JOINT EUROPEAN RESEARCH INFRASTRUCTURE NETWORK FOR COASTAL OBSERVATORIES

REVIEW ON OXYGEN SENSORS FOR OCEANOGRAPHIC APPLICATIONS AND THEIR PERFORMANCE WITH RESPECT TO BIOFOULING. PRELIMINARY RESULTS

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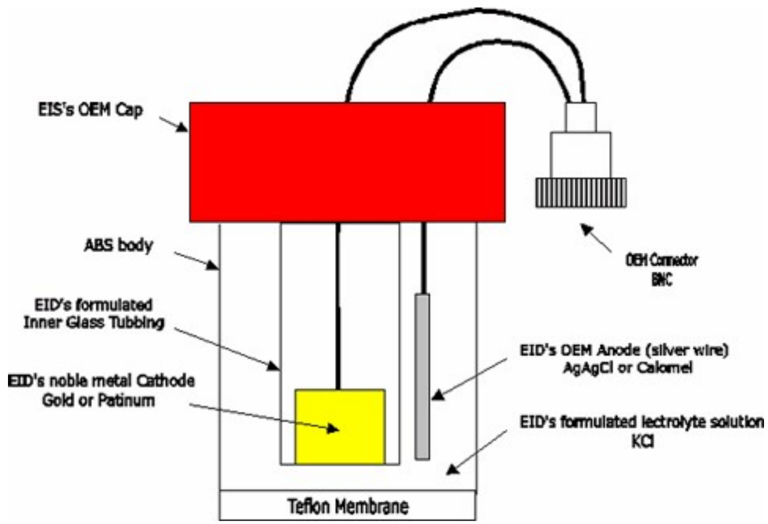
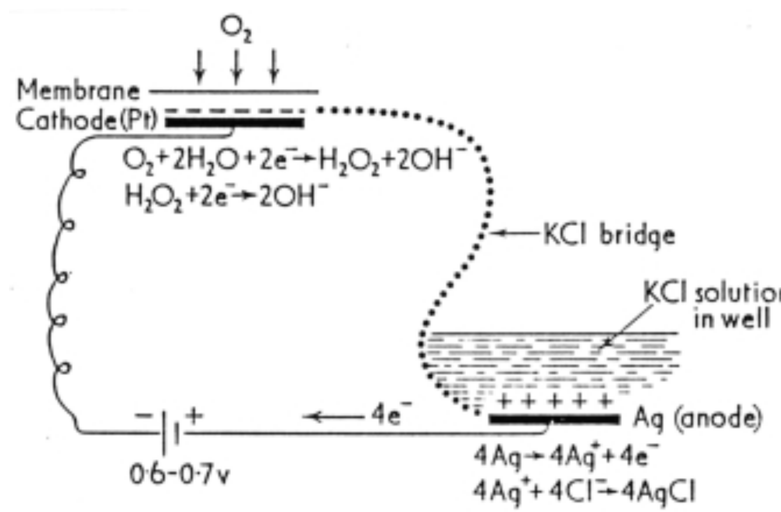
Electrochemical (polarographic) DO sensors - 1

Principle: based on an amperometric cell (*dr. Leland Clark, 1959*) polarised at ≈ -0.8 V. In conditions of a complete polarisation ($[O_2] = 0$ on cathode surface), the current is proportional to the diffusion (i.e. partial pressure) of DO in the liquid media. Oxygen is consumed, need of a constant water flux.

Anode (Ag/AgCl with electrolyte KCl) $2Ag + 2Cl^- \rightarrow 2AgCl + 2e^-$
Cathode (Platinum, gold, palladium) $2e^- + \frac{1}{2} O_2 + H_20 \rightarrow 2 OH^-$
Net result: $2Ag + \frac{1}{2} O_2 + H_20 + 2Cl^- \rightarrow 2 AgCl + 2OH^-$





Electrochemical (polarographic) DO sensors - 2

Main types:

- Steady-state sensors with permeable membranes (e.g. teflon or polyethylene) and electrolyte (KCl or KBr solutions);(e.g. **SBE 43**)
- Rapid-pulse sensors with membrane and electrolyte (three electrodes, pulse voltage to avoid the depletion of DO at the surface of the membrane);
- Micro-hole potentiostatic sensors (three electrodes: cathode, anode, reference); without membrane and electrolyte, they are based on the direct diffusion of DO;

Others:

Steady-state electrochemical (galvanic) sensors, with membrane and electrolyte. They measure a current proportional to DO partial pressure in KCl solution in a galvanic cell (cathode: silver / anode: zinc), without the application of an external constant voltage (i.e. similar to a battery).

Optical DO sensors - 1

Principle: (since the 2000s) based on a sensing foil containing a chemical dye in contact with seawater that is excited by a monochromatic (blue) light. Oxygen dissolved in the water quenches both decay time and intensity of the (red) luminescence emitted by the foil (i.e. emission of photons at a lower energy than those absorbed). The sensor also emits a red light that is reflected by the dye layer. The reading of this reflected light is used as reference.

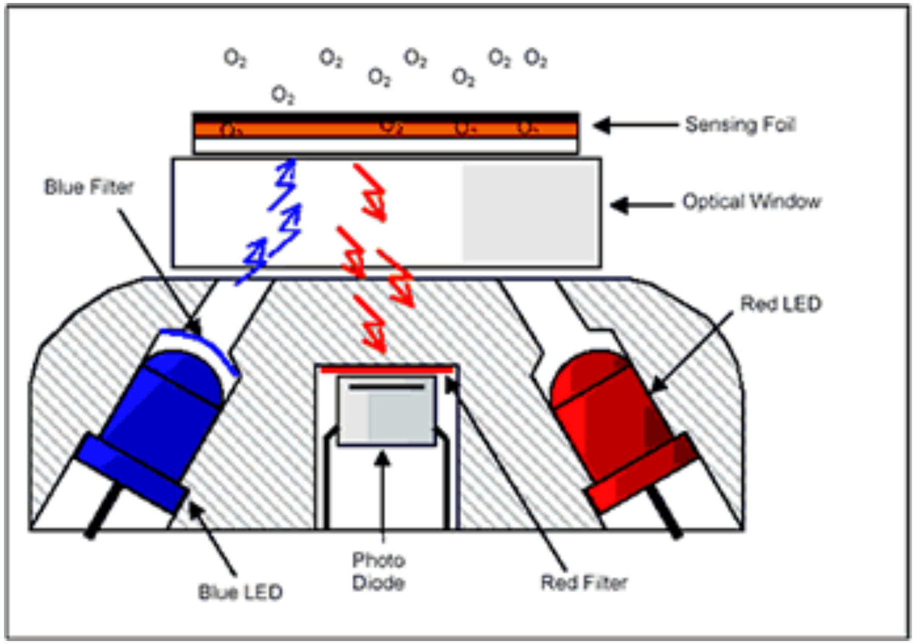
Stern-Volmer equation:

$$[O_2] = \frac{1}{K_{sv}} \cdot \left(\frac{T_0}{T} - 1 \right)$$

relationship between $[O_2]$ and luminescence lifetime/intensity:

T = lifetime/intensity, T_0 = lifetime/intensity in the absence of oxygen, KSV = Stern-Volmer constant (the quenching efficiency for the selected dye).

Lifetime measure more used: less affected by dye degradation



Optical DO sensors - 2

Oxygen is not consumed during the measure. No need of water flux.

Main types of sensing dyes:

- Polymer layer with fluorophores (polycyclic aromatic hydrocarbons; e.g. pyrene and fluoranthene), metal (e.g. platinum) porphyrins, longwave absorbing dyes, transition-metal (e.g. ruthenium) organic complexes.

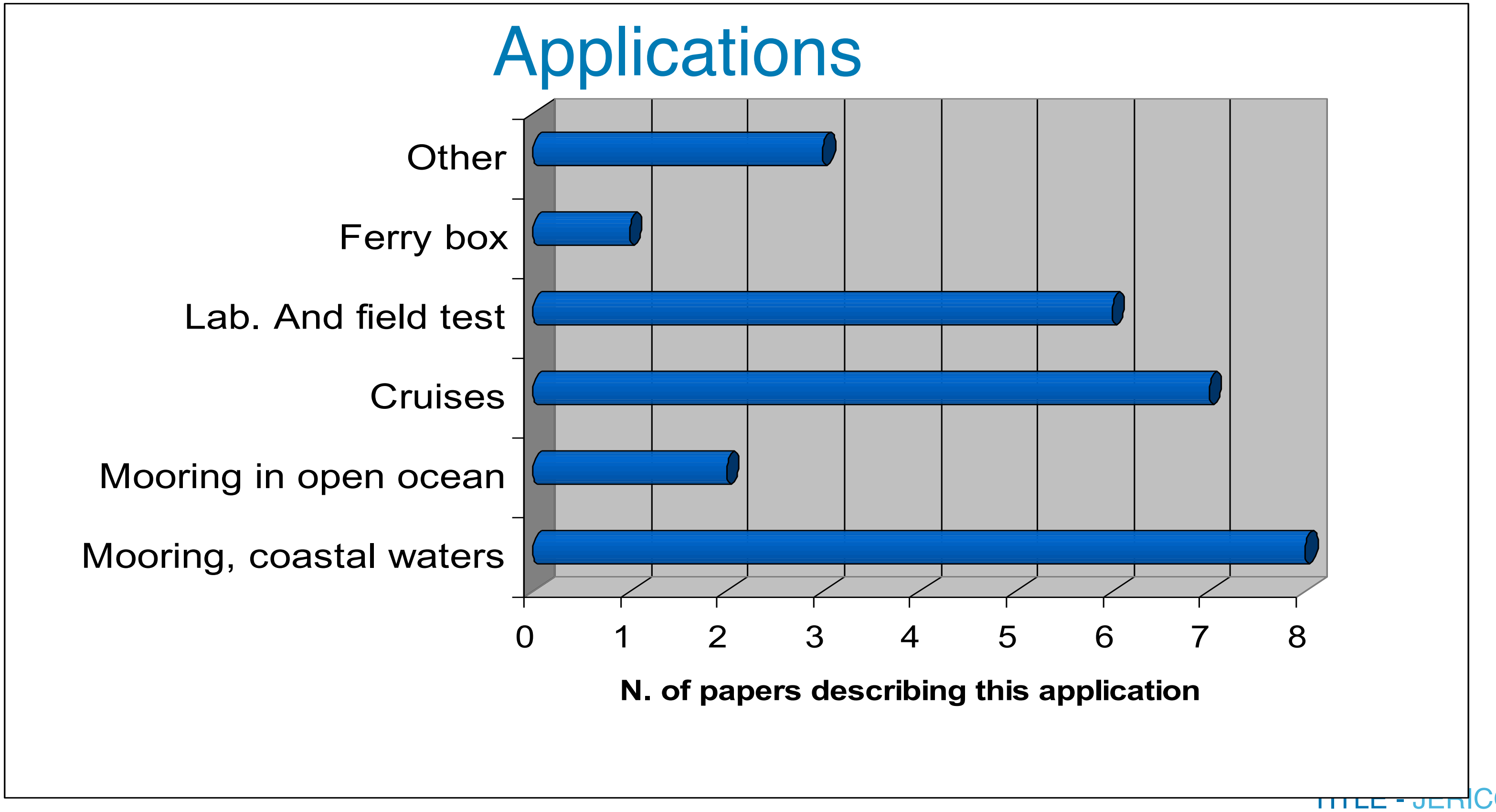
Structure:

- Optodes or micro-optodes;
- Planar foils or porous plastic supports;
- Presence/absence of an oxygen permeable diffusion cover to protect the foils (e.g. silicon membrane).

Literature review: applications

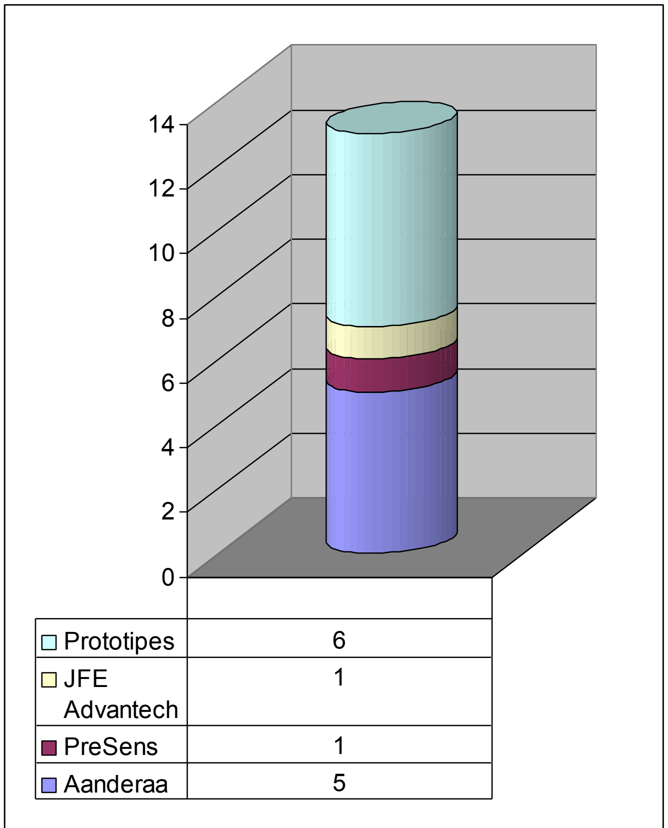
17 Peer-reviewed papers from 1995, independent authors

4 Performance Verification Statement – ACT 2004

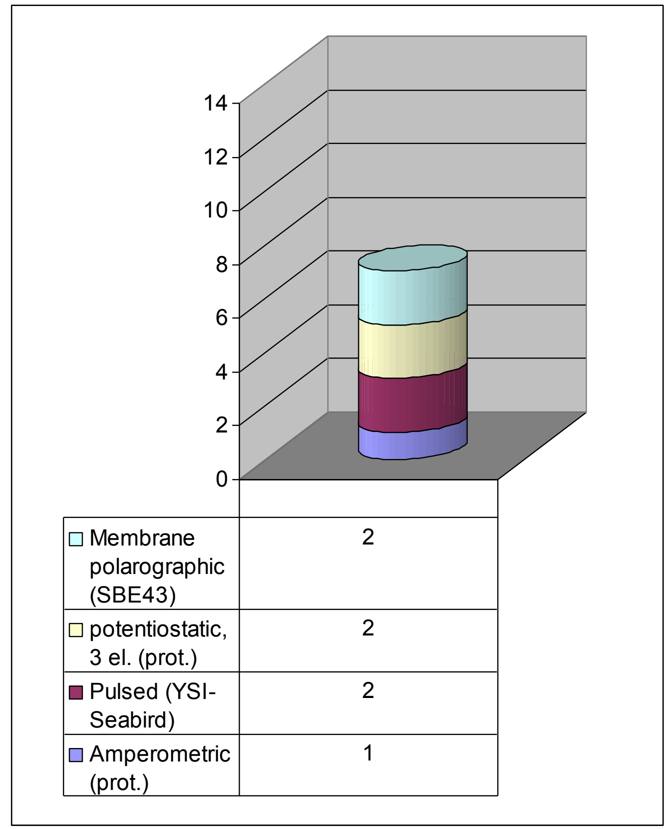


Literature review: kind of sensors

OPTODES



ELECTROCHEMICALS



Effect of environmental conditions on DO sensors

Temperature

Changes in temperature modify molecular activity in the water media, with consequences on the diffusion of DO through the membrane of an electrochemical probe or on the sensing element of an optical probe The temperature affects both electrochemical and optical DO sensors and its effects have to be corrected through calibration or algorithms that use the temperature readings from the probe's thermistor.

Salinity

The presence of permeable diffusion membranes protect polarographic and optical sensors by the contact with water and salt. However, increases of salinity decrease the solubility of DO in seawater. Thus, salinity must be derived by the conductivity sensors and factored into the instrument's algorithms for the calculation of DO concentration.

Pressure

An increase of the pressure decreases the permeability of membranes, reducing the current outputs of polarographic sensors, while the response of micro-hole sensors is slightly increased. The response of optodes also decreases with an increasing pressure (≈ -4% for +100 bar), but the effect is fully reversible and predictable without remaining effects of hysteresis.

Effect of environmental conditions on DO sensors

DO concentration

Optodes have a greater precision at lower oxygen concentrations (hypoxic conditions) that at higher levels (300-500 µM).

Chemical contamination

Contamination by hydrogen sulfide (H_2S) is reported for electrochemical sensors that used silver as the cathode element. Sensor that use noble metals (gold) as the cathode and silver as the anode, are not affected by sulfur contamination. Optodes are insensitive to H_2S poisoning, but a cross-sensitivity with gaseous sulfur dioxide (SO_2) and chlorine (Cl_2) has been observed.

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Effect of biofouling on DO sensors

From a theoretical point of view

- Biofouling alters the membrane permeability to DO diffusion, both for electrochemical and optical sensors
- Biofouling creates a microenvironment (production/ respiration) that is not representative of the surrounding seawater

From: Alliance for Coastal technologies. Performance verification Statement for Aanderaa Instruments Inc. Dissolved Oxygen Optode 3830/3930/3838 - 2004

Unprotected

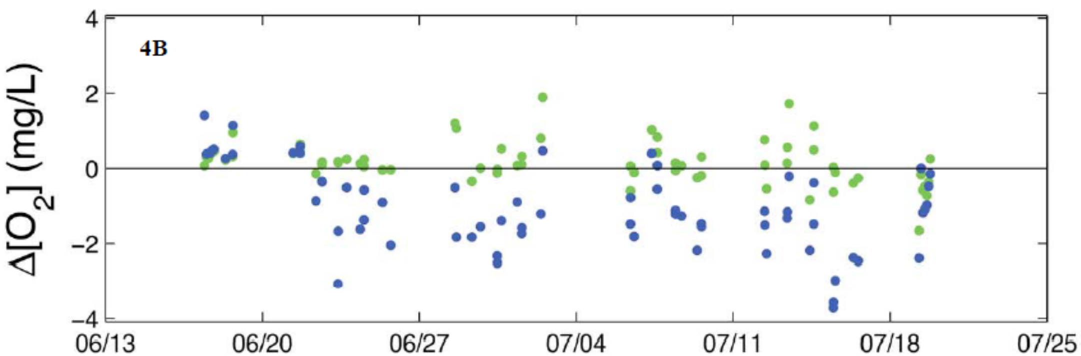
Sensor without the biofouling prevention system after four-week field deployment.

Protected

Sensor with the biofouling prevention system after four-week field deployment.

Belleville Lake, Michigan.
4 weeks deployment.
2 Optodes + Winkler measures

- Unprotected (green)
- Protected (blue)



Difference with respect to Winkler data

Sensor with the biofouling prevention system drifted more than the unprotected

➢ The best: unprotected

From: Alliance for Coastal technologies. Performance verification Statement for Aanderaa Instruments Inc. Dissolved Oxygen Optode 3830/3930/3838 - 2004

Unprotected

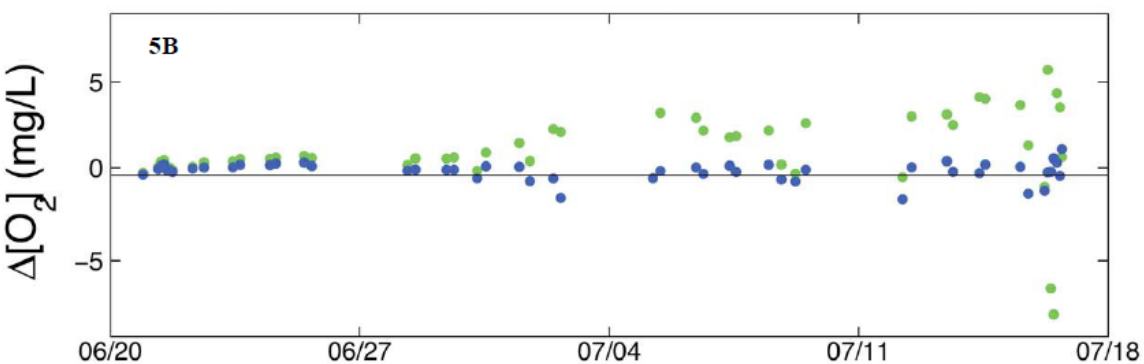
Sensor without the biofouling prevention system after four-week field deployment.

Protected

Sensor with the biofouling prevention system after four-week field deployment.

Kaneohe Bay Reef, Hawaii.
4 weeks deployment.
2 Optodes + Winkler measures

- Unprotected
- Protected



Difference with respect to Winkler data

Sensor with the biofouling prevention system drifted less than the unprotected

➢The best: protected

From: **M. Martini and B. Butman. J. Of Atm. And Ocean Tech. Long-term performance of Aanderaa Optodes and Sea-Bird SBE-43 DO sensors Bottom Mounted at 32m in Massachusetts Bay. - 2007**

November 2007 MARTINI ET AL. 1931

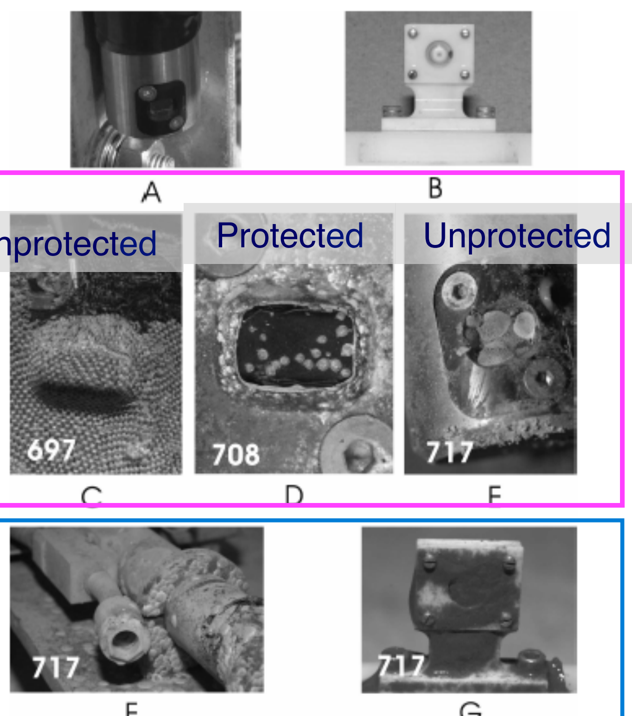


FIG. 4. Images of clean (a) optode and (b) SBE43 membrane assembly before deployment. Optode following recovery from (c) tripod 697 with a plastic window frame, (d) 708 with a copper window frame, and (e) 717 with a plastic window frame. SBE43 from tripod 717 on recovery showing (f) the antifouling tip on the intake and (g) membrane assembly with sediment.

Massachusetts Bay, 32m.
7 months deployment with 1-2 months of measures with two sensors.
Optode (Aand.3830), Polarographic (SBE43), Winkler measures

697 Sensing foil window completely covered by a bryozoan colony. Not working anymore

708 Copper frame, new design. Less fouled, good DO data

717 severe fouling conditions, sensing window nearly blocked. However only small drift in DO values!

Sea-Bird SBE43 Flushing and tributyl-tin leaching tips.

No fouling. Membrane covered by sediments but still good data – 112 days.

From: Tengberg et al., Limnol. Ocean. Methods. Evaluation of a lifetime-based optode to measure oxygen in aquatic systems - 2006

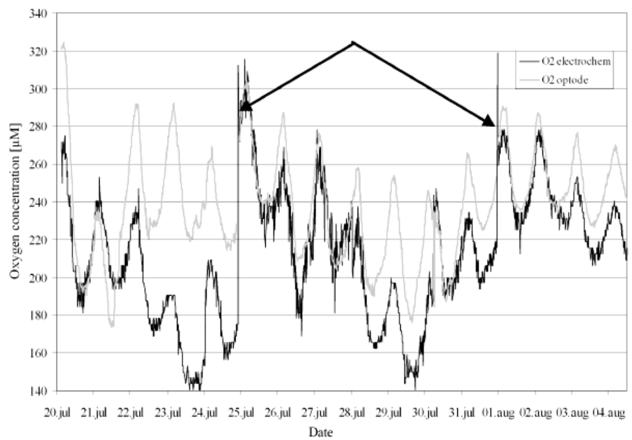


Fig. 6. Oxygen data from a comparison between an optode and an electrochemical sensor at a monitoring station in the River l'Orge (France). Two occasions when the electrochemical sensor was taken up, cleaned, and recalibrated are marked with arrows in the figure. The optode was not cleaned during this experiment.

- Monitoring station in River l'Orge (France)
  Heavy fouling environment, bacterial biofilm.
  20 days deployment.
  Optode (Aa3830), Electrochemical sensor.

  Electrochemical sensor affected by fouling after 2 days; optode without protection no influence of fouling within 20 days

- Waste water treatment plants
  14 days unprotected and not cleaned optodes
  90 days unprotected and cleaned with tap water spry to remove the organic material accumulated near the foil.

- Shallow coastal waters
  Use of a berillyum-copper alloy net (for domestic cleaning) wrapped around the sensor.
  Service interval prolonged from 7-10 days to 40-60 days.

Effect of biofouling on DO sensors

Summarizing the effect of Biofouling

Optodes are less affected by fouling than polarographic sensors.

- In polarographic sensors, fouling alters the characteristics of the membranes and they need accurate cleaning and recalibration.
- Optodes are tolerant of fouling as long as some part of the window remains clear

However ….

- The anti-fouling technique used by Sea-Bird is proved to be effective also under severe fouling conditions.
- Care is needed in the choice of fouling protection for optodes. If it reduces water circulation at the membrane surface, the effect could be opposite.

Conclusions

	ELECTROCHEMICAL SENSORS	OPTODES
Reliability	Proven technology	Not always approved for environmental monitoring
Calibration and maintenance	More frequent	Less frequent
Power	Higher consumption (pumping system is needed)	Lower consumption
Response time	Faster measurements	Slower measurements (not always suitable for CTD cast applications)
DO consumption in the samples	Yes (not suitable for micro-environments and for not stirred samples)	No
Costs	Lower initial costs	Higher initial costs
Biofouling	More sensitive, but good antifouling systems available	Less sensitive
Chemical contamination	Recent sensors are scarcely affected	Scarcely affected
Winkler calibration	Always necessary for high precision DO determinations	Always necessary for high precision DO determinations