An Example: Biofouling Protection for Marine Environmental Sensors by Local Chlorination

L. Delauney (✉) and C. Compère

Abstract These days, many marine autonomous environment monitoring networks are set up in the world. Such systems take advantage of existing superstructures such as offshore platforms, lightships, piers, breakwaters or are placed on specially designed buoys or deep sea fix stations. The major goal of these equipments is to provide in real time reliable measurements without costly frequent maintenance. These autonomous monitoring systems are affected by a well-known phenomenon in seawater condition, called biofouling. Consequently, such systems without efficient biofouling protection are hopeless. This protection must be applied to the sensors and to the underwater communication equipments based on acoustic technologies. This paper presents the results obtained in laboratory and at sea, with various instruments, protected by a localised chlorine generation system. Two other major protection techniques, wipers and copper shutters, are presented as well.

1 Introduction

Monitoring networks commonly use various sensors such as dissolved oxygen, turbidity, conductivity, pH or fluorescence units and, for specific matters, some underwater video systems such as cameras, video equipments and lights. For surface application the data gathered are generally transmitted in real time via satellite and for deep sea application data logger or wired networks are involved. In most cases the monitoring stations are autonomous, especially concerning the energy needs.

In addition to the numerous environmental monitoring stations used along continents, some specific measuring stations are deployed for other purposes in some specific areas where biofouling is very much present.

L. Delauney
Ifremer–*In Situ* Measurements and Electronics, B.P. 70, 29280, Plouzané, France
e-mail: laurent.delauney@ifremer.fr

Springer Series on Biofilms, doi: 10.1007/7142_2008_9

For example, systems for the monitoring of polluting wrecks (Marvaldi et al. 2006) are based on autonomous and real-time stations deployed in order to measure critical data nearby wrecks and to transmit them. These stations are equipped with conventional seawater physicochemical sensors and with acoustic transducers for underwater data communication (for an example, see Fig. 1). They are generally deployed from 15 m depth down to whatever is needed, and for long-term monitoring they are deployed for 1 month up to 6 months during which no maintenance is possible.

For deep sea research, down to 3,000 m, specialized autonomous stations measure physicochemical parameters and record pictures and movies. Some areas of interests are, for example, fumes of hydrothermal sites (Sarrazin et al. 2007). For these applications the autonomy must be provided up to 1 year. The compactness of these stations is crucial, since the equipment is deployed by a remotely operating vehicle.

These autonomous monitoring systems are affected by a well-known phenomenon in seawater condition, called biofouling. The major goal of these equipments is to provide in real time reliable measurements without costly frequent maintenance. In deep sea conditions this maintenance is nearly impossible to provide. For coastal applications it is quite well accepted now, that for economically viable in situ monitoring systems, the maintenance must not be performed more frequently than 2 month (Blain et al. 2004). Consequently, such systems without efficient biofouling protection are hopeless. This protection must be applied to the sensors and to the underwater communication equipments that are based on acoustic technologies.

Biofouling in seawater, during productive period, can occur very rapidly and lead to poor data quality in less than 2 weeks. As shown in Figs. 2 and 3, the biofouling species involved differ very much from one location to another (Le Haitre et al. in press).

Very often, this biofouling gives rise to a continuous shift in the measurements. Consequently, the measurements can be out of tolerance and the data become useless. Video systems such as cameras, video equipments and lights are also

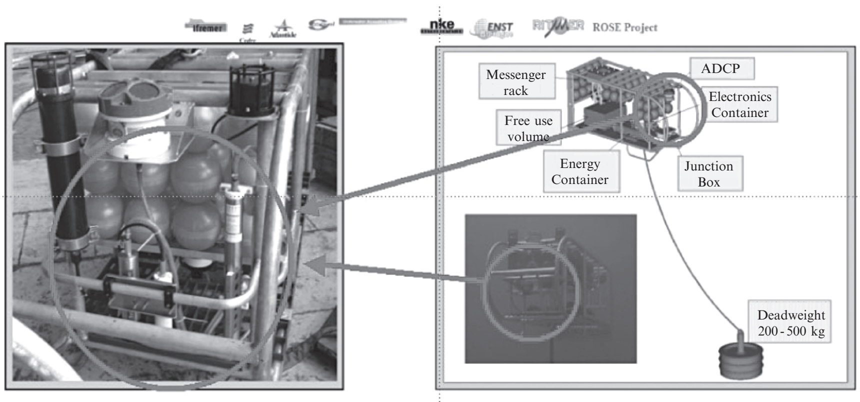

Fig. 1 Autonomous monitoring station for polluting wreck surveillance (Ifremer – ROSE project)

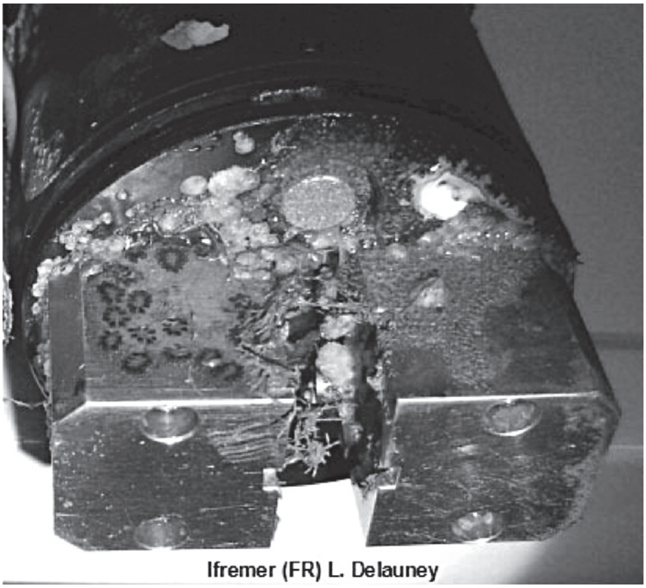

Fig. 2 Fluorometer after 30 days in Helgoland (Germany) during summer

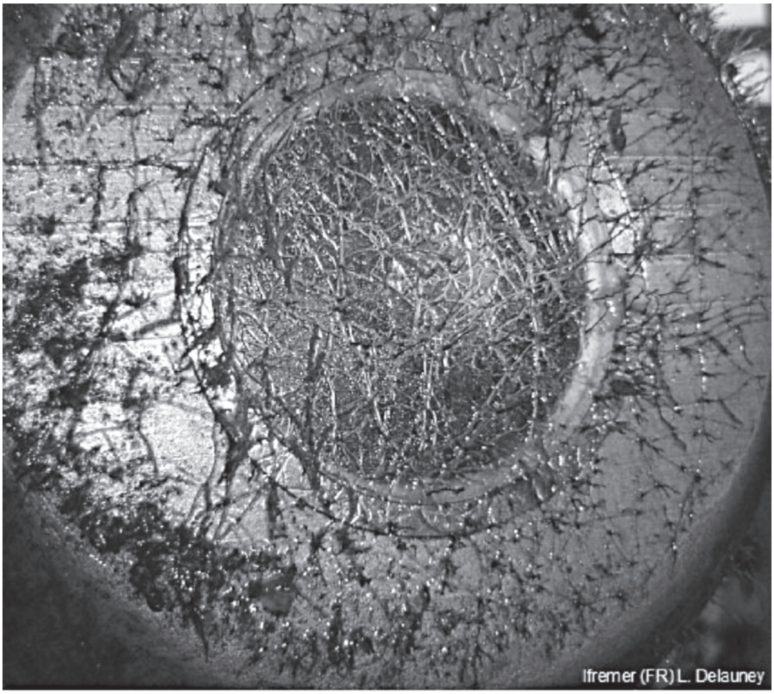

Fig. 3 Transmissometer after 40 days in Throndheim harbour (Norway) during summer

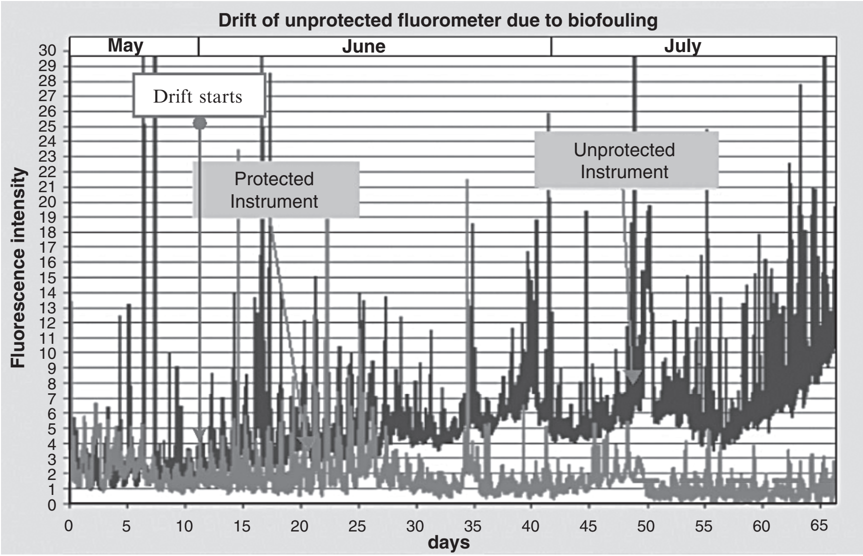

Fig. 4 Drift of an unprotected fluorometer due to biofouling development on the optics

compromised by biofouling. Pictures become blurred or noisy, and lights lose efficiency since their intensity decreases because of the scattering effect of biofilm and macro-fouling.

As shown in Fig. 4, after 7 days, owing to biofouling on the sensitive part of the sensor, a drift can be observed in the measurements produced by a fluorescence sensor (Delauney and Cowie 2002). This kind of optical sensor is very sensitive to biofouling since even a very thin biofilm on the optics interferes with the measurement process and gives rise to over-evaluated measurements.

2 Biofouling Protection Methods for Oceanographic Sensors

Biofouling protection for oceanographic sensors is a difficult task requiring specifications driven by three important characteristics:

1. It should not affect the measurement.
2. It should not consume too much energy in order to preserve the initial autonomy of the autonomous monitoring system.
3. It should be reliable even in aggressive conditions for technological systems (seawater corrosion, sediments, hydrostatic pressure, etc.).

Consequently, few techniques are actually used, and none of them are based on an antifouling paint because the area to be protected cannot be coated with any opaque substance.

Otherwise the measurements taken by the sensor can be completely compromised. We must know that the goal of a biofouling protection is to limit as best as possible the growth of biofouling on the sensitive part of the sensor. For every type of sensor, such as optical sensors (fluorometer, turbidimeter, transmissometer, dissolved oxygen), membrane sensors (pH, dissolved oxygen) or electrochemical sensors (conductivity), the interface between the media to measure and the sensitive area of the sensor must remain clear.

Currently, three biofouling protection systems for oceanographic sensors are in use for operational deployments:

4. Strictly mechanical devices – wipers
5. An "uncontrolled" biocide generation system based on a copper auto-corrosion mechanism
6. A "controlled" biocide generation system based on a localized seawater electro-chlorination system

These three techniques are commonly used on oceanographic sensors, each having both advantages and disadvantages.

2.1 Mechanical In Situ Wiper Systems

Biofouling protection system using wipers are based on a mechanical process that has to be adapted to the instrument from the early stages of design. Consequently, such systems can be found on the instruments if the sensor manufacturers have taken biofouling problem into account. Figure 5 shows such a biofouling protection system based on wipers on a commercial multiparameter probe (YSI 6600 EDS).

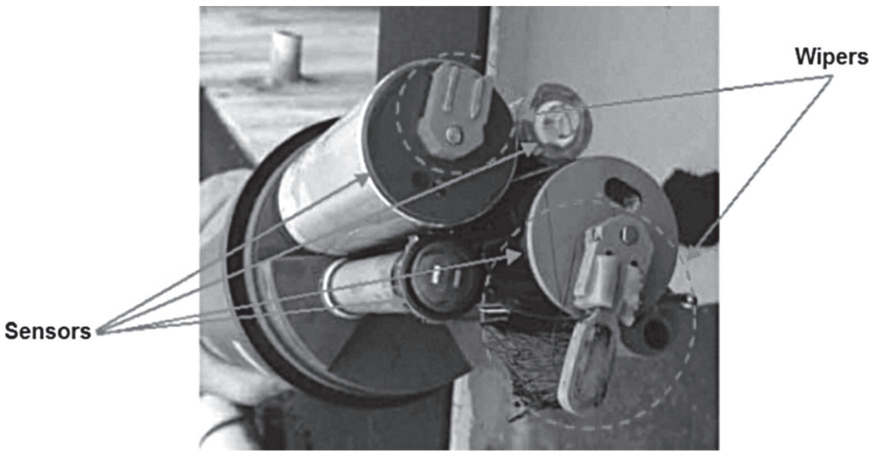

Fig. 5 Multiparameter probe with a mechanical biofouling protection based on wipers (photo: L. Delauney, Ifremer, France)

Fig. 6 Wiper biofouling protection after 150 days of operation (photo: L. Delauney, Ifremer, France)

The device consists of two distinct wipers that use three "scrapers". Two of them are made of sponge and directly wipe the sensors' optical interfaces for fluorescence and turbidity measurements and a brush with long bristles has been implemented to clean the non optical sensors such as pH and oxygen sensors that are based on membrane techniques.

This biofouling protection technique is effective as long as the scrapers are in good condition and as long as the geometry of the sensor head is suitable for this cleaning process. The problems with this technique are mainly the mechanical complexity of the system. The water tightness of the wipers' axles as well as the short-term robustness of the wiper motion device are major weaknesses. As said earlier, sensors with a non-flat measurement interface, as shown on top right of Fig. 6, cannot be protected with this technique. Currently, sensor manufacturers are searching for new, alternative biofouling protection techniques to simplify their instruments and consequently to improve their reliability.

2.2 Biofouling Protection by "Uncontrolled" Biocide Generation: Copper Release

Copper is known for its biocide properties (Manov et al. 2004). As copper corrodes in seawater, oxidized molecules are released into the water rather than remaining on the metal surface. Copper interferes with enzymes on cell membranes and prevents cell division.

Copper is toxic at high concentrations, and to achieve this, the principle is to catch in a "copper cell" a small volume of seawater on the sensor measurement interface. In this way, the sensor interface will be in contact with a solution having increasing concentration of Cu^{2+} ions as long as the cell is closed.

Many manufacturers use this protection technique. Some of them build the sensor head totally in copper and add a wiper system to scrap the optics.

A specific equipment can be found that allows to equip any sensor with a copper cell system more commonly named a "copper shutter." A motor drives the mechanism for shutters that open for measurements and close for biofouling protection over the optical windows. It keeps the sensor very close to the copper system releasing toxic copper, and the closed cell allows darkness, thereby reducing biofouling.

Such protection is not easy to implement on an existing sensor. The copper screen with the stepper motor needs to be placed on the sensor in a way that the copper screen includes a small volume of water over the sensor measurement interface. An example of such a system on a Seapoint fluorometer is shown in Fig. 7. To maximize the effectiveness of the protection, it was necessary to implement a copper cell and to coat the entire sensor head with copper.

Results obtained with such a system (Delauney and Compère 2006), when the implementation is made exactly as described earlier, can be satisfactory for long-term deployment. The optics remained clean during the 3 months of deployment in coastal area in Brest (FR) and during summer season.

Some results obtained with copper tubing and copper shutter on optical instruments are presented by Manov et al. (2004). They conclude that "copper-based antifouling systems have shown marked improvement in obtaining long-term dataset for acquisition of optical measurement."

However, this method can lead to the following problems:

- Copper corrosion produces copper oxide precipitates, which can interfere with the measurements.
- Copper corrosion produces bubbles on the copper-coated surfaces, which are trapped in the copper cell close to the measurement interface. This can interfere

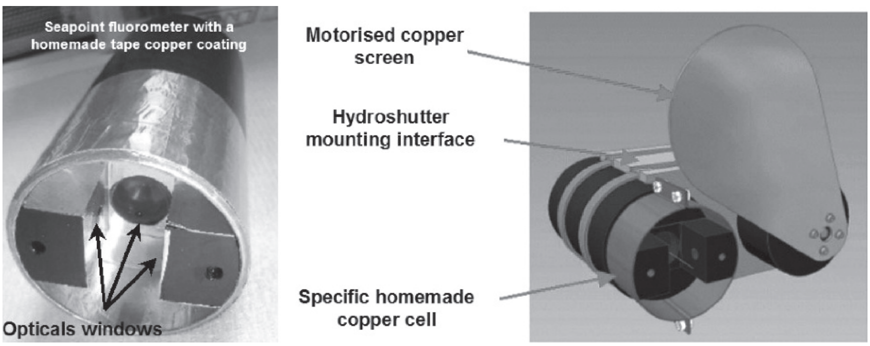

Fig. 7 Biofouling protection with a HOBI Labs copper shutter HydroShutter-HS (HOBI Labs, http://www.hobilabs.com) (photo and drawing: L. Delauney, Ifremer, France)

with the measurements, especially if the sensor is based on an optical technology. Bubbles are trapped easily since the system is based on a closed cell.
- When the copper screen is closed, it is of course impossible to take any measurements. The screen must be closed for sufficient time in order to get an effective protection, but then, it is impossible to take high-frequency measurements. And actually, with the wide band data transmission systems getting more and more common, and because of tide duration for which scientists need a good time resolution, copper shutter can be a limitation.
- The mechanical system involved is quite fragile. It is based on a stepper motor that cannot tolerate any mechanical obstacles; otherwise, the fragile gear box system will break. Consequently, the copper screen must be adjusted very precisely in order to fit sufficiently watertight to the copper cell. Any misplacement of the copper screen with the copper cell can lower the biofouling protection or interfere with the mechanism.

2.3 Biofouling Protection by "Controlled" Biocide Generation: Localized Seawater Electro-Chlorination System

This technique is the adaptation for biofouling protection of in situ oceanographic sensors, of a largely used technique to protect seawater cooling system for industry (Satpathy 2006). For our application, only the sensor transducing interface area will be protected, which explains the term "localized." Biocide generation is obtained by seawater electrolysis. With this technique, we can achieve a powerful biocide generation, hypochlorous acid, which can be concentrated as best as possible, on the sensor transducing interface area.

This technique has many advantages:

- Biocide generation is controlled. Consequently, the biocide quantity can be adjusted and on/off periods can be arranged as needed. On/Off periods are useful in arranging biocide-free periods so as to obtain the measurements in good environmental conditions. Moreover, the control of the biocide generation intensity is very important in order to adapt the biocide generation in function of the biofouling colonization.
- The energy needed for such systems is fully compatible with autonomous coastal monitoring systems and deep sea autonomous monitoring stations.
- The system is very robust and reliable since no mechanical parts are in motion.
- The system is easily adaptable to existing sensors even for usage at high depth.
- The system can be integrated to the sensors by manufacturers.

As shown in Fig. 8, the system is made of an electrode placed around the sensor transducing interface area, in this case the optic. This electrode is connected to an electro-chlorination unit. This unit can be a separate electronic container as shown in Fig. 8 or can be integrated inside the instrument.

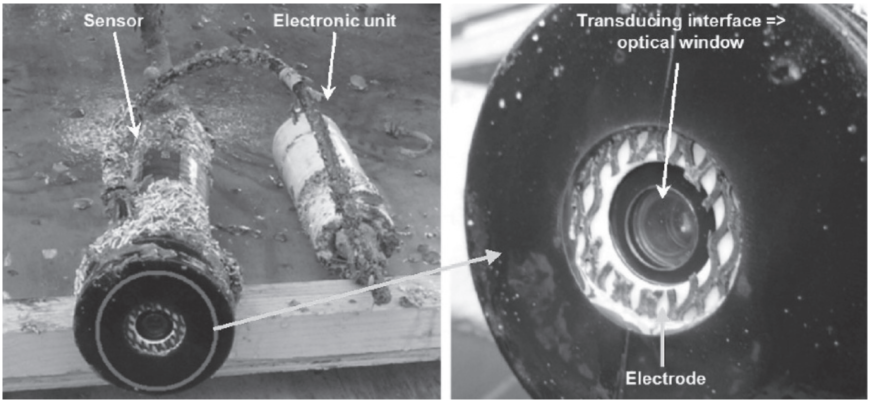

Fig. 8 Biofouling protection of a fluorometer by localized seawater electro-chlorination (©Ifremer) – Protection system under Ifremer licence – NKE, Hennebont (56), France (photo: Ifremer, France)

This biofouling protection technique has been successfully used for many in situ coastal monitoring systems (Delauney et al. 2002) even immersed at low depth, 2 or 3 m, where biofouling development is intense (cf. Fig. 4), as well as for medium-depth (15–100 m) stations (Marvaldi et al. 2006) or even for high-depth stations down to 2,000 m where biofouling can appear close to hydrothermal vents (Sarrazin et al. 2007).

3 Localized Electro-Chlorination Biofouling Protection Results

The local chlorination technique was applied on various instrumental technologies, optic (turbidity, fluorescence, oxygen), electrodes (conductivity) and glass membrane (pH). For every test, in the laboratory or at sea, two sensors were placed simultaneously, one unprotected and one protected by the local chlorination device. The measurements were internally recorded or when possible recorded by a laptop for real time data analysis. When possible, some water was sampled and reference analysis was done in order to follow the eventual drift of the sensors in real time.

3.1 Determination of Possible Interference of Electro-Chlorination with the Measurement

Before implementing the system on the instruments, it is necessary to check possible interfering effects on the measurements. Electrodes in the vicinity of a sensor may perturb measurement. Consequently, a “Laboratory check” and a specific calibration is necessary. In the same way, biocide molecules can interfere with membranes or induce local water property modifications, and this effect must be studied even if it can be overcome by scheduled chlorination.

All instruments have been tested in the laboratory with standard solutions or standard analytical methods in order to calibrate the signal of a protected instrument vs. an unprotected one (Delauney and Compère 2006). Depending on the parameter measured, the following standard methods were used:

- Oxygen: Winkler titration (Aminot and Kerouel 2004)
- Fluorescence: Ifremer Fluorescein protocol (Delauney and Le Guen 2003)
- Conductivity: natural seawater sampling and Reference Guildline salinometer analysis (Aminot and Kerouel 2004; Fofonoff and Millard 1983)

The laboratory check for interference of chlorine with the measurement consists in comparing the responses of two instruments, one of them equipped with the local chlorination device. Two steps are involved. The first one determines the adverse effect of the local chlorination hardware. This can possibly be overcome by a specific calibration. The second determines the adverse effect of the chlorine generation, which can possibly be overcome by a scheduling of the chlorination generation.

3.2 Biofouling Protection Field Test on Conductivity Sensor

Local chlorination protection device was tested on the conductivity instrument at St. Anne du Portzic, Brest, in France. Two instruments were placed on site, one protected and one unprotected. The local chlorination scheduler is adjusted to last for 3 months with no maintenance.

Figure 9 shows the measurement obtained during the field test in St. Anne du Portzic, Brest, in France. The dark top curve shows measurement from the protected instrument. The light top curve that then drops shows measurement from the unprotected instrument. The bottom curve shows the difference between the two signals. The drift started after 80 days; it remained linear up to the 110th day and then became exponential until the end (133 days).

The reference measurements obtained from water withdrawn and subjected to Guildline salinometer conductivity analysis (large dots in Fig. 9) show a slight shift of the protected instrument (0.5 PSU). This drift is probably due to a stop in the chlorination process after the 100th day due to a lack of energy (failure of battery).

Figure 10 shows the unprotected conductivity sensor (left) and the protected one (right) after 133 days of deployment. Visually, we can perceive the effectiveness of the biofouling protection. It is even surprising how the local chlorination system placed inside the white probe housing has protected the outside.

The local chlorination biofouling protection for the conductivity sensor is efficient as was clearly shown during St. Anne du Portzic Brest test for a continuous period of 133 days. The drift of the unprotected instrument started after 80 days, in August.

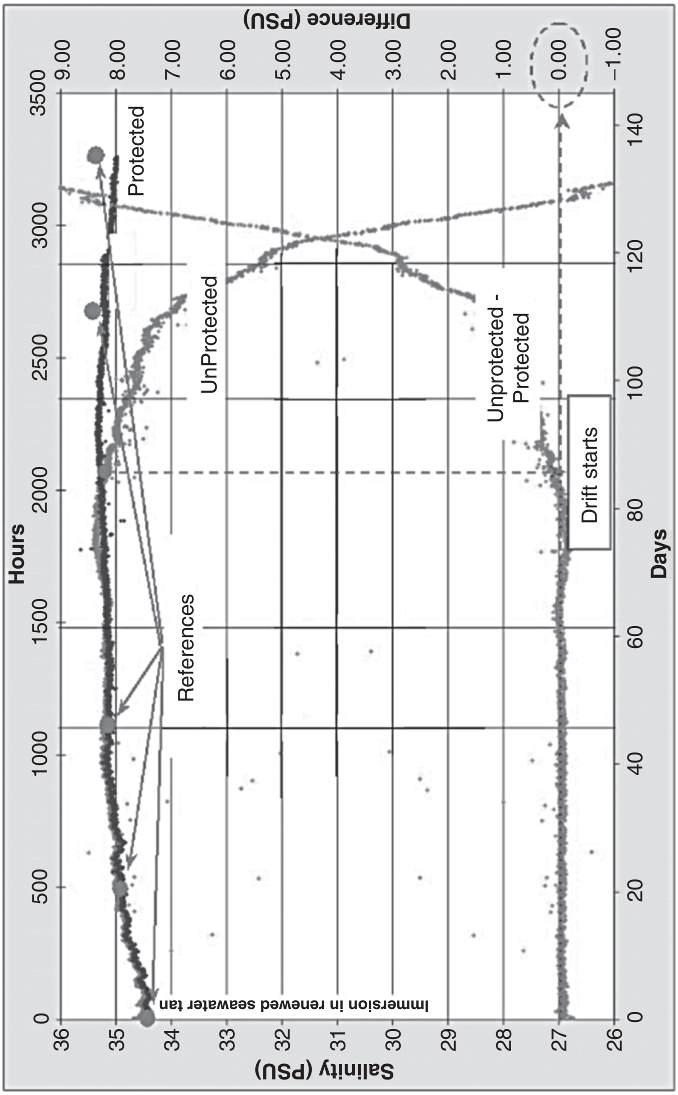

Fig. 9 Conductivity sensor in situ results (133 days duration), 3 June–16 October 2003, Brest

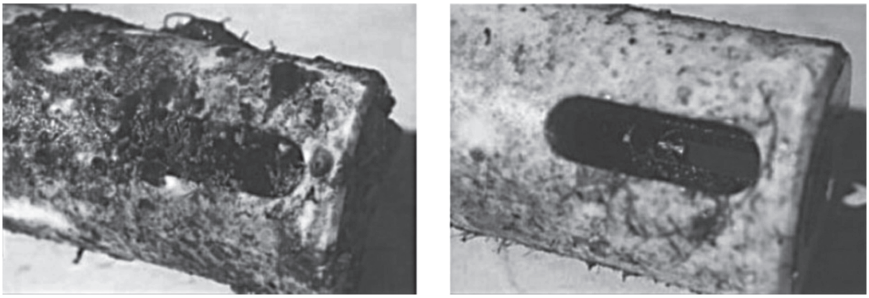

Fig. 10 Conductivity sensor: unprotected (*left*), protected (*right*) (photo: Ifremer, France)

3.3 Biofouling Protection Field Test on Optical Oxygen Sensor

The local chlorination protection device was tested on the oxygen instrument at St. Anne du Portzic, Brest, France. Two instruments were placed on site, one protected and one unprotected. As previously, the local chlorination scheduler was adjusted to last for 3 months with no maintenance.

Figure 11 shows the measurement obtained from day 110 to day 140 during the field test in St. Anne du Portzic, Brest.

The top dark curve shows measurement from the protected instrument. The top light curve that then drops shows measurement from the unprotected instrument. The bottom curve shows the difference between the two signals. The drift started after 127 days. The protected optode signal is very good up to day 160. The Winkler analysis, which was done until the 160th day, confirms this result.

The local chlorination biofouling protection for the oxygen optode sensor is efficient as was clearly shown during St. Anne du Portzic Brest test for a continuous period of 160 days. The drift started after 130 days, in April. The protected sensor showed a temporary failure from day 160 to day 170.

3.4 Biofouling Protection Field Test on Fluorescence Sensor

A local chlorination protection device was tested on fluorescence measurement instruments at Millport island, Scotland, for 100 days. Two instruments were placed on site, one protected and one unprotected. The local chlorination scheduler was adjusted to last for 3 months with no maintenance.

Figure 12 shows the measurement obtained during a field test at Millport Island. For this experiment the two fluorometers were immersed at 1.5 m depth on Millport island (Scotland) in 2004, with the collaboration of Dr P. Cowie (GMTC, UK) during the European BRIMOM Project. The dark curve shows measurement from the unprotected instrument. The light curve shows measurement from the protected

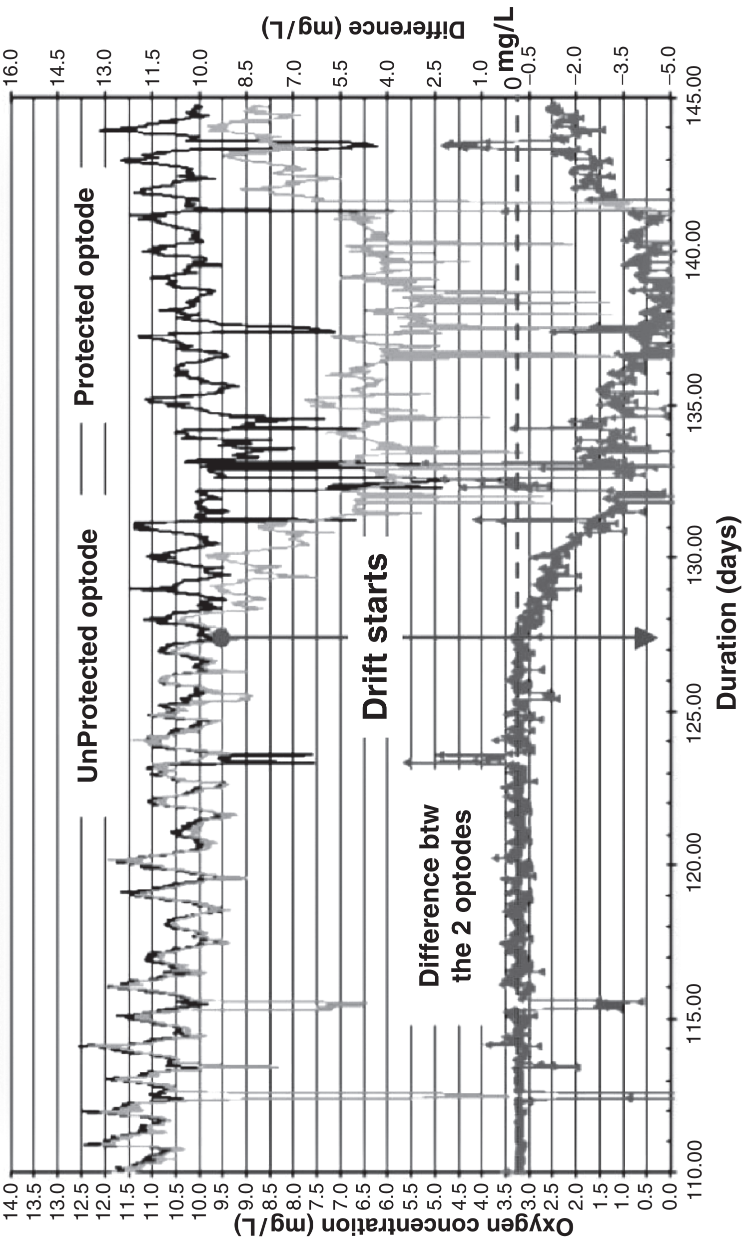

Fig. 11 Oxygen optode sensor in situ results (190 days duration), January–July 2004, Brest

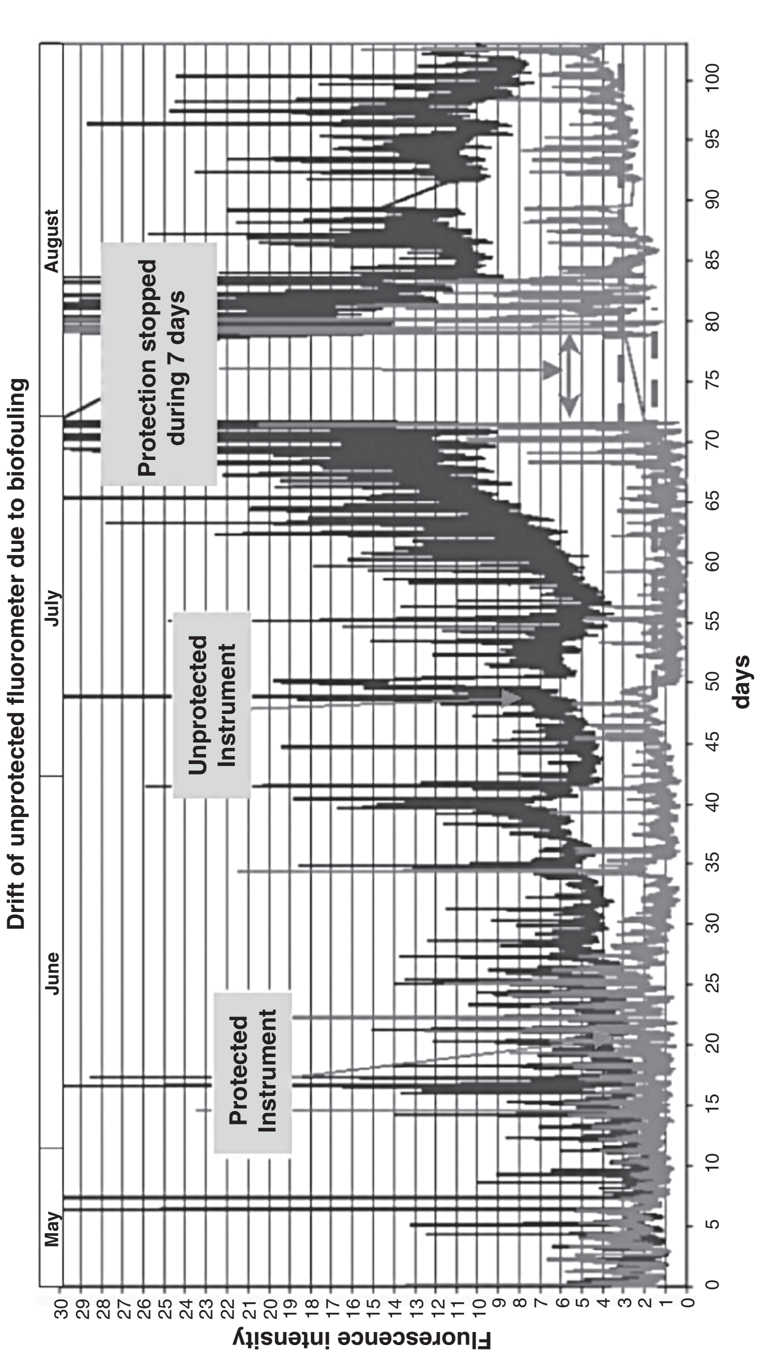

Fig. 12 Fluorescence sensor in situ results (100 days duration), May–August 2004, Millport Island

instrument. The unprotected fluorometer starts to drift after 7 days of immersion and keeps drifting during the 80 days of experiment. The protected fluorometer does not show any drift until day 70. It is very interesting to see that after day 70, the protected instrument was not protected for 7 days. Consequently, biofouling started and a non-negligible measurement drift was observed. This incident shows that if the protection system is not mechanical, but rather chemical, any beginning biofouling will induce a bias on the measurement which will be difficult to remove.

The local chlorination biofouling protection for the fluorometer sensor was effective as was clearly shown during the Millport Island test for a continuous period of 70 days. After 70 days, the small drift observed is mainly due to a chlorinator batteries failure for 7 days.

4 Conclusion

For the last 10 years, oceanographic sensor biofouling protection has improved quite a lot. Owing to the intense technological development of in situ autonomous monitoring systems, the biofouling problem for such systems has been a technological one which needed to be solved. The prohibition of tributyl tin as a biocide, which was used by some manufacturers to protect their sensors, has pushed researchers to find alternative methods to protect sensors from biofouling.

Wipers, scrapers, and other mechanical systems are interesting solutions but very often lead to mechanical failure, resulting in water leakage inside the instruments and, thus, destroying the entire equipment.

Copper shutter scan work quite well but are still complicated to implement, and the biocide generation is uncontrolled, which can lead to problems if the biocide formation interferes with the sensor measurements.

Localized electro-chlorination biofouling protection is actually a promising and an advanced solution for in situ oceanographic sensors, since many successful in situ results have been obtained and sensor manufacturers can integrate in their instruments a compact, simple, robust and low energy requiring solution.

This technique has been tested on many oceanographic instruments for coastal and deep sea monitoring. Very encouraging results have been obtained for the parameters commonly measured for marine monitoring. Every deployment has been a success for a duration of up to 160 days. Various types of biofouling, such as biofilm, algae, and barnacles, have been prevented on different types of instruments and different types of measurement technologies. The system can be adapted to many kinds of instruments quite easily. The energy requirement is compatible with autonomous monitoring.

Special care should be taken for some sensitive parameters such as oxygen or fluorescence. The chlorination period must be scheduled in order to leave free time intervals to take the measurements. The system is now used by Ifremer for autonomous coastal monitoring and allows a reasonable maintenance frequency of 3 months, with high-quality measurements obtained.

Acknowledgements Ifremer thanks Phil Cowie from UMBS, Millport, Scotland, for taking very good care of the Fluorometer experiment in Millport.

References

Aminot A, Kerouel R (2004) Hydrologie des écosystèmes marins, paramètres et analyses, mesure de la concentration en oxygène dissous, Chap. VII. pp 92–118. Publisher: INRA Edition. F-78026 Versailles France

Blain S, Guillou J, Tréguer P, Woerther P, Delauney L (2004) High frequency monitoring of the coastal marine environment using the MAREL buoy. J Environ Monit 6:569–575

BRIMOM (biofouling resistant infrastructure for measuring, observing and monitoring), project no. EVRI-CT-2002-40023

Delauney L, Compère C (2006) Biofouling protection for marine environmental optical sensors. International conference on recent advances in marine antifouling technology (RAMAT), Chennai (Madras), India. Proceedings of the International Conference on recent advances in marine antifouling technology. Allied Publishers Pvt. Ltd

Delauney L, Cowie P (2002) BRIMOM (biofouling resistant infrastructure for measuring, observing and monitoring) report (project no. EVR1-CT-2002-40023). http://cordis.europa.eu/data/PROJ_FP5/ACTIONeqDndSESSIONeq112362005919ndDOCeq221ndTBLeqEN_PROJ.htm

Delauney L, LeGuen Y (2003) Calibration procedure for in-situ marine fluorometer. In: International metrology conference 2003 proceedings, Toulon, France. CD Publisher: Collège Français de métrologie. 75015 Paris

Delauney L, Lepage V, Festy D (2002) BRIMOM (biofouling resistant infrastructure for measuring, observing and monitoring), project no. EVR1-CT-2002-40023. http://cordis.europa.eu/data/PROJ_FP5/ACTIONeqDndSESSIONeq112362005919ndDOCeq221ndTBLeqEN_PROJ.htm

Delauney L, Compère C, Lehaitre M (2005) Office for official publications of the european communities - Luxembourg. Proceeding of the fourth international conference on EuroGOOS. pp 397–403

Fofonoff NP, Millard RC (1983) Algorithms for computation of fundamental properties of seawater, UNESCO Technical papers in marine science 44, UNESCO Division of Marine Science, Paris, France, 53 pp

Lehaitre M, Delauney L, Compère C (in press) Oceanographic Methodology series, Real Time Coastal Observing Systems for Marine Ecosystem Dynamics and Harmful Algal Blooms: Theory, Instrumentation and Modelling. 2008, ISBN 978-92-3-104042-9. UNESCO Publishing

Manov DV, Chang GC, Dickey TD (2004) Methods for reducing biofouling on moored optical sensors. J Atmos Ocean Technol 21(6):958–968

Marvaldi J, Coail Y, Legrand J (2006) ROSE, CMM'06 Caractérisation du Milieu Marin, 16–19. SeatechWeek 2006 - Brest -France

Sarrazin J, Blandin J, Delauney L (2007) TEMPO: a new ecological module for studying deep-sea community dynamics at hydrothermal vents (IEEE catalogue no. 07 EX). Oceans 2007 IEEE conference proceedings, Aberdeen, Scotland, 18–21 June 2007

Satpathy KK (2006) Biofouling and its control in power plants cooling water system. International conference on recent advances in marine antifouling technology (RAMAT), Chennai (Madras), India. Proceedings of the international conference on recent advances in marine antifouling technology. Allied Publishers Pvt. Ltd

YSI 6600 EDS (Extended Deployment System) – Clean SweepTM – http://www.ysi.com