

Annual Review of Analytical Chemistry Sensors for Coastal and Ocean Monitoring

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Abstract

In situ water monitoring sensors are critical to gain an understanding of ocean biochemistry and ecosystem health. They enable the collection of high-frequency data and capture ecosystem spatial and temporal changes, which in turn facilitate long-term global predictions. They are used as decision support tools in emergency situations and for risk mitigation, pollution source tracking, and regulatory monitoring. Advanced sensing platforms exist to support various monitoring needs together with state-of-the-art power and communication capabilities. To be fit-for-purpose, sensors must withstand the challenging marine environment and provide data at an acceptable cost. Significant technological advancements have catalyzed the development of new and improved sensors for coastal and oceanographic applications. Sensors are becoming smaller, smarter, more cost-effective, and increasingly specialized and diversified. This article, therefore, provides a review of the state-of-the art oceanographic and coastal sensors. Progress in sensor development is discussed in terms of performance and the key strategies used for achieving robustness, marine rating, cost reduction, and antifouling protection.

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1. INTRODUCTION

The biochemistry and biology of the ocean play a central role in the world economy and climate regulation. Anthropogenic activities have altered the state of the ocean, leading to warming, acidification and deoxygenation, eutrophication, pollution, nutrient flux reduction, the decline in fishery resources and biodiversity, and habitat loss (1-4). Recent observation-based estimates show that ocean warming has accelerated over the past few decades (5) and has caused a decline in glaciers, ice caps, and ice sheets in the polar region, a decrease in primary production, rising sea levels, and changes in ocean stratification (6). In response, in situ ocean observing networks have been established on a regional-to-global scale to provide the basis for understanding complex ocean dynamics. Examples of such networks include the Global Ocean Observing System (GOOS; https://www.goosocean.org/), the US Integrated Ocean Observing System (IOOS; https://ioos.noaa.gov/), the Ocean Observatories Initiative (OOI; https://oceanobservatories. org/), the Australian Integrated Marine Observing System (IMOS; https://imos.org.au/), the Biogeochemical-Argo program (BGC-Argo; https://biogeochemical-argo.org/), and the Export Processes in the Ocean from Remote Sensing (EXPORTS; https://oceanexports.org/). For coastal areas, legislation is in place to limit the transport of anthropogenic pollutants to the marine environment. For example, the Marine Strategy Framework Directive (MSFD, 2008/56/EC) aims to achieve "good environmental status of the EU's marine waters" (7), and the Water Framework Directive (WFD, 2000/60/EC) aims to achieve "good ecological status" (8). In situ sensing technology has been instrumental in both oceanographic and coastal monitoring. Sensor networks are providing the most promising approach to date for collecting temporally and vertically resolved observations of biogeochemical processes throughout the ocean (9), real-time data for decision support in coastal areas (10, 11), validation of space and airborne observations (12), high-frequency data for forecasting models, and big data analytics (13).

Sensors operating in the marine environment are exposed to extreme conditions and must endure long deployments to be cost-effective. To withstand the harsh marine environment, sensors have to be robust, power efficient, and equipped with suitable antifouling protection (14). There are numerous in situ sensors available both commercially and at a research stage with various technology readiness levels. This review provides up-to-date information on in situ technologies that are available, either at the laboratory and prototype stages or commercially, and suitable for deployment in the marine environment. Therefore, (*a*) this article provides a review of existing sensors for coastal and ocean monitoring; a focus is placed on commercially available technologies with a comprehensive list of sensors and manufacturers provided. State-of-the-art developments are discussed, including recent progress in wet chemistry-based, hybrid, and optical-based sensors. (*b*) It provides a breakdown of contemporary materials and technologies used in sensor manufacture and key strategies used for achieving robustness, marine rating, and cost reduction. (*c*) This review discusses the critical challenge of antifouling protection, which is universal to all submersed sensors.

2. EXISTING IN SITU MONITORING TECHNOLOGIES

Based on the sample measurement principle, in situ water monitoring sensors and instrumentation can be largely classified in two main categories: sample draw-based and interface-based (Table 1).

2.1. Sample Draw-Based Sensors

Sample draw-based sensors rely on transfer of the sample from the outside environment into the sensor. Sample processing steps, including filtration, mixing with on-board stored reagents, or incubation to predefined temperatures, are carried out prior to the detection step or during

Туре	Sensor	Parameter	Manufacturer	URL		
Flow injection sensors						
Nutrients	HydroCycle-PO ₄	SRP	Sea-Bird Scientific, Washington	https://www.seabird.com/		
	A1000-200	SRP	Dartmouth Ocean Technologies Inc., Canada	https://dartmouthocean.com/ products/phosphate-sensor		
Fecal indicators	ALERT System	<i>E. coli</i> , coliforms, or enterococci	Fluidion SAS, France	http://fluidion.com/en/products/ alert-system-2		
	Colifast ALARM	Coliforms, E. coli	Colifast AS, Norway	https://www.colifast.no/ products/		
	ColiMinder CMI-02	GUS activity	VWMS GmbH, Austria	https://www.coliminder.com/		
	BACTcontrol	GUS, GAL activity	MicroLAN B.V., The Netherlands	http://www.microlan.nl		
рН, <i>р</i> СО ₂	SAMI-pH, iSAMI-pH	pH	Sunburst Sensors LLC, Montana	http://www.sunburstsensors.com/		
	SAMI-CO ₂	pCO ₂				
Interface sensors				•		
Hybrid systems and sensors	VIP system	Trace metals Cu(II), Pb(II), Cd(II), Zn(II) (ppt level) Mn(II), Fe(II) (ppb level)	Idronaut S.r.l., Italy	https://www.idronaut.it/		
	CO ₂ -Pro CV	pCO ₂	Pro-Oceanus, Canada	https://pro-oceanus.com/		
	CO2-Pro ATM	CO ₂ flux				
	Mini CH4	pCH ₄				
	C-sense	pCO ₂	Turner Designs, California	https://www.turnerdesigns.com/		
	SeaFET V2	pH	Sea-Bird Scientific, Washington	https://www.seabird.com/		
	Oxygen sensors 4835, 4831, 4330, 4531	DO	Aanderaa, Norway	https://www.aanderaa.com/		
	HydroC CO ₂	pCO ₂	CONTROS Systems & Solutions GmbH, Germany	https://www.4h-jena.de/en/ maritime-technologies/ sensors/hydrocrco2/		
Single/ multiwavelength absorption, scatter, and fluorescence probes	Spectro::lyser V3	Turb, <i>Chl a</i> , TOC, DOC, BOD, T	s::can GmbH, Austria	https://www.s-can.at		
	Nitratax plus sc	NO ₃ -	Hach Lange GmbH, Germany	https://de.hach.com/		
	SUNA V2	NO ₃ -	Sea-Bird Scientific, Washington	https://www.seabird.com/		
	ECO Triplet	<i>Chl a</i> , fDOM, Rho, PC, PE				
	SeaOWL UV-A	Crude oil, Chl a				
	ECO NTU, ECO BB9	Turb, OBS				
	VLux series	BGA (PC, PE), Try, <i>Cbl</i> <i>a</i> , <i>b</i> , <i>c</i> , Turb, fDOM, BTEX, PAH	Chelsea Technologies, United Kingdom	https://chelsea.co.uk/		

Table 1 Commercially available water quality sensors and instrumentation for in situ applications

(Continued)

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Table 1 (Continued)

Туре	Sensor	Parameter	Manufacturer	URL
	EnviroFlu, matrixFlu VIS, nanoFLU, microFlu V2	<i>Chl a</i> , PC, Rho, CDOM, PAH, Try, PC	TriOS Mess- und Datentechnik GmbH, Germany	https://www.trios.de/en/index.php
	TTurb	Turb		
	NICO, LISA, OPUS	NO ₃ ⁻ , NO ₂ ⁻ , SAC254, TOC		
	OBS501	Turb	Campbell Scientific, Utah	https://www.campbellsci.com/
	C3, CP6	T, D, Try, Rho, fDOM, crude and fine oil, PC, PE, <i>Chl a</i>	Turner Designs, California	https://www.turnerdesigns.com/
	PhytoFind	Algae speciation		
	Hyperion series	Turb, Chl a, PC, Rho	Valeport Ltd., United Kingdom	https://www.valeport.co.uk/
	AlgaeTorch	BGA, Chl a	bbe Moldaenke GmbH,	https://www.bbe-moldaenke.de/ en/
	FluoroProbe	Algae speciation, Chl a	Germany	
	Turbidity Sensor 4296	Turb	Aanderaa, Norway	https://www.aanderaa.com/
	The Pixie	Chl a, PC, PE, fDOM	Dartmouth Ocean Technologies Inc., Canada	https://dartmouthocean.com/
Multiparameter sondes	YSI EXO series	C, T, D, pH, ORP, fDOM, BGA, Rho, NO_3^- (optical), <i>Chl a</i> , DO, Turb, NH_4^+	YSI, a Xylem brand, Ohio	https://www.ysi.com
	Sea-Bird HydroCAT-EP	C, T, D, pH, Turb, <i>Chl a</i> , DO	Sea-Bird Scientific, Washington	https://www.seabird.com/
	DS5X, HL7	C, T, D, pH, ORP, BGA, Rho, NO ₃ ⁻ (ISE), <i>Chl a</i> , DO, Turb	HYDROLAB, Colorado	https://www.hydrolab.com/
	Eureka Trimeter	C, T, D, pH, ORP, DO, <i>Chl a</i> , BGA, Rho, crude and refined oil	Eureka Environmental, Texas	http://rshydro.ie/eureka-m- 20.html
	Proteus	C, T, D, pH, ORP, DO, crude and refined oil, Try, CDOM	Proteus Instruments Ltd., United Kingdom	https://www.proteus- instruments.com/
	MIDAS CDT+	C, T, D, pH, ORP, DO, <i>Chl a</i>	Valeport Ltd., United Kingdom	https://www.valeport.co.uk/

Abbreviations: BGA, blue-green algae; BOD, biochemical oxygen demand; BTEX, benzene, toluene, ethylbenzene, and xylene; C, conductivity; CDOM, chromophoric dissolved organic matter; *Chl a, b, c*, chlorophyll a, b, c; D, depth derived from pressure; DO, dissolved oxygen; DOC, dissolved organic carbon; *E. coli, Escherichia coli* marker enzyme; fDOM, fluorescent dissolved organic matter; GAL, β galactosidase (total coliforms marker enzyme); GUS, β glucuronidase; ISE, ion-selective electrode; OBS, optical back scattering; ORP, oxidation reduction potential; PAH, polycyclic aromatic hydrocarbon; PC, phycocyanin; *p*CO₂, partial CO₂ pressure; PE, phycocrythrin; Rho, rhodamine; RT, real-time; SRP, soluble reactive phosphorus; T, temperature; TOC, total organic carbon; Try, tryptophan; Turb, turbidity.

detection. The analyte detection and quantification are achieved under strictly controlled conditions for good analytical performance. Such systems widely known as wet chemistry-based sensors or analyzers are particularly successful for species and analytes that are challenging or impossible to measure using interface-based sensors. These devices are becoming commonplace due to recent advancements in microfluidics and lab-on-chip (LOC) devices, which require small

454 Briciu-Burghina et al.



Figure 1

Wet chemistry–based sensors. (*a*) Lab-on-chip phosphate sensor. (*i*) A fully assembled sensor with reagent housing. (*ii*) A lab-on-chip sensor prior to placement in the watertight sensor housing. (*iii*) One of the poly(methyl methacrylate) layers of a phosphate lab-on-chip showing the microfiluidic channels prior to sealing with the other layers of the microfiluidic chip phosphate–based sensors. Panel adapted from Reference 19 (CC BY 4.0). (*b*) A submersible phosphate analyzer for marine environments. (*i*) The A1000-200 phosphate sensor and reagent canister (https://dartmouthocean.com/products/phosphate-sensor). Phosphate sensor image provided by Dartmouth Ocean Technologies Inc., Dartmouth, Nova Scotia, Canada. (*ii*) Cross section of the interior of the phosphate sensor. Fluid is pulled and directed into the lab-on-chip by stepper motor-actuated syringes and active solenoid valves. Valve control, data logging, and optical control are handled using three separate electronics boards. Panel reproduced with permission from Reference 20 (CC BY-NC 3.0). (*c*) Nitrate and nitrite sensor. (*i*) Schematic showing the fluidics of the sensor and mode of operation. (*ii*) Finished sensor incorporating fluidics, heater, flow cells, and control electronics. Panel adapted with permission from Reference 44; copyright 2019 American Chemical Society. Abbreviations: LED, light-emitting diode; PCB, printed circuit board.

volumes of sample, reagents, and ultimately on-board power (**Figure 1**). They are commonly used for nutrients (15), fecal indicator bacteria (16), and algal toxins (17) (see **Table 1** for commercially available sensors). Wet chemistry–based sensors are generally more expensive and bulky than their interface-based counterparts (e.g., ion-selective and optical sensors), but they provide better accuracy, precision, and resolution (18). Submersible sensors exist at different technology readiness levels for phosphate (19–21), nitrate (22, 23), silicate (24), ammonium and iron (25), nitrate and provide deference of the provide sensors of the provide deference of the provide sensor of the provide senso

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sulfide (22), and iron and sulfide (26), with more advanced systems performing electrochemical desalination and passive acidification to remove interfering ions (27).

For coastal regions, particularly around recreational sites, it is critical to detect fecal pollution in a manner that allows decision support. This has led to the development of different systems for the detection of coliforms, *Escherichia coli*, and enterococci and their respective marker enzymes. Examples include the ColiSense system (28–30), Colifast ALARM (31), ColiMinder (16, 32–35), BACTcontrol (36), and the ALERT System (37, 38) (Table 1). Systems that rely on selective bacteria growth (Colifast ALARM, ALERT System) require longer times to provide results (2–15 h), whereas systems relying on direct enzyme activity (ColiMinder, BACTcontrol) provide results in 15–75 min. The methods used mostly rely on proprietary or already commercially available growth media, synthetic substrates for marker enzymes, and selective incubation temperatures. Among them, the ALERT System is the only sensor that can be deployed autonomously. In contrast with a flow-through system, where the sample is drawn, analyzed, and discarded, the ALERT System uses multiple disposable cartridges for sample incubation and detection. These cartridges are stored on-board within the sensor and replaced by the operator during maintenance windows (37, 38). Other wet chemistry-based sensors are used to determine carbonate system parameters: total dissolved inorganic carbon, partial pressure of CO₂ (pCO₂) or CO₂ fugacity (fCO₂), pH, and total alkalinity (39) through the use of spectrophotometric methods (40, 41). For example, the SAMI-pH system is based on the spectrophotometric pH method using a meta-cresol purple indicator (42) and is described in detail elsewhere (43).

2.2. Interface-Based Sensors

A second category of sensors relies on measurements carried out at the interface with the environment and is available for an extensive range of parameters. From a measuring principle perspective, they can be grouped into electronic sensors (temperature, conductivity, and pressure), optical sensors (measuring scatter, absorption, and fluorescence) and hybrid sensors. In addition to the electrical or optical detection, hybrid sensors leverage gas diffusion membranes, selective analyte recognition membranes, and chemical transducers to achieve selectivity. Common examples include the membrane-based optical dissolved oxygen (DO) sensor or DO optode (45), ion-selective electrode sensors, and the polarographic or galvanic cell oxygen sensors (46). The DO optode was first described by Kautsky (47), but a mature technology now provides robust and sensitive sensors used worldwide on observational platforms (48). Oxygen optodes are based on the principle of luminescence quenching by oxygen and rely on luminophores with long luminescence lifetimes (42). Luminescence lifetime rather than its intensity is used, as the latter is prone to drift and variability due to changes in the excitation light source intensity, ambient scattering, and other matrix effects (45). A more in-depth discussion of DO measurement principles, analytical performance, and luminophores used can be found elsewhere (49).

Other hybrid sensors include the pH and pCO_2 sensors (**Table 1**). The ion-sensitive field effect transistor (ISFET)-based pH sensors (50–52) together with the spectrophotometric-based sensors are most commonly employed in oceanographic studies and considered to be more stable and precise than the electrochemical-based pH electrode. The performance of the commercially available ISFET-based pH sensor (SeaFET) developed in 1993 at the University of South Florida by Robert Byrne and coworkers (50) has been recently evaluated (53).

Commercially available pCO_2 sensors use nondispersive infrared detectors to measure the partial pressure of CO₂ dissolved in water (e.g., HydroC CO₂, Pro-Oceanus CO₂, C-sense) or for colorimetric detection (SAMI-CO₂) (**Table 1**). At the research stage, progress has been made toward the development of pCO_2 optodes (54–56) and, more recently, the Aanderaa 4797 CO₂ optode has been successfully used on a sea glider (57) and profiler (58). Such sensors rely on the equilibrium between dissolved CO_2 and a pH-sensitive fluorescent dye followed by fluorescence detection (56).

Another class of environmental sensors that have recently attracted attention are optical sensors. The main advantage of these sensors is the simple measurement principle, which relies on the interaction of ultraviolet (UV), visible (VIS), and infrared radiation with matter. These sensors use absorption, fluorescence, or scatter to detect a wide range of parameters (Table 1). The most employed optical parameter in coastal monitoring is turbidity. The measurement of turbidity is split into two basic methodologies: turbidimetry, in which the degree of transmission of light is determined, and nephelometry, in which the degree of light scattering is determined (59). Both principles are derived from mathematical models for real-world observations. In case of turbidimetry, the principles rely on Beer-Lambert laws, whereas for nephelometry, many theories and models have been developed to describe a range of scattering processes, and these models are mostly derived from Mie theory (59). Optical back scattering (OBS) can be determined at multiple angles with one or multiple detectors or at multiple wavelengths. The most common configuration uses a single detector at 90° and a light source in the infrared region of the spectrum. A light-emitting diode (LED) with a wavelength of 860 nm and a spectral bandwidth less than or equal to 60 nm is specified by the ISO 7027 as the light source (60). OBS sensors are now a mature technology, available from multiple manufacturers in either stand-alone configurations, coupled with other optical measurements like fluorescence, or part of multiparameter sondes (Table 1).

Fluorometers are another category of optical probes, which are commercially available for a range of parameters. Fluorometers have been traditionally used for chlorophyll a, b, c (Chl a) measurements but are now available for a range of other pigments such as phycocyanin and phycoerythrin and for algal speciation. Fluorescence signals are known to be affected by temperature, turbidity, pH, quenchers, and ionic strength. Therefore, interpretation of such data has to be done with caution (61). Quantifying phytoplankton biomass in situ using in vivo Chl a fluorescence has become a routine observation. Uncertainties in the data arising from interferences like the chromophoric dissolved organic matter (CDOM) concentration, nonphotochemical quenching, and phytoplankton physiology exist, although they can be corrected thorough discrete sampling followed by in vitro laboratory analysis (62, 63). For example, a correction by a factor of two is recommended for factory calibrated in situ fluorometers to produce a relatively small bias compared to global average high-performance liquid chromatography-measured values (64). In general, Chl a in situ measurement is accompanied by the measurements of other photosynthetic pigments like phycocyanin, phycoerythrin, and/or OBS and fluorescent dissolved organic matter (fDOM). Such configurations enable the gathering of robust data for oceanographic applications and allow pollution identification in coastal areas. Sensors with such configurations are in general purely optical (e.g., ECO Triplet, VLux series) or part of multiparameter sondes (e.g., a blue-green algae probe on YSI EXO series).

Fluorometers operating in the UV region are even more susceptible to errors, particularly due to overlapping absorption and emission bands from multiple dissolved and particulate components. Examples of species absorbing in the UV region and emitting in the UV-VIS include marine and terrestrial humic-like material, crude oil, refined oil, a range of amino acids including tryptophan that are often linked to bacterial contamination and biological oxygen demand, and CDOM/fDOM (65–67). To differentiate between the different species, fluorometers use multiple excitation/emission wavelengths finely tuned for the analyte of interest, and some apply signal correction algorithms for interferences like background fluorescence or turbidity. A range of submersible fluorometers with excitation in the UV region are available commercially (**Table 1**) for petroleum compounds (68), fDOM (69, 70), and tryptophan (71).alreviews.org.

The last measurement principle used by the optical probes relies on absorption derived from light attenuation. Such probes perform single or multiwavelength sensing in the UV to infrared spectral regions and rely on data processing via wavelengths based algorithms and partial least squares regressions to calculate nutrient concentrations (72). Examples of such sensors include Spectro::lyser or nitro-/multi::lyser (s::can GmbH, Vienna, Austria), TriOS NICO, (TriOS Messund Datentechnik GmbH, Rastede, Germany), and the SUNA V2 Nitrate Sensor (Sea-Bird Scientific, Bellevue, Washington) (**Table 1**).

However, to date, the powerhouse of environmental monitoring has been the multiparameter sonde (**Table 1**). These sensors bring together a multitude of probes in a modular plug-and-play design, where in addition to the electrical conductivity, temperature and depth/pressure (CTD) probes (provided as fixed in the configuration), users can select a wide range of hybrid or optical probes to suit their application. Among the most widely used parameters are Turb, DO, and *Chl a*, although with recent advancements, NO₃⁻ optical probes are now available (see the YSI EXO series). The plug-and-play design offered by these sensors suits a wide range of monitoring needs, and the same sonde can be used to address different monitoring requirements by simply replacing the probes. High-end multiparameter sondes have now up to seven available ports, which allow monitoring of a wide range of parameters simultaneously.

3. ROBUST LOW-COST ENGINEERING DESIGN

Sensors for in situ ocean monitoring must meet stringent international standards of robustness, reliability, and accuracy to be used commercially, as outlined in ISO 22013 (73). Enclosures and cables used must also be able to withstand hydrostatic pressures at depth and maintain a watertight seal to meet IP68 standards. Deterring corrosion is a major requirement for any components used in direct or indirect contact with the marine environment, including the external enclosure, fasteners, cables, optical components, and electronic components. ISO 9223 outlines standards for corrosion of metals and alloys, and time of wetness is defined as the amount of time a metal surface remains wet during atmospheric exposure (74).

The major components of a simple submersible optical sensor can be split in sensor housing or body, sensor head, and internal electronics (**Figure 2***a*,*e*). The enclosure houses all of the internal components and isolates them from the external environment. In general, O-rings are used to provide waterproofing when joining adjacent components. Enclosure designs and packaging of sensors have improved with advancements in materials, manufacturing techniques, and the increasing popularity of hobby submersibles from companies such as Blue Robotics (Torrance, California; https://bluerobotics.com/store/watertight-enclosures/wte-vp/#tube) and Develogic (Hamburg, Germany; http://www.develogic.de/products/underwater-housingsystems/) (Figure 2*d*), which provide off-the-shelf commercial housings at lower costs.

The materials used, manufacturing methods, and assembly of the components can mitigate risks of damage by creating a rigid, watertight structure. External materials used for the outer casing can withstand environmental damage and internal structures inside the housing are able to protect the vulnerable electronic components from damage. To counter saltwater corrosion, manufacturers apply superior metal materials known as especially corrosion-resistant alloys with specific properties to resist chemical corrosion (75). A range of materials are being used in sensor manufacturing (**Table 2**). Metal housing made from stainless steel 316 or titanium alloy are manufactured using deep drawing, extrusion, and rolling from stock material such as sheet, block, or tube. For finer detailing, drilling, milling, and lathe work may be required. Processing of harder metals generally results in higher manufacturing costs from tool wear and longer manufacturing times (76). Injection molding, extrusion, die casting, or blow molding is used for plastics such as



Figure 2

Example of marine sensor design. (*a*) Exploded view of an optical marine sensor showing the different sections that compose it. (*b*) Example of a commonly used IP68-rated marine cable connector used on YSI 6 series sondes. (*c*) Example of a wet-mate bulkhead connector from an in-house-built sensor. (*d*) Example of a sensor enclosure designed in-house and fabricated via computer numerical control machining. (*e*) Labeled diagram example of different engineering sections of a marine sensor. (*f*) Example of an internal frame structure design used for mounting of electronic and optical components and (*g*) fabricated frame with mounted components. (*b*, *i*) Example of light source and detector optical windows at the interface with the environment in an optical detection system. (*b*) Collimating fused silica lenses in an in-house-built sensor. (*i*) Exposed optical fiber ends in a turbidity probe used on YSI 6 series sondes. Red arrows point to the optical windows.

methylene polyoxide (POM), whereas additive manufacturing techniques are ideal for rapid prototyping. Specific cables and connectors are required for any hardwire connections made between devices in the marine environment with an IP68 rating to ensure complete isolation of the electrical connections from the environment. The cables are now stronger and can hold more weight, and the integrated strain relief takes additional pressure off the wet-mate bulkhead connector, which ultimately provides a much more durable and rugged cable (**Figure 2***b,c*).

An environmental sensor's electronic system consists of many interconnected parts allowing it to perform the required functionality of the sensor to gather data reliability and consistently and then output those data to be used by another external system. The capabilities of environmental sensors have expanded dramatically while costs have been reduced, which is due to a few factors. Miniaturization of electronic components due to Moore's law (77) has made certain sensing components more practical to integrate. Mass production of components and materials has led to

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On: Sun, 30 Jun 2024 14:32:2

Grade	Material	Sensors			
Metal-based materials					
316	Stainless steel alloy (contains molybdenum)	YSI, Sea-Bird, Turner			
AH36	Carbon steel	YSI			
6061-T6	Aluminum	Blue Robotics ROV (remotely operated underwater vehicle)			
	Titanium	YSI, Sea-Bird, Chelsea, TriOS, s::can, Turner			
1.4571/1.4404	Stainless steel	TriOS			
	Copper	Sea-Bird, TriOS, HydroCAT-EP, Chelsea, Turner, HYDROLAB			
Polymers					
Xenoy	Blend/resins	YSI			
Lexan	Polycarbonates/thermoplastic	YSI			
Victrex PEEK	Thermoplastic	Quantum Analytical			
PPS (polyphenylene sulfide)	Thermoplastic	Chelsea			
Acetal C	Thermoplastic	TriOS			
Rigid polyurethane	Thermoplastic/thermoset	Seapoint Sensors			

Table 2 Materials used in sensor manufacturing

reduced costs, thus making the technology more accessible. In the last decade, LEDs have become cheaper, smaller, and more available in a wide spectral range (from deep UV to infrared) (78), which has led to their increased use in environmental optical sensors. LEDs are more efficient and brighter than alternative light sources (79), making them suitable for use in power-limited remote applications such as in situ sensors. LEDs can be used together on the same device to provide multispectral data readings (80). LEDs come in two basic packages, through-hole and surface mounted. Through-hole LEDs tend to be larger and more expensive when used in a mass-produced product owing to difficulties in assembling components. Surface-mounted LEDs are much cheaper, smaller, and conducive to the automated assembly of printed circuit board, making them more suitable to mass production. The smaller size of current LED packages allows for multiple LEDs to be positioned together to form a low-profile, multispectral LED array light source.

Photodetectors are used to convert the emitted fluorescence into an electrical signal that can be quantified. Photodiodes are most used in fluorometers and are semiconductors that generate an electrical current proportional to the light intensity. However, single photodiode detectors are limited to just intensity measurements and require optical filtration to isolate the targeted wavelength of interest. The use of mini spectrometers in marine/underwater scientific instruments has increased. Over the last two decades, advancements in spectrometer optical design, software, hardware, and fabrication techniques have produced ultracompact microspectrometer systems that maintain an acceptable level of performance and a sufficient resolution in the visible range that is adequate for in situ sensors (81–83). If higher resolution is needed in the system, a complementary metal-oxide-semiconductor spectrometer can be used, which can supply individual intensity readings over a spectral range. Light enters the spectrometer though a narrow aperture called an entrance slit, and the slit vignettes the incoming light. A concave mirror is used to collimate the light, and a grating disperses the light into its spectral components, which are directed away at slightly different angles. An array of photodetectors can be lined up with the respective angles of the dispersed light to measure the individual components of the light as wavelength regions. Optical lenses and windows are used primarily at the interface with the environment and in general serve two purposes: optical-coupling (collimation or focusing) and protection of internal components from the outer environment (**Figure** *2b,i*). They must keep a watertight seal while also withstanding hydrostatic pressure, fouling, abrasion, and impact.

4. BIOFOULING PROTECTION

The adhesion and growth of microorganisms at the interface between any nonsterile medium and a solid surface are widespread phenomena that occur in most environments on Earth. The development of biofilms on surfaces and accumulation of biomass on components and structures that are immersed in water are major challenges for industries conducting research on materials, coatings, corrosion, structural failures, or loss of performance, among others. This adhesion and undesirable biological growth on surfaces have been termed biofouling (84, 85). Fouling and, in particular, biofouling have long been considered limiting factors for sensors operating in the marine environment and are recognized as main obstacles to in situ environmental monitoring (86, 87). All immersed components, including operational components (membranes, optical windows, and electrodes), housings, and mooring components are subject to biofouling and prone to irreversible damage (88). For a large percentage of deployed instrumentation, biofouling is the single biggest factor affecting the operation, maintenance, and data quality. The Alliance for Coastal Technologies in the United States has estimated that up to 50% of operational budgets are attributed to biofouling, depending on location and season (89). Such costs are associated with shorter deployment periods, loss of data due to sensor drift, frequent maintenance requirements, and a shorter lifespan of the instruments. To date, sensor manufacturers have employed a wide range antifouling strategies to deter fouling (for a detailed review, see 14). In general, these strategies can be grouped into passive and active strategies. Active protection is applied to the critical active sensing or transducer areas, which lie at the interface with the environment. Based on sensor type, these can be optical guides (optical windows, lenses, or optical fiber), gas-permeable membranes, or conductivity cells. Among active protection strategies, the most widely implemented in commercial systems are wipers, biocide injection systems, and shutters (14) (Figure 3a-d). Wipers rely on mechanical cleaning and can be built-in [such as the YSI EXO series central wiper from YSI, a Xylem brand, Yellow Springs, Ohio (Figure 3a) or self-cleaning sensors from HY-DROLAB, Loveland, Colorado] or stand-alone [see Hydro-Wiper, Zebra Tech Ltd., Nelson, New Zealand (Figure 3c); https://www.zebra-tech.co.nz/hydro-wiper/]. Other manufacturers use shutters for light blocking and active cleaning. For example, the ClearSensor Method from Campbell Scientific (Logan, Utah) uses a copper shutter constructed to prevent sand grains or packed sediment from getting wedged between the shutter and sensor body (90). Another active strategy is the use of biocide generation systems. For example, systems based on the use of compounds such as peracids, quaternary ammonium compounds, and chlorination have been used for years in industrial applications to combat biofouling (14). Sea-Bird Scientific uses bleach injection and electrolytic chlorination in conductivity cells coupled with tributyltin rings (Figure 3b). Another active strategy that shows promise for future implementation is the use of in situ UV radiation. To that extent, ongoing research is looking at the potential for integration in ship hulls (91–93). For sensor applications, Mariscope (Kiel, Germany; https://www.mariscope.de/product/uv-ledantifouling/) and AML Oceanographic (Dartmouth, Nova Scotia, Canada; https://amloceano graphic.com/uv-biofouling-control) offer UV-based solutions that can be integrated into multiple sensing platforms (Figure 3e). Passive antifouling strategies have been used throughout, on the sensor body, wipers, probe housing, mounting plates, and guards. The method of tributyltinbased paints has been widely used in the past, but since its prohibition by the International Maritime Organization in 2008, manufacturers have had to look for other similar alternatives.



Summary of antifouling strategies used in sensor protection. (*a*) Built-in antifouling wipers: (*i*) central wiper on a YSI EXO series multiparameter sonde and (*ii*) individual wipers on a YSI V6 series sonde. (*b*) Biocide container on a water quality monitor WET Labs and Sea-Bird Scientific sensor (https://www.ott.com/download/sea-bird-scientific-wqm-manual/). Subpanels reproduced with permission from Sea-Bird Scientific, Bellevue, Washington. (*c*) Stand-alone antifouling wiper example (https://www.zebra-tech.co.nz/hydro-wiper/). Panel reproduced with permission from ZebraTech Ltd., Nelson, New Zealand. (*d*) Copper shutter in the ECO fluorometers line (https://www.seabird.com/eco-fluorometer/product?id=60429374754#). Panel reproduced with permission from Sea-Bird Scientific. (*e*) Effectiveness of (*i*) an ultraviolet C-band (UV-C) irradiated probe versus (*ii*) an unprotected probe against biofouling after nine months of deployment (https://amloceanographic.com/). Panel reproduced with permission from AML

Oceanographic, Dartmouth, Nova Scotia, Canada.

One is the use of copper in the form of copper alloys, copper coatings, and copper-based antifouling paints (14) (**Figure 3**). Slow-release coatings release cuprous oxide into the surrounding environment, whereas ablative antifouling paints rely on the biocidal effect. The released bivalent Cu^{2+} interferes with cell membrane enzymes, preventing cell division (94). Although they are in an incipient stage, nature-inspired engineered biomimetic surfaces have shown potential as a complementary passive solution (95, 96) and application to sensor components and housings. Deployment platforms could become a reality in the future.

The most successful solutions implemented to date use both passive and active strategies in tandem. Examples include the combination of wipers with biocidal materials (mainly copper, copper alloys, and copper-based paints) or the combination of wiper/shutter systems with bleach injection, tributyltin-controlled release, and biocidal materials (copper components). In general, manufacturers of highly specialized equipment are going to great extents to ensure cost and antifouling efficiency. A good example is the transition to a central wiper on the latest EXO series multiparameter sonde (Figure 3a, subpanels i, ii) that has replaced individual wipers on optical and hybrid probes in the V6 series sonde. The latest design coupled with a reengineered conductivity probe allowed full reach of the mechanical wiper into the conductivity cell,

providing fouling protection to previously vulnerable areas (97). The variety of sensor types, their deployment scenarios, and their application preclude a single antifouling strategy. To date, there is no universal strategy that is effective, but rather a combination of strategies has extended deployment times and maintenance-free periods from days to months.

5. DISCUSSION

The main challenge to the realization of high-density coastal and oceanographic sensor networks is cost, which includes the capital and operational cost. While the former is needed for sensing instrumentation and deployment infrastructure, the latter is needed for maintenance, service, and site visitations. Deployment strategy is thus important for cost-effective data collection. Multiple deployment platforms exist for in situ instrumentation, capable of providing three-dimensional spatial resolution at high temporal frequency, and are covered in depth elsewhere (98-100). Stateof-the-art autonomous surface platforms (gliders, floats), new fixed location moorings, and the use of boats of opportunity have all decreased the cost of deploying sensors. This has been in part allowed by an overall decrease in payloads mainly driven by recent miniaturization of sensing technologies. For most scenarios, the sensor payload on these platforms represents the highest capital cost. An extensive range of sensors is available for coastal and oceanographic applications (Table 1). A clear trend toward smaller, smarter, and cheaper sensors is observed with three priorities: miniaturization, use of lower-priced materials, and the use of innovative approaches for sensor design, integration, and signal transduction. For example, while a traditional CTD instrument costs approximately US\$10,000, a new micro-electro-mechanical-system (MEMS)-based CTD sensor has an approximately tenfold lower cost. Although a typical DO optode may cost upward of US\$10,000, repackaging it using low-cost materials and electronics can decrease the cost by five- to tenfold (39).

The emergence of LOC technology has catalyzed the development of wet chemistry-based sensors into robust, low-cost, and compact technologies. The modest size and power consumption, low reagent requirement, and imbedded in situ calibration protocols (which provide high-quality data) have lowered the overall deployment cost and extended deployment times to months without maintenance (23, 101–103). Although the technology is still in a growth stage, it has excellent potential for further development. Immediate development could see an increase in the complexity of such sensors through integration to allow detection of multiple parameters within one unit. The future is also likely to see the realization of LOC sensors for algal toxins (17), the identification and quantification of key groups of bacteria and archaea through detection and enumeration of DNA or RNA sequences (104), where an innovation pipeline already exists from the medical device sector (105), and environmental DNA (106). Molecular biology techniques require small sample and reagent volumes (microliter scale), which makes them ideal for LOC integration. By comparison, interface-based sensors are a more established technology for the marine environment (9), with sensors such as the DO optode, OBS instrument, and Chl a sensors reaching maturation. Innovation exists at the development stage, with efforts made toward the development of more robust and reliable technologies and new detection and transduction mechanisms (e.g., quantum dots for phycoerythrin) (107, 108).

To date, there are two main trends among sensor manufacturers. Manufacturers of highspecification instrumentation (e.g., YSI and Sea-Bird Scientific) place the requirements of the end user at the center of product design and provide solutions for an extended range of applications. Such sensors are the result of many years of experience, in-house know-how, research, and continuous engagement with end users. The performance of such sensors is in general excellent and takes precedent over cost. The second trend is a focus on low-cost, optical-based sensors. Progress in this field has been mainly catalyzed by progress in optical components, low-cost electrical components (e.g., single-board microcomputers and microcontrollers and radio frequency transceivers) and manufacturing technologies (see Section 4). Optical sensors and optodes are slowly replacing their ion-selective electrode counterparts mainly due to analytical performance, stability over time, robustness, and longer lifetime. With a growing environmental sensor market and new solid state sensors available for a wide range of parameters, sensor performance is a critical factor in the selection process. Emerging sensors that have not been fully validated and tested in environmental applications rely on verification by third parties. This is accomplished mainly by peer-reviewed, published scientific literature coming from both academia and independent organizations. For example, the Alliance for Coastal Technologies provides verification reports on performance testing of emerging technologies in operational environments (https://www. act-us.info/evaluations.php) and maintains a database of sensors for oceanographic applications. In terms of physical or biological fouling of sensors, which affects integrity of the data and increases operational costs, there is no ideal solution available, but rather a combination of multiple approaches can be used (14). In general, for manufacturers of high-specification instrumentation, the antifouling strategy is an essential performance indicator, whereas other manufacturers rely on the end user to implement the antifouling strategy or collaborate with specialized companies for the implementation of active protection. Such companies are now emerging and offer wiper-based and UV-based solutions that can be retrofitted to a wide range of sensors.

6. CONCLUSIONS

There is a pressing demand for an increase in operational architectures (autonomous and in situ) at regional and global scales for monitoring coastal and oceanographic zones. Coastal sensor networks for real-time decision support and marine networks for ocean observations are instrumental to our understanding of ocean biochemistry, the impacts of anthropogenic pollution, and mitigation.

This article reviews in situ sensors that are available commercially or at a research stage and are suitable for deployment in the marine environment. In situ sensors are becoming smaller, smarter, more cost-effective, and increasingly specialized and diversified. In terms of innovation, progress has been made in the development of wet chemistry–based sensors through the integration of microfluidic platforms and LOC devices and development of interface sensors through new optodes for pCO_2 and lower-cost optical sensors. Current antifouling strategies are reducing the maintenance cost of in situ sensors, and there is potential for further reductions through the use of emerging technologies such as UV radiation and nature-inspired surfaces. The capital cost of sensors has also decreased owing to low-cost electrical and optical components and manufacturing without a loss in performance.

Although most sensors have been prototyped and demonstrated in academic research, it is industry that has perfected them through innovative design and smart engineering. The most notable developments and advancements come from industry, with the development of specialized, tailor-designed solutions for various applications. The collaboration between academia and industry is thus critical for the realization of next-generation, cost-effective technologies.

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