

Reliable in-Situ Sensing of Water Quality Parameters using Low Cost Autonomous Analysers

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Abstract

A sensing platform for the in situ, real-time analysis of phosphate in natural waters has been realised using a combination of microfluidics, colorimetric reagent chemistries, low-cost LED-based optical detection and wireless communications. Prior to field deployment, the platform was tested in the laboratory where a total of 459 autonomous measurements were performed (153 each of low calibration standard, high calibration standard and sample). The platform was subsequently field-deployed in Dublin Bay at the mouth of the Tolka Estuary, County Dublin, Ireland, to track changes in phosphate continuously at a transitional water body site previously identified as at risk. Initial data from 10/04/19 to 17/04/19 is presented, comprising 168 autonomous measurements (56 each of low calibration standards, high calibration standards and sample).

Keywords: water quality; phosphate; eutrophication; colorimetric chemistries; autonomous analysers

1. Introduction

Excessive nutrient loading in both fresh and marine ecosystems can have adverse effects on aquatic ecosystems [1]. Eutrophication as a result of elevated nutrients levels can result in the formation of harmful algal blooms leading to oxygen depletion, the release of algal toxins, formation of dead zones and contamination of drinking water supplies [2]. Traditionally, phosphate levels in natural waters are taken by manual collection and subsequent laboratory analysis [3]. This process is not only labour intensive and costly but provides limited information regarding the spatial and temporal variation of the nutrient within the waterbody. Real-time monitoring provides reliable in situ measurements, which can provide spatial data that can enhance our understanding of the processes that drive increases in nutrient levels [4]. These data can be used to strengthen the development of projection models for mitigation measures to reduce economic and environmental impacts caused by nutrient stresses [5]. In recent years, advances in rapid prototyping related to 3D printing and fabrication technologies have dramatically improved the efficiency of producing in situ reagent-based analysers for monitoring key environmental parameters, such as phosphate levels in natural waters [6,7]. This improved prototyping efficiency is opening the way to more

effective analytical platforms, combined with lower unit costs, higher frequency sampling, and longer service intervals for sensing platforms for nutrients (PO_4^{3-} , NO_2^- and NO_3^-) and other analytical targets in natural waters. Despite these advances, measurement uncertainty, reliability, robustness and cost of in situ analysers for long term deployments still significantly inhibit wide scale deployments necessary to generate data with enhanced spatial and temporal frequency to meet user and regulatory requirements. In this paper we describe the testing carried out on a prototype nutrient platform in lab and in the field as seen in figure 1.

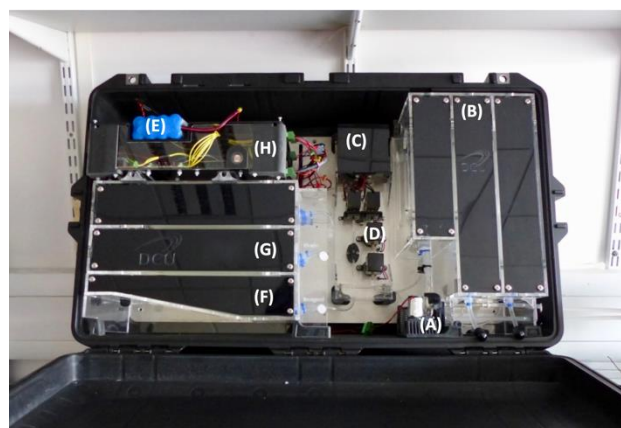


Figure 1. Sensing Platform with (A) Inlet System, (B) bags holding sample, high calibration standard, and low calibration standard, (C) Detection chamber housing the microfluidic chip, LED (375nm), and photodiode, (D) Fluidic Control Board, (E) battery, (F) Reagent Bag, (G) waste bag and (H) electronics.

The sensing platform is completely autonomous, incorporating sampling, automatic calibration, waste containment, and wireless communication. Automation is achieved via Arduino microcontrollers, while low cost pumps and solenoid valves allow precise fluidic handling. Microfluidics facilitates effective sample-reagent (1:1) mixing using shear forces in a serpentine channel, followed by colorimetric detection via an integrated 2.25 cm path length flow cell using a pulse width modulated LED, coupled with an in-line photodiode detector.

2. Results and Discussion

2.1. In lab Testing

The Sensing platform was tested in lab in fully autonomous operational mode prior to initiating field deployments. The measurement cycle (ca. 70 min) consisted of (i) blank solution measurement ($0 \mu\text{M PO}_4^{3-}$), (ii) high standard measurement ($50 \mu\text{M PO}_4^{3-}$), and (iii) sample measurement. During this test, the platform generated 153 measurements of each test solution, blank, high and sample. Samples were obtained from a tank containing $25 \mu\text{M PO}_4^{3-}$.

Figure 2 shows the platform response obtained over the test period. The red square, representing the PO_4^{3-} concentrations determined using the UV-Vis Spectrophotometer reference method, are clearly in excellent agreement with the concentrations determined by the sensing platform (Table 1). Overall, the response of the platform was encouraging, with the response remaining reasonably consistent with the reference measurements throughout.

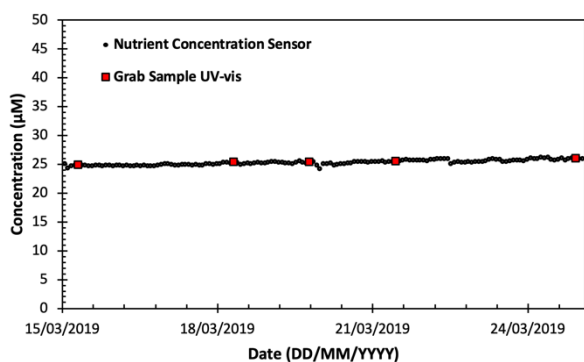


Figure 2. Laboratory analysis of $25 \mu\text{M}$ phosphate standard with autonomous sensing platform (black dots) and the UV-Vis spectrometer reference method (red squares).

Reference PO_4^{3-}		Sensing Platform PO_4^{3-}	
Mean \pm %RSD	%RE	Mean \pm %RSD	%RE
25.51 ± 1.66	1.50	25.38 ± 1.60	1.98

Table 1. Summary of the analytical performance at $25 \mu\text{M}$ phosphate during in lab testing.

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2.2. Dublin Bay Deployment

Following extensive lab trials, the systems field performance was assessed through a deployment during which it operated in completely autonomous mode in Dublin Bay. Figure 3 shows the phosphate concentration data generated during the deployment. From the 10/04/2019 to 17/04/2019, a total of 168 in situ measurements (i.e., 56 sample, 56 blank ($0 \mu\text{M}$) and 56 high standard ($50 \mu\text{M}$) were obtained. The sample was filtered through a $0.45 \mu\text{M}$ filter membrane at the inlet.

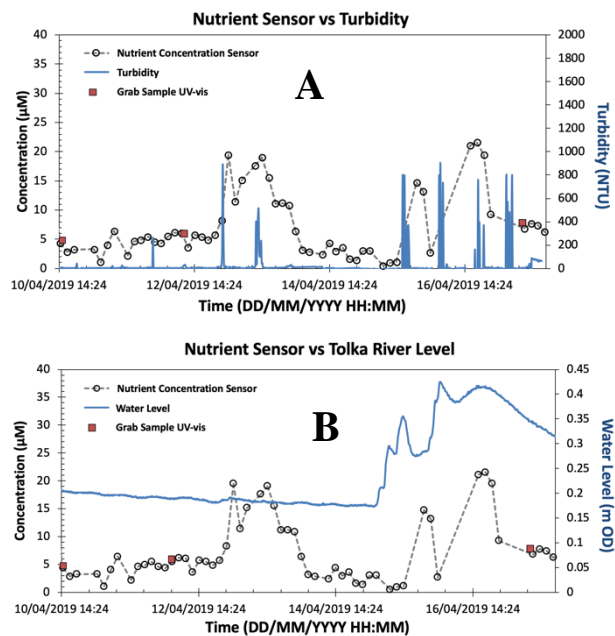


Figure 3. Variation in phosphate concentration (PO_4^{3-}) measurements in Dublin bay, (A) Nutrient concentrations vs Turbidity and (B) Nutrient concentrations versus river outflow into sampling site.

Figure 3 shows elevated phosphate concentration events, the first centred on 13/04/2019 and the second centred on 16/04/2019. Elevated turbidity can be seen during both events (A) and elevated water level seen during the second event on the 16th (B). Several reference measurements from grab samples correlate closely with data obtained from the in-situ analyser. During the deployment, the phosphate concentrations measured by the platform ranged from 0.51 to $32.51 \mu\text{M}$, with an average concentration of $9.12 \mu\text{M}$.

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