An Autonomous Microfluidic Sensor for Phosphate: On-Site Analysis of Treated Wastewater

John Cleary, Conor Slater, Christina McGraw, and Dermot Diamond

***Abstract*—A microfluidic sensor for long-term monitoring of phosphate levels has been developed that incorporates sampling, reagent and waste storage, detection, and wireless communication into a compact and portable device. The sensor is based on the yellow method for phosphate determination, a simple colorimetric technique involving the formation of vanadomolybdophosphoric acid when a phosphate-containing sample is mixed with an acidic reagent containing ammonium molybdate and ammonium metavanadate. This paper describes the application of the phosphate sensor to the on-site analysis of effluent from a wastewater treatment plant. The data was validated by comparison with the plant's existing online monitor, and a good correlation between the two sets of data was achieved, showing that the phosphate sensor is capable of operating satisfactorily at low mg L^{-1} levels over extended periods of time.**

***Index Terms*—Environment, microfluidic, phosphate, wireless sensor network.**

I. Introduction

PHOSPHORUS is an essential nutrient for plant and animal species, and is a limiting nutrient in many aquatic ecosystems. It is typically present in the form of phosphate, of which the inorganic orthophosphate form is the most stable. Eutrophication (overenrichment of natural waters with phosphate or other nutrients) is one of the most common water quality issues for many regions, occurs primarily due to human activities, and leads to excessive growth of algae and other aquatic plants [1]. This, in turn, deteriorates the health of aquatic ecosystems [2], [3] by decreasing the amount of dissolved oxygen available for other organisms, sometimes resulting in large-scale fish kills. Other harmful effects of eutrophication include the development of unsightly and sometimes toxic algal blooms, with associated health risks to animals and humans, as well as impairment of the use of water bodies as drinking water, recreational, and amenity resources. Major sources of phosphate in natural waters include wastewater (treated and untreated), agricultural sources such as fertilizers and farmyard runoff, and industrial sources [4].

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J. Cleary, C. Slater, and D. Diamond are with the AIC Adaptive Sensors Group, Dublin City University, Dublin 9, Ireland (e-mail: john.cleary@dcu.ie; conor.slater@dcu.ie; dermot.diamond@dcu.ie).

C. McGraw was with the AIC Adaptive Sensors Group at Dublin City University. She is now with the Department of Chemistry, University of Otago, Dunedin, New Zealand (e-mail: cmcgraw@chemistry.otago.ac.nz).

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Currently, measurements of phosphate levels in natural waters are typically made by manual collection and filtering of samples, followed by laboratory analysis. Manual sample collection is not only labor intensive and costly, but provides limited information about the spatial and temporal distribution of phosphate throughout a water system, as highlighted by the work of Donohue *et al.* [5], Irvine [6], and Jordan *et al.* [7]. Moreover, in the European context, the implementation of the Water Framework Directive (WFD) [8], aimed at maintaining and improving the aquatic environment in the European Community, has provided an impetus towards enhanced water quality monitoring. The WFD envisages three types of monitoring, namely: (i) *surveillance monitoring*—involving assessment of long-term trends in water quality; (ii) *operational monitoring*—to be carried out where pollution or other impacts on ecological status are apparent; and (iii) *investigative monitoring*—"snapshot" monitoring to help ascertain the reason for poor quality at a particular location, or to assess the impact of a pollution incident.

The objective of this work is to develop a phosphate sensor capable of being deployed in large numbers on rivers, lakes or any body of water in order to allow rapid detection and location of phosphate pollution, thereby facilitating identification of polluters and ultimately helping to minimize damage to the aquatic ecosystem. Dynamic tracking of trends using such sensor networks would facilitate early warning of emerging problems and assessment of the effectiveness of remedial strategies. In order to fulfill this vision for the future of environmental monitoring, the analytical system developed must be portable, environmentally compatible, robust, inexpensive to own and operate, and capable of providing reliable analytical information over extended periods of autonomous operation [9].

To date, a system for the detection of phosphate in natural waters has been miniaturized, assessed, and packaged into a compact and portable system, as described previously [9]–[13]. This completely autonomous device incorporates sampling, reagent handling, mixing of sample and reagent, colorimetric detection, waste containment, wireless communication, and a power supply. Microfluidic technology is used to minimize the volumes of reagent and sample required, which in turn enables the use of a low powered pumping system. The system also employs a low-power detection and communication system, so the entire instrument can operate autonomously for 7 days on a 12 V battery. Integration of a wireless communication device allows acquisition parameters to be controlled remotely and adjusted according to individual needs, in addition to enabling data transfer [13].

The sensor is based on the yellow vanadomolybdophosphoric acid method for phosphate detection. The yellow method is a simple colorimetric technique which involves the formation of vanadomolybdophosphoric acid when a phosphate containing

sample is mixed in a 1:1 ratio with an acidic reagent containing ammonium molybdate and ammonium metavanadate. The resulting solution absorbs strongly below 400 nm. The measured absorbance of the yellow solution is used to determine the concentration of phosphate in the original sample. The current system has a linear range from 0–20 mg L^{-1} P-PO_4^{3-} and limit of detection (LOD) of 0.3 mg L^{-1} P-PO_4^{3-}. A preliminary field trial of the sensor was carried out in March 2006 [13].

This paper describes a more extensive field trial in which the phosphate sensor was applied to monitoring effluent at Osberstown Wastewater Treatment Plant in Co. Kildare, Ireland. The trial was carried out during a three-week period in September and October 2006, during which time the sensor performed a total of 430 measurements at an average measurement frequency of 1 sample/70 min. Control of the sensor, and data download, was achieved using wireless communication between the sensor and a laptop computer. The data was validated by comparison with the plant's existing online monitor, and a good correlation between the two sets of data was achieved, showing that the phosphate sensor is capable of operating satisfactorily at low mg/L levels over extended periods of time.

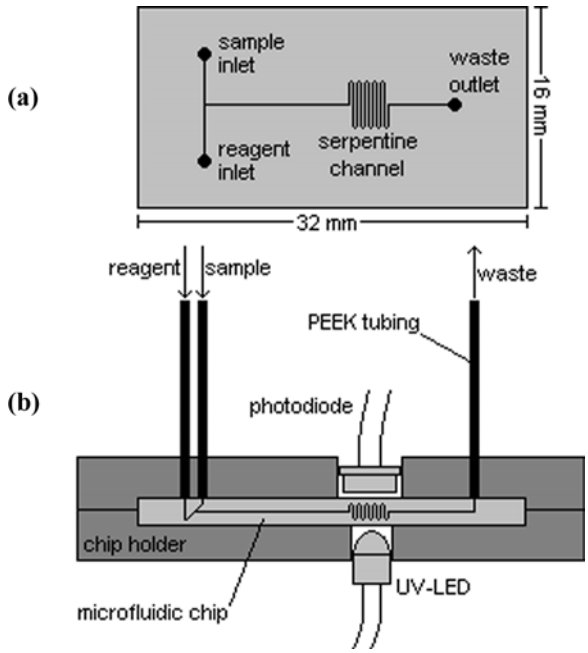

Fig. 1. Schematic diagram of (a) the microfluidic chip and (b) the chip/chip holder/optical detection system assembly.

II. Experimental Section

A. Microfluidic Chip Design

The microfluidic chip is fabricated in a 4 mm $\times$ 16 mm $\times$ 32 mm piece of clear polymethyl methacrylate (PMMA) using micromilling techniques. After milling, the chip is sealed with a second layer of PMMA using pressure sensitive adhesive. The sample and reagent are introduced into the chip through separate inlets and mixed in equal volume at a T junction. Channels of 200 μm width and 200 μm depth ensure that mixing of the reagent and sample occurs through diffusion on the time scale of the experiment. The solution flows through a serpentine channel, designed to cover the entire active area of a photodiode detector, before exiting the chip through a waste outlet. The chip design is illustrated schematically in Fig. 1.

B. Sensor Design

The microfluidic chip is integrated into a portable analytical system that incorporates all sampling, detection, and communication components. Polyetheretherketone (PEEK) tubing (175 μm inner diameter), is used for the introduction and removal of the sample, reagent, and waste into the chip inlets and outlet. Epoxy resin adhesive provides leak-free connections between the PEEK tubing and the microfluidic chip. The detection components and the microfluidic chip are held in place with a nylon chip holder which excludes ambient light. The chip is secured between the two plates of the chip holder, while a hole in the top plate houses a photodiode (S1227-33BR, Hamamatsu Photonics UK Limited, Hertfordshire, U.K.) and a hole in the bottom plate holds a 380 nm LED (NSHU550E model, Nichia Corporation, Tokushima, Japan). The photodiode detector and LED are aligned on opposite sides of the chip's serpentine channel, so that absorbance measurements of the yellow complex can be made.

A miniature dual-channel peristaltic pump (2PP10.S, Eurolink Associates, Tyne&Wear, U.K.) controls the flow of the sample solution and reagent into the microfluidic chip. Reagent and blank solutions are each stored in a plastic container with a PEEK tubing outlet. A solenoid switching valve (Y Valve C 3200, Lee Products, Ltd., Buckinghamshire, U.K.) is used to alternate between the sample and blank in order to compensate for drift in the sensor output over time. The valve delivers the appropriate solution to one channel of the peristaltic pump; the second channel of the pump is attached to the water sampling port, which is described further below. Fluid from the waste outlet of the microfluidic chip is contained in a third plastic container. The entire system is packaged into two waterproof polycarbonate boxes (Fig. 2). A 28.0 cm $\times$ 18.5 cm $\times$ 13 cm box contains the power supply, hardware, and communication components; a 16.5 cm $\times$ 13.5 cm $\times$ 9.5 cm box houses the peristaltic pump, microfluidic chip, thermistor, light source, detector, and reagent and waste containers. These boxes are connected by an 8 m communication cable. This design was used to separate the sampling and wet chemistry from the control and communications electronics.

The sampling port consists of a 13 mm piece of 0.50 mm inner diameter PEEK tubing placed through the wall of the sensor box. One end of the PEEK tubing is flush with the outer wall of the box and sealed by a polyethersulfone filter membrane with 0.45 μm micropores (Supor 450, Pall Corporation, East Hills, NY); the other end of the PEEK tubing is attached to the pump tubing. The pump draws the water through the membrane, filtering out large particulate matter, before the fluid enters the microfluidic chip.

The base station (Whistonbrook Technologies, Ltd., Luton, U.K.) consists of electronic control, data acquisition, and communication components powered by a 12 V, 7 Ah lead acid battery, all of which are sealed in the larger waterproof box. The system parameters can be changed via a laptop computer, which communicates with the base station through either a GSM

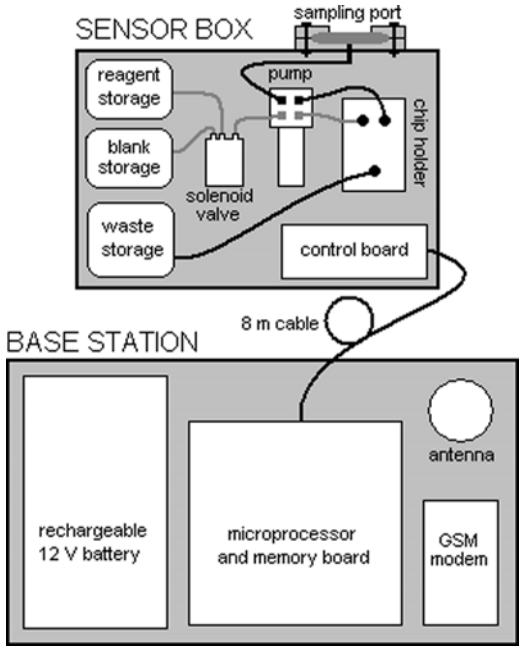

Fig. 2. Schematic diagram of the sensor design showing the major components of the sensor box and basestation.

modem or a serial port. Customized software allows the user to set the pumping time, define a measurement delay to ensure completion of the reaction, choose the number of measurements to be made, and decide whether communication with the system is done through the serial port or the GSM modem.

C. Reagents and Standards for Vanadomolybdophosphoric Acid Method

All solutions were prepared with Milli-Q deionized water (Milli-Ro Plus 30 System, Millipore, Billerica, MA). A 50 mg L^{-1} stock solution of phosphorus, in the form of phosphate, was made by dissolving 0.2195 g of anhydrous potassium dihydrogen phosphate (60218, Fluka, Buchs, Switzerland) in 1 L of deionized water. 2.25 mL of sulfuric acid (S/9200/PB17, Fisher Chemicals, Leicestershire, England) was added to preserve the stock solution. 0–20 mg L standard solutions were prepared from dilutions of the stock solution with deionized water. The reagent was prepared by dissolving 7.143 g of ammonium molybdate (A-7302, Sigma, Dorset, England) and 0.358 g of ammonium metavanadate (20555-9, Aldrich, Dorset, England) in 95 mL of concentrated hydrochloric acid (37% wt. in water) (926, BDH Laboratory Supplies, Dorset, England) and 905 mL of water. The reagents and reaction have been shown to be stable over long periods [10].

D. Field Trial Setup and Procedures

The trial was carried out within the wastewater treatment plant's effluent monitor building. The effluent is pumped from the adjacent effluent chamber to this building via a sample line, which is then split to deliver sample to each of the plant's on-line monitors which measure phosphate, nitrate and ammonia levels in the effluent. To facilitate direct validation of the results from the sensor, sample was obtained from the end valve on

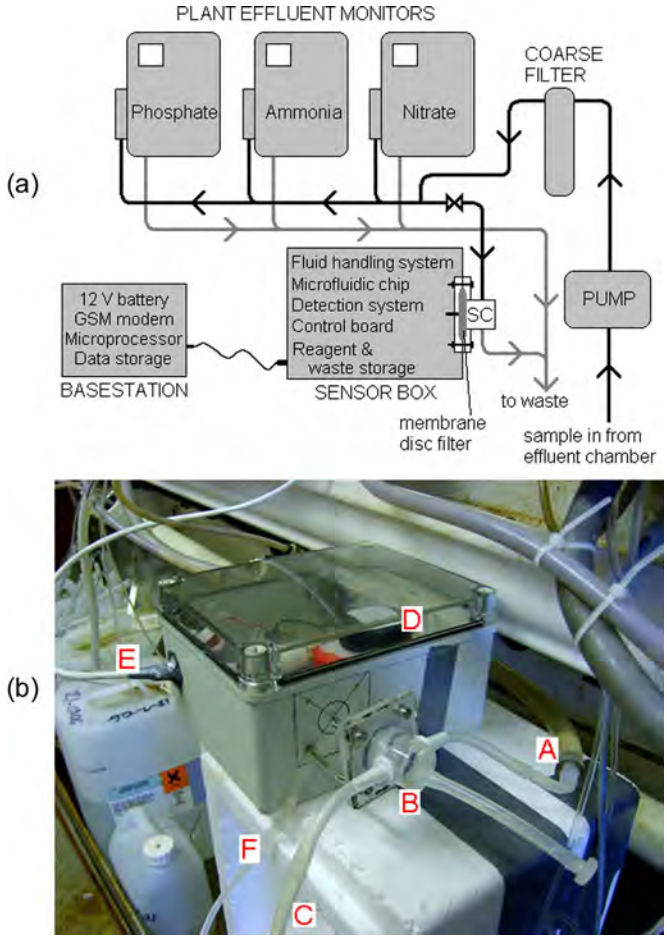

Fig. 3. (a) Schematic diagram of the experimental setup during the sensor trial. (b) Photograph of the sensor box *in situ*. Some of the visible features include: A–effluent line in, B–sample chamber, C–effluent line out, D–Reagent storage container, E–connection to basestation, and F–sensor waste outlet.

this sample line, via a sample inlet chamber, where the membrane filter was located. Mains power was readily available and was used throughout this trial. The sensor was controlled, and data was downloaded, via wireless communication between the sensor and a laptop computer using a GSM modem. On some occasions data was downloaded directly to laptop using a serial connection. The setup for the trial is illustrated schematically in Fig. 3.

In the configuration used, it was necessary to disconnect the sample line from the sample inlet and reconnect it to a container of standard solution in order to calibrate the system, which meant that sample measurements could not be performed during the calibration run. Such calibration solutions were introduced at three occasions during the trial. The sampling system is shown in a more detailed schematic in Fig. 4. The sample chamber (volume 8 mL approximately) was fabricated from a section of polyethylene oxide sample vial (internal diameter 20 mm), to which flexible tubing was attached using adapted tubing connector fittings (tubing and fittings from Cole-Parmer Instrument Company, IL, USA) and epoxy adhesive (Bondloc U.K., Ltd., Worcestershire, U.K.). Effluent entered and exited the sample chamber through two of these tubes, while the third tube was used to vent air bubbles which occasionally became trapped in the sample chamber. One side of the sample chamber

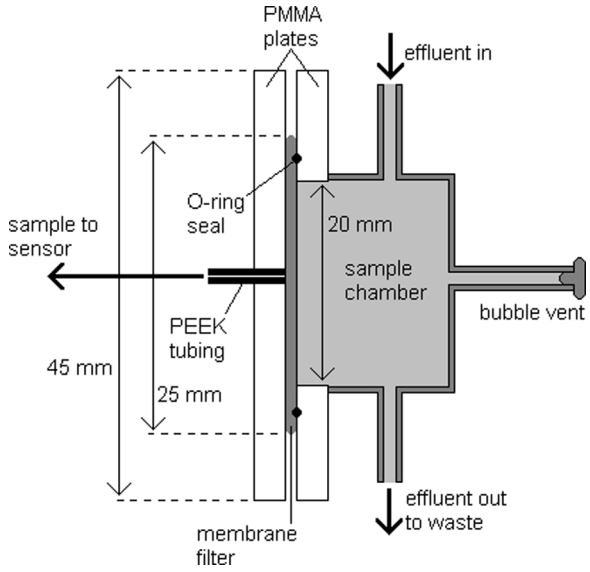

Fig. 4. Schematic cross section of the sampling system.

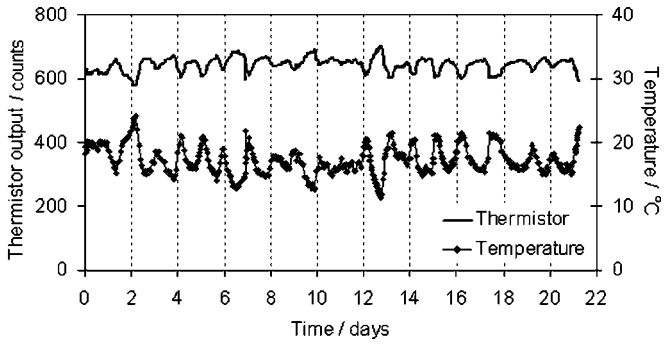

Fig. 5. Output from the phosphate sensor's inbuilt thermistor and corresponding temperature values over the duration of the trial.

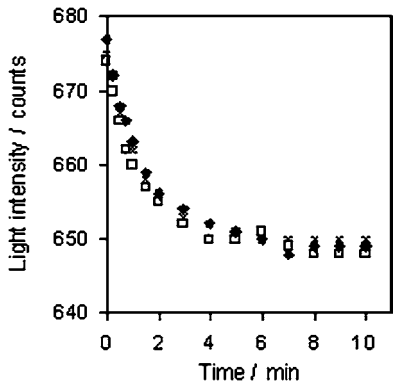

Fig. 6. Reaction profiles for the colorimetric reaction between the yellow reagent and a phosphate solution (5 mg L^{-1}) in the sensor at 10 °C. Data is presented as light intensity, measured in counts ranging from 0 to 1024 on a scale corresponding to the full range (0–5 V) of the photodiode output voltage.

was exposed to the membrane filter, through which effluent was drawn, via a length of polyetheretherketone (PEEK) tubing (Upchurch Scientific, Inc., Washington, USA) into the sensor by the peristaltic pump. The flow-rate of effluent through the sample chamber varied between 10 and 30 mLmin^{-1} during the trial, while the flow-rate drawn by the peristaltic pump was approximately 100 μLmin^{-1}.

E. Collection, Digestion, and Analysis of Effluent Samples

Sample Collection: Samples for laboratory analysis were collected in acid-washed containers which were rinsed with sample before collection, in accordance with the procedure described by Worsfold *et al.* [14]. Samples were filtered (where appropriate) using 0.45 μm membrane filters identical to that used in the sensor's sampling port. Each sample was chilled immediately after collection, and frozen within 90 min of collection.

Digestion: The digestion procedure was adapted from a procedure described by Lambert and Maher [15]. Concentrated nitric acid (5 mL) and concentrated sulfuric acid (1 mL) were mixed with 10 mL of sample in 50 mL borosilicate test tubes and heated until the solution became colorless and the acid volume reduced to about 1 mL. The digests were cooled, 10 mL of distilled deionized water and two drops of phenolphthalein were added and the solution was neutralized with 1 M sodium hydroxide. The solution was then made up to a volume of 100 mL using deionized water.

Analysis: The solutions were analyzed for phosphate using the vanadomolybdophosphoric acid method. Samples were mixed with an equal volume of the yellow reagent and mixed for 30 min at room temperature to ensure the reaction proceeded to completion. The absorbance of the yellow solution thus formed was determined at 380 nm using a bench-top spectrophotometer (Cary 50, Varian, Inc., CA, USA) and the corresponding phosphate concentration was determined from a standard curve obtained using phosphate solutions of known concentration. The concentration of the original (undiluted) sample was then calculated based on the dilution factor of 1 in 10.

III. Results and Discussion

A thermistor located inside the sensor box gives temperature information. This information is presented in Fig. 5 in the form of thermistor output and temperature. The temperature values were calculated based on a laboratory calibration of the thermistor which gave a linear relationship between the thermistor output (in counts ranging from 0 to 1024 on a scale corresponding to the full range of the thermistor output voltage) and the temperature (T) in °C as described by the equation

$$T = -0.100 \times (\text{thermistor output}) + 81.507. \quad (1)$$

The correlation coefficient associated with the calibration equation was $R^2 = 0.978$.

The diurnal temperature variation is apparent in Fig. 5. It should be noted that the monitoring building in which the trial was carried out had a basic heating system so the sensor was not exposed to full environmental temperature variations. The minimum and maximum temperatures observed over the three weeks of operation were 11.4 °C and 24.0 °C, respectively. Temperature is an important parameter in the system as it determines the length of time required for the colorimetric reaction to reach completion, and, therefore, the minimum interval between measurements [16]. Fig. 6 shows the reaction profile (in triplicate) which was obtained in the sensor under laboratory conditions at 10 °C. For each of the three reactions, the light intensity had reached its minimum value, indicating completion of the reaction, after 7–8 min. In the field trial, the time interval between

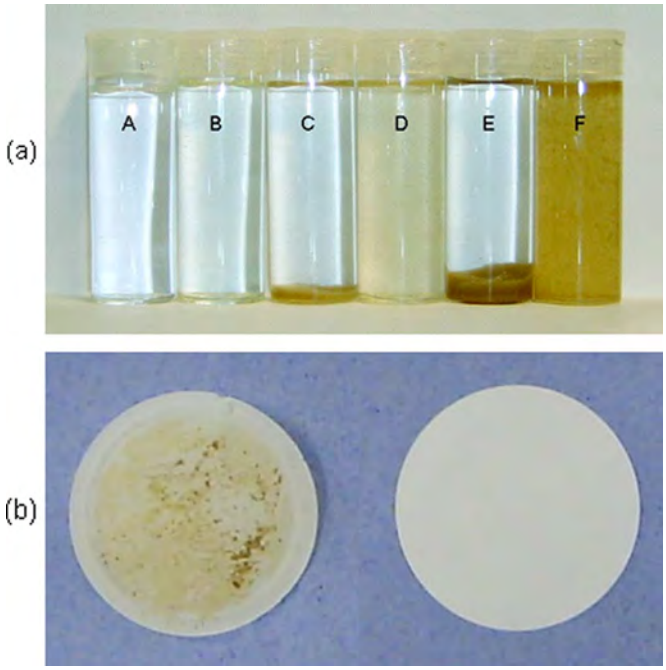

Fig. 7. (a) Photograph showing effluent samples, with varying solids contents, collected during the trial: A–DIW, shown for comparison, B–effluent with low solids and good clarity, C and D–effluent with moderate solids content, shown after and before settling, respectively, E and F–effluent with high solids content, shown after and before settling, respectively. (b) Photo showing the membrane filter before (on right) and after 21 days exposure to the effluent.

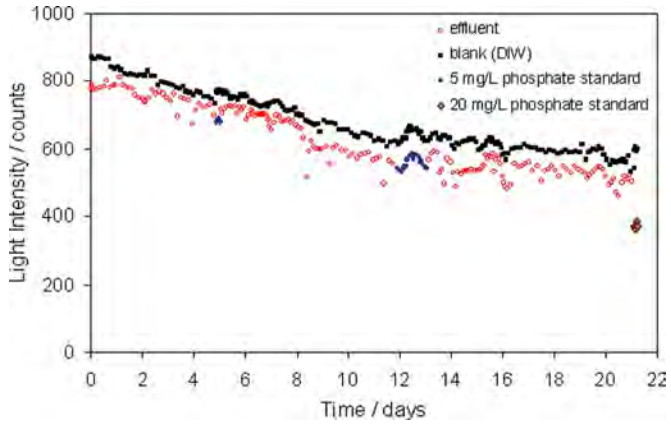

Fig. 8. Raw data from the phosphate sensor for the duration of the trial. Data is presented as light intensity, measured in counts ranging from 0 to 1024 on a scale corresponding to the full range (0–5 V) of the photodiode output voltage.

mixing of the sample and reagent and the measurement being taken was 8 min, and given the minimum temperature of 11.4 °C observed during the trial, this interval was clearly sufficient to allow completion of the reaction in each case. When combined with the required pumping time of 6 min to draw sample from the effluent sampling chamber to the microfluidic chip, the minimum interval between measurements was 15 min. In practice, the shortest interval used was 20 min, and the longest interval used was 2 h. The average measurement frequency over the entire duration of the trial was 1 sample/70 min.

No issues were caused by fouling during the trial, despite the nature of the sample to which the filter was exposed. As shown in Fig. 7(a), the effluent contained varying, and sometimes significant amounts of solids. Fig. 7(b) shows the membrane filter before and after the trial. Some accumulation of solids on the surface of the membrane is apparent, as might be expected, however, the flow rate of sample to the sensor was not affected to any significant extent.

As mentioned in the experimental section, air bubbles which occasionally became trapped in the sample chamber, without interfering with sample flow to the sensor, were vented manually via an outlet added to the sample chamber for this purpose. Throughout the duration of the trial, no bubbles were observed within any of the tubing associated with the sensor proper. Bubbles within the detection area of the microfluidic chip interfere with the light passing through the chip and thereby give rise to false high readings, which were not a feature of the results obtained (Fig. 9). It is possible that the relatively high flow rate used (100 μLmin^{-1}) helped prevent trapping of any small bubbles by flushing them through the microfluidic system.

Fig. 8 shows the output of the phosphate sensor over the entire 21-day duration of the field trial. This data is in the form of light intensity measured by the photodiode and so the values for the sample and standard solutions are lower than those for the blank solution. There is a fairly consistent downward drift in the light intensity throughout the trial. This is not caused by any decrease in the reactivity of the reagent over time [12], nor is it due to instability of the detection system, as the intensity values returned to a level approximately equal to the initial readings when the chip was thoroughly rinsed after the trial. The drift is, therefore, ascribed to staining of the inside of the microfluidic channel by the colored compound generated (vanadomolybdophosphoric acid), with a possible contribution by any particulate matter capable of passing through the 0.45 μm filter. This suggests that rinsing of the microfluidic chip between measurements in order to remove any material interfering with the optical measurement is desirable. As the colored compound is acidic, a basic solution (1M NaOH) has been assessed for this purpose and has been found to effectively decolorize the yellow solution. This suggests that a dilute solution of NaOH (or possibly another, less aggressive base) is suitable for use as a cleaning solution which could be used to remove the colored agent from the channel so as to eliminate the gradual decrease in the amount of light reaching the photodiode, and hence the downward drift in the sensor output.

To compensate for the drift in sensor output in this trial, alternate blank and sample measurements were carried out using the solenoid valve to switch between the blank and sample input lines. This allowed the results in Fig. 8 to be converted to absorbance readings using the equation

$$A = \log(I_o/I) \tag{2}$$

where A is absorbance, I_o is the light intensity reaching the photodiode when the detection area contains blank + reagent, and I is the light intensity reaching the photodiode when the detection area contains sample (or standard solution) + reagent. The corresponding concentration can then be determined based on the absorbance of the standard phosphate solutions. The concentration values thus obtained are plotted in Fig. 9, along with

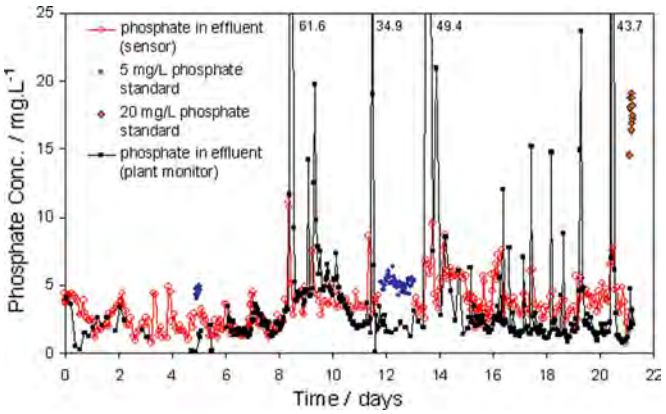

Fig. 9. Effluent phosphate concentrations obtained from the phosphate sensor and the plant's existing phosphate monitor. Results for 5 mg L^{-1} and 20 mg L^{-1} standard phosphate solutions are also shown. The y axis is truncated to show the sensor data at an appropriate scale. Phosphate peaks which exceeded the range shown are labeled (to the right of each such peak) with the maximum phosphate concentration measured.

TABLE I
SUMMARY OF CONCENTRATION VALUES OBTAINED FOR SOLUTIONS OF KNOWN PHOSPHATE CONCENTRATION

Concentration of standard solution (number of measurements)	Measured concentration / mg L^{-1} Average	Standard deviation
5.0 mg L^{-1} – run 1 (n = 12)	4.58	0.32
5.0 mg L^{-1} – run 2 (n = 41)	5.13	0.43
20.0 mg L^{-1} (n = 10)	17.91	0.89

the corresponding data obtained from the plant's existing online phosphate monitor.

In the early stages of the trial (days 1 through 6), the data from the plant's phosphate monitor was only sporadically available, due to airlocks in the lines delivering effluent to the plant's various online monitors, arising from problems with the effluent pump. In contrast, the sensor did generate data throughout this period due to the relatively minuscule volume of sample required. However, in the absence of data for comparison, and in light of the possibility that the effluent flow through the sensor's sampling chamber may have been interrupted, this data is of limited usefulness. From day 6 onwards, however, the sensor data is generally in good correlation with that of the plant monitor, with peaks in both sets of data coinciding on the time axis. The exception to this overall good correlation is that many of the very high phosphate concentrations detected by the plant monitor are not seen to the same extent in the sensor data—this discrepancy is discussed in more detail below.

In some cases, there is a slight time offset (for example, the peaks occurring at 8.5 days and 11.5 days). This is due to differences in the times at which measurements were carried out; as mentioned earlier the sensor took measurements at intervals between 20 and 120 min. The plant monitor took measurements at 15 min intervals, but the data shown in Fig. 9 is aggregated to show hourly averages. Towards the latter end of the trial period (days 15–21) there is a noticeable offset in the concentration levels obtained, with the sensor giving consistently higher concentrations than the plant monitor. This highlights the need for a more frequent calibration protocol than was implemented in this experiment. This has been catered for in a revised design of the phosphate sensor currently undergoing laboratory assessment.

The concentration data obtained for the standard phosphate solutions are summarized in Table I. These data show that the measured values were reasonably well correlated with the known values, with the average value for the first run with 5 mg L^{-1} standard and the run with 20 mg L^{-1} standard resulting in a slight underestimation of the actual phosphate concentration.

As mentioned above, the most obvious discrepancy between the two sets of data occurs at the higher phosphate concentrations, with the plant monitor giving significantly higher phosphate concentrations than the sensor. These peaks were observed to occur after significant rainfall events, when the flow of effluent was increased and the solids content in the effluent was also visibly higher [as illustrated by the samples in Fig. 7(a)]. The plant monitor was a Capital Controls instrument (Aztec P1000 model) in which the effluent passes through only a coarse filter prior to entering the monitor, which utilizes acid hydrolysis with heating, followed by phosphate detection based on the blue molybdate method [17]. We hypothesized that the discrepancies observed at high phosphate levels were due to the exclusion of solids from the sensor by the 0.45 μm membrane filter at the sample inlet in our sensor, while solids could enter into, and be digested by, the plant monitor.

In order to test this hypothesis, a sample with particularly high solids content was collected, and divided into two portions, one of which was filtered using an identical (0.45 μm) membrane filter to remove solids, while the other remained unfiltered. An aliquot of each sample was then digested by heating to boiling with mixed HNO_3/H_2SO_4. Following digestion the samples were analyzed for phosphate using the yellow method. The phosphate concentrations were found to be 3.78 and 50.48 mg L^{-1} for the filtered and unfiltered samples, respectively, representing a 13-fold increase in the measured phosphate concentration due to digestion of the solids content in the unfiltered sample. It is, therefore, reasonable to suggest that the discrepancies observed between the sensor output and that of the online monitor can be explained by this effect. In fact, the 13-fold difference in phosphate concentration is significantly greater than the corresponding ratios observed in Fig. 9—this may be explained by the selection of a sample with particularly high solids content for the digestion experiment. This finding also highlights that only a small proportion of the phosphorus (P) contained in the effluent with high solids content is in the readily bioavailable dissolved reactive phosphorus (DRP) form which is detected by the phosphate sensor. When evaluating P inputs to water bodies, it is important that the bioavailability of the overall P content is taken into consideration.

IV. Conclusion

In this work, the application of the phosphate sensor previously developed to the analysis of effluent from a wastewater treatment plant has been described. The sensor operated successfully over an extended period of time (21 days) in a sample with varying, and frequently high, solids content, and yielded data in good agreement with those obtained in parallel from the plant's existing, commercially available, online phosphate monitor. Control and data download were performed wirelessly via a GSM modem. A discrepancy between the sensor and the plant monitor at high phosphate concentrations was shown to be due to the detection by the plant monitor of phosphate associated with solids which were excluded from the sensor by the filtration system used. This highlights the importance of being cognizant of, and correctly identifying, the fraction of the total phosphorus content which is detected in a given sample/sensing regime.

Concurrent with the laboratory and field trials described in this and previous works, a "Mark II" phosphate sensor has been designed and fabricated to address the limitations and to expand the functionality of the system described here. Key improvements include greater robustness, more versatile fluid handling system, improved power efficiency, an improved detection system, an automatic chip-cleaning cycle between measurements, and energy harvesting functionality via solar panel. The revised design also allows for a more frequent and more integral two-point calibration protocol. This new system is currently undergoing laboratory and field trials.

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References

[1] K. Robards, I. D. McKelvie, R. L. Benson, P. J. Worsfold, N. J. Blundell, and H. Casey, "Determination of carbon, phosphorus, nitrogen and silicon species in waters," *Anal. Chim. Acta*, vol. 287, no. 3, pp. 147–299, Mar. 1994.

[2] V. H. Smith, G. D. Tilman, and J. C. Nekola, "Eutrophication: Impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems," *Environ. Pollut.*, vol. 100, no. 1–3, pp. 179–196, Aug. 1999.

[3] C. P. Mainstone and W. Parr, "Phosphorus in rivers—Ecology and management," *Sci. Total. Environ.*, vol. 282–283, pp. 25–47, Jan. 2002.

[4] D. M. Anderson, P. M. Glibert, and J. M. Burkholder, "Harmful algal blooms and eutrophication: Nutrient sources, composition, and consequences," *Estuaries*, vol. 25, no. 4b, pp. 704–726, Aug. 2002.

[5] I. Donohue, D. Styles, C. Coxon, and K. Irvine, "Importance of spatial and temporal patterns for assessment of risk to diffuse nutrient emissions to surface waters," *J. Hydrol.*, vol. 304, no. 1–4, pp. 183–192, Aug. 2005.

[6] K. Irvine, "Classifying ecological status under the European Water Framework Directive: The need for monitoring to account for natural variability," *Aquat. Conserv.: Mar. Freshwat. Ecosyst.*, vol. 14, no. 2, pp. 107–112, Feb. 2004.

[7] P. Jordan, J. Arnscheidt, H. McGrogan, and S. McCormick, "High-resolution phosphorus transfers at the catchment scale: The hidden importance of non-storm transfers," *Hydrol. Earth Syst. Sci.*, vol. 9, no. 6, pp. 685–691, Dec. 2005.

[8] "Directive 200/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy," *Official Journal L 327/1*, Dec. 2000.

[9] M. Bowden, M. Sequiera, J. P. Krog, P. Gravesen, and D. Diamond, "Analysis of river water samples utilizing a prototype industrial sensing system for phosphorus based on micro-system technology," *J. Environ. Monit.*, vol. 4, no. 5, pp. 767–771, Aug. 2002.

[10] M. Bowden, M. Sequiera, J. P. Krog, P. Gravesen, and D. Diamond, "A prototype industrial sensing system for phosphorus based on micro system technology," *Analyst*, vol. 127, no. 1, pp. 1–4, Jan. 2002.

[11] M. Bowden, O. Geschke, J. P. Kutter, and D. Diamond, "CO_2 laser microfabrication of an integrated polymer microfluidic manifold for the determination of phosphorus," *Lab Chip*, vol. 3, no. 4, pp. 221–223, Sep. 2003.

[12] M. Bowden and D. Diamond, "The determination of phosphorus in a microfluidic manifold demonstrating long-term reagent lifetime and chemical stability utilizing a colorimetric method," *Sens. Actuators B*, vol. 90, no. 1–3, pp. 170–174, Apr. 2003.

[13] C. M. McGraw, S. E. Stitzel, J. Cleary, C. Slater, and D. Diamond, "Autonomous microfluidic system for phosphate detection," *Talanta*, vol. 71, no. 3, pp. 1180–1185, Feb. 2007.

[14] P. J. Worsfold, L. J. Gimbert, U. Mankasingh, O. N. Omaka, G. Hanrahan, P. C. F. C. Gardolinski, P. M. Haygarth, B. L. Turner, M. J. Keith-Roach, and I. D. McKelvie, "Sampling, sample treatment and quality assurance issues for the determination of phosphorus species in natural waters and soils," *Talanta*, vol. 66, no. 2, pp. 273–293, June 2005.

[15] D. Lambert and W. Maher, "An evaluation of the efficiency of the alkaline persulphate digestion method for the determination of total phosphorus in turbid waters," *Water Res.*, vol. 29, no. 1, pp. 7–9, Jan. 1995.

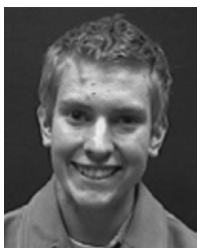
[16] M. Bowden, "Smaller, smarter, faster: The development and application of microfluidic devices to the determination of phosphorus in natural waters," Ph.D. dissertation, School of Chemical Sciences, Dublin City Univ., Dublin, Ireland, 2003.

[17] *Aztec Series 1000 Colorimetric Range: Operation and Maintenance Manual*. Colmar, PA: Severn Trent Services, Colmar Operations, Jan. 2006.

John Cleary received the B.Sc. and Ph.D. degrees from the University of Limerick, Limerick, Ireland, in 1998 and 2005, respectively.

He was a Research Fellow at the Electrochemistry Research Group, University of Limerick, where he developed an amperometric sensor for heavy metal ions. He is currently a Research Fellow at the Adaptive Sensors Group, Dublin City University. His research interests include sensors for environmental monitoring and microfluidic systems for chemical sensors.

Dr. Cleary was the recipient of a Research Award at the Seventh United Kingdom-Ireland Controlled Release Society Symposium, King's College London, London, U.K.



Conor Slater received the B.Eng. degree from Dublin City University, Dublin, Ireland, in 2005. He is currently a research postgraduate student with the Adaptive Sensors Group, Dublin City University, Dublin, Ireland.

In 2004, he worked with BMW, Steyr, Austria designing online monitoring systems. His research interests include field deployable sensors for environmental monitoring and the manufacture of lab-on-a-chip devices.

Mr. Slater has been an Ordinary Member of Engineers Ireland since 2005. In 2004, his team was given the Award of Most Innovative Design in a mobile robotics competition at Dublin City University.

Christina McGraw received the B.Sc. degree from the University of Alaska Fairbanks, Fairbanks, in 1999 and the Ph.D. degree from the University of Washington, Seattle, in 2004.

She is currently an Assistant Lecturer of Marine Chemistry at the University of Otago, Dunedin, New Zealand. Previously, she was a Research Fellow in the Adaptive Sensors Group, Dublin City University, Dublin, Ireland. Her research interests include environmental sensors and portable instrumentation.

Dr. McGraw is a member of the American Chemical Society and the New Zealand Institute of Chemistry.

Dermot Diamond received the Ph.D. and D.Sc. degree from Queen's University Belfast, Belfast, Ireland, (chemical sensors, 1987, Internet scale sensing, 2002).

He was Vice President for Research at Dublin City University, Ireland, from 2002 to 2004. He has published over 150 peer reviewed papers in international science journals, is a named inventor of 12 patents, and is coauthor and editor of four books. He was a founding member of, and is currently Director of the National Centre for Sensor Research. He was formerly Director of the "Adaptive Information Cluster" (AIC), a major research initiative in the area of wireless sensor networks. He is a member of the editorial advisory boards of the international journals *The Analyst* and *Talanta*.

Prof. Diamond was awarded the Inaugural Silver Medal for Sensor Research by the Royal Society of Chemistry, London, in 2002.