High temporal resolution field monitoring of phosphate in the River Frome using flow injection with diode array detection

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Abstract

The design and deployment of an in situ flow injection (FI) monitor for high temporal resolution monitoring of phosphate in the River Frome, Dorset, UK, is described. The monitor incorporates solenoid, self-priming micropumps for propulsion, solenoid-operated switching valves for controlling the fluidics and a miniature CCD spectrometer for full spectrum (200–1000 nm) acquisition and operates in a graphical programming environment. A tangential filtration unit is attached to the sample inlet line to remove suspended particulate matter and prevent blockage of the micropumps and valves. Detection

Frome performed in October 2000 are presented, and the implications of the data for refining an export coefficient model for phosphorus from the catchment are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Flow injection; Eutrophication; Solenoid

1. Introduction

Phosphorus export (loading) into catchments from both point and diffuse sources can result in eutrophication, i.e. an enrichment of nutrients, which can in turn lead to an increase in biomass and primary productivity within aquatic communities [1,2]. Eutrophication of natural waters has become a subject of increasing public concern which, in the European Union, has been recognised by legislation setting $0.1\,\mathrm{mg\,l^{-1}}$ PO_4 as an indicator level for possible problematic algal growth in rivers [3]. An assessment of water quality is an essential prerequisite for the implementation of successful management strategies for minimising the likelihood of eutrophication. Phosphorus loading is an important factor in this assessment and is often the best indicator of the nutrient status of receiving waters. Models have been implemented to predict nutrient loads and their sources and sinks [4–7] and for this study a simple export coefficient model for the River Frome, Dorset, UK, was constructed. The annual and seasonal total phosphorus (TP) loads were predicted as the sum of the export of phosphorus from each nutrient source [8]. However, the transfer of phosphorus from land and its concentration in catchments such as the River Frome are strongly influenced by rainfall.

There are extensive data on instantaneous (grab sample) phosphorus concentrations in rivers but very

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little information that shows short-term changes in phosphorus concentration occurring, for example, immediately before, during and after a rain event. Consequently, field instrumentation capable of acquiring high quality analytical data with good temporal resolution, i.e. every 15–30 min, would be a useful development in its own right [9,10]. In addition such data are essential for building improved models for predicting the transport and biogeochemical behaviour of phosphorus in catchments.

This paper describes the design and deployment of an in situ flow injection (FI) monitor for high temporal resolution monitoring of phosphorus in the River Frome. The monitor incorporated a miniature diode array detector, self-priming micropumps and electronic switching valves for controlling the fluidics. Analytical performance, in the laboratory and in the field, is presented and the influence of the data on an export coefficient model for phosphorus in the Frome catchment considered.

2. Experimental

2.1. Reagents

All solutions were prepared in ultra-pure water (Elga Maxima®, 18.2 MΩ) and all reagents were of AnalaR (or equivalent) grade and purchased from BDH Merck, unless otherwise stated. All containers, bottles and glassware used during this study for manipulating and storing reagents, samples and standards

were first cleaned overnight with nutrient free detergent (Neutracon®, Decon Laboratories), rinsed three times with ultra-pure water and soaked in 10% (v/v) HCl for at least 24 h. All were then rinsed three times with ultra-pure water and dried at room temperature.

2.1.1. Flow-injection manifold

The optimum concentrations for the two phosphorus reagent streams were: ammonium molybdate solution ($10 g l^{-1}$ ammonium molybdate in $35 ml l^{-1}$ sulphuric acid), and tin(II) chloride solution ($0.2 g l^{-1}$ tin(II) chloride and $2 g l^{-1}$ hydrazinium sulphate in $28 ml l^{-1}$ sulphuric acid). Working standard solutions in the range of 0.8–8.0 μM PO_4 were prepared by dilution from a 3 mM stock solution (0.4393 g of oven dried potassium dihydrogenorthophosphate diluted to 1000 ml with water). The carrier stream was ultra-pure water.

2.1.2. Batch method

The three reagents used for batch determination were: ammonium molybdate (15 g diluted to 500 ml with water), ascorbic acid (5.4 g diluted to 100 ml) and potassium antimonyl tartrate (0.34 g diluted to 500 ml). Working standard solutions in the range 0.3–12.0 μM PO_4 were prepared by dilution from a 3 mM stock solution (0.4393 g of oven dried potassium dihydrogenorthophosphate diluted to 1000 ml).

2.2. Flow injection (FI) manifold

The manifold used is shown in Fig. 1. It consisted of four solenoid-operated self-priming micropumps
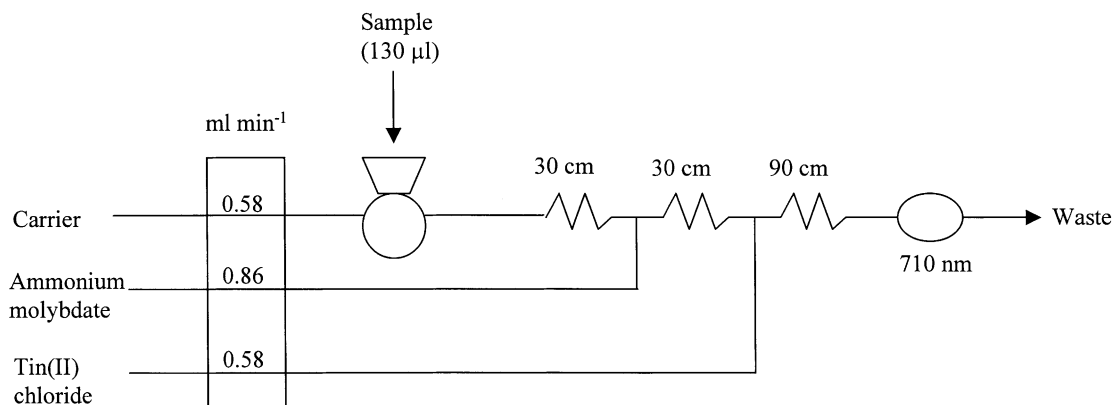

Fig. 1. FI manifold for the determination of PO_4 in freshwaters.

(Bio-Chem Valve series 120SP12-25, PD Marketing, Chichester, UK) connected to solenoid-operated PTFE switching valves (Bio-Chem Valve series 075T12-32, PD Marketing) with PTFE tubing (0.8 mm i.d.). The fluidics and the operation of the system are discussed in detail in Section 3.1. An Ocean Optics PSD-1000 miniature fibre-optic spectrometer (Anglia Instruments Ltd., Cambridge, UK) consisting of two 1024 element linear CCD arrays was used for detection. The master channel (UV–VIS range), with $600\,lines\,mm^{-1}$ blazed at $300\,nm$, enabled a spectral range of 200–$700\,nm$. The slave channel (VIS–NIR range), with $600\,lines\,mm^{-1}$ blazed at $750\,nm$, enabled a spectral range of 500–$1000\,nm$. The light source was a miniature halogen lamp (LS-1 Ocean

Optics Inc.). Data communication was performed using a type II PCMCIA DAQ-DIO-24 card (National Instruments Corp., Berks, UK) and a Toshiba Satellite 4030 CDS notebook PC (Toshiba Information Systems Ltd., Surrey, UK). Automation of the manifold and data acquisition was controlled using an in-house graphical program (LabView^{TM} 5.0, National Instruments Corp.). A schematic diagram of the complete system is shown in Fig. 2.

2.3. Field study site

The River Frome rises on the North Dorset Downs near Evershot and flows into Poole Harbour in the Southwest of the UK. The most important geological
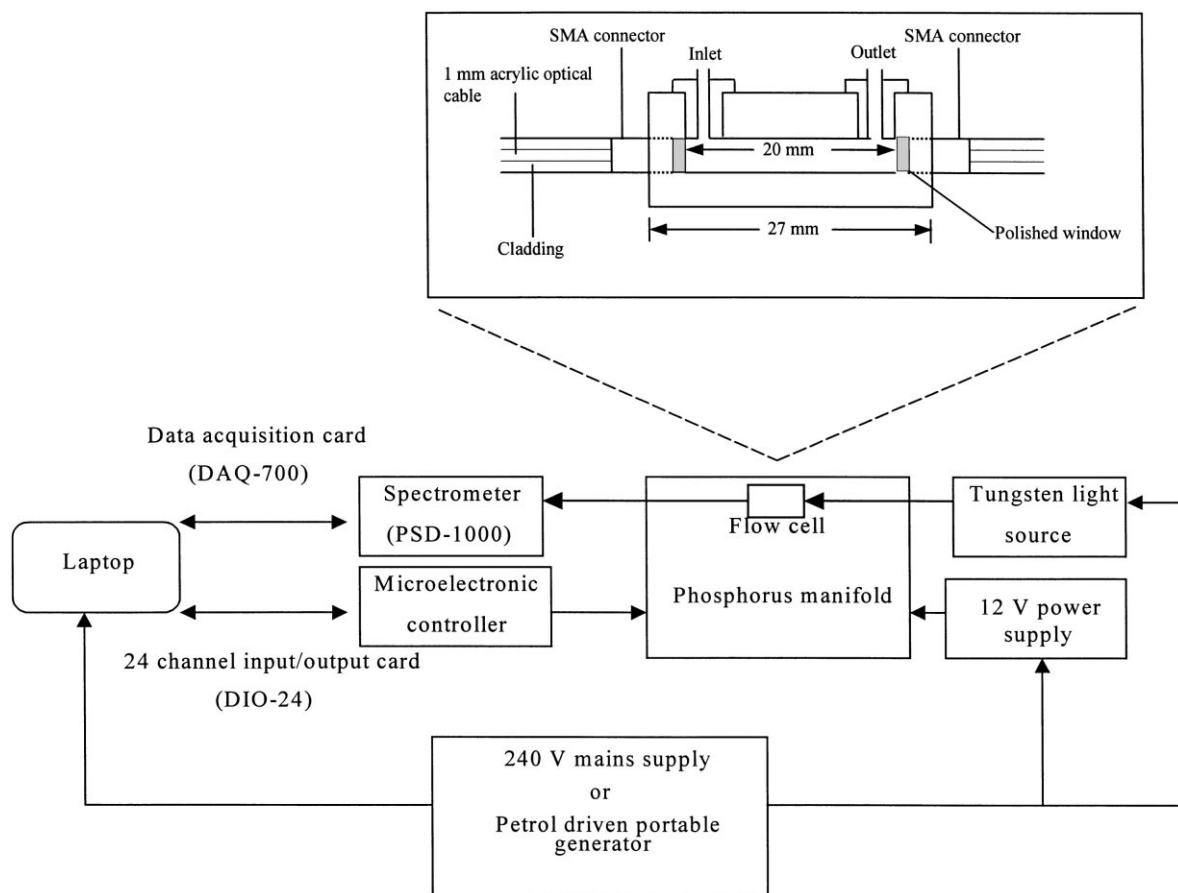

Fig. 2. Schematic diagram of the complete FI system for PO_4 determination with an insert showing the PVC flow cell incorporating 1 mm acrylic optical fibre cables.

formation is chalk, which comprises nearly 50% of the $414 km^2$ catchment [11]. Land use in the catchment is predominately permanent grassland, dairying or stock rearing, cereals and natural wetlands. The hydrology of the Frome catchment is dominated by a highly reactive aquifer passing beneath the lower catchment and Poole Harbour. River flow is dependent on upper reach streams and groundwater levels and drains into Poole Harbour, UK.

2.4. Procedures for field trial

A 3 day high temporal resolution campaign was undertaken on the River Frome at the Environment Agency gauging station, East Stoke (grid reference SY866867). River water was pumped up a vertical height of 2 m into the filtration unit, incorporating a 0.45 μm cellulose acetate filter (0.47 mm o.d.), using a rotary pump (Cole-Parmer 7532-02). Calibration was performed each morning and evening using 0.8, 1.5, 4.0, 6.0 and 8.0 μM PO_4 standards, with a 4.0 μM standard injected after every fourth or fifth river sample as a quality control (QC) sample. Calibration was then adjusted according to the QC result. The sampling cycle was configured to sample every 30 min. Samples for batch analysis were collected in 125 ml HDPE sample bottles (Nalgene®) at the same time as sample was introduced into the FI monitor. Bottles were first rinsed twice with filtrate then filled with approximately 50 ml aliquots of sample. Samples were then preserved with 0.1% (v/v) chloroform, labelled, placed in resealable plastic bags and stored at 4°C in the dark. Upon return to the laboratory (within 6–12 h), samples were allowed to warm to room temperature and then analysed immediately for PO_4 using a Beckman DU-8 spectrophotometer according to the method of Eisenreich et al. [12].

3. Results and discussion

3.1. Instrument design

Previous field FI systems have typically incorporated solid-state detection based on light-emitting diodes (LEDs) and photodiodes, peristaltic pumps and text-based software. Such solid-state detection is limited in that it can only provide an integrated response over the spectral bandwidth of the LED (typically 20–30 nm). In addition, peristaltic pumps require frequent recalibration and maintenance as well as regular replacement of pump tubing. The use of text-based software allows instrument control, but is difficult to use and has limited data acquisition and processing capabilities. The instrumentation reported here therefore provides major advantages in terms of spectral acquisition and signal processing, component reliability and ease of operation.

A prototype instrument, used to determine nitrate in the River Frome, has been previously reported [13]. The current instrument has several design modifications to improve reliability for field use. Firstly, the conventional quartz flow cell was replaced by a rigid, in-house 20 mm bore PVC flow cell incorporating 1 mm acrylic fibre optical cables (see Fig. 2 insert). Secondly, an on-board tangential flow filtration unit [14] was incorporated to prevent blockage of the micropumps (a limitation of the original design) and thereby significantly extend operating lifetime and reliability in the field. In addition, the system was housed in a secure, impact resistant IP67 rated polycarbonate box (FIBOX, Finland) for adequate protection during field use and the software was modified to allow for replicate analyses and in-field adjustment of the calibration.

The self-priming micro pumps and miniature solenoid valves provided a viable alternative to peristaltic pumps. Fig. 3 shows the fluidic layout of the FI automation injection sequence. Switching valves were set to normally open — common (NO/COMM) when de-energised and to normally closed — common (NC/COMM) when power was supplied to the valves. The advantages of the system are low maintenance (and therefore potentially longer deployments) and electronic control of the flow rates. The two drawbacks are the additional pulsing of the micropumps compared with peristaltic pumps and their susceptibility to blockage from particulate matter. The first problem was overcome by using the spectral capability of the detector to subtract the signal at a non-absorbing wavelength and the second problem by incorporation of the tangential flow filter.

The phosphorus FI manifold was based on a published design [15] but the limit of detection was improved to meet the needs of the study site (annual variability of 1–4 μM PO_4) [9,15]. This was achieved
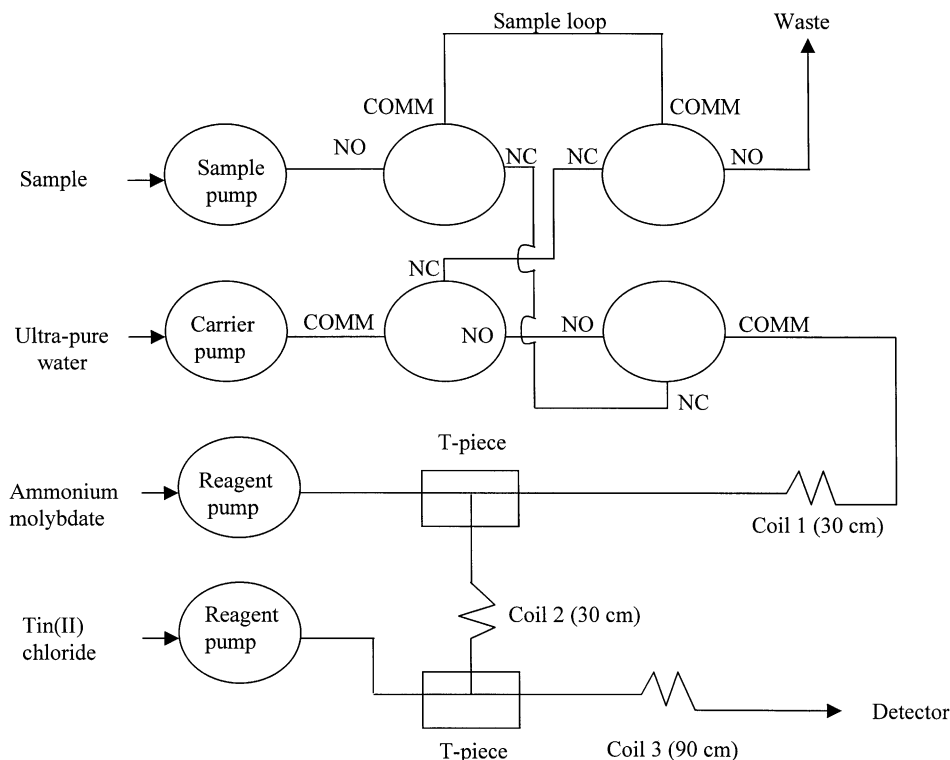
Fig. 3. Fluidics of the automated FI monitor for PO$_4$ determination. Switching valves were set to normally open — common (NO/COMM) when de-energised and to normally closed — common (NC/COMM) when power was supplied to the valves.

by increasing the sample volume from 40 to 130 µl and monitoring the phosphomolybdenum blue species produced at 710 nm (instead of 690 nm).

3.2. Laboratory FI calibration

The FI determination of PO$_4$ was based on the standard reaction with acidic molybdate to form 12-molybdophosphate, which was then reduced to form an intensely coloured molybdophosphate blue species [16]. Five phosphate standards covering the range 0.8–8.0 µM PO$_4$ gave linear calibration graphs ($r^2 > 0.998$), with a gradient of 0.0043 absorbance µM^{-1} and an intercept of −0.009 absorbance. The relative standard deviations (R.S.D.) for these standards were typically in the range of 0.0–1.3% ($n = 3$) and the limit of detection (calculated from the mean of the blank plus three times the standard deviation of the blank) was 0.67 µM PO$_4$. All measurements were made at 710 nm (λ_{max}) and processed by sub-

tracting the absorbance at a non-absorbing reference wavelength (447 nm). Fig. 4a and 4b compare the single (710 nm) and dual wavelength (710–447 nm) FI responses for the standards and clearly demonstrates the success of using the non-absorbing wavelength to remove the effect of pulsations caused by the micropumps.

The linear calibration range was extended to 0.8–50 µM PO$_4$ by reducing the sample volume injected from 130 to 90 µl and monitoring at 650 nm (selected as the wavelength giving 50% of maximum absorbance at 710 nm). This gave a linear calibration graph ($r^2 = 0.994$, $n = 6$) with a gradient of 0.0034 absorbance µM^{-1} and an intercept of 0.009 absorbance. Good reproducibility was also observed throughout the range, with R.S.D.s typically <3.0% ($n = 7$). This shows that the linear range can easily be adjusted in the field to suit local conditions and changing circumstances, e.g. storm events. For this deployment, 710–447 nm with a sample loop volume
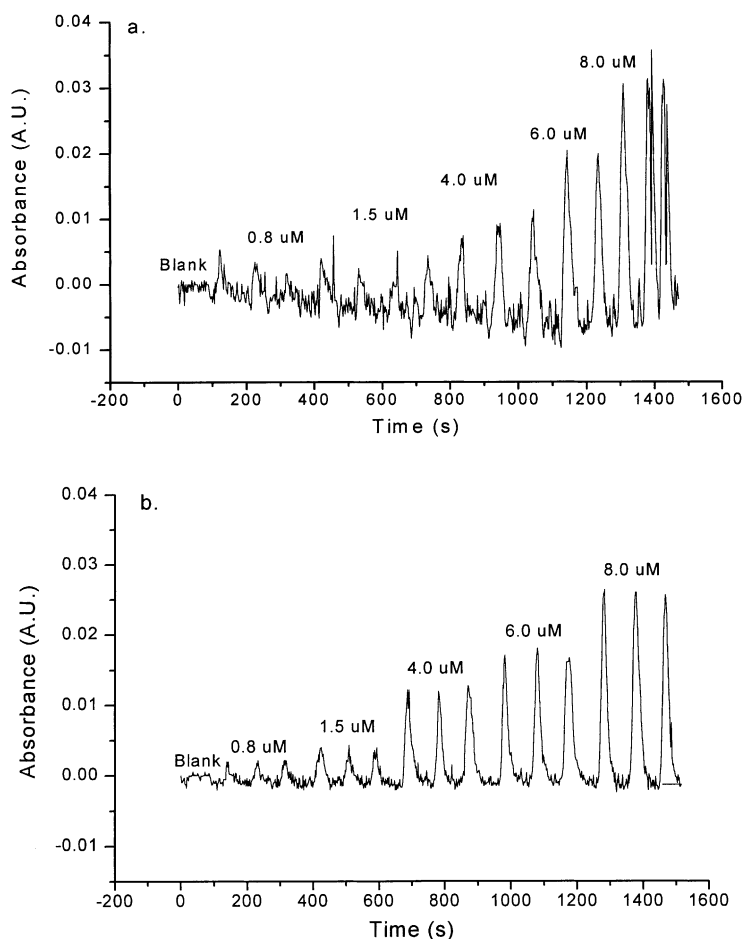
Fig. 4. (a) Single wavelength (710 nm) and (b) dual wavelength (710–447 nm) scan of a PO$_4$ calibration series (0.8–8.0 μM).

of 130 μl was considered the best measurement protocol for the levels typically found in the River Frome in October. The addition of the QC (4.0 μM PO$_4$) after every fourth or fifth sample allowed for correction of drift arising from, e.g. changes in air temperature.

3.3. River Frome field study (October 2000)

A comparison of the data for the three field calibrations (1–3 October 2000) is given in Table 1. Reproducibility for replicate injections of standards was typically <4.0% R.S.D. ($n = 3$) and the pooled data (between batch) also showed R.S.D. of <4.0%, with a linear correlation coefficient (r^2) of 0.997. The QC sample was analysed 15 times over the 3 day period and the results were all within 3.7% (range 3.81–3.95 μM PO$_4$), showing that external factors did not significantly affect the response. Fig. 5 shows the diurnal PO$_4$ concentration profile over the course of the 3 day monitoring campaign, during which the monitor ran continuously after initial installation except for deliberate stoppages for the calibrations and subsequent changes of filter in the tangential flow filtration unit. The environmental significance of the data is discussed in Section 3.5.

3.4. Intercomparison study

An intercomparison study between the FI instrument and the batch method on 30 samples was

Table 1
Table of field calibration data for PO$_4$ obtained during the field deployment on the River Frome.

[PO$_4$] (μM) ($n = 3$)	Day 1		Day 2		Day 3		Pooled Data	
	Mean absorbance	R.S.D. (%) ($n = 3$)	Mean absorbance	R.S.D. (%) ($n = 3$)	Mean absorbance	R.S.D. (%) ($n = 3$)	Mean absorbance	R.S.D. (%) ($n = 3$)
0.8	0.0027	2.7	0.0021	3.7	0.0019	1.5	0.0020	2.6
1.5	0.0040	6.0	0.0049	2.3	0.0040	2.7	0.0043	3.7
4.0	0.0121	0.9	0.0135	4.3	0.0121	0.8	0.0126	2.0
6.0	0.0168	1.0	0.0181	0.7	0.0166	2.3	0.0172	1.3
8.0	0.0260	1.6	0.0276	2.0	0.0257	1.9	0.0263	1.8
r^2	0.993	0.993	0.998	0.998	0.995	0.995	0.997	0.997
Gradient (absorbance, μM^{-1})	0.0038	0.0038	0.0043	0.0043	0.0038	0.0038	0.0038	0.0038
Intercept (absorbance)	0.0003	0.0003	−0.009	−0.009	0.0004	0.0004	0.0007	0.0007

undertaken. Samples were analysed immediately using the FI monitor (range 4.74–5.13 μM PO$_4$) and also collected manually, stored and analysed later (within 8 h) using the batch method (range 4.75–5.34 μM PO$_4$). A paired t-test showed no significant difference at $P = 0.05$ (the critical value of $|t|$ was 1.96 and the calculated value of $|t|$ was 0.88). This means that data acquired using the field instrumentation can be directly compared with historical data acquired using the batch method and can therefore also be incorporated into the export coefficient model.

3.5. Effect of FI data on the export coefficient model

The export coefficient model for the Frome catchment [8] predicted a TP load of 26,100 kg per year,
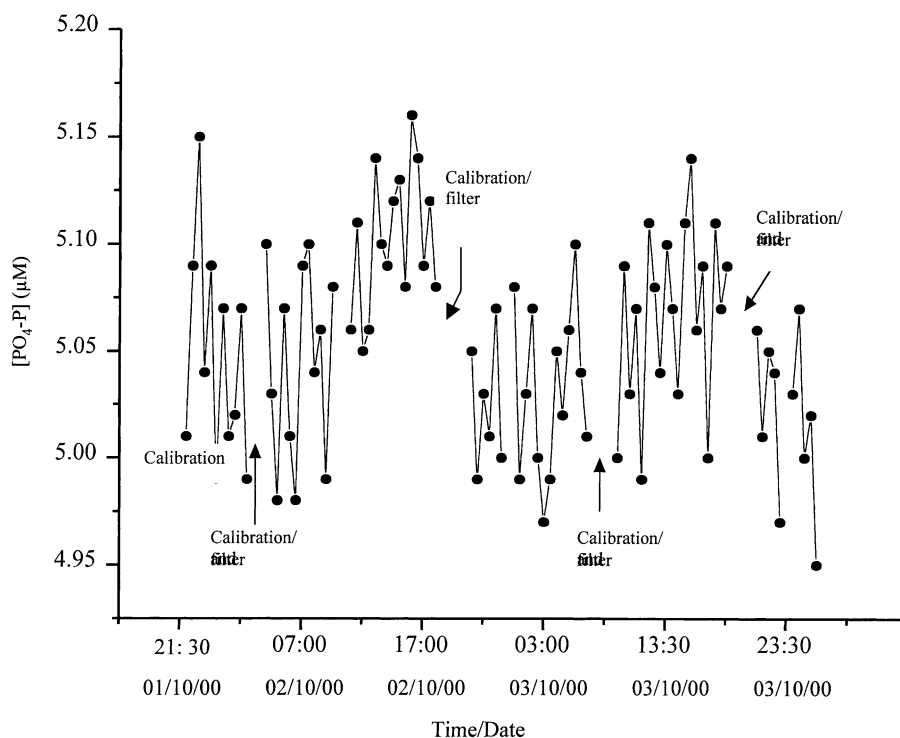

Fig. 5. Time series plot of PO$_4$ concentration obtained over a 3 day sampling campaign on the River Frome in October 2000.

compared with an observed (measured) load of 23,400 kg per year for 1998. Data for the observed load were obtained from manually collected samples (four per month) analysed in the laboratory using the batch method. The concentration data were integrated with flow data from the same sampling point and the observed annual load determined. Due to the variation in number of days between measurements, the loads were calculated on a time interval basis and aggregated to obtain the annual load. The observed load for 1998 was 11% less than the predicted load, due in part to the lack of resolution of the manual sampling programme, which meant that insufficient samples were collected during periods of peak river flow (when phosphorus loads are at their highest).

During the 3 day deployment, and for 10 days prior to that, it remained dry and therefore it is not surprising that Fig. 5 does not show major changes in PO_4 concentration. Nonetheless the difference between the highest and lowest concentrations of PO_4 observed would have resulted in an annual difference of 770 kg in an aggregated calculation which, assuming a constant ratio of TP to PO_4 of 1.6:1.0 [8], is equivalent to 1230 kg TP. It is reasonable to assume that over the lifetime of a rain event the PO_4 concentration will fluctuate much more rapidly and that this data will have significant leverage on the aggregated observed annual load. The above hypothesis will be tested during future deployments but this paper demonstrates the feasibility of acquiring the necessary high temporal resolution data using FI based field instrumentation.

4. Conclusions

The FI field monitor described is effective and reliable for measuring PO_4 in freshwaters, with a detection limit of 0.67 μM and the ability to respond to changes in environmental conditions by adjusting the wavelength used for detection. The addition of the tangential flow filtration unit prevented blockage of the micropumps seen in earlier deployments, which allowed extended and uninterrupted introduction of samples. The monitor can sample with high temporal resolution (every 30 min) which is necessary to measure short-term changes in PO_4 concentration. In

addition, the acquired data can be used to refine the export coefficient model for phosphorus loading in the Frome catchment.

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