



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

# Flash study

## The need for water monitoring in aquaculture



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# Introduction

In 2014, the world fish supply reached 16.2 million tonnes, which represent 20kg of fish per person (FAO, 2016). It reached a new record, mostly due to the tremendous growth of aquaculture, which provides now almost half of the fish stock (73.8 million tonnes in 2014), while capture production is saturating since 1990 (**figure 1**). Experts all agree that aquaculture will contribute significantly in the future to food security and adequate nutrition for a global population expected to reach 9.7 billion by 2050.

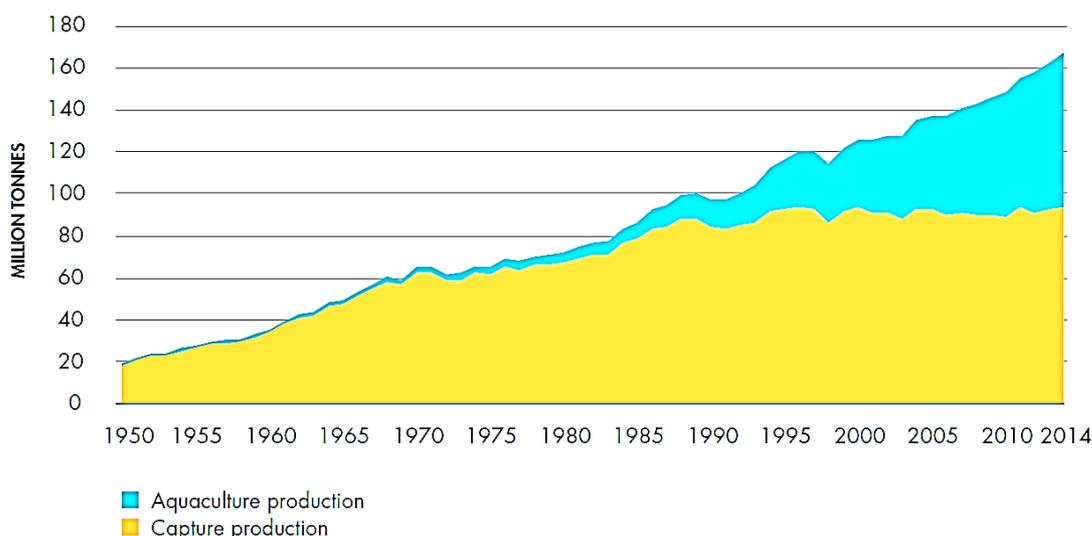


Figure 1 – Global aquaculture and capture fisheries production in million tonnes since 1950 (FAO, 2016)

In a recent study (Merino et al., 2012), authors investigated the feasibility of sustaining current and increased per capita fish consumption rates in 2050 based on extensive data: predictions of changes in global and regional climate, marine ecosystem and fisheries production estimates, human population estimates, fishmeal and oil price estimations and projections of the technological development in aquaculture technology. They conclude that meeting current and larger consumption rates is feasible, despite a growing population and the impacts of climate change on potential fisheries production. However, it is possible only if fish resources are managed sustainably and fisheries management are effective.

The fisheries management relies totally on the water quality monitoring. Fish diseases are very frequent and impact directly the harvesting yield (Lafferty et al., 2015). A low water quality can also impact the fish growth and delay the harvest. Today, the water monitoring systems are very expensive and lack of sensitivity. Implementing and maintaining this kind of system is resources consuming. A lot of small producer choose not to use it and take the risk to get a smaller yield. That is why water quality is the key to success in aquaculture and improve water quality is a big challenge, especially in small fish farms in developing countries.

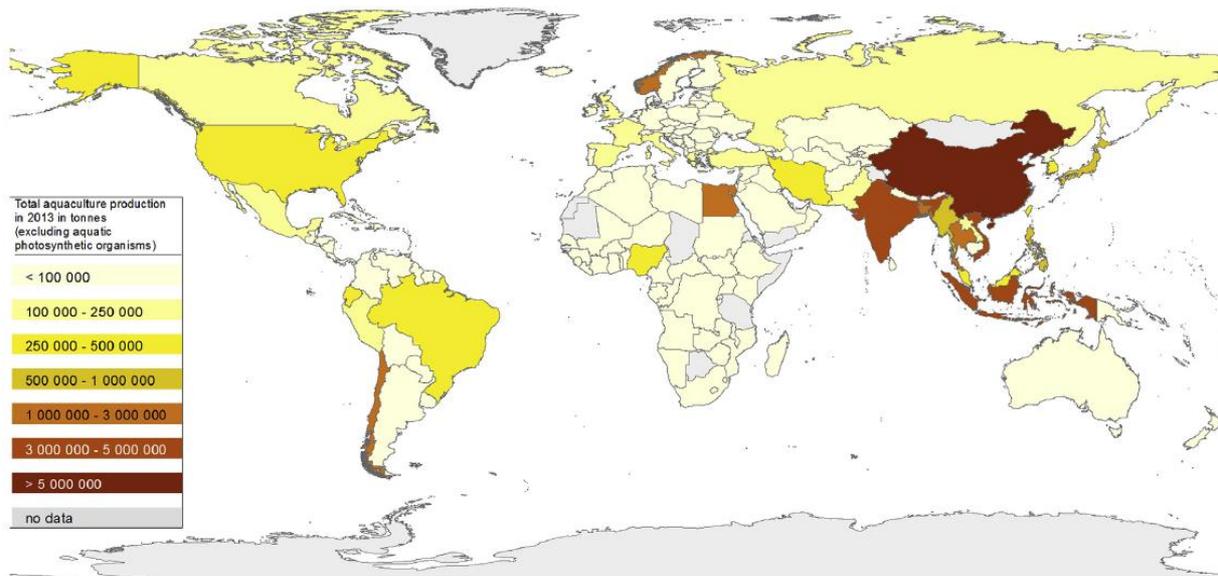


Figure 2- Map of global aquaculture production in 2013 (Ottinger, 2016)

Indeed, aquaculture has exponentially grown in developing countries, especially in Asia where the top 5 aquaculture producers come from (**figure 2**). In these countries, the rapid increase of aquaculture and the high trade shares of aquatic product has induced positive social and economic changes, mainly caused through the creation of employment opportunities (Ottinger et al., 2016). It is also estimated that a large amount is produced by small-scale farmers entering only domestic market (Allison, 2011). Those farmers generally don't have the management capability to monitor the water due to the cost of the water monitoring existing systems.

In this short study, we present the new PROTEUS carbon-nanotube innovative sensors, a highly sensitive multi-parameters sensors that cost up to 50 times less than the current water monitoring systems.

# 1. Water quality: the key to success

Although most aquaculture systems rely on low or uncostly environmental goods and services (Bostock et al., 2010), many different aquaculture systems exists (**figure 3**), from smallholder ponds in Asia and Africa with low investment requirements to commercial, highly industrialized offshore cage farms in Norway and Chile with immense input of feeds and use of advanced technologies (Ottinger et al., 2016).

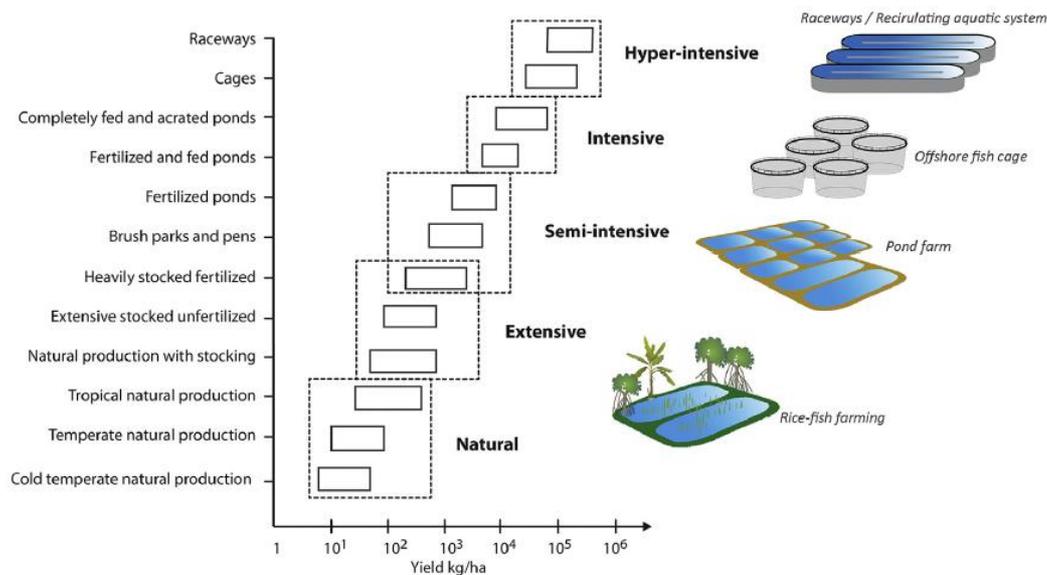


Figure 3- Production from different aquaculture systems (Ottinger, 2016)

Nevertheless, the optimum fish production is totally dependent on the physical, chemical and biological qualities of water (Bhatnagar and Devi, 2013) no matter the type of facility. Therefore, water quality is the key to succeed a good fishery management. It is determined by variables like temperature, turbidity, carbon dioxide, pH, alkalinity, ammonia, nitrite, nitrate, etc...

Amongst them, the most critical are temperature, dissolved oxygen and pH.

Optimum temperature is dependent of the fish species, but as fish are cold blooded animals, it is vital that the temperature is controlled and maintained in the correct range. And even in the correct range, higher temperature increases the rate of bio-chemical activity of the micro biota and so increase the oxygen demand. To limit disease and oxygen consumption, temperature as to be fine regulated.

Optimum dissolved oxygen should always be above 5 ppm. Fish needs enough oxygen in the water to survive, otherwise they stay at the surface to catch up more oxygen, have slower metabolism and grow slower, and ultimately can die of lack of oxygen. It is even a bigger problem for aquatic organism to obtain sufficient oxygen than for terrestrial ones, due to low solubility of oxygen in water.

Optimum pH for fish life is between 7 and 8.5, ideal for biological productivity, otherwise fished can become stressed in water, slowing down their growth.

Many other parameters may be also monitored, but they generally influence directly the 3 main parameters mentioned above. Monitor and control them is the basis of a good water quality. The key is to monitor them in real-time to react quickly.

## 2. Monitoring the water in real-time

Real time sensors for aquaculture are used in both freshwater and sea water. Generally sensors are used to monitor critical environmental parameters such as dissolved oxygen, temperature and pH. They are also used to measure nutrient levels and the build-up of wastes such as ammonia ( $\text{NH}_4^+$ ) and carbon dioxide ( $\text{CO}_2$ ). Such sensors are particularly vital in systems where water is recirculated and where stocking levels are high. To be of most use such sensors are often linked to alarms triggered when parameters such as dissolved oxygen or temperature are measured outside of safe limits. Oxygen sensors can be linked to oxygen or aeration banks to supply supplementary oxygen when needed.

There are a range of environments where sensors are required. In hatcheries or facilities for production of juveniles sensors are deployed within ponds or tanks within buildings. There is usually access to mains electricity, so power is not an issue. The facilities are also weather-proof and easily accessed for servicing and maintenance. At the other end of the range sensors are deployed on floating structures such as net pens or feed barges at sea and on freshwater lakes and ponds. Here they are exposed to weather and tough environmental conditions. In addition there may not be direct access to mains power. In such locations the power consumption of the sensors and of the communication system to relay the data can be a major issue.

In most environments where sensors are deployed there is a potential for fouling of the instruments by both detritus and biofouling organisms. Therefore in all cases the robustness of the sensor and its ability to withstand fouling is a major consideration. Self-cleaning or fouling resistant instruments will have a major advantage followed by those which have a simple and low frequency preventative maintenance programme.

The key considerations for aquaculturalists when considering sensors are as follows:

- Reliability & Accuracy: this is especially true where measuring critical environmental parameters such as dissolved oxygen.
- Cost: aquaculture is a food production industry often operating on tight margins and expenditure of automated equipment needs to have a proven cost-benefit before it will be availed of.
- Maintenance schedules and costs: this has proven to be a major issue with many systems, from feeding systems to sensors and water purification/filtering. New equipment will need to prove itself in terms of length of life and maintenance costs.

PROTEUS innovative sensor respond to this key considerations:

- It is highly sensitive and specific, thus accuracy and reliability can be mastered.
- The cost is up to 50 times less than classical water monitoring system.
- Lifetime of the sensor will be up to 2 years with 24/7 operation and real-time communication, thus reducing the maintenance costs. Moreover, the re-calibration frequency will not be higher than twice a year.

The technology of the PROTEUS sensor is detailed in next section.

### 3. 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.

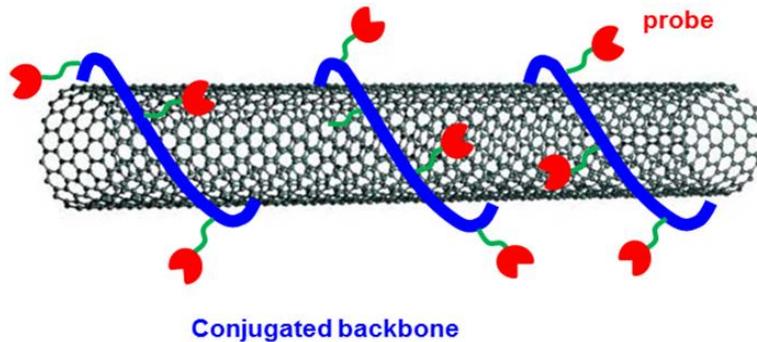


Figure 4- Non covalent functionalization of carbon nanotubes by conjugated polymers for selective sensing.

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.

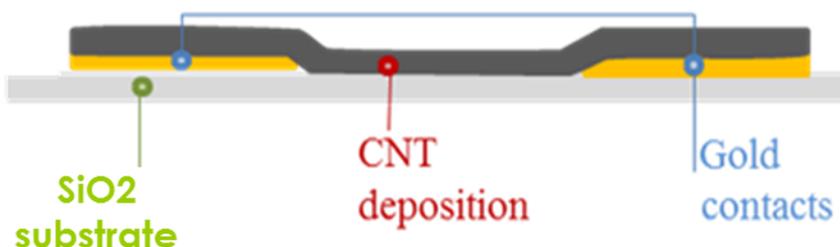


Figure 5-Side view of an ohmic carbon nanotube sensor

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  $\pm 0.01$  pH unit between pH 7 and pH 9, at temperature ranging from  $-5^{\circ}\text{C}$  to  $30^{\circ}\text{C}$ .

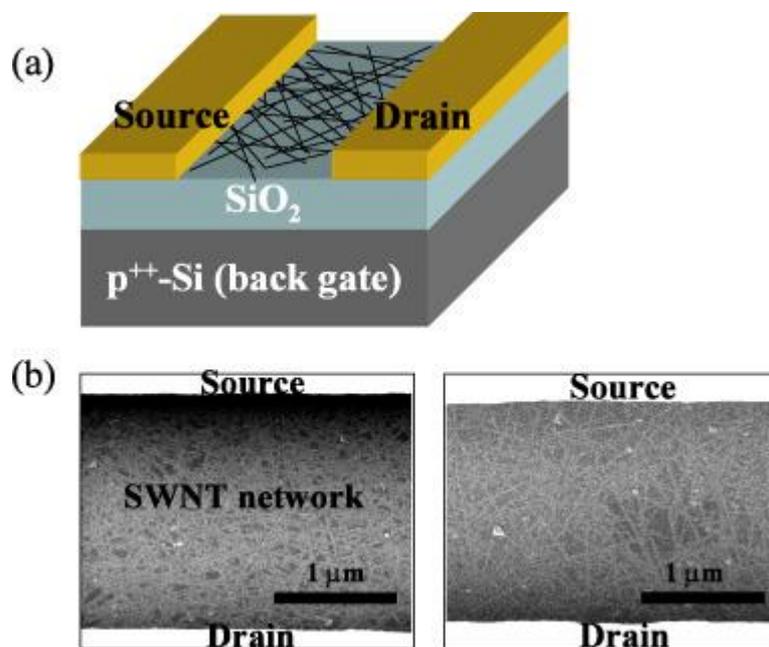


Figure 6-Architecture and SEM image of a carbon nanotube field effect transistor (Hong, 2006)

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  $1\text{cm}^2$  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 sensor is bringing a new perspective in the aquaculture challenge of water monitoring. In 2050 aquaculture is expected to be a major source of feed for 9 billion human. To ensure that the world production is safe and sufficient enough, water quality is fundamental. Most of fish production come from small farms with low investments capacities for complex water monitoring systems. PROTEUS carbon nanotube sensors brings a new possibility for low-cost, high sensibility, multi-parameters water monitoring.

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