode via a blue band-pass filter in the range 400-500 nm and a plano-convex lens, which allow focusing of the radiation to the surface of the photosensitive element.

To identify the best optical configurations of the electro-optical components (e.g., LEDs, diodes, and filters) for the detection of the CDOM florescence with the T-FLaP fluorimetric cell, an optical circuit has been realized consisting of three experimental measuring cells placed in a closed continuous flow hydraulic system (Fig 19 a). Many laboratory experiments were conducted using sequential dilutions of natural waters of various origins and of quinine sulfate (Sigma-Aldrich) dissolved in H_2SO_4 0.05 M solutions (Coble et al. 1993).

To evaluate the performance of the developed sensor, an experimental prototype was tested during an in situ survey conducted along the Latium coast (Fig 19 b). The sensor measures were compared with the results of the spectrophotometric analysis of CDOM absorption at 375 nm carried out on seawater surface samples collected throught a Niskin bottle.[14] The samples for the laboratory analysis were stored in borosilicate glass bottles, kept in the dark and analyzed within 4 hours of collection.

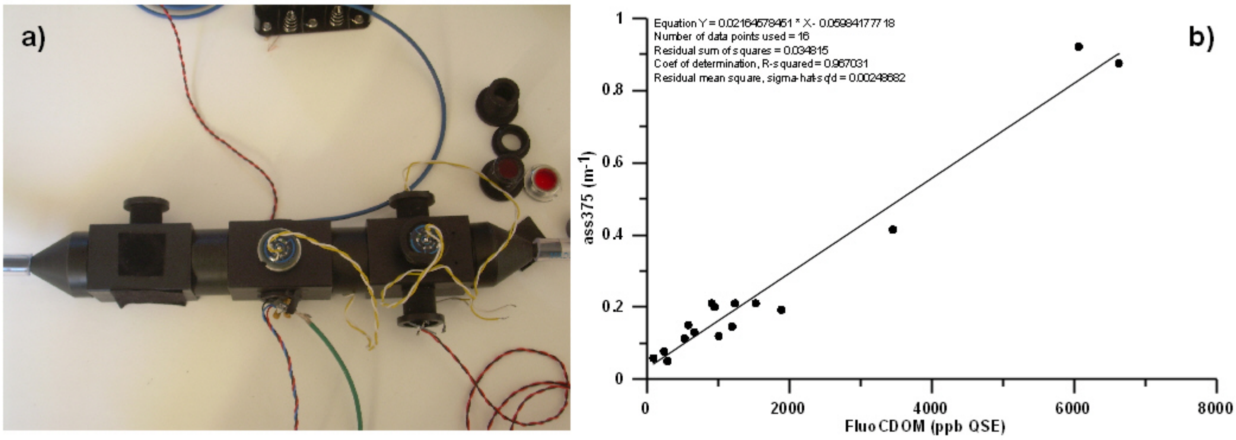

Fig 19 detail of the experimental circuit used for the identification of the best optical configurations of the electro-optical components; b: comparison between CDOM absorption at 375 nm and CDOM fluorescence data acquired with the new prototype

Low cost Conductivity sensor

The low cost conductivity cell, realized in plexiglass, contains four platinum rings placed on the flow line. Inside the four-pole cell an alternating current is applied to the two outer rings while the voltage is measured on the inner rings, thus avoiding errors due to polarization effects, and ensuring the accuracy of the measurement. The conductivity cell combines the advantages of the four-pole design with the presence of an internal temperature sensor, which allows to calculate the salinity. Many experimental tests were conducted to achieve the best compromise between low-cost, mechanical design and high performance detection. The developed prototypes were calibrated using a MicroTSG (MicroThermosalinograph) SBE 45 (temperature resolution: 0.0001 °C; conductivity resolution: 0.0001 mS/cm) connected with a thermocryostate Haake Thermo Scientific DC10/K10 Fig 20 a.

The performance of the sensor was tested during an in situ survey comparing the acquired measures with the conductivity sensor of the IDRONAUT 316 multiparameter probe. The salinity calculated by both the instruments shows a good correlation, as reported in Fig 20 b.

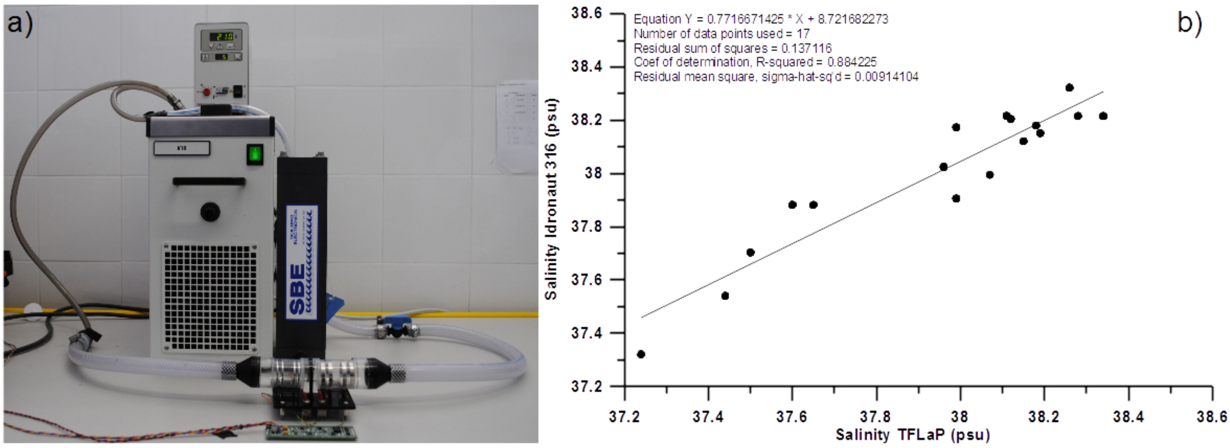

Fig 20 a): laboratory tests on the experimental conductivity cell; b): comparison between salinity measures obtained with IDRONAUT 316 and the developed conductivity sensor during an *in situ* test

Operative implementations in oceanographic surveys

These advances allowed significant improvement of the expendable probe and the development of two additional applications: the recoverable TFLaP vertical profiler, and the mini-ferrybox system, *Spectra*, for surface mapping of the marine bio-physical properties.

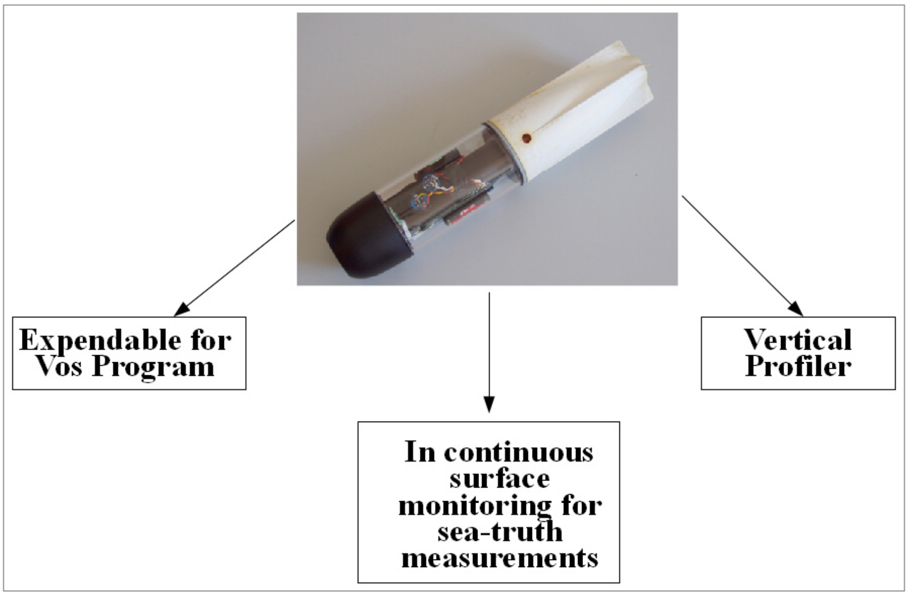

Fig 21 T-FLaP applications

The different applications were extensively used during several oceanographic and coastal surveys, both from research vessels and little boats, to verify the instrument effectiveness in the description of marine processes and at the same the handiness.

The ADRICOSM-STAR survey

The ADRICOSM-STAR Project (integrated river basin and coastal zone management system: Montenegro coastal area and Bojana river catchment)[15], coordinated by CMCC (Euro-Mediterranean Centre for Climate Change), was launched as a Type II initiative at the World Summit on Sustainable development (WSSD), in Johannesburg in 2002, by the Italian Ministry for the Environment, Land and Sea. Within the project the Laboratory of Experimental Oceanology and Marine Ecology was recruited to support the upgrade of the VOS (Voluntary Observing Ship) monitoring system of the Adriatic Sea. During the project, the ADR0208 survey was conducted and five prototypes of the expendable probe were used to test the optical components and combinations and to analyze the instrument accuracy. The five prototype T-FLaPs, calibrated before the survey (Marcelli et al. 2014), were launched just after the standard CTD (SBE 911, Aquatraka III fluorometer) casts, along the Dubrovnik-Bari transect (Fig 22 a and 22 b).

The objective was to verify the possibility of describing mesoscale processes with sufficient accuracy. For this reason the Southern Adriatic Sea was ideally suited to the T-FLaP fluorescence measure tests, because of the gyre presence, which strongly influences the distribution of phytoplankton biomass.

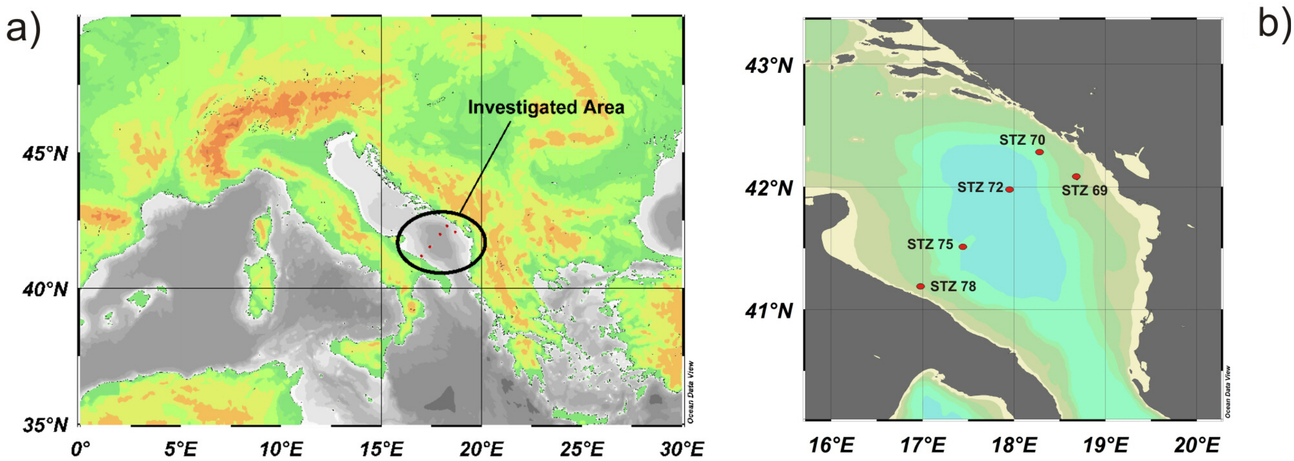

Fig 22 a): The ADR0208 study area and b): the Dubrovnik-Bari transect

The CTD and T-FLaP data were represented in depth-distance sections, along the Dubrovnik-Bari transect. The objective was to test the possibility of detecting mesoscale structures, particularly the Southern Adriatic gyre.

This gyre influences and modulates the DCM distribution, which has the highest chlorophyll *a* values near the Balkan coast, during the ADR0208 cruise.

The temperature sections show a similar trend for both TFLaP and CTD probes, which detect the mesoscale structure with a good accuracy, as shown in Fig 23 c and 23 d. Both the sections show a dooming connected to the cyclonic gyre in the center of the Southern Adriatic Sea.

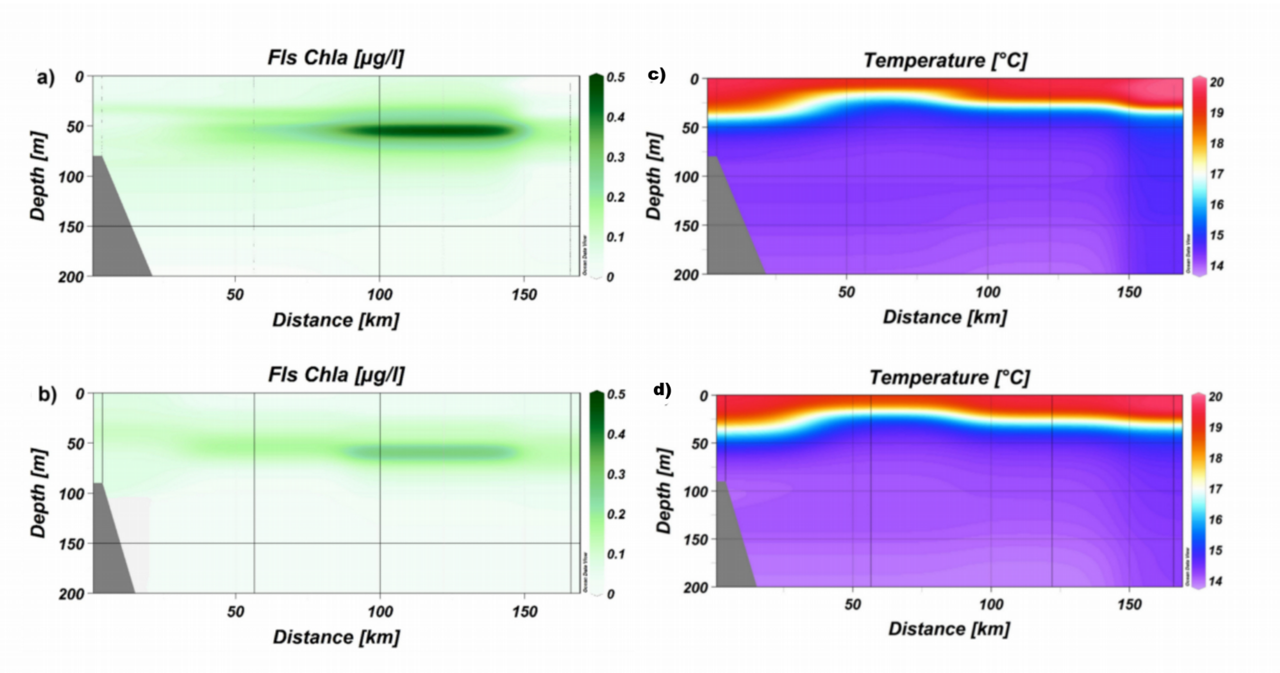

Fig 23 distribution of a) T-FLaP and b) Chelsea Aquatraka III fluorescence and c) T-FLaP d) CTD SBE 911 temperature acquired along the Dubrovnik-Bari transect

The chlorophyll *a* fluorescence data differed between the two probes, provide some opportunity for discussion, as shown in Fig 23 a and 23 b. The differences between the fluorescence measured by the probes (both T-FLaP and AquatraKa III) and the chlorophyll concentration is about 40%. The maximum value of chlorophyll *a*, as obtained by laboratory analyses, was located in the DCM of station 72 and was about 0.72 µg/l, while the fluorescence values measured by the T-FLaP and for Aquatraka III probes were 0.5 and 0.41µg/l respectively. The DCM position and intensity was identified by T-FLaP, similarly to Chelsea Aquatraca III, while in the areas of lower concentration the T-FLaP chlorophyll signal is less intense. Above and below the DCM zone, T-FLaPs show a higher concentration with a more intense signal.

Tyrrhenian Sea survey: Elba Isle

The recoverable T-FlaP vertical profiler was tested and extensively used during different surveys off the Elba Isle (Fig 24 a and 24 b), carried out with the Italian Coastal Guard on board the CP406 boat. In order to study the distribution of phytoplankton biomass, various transects were performed during August 2012.

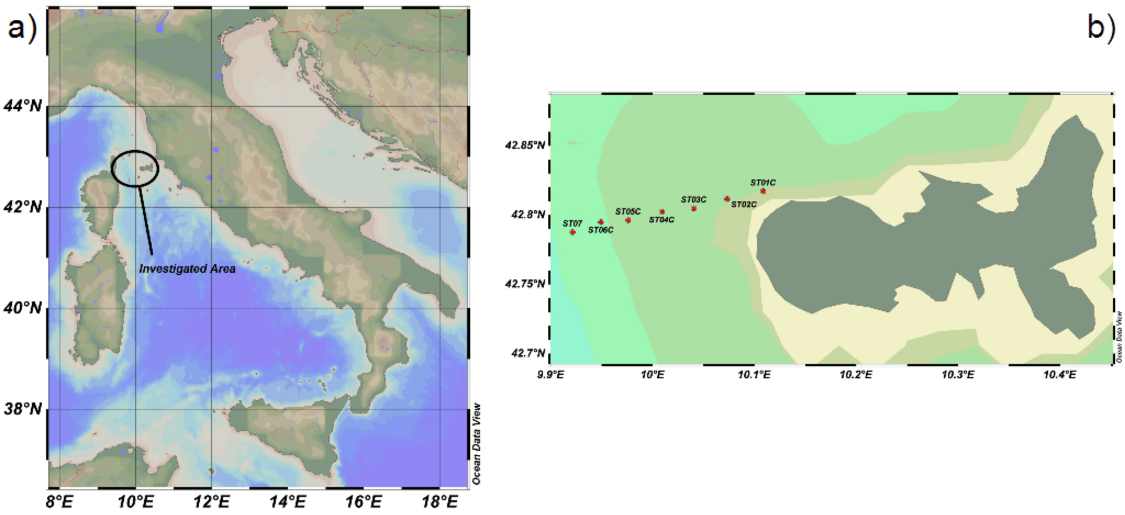

Fig 24 a): The Elba survey study area and b): the Elba-Corsica transect

The instrument allows to observe a strong vertical stratification, typical of the summer period, with a marked thermocline (Fig 25 a). As regards the distribution of phytoplankton biomass, the chlorophyll *a* fluorescence shows higher concentrations at the bottom above 60m depth, with a maximum peak of 1.25 rel.un. (Fig.25 b).

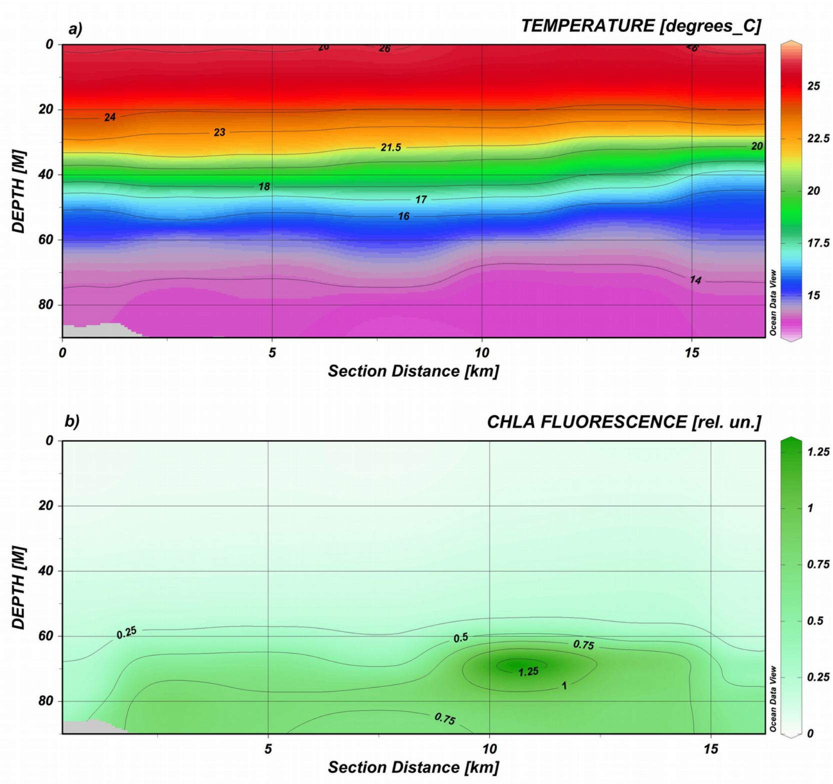

Fig 25 distribution of a) temperature and b) fluorescence acquired along the Elba-Corsica transect with the recoverable vertical profiler

In each T-FLaP station standard CTD casts (multiparameter probe IDRONAUT 316 with a Seapoint fluorometer) and water sampling were performed. The comparison of the vertical temperature and chlorophyll *a* fluorescence profiles, shown in Fig 26 a, confirms the capacity of TFLaP probe to describe the vertical structure of the investigated variables.

The results of water samples collected for chorophyll a analyses (Jeffrey & Humphrey 1975; ISO 10260 1992) were compared with the data acquired by the TFLaP showing a good correlation, as reported in Fig 26 b.

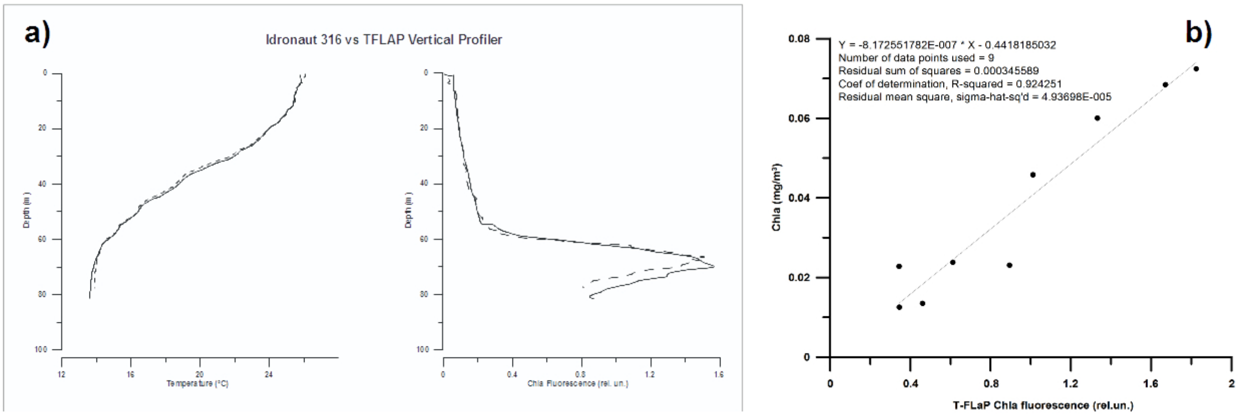

Fig. 26 a): comparison between T-FLap (solid line) and Idronaut 316 (dashed line) temperature and chla fluorescence profiles and b): linear regression between T-FLaP chla fluorescence and chla laboratory analysis

IOSMOS survey

The Ionian Sea water quality MOnitoring date by Satellite (IOSMOS) project, in collaboration with the IMAA-CNR of Potenza, was aimed at monitoring the bio-optical properties of the waters of the stretch of Ionian coast between the estuary of the river Basento and that of Sinni (Fig 27), by analyzing multi-temporal data and advanced satellite products. For this purpose, several *in situ* surveys were performed for the intercalibration between local scale remote satellite and airborne observations.

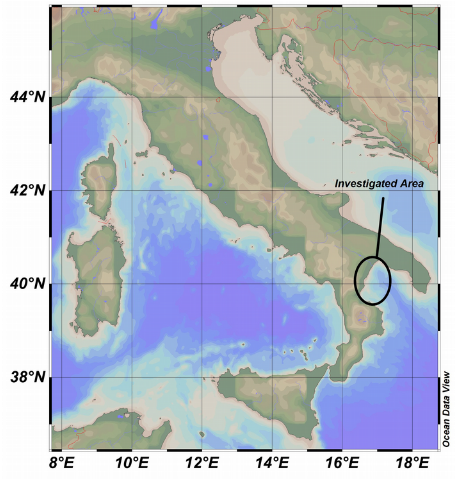

Fig.27 The IOSMOS study area

During these surveys a series of transects were carried out using the *Spectra* system in correspondence of the rivers, in order to analyze the different coastal-offshore gradients.

Figure 28 shows the results of the survey carried out in July 2013 on-board a class 200 italian coastal guard boat.

The data acquired through the *Spectra* were represented through isosurfaces, representing the distribution of the temperature, chlorophyll *a*, and CDOM fluorescence variables along the surface.

The temperature measured in the area varies between 24.5 and 27°C, as recorded at the mouth of the River Agri and off the mouth of the river Basento, respectively. The values of chlorophyll *a* fluorescence show a maximum of 2.35 rel.un. along the transects of the Sinni and the Cavone rivers.

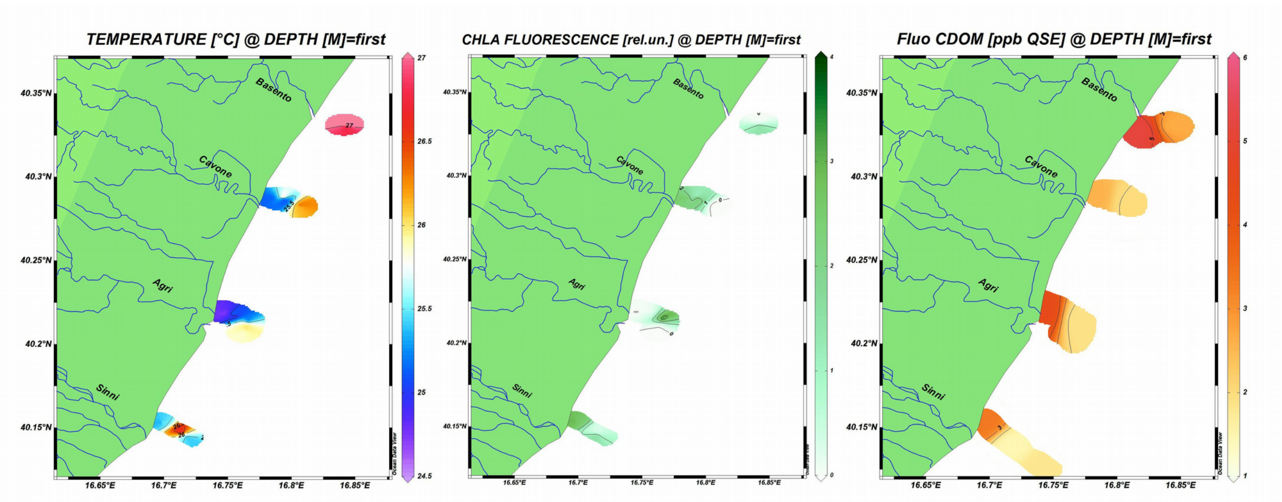

Fig 28 Surface distribution of temperature,chlorophyll a and CDOM fluorescence

The distribution of CDOM fluorescence has a characteristic coast-offshore pattern along all of the transects monitored, with higher values in the proximity of river mouths (5.69 ppb - river Basento, 2.56 ppb - River Cavone, 4.40 ppb Agri River, 3.34 ppb river Sinni) compared to the corresponding offshore stations.

Conclusions

The developed technology presents some advantages as below listed.

- The modularity allows the integration of different sensors. Four measurement channels for each flow cell can be duplicated and the payload sensors can be easily replaced. For example, during the *in situ* free fall testing, the T-FLaPs had been equipped with triaxial accelerometer, gyro, temperature, and pressure sensors, instead of chlorophyll *a*, temperature, and pressure sensors.
- Performing measures within a flow cell decreases environmental interferences and, with a minimum effort, makes it possible to apply the instruments in different operating modes (e.g., expendable, recoverable vertical profiler, and mini-ferrybox).

The integration of new sensors in the developed modular technology is another over conventional measurements, which were limited to pressure, temperature and chlorophyll *a*. The new CDOM and conductivity sensors further improve the performance of the T-FLaP technology and extend its use to a broader range of applications.

In order to confirm the reliability of the technology for the description of marine processes this paper presents the results of the three main applications tested in oceanographic cruises. During the ADR0208 survey, five expendable T-FLaP were launched. SBE911 CTD profiles and water samples were also performed for chlorophyll *a* analysis. The T-FLaP data were then calibrated and compared with CTD data. The temperature and chlorophyll *a* T-FLaP data sections, between Italy and Balkan Peninsula, allow us to correctly describe an upwelling in the southern Adriatic, an area already featuring typical Mediterranean oligotrophia.

During the Elba survey performed with the Italian Coast Guard CP406 between Elba and Corsica, we used a T-FLaP profiler that allowed us to describe the change in temperature and chlorophyll *a* fluorescence in this area of the Tyrrhenian Sea. The water samples allowed us to analyze the content of chlorophyll *a*, validating the T-FLaP profiler data with laboratory results. In this case the T-FLaP was used as the sole fluorometer during three short measurement campaigns.

Finally, during the IOSMOS campaign *Spectra* was used to characterize the trophic conditions of the coastal area under investigation (i.e., at the immission of the four main rivers present along the Ionian coast), allowing us to detect strong coastal-offshore gradients of dissolved organic materials of continental origin.

5.4 A new approach to assess the effects of oil spills on phytoplankton community during the "Serious Game" experiment (MEDESS-4MS Project)

Adapted from:

Fiori E., Servadei I., Piermattei,V., Bonamano,S., Madonia,A., Guerrini,F., Marcelli,M. & Pistocchi R. (2016). A new approach to assess the effects of oil spills on phytoplankton community during the "Serious Game" experiment (MEDESS-4MS Project). Deep Sea Research Part II: Topical Studies in Oceanography.

Deep-Sea Research II 133 (2016) 76–87

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

A new approach to assess the effects of oil spills on phytoplankton community during the "Serious Game" experiment (MEDESS-4MS Project)

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ARTICLE INFO

Available online 8 June 2016

Keywords:
Phytoplankton
Oil spill
Hydrocarbon
Chlorophyll
Fluorescence
Cell volume
Carbon
Nitrogen
Tyrrhenian Sea

ABSTRACT

The "Serious Game" experiment was focused on the development of an integrated monitoring approach to oil spill events in the Mediterranean Sea; it was carried out in the Northern Tyrrhenian Sea, an area that is reported to have intense marine traffic often connected to operational oil discharges. Our experiment was designed in order to develop a rapid assessment of oil spill effects on phytoplankton community through the integration of satellite imagery, *in situ* sampling and new low-cost technologies. In particular, satellite images were frequently acquired to monitor the study area. When the oil slick was detected, a real time sampling survey was carried out with the support of the Italian Coast Guards, employed as Voluntary Observing Ships for the identification of the polluted area, as well as for sampling and measuring activities. During the experiment, numerous analyses were carried out on the controls (C1, C5, E1, E5) and oiled (M1, M2, M4) stations to assess the most useful methods to quantify the impact of oil slick on the phytoplankton community. Among the numerous methods used, phytoplankton qualitative and quantitative evaluation was indispensable to appreciate subtle changes among the different phytoplankton groups; it is therefore a crucial analysis to observe the short negative effects of oil exposure on microalgae. In addition, the C:N ratio was shown to be a reliable parameter to evaluate the presence of oil compounds in the particulate fraction. Also the new low-cost technology used (the vertical profiler T-FLaPpro) was proved to be an efficient support to the rapid assessment of the oil impact along the water column.

Introduction

The global development of marine transportation and the use of oil during the last centuries have led to widespread and regular marine oil spills. The main systems to monitor sea-based oil pollution consisted in the use of airplanes and of satellite images (Coppini et al., 2011; Fingas and Brown, 2014). This allowed to ascertain that sea inputs are represented by discharges coming from ships or offshore platforms and that the origin of the pollution can be accidental or deliberate (operational), the latter consisting in the illegal discharges of oily residues and oily ballast water due to tank washing into the marine environment.

Operational pollution from ships has become a major problem in the Mediterranean Sea, which represents an important route for transportation, due to its strategic position. As reported in the literature, the spills distribution was highly correlated with the major shipping routes (Ferraro et al., 2007). High oil spill densities were reported during 1999 and 2004 in the region between the Corsica Island and the Italian Peninsula (Ferraro et al., 2007). The number of operational spill detections generally increases during summer months due to the lower wind speed, which allows the formation of visible surface films (Ferraro et al., 2007; Gade et al., 2000). In particular areas, such as the area between the Corsica Island and the Italian Peninsula, the increasing number of summer detections could also be due to the increment of maritime traffic during the touristic season (Gade et al., 2000). In this context the Voluntary Observing Ship (VOS) Program plays a crucial role to rapidly assess the effects on marine ecosystems in case of accidental pollution events (Renner and Kuletz, 2015). In particular this program utilizes a variety of ships, i.e. merchant or military vessels, ferries, which can be used operationally for the measurement of the principal water parameters giving an important contribution to the marine datasets. The employment of VOS provides a cost effective way to frequently and timely collect data necessary for assessment of the marine environment health and changes (Manzella et al., 2003).

Once oil enters into the environment, it is immediately subjected to a series of natural processes (oil weathering processes) including evaporation, dissolution, dispersion, emulsification, photo-oxidation, sedimentation, etc. These processes highly depend on the nature of oil and on the weather conditions (temperature, wave movement, wind speed and sun incidence) during and after the spill. Crude oils consist in complex mixtures of hydrocarbons, which represent the main components, and other elements ranging from smaller, volatile compounds to very large, nonvolatile compounds (Kinghorn, 1983). Oils may also contain varying amounts of sulfur, nitrogen, oxygen and trace metals such as nickel, vanadium and chromium. Nitrogen compounds are abundant in most crude oils and constitute about 0.1–2 percent of the total by weight (Zhang et al., 2010). Oil spills can cause serious damages to the marine environment and numerous studies have been carried out with different approaches to study the influence of oil on phytoplankton: monospecific cultures (Echeveste et al., 2010; Garr et al., 2014; O'Brian and Dixon, 1976; Ozhan and Bargu, 2014), mesocosm studies (Gilde and Pinckney, 2012; González et al., 2013; Ohwada et al., 2003), in situ observations (Varela et al., 2006). However, oil effects on marine algal species are still unclear and sometimes contradictory (Soto et al., 2014). The impacts of oil on marine organisms depend on the concentration of oil, oil type, sensitivity of organisms and duration of exposition. In fact, plankton organisms living in the upper layers of the sea are exposed to the highest concentrations of oil (Hoong Gin et al., 2001). However, the variability in physical parameters, such as the direction and speed of water movement through the water column, could reduce the duration of exposure of plankton to floating oil (O'Brian and Dixon, 1976). Oil effects on phytoplankton also differ depending on natural environmental conditions; i.e. the inhibition of growth rate due to oil is highly temperature-dependent (de la Cruz, 1982). Indirect effects could be represented by the fact that oil slicks cover the sea surface limiting gas exchanges through the air interface and can also reduce light penetration into the water column affecting photosynthesis. This study was conducted within the MEDESS-4MS (Mediterranean Decision Support System for Marine Safety) project, which is dedicated to the maritime risks prevention and to the strengthening of maritime safety related to oil spill pollution in the Mediterranean Sea (http://www.medess4ms.eu/). The goal of this study was to set up and test an experimental and innovative integrated monitoring approach in response to oil spill events in the Mediterranean Sea. Among the several activities performed during the experiment, a big effort was also made to find a rapid approach useful to assess the impact of oil slick on the phytoplankton community of the study area.

Materials and methods

Sampling strategy

Within the "Serious Game" experiment, to promptly intervene in case of oil spill events, an "emergency" system has been developed in cooperation with the Italian Coast Guard (ITCG). The system combined: (1) the support of frequently acquired (every 12 h) satellite images to detect possible oil slick events (CleanSeaNet2, CSN-2); (2) in case of oil spill detection, the immediate departure, from the closest port, of the Italian Coast Guard vessels to confirm the position of the warning and to collect in situ data and oil/seawater samples; (3) the release of drifters to monitor the oil slicks movements; (4) the model forecasting of the oil spill trajectory. To test the efficacy of the proposed operative protocol a "Serious Game" experiment was conducted in the Northern

Tyrrhenian Sea, between the Elba and Capraia Islands from 17th to 26th of May 2014 (Fig. 29). During the period, two intensive sampling surveys were scheduled on the 17th and on 21st of May 2014 for the physical, chemical and biological characterization of the study area. The study area was subdivided in advance in a sampling grid based on 9 stations (named A1, C1, E1, A5, C5, E5, A9, C9, E9) where biological analyses on seawater samples and vertical profiles with multiparametric probes and low cost instruments were carried out. The operative base was localized at the ITCG Station of Portoferraio (Elba Island), where a laboratory for the execution of the most urgent analyses, the stocking of the collected samples and the provision of the oceanographic instrumentations was set up. An informatic center for the visualization of satellite images and the use of forecasting models was also available.

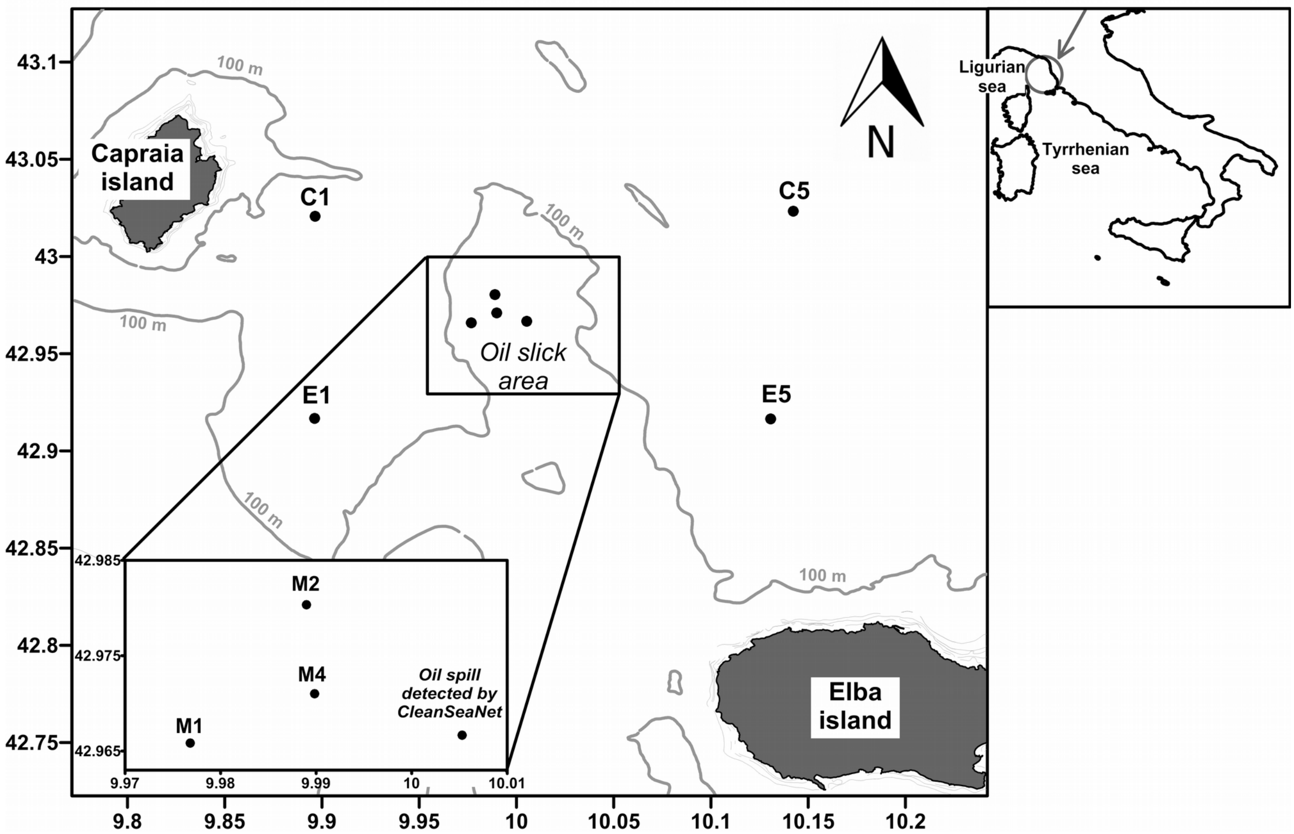

Fig 29 Map of the sampled stations: controls (C1, E1, C5, E5) and oil-polluted stations (M1, M2, M4)

On the 17th of May 2014 at 05:38:15 UTC, an elongated oil slick (covering an area of 1.78 km2: 6.24 km length, 0.25 km width) was sighted at the South-East of the Capraia Island from CleanSeaNet2 (De Dominicis et al., 2016). The M/V CP 286 patrol boat immediately left the Portoferraio harbor, equipped with the multiparametric probe Idronaut 316, the low-cost fluorimeter T-FlaPpro (Marcelli et al., 2014), and two kinds of Niskin bottles: 12 L PVC for control seawater, and 1.2 L teflon-coated, specific for organic compounds, for oil polluted seawater sampling. When the operators reached the presumed discharge position the oil slick was moving in the North-West direction and appeared subdivided in different patches, within which three sites (named M1, M2 and M4) were sampled starting at 07.00 UTC (Fig. 1). Surface water samples were collected within 6 h in the three sites inside the slick, and then in all the 9 prefixed stations. Four stations that were located around the area interested by the oil slick were considered as controls (C1, E1, C5, E5). Both controls (C1, E1, C5, E5) and oiled (M1, M2, M4) stations were subjected to the following analyses: phytoplankton qualitative and quantitative evaluation, algal biomass (cell counting, cell volume), phytoplankton intracellular components (chlorophyll-a, carbon, nitrogen).

Vertical profiles of fluorescence were carried out using a vertical profiler (T-FlaPpro).

Chemical analyses of the slick samples (M1, M2, M4) were performed to evaluate the concentration of total hydrocarbons.

The phytoplankton qualitative and quantitative analysis and the fluorescence profiles were also performed in all the 9 prefixed stations during both samplings.

In order to perform the filtrations and analyses of the seawater samples as soon as possible, at one extremity of the sampled area a CP patrol boat (class 500) took the samples from M/V CP 286, which were delivered within 2 h at the biological laboratory in Portoferraio.

Data collection – surface

<u>Phytoplankton qualitative and quantitative analysis</u>

Surface water aliquots were transferred from Niskin bottles to dark glass bottles (250 mL) and fixed with acid LUGOL solution. For the microscope analysis, after gentle swirling, 50–100 mL sub-samples were taken, allowed to settle for 24–48 h and examined following the Utermöhl (1931) method using an Axiovert 100 microscope (Zeiss GmbH, Oberkochen, Germany) at 320 magnification.

The detection limit was defined as the minimum concentration, which allowed the detection of a specific taxon or group with a specified probability (CEN, 2005). For a single taxon, the detection limit was determined by Poisson statistics according to

$$n_{det} = -\ln(\alpha) * f_{total}/(V * f_{counted})$$

where

n_{det} is the detection limit;

α is the level of significance;

f_{total} is the total number of microscope fields in the chamber;

$f_{counted}$ is the number of fields counted;

V is the volume of the sub-sample in the chamber.

The detection limit corresponded to 30 cell L^{-1} for subsamples of 100 mL, and 60 cell L^{-1} for sub-samples of 50 mL. During countings, only micro-phytoplanktonic (20–200 mm) and nano-phytoplanktonic (2–20 mm) fractions were considered. Microphytoplankton taxa were finally clustered into three major groups: Bacillariophyceae (including for simplification all the diatoms), Euglenophyceae and Dinophyceae. The species composition of the microphytoplankton size class was defined according to Tomas (1997), while nanophytoplankton species were not determined. Cell volumes were calculated according to Hillebrand et al. (1999).

Chlorophyll-a

Seawater for the analysis of chlorophyll-a concentration was collected with the Niskin bottles, immediately pre-filtered with a 250 mm pore size mesh, for the removal of mesozooplankton and larger-size particles, and stored in 5 L PTFE containers at 4 °C in the dark prior to laboratory deliver. Upon arrival at the laboratory in Portoferraio, sub-samples (3 L) were filtered in a Gelman Science filtration system equipped with 300 mL funnels using GF/F glass fiber filters (diameter: 25 mm). The filters were stored at -20 °C in acetone 100 percent and successively analyzed (within 1 month) with a UV-mini Shimadzu spectrophotometer according to Lazzara et al. (2010).

Carbon and nitrogen content

Sampled water (volumes from 1.2 to 1.7 L) was filtered on Whatman glass microfiber filters (GF/F, diameter: 25 mm), previously dried at 450 °C in a muffle furnace for 4 h. Samples were stored at -20 °C then, before performing the analyses, were dried at 60 °C for 2 h in order to remove any water content. Analyses were conducted in duplicates using a CHNSO elemental analyzer (ThermoFisher, Flash 2000).

Hydrocarbons analyses

Chemical analyses on seawater samples, collected inside the oil slick (M1, M2 and M4), were performed according to UNI EN ISO 9377-2:2002 using solvent extraction and gas chromatography. In each station fluorescence vertical profiles were performed by means of a new low-cost vertical profiler, the T-FLaPpro, developed to measure marine temperature and fluorescence of chlorophyll-a onboard of Voluntary Observing Ships and, at the same time, by the Idronaut Ocean seven 316Plus probe equipped with a Seapoint fluorometer. The comparison between the two different measurements confirmed the good quality of the T-FLaPpro data, due to a very high correlation (R21⁄40.90), as shown in Fig. 30.

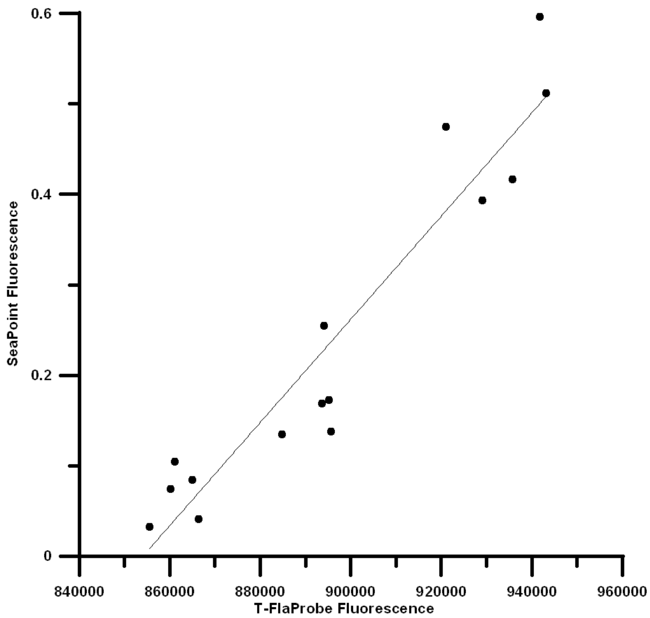

Fig 30 Scatterplot showing the linear regression between T-FlaPpro and Seapoint chlorophyll-a fluorescence data

Statistics analyses

MATLAB statistical program (MATLAB R2011a) was used to conduct one-way analyses of variance (ANOVA) on C:N ratio results, performed among controls (C1, C5, E1, E5) and oiled (M1, M2, M4) stations. Prior to carrying out the ANOVA analysis, data were checked for normal distribution (Lilliefor0s test) and homogeneity of variance (Barlett0s test). Consequently Tukey's honesty significant difference (HSD) was performed. For the purposes of the present study, phytoplankton community richness, diversity and evenness were assessed applying three statistical indices: Margalef index (H), Shannon index (H) and Pielou index (J) (PRIMER-6). The indices were calculated using the Bacillariophyceae and Dinophyceae genera detected in the controls (C1, E1, C5, E5) and in the oiled stations (M1, M2, M4). The Shannon diversity index (H) takes into consideration both abundance and evenness of the genera present (Shannon, 1948; Shannon and Weaver, 1949).

$$H = -\sum_{i=1}^{S} p_i ln(p_i)$$

where p_i=S/N; S is the number of individuals of one genus; and N is the total number of all individuals in the sample. The index is based on the principle that polluted waters present low species richness.

The Margalef index was used as a simple measure of species richness (Margalef, 1958)

$$D = (S-1)/\ln N$$

where S is the total number of phytoplankton genera; and N is the total number of all individuals in the sample. Low values of D represent low phytoplankton genus richness.

The evenness of the phytoplankton community can be represented using the Pielou index (Pielou, 1966).

$$J = H/\ln S$$

where H is the Shannon index and S is the total number of phytoplankton genera. The present index ranges between 0 and 1. The closer is the value to 1 the more even is the distribution of phytoplankton.

Results

Chemical analyses, performed in surface water samples of the three stations where the oil presence was noticed (M1, M2, M4), underlined the presence of hydrocarbons in all the samples analyzed. The total hydrocarbon concentration could not be precisely determined due to the low sensitivity of the chemical analysis applied: in all the samples the oil concentration was observed in amounts lower than the detection limit (<100 $\mu g\ L^{-1}$). Nevertheless high iridescence was observed in M2 during the sampling activities (Fig. 31).

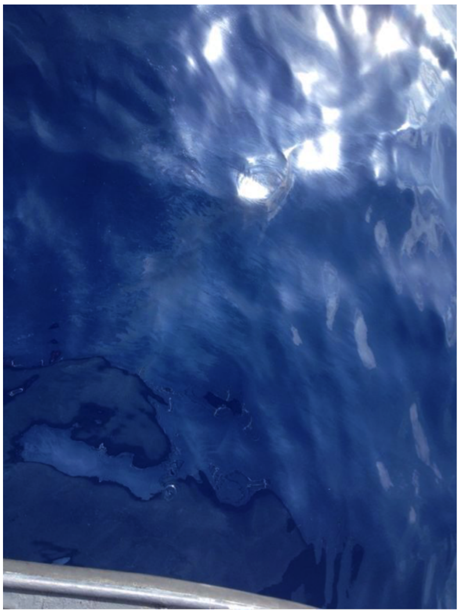

Fig 31 Picture taken on-board of the M/V CP 286 patrol boat of the oil slick in M2 station. Iridescence is visible on the south-west corner of the picture

In addition, results of the carbon (C) and nitrogen (N) analyses, performed on the particulate fraction collected on the filters, could be used to understand in which samples the total hydrocarbons were more concentrated. The molar C:N ratio measured in M2 was significantly higher (11.82±1.43) than the C: N ratio of the control stations (C1, E1, C5, E5) (Fig. 32).

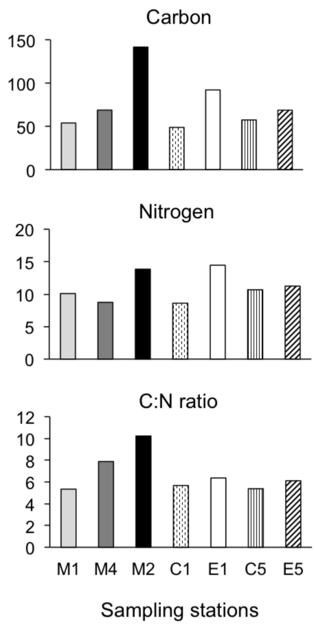

Fig 32 Particulate carbon and nitrogen (mg/m^3) and C:N ratio measured in the control (C1, E1, C5, E5) and in the polluted (M1, M4, M2) stations.

All the controls displayed C:N ratio values around 7 (6.62–7.45), which is the range typical of marine phytoplankton. Conversely, the C:N ratio in M4 was found to be slightly higher (9.6±71.91), while in M1 (6.23±0.02) the value was in the same range as the control stations (M2> M4>M1) (Fig. 32). However, no significant differences were detected among M4, M1 and the control stations. The total phytoplankton biomass, in terms of enumeration (cell L^{-1}) and cell volume measures (μm3 L^{-1}), followed the same trend in all the sampled stations (Fig. 33).

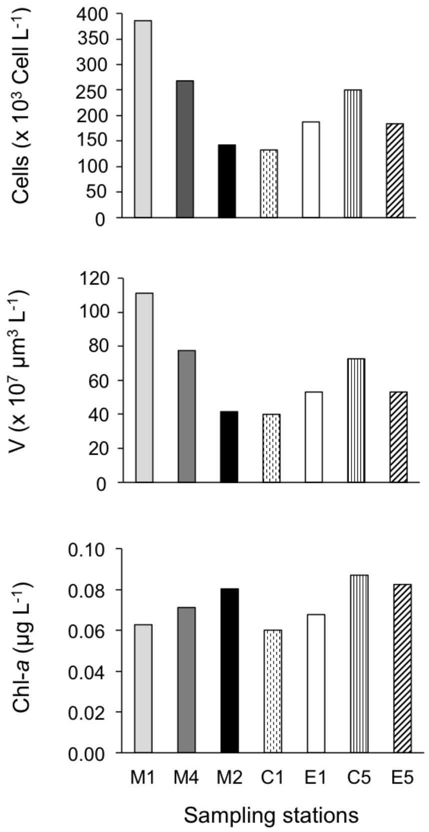

Fig 33 Phytoplankton abundance (Cells, cell number L^{-1}) cell volume (V, $\mu m^3 L^{-1}$) and chlorophyll-a content (Chl-a, μg L^{-1}) in the control (C1, E1, C5, E5) and in the polluted (M1, M4, M2) stations.

With regards to the control stations, C5 presented the highest phytoplankton biomass, while in C1 the lowest values were registered. In the stations where the oil slick was detected, the total phytoplankton biomass drastically decreased from M1, which presented the highest phytoplankton abundance, to M4 and to M2 (M1>M4>M2). Both cell densities and cell volumes were higher in the M1 and the M4 station than in the controls (Fig. 33). On the contrary, the M2 station displayed lower cell numbers and cell volumes than the majority of the control stations (E1, C5 and E5) (Fig. 33). Only the C1 station was characterized by phytoplankton biomass and cell volume values in the same range of that detected in M2 (Fig. 33). The M2 and the C1 stations had the lowest cell numbers also when compared to all the stations sampled in the study area (Table 1).

Table 1

Cell enumeration (x10^3 L^{-1}) during the two sampling days (17th and 21st May) in all the prefixed sampling stations.

Stations	Sampling 1	Sampling 2
M1	385.92	–
M4	268.04	–
M2	142.35	–
C1	132.58	88.74
E1	187.57	181.62
C5	250.20	203.60
E5	184.01	87.88
C9	412.72	315.70
E9	414.03	157.21
A1	301.52	225.57
A5	517.33	337.60
A9	273.88	238.36

The results of the second sampling evidenced a decrease in phytoplankton abundance in all the sampling stations due to variations in the meteorological and oceanographic conditions between the two sampling days (Table 1). Chlorophyll-a (mg L^{-1}) followed the same trend as the variables reported above (cell density and cell volume) in the four control stations (Fig. 33): the highest chlorophyll-a concentration was obtained in C5, while C1 presented the lowest value. On the contrary, in the stations were the oil was detected a different pattern was observed: a high chlorophyll-a value was measured in M2, which presented the lowest phytoplankton abundance and cell volume data; chlorophyll-a concentrations decreased from M2 to M4 to M1 (M2>M4>M1). In addition, chlorophyll-a content was higher in the polluted samples compared to the control stations C1 and E1, while the C5 and the E5 stations presented slightly higher chlorophyll-a contents respect to the polluted stations (Fig. 33). Chlorophyll-a per cell values were in the range of 0.16–0.56 pg $cell^{-1}$ (Table 2). The highest values were registered in the M2, C1 and E5 stations. Slightly lower values were reported for the other control stations (E1 and C5), while the polluted stations M4 and M1 presented the lowest chlorophyll-a cell contents (Table 2).

Table 2

Chlorophyll cell content (pg $cell^{-1}$) and Chl:C ratios measured in the controls and oiled stations.

Stations	Chl-a	Chl: C
M1	0.16	1.16
M4	0.27	1.03
M2	0.56	0.57
C1	0.45	1.23
E1	0.36	0.74
C5	0.35	1.51
E5	0.45	1.20

The evaluation of chlorophyll-a: carbon ratios (Chl:C) reported more homogeneous results in all the control and oiled stations. The lowest value was detected in the M2 station (0.57) where high carbon content was registered (Table 2).

The analysis of the vertical profiles, acquired by T-FlaPpro, showed that the fluorescence values ranged from a minimum of 0.02 (rel.un.) at the surface layer to 0.3 (rel.un.) at the bottom in the control stations (C1, E1, C5, E5) and in the M1 station (Fig. 34). However, the vertical profile carried out in M2 underlined a pronounced decrease of fluorescence values in the upper layers of the water column (0 - 10 m). In addition, the chlorophyll fluorescence values along the water column did not exceed 0.14 (rel. un.) despite the lower depth of this station (Fig. 34).

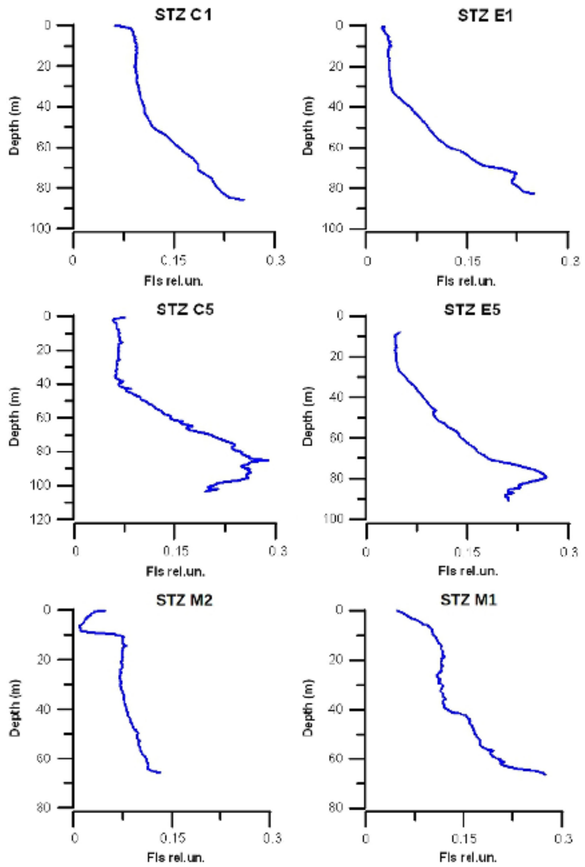

Fig 34 Vertical profiles of chlorophyll-a fluorescence in the control stations (C1, E1, C5, E5) and in the oil polluted stations (M2, M1).

The composition of the phytoplankton community and quantitative data of the main groups (Bacillariophyceae, Dinophyceae, Euglenophyceae and nanoplankton) were also determined for all the stations (Figs. 35–38). The nanoplankton was the most abundant phytoplankton group (in the range of 400.000 cell L^{-1}), with Bacillariophyceae and Dinophyceae being nearly two orders of magnitude lower (in the range of 6000–9000 cell L^{-1}) and Euglenophyceae lower than 200 cell L^{-1} (Fig. 35).

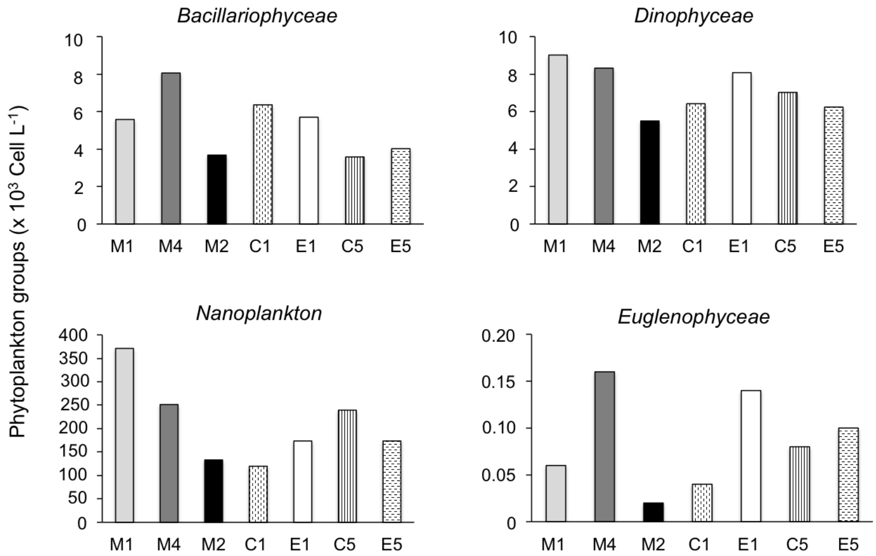

Fig 35 Phytoplankton abundance (cell number L^{-1}) for each group (Bacillariophyceae, Dinophyceae, nanoplankton and Euglenophyceae)

Cell volume measurements performed individually on each species (data not shown) underlined that small size cells dominated also the microphytoplankton groups (Bacillariophyceae, Dinophyceae and Euglenophyceae) detected. In particular, all the species belonging to the Bacillariophyceae had cell volumes in the range of 30–3723 µm3. The majority of the Dinophyceae species had cell volume values in the range of 374–3937 µm3, except 4 species (Diplopsalis spp., Tripos furca, Protoperidinium spp., Oblea rotunda), which belonged to the size range 22.187–70.685 µm3. The M1 and M4 stations had phytoplankton densities generally higher than those of the control stations. Conversely, in the M2 station the abundance of all the phytoplankton groups was generally lower with respect to all the other stations (M1, M4, C1, E1, C5, E5). The M2 station presented a nanoplankton abundance in the same range as those obtained in the control station C1 (Fig. 35).

Concerning the Bacillariophyceae class, a lower amount of Cyclotella sp. (200 cell L^{-1}) was observed in M2 compared to all the other stations, and species of the genus Chaetoceros were not detected at all in the same station (Fig. 36). Furthermore, Cyclotella sp.(ranging between 660 and 3880 cell L^{-1}) and Chaetoceros spp. (ranging between 40 and 720 cell L^{-1}) were detected in all the study area (9 sampling stations) (data not shown).

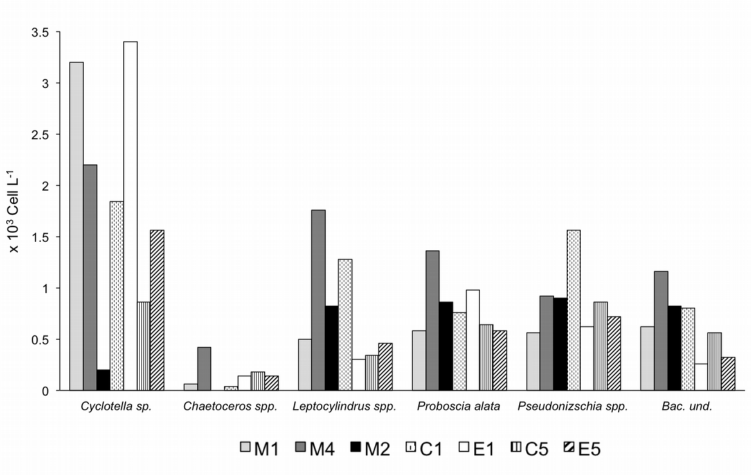

Fig 36 Most abundant Bacillariophyceae species detected in the sampling stations

The largest centric species and the pennate forms presented similar values between the oiled stations and the controls. The lower Dinophyceae number reported in M2, with respect to all the other stations, can be attributed to a decrease of the most abundant species (4400 cell L^{-1}) (Fig. 37), among which, the undetermined Dinophyceae had lower abundance in M2 compared to all the other stations, Gyrodinium spp. were lower compared to all the other station with the exception of C1, and Scrippsiella spp. cell number was lower compared to M1, M4, E1, C1 and C5 (Fig. 37).

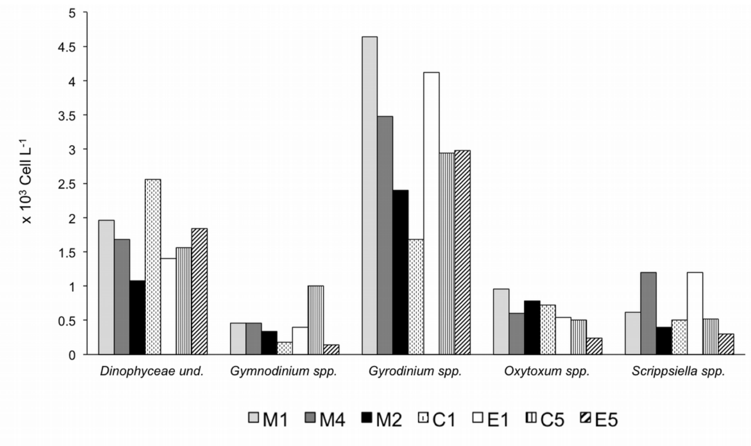

Fig 37 Dinophyceae species detected in the sampling stations at concentrations above 400 cell L^{-1}

Other Dinophyceae species were detected at much lower abundance (<400 cell L^{-1}) (Fig. 38). Among these, Prorocentrum spp. was not detected in M2 but was present in all the control stations (Fig. 10), in particular, during the first sampling, Prorocentrum spp. were detected in all the 9 sampling stations ranging between 20 and 440 cell L^{-1} (data not shown). Also Protoperidinium spp. were lower in M2 compared to M1, C1, C5 and E5 (Fig. 38).

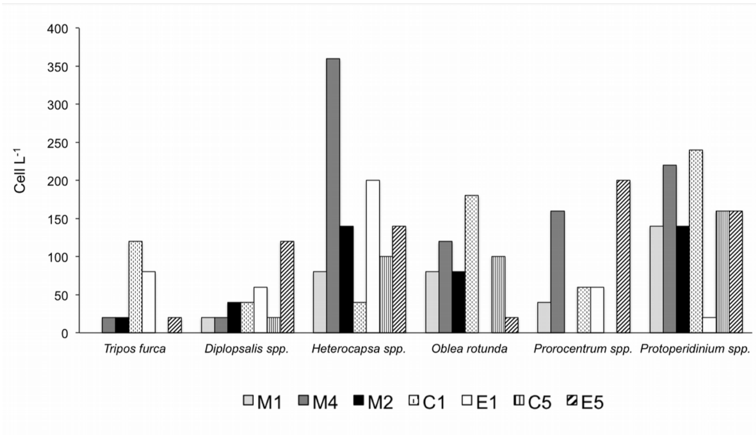

Fig 38 Dinophyceae species detected in the sampling stations at concentrations below 400 cell L^{-1}

Three indices (Shannon (H), Margalef (D) and Pielou (J)) were applied to the results on Bacillariophyceae and Dinophyceae composition at genus level (Table 3).

Table 3

Results of the statistical analyses: Shannon (H), Margalef (D) and Pielou (J) indices, calculated on the Bacillariophyceae and Dinophyceae genera detected in the controls (C1, E1, C5, E5) and in the oil polluted stations (M1, M4, M2)

Sampling stations	Bacillariophyceae			Dinophyceae		
	H	*D*	*J*	*H*	*D*	*J*
M1	1.35	0.81	0.65	1.44	1.00	0.63
M4	1.80	1.00	0.78	1.71	1.01	0.74
M2	1.61	0.73	0.83	1.68	1.16	0.70
C1	1.64	0.91	0.75	1.72	1.25	0.69
E1	1.24	0.58	0.69	1.49	1.00	0.64
C5	1.83	0.98	0.82	1.67	1.35	0.65
E5	1.77	1.20	0.74	1.49	1.03	0.65

For the Bacillariophyceae class, lower values of Margalef and Shannon indices were obtained for M2 station compared to all the controls (C1, C5, E5), except for the E1 station, suggesting low richness and diversity in the oil-polluted station (M2). Regarding the Dinophyceae class lower values of Margalef and Shannon indices were found in M2 station compared to two control stations (C1 and C5). Finally, the evenness index (Pielou index) calculated for the Bacillariophyceae and the Dinophyceae classes showed lower values in all the control stations compared to the M2 station, indicating a lower variation of the phytoplankton community in the oiled station (Table 3).

Discussion

Our study was performed in a transition zone between the Tyrrhenian and the Ligurian Sea characterized by a high dynamic variability and low chlorophyll values (ARPAT, 2015; Lazzara et al., 1989; Marchese et al., 2015; Volpi et al., 2009). The low chlorophyll-a concentrations and the scarce phytoplankton biomass detected during the experiment clearly indicated that the sampling period represented a post algal bloom event (Innamorati et al., 2003; Lenzi Grillini and Lazzara, 1978; Nuccio et al., 1995).

During our sampling campaign the nanoplankton resulted the most abundant group in agreement with the ARPAT monitoring data, which evidenced that two sampling sites situated near to our study area (“Capraia” and “Elba nord”), presented the lowest phytoplankton abundances among 20 stations (ARPAT, 2015). In particular, these sampling sites were characterized by high abundances of nano-phytoplankton of different taxa respect to the Bacillariophyceae and the Dinophyceae groups. Other studies also underlined the nanoplankton as the major component, in terms of abundance, of the phytoplankton community of the Northern Tyrrhenian Sea (Cappella et al., 2008; Innamorati et al., 1990, 1992; Nuccio et al., 1995; Volpi et al., 2009). Lenzi Grillini and Lazzara (1980) studied the temporal variability of the phytoplankton community and evidenced a decrease in diatoms abundance, from May to June, while the flagellates species increased. However, within the Bacillariophyceae group, Rhizosolenia alata (1⁄4Proboscia alata) and Leptocylindrus danicus continued to be the dominant species, while Chaetoceros spp. decreased (Lenzi Grillini and Lazzara, 1980). A low Bacillariophyceae biomass was detected also in our samplings and the obtained results on phytoplankton diversity underlined the prevalence of Cyclotella sp., Chaetoceros spp., Leptocylindrus spp., Proboscia alata and Pseudo-nitzschia spp., while within the Dinophyceae group the most abundant genera were Gyrodinium spp., Gymnodinium spp., Oxytoxum spp. and Scrippsiella spp. Many of these Dinophyceae were also reported by Nuccio et al. (1995) as part of a permanent community during all seasons. According to our results Innamorati et al. (1990) reported Table 3 Results of the statistical analyses: Shannon (H), Margalef (D) and Pielou (J) indices, calculated on the Bacillariophyceae and Dinophyceae genera detected in the controls (C1, E1, C5, E5) and in the oil polluted stations (M1, M4, M2). the presence of Gymnodinium spp. and Gyrodinium spp. during the summer period. Although the studied area was reported to have high frequency of operational oil spill events (Ferraro et al., 2007; Gade et al., 2000), there are no studies in literature concerning the effects on phytoplankton community. Our results, although limited to two sampling days, can add some information concerning the phytoplankton composition and size of this area and the effects of low oil concentrations and short-term exposure on the phytoplankton community. The majority of the oil spill studies are in fact addressed to understand the long-term effect on phytoplankton growth or population composition changes, and thus not evidencing the acute effects and possible physiological responses. Despite we were not able to quantify the exact hydrocarbon concentration in the oil polluted stations (M1, M2 and M4), due to the low sensitivity of the chemical analyses applied, the M2 station resulted as the most polluted. In fact, it was characterized by high iridescence signals and a C:N ratio higher than the value typical of marine phytoplankton (Kepkay et al., 1997; Redfield et al., 1963). This finding was confirmed by other results obtained within the "Serious Game" experiment: Santinelli et al. (2016) carried out a study on CDOM analyses and demonstrated that M2 was the most oiled station; M2 resulted the most affected station by the oil spill event also from model studies (De Dominicis et al., 2016). Concerning the other two oil polluted stations (M1 and M4), according to iridescence observations and C:N ratio values, it was possible to deduce an oil pollution trend in the order M2>M4>M1 (with hydrocarbons presumably almost absent in the latter). Finally, the low cell numbers and low cell volumes which characterized the community found in M2 also supported the conclusion that the high carbon and nitrogen concentrations observed in this station were not due to the presence of large species of microalgae with high cell volume but were due to oil components. With regard to the effect of oil on phytoplankton, our study differed from those previously performed in situ since it was not related to an extensive spill event, and it was focused on possible short-term toxic effects. There are a number of studies reporting the increase in phytoplankton biomass occurring months after oil spill events, presumably due to growth stimulation by oil degradation products (Pan et al., 2012; Parsons et al., 1976; Peterson et al., 2003; Riaux-Gobin, 1985; Sheng et al., 2011) or to a decrease in zooplankton grazing pressure (Johannson et al., 1980). Since in our study the samples were taken not later than 6 h after the oil slick detection, this kind of response could not be taken in consideration. Generally, field observations and experimental studies on the effects of oil spills on phytoplankton are limited and often contradictory because of problems involved in differentiating between the effects of the pollutants and the ranges of natural variability (O'Brian and Dixon, 1976; Teal and Howarth, 1984; Varela et al., 2006). Hence, our different approach could also be of help in understanding the acute effects on phytoplankton during highly impactful events. Our study seemed to highlight a possible short-term negative effect of hydrocarbons on marine algae even at low concentrations (<100 μg L^{-1} of total hydrocarbons). In particular, in the M2 station the phytoplankton community was low in terms of abundance and especially in terms of species composition, being all the phytoplankton groups (Bacillariophyceae, Dinophyceae, Euglenophyceae and nanoplankton) less abundant in M2 than in all the other sampled stations, with the exception of C1. This effect could be regarded as due to the toxicity of the oil compounds towards phytoplankton cells, as low oil concentrations were previously reported to produce effects: González et al. (2009) observed changes in the structure of the plankton community at 8.6 and 23 μg L^{-1} chrysene equivalents, and Gilde and Pinckney (2012) suggested that low levels (10, 50 and 100 µl L^{-1}) of crude oil exposure might reduce total biomass and alter phytoplankton community composition. These observations were made in microcosms, while going to higher volumes (mesocosms) the negative effects of oil were reduced (González et al. 2013). Recent studies demonstrated a high correlation between the oil effects on phytoplankton and the cell dimension or volume. A strong positive linear relationship between the negative effect (LC50) of 2 polycyclic aromatic hydrocarbons (pyrene and phenanthrene) and the cell volume was observed for diatoms and phytoflagellates (Echeveste et al., 2010). The authors determined a high sensitivity to hydrocarbons for small sized species, both in cultures and in natural communities, on the contrary, large phytoplankton species (Thalassiosira sp.) were the most resistant to the pollutants. These results were attributed to the high surface to volume ratio of small cells, which could have allowed the increased hydrocarbon incorporation through the membranes (Del Vento and Dachs, 2002; Echeveste et al., 2010). Possible higher incidence of hydrocarbons in oligotrophic waters, due to the prevalence of small sized phytoplankton, was thus highlighted (Echeveste et al., 2010). Our results underlined negative effects due to oil exposition both on nanoplankton and on cell size 4 20 µm (micro-phytoplankton class) which was nevertheless dominated by small size species. In addition, the most polluted sample M2 showed lower amount of phytoplankton organisms characterized by small size or cell volume.

The oil effects on algae were shown to be species-specific, strongly dependent on the phytoplankton community involved (Licea et al., 1982, Ostgaard et al., 1984; Thomas et al., 1981; Throndsen, 1982). In agreement with previous studies, our results may highlight a different sensitivity to oil pollution among different phytoplankton species. In fact a drastic decrease of Cyclotella sp. and Chaetoceros spp. (centric diatoms) was evidenced; in particular, species of the genus Chaetoceros were not detected in the M2 station. In agreement with our results, acute toxicity (growth inhibition and mortality) to oil and dispersed oil was demonstrated for Chaetoceros sp. (Garr and Laramore; 2014) and Varela et al. (2006) reported a decrease of Chaetoceros spp. after the Prestige shipwreck. Our results underlined a higher sensitivity to oil exposure of some species of small centric diatoms (Cyclotella sp., Chaetoceros spp.) compared to pennate diatoms (Pseudonitzschia spp.). Other studies reported that pennate diatoms were not affected by 40 µg L^{-1} fuel oil contrarily to large centric diatoms (Cerataulina) (Lee et al., 1977). Different studies reported the predominance of pennate diatoms when the phytoplankton community was exposed to oil, especially under nutrient-enriched conditions (Ozhan and Bargu, 2014), or to oil plus dispersant (Jung et al., 2012) and not to oil alone. Additional studies are thus necessary to understand if pennate diatoms are less sensitive than the centric organisms. We observed a reduction also in the Dinophyceae class, in particular for the undetermined Dinophyceae (among the smallest in size) and Gyrodinium sp., which was the most abundant organism. Among the species present in low amounts (<400 cell L^{-1}), it is worth noticing that the genus Prorocentrum was not detected at all in the M2 station; conversely, from 2 to 5 species were detected in all the other stations and also in the second sampling (data not shown). Previous results on this genus were contradictory: Ozhan and Bargu (2014) affirmed that Prorocentrum minimum growth was inhibited when exposed to crude oil from the concentration of 2.75 µg L^{-1}. On the contrary, Morales-Loo and Goutx (1990) reported stimulation effects on Prorocentrum minimum growth and chlorophyll-a content in water-soluble fractions of crude oil treatments. Our results showed low chlorophyll-a values (o0.10 µg L^{-1}) in all the sampling stations. Similarly, Lazzara et al. (1989) described a chlorophyll surface distribution generally scarce in the Northern Tyrrhenian Sea (0.084–0.112 µg m^{-3}), while higher values were recorded along the northern coast of the Elba Island (0.14– 0.24 µg m^{-3}) (Lazzara et al., 1989; Marchese et al., 2015). The vertical profiles, acquired by T-FlaPpro, showed an increase of florescence of chlorophyll-a with depth according to a previous report on the vertical distribution of chlorophyll showing higher concentrations (4 to 5-fold higher than the surface values) close to the thermocline (50–100 m) (Lazzara et al., 1989).

Chlorophyll-a concentrations in all the control stations were in good agreement with cell number and cell volume measured. On the contrary, in the oil polluted stations the chlorophyll-a amounts (M1 o M4 o M2) did not match with the measured biomass (M2 o M4 o M1). Decreasing chlorophyll concentration in phytoplankton exposed to oil was previously observed after 24h (González et al., 2009) and 33 h (Gilde and Pinckney, 2012) and can be explained as decreased biomass or as pigment loss due to the increased membrane permeability caused by oil toxicity. On the contrary, very few studies were addressed to the effects of hydrocarbons on cell biochemical changes: Morales-Loo and Goutx (1990) observed a decrease in chlorophyll cell content in algae displaying a retarded growth and reported an enhancement in cells which were stimulated by oil exposure. Oberholster et al. (2010) observed a relative increase of chlorophyll-b respect to chlorophyll-a within 24 h exposition of Selenastrum to sunflower oil. Chlorophyll synthesis stimulation could represent a response to photosynthesis inhibition, as observed for different pollutants (Fiori and Pistocchi, 2014), or a photoacclimation response to the decreased light penetration due to the oil presence at the surface. In our study chlorophyll *a* nalyses were carried out on samples collected within 6 h from the oil spill event and the observed changes could be ascribed to a photoacclimation response presumably occurring during the first half of the day in the phytoplankton collected in the M2 and, to a lesser extent, in the M4 stations.

Fluorescence vertical profiles carried out in the M2 station displayed a very different pattern from all the other stations showing low values both at the surface and at the bottom. The pronounced decrease of fluorescence values could be attributed to: a low biomass, a different distribution of the phytoplankton, or photosynthesis efficiency changes. Therefore, additional analyses on chlorophyll *a* and phytoplankton abundance are necessary all along the water column to better explain these results.

Conclusions

Illegal discharges from ships can be eliminated by strict regulations and monitoring activities of the maritime traffic. There is an urgent need for an enhanced surveillance and monitoring activity over the entire basin in order to prevent and control illicit discharges from ships.

Satellites are essential to detect oil discharges, thanks to the high frequency monitoring of large areas. In case of oil spill events a well-designed real time early-warning system is necessary, where the responsible authorities, as coastal guards, can play an important role. Besides, chemical analysis of the pollutants and biogeochemical studies of the phytoplankton community are important in order to evaluate the possible oil effects on the marine ecosystem. Oil spills can lead to changes in the phytoplankton community structure and cause possible alteration on the pelagic food web.

The aim of this study was to assess the oil spill effects on the phytoplankton community during small entities events in an area of high maritime traffic. Our results suggested that phytoplankton qualitative and quantitative evaluation was indispensable to evaluate the changes occurring among the different phytoplankton groups. It is also worth to notice that the analyses of the C and N contents carried out on the particulate fraction represent a simple screening to detect the oil presence. Chlorophyll-a measurement did not appear a suitable method to measure phytoplankton abundance in case of oil spill events, due to the physiological variations often occurring. The new low-cost vertical profiler (T-FLaPpro) utilized during the experiment appeared as a good support to perform a real time assessment of the water column in the oil polluted sites, making Coast Guard vessels, used like voluntary observing systems, suitable to monitor illegal discharges from ships. This study is part of a project that, for the first time in the Mediterranean sea, allowed to test a new kind of approach to define a protocol, for analysis of acute effects of oil spills on the marine ecosystem.

6. WORK IN PROGRESS: REMOTE SENSING APPLICATION

The last part of my research work is dedicated to the analyses of how data can be integrated with large, middle, and small scale remote sensing data to create a cost effective tool for a quality improvement of coastal ecosystems analyses and monitoring. The integration of a low-cost device with ship of opportunity platforms can give an important contribution to remote sensing data validation.

The following part of the work reports preliminary analyses and results of the application of Spectra to the validation of temperature, chlorophyll *a* and turbidity obtained from middle (Landsat 8 OLI) and small scale (airborne Sensytech AA1268 EM3 – IITCG) remote sensing.

This research work is driven by the necessity of monitoring highly dynamic ecosystems such as coastal waters, which require dense sampling in space and time so as to capture short-term events . These events are related to important phenomena and processes which could have critical impact on coastal systems, such as unexpected phytoplankton blooms (Krasemann 2007) or exceptional suspended solids and organic matter concentrations. This is particularly true in coastal seas, which are subjected to multiple anthropic pressures and where the optical properties of inorganic suspended matter and colored dissolved organic matter must be considered and separated by the chlorophyll *a* contribution. The lack of continuous monitoring systems, related both to physical and biological characteristics, directly influences the robustness both of ocean operational oceanography and remote sensing data, particularly in the biological fileds.

This work has been submitted for a presentation at the EGU 2017 and a paper is in progress for the submission to an international journal.

The research acitivity was implemented in strong connection with the Italian Coast Guard, who made available both ships and aircraft equipped with high resolution devices for remote sensing and in situ measurements.

Methods and preliminary results

The survey described below were carried out in two different coastal areas in the Northern part of Tyrrhenian Sea a both to multiple anthropic pressures: Portoferraio (Elba Island, Italy) and Civitavecchia (Latium, Italy).

The first experiment was planned *ad hoc* together with the Italian Coast Guard (ITCG) in the Elba Island on 6th September 2016. The mission combined: remote sensing data acquisition through a multispectral system Sensytech AA1268 EM3, provided by 3° Nucleo Aereo (ITCG) Pescara and boarded on the aircraft ATR42 (ITCG); n.2 Italian Coast Guard vessels to collect in situ data and seawater samples, one for the innovative device (Spectra) (Marcelli et al. 2014, Marcelli et al. 2016) and the other for traditional survey. Moreover an operative base was localized at the ITCG Station of Portoferraio (Elba Island), where a laboratory for the execution of analyses, the stocking of the collected samples and the provision of the oceanographic instrumentations was set up.

Fig 39 Aircraft trajectories and corresponding Sensytech AA1268 EM3 acquisitions

The Sensytech 1268 AA multispectral scanning sensor detects the surface reflected energy covering the range of visible, near and middle IR bands with 12 channels which range between 0.42µm and 14.99 µm. The mission was planned to cover the whole isle with 12 sections at an altitude of 1524 m which allows a 3084 m swath and a ground resolution of 1.9 m.

The Spectra was installed on board a 2000 class patrol boat of ITCG and continuously acquired surface temperature, conductivity, chlorophyll *a* and CDOM fluorescences, turbidity over water samples.

In this work we chose a part of the section n.8 which covers our area of interest: the Gulf of Portoferraio.

In this area the Spectra survey were performed during the Sensytech acquisition, as shown in Figure 40 which represents the Spectra trajectory overlaid on the multispectral image acquired by Sensytech system.

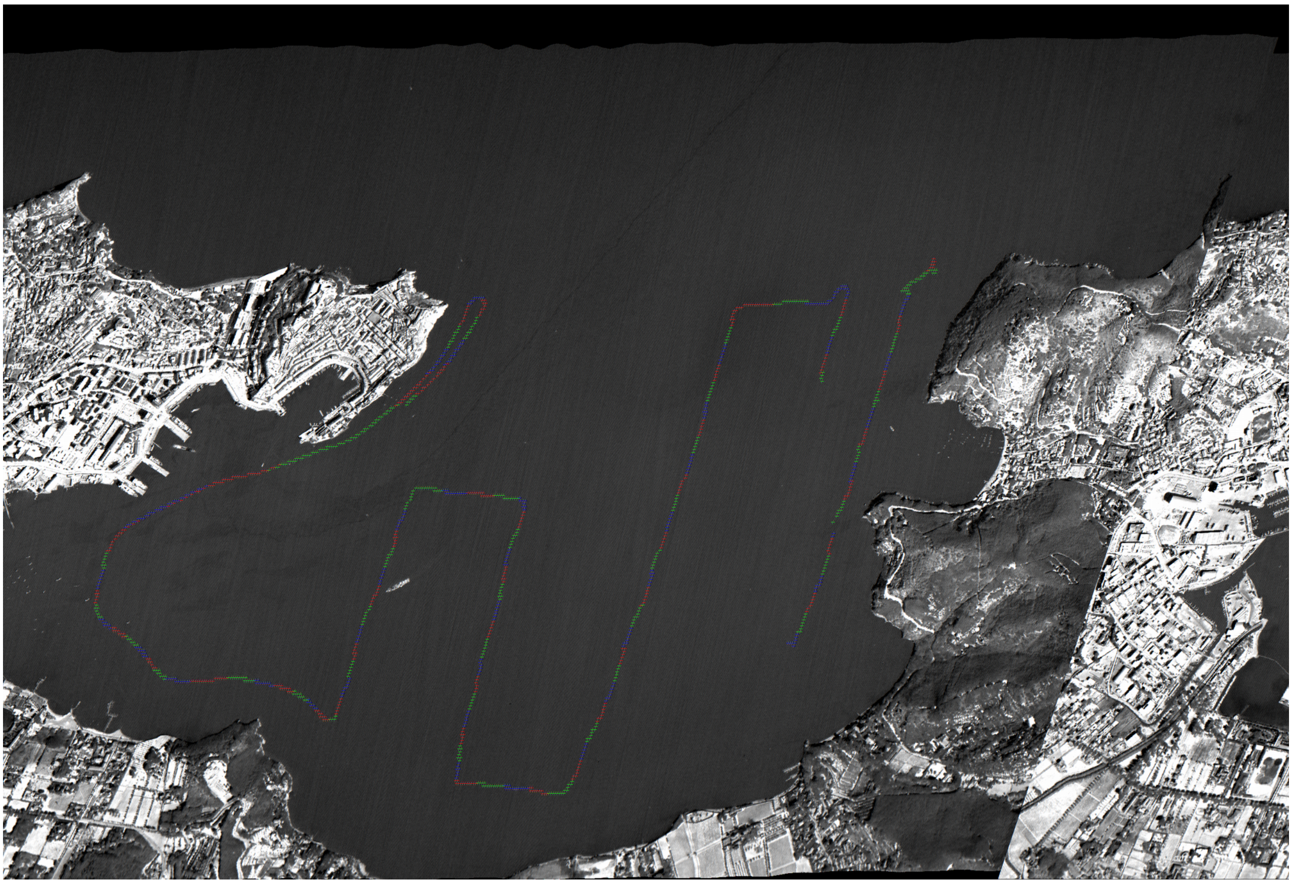

Fig 40 Spectra trajectory overlaid on the n.8 Sensytech section

The Sensitech data were processed by qualified staff of ITCG who obtained georeferenced maps for the each channel acquired by the multispectral sensor. The Spectra temperature and conductivity data were compared with the reference sensors (multiparametric probe Idronaut 316 Plus) used during the survey, while fluorescence of chlorophyll *a* and CDOM were calibrated with the results of water samples analyses. The data were processed with ENVI software which allowed to extract the Sensytech observations corresponding to the Spectra once.

Figure 41 shows an example of temperature data comparison.

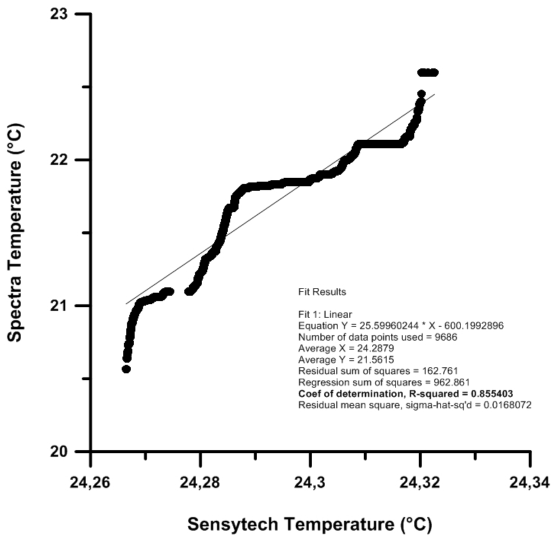

Fig 41 Comparison between Spectra and Sensytech temperature data

The second experiment was performed along the cost of Civitavecchia (Latium, Italy) on 20th August 2016, and it was focused on the acquisition of Spectra data during the Landsat 8 OLI passage.

Fig 42 Landsat 8 OLI image

The Operational Land Imager (OLI) measures in the visible, near infrared, and short wave infrared portions of the spectrum and has a 16-day ground track repeat cycle. The images have 30 m multispectral spatial resolutions along a 185 km wide swath, covering wide areas of the Earth's landscape and providing a good resolution to distinguish several features. The data were processed through Acolite software, which was specifically developed for Landsat 8 OLI including the atmospheric correction procedures and a collection of algorithms to obtain different products such as chlorophyll *a* or turbidity.

The Spectra was installed on board a little coastal vessel and continuously acquired surface temperature, conductivity, chlorophyll *a* and CDOM fluorescences, turbidity and water samples. Figure 43 represents the Spectra trajectory overlaid on the multispectral image acquired by Landsat 8.

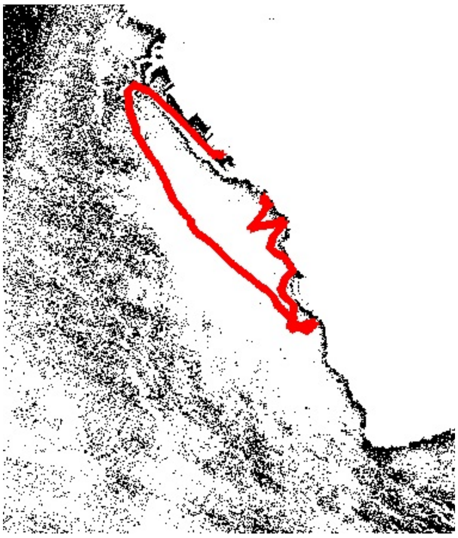

Fig 43 Spectra trajectory overlaid on the Landsat 8 cholrophyll *a* image

7. CONCLUSIONS

Knowledge and understanding is the key to sustainable development and good ocean governance. Everyday new knowledges and technologies emerges in all marine science sector to facilitate a better understanding of the world in which we live.

New innovative tools provide an array of possibilities which can be used to add value to traditional marine sectors, such as seafood, fisheries and aquaculture, maritime safety and transport, blue biotechnology and environmental protection, monitoring and assessment, providing solutions to prevent and forecast climate change and marine pollution.

The routine generation of ocean climate products will provide essential ocean data for global climate and weather models needed by both scientific community and governments. All actions are technologically feasible and can be accomplished with established coordination mechanisms and agreements. An integrated and coordinated approach is also essential for meeting the requirements of european environenmental policy toward a .sustainable Blue Growth

Infact the major weaknesses of the current marine observing system are the lack of global coverage of the ocean, the need for autonomous and remote instruments for the entire oceanic variables list, particularly the biological and biogeochemical once, the need for expanded and more effective data and product systems, and the need for long-term continuity of national efforts along with international coordination. Present global effort depends heavily on the efforts and funds of the research community so a continued research is required to improve and develop observing capabilities and to make systems more robust and cost-effective.

Though many advances have been made in the technological innovation for the study of the seas and oceans, nowdays there is still an increasingly need for technological development, both as regards the development of measurement platforms and so far with respect to the innovative sensors. In fact, in most cases, either the measurement platforms are still too costly or they are limited in the use by the operational capabilities (eg, autonomy, depth, etc..).The big effort applied to the development of new measurement platforms is needed also for the development of new sensors, especially for the physical measurement of biological variables.

These developments must take into account the spatial and temporal scales of oceanographic phenomena, but also the cost-effectiveness in order to be efficiently used like sea truth for satellites data and to be assimilated in mathematical models, that require large amounts of data for their calibration/validation. This point is particularly valid for the biological measures. In fact, many solutions are still to be explored both for the measurement of nutrients and for the measurement of bio-optical variables, able to measure the optical absorption of light by phytoplankton.

This thesis work was focused on the improvement and application of new low-cost sensors and platforms developed to measure the principal physical and biological variables of marine water, in order to study pelagic and coastal marine processes and dynamics at different temporal and spatial scales. The general objectives of this research were to meet the specific measurement requirements and lack that the ocean observing international programs identify like priorities.

The technologies shown in this research work bornt with the aim to realize:

- a modular measurement technology, cost-effective and user-friendly, available for different measurement platforms;
- a measurement platform for the study of surface marine water with high spatial and temporal resolution, which could be used also for the validation of remote sensing data;
- an accurate system which could give important and fast informations on marine phytoplankton dynamics both of pelagic and coastal ecosystems.

Despite the lower prototype costs, the measurement accuracy of the different variables is very high and comparable with standard commercial instrument and reference toolss. A comparison between the data acquired by the new technological developments and traditional probes yields strong consistency, satisfying the resolution requirements for the description of the physical and biological structures with good accuracy.

The expendable and the vertical profiler were shown to be capable of identifying the distribution of phytoplankton populations along the water column both in eutrophic and oligotrophic marine waters. The in situ application of the Spectra prototype confirmed the validity of the measurement system developed for temperature, conductivity, Chla and CDOM fluorescence acquisition on the surface layer of the sea, which can be a useful tool for calibrating and validating remotely sensed data and mathematical models.

These technological solutions were specially designed to be used onboard ships of opportunity and for the implementation of oceanographic monitoring networks, in order to improve the quality of operational oceanography products. The availability of extended datasets is fundamental to our understanding and forecasting of physical and biological marine processes.

Incorporating such innovative tools in our marine observational arsenal, we can begin to realise aims and objectives of the Integrated Maritime Policy, the Marine Strategy Framework Directive (MSFD) and the Europe 2020 Strategy and consolidate Europe’s role in global ocean developments and governance, allowing to find relevant solutions to prevent and forecast climate change and marine pollution.

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