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Report to United Utilities

High resolution and in-situ phosphorus monitoring: a comparison of equipment, deployment and maintenance requirements and cost

[redacted]

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CONFIDENTIALITY STATEMENT

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SUMMARY

This report outlines four available options for high resolution and in-situ phosphorus monitoring equipment. These are the Wetlabs Cycle-PO_4, the Systea WIZ probe, the Hach Lange PHOSPHAX sigma and the ISCO autosampler with laboratory analysis. These options are presented in terms of their equipment specification, field deployment, maintenance requirements and cost in relation to seven considerations for identifying a suitable piece of equipment for a particular situation. These considerations are the location of the monitoring site, required frequency of sampling, the number of analytical determinands measured, the disposal of waste chemicals, the ease of deployment, the maintenance requirements and costs. Information was gained from manufacturer specifications, published papers and discussions held with users of the different pieces of equipment to establish the field requirements for their use. A comparison is made of these options against the different considerations to highlight the advantages and disadvantages of each one.

INTRODUCTION

Improving our understanding of nutrient fluxes from catchments, their sources and dynamics requires high resolution, in-situ monitoring of nutrient concentrations. It is now well established that a high proportion of total nutrient loading to rivers occurs during high flow events and often over very short periods of time, resulting in the underestimation of the true nutrient loads received by streams where nutrient concentration data are obtained from conventional, routine spot sampling (Cassidy and Jordan, 2011). In addition, different nutrient sources may be more or less important depending on flow conditions. For example, point sources discharging directly into a river or lake are likely to be flow independent and can therefore be an important contribution of nutrients at low flow levels, while diffuse sources must be mobilised and moved into a waterbody, often during high flow events and are therefore more likely to be flow dependant with higher concentrations associated with higher flow levels (Jones et al. 2011).

In the past, in-situ monitoring of phosphorus has proved difficult due to the analytical requirements of the wet chemistry technique used to determine phosphorus concentration and the low concentrations of phosphorus, particularly phosphate, frequently found in the environment. More recently, technological developments by a number of different scientific monitoring equipment manufacturers has resulted in several different in-situ phosphorus monitoring systems being available commercially. Further developments in this field are also occurring, with new generations of sensor types such as the ‘lab on a chip’ (Wade et al. 2012) likely to become available in the future.

A range of considerations are necessary to identify the best monitoring system for the particular situation and the data that is required. These are:

- Location of monitoring site
- Frequency of sampling
- Analytical determinands measured
- Disposal of waste chemicals
- Ease of deployment
- Maintenance requirements
- Costs

In-situ phosphorus monitoring systems can generally be divided into two different categories, those which are deployed directly in the water and those which require housing within cabinets alongside the waterbody, with water being pumped from the waterbody into the cabinet before being analysed. In addition, automated sampling of water can be carried out and the water collected and analysed in a laboratory. The choice of system is therefore dependant on the requirements of the monitoring situation. Systems also differ in terms of the particular fractions of phosphorus they can analyse such as dissolved phosphate (PO_4-P), particulate or total phosphorus (TP) forms and whether filtration steps through small pore sized filters (typically 1.2 – 0.45 µm) are included in the process such as for Soluble Reactive Phosphorus (SRP) but not Total Reactive Phosphorus (TRP). In general, most systems currently available utilise the molybdate-blue reaction method of phosphate determination, where an acidified molybdate reagent is reacted with a sample to create a phosphomolybdate complex, which is reduced to a molybdenum blue compound and read spectroscopically (Murphy and Riley 1962). The intensity of the blue colour is proportional to the concentration of phosphate in the sample and therefore the use of calibration standard concentrations allows the determination of phosphate in the sample. This method is analogous to the common analytical technique used by chemistry laboratories, with additional digestion steps required for the determination of TP.

Given the range of options for in-situ monitoring and phosphorus forms that can be analysed, this report considers four potential high frequency phosphorus monitoring systems currently available; the Wetlabs Cycle-PO4, the Systea WIZ probe, the Hach Lange PHOSPHAX Sigma and ISCO autosampler. The report provides information on the equipment specification, field deployment and maintenance for each system, followed by a cost comparison and recommendations.

EQUIPMENT SPECIFICATION

Wetlabs Cycle-P

Description:

The Cycle-P analyser is an in-situ monitor for the determination of TRP (Figure 1). It can be deployed directly in a water body and fully submerged.

Figure 1 Wetlabs Cycle-PO4 Analyser. Source: http://wetlabs.com/cycle-phosphate-sensor

Dimensions and operational requirements:

Feature	**Value**
Height	0.56 m
Diameter	0.18 m
Weight (in air)	6.8 kg
Weight (in water)	0.37 kg
Maximum depth of deployment	200 m
Operational temperature range	0 – 35 °C
Electrical input	10.5 – 18.0 V DC
Current draw during operation	115 mA average, 2 A max
Current draw during low power	30 µA
Data storage	1 GB compact flash car type II
Number of samples	1000 per reagent cartridge change
Length of deployment	Up to 3 months
Cycle time per analysis	30 minutes

Analytical detection method, range of instrument and detection limit:

- The Cycle-P measures TRP, although the water is filtered on 10 µm filters prior to the molybdenum blue analysis.
- The instrument range is 0 – 0.3 mg/L PO_4-P
- The limit of detection is 0.0023 mg/L PO_4-P

Systea WIZ probe

The WIZ probe is an in-situ monitor capable of measuring up to four chemical compounds, including ammonia, nitrate + nitrite, Nitrite, total nitrogen, phosphate, organic phosphorus, total phosphorus, silica, total organic carbon, chemical oxygen demand, biological oxygen demand and turbidity (Figure 2). They offer a phosphorus set up for the probe which can measure phosphate, organic phosphorus and total phosphorus on one instrument. It can be deployed in water and fully submerged.

Figure 2 WIZ probe. Source: http://www.systea.it/index.php?option=com_content&view=article&id=58&Itemid=45&lang=en

Dimensions and operational requirements:

Feature	**Value**
Height	0.52 m analytical unit + 0.2 m reagent canister
Diameter	0.14 m analytical unit, 0.07 m reagent canister
Weight (in air)	8 kg (without reagents)
Weight (in water)	-
Maximum depth of deployment	10 m
Operational temperature range	4 – 40 °C
Electrical input	12 V DC
Current draw during operation	8W average, 1.5 A max
Current draw during low power	3 W
Data storage	Internal memory

Number of samples	500 complete analyses (up to 4 determinands) per reagent cartridge change
Length of deployment	Up to 2.5 months – reagents stable for 4 – 10 weeks (temperature dependent)
Cycle time per analysis	40 to 60 minutes

Analytical detection method, range of instrument and detection limit:

- The WIZ measures SRP as the water is filtered on 10 µm filters and an optional self-purging 0.25 µm microfilter prior to the molybdenum blue analysis. For TP analysis the sample is first hydrolysed, which involves the injection of sulphuric acid, heating, injection of potassium peroxodisulphate and UV irradiation and then analysed using the same molybdenum blue method as for SRP
- The instrument range is 0 – 0.5 mg/L PO_4-P and 0 – 1 mg/L for TP
- The limit of detection is 0.005 mg/L PO_4-P and TP

Hach Lange PHOSPHAX sigma

The PHOSPHAX sigma is a photometer which can alternately measure TP and TRP, as no micro-filtration step is included in the analysis procedure. It requires a cabinet-type installation as it is not ruggedized for direct deployment in a water body (Figure 3). Samples which could contain particulates are also required to be homogenised with a SIGMATAX 2 control unit and ultrasonic harmogenisation before being taken into the analyser.

Figure 3 Example of a PHOSPHAX sigma deployment as part of the EdenDTC project (http://www.edendtc.org.uk/) Source: Dr Clare Benskin.

Dimensions and operational requirements:

Feature	**Value**
Height	1.19 m
Diameter	0.55 m
Weight (in air)	43 kg
Weight (in water	NA
Maximum depth of deployment	NA
Operational temperature range	5 – 40 °C
Electrical input	230 V AC
Current draw during operation	310 VA
Current draw during low power	NA
Data storage	Via datalogger
Number of samples	Reagent supply lasts approximately 3 months, standards approximately 1 year
Length of deployment	Maintenance interval 3 months, plus ½ hour required per week
Cycle time per analysis	10 minutes

Analytical detection method, range of instrument and detection limit:

- The PHOSPHAX sigma measures TRP using the molybdenum blue method. For TP analysis the sample is first heated and digested by sodium peroxide sulfate and then analysed using the same molybdenum blue method as for TRP
- The instrument range is 0.01 – 5 mg/L PO_4-P and TP in 0.1 mg increments
- The limit of detection is 0.02 mg/L and uncertainty is +/- 2% of the measurement value

Autosampler and lab-based analysis

The ISCO autosampler is a portable sampling unit which can be used to take sequential or composite water samples at programmable intervals. It consists of a controller, pump, battery and sample bottles (Figure 4). The unit is installed next to the water body with an inlet pipe secured in the water for sampling. Sampling can be triggered either directly on the controller or remotely via a telemetered link or in response to an exceedance threshold of linked ESNET units such as flow level, turbidity or rainfall. Sampling intervals are user defined. Following the triggering of sampling, samples must be collected for transport to a laboratory within a short period of time, typically 24 – 48 hours to ensure that samples do not degrade for the required chemical analyses.

Figure 4 ISCO autosampler. Source: http://www.isco.com/products/products3.asp?PL=201101030

Dimensions and operational requirements:

Feature	Value
Height	0.64 m
Diameter	0.55 m
Weight (in air)	16.8 kg (excluding battery)
Weight (in water)	NA
Maximum depth of deployment	NA
Operational temperature range	0 – 49 °C
Electrical input	12 V DC
Current draw during operation	-
Current draw during low power	-
Data storage	NA
Number of samples	Up to 24 but dependant on the number of chemical determinands or volume required in the laboratory
Length of deployment	Usually over a 24 hour cycle
Cycle time per analysis	NA

Analytical detection method, range of instrument and detection limit:

- The analytical method will be laboratory specific but most are likely to use some form of the molybdenum blue method, with an added digestion step for the determination of TP.
- The limit of detection is dependent on the laboratory carrying out the analysis but might be typically 0.02 – 0.001 mg/L SRP, TRP or TP.

FIELD DEPLOYMENT AND MAINTENANCE

To gain a better understanding of the deployment and maintenance requirements of the different in-situ measurement or sampling systems, where possible, discussions were held with people who had experience of using the different pieces of equipment. Questions were asked about the ease and requirements for equipment deployment, the frequency of maintenance trips, the reliability of the system for long field deployments and the quality of the data obtained. A summary of these discussions is provided below.

Wetlabs Cycle-P

Information on the deployment and use of a Cycle-P was gained from [redacted] from EAWAG, Switzerland and [redacted] from South Cumbria Rivers Trust.

- The equipment is thought to be easy to deploy and robust for field use. In Elterwater [redacted]), the Cycle-P is deployed at 0.4x the water depth from the sediment surface. Once in situ, the unit is purged of air bubbles and then set to log samples.
- Deployment in Elterwater is from a post in the centre of a channel, which requires cable connections to the shore where batteries and telemetry equipment are based.
- An external battery is required to maintain an adequate voltage for operation.
- Maintenance schedules seem to vary between sites, with the unit used by [redacted] in a eutrophic lake being visited and cleaned every week, while the Elterwater deployment is only visited when the reagent cartridges are swopped out, every six months.
- The data acquired for the Elterwater work so far, is of good quality and consistency even at low values (~4 µg L^{-1}).
- The only problem with the Elterwater deployment has been as a result of flooding in November 2014, where a lake level rise of 1.5 m caused the flooding of the telemetry control box and a loss of contact with the Cycle-P.
- Waste disposal of reagents is an additional necessary consideration and requires an external storage solution to be found.

Systea WIZ probe

Unfortunately, it wasn't possible to contact anyone to discuss the WIZ phosphorus probe. However there are two papers supplied by the manufacturer which describe some aspects of the field deployment and maintenance requirements (Moscetta et al. 2009; Copetti et al. 2014).

- Biofouling of the exterior of the probe during deployment can affect results and therefore frequent cleaning is required (approximately every 10 days, but this depends on the trophic status of the site), an online filter can be added to the sample line to prevent biofouling.
- WIZ reagent canister designed to be simple and quick to change.
- Waste chemicals are stored within the reagent canister and can be removed when changing this equipment (~3-4 weeks depending on sampling schedule).
- A study comparing the WIZ and laboratory methods for samples analysed for SRP and TP revealed a coefficient of determination (r^2) of 0.91 for SRP and 0.56 for TP between methods, with a tendancy for the WIZ to overestimate the lowest concentrations and underestimate the highest concentrations (Copetti et al. 2014).

Hach Lange PHOSPHAX Sigma

A discussion was held with [redacted] from the EdenDTC project about their use of a PHOSPHAX sigma and Sigmatax control unit.

- Requires a weather-proof structure (usually some kind of cabinet see Figure 3) and mains power for operation. It is also important to have insulated intake pipes and heating in the cabinet to ensure sample lines do not freeze and the operating temperature is maintained.
- Maintenance trips are required every 7 – 10 days for approximately ½ hour cleaning checks, bi-weekly removal of waste and reagent changes every 3 months. In addition a service contract is likely to be required for breakdowns and parts replacement/ renewal.
- The system is robust and reliable for long term use, once set up and correctly maintained. In general, equipment problems that occur are often possible to fix

by an experienced field technician with the aid of the Hach Lange manuals, although for some issues a site visit will be required by a technical engineer.

- The data produced is of good quality but does require 'cleaning' to remove erroneous values such as below limit of detection or when maintenance occurred. These decisions are user specific but might typically result in ~40% data being discarded.

Autosampler and lab-based analysis

Discussions were held with [redacted] from the EdenDTC project and [redacted] from the Environment Agency (EA) about their use of ISCO autosamplers.

- Relatively little infrastructure is required to deploy an autosampler. For remote triggering via GSM, telemetry infrastructure is necessary and for the purposes of security the EA use either existing buildings or a cage next to the river. There is a limit of 15 m on the length of the intake tubing and the height over which the sample can be drawn from the waterbody. Autosamplers are relatively easy to move around and change the location of interest.
- Setting up the autosampler, deploying and collecting bottles are fairly straightforward but if several people are involved, a crib sheet or check list is recommended to ensure consistency in the method and approach used.
- Power requirements are via a battery and solar panels. These shouldn't need changing if the equipment is only triggered twice per month and the solar panel is able to trickle charge the battery.
- Sites for using this equipment need to be relatively accessible to vehicles owing to the weight of samples on collection and for the initial deployment of the equipment.
- The equipment has been found to be relatively robust for long term deployments, although telemetry would need regular testing to ensure that triggering occurred when an event was selected for sampling.
- The main consumable for the equipment is pump tubing. Warnings can be programmed into the controller to trigger an alarm to change tubing after a defined number of rotations (usually 10,000), however the regularity of

replacement should also be based on how often the unit is triggered and the distance the unit has to extract water from the water body.

- The filter on the intake tubing should be regularly checked for blockages and to ensure the location for sampling is correct.
- Various options are available in terms of numbers of bottles and sampling frequencies. Typically on the EdenDTC sites a 24 bottle configuration is used and samples collected hourly. On retrieval of samples for analysis, not all may be analysed, but this depends on the question being asked. The EA configuration on the River Ehen has been to use eight, two litre bottles and to analyse a range of determinands on each sample. There is also an option for eight glass bottles, suitable for pesticide or herbicide monitoring.
- One of the most crucial issues with the use of autosamplers is the requirement to have manpower and logistical support to firstly trigger the sampler and then to return and collect samples in a timely manner. This can be a labour intensive process.
- A key consideration needed when using this method to sample events is the threshold value and variable used for triggering the sampling. An understanding of how the catchment behaves such as the antecedent conditions, flashiness, time of year, is very useful for establish these values and whether flow or rainfall are the indicator required. It is also important to be clear on what question you are collecting the data for, a more precise question will help to focus sampling effort where it is needed. Someone is needed in every case to make the decision on when to sample and this requires time to observe changes in the catchment.

COST COMPARISON

The costs provided in this section are indicative and approximate. They are intended to give an illustration of typical costs for each option to provide a broad basis for comparison of the different equipment types.

Wetlabs Cycle-P

Cost of equipment is approximately £13,100 +VAT. This includes one set of reagents, software and a spare parts kit. Additional items such as a service contract, reagent refills, power cables and external power supply are extra costs to consider.

Systea WIZ probe

Cost of equipment is approximately £15,300 +VAT. This analyser would provide TP, TRP/SRP and organic phosphorus. The package includes one set of reagents, submersible cable, software, 12V DC power supply for maintenance and set up. Additional items such as a service contract, reagent refills and deployment power supply are extra costs to consider.

Hach Lange PHOSPHAX Sigma

The approximate cost of the set up at the EdenDTC site at Morland was around £40-50,000. This included the cabinet, all the required instruments and the costs of installation. Additional items such as a service contract, reagent refills and power supply are extra costs to consider.

Autosampler and lab-based analysis

The cost of an ISCO autosampler set up is approximately £2,300 per annum on a commercial lease basis from NWQIS, including the control unit, pump and bottles. Additional items would include the cost of laboratory analysis. The cost of laboratory analysis can be a significant proportion of the ongoing costs of using an ISCO autosampler. This will vary depending on the number of determinands analysed and which laboratory is used.

DISCUSSION AND RECOMMENDATIONS

Based on the considerations given in the Introduction, the following discussion provides an overview of each consideration in turn.

- When selecting equipment, it is important to have a clear idea of the question or questions that it is being used to answer. This also includes a consideration of the logistical constraints of the likely sampling sites in terms of access, power supply and suitable location for siting necessary infrastructure such as cabinets or telemetry equipment. This is also relevant when considering if an in-situ monitor is required for continuous monitoring of all conditions, as opposed to an ISCO autosampler, which can only be used for short-term event sampling.
- Site location – The four different high resolution and in-situ options considered have different requirements for a deployment site. The Cycle-P and WIZ are both fully submersible units which means they can be deployed both in river and offshore lake locations, provided that there is some surface infrastructure for attachment and the location of a battery power supply and possible telemetry equipment such as on a monitoring buoy. The PHOSPHAX sigma and ISCO autosamplers are both samplers which require either a cabinet in the case of the PHOSPHAX sigma or an accessible bank side site for the ISCO sampling unit and bottles.
- Sampling frequency – the PHOSPHAX sigma offers the most frequent sampling option of the three in-situ measurement options at up to a 10 minute frequency (20 minutes for both determinands). The Cycle-P has a maximum frequency of 30 minutes, while the WIZ can do all three analyses within 1 hour. The sampling frequency of the ISCO autosamplers is also user defined and dependant on the bottle configuration and the type of event targeted.
- Determinands measured – The Cycle-P is a single determinand system, measuring TRP following a 10µm filtration. The PHOSPHAX sigma can measure both TP and TRP, while the WIZ can be configured to measure TP, TRP/SRP and organic phosphorus. As chemical analysis is carried out in a laboratory following collection from the ISCO autosampler a wide range of determinands are available but a rapid transfer from the sampler to the laboratory is necessary to ensure the sample integrity. Limit of detections for the three in-situ options are 0.0023 mg/L for the Cycle-P, 0.005 mg/L for the

WIZ and 0.02 mg/L for the PHOSPHAX sigma. The Cycle-P and WIZ are therefore best suited to sites with low phosphorus concentrations.

- Disposal of waste – All three in-situ measurement options produce waste chemicals that require arrangements for appropriate collection and disposal.
- Ease of deployment – All options require some form of structure in order to deploy the equipment. In the case of the Cycle-P and WIZ this could be a monitoring buoy on a lake or a secure in-stream structure. For the PHOSPHAX sigma system, a larger cabinet-type structure is required. In all cases consideration should be given to the security of the equipment. Feedback from users suggested that the Cycle-P, WIZ and ISCO autosampler units were relatively straightforward and quick to deploy in the field.
- Maintenance requirements – The maintenance needs of each in-situ option need careful consideration based on the situation and environment the equipment is exposed to. Amongst the users of the systems the number of site visits varies from weekly or fortnightly to several months. Reagent changes and waste collection will be dependent on the sampling frequency required, however checks for blockages and biofouling may necessitate frequent weekly visits to ensure the quality of the data is maintained. A benefit of telemetering the data is that real time interrogation can occur, to help flag up issues and prompt a site visit.
- Cost – In terms of capital investment, the ISCO autosampler has the lowest cost, followed by the Cycle-P, WIZ and PHOSPHAX sigma. The latter two in-situ monitors do however measure more than one phosphorus species. Ongoing running costs are likely to be dependent on sampling frequency for reagent use and the use of service agreements.

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