



ADAPTIVE MICROFLUIDIC - AND NANO - ENABLED SMART SYSTEMS FOR WATER QUALITY SENSING

Flash study

The need for water monitoring in oceans



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Table of content

Introduction	4
1. Ocean monitoring: a field of increasing interest	5
2. Multi-sensors platforms	6
3. New developments and remaining issues.....	8
4. PROTEUS carbon nanotube approach	9
Conclusion	11
References	12

Introduction

In 2017, climate change and global warming are a widely-acknowledged reality, from which the ocean equilibrium suffers. Even though ocean ecosystems have been extensively studied for decades, we still do not have enough data to fully understand how they are impacted by human activities. The scarcity of data is mainly due to the fact that monitoring systems – buoys, multisensors platforms, gliders...- suitable for use in oceans are very expensive to deploy and maintain.

Lately, the development of lower cost sensing platforms with lower energy-consumption is opening up a wide range of new opportunities for sea water monitoring. Smaller ecosystems can be investigated, denser network of sensors can be deployed, and more parameters can be monitored.

The H2020 European project PROTEUS is developing a cutting-edge water monitoring sensor based on carbon nanotube technology. We believe that this kind of highly sensitive, low cost and low energy sensor will accelerate even more the development of a global sea water monitoring network.

1. Ocean monitoring: a field of increasing interest

In a 2001 Science publication, Levitus et al. raised a lot of concern and controversy (Levitus et al., 2001) when demonstrating for the first time that the anthropogenic gases in Earth's atmosphere cause an increase in ocean temperature. In 2005, this result was confirmed by Hansen et al. based on precise measurements over 10 years showing increasing ocean temperatures between 1995 and 2005 (Hansen et al., 2005). The Earth's energy imbalance was calculated and a first estimation of global warming by 0.6°C was proposed. Today, the global warming is estimated between 2°C and 6°C at the end of the 21st century and, together with climate changes, it is an uncontested fact for the scientific community. It is also acknowledged by most governments, as the 2015 Paris Agreement shows.

To understand the complexity of the global warming of the ocean, which has a direct impact on climate changes, ocean monitoring has become a major field of interest. Despite the importance of accurately deriving the thermal energy of the ocean, it remains a challenging problem for climate scientists (Abraham et al., 2013). Accurate temperature measurements covering extensive spatial and temporal scales are required for a determination of the energy changes over time. While there have been significant advances in the quantity and quality of ocean temperature measurements, coverage is not yet truly global. Furthermore, past eras of ocean monitoring have provided extensive data but variable spatial coverage.

Temperature increase is not the only consequence of CO₂ rising. Ocean acidification is also a major problem due mainly to human fossil fuel combustion (Doney et al., 2009). The reduction of ocean pH causes shifts in seawater carbonate chemistry: it alters seawater chemical specification and biogeochemical cycles of many elements and compounds. One well-known effect is the impact on shell-forming marine organisms from plankton to benthic molluscs and corals.

Probably as a consequence of global warming and rising CO₂, transient phenomenon like Harmful Algae Blooms (HAB) are also more frequently observed (Visser et al., 2016). The HAB can cause death of fishes in a large area, either because algae are toxic, or more frequently because the quantity of the algae is so dense that the fish lack of oxygen in water. The increase of anthropogenic nutrients (fertilizers, sewage, animal wastes, coastal aquaculture) is also likely to favour the appearance of HAB (Davidson et al., 2014). But the localisation, coverage and frequency of these phenomena is still very difficult to apprehend (Paerl and Otten, 2013). Scientists cannot predict where they will appear and for how long - sometimes for a few hours only, and they are in demand for global ocean monitoring systems to understand these transient phenomena.

Following scientific work, public awareness has strongly risen. Oceans are back to being considered "national wealth". Henceforth seawater quality and its impact on the ecosystem has also become a major interest for the governments around the globe (Karydis and Kitsiou, 2013). For instance, heavy metals, organometallic compounds, oils and hydrocarbons, pesticides are regularly monitored.



2. Multi-sensors platforms

To understand the climate change, we need a global *in-situ* observation system. Since the 1950s, neutrally buoyant floats have been used under various forms to explore and to discover many aspects of the ocean water circulation (Gould, 2005). Launched in 2000, Argo¹ is the first-ever global, *in-situ* ocean-observing network in the history of oceanography, providing an essential complement to satellite systems to observe, to understand and to predict ocean and global climate changes. Argo project - a consortium of 30 countries - deployed a global array of 3,000 autonomous profiling floats measuring in real time and every 10 days temperature and salinity throughout the deep global oceans, down to 2,000 meters. They are expensive to deploy and to maintain as a single buoy cost between 15 and 20 k€ per year but they offer high precision measurements that are crucial for ocean monitoring.



Figure 1- Argo float being deployed in sea (©ABC Radio Australia)

Later were developed the underwater gliders (Rudnick et al., 2004). They are autonomous vehicles that achieve vertical profiles of parameters by controlling buoyancy and by moving horizontally on wings. They constitute a good approach to achieve the subsurface spatial and temporal high resolution necessary for ocean research. They yield information like the ocean's thermal stratification and can also make samplings (Rudnick and Cole, 2011). More expensive than Argo floats (between 50 and 70 k€), they demand a big infrastructure to deploy them. Figure 2a and 2b show pictures of two different gliders.



Figure 2 - The gliders (a) The underwater glider Spray (b) The towed vehicle SeaSoar (Rudnick, 2011)

¹ <http://www.argo.net/>



The need for *in-situ* observations is not limited to chemical parameters. Marine microorganisms are central to biogeochemical process that can be perturbed by climate change (McQuillan and Robidart, 2017). Today, ocean-deployable sampling and sensing instrumentation is generally too large, complex and expensive for wide-spread use. Figure 3a shows a sampling system designed to collect geochemical and microbial samples from the rising portion of deep-sea hydrothermal plumes. Figure 3b shows an Environmental Sample Processor for HAB detection with filtration, rRNA and protein hybridization and gene quantification. Their deployment demands a huge infrastructure and has a high cost (up to 200k€).

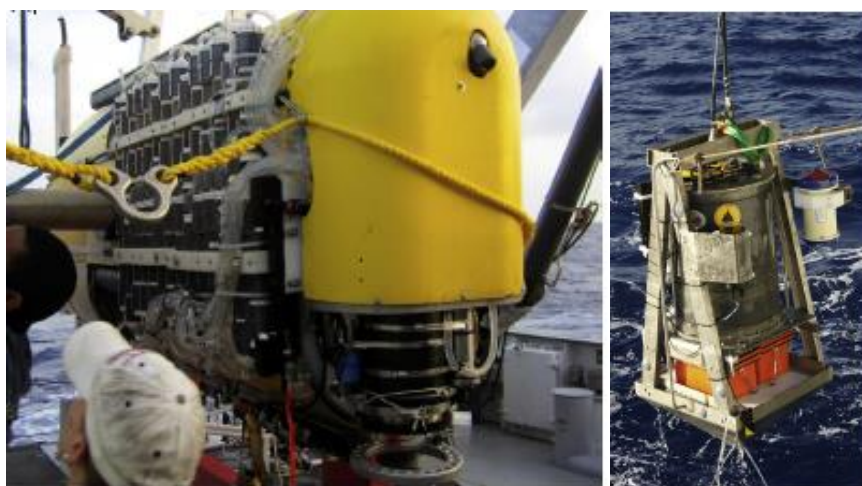


Figure 3 – (a) Suspended Particulate Rosette on HROV Nereus during the 2013 Cayman cruise led by C.R. German (b) Environment Sample Processor drifter from BioLINCS cruise, September 2011 (McQuillan,2017)

3. New developments and remaining issues

Today, one of the most innovative aspects of oceanographic research is the development of low-cost instrumentation (Marcelli et al., 2014). As low-cost instruments can be installed on existing platforms or on marine buoys, multi-parameters platforms are no longer reserved to high-level research programs. Small ecosystems, particularly vulnerable to the effects of human activity, can also be studied at lower cost. In 2012, a low-cost multi-sensor buoy was deployed in the Mar Menor lagoon, close to Carthagena in Spain (Albaladejo et al., 2012), and is still operational today. This buoy is communicating with radio frequency and has thus a lower energy consumption than the platforms communicating via satellite. On the other hand, low-cost instruments are less sensitive, less precise and their life time is smaller. That's why, to study an ecosystem with low-cost instruments, it is crucial to significantly increase the number of devices to have a good spatial and temporal coverage in order to seize the changes that can occur in water.

The availability of high frequency water quality measurements is also catalysing new understanding of the ocean (Rode et al., 2016). While traditional laboratory sampling has increased in the last 50 years, the transformation of ocean science is due to increasing availability of automated *in situ* sensors. Available sensor technologies have been extended through the development of methods such as optical or flow cytometry techniques, through advances in field deployment engineering (antifouling, batteries, micropumps), and through new electronics (detectors, emitters) with reduced costs. This has increased the number of sites at which *in situ* measurements are now achieved as well as the frequency of data collection.

Miniaturisation has also been a major area of improvement with the development of “lab-on-chips” systems (Jang et al., 2011) – a combination of microfluidic and sensor chip, with fluidic and electrical interfaces. Laboratory analyses of field-collected samples are achieved at lower effort and cost using such types of electrochemical-based portable monitoring systems. They can be brought in oceanographic campaigns or installed near contaminated sites for quick analyses. Despite the considerable technology breakthrough, they represent, they are still usable only on sampled water, not for in-situ continuous monitoring.

In conclusion, the overall issues in the sea-water monitoring field are the following:

- The actual cost that can go up to 200k€ for a single multi-sensor platform.
- The complexity of the sensors that request high sensitivity
- The need for multi-parameter measurements which can increase the cost with purchase of several expensive probes
- The need for chemical measurement but also bio-related measurement



4. PROTEUS carbon nanotube approach

Carbon nanotubes based chemical sensors have been widely studied for their high sensitivity and the large range of detectable analytes. Their main drawback is the lack of selectivity, because carbon nanotubes respond similarly to a wide range of different analytes. To counter this, functionalization of the carbon nanotubes is the classical approach: the functionalization is tuned to the target analyte, while the carbon nanotubes themselves act as highly sensitive transducers.

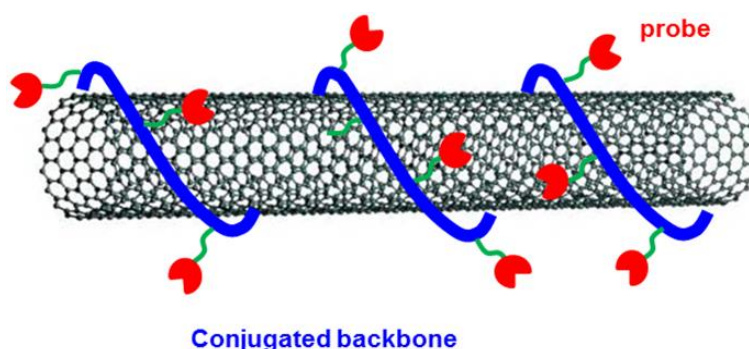


Figure 4- Non covalent functionalization of carbon nanotubes by conjugated polymers for selective sensing.

LPICM (joined research unit between Ecole Polytechnique and CNRS) and IFSTTAR have developed a patented chemical sensing strategy, where new functionalization molecules can be easily proposed for any given analytes based on a conjugated polymer backbone. When associated with carbon nanotubes, the result is a wide range of highly sensitive and highly selective chemical sensors.

This approach was tested along the course of the H2020 Proteus project on drink water quality monitoring: ohmic sensors based on percolating networks of functionalized carbon nanotube were elaborated by ink-jet printing. Using ink-jet printing yields strong process stability in an easily upscalable approach. The resulting devices showed sensitivity and selectivity to pH as well as chloride and hypochlorite ion concentrations, validating the global approach.

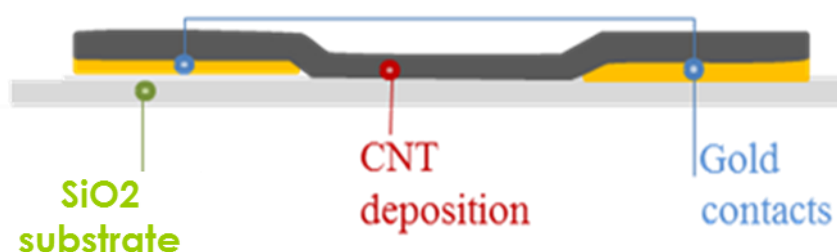


Figure 5-Side view of an ohmic carbon nanotube sensor



In addition, the devices PROTEUS proposes respond to all criteria in terms of low cost, possibility of multiplexing as well as compatibility with various technological processes (for cointegration). Such sensors work under low-operating voltages (a few volts), they can be made at low-temperature processing (and especially low-cost processing techniques such as printing), and they have a good mechanical flexibility.

The current limitation to the technology is the sensitivity of the devices, limited to a few dozens of ppb level by the ohmic transduction scheme. But the sea water use case is much more demanding in terms of sensitivity. To meet this challenge, a direct follow-up of PROTEUS work will consist in exploiting architectures based on functionalized carbon nanotube field effect transistors as an alternative to ohmic sensors. It has been recently shown that field-effect transistor-based sensors provide highly sensitive detection with stability in the marine environment. The sensitivity is notably enough for the detection of heavy metals at a micromolar concentration (Knopfmacher, 2014). Based on this approach, one would expect to achieve precision of ± 0.01 pH unit between pH 7 and pH 9, at temperature ranging from -5°C to 30°C .

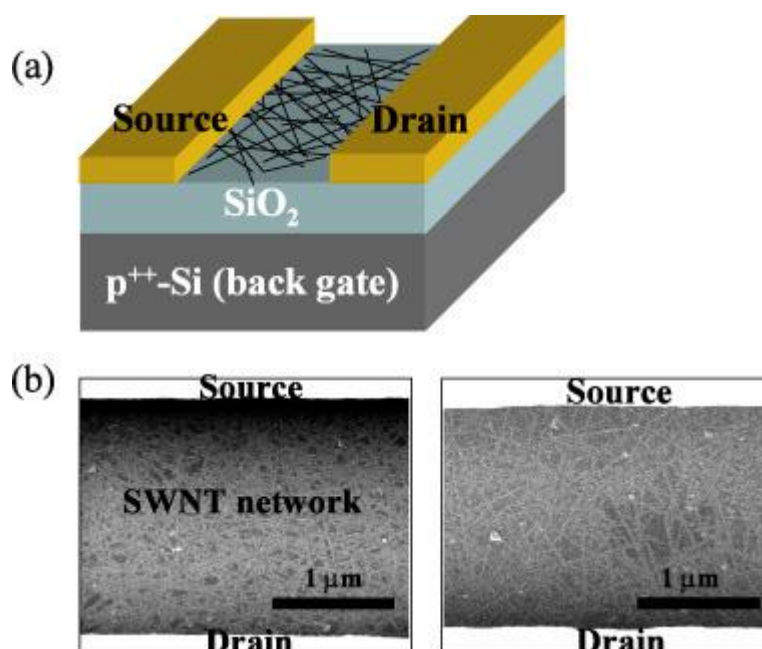


Figure 6-Architecture and SEM image of a carbon nanotube field effect transistor (Hong, 2006)

In conclusion, using a carbon nanotube approach, the answer of PROTEUS to the sea-water monitoring needs is a multi-parameter sensor chip for in-situ measurement with:

- Lower sensor cost, that could be reduced even further by a factor of 50
- Heavy multiplexed chemical measurements (4 different analytes in parallel validated today, over 12 possible over a only 1cm² chip)
- Potential for considerably higher sensitivity (via a transistor approach to be validated)
- Potential for biological measurement (in the development roadmap)

Conclusion

PROTEUS carbon nanotube technology is bringing a new perspective to ocean monitoring challenges. With these cutting-edge sensors, deployments will become possible at larger scale, at lower-cost and will turn into a reality, opening the path toward a fuller understanding of climate change, toward the immediate detection of human pollutions and the protection of coastal ecosystems.

After adapting PROTEUS technology for optimal use in sea water, additional challenges will have to be met, for instance making those sensors more resistant to biofouling, an acute problem in sea water (Delauney et al., 2010). Some solutions already exists (Hsu et al., 2014), which could be combined with PROTEUS carbon nanotube technology. Beyond this, nanomaterial bacteria sensing is a field of major interest (Chen et al., 2017) as we know microorganisms play a key role in ocean equilibrium. Carbon nanotube biosensors are already identified as future challenges to be explored beyond PROTEUS scope.

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