Monitoring the Marine Environment using a low-cost Colorimetric Optical Sensor

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Abstract— Anthropogenic activities have led to increased stress on our marine and other aquatic environments. There is a pressing need to monitor, measure, understand and mitigate the causes of these pressures. This paper presents the development and preliminary testing of a low-cost colorimetric optical sensor to detect colour-linked events in the marine environment. Potential applications may include the detection of Harmful Algal Blooms (HAB), which due to the production of toxins have deleterious effects on marine ecosystems and can ultimately lead to human, fish, bird and mammal deaths. Preliminary results indicate the capability of the sensor to differentiate between the colour signatures of several environmental samples.

Keywords-environmental monitoring; colorimetric sensor; marine sensing; optical sensor.

I. INTRODUCTION

Recognition of the incontrovertible facts that the marine environment (1) plays a vital role in sustaining life and (2) is rapidly deteriorating, has led to a greater focus on the health of the European marine environment [1]. European frameworks such as the Water Framework Directive [2], the Bathing Water Directive [3] and the Marine Strategy Framework Directive [4] acknowledge that the marine environment, and water in general, are heritages and "*must be protected, preserved and, where practicable, restored with the ultimate aim of maintaining biodiversity and providing diverse and dynamic oceans and seas which are clean, healthy and productive* [4]".

Several water quality monitoring requirements are identified in the aforementioned directives and current FP7 projects address several of these areas of concern. For example, the focus of EPOCA [5] is ocean acidification (the drop in ocean pH caused by absorption of atmospheric CO_2). MedSeA [6] is again concerned with ocean

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acidification but specifically in relation to the Mediterranean Sea. The overall objectives of Hypox [7] and Viroclime [8] are to continuously monitor oxygen depletion in aquatic systems and to investigate the impact of climate change on viral flux (i.e., the growth, death and transport of viruses) respectively. Despite this significant increase in marine monitoring activity, there remain several important research areas that require detailed investigation, for example:

- 1. Continuous real-time monitoring of harmful bacterial species;
- 2. Improvement in continuous, long-term marine monitoring capabilities in terms of both sensor development and deployment e.g. antifouling and sensor marinisation (i.e., the design of a system for survival in the harsh marine environment).

To put some of these contamination risks in context, harmful bacterial species in the marine environment such as microcystins can lead to severe human and animal intoxication [9]. Symptoms can range for vomiting to liver and neurological dysfunctions which, in severe cases, can ultimately result in the death of consumers.

Certain harmful bacterial species of interest have specific colour footprints. For example, cyanobacteria, which include the microcystins, are characterised by bright green algal blooms [10]. Other harmful algal blooms, which contain species such as *Karenia brevis* and *Alexandrium* are characterised by the colour red, commonly known as red tides [11, 12]. Therefore, the application of low-cost colorimetric optical sensors may potentially be very beneficial to detect colorimetric events such as harmful algal blooms and to serve as an early warning alarm and decision support tool for more sophisticated bacterial sensors.

Traditional approaches to monitor and detect harmful bacterial species have typically involved the intermittent

collection of samples at the relevant monitoring location (grab sampling), the transportation of the samples to the laboratory, the analysis of samples using various lab-based analytical techniques and the evaluation of results. This approach is not always ideal for a number of reasons, including: (1) the possibility of missing events due to low sampling frequencies, (2) the potential for sample contamination during transport from the point of collection to the laboratory, and (3) the inherent lead time from sample collection to analytical results. This can be problematic with regards to delayed reaction protocols and cause traceability. Lead times can be considerable in the analysis of bacterial samples which require culturing in the laboratory. There is therefore a strong argument for continuous in-situ monitoring. However, the development of long-term, continuous bacterial sensors in the marine environment is far from trivial. The objective of this research is to develop a low-cost, continuous, long-term, optical colorimetric sensor to detect colorimetric events, and thus act as a decision support tool for more sophisticated bacterial sensors, for example, to inform sampling frequency.

Much research has been conducted in the area of monitoring the inherent optical properties (IOP) of water and its relation to biological content. This is mainly done using satellite imaging of the ocean surface. Woods Hole Oceanographic Institution has reported vertical profiling of attenuation and scattering characteristics of New England coastal waters using a Wetlabs AC-9 meter. [13]

The Wetlabs AC-S *in-situ* spectrometer [14] a descendent of the AC-9 is a highly sensitive device with high spectral resolution for the detection of IOP, using a flow through detection system.

The OCS is an inexpensive, imprecise sensor intended for detecting significant changes in the bulk optical properties of marine waters. The OCS has several important advantages. First, it is low cost (less than \in 500 per unit for parts). A second advantage is ease of deployment; the sensor requires no support structure, only a mooring. These features allow for multiple strategic deployments to allow both temporal and spatial monitoring.

II. DEVELOPMENT OF OPTICAL COLORIMETRIC SENSOR

The Optical Colorimetric System (OCS) was based on a first generation prototype developed by researchers in CLARITY, Centre for Sensor Web Technology, Dublin City University (Fig. 1).

Prototype 1 was essentially a laboratory version and features included;

- LED array light source (IR, red, amber, green, blue)
- Photodiode detectors (90° and 180° to the light source)
- Short-range wireless communications.

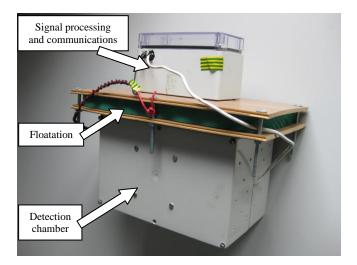


Figure 1. Prototype 1 showing measurement system below the water and communications above the water – separated by the float.

Prototype 2, the Optical Colorimetric Sensor (OCS), was developed to be a more robust field version of the original (Fig. 2). Additional features include:

- Robust marine deployable design
- Antifouling measures
- GSM communications.

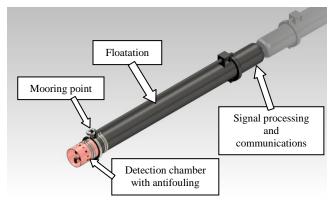


Figure 2. Prototype 2.

The Prototype 2 OCS is deployed using a single point mooring. It floats at the surface with the sensing elements submerged at 1 m. GSM telecommunications equipment is housed in the upper compartment above the water line. The OCS is designed for inshore use thus GSM communication is adequate in most Irish scenarios. Detection involves the use of 5 LEDs at differing wavelengths as a light source and photodiode detectors at 180 degrees and 90 degrees to the source. The detectors measure attenuation and reflectance respectively.

Optical detection in the marine is subject to interference such as scattering due to suspended particulate matter. Also significant drift in readings over time will be expected due to the formation of biofilms on optical windows. Antifouling research previously carried out by MESTECH has been incorporated into the sensor design to mitigate fouling effects. The objective of the OCS is to inform of shifts in colour or particle density with respect to a baseline, but not to quantify these changes accurately. Issues of sensor robustness will be addressed as part of future testing in the marine environment.

III. RESULTS TO DATE

Preliminary system evaluations were carried out using varying concentrations of food dye in tap water, which were chosen as being representative of typical environmental colorations. Fig. 3 and Fig. 4 show the system response (per LED) to changes in concentrations of red and green food dyes in tap water respectively. The percentage attenuation refers to the reduction in light transmission through the sample from a baseline of transmission in tap-water. Based on these initial results, the system demonstrates sensitivity to dye concentration changes in water, and can, therefore, distinguish between differing depths of colour. For example, the red dve (Ponceau 4R E124) absorbs light from 350 nm to 500 nm (i.e., UV to green). Thus in Fig. 3 the blue and green light is attenuated strongly by the red dye. In Fig. 4, the green dye (Tartrazine E102, Green S E142) absorbs light between 350 nm and 450 nm and also between 570 nm and 700 nm, thus the blue, amber and red lights are attenuated. In both Fig. 3 and Fig. 4, it can be seen that IR (850 nm) is not attenuated by either dye. However, it can be seen to attenuate strongly in environmental samples; see Fig. 5. This can be due to absorption in dissolved organic matter.

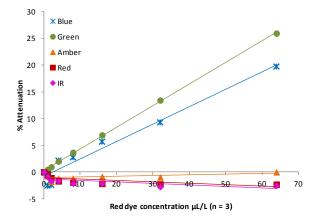


Figure 3. Response of the prototype 2 sensor to red dye.

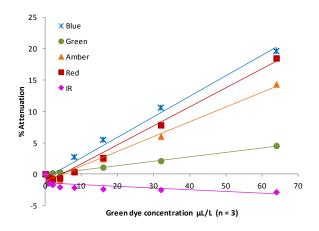


Figure 4. Response of the prototype 2 sensor to green dye.

A follow-on objective of the research was to establish the ability of the OCS to differentiate between the colours of samples taken from various aquatic environments. Samples from several locations throughout Dublin were analysed *insitu* using the sensor. These samples included both riverine and estuarine waters. The percentage changes in light transmission through samples were recorded and were referenced against clean tap-water. The results are shown in Fig. 5, which clearly demonstrate the capability of the sensor to distinguish between the different absorbance signatures of the various water samples. These preliminary results are significant and point towards potential marine monitoring applications.

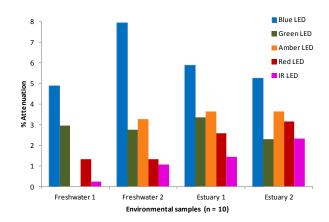


Figure 5. Field analysis of environmental samples using OCS.

IV. CONCLUSION AND FUTURE WORK

Based on preliminary tests and results, the OCS shows promise for marine environmental applications. The OCS system is robust and deployable in the aquatic environment. Of particular importance, the OCS shows potential to detect events in the environment such as a shift in water colour due to a pollution event. Future work includes longer-term deployment in the marine environment (SmartBay, the National Test and Demonstration Infrastructure, Galway). Events detected will be cross referenced against commercial sensing equipment (YSI sonde 6600) and standard laboratory analysis as part of an ongoing sampling programme. Future research will also involve the characterisation of the colorimetric response to simulated environmental events.

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REFERENCES

[1] European Commission Fact sheet: protecting and conserving the marine environment, [on-line], http://ec.europa.eu/environment/pubs/pdf/factsheets/marine.p df, (Accessed April 2012).

- [2] European Water Framework Directive, DIRECTIVE 2000/60/EC.
- [3] European Bathing Water Directive, DIRECTIVE 2006/7/EC.
- [4] European Marine Strategy Framework Directive, DIRECTIVE 2008/56/EC.
- [5] EPOCA website, [on-line], http://www.epoca-project.eu/, (Accessed April 2012).
- [6] MedSeA website, [on-line], http://medsea-project.eu/, (Accessed April 2012).
- [7] Hypox website, [on-line], http://www.hypox.net/, (Accessed April 2012).
- [8] Viroclime website, [on-line], http://www.viroclime.org/, (Accessed April 2012).
- [9] B. Byrne, E. Stack, N. Gilmartin, and R. O'Kennedy, 2012, "Antibody-based sensors: Principles, Problems and Potential for Detection of Pathogens and Associated Toxins", Sensors, 9(6), 4407-4445.
- [10] M.T. Madigan, J.M. Martinko, P.V. Dunlap, and D.P. Clark, *Brock Biology of Microorganisms*, 12th edition, 2009, Pearson, San Francisco, United States.
- [11] J. T. Turner, V. Roncalli and P. Ciminiello, 2012, "Biogeographic Effects of the Gulf of Mexico Red Tide DinoflagellateKareniaBrevis on Mediterranean Copepods," Harmful Algae, 16(0) pp. 63-73.
- [12] Woods Hole Oceanographic Institution website, [on-line], http://www.whoi.edu/oceanus/viewArticle.do?id=13406, (Accessed April 2012).
- [13] Woods Hole Oceanographic Institution website, [on-line], http://www.whoi.edu/science/B/sosiklab/063.pdf, (Accessed, July, 2012)
- [14] WetLabs AC-S specification sheet (Accessed July, 2012) http://www.wetlabs.com/products/pub/specsheets/acsssd.pdf