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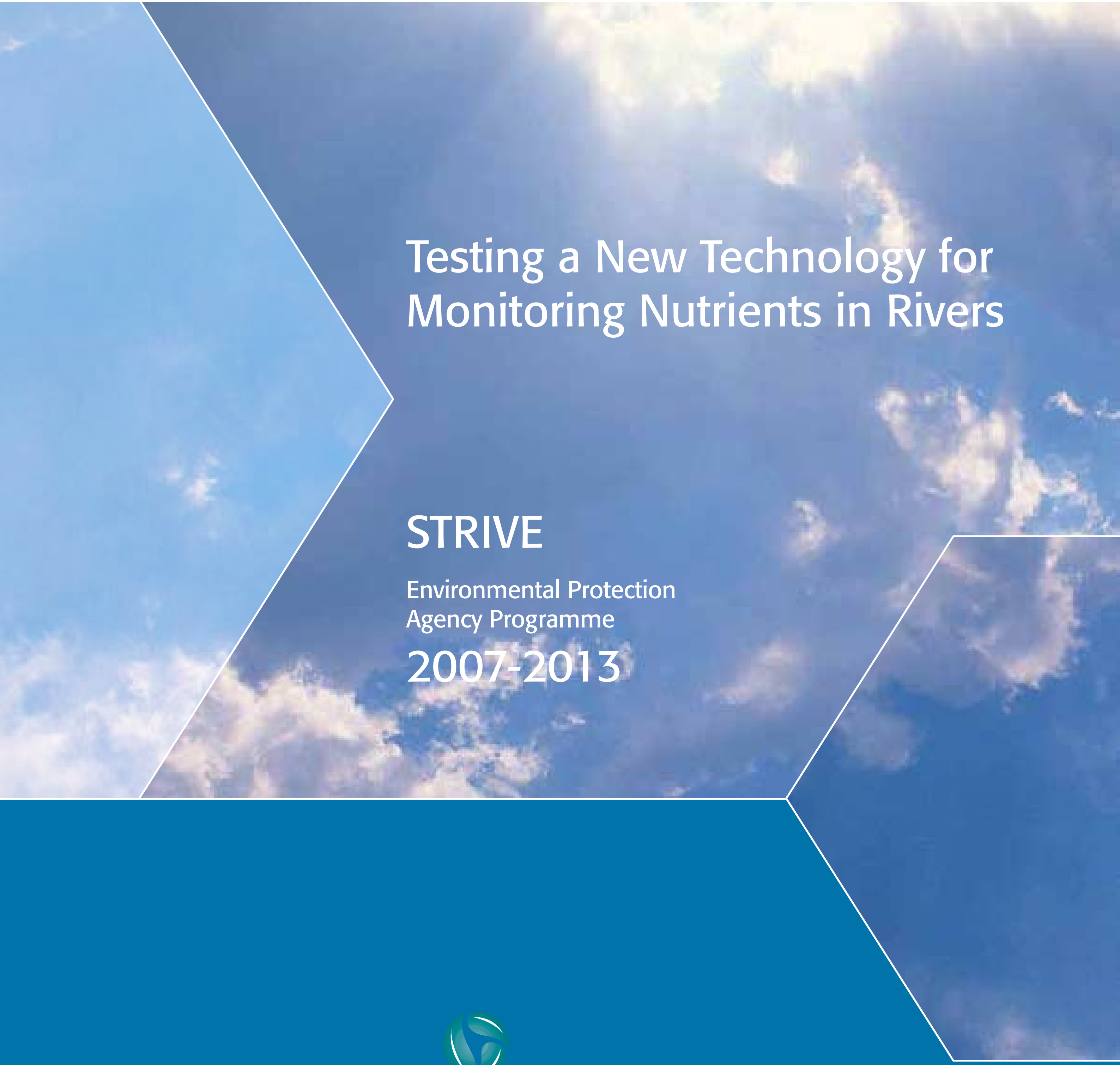
An Ghníomhaireacht um Chaomhnú Comhshaoil

STRIVE
Report Series No.81



Testing a New Technology for Monitoring Nutrients in Rivers

STRIVE

Environmental Protection
Agency Programme

2007-2013

SSTI
Strategy for Science, Technology and Innovation

Comhshaol, Pobal agus Rialtas Áitiúil
Environment, Community and Local Government

Environmental Protection Agency

The Environmental Protection Agency (EPA) is a statutory body responsible for protecting the environment in Ireland. We regulate and police activities that might otherwise cause pollution. We ensure there is solid information on environmental trends so that necessary actions are taken. Our priorities are protecting the Irish environment and ensuring that development is sustainable.

The EPA is an independent public body established in July 1993 under the Environmental Protection Agency Act, 1992. Its sponsor in Government is the Department of the Environment, Community and Local Government.

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- Office of Environmental Enforcement
- Office of Environmental Assessment
- Office of Communications and Corporate Services

The EPA is assisted by an Advisory Committee of twelve members who meet several times a year to discuss issues of concern and offer advice to the Board.

EPA STRIVE Programme 2007–2013

Testing a New Technology for Monitoring Nutrients in Rivers

Flow-proportional Passive Sensor Validation of Phosphorus and Nitrogen in Irish Rivers (Flow-Pro)

(2008-ET-MS-5-S2)

STRIVE Report

Prepared for the Environmental Protection Agency

by

University of Ulster

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ACKNOWLEDGEMENTS

This report is published as part of the Science, Technology, Research and Innovation for the Environment (STRIVE) Programme 2007–2013. The programme is financed by the Irish Government under the National Development Plan 2007–2013. It is administered on behalf of the Department of the Environment, Heritage and Local Government by the Environmental Protection Agency which has the statutory function of co-ordinating and promoting environmental research.

DISCLAIMER

The EPA STRIVE Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

EPA STRIVE PROGRAMME 2007–2013

Published by the Environmental Protection Agency, Ireland

ISBN: 978-1-84095-404-3

Price: Free **Online version**

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Executive Summary

The Environmental Protection Agency (EPA) is the statutory authority in Ireland for the protection of the environment. Along with other competent authorities, such as the River Basin Districts and local authorities, the EPA is charged with monitoring the ongoing chemical and biological state of water bodies. This is in alignment with the implementation of the Water Framework Directive (WFD; *Official Journal of the European Community* (*OJEC*), 2000) and the associated programmes of measures. Rivers, for example, which can be spatially and temporally variable, require monitoring networks that are extensive and are potentially an expensive commitment. In Ireland, spatial coverage has been favoured over temporal coverage in many monitoring programmes. However, as chemical pollutant transfers can be related to short-term discrete events or events related to storm hydrology, absence of a temporal emphasis to monitoring may result in an under-representation of these types of transfer from year to year.

As phosphorus (P) and nitrogen (N) transfers are considered to be persistent in Irish catchments, from multiple point and diffuse (including domestic and agricultural) sources, the purpose of this research project was to validate a commercially available passive flow-proportional sampling solution for P and N in Irish rivers. This is especially pertinent in the context of the WFD objectives of achieving and/or maintaining good status. Moreover, the project aims were to test an alternative to discrete grab sampling in rivers for nutrient concentrations using an approach that purported to give a more representative, integrated concentration over a deployment period, ideally synonymous with flow-weighted mean concentrations.

The passive sampler is possibly a cost-effective compromise between low-cost and data-poor grab sampling (spatial emphasis), and high-cost and data-rich automated sampling (temporal emphasis). The passive technology is based on adsorbent filled cartridges that are exposed to flowing water over defined time periods. The volume of water that has passed through the passive sampler is determined relative to the dissolution rate of a calcium citrate tracer salt. The passive system in groundwater (phreatic zone) and soil water (vadose zone) environments and controlled river flow environments (since the start of this study) had been shown to perform well in other studies but had not been tested in ambient river flows of high gradient (low to high flows) with multiple signals of P and N transfer.

In this study, predefined exposure periods and subsequent laboratory extractions were compared with high-resolution data sets for total oxidisable nitrogen, total phosphorus and total reactive phosphorus that were collected at established monitoring stations.

Multiple cartridges were deployed on 14 occasions in a variety of river systems in an effort to rigorously validate their use in rivers. These transfer risk patterns are summarised as showing indications of high P or N in storm flows and/or in inter-storm periods and from a variety of point and diffuse sources, the latter from both lateral (P) and vertical (N) flows. This allowed the accurate determination of time- and flow-weighted mean concentrations for the sampling periods that ranged from 3 to 5 weeks. A departure from the original systematic experimental design (a single river system, multiple deployment periods) occurred due to emerging factors relating to variable and under-estimation of flow-weighted mean concentrations. Hence the deployment strategy was extended to a number of river systems with different hydrological responses and nutrient transfer risks to ensure that any issues were not related to one particular site. Variability existed in the P and N concentrations returned by the cartridges compared to those measured by the high-resolution monitoring equipment. It included under- and over-estimates of nutrient fluxes (as flow-weighted mean concentrations) from near-continuous time series data. Experiments were subsequently conducted to investigate the discrepancies that existed between passive sensor results and high-resolution data.

Hydrodynamic simulations were conducted using a two-dimensional lattice Boltzmann discrete element methodology. This allowed fluid movement around the cartridge to be modelled as discrete particles, and simulations demonstrated flow divergence round the cartridges rather than into them. Issues were raised regarding the accumulation of detritus around the cartridges during storm events, the effectiveness of the cartridges during low flow, and the implications of invertebrate and algal colonisation.

To test adsorbance and tracer salt loss, and to eliminate external environmental variables, cartridges were exposed to standard solutions of known (P and N) concentration and ambient river samples via controlled pumping. Concentrations of P and N determined by cartridges in the pump test trials still displayed discrepancies in comparison to actual concentrations determined by standard methods in the river samples. However, estimation of cartridge throughflow using tracer salt dissolution rate appeared to be a reliable methodology, but only when flow was forced through the cartridge under pumped pressure.

The issues of temporal coverage for chemical monitoring in rivers remain highly important for future evaluation of catchment policy measures. Multiple factors have been highlighted regarding the performance of the cartridges and their variable recoveries when compared with flow-proportional data. Further investigation into these factors would allow the true effectiveness of the passive sensor cartridge to be quantified in Irish river systems and informed adaptations made to the cartridge design to improve function. As these issues become resolved, the passive system could be extremely useful to the WFD authorities mentioned above, in tandem with current monitoring programmes, and possibly form part of a complementary suite of ‘smart’ infrastructure for ongoing and future water monitoring programmes.

1 Introduction

1.1 Principles of Nutrient Monitoring

Managing the eutrophication of fresh, transitional and coastal waters caused by excessive transfers of nutrients from land to water remains one of the key water quality challenges of the twenty-first century. In Ireland and the rest of the European Union (EU), managing eutrophication will form part of (international) River Basin District (RBD) management plans and programmes of measures (POMs) under the Water Framework Directive (WFD; *OJEC*, 2000) with a view to attaining at least 'good' ecological status by 2015. Managing and monitoring issues pertaining to eutrophication in Ireland fall under the remit of the Environmental Protection Agency (EPA), RBDs and local authorities.

The drivers of anthropogenic eutrophication are largely excessive inputs of phosphorus (P) and nitrogen (N) from a multiplicity of diffuse and point sources, each source varying in importance according to water-body type, hydrological regime (and connectivity) and source-magnitude in any given catchment or watershed (Tilman et al., 2002; Gburek et al., 2005).

In large rural Irish catchments, identification of diffuse and point source influences would help to decipher nutrient transfer. Diffuse loss from critical source areas in a landscape delivers the bulk of annual loads via storm hydrological pathways and has the greatest impact on standing water bodies. These areas pose particular risks when surface storm pathways interact with land that has a historically high accumulation in upper soil layers or when they interact with recently slurried/fertilised soils (Haygarth et al., 2005; Douglas et al., 2007). Point source loss tends to deliver a constant but low-level nutrient load that would have a greater impact on flowing waters over a prolonged timescale (Foy, 2007; Bowes et al., 2010). Somewhere in between these two extremes are the very many small rural point sources that exist in a diffuse pattern across the Irish landscape. These form a unique typology of 'diffuse-point' nutrient sources that may or may not be linked to storm hydrology (according to site, engineering, age or maintenance) and that consist of single-dwelling domestic septic systems, farmyard infrastructure, and cattle access to streams and rivers (Jordan et al., 2008; Arnscheidt et al., 2007). Furthermore, these can be augmented by accumulated nutrients in streambed sediments that can be released under both low-flow (redox-related desorption) conditions (Jarvie et al., 2005) and high-flow (flushing) conditions (McDowell and Sharpley, 2001). This combination of 'diffuse-point' sources is a typology that can therefore augment both diffuse and point nutrient transfers in time and space.

Under the terms of the WFD, bodies such as the EPA and local authorities are required to undertake baseline biological and chemical water quality monitoring in rivers, identify pressures and instigate programmes of measures to alleviate pressures, and then monitor the effectiveness of those measures. In Irish rivers, reach by reach up to catchment outlet, routine nutrient monitoring is carried out on a monthly basis (up to 12 grab samples per year), and this regime forms the basis of assessing the effectiveness of catchment management strategies. Indeed, estimating a gross annual nutrient (or sediment or pathogen) load or mean annual concentration is fundamental to environmental accounting in riverine fluxes (albeit with reference to inter-annual hydroclimatic differences; see, for example, Johnes, 2007). As an introduction to this report on passive sensors, a summary review is provided on the background to sampling and the evolution of the passive sensor technology.

1.2 Grab Sampling

The most frequently employed method for the analysis of environmental parameters, in soil, sediment or water, is discrete grab sampling (Facchi et al., 2007). This sampling regime is widely used by many government agencies and monitoring bodies within Ireland and the UK. Grab sample frequency tends to occur on a monthly, fortnightly or sometimes weekly basis (Bowes et al., 2009). The technique does have limitations, including the expense and labour-intensiveness of the sampling process (de Jonge and Rothenberg, 2005). It is also widely acknowledged in the scientific community that grab sampling delivers only a 'snapshot' of prevailing environmental conditions at the time of sampling

(Facchi et al., 2007). This is particularly problematic when monitoring dynamic water bodies, where nutrient levels can change rapidly over a very short timescale (Kronvang and Iverson, 2002; Jordan et al., 2005a; Facchi et al., 2007; Bowes et al., 2009).

By its very nature, grab sampling in rivers is both coarse and time-discrete. It is ineffective at delineating the precise dynamics of nutrient transfers during high- and low-flow events, and as a result, it is difficult to accurately estimate load and average concentrations from data collected using the methodology (Jordan et al., 2007). In an effort to improve the resolution of grab sample data it is therefore necessary to increase the sampling frequency (Johnes, 2007). However, this is not always possible in many monitoring regimes due to the excessive costs that are likely to be incurred through increased laboratory analysis and labour. An implicit assumption with this regime is that due to the likelihood of low coverage of high-flow events, many years of data will eventually include this important flow pattern to enable an assessment of both point and diffuse nutrient transfer patterns. In terms of trajectories of change, however, as grab sampling will always tend to over-sample low-flow patterns and under-sample high-flow patterns, the main changes noted will always be biased towards the lower flows that can, in some catchments, be overwhelmed by point source impact patterns.

1.3 Automatic Samplers

The necessity for increased sample frequency and an improvement in data resolution led to the use of portable automatic samplers to capture higher, episodic flow samples. Automatic samplers are used within the freshwater research community for the collection of both composite and time-integrated samples (Lennox et al., 1997). Composite sampling consists of the accumulation of several 'high-frequency grab samples', which are taken over a known period of time (Facchi et al., 2007). Composite samples therefore aim to capture the mean concentration for the entire sampling period, due to the cumulative nature of the technique. When combined with or controlled by a flow measuring device, the composite samples can be collected on a flow-proportional basis (Douglas et al., 2007), thus taking account of the larger influences that higher flows will have on nutrient (or other parameter) flux.

Automatic samplers are also designed to take multiple water samples over a predefined time period or flow regime. The number and volume of samples to be collected is dependent on the size of the automatic sampler and the number of collection vessels housed within. The frequency of sample collection can be programmed to occur on a time- or flow-proportionate basis. With time-proportional sampling, water is collected on a time-integrated basis, whereas with flow-proportional sampling it is triggered by the passage of pre-programmed volumes of water. The use of on-site automatic samplers facilitates the collection of multiple water samples, which can then be transported back for laboratory analysis. Rapid transportation and analysis of samples is essential to avoid degradation in the absence of preservation techniques. Automatic samplers help to improve sample resolution without excessive cost, and can augment standard grab sampling regimes. However, there are limitations, including purchase expense when used at multiple sites, maintenance, installation, capacity and sampling duration.

1.4 High-resolution Continuous Monitoring

High-resolution nutrient monitoring has developed within academic and research institutes to address the inherent limitations of low-resolution sampling techniques. Johnes (2007) reports how the under-estimation of P loads occurs as a consequence of infrequent sampling and the under-representation of storm events. The use of bank-side auto-analysers provides state of the art, *in situ* equipment for the collection of continuous high-frequency river data. The collection of high-frequency data sets has therefore improved current estimates of periodic nutrient load, expanded the potential of environmental modelling, and facilitated the capture of low- and particularly high-flow events (Jordan et al., 2005a*,* 2005b, 2007; Kronvang et al., 2005; Sharpley et al., 2009; Fealy et al., 2010). One major limitation to the use of auto-analysers is capital required to purchase, install and maintain such equipment.

In 2001, the Blackwater Trans-boundary River-basin Action for Community and Environment (TRACE) project commissioned and installed high-resolution bank-side auto-analysers in two catchments in Northern Ireland and one in the Republic of Ireland (Jordan et al., 2008). The research was a water quality project funded by EU INTERREG IIIa that operated in the Irish cross-border drumlin region in the Blackwater River catchment. This project sought to capture both episodic and background continuous P transfers in a dynamic and flashy catchment, predisposed to storm flow pathways.

As part of the TRACE project, total phosphorus (TP) measurements were taken using a Dr Lange Sigmatax-Phosphax instrument suite, which is located in a glass reinforced plastic (GRP) kiosk powered by 240 V. This equipment can extract, homogenise, digest and determine TP colorimetrically every 10 minutes. Sample delivery by the Sigmatax is to an enclosed stainless steel sampling chamber located within the stream water, which is operated by positive air pressure. The 100 ml sample is homogenised by ultrasound to disperse particulates, and a 10 ml aliquot is then delivered to the Phosphax unit. Digestion is performed using sulphuric acid and potassium persulphate, according to the method of Eisenreich et al. (1975). TP is measured photometrically following the automated addition of molybdate antimony and ascorbic acid. Performance characteristics of the Dr Lange instrumentation are detailed in Jordan et al. (2007).

Also housed within the TRACE bank-side kiosk are the following pieces of hydrometric equipment:

- YSI 6600EDS sonde for the measurement of turbidity, conductivity, pH, temperature and dissolved oxygen;
- Starflow velocity–area discharge gauge;
- Rated OTT Thalimedes gauge for the measurement of stage height;
- Flow-proportional ISCO 6700 automatic water sampler.

Data recording is performed by a Campbell CR 10X datalogger, and results are delivered telemetrically to the University of Ulster at Coleraine. Figure 1.1 illustrates the bank-side kiosk located at the Co. Monaghan site.

Figure 1.1. High-resolution water quality and hydrometric station located in Co. Monaghan.

Linked to high-resolution monitoring, there is also a growing requirement for the accurate determination of nutrient fluxes during high-flow storm events (Jarvie et al., 2002; Johnes, 2007; Jordan et al., 2005a, 2007; Withers and Jarvie, 2008). Haygarth et al. (2004) recognised the need to 'monitor P concentrations at the same resolution as stream water discharge'. This is particularly relevant in relation to P, as the bulk of nutrient transfer occurs during storm events via diffuse sources (Jordan et al., 2007). Bowes et al. (2009) noted that a few high-flow storm events are responsible for the majority of annual TP transfers from catchments, yet these events constitute a relatively small proportion of the total monitoring period. P transfer is therefore positively correlated with flow during storm events. This relationship is due to increased surface and near-surface flow, and the diffuse transfer of P, particularly from agriculturally enriched soils, into receiving water bodies (Kurz et al., 2005; Jordan et al., 2007).

The very nature of storm events within many Irish catchments makes measurement difficult, owing to their clay-dominated soils and flashy hydrology. As a result, it is widely acknowledged that coarse, time-discrete sampling regimes are not likely to be coincident with many storm events. This was demonstrated by the Blackwater TRACE project, which highlighted that monthly, weekly and even daily grab samples grossly under-estimated annual TP loads by up to 60% (Fig. 1.2) compared with data collected every 10 minutes (Jordan et al., 2005a; Scholefield et al., 2007).

This was further corroborated by Kronvang and Iversen in 2002, who discussed the under-estimation of mass P fluxes as a result of storm event under-representation. In addition to this, it is also recognised that high-resolution data sets provide an insightful discrimination between continuous and episodic nutrient transfers within catchments (Arnscheidt et al., 2007).

1.5 Passive Sampling

It is widely acknowledged in environmental research that the process of sample collection and preparation constitutes a large proportion of the total analysis time and cost. Many analytical procedures within laboratories consist of multi-step processes that are both time and labour intensive. The growing necessity for high-resolution sample collection further substantiates the need for a reduction in analysis time and cost, to make monitoring an economically viable process. A move towards passive sampling techniques may provide the answer to this problem (Gorecki and Namiesnik, 2002; Namiesnik et al., 2005).

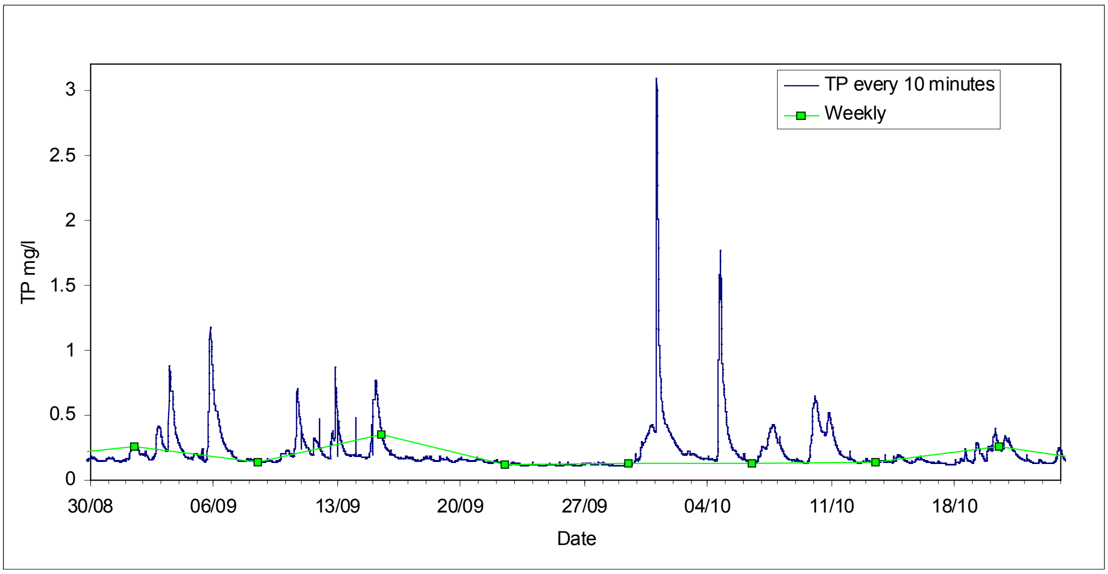

Figure 1.2. Blackwater Trans-boundary River-basin Action for Community and Environment high-resolution total phosphorus (TP) data collection compared to weekly grab sampling in Co. Monaghan (Jordan et al., 2005a; Arnscheidt et al., 2007).

The use of passive technologies not only facilitates a reduction in field and laboratory activities, but also improves sampling resolution. Passive sensors are deployed *in situ* for a predefined period of time and then collected for analysis. Another auxiliary benefit from the use of passive samplers is the reduction in sample degradation during transport and storage, through the use of 'semi-infinitive absorptive resins' (de Jonge and Rothenberg, 2005; Namiesnik et al., 2005). Passive samplers can therefore fix the analyte in a relatively stable state compared to grab sample transportation in sample bottles.

Passive sampling is defined as the measurement of an analyte as a weighted function of the time of sampling, which delivers time-weighted average concentrations relative to sampling duration (Kot et al., 2000; Vrana et al., 2006). Vrana et al. (2005) recognise the potential for passive samplers to measure a variety of pollutants *in situ*, which eliminates many of the problems associated with grab sampling and automatic samplers. Passive technology therefore simplifies the sampling procedure and removes the need for an external power supply. The principal limitation of passive samplers, for water quality monitoring, is their use in hydrologically controlled systems, such as rivers and streams, where nutrient flux is flow related rather than time related.

1.5.1 Time-integrated Passive Sampling Using Diffusive Gradient in Thin-film and Diffusive Equilibrium in Thin-film

Passive sampling methodologies have evolved through the development of diffusive gradient in thin-films (DGT) and diffusive equilibrium in thin-films (DET). Gel probe technology is both passive and time-integrated, and can be deployed *in situ* for the measurement of metals and more recently nutrients (Zhang et al., 1998a; Pichette et al., 2007, 2009). Data provided by passive technology facilitate the estimation of nutrient and metal mass balances, fluxes and transport, within deployed environments (Jarvie et al., 2008; Bottrell et al., 2007). Research to date has documented gel deployments in natural waters (Zhang et al., 1998a; Dahlqvist et al., 2002), soils (Zhang et al., 1998b; Harper et al., 1998), sediment pore waters (Zhang et al., 2002; Fones et al., 2004; Leermakers et al., 2005; Gao et al., 2006), and marine and lacustrine sediments (Mortimer et al., 1999; Zhang et al., 2002).

DGT (Zhang and Davison, 2000) uses a diffusive polyacrylamide gel and a secondary binding layer impregnated with either Chelex or iron oxide. (Chelex is a cation-exchange resin used for the absorption of metals; Gao et al., 2007.) Iron oxide is used as a binding agent for the determination of P. Adsorption is based on the theory of mass transport, where solutes pass through the filter and diffusive gel, then bind to the resin layer (Pichette et al., 2007). The establishment of a constant concentration gradient enables the transport of the dissolved substances onto the resin layer. Concentrations adsorbed by the resin are then determined using atomic adsorption (AA) or inductively coupled plasma (ICP), following acid elution. Time-weighted mean concentrations are then calculated using Fick's first law of diffusion (Docekalova and Divis, 2005). The use of differing gel types allows the measurement of a variety of organic and inorganic species (Zhang and Davison, 2000).

DET uses similar gel technology to DGT, but operates on equilibration of the resin with the adjacent medium. The DET probe also contains a polyacrylamide gel that equilibrates with the surrounding environment over time (Davison et al., 1991; Mortimer et al., 1998; Gao et al., 2007; Jarvie et al., 2008). After deployment, the gel is removed from the probe and analysed for solute concentration in relation to Fick's first law (Mortimer et al., 1998). Until recently, the application of DET was restricted to trace metal analysis in freshwater systems (Davison et al., 1994; Davison and Zhang, 1994). Limited research had been conducted in the use of gel technologies for the analysis of nutrients. However, Jarvie et al. (2008) successfully tested the application of DET gel probes for the measurement of soluble reactive phosphorus (SRP) profiles and fluxes in riverbed sediments. Probes were deployed within the riverine sediments for approximately 24 hours, eluted using 0.25 M sulphuric acid, and the concentration of SRP was finally measured colorimetrically using the method of Murphy and Riley (1962).

One practical limitation of gel technology is the accumulation of particulate matter on the filter surface. This occurs when probes are deployed in environments containing high concentrations of suspended matter and nutrients (Pichette et al., 2009). The development of biofilms on the gel surface is also problematic, and accrual levels are dependent on nutrient enrichment and deployment duration. When using DGT probes it is important that the influence of fouling films is limited to avoid bias. Pichette et al. (2007) conducted research into methods for reducing algal growth and thus extending the deployment period of DGT devices. Results concluded that it is possible to prevent algal colonisation on gel surfaces by using anti-biofilm agents, such as copper or silver iodide, for the analysis of P. The choice of algal deterrent is governed by the characteristics of the measured solute; for metal analysis it must not interfere with the adsorption or speciation of the metal.

Current application of DGT and DET passive samplers takes place in aquatic systems where solute flux rate is not overly influenced by large changes in flow rate, as in lakes or sediment–water interfaces. In such stable environments, the gel presents a constant exposure area of adsorbant resin to the solute. The use of gel technology for riverine systems has not yet been developed. In rivers, where flow rates have a high variation, the exposure area of the adsorbant must become dynamic relative to flow. Also, the range of nutrient flux in rivers is highly dependent on antecedent weather conditions and catchment hydrometrics, and as a result, nutrient levels can change rapidly and vary considerably in hydrologically active systems. To effectively capture such variation, passive sensors must have an equally dynamic chemical adsorbance mechanism, to allow an accurate measurement of nutrient range relative to flow. The resin or gel must therefore be capable of increasing and decreasing its chemical adsorbance relative to river velocity and discharge. Passive sensor technology for use in a riverine system should aim to be flow-proportional or flow-integrated.

With flat-surface adsorbents, such as those used in DGT and DET probes, there is currently no technology present to increase and subsequently decrease adsorbance area relative to flow. Passive sensors in their current form lack the dynamic capabilities to account for increasing and decreasing velocity or discharge. As a result, solute concentrations eluted from the deployed resin would be analogous with the time-proportional (rather than flow-proportional) mean concentration. True flow-proportional concentrations, for example, are calculated using the summation of all time-step loads, by multiplying discharge by concentration and then dividing by total discharge.

1.5.2 Sorbisense Flow-proportional Passive Sensors

Sorbisense is a Danish company that offers a passive sensor solution to the adsorption of solutes in environments where nutrient flux is hydrologically controlled. This emergent technology, called the Sorbicell sampler, utilises a cartridge-type adsorbant that sequesters the solute, proportional to the velocity of influent water. The primary advantage of this cartridge-style device is that flow can pass through, rather than onto, the adsorbant material. This enables the rate of nutrient adsorption by cartridge to be dynamic in relation to stream flow. The adsorbant resin housed within the cartridge therefore operates as a ‘semi-infinite sink for passing solutes of interest’ (de Jonge and Rothenberg, 2005). Also contained within the cartridge is a salt tracer, which is designed to quantify the volume of water that passes through the sensor during a deployment period. Salt dissolution rate is relative to the volume of water that passes through the cartridge. Solute extraction is finally performed by Sorbisense laboratories, using hydrochloric acid elution of the absorptive resin.

De Jonge and Rothenberg (2005) published on the proof of concept for this device, which was initially designed for the *in situ* sampling of dissolved solutes and/or colloids within soil and groundwater systems. In these environments, matrix flow in a saturated media dominates, so flow rate gradients would be low. Rozemeijer et al. (2010) also demonstrated the use of the samplers in controlled flume experiments – of varying flow – measuring nitrate, although rates of change were low over a one-year cycle. The sampler is marketed as a ‘smart filter’ that is passive and acts as a ‘water-permeable porous sampler that is in continuous capillary contact with its surroundings’ (de Jonge and Rothenberg, 2005). The principal advantage of this technology is its ability to continuously sample over an extended period of time, under varying hydrometric conditions, at a reduced cost compared to high-resolution monitoring. Sorbicell data therefore deliver dynamic solute concentrations that are indicative of the sampling period as a whole.

The Sorbicell sampler is designed to measure average concentrations over periods of time extending up to a month, dependent on influent velocities (Rozemeijer et al., 2010). The cartridge is constructed as a multi-porous system consisting of macropores of up to

0.1 mm and small nanopores of less than 1–10 nm. The macropore system ensures capillary contact and a high hydraulic conductivity. Contained within the cartridge is an adsorbant resin and tracer compound. The resin type varies relative to the solute, and the tracer compound is an environmentally neutral salt, such as calcium citrate. The technology is based on advective flow through the cartridge, in comparison to the equilibrium or kinetic diffusion that is used with DET and DGT gels. As a result, it appears potentially viable to deploy such technologies in hydrologically active river and stream systems. The Sorbisense InStream sampling method offers a cost-effective system for the continuous sampling of surface waters, and cartridges can be deployed in stream environments for between one and four weeks, dependent on high flow velocity (which may reduce the sampling period due to rapid tracer loss). Optimum salt loss from the cartridge is between 20% and 80% to allow an accurate determination of influent water.

Flow-proportionate passive sensor technology therefore offers an inexpensive alternative to high-resolution data collection, with a theoretical advantage over flat-surface gels. Flow-through passive sensors are an emerging technology that has only just become commercially available, and initial development and testing have been well received by the scientific community (de Jonge and Rothenberg, 2005). Nevertheless, further rigorous testing and validation are required to ascertain cartridge effectiveness in dynamic riverine systems that drain varying catchment types. Validation of the Sorbicell passive sensor cartridge, for use in Irish river systems, forms the basis of this research project.

2 Methodology

2.1 Aims and Objectives

The overall aim of the project was to validate a new passive flow-proportional sensor designed for sampling P and N in Irish rivers.

2.1.1 Objective 1

To facilitate N validation of the Sorbisense cartridges, it was necessary to procure, install and commission ultraviolet (UV) nitrate probes at existing water-quality stations for continuous monitoring. A probe was installed as part of the EPA Science, Technology, Research and Innovation for the Environment (STRIVE) Flow-Pro project in Co. Monaghan, with an additional probe as part of a Northern Ireland Environment Agency (NIEA) funded project in Co. Tyrone. The UV probes were validated by sampling across a high- to low-flow gradient and analysing using standard laboratory methods. Additional data were used selectively from other stations around Ireland where total oxidisable nitrogen (TON) probes (and P analysers) had subsequently been deployed.

2.1.2 Objective 2

High-resolution data capture was provided by existing P analysers and the newly installed and commissioned nitrate probe(s). Passive P and N sensors were then procured and deployed at water-quality and hydrometric stations, over a variety of time periods. Entry velocity into passive sensor arrays was monitored in detail around the deployment using an Ott Nautilus velocimeter at the start and end of exposures. Comparison of data sets from high-resolution analysers and passive sensors formed the basis of the validation procedure.

2.2 Site Descriptions

For field monitoring, the main station used in this project was a 5 km^2 sub-catchment of the Blackwater River in Co. Monaghan. These data were augmented by a similar station in Co. Tyrone, also a 5 km^2 sub-catchment of the Blackwater River. Both sites were part of a previous large-scale project, Blackwater TRACE (Jordan et al., 2008). These two sites were typical of flashy drumlin hydrological systems with both point and diffuse pressures, typically with high P and low N background and storm concentrations. Subsequent to the start of the project, a number of other sites were used that had the potential for: high P and high N concentrations (part of the Dee system in Co. Louth); low P and high N concentrations (part of the Slaney system in Co. Wexford); and low P and low N concentrations (part of the Robe system in Co. Mayo); see Fig. 2.1. Each site had hydrometry and water-quality instrumentation measuring discharge, P and N on a sub-hourly basis (e.g. Fealy et al., 2010); see Fig. 2.2.

2.3 Ultraviolet Nitrate Probes

To provide nitrate validation data for the passive sensors, a suitable probe was procured. After a tender process, the Nitratax UV-nitrate probe by Hach Lange was used to enable retrofitting to existing equipment. Stations were maintained on a weekly basis, and all equipment, pipes and tanks were rigorously cleaned and tested. Data were also downloaded on a weekly basis.

These reagentless nitrate probes use UV excitation and emission detection to predict TON (NO_3-N plus NO_2-N) in a water sample. The probe optics are designed to compensate for varying turbidity and colour changes in the monitored water by using a narrow band of wavelengths, while biofouling is avoided by using an optical wiper that cleans the sensor prior to measurement. To test the accuracy of the probes and their sensitivity to the presence of turbidity or humics within the Blackwater River catchments, the output was compared with a validation data set that was analysed independently at Dundalk Institute of Technology. Similar validation data sets are being prepared for the other sites.

Figure 2.1. Locations of deployment sites: 1 – Co. Tyrone; 2 – Co. Monaghan; 3 – Co. Mayo; 4 – Co. Wexford; 5 – Co. Louth.

Figure 2.2. Typical setup of a high-resolution water-quality and hydrometric station.

Validation water samples were extracted from the rivers using an ISCO 6700 automatic sampler. At the end of each run, the samples were refrigerated and transferred immediately to Dundalk Institute of Technology, where analysis was completed within two hours to minimise the risk of degradation. Sampling normally ran through the night to facilitate collection in the morning, thus avoiding higher daytime temperatures accelerating biological activity within the samples. A number of blank and spiked samples were also included for quality assurance purposes. Colorimetric analysis for nitrate and nitrite was undertaken using a flow-injection auto-analyser (Lachat Quickchem®), and a set of standards was periodically tested to ensure accuracy.

2.4 Sorbisense Cartridge Technology and Deployment

Sorbisense InStream technology is designed using smart, porous nano-materials. The cartridge contains an adsorbent that is in constant capillary contact with the surrounding medium. The type of adsorbent housed within the cartridge is specific to the solute of interest. Also contained within the cartridge is a partially soluble tracer compound (see Section 1.5.2). Cartridges are manufactured in two adsorbant capacities, 3 ml and 10 ml, dependent on instream concentrations of P and N (Fig. 2.3).

Water enters the cartridge via the frit and passes through a block of adsorbent resin (Figs 2.3 and 2.4) of acrylic polymer that adsorbs P and N. The frit is a glass or polyethylene (PE) mesh located at the upstream end of the cartridge, designed to filter the influent water. As water leaves the resin, it enters a section of the cartridge that contains a soluble tracer compound. Dissolution of the calcium citrate tracer is designed to be proportional to the volume of water passing through the cartridge as determined by the tracer solubility constant (Rozemeijer et al., 2010). Optimal tracer loss to ensure accurate determination of influent flow is between 20% and 80% of the total salt contained in the cartridge. After passing through the tracer compound, water leaves the cartridge and returns to the river system.

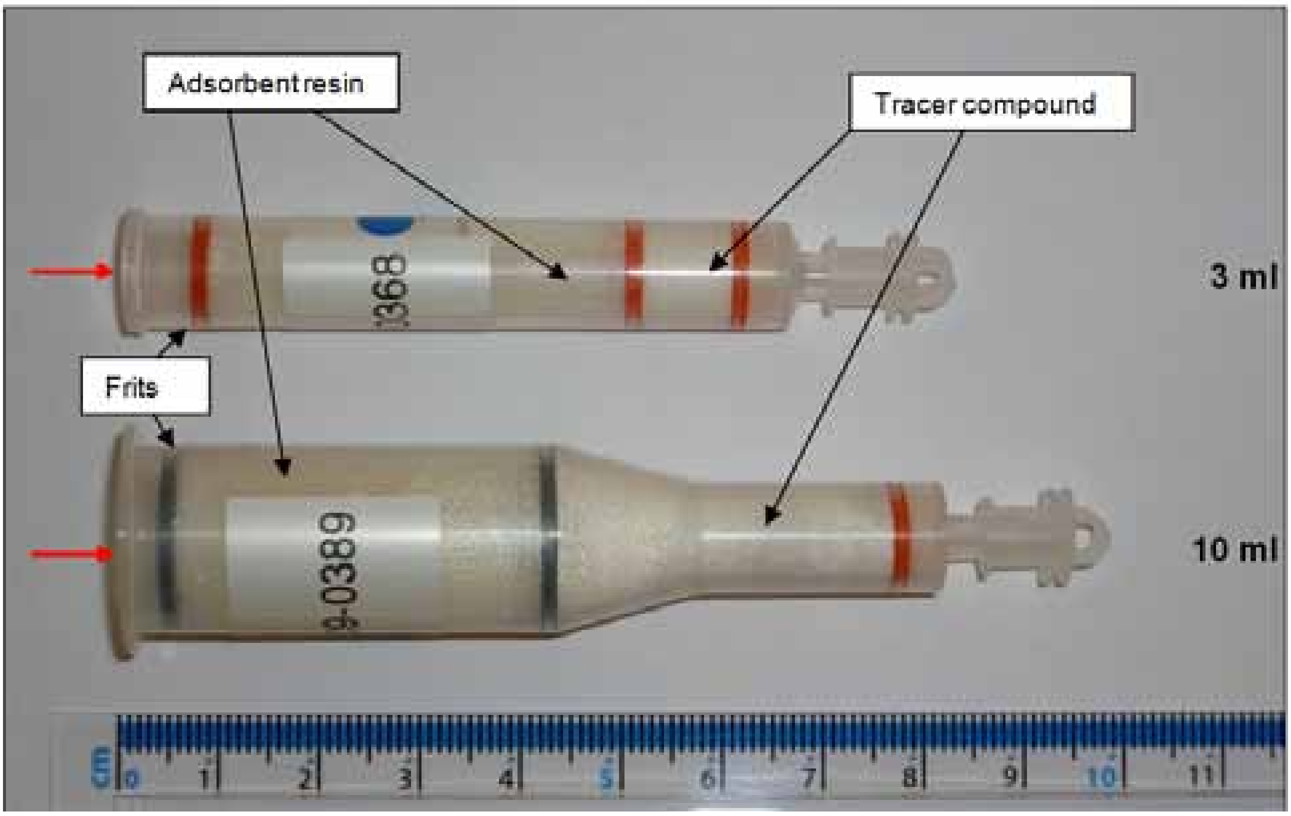

Figure 2.3. Sorbisense flow-proportional instream cartridges of capacity 3 ml and 10 ml. Direction of influent water is depicted by red arrows.

Figure 2.4. Sorbisense flow-proportional instream cartridges. Direction of influent water is depicted by red arrows, and frits are shown at the entrances of the cartridges.

Prior to deployment, the cartridges were pre-wetted by pushing deionised or stream water though the cartridge using a syringe. To maintain capillary contact, it was important to ensure that all air bubbles were removed from the cartridge prior to use. Once pre-wetted, the cartridge was attached horizontally into clips mounted on the instream rack (Figs 2.5 and 2.6). The adsorbent end of the cartridge was orientated in the direction of the stream flow.

After the deployment period, cartridges were removed from the stream, capped at either end, and placed in a self-sealing bag for transportation to the Sorbisense laboratory for analysis. To limit degradation, samples were stored in a cool, dark environment. P and N adsorbed to the resin was then acid eluted, and the solute mass (*M*) determined. The mass of tracer compound remaining was also measured, and the volume (*V*) of water that passed through the cartridge was determined relative to the solubility of the tracer. The flow-proportional concentration of solute measured during the deployment period, was then calculated as the ratio *M*/*V* expressed in µg l^{-1}.

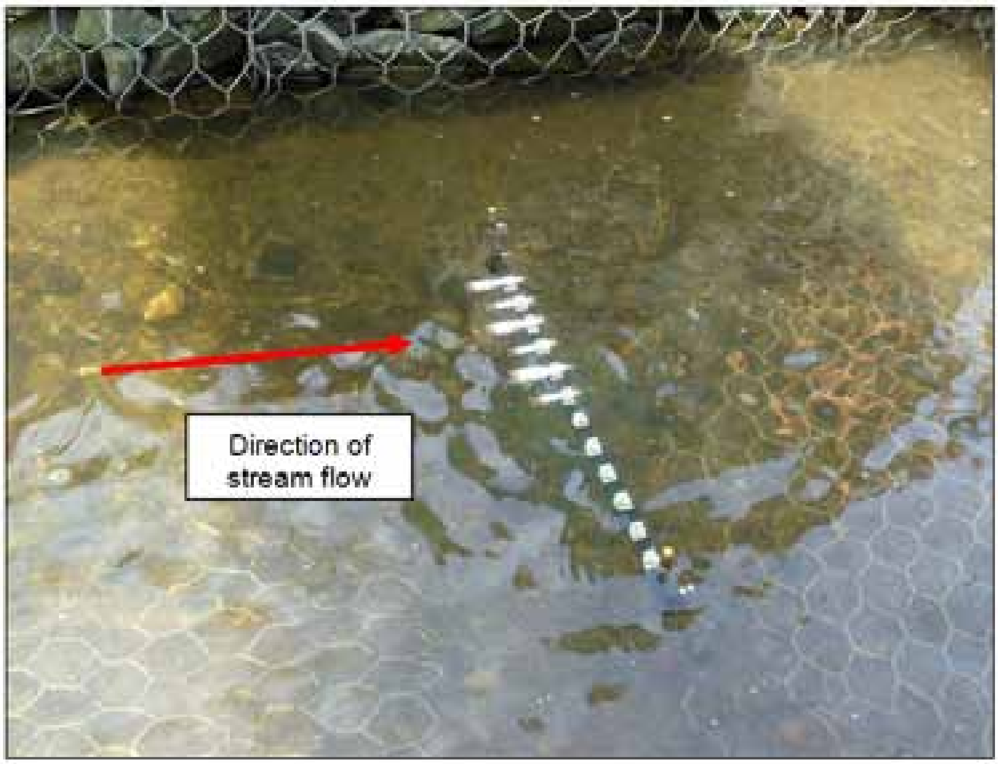

Figure 2.5. Instream rack and clips for mounting Sorbisense cartridges.

Figure 2.6. Deployment of cartridges using clips mounted on instream rack.

2.5 Calculation of Time- and Flow-weighted Mean Concentrations

Time- and flow-weighted mean concentrations (TWMC and FWMC) for each deployment period were calculated using high-resolution P, N and discharge (Q) data, as recorded by water-quality and hydrometric stations at sub-hourly intervals. Mean hourly discharge, N and P concentrations were then calculated. FWMC was calculated as total load (discharge multiplied by concentration for all time-step loads) divided by total discharge, for the deployment period. TWMC was calculated as the mean concentration during the deployment in the absence of stream flow. If the Sorbisense InStream cartridges behaved flow-proportionally, as desired, then concentrations returned by the cartridge should be comparable to the FWMC, as measured by the continuous monitoring stations.

3 Results

3.1 Validation of Ultraviolet Nitrate Probes for Continuous Monitoring

Sampling and analysis to provide a validation data set for the UV TON probe(s) sought to capture as broad a range of concentrations as possible. For the Co. Monaghan and Co. Tyrone sites, results are illustrated in Fig. 3.1. UV TON data used for passive sensor validation in Co. Monaghan and Co. Tyrone were corrected using the best-fit equation derived from the calibration data sets shown in Fig. 3.1.

There are significant positive relationships between the concentrations predicted by the UV nitrate probe and those determined colorimetrically for Co. Monaghan ($r = 0.989$, $n = 22$, $p < 0.001$) and Tyrone ($r = 0.966$, $n = 25$, $p < 0.001$). Analysis of covariance (ANCOVA) was used to compare the slopes and intercepts of the two regression lines (Quinn and Keough, 2002). ANCOVA demonstrates that there is a significant difference between the slopes of the lines ($F_{1,43} = 24.875$, $p < 0.001$). The difference in slopes between rivers and their deviation from unity is indicative of an additional contribution to the wavelengths detected by the sensor in response to UV excitation. This is most likely to be attributed to different levels of organic compounds and/or humics present in each catchment (although this assertion was not tested under laboratory conditions).

Organic material is known to respond to UV excitation and may not be completely excluded by the sensor optics. No mechanical problems are suspected, as the sensors are cleaned and tested at least once a week and produce an identical and correct response when tested with standard concentrations. Turbidity interference also appeared not to be a factor in signal output (Fig. 3.2), and this indicated that the probe is fairly robust as a device for isolating the N signal.

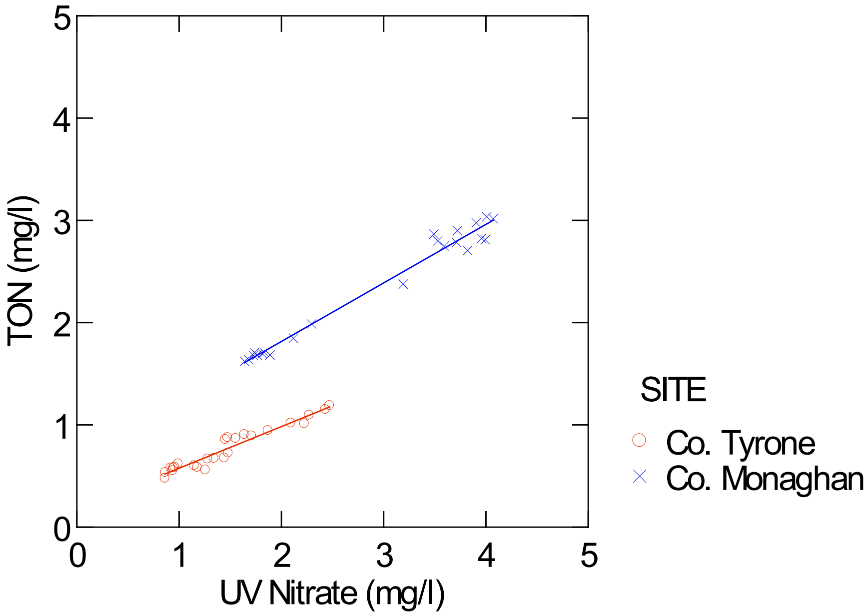

Figure 3.1. Calibration data sets for ultraviolet (UV) nitrate probes located in Co. Tyrone ($y = 0.407x + 0.168$) and Co. Monaghan ($y = 0.573x + 0.670$).

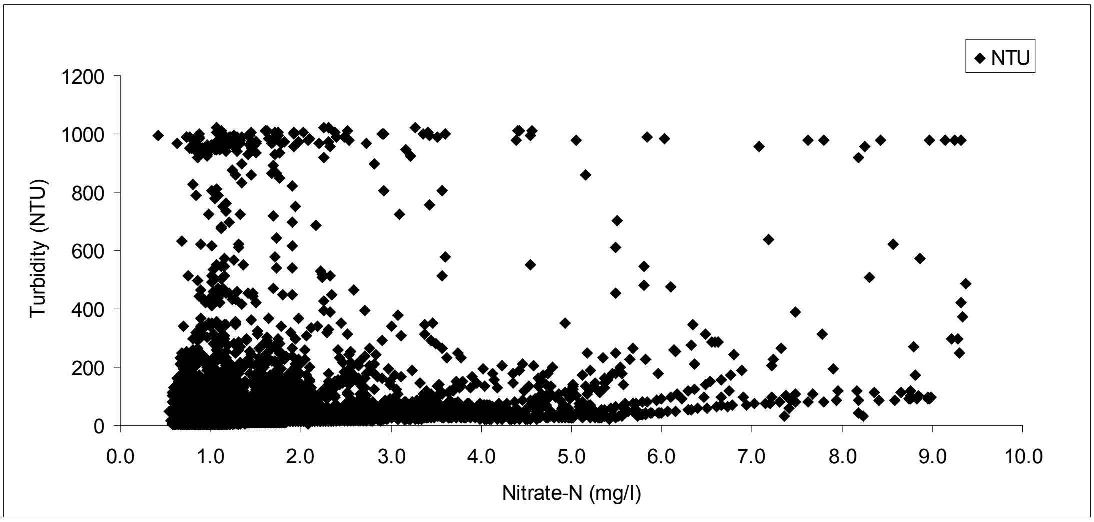

Figure 3.2. Nitrate determined by ultraviolet probe compared with turbidity. There appears to be no overall optical interference from sediments at the Co. Tyrone site.

Anecdotal evidence from the other sites (not presented here[1]) where humics were not as evident suggested that the relationship between laboratory and UV probe data was closer to unity. This also suggests that site-specific calibration (as distinct from validation) curves would be required at each station deployment.

3.2 Sorbisense Flow-proportional Passive Sensors

3.2.1 Initial Trials

Initial trials of the 3 ml cartridge revealed that P recovery was an order of magnitude lower than that measured by the high-resolution hydrometric stations for the period of deployment (Table 3.1). This was initially attributed to the blockage of the glass frits with suspended material contained within stream water. Glass frits are contained within the cartridge to filter flow into the adsorbent resin and then into the tracer compound. If the aperture size of the frit is too fine, then it could block, thus impeding throughflow onto the adsorbent resin. Conversely, if the frit is too coarse, then large particulate material may enter the flowcell to a greater degree. If this occurs, it is possible that advection and sequestration of P and N could occur, but in the absence of any tracer salt loss. To address this issue, a series of tests using a variety of frit sizes was conducted before the scheduled field deployments.

Prior to the frit size investigation, a technical examination of the cartridge design was conducted to identify other potential issues that may contribute to the under-estimation of concentrations. Published results, pertaining to the use of Sorbicell passive samplers, primarily detail their use within soil and groundwater (de Jonge and Rothenberg, 2005). In such environments, cartridges are embedded in a soil matrix and flow is induced through the soil. Recoveries from soil and groundwater deployments have to date provided good recoveries. In the soil environment, fluid is not less likely to pass through the cartridge than through the soil pore space. As a result, groundwater movement into the cartridge is representative of that in the soil matrix. In river systems, however, fluid flow is markedly different to that of groundwater. Increased velocity in river channels will encourage flow divergence around an obstacle, rather than move through it. The design of the Sorbicell should therefore be modified to reflect this in an effort to maximise flow and minimise resistance. The controlled flume experiments and cartridge deployments described by Rozemeijer et al. (2010) were compared with discrete and optical N probe data and appeared to follow seasonal trends of N transfer. The variations in flow and nitrate concentration were, however, not large, albeit much larger than phreatic or vadose systems.

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[1] A constraint of the results is that TON data presented are uncorrected for sites other than Co. Tyrone and Co. Monaghan, but are known to have less dissolved organic matter influence.

Table 3.1. Initial 28-day trial using a 3 ml cartridge deployment in Co. Tyrone.

Co. Tyrone Deployment from: 01/10/08 11:00 to 29/10/08 11:00		
	TP (mg l^{-1})	TRP (mg l^{-1})
Flow-weighted mean concentration (FWMC)	0.247	0.115
Time-weighted mean concentration (TWMC)	0.149	0.080
Passive sampler extracts	P (mg l^{-1})	
Cartridge 1	0.017	
Cartridge 2	0.028	
Cartridge 3	0.016	
Mean	0.020	

3.2.2 *Hydrodynamic Simulations*

Hydrodynamic simulations were undertaken using a two-dimensional modified lattice Boltzmann discrete element methodology (Abe, 1997; Martinez et al., 1994). The hydrodynamics of a fluid are modelled by representing the fluid as discrete particles, located at the nodes of a hexagonal lattice, moving in one of six directions and described by their interaction with nearest neighbour nodes at each discrete time step. Flow is induced by applying a small body force to each node in the direction of propagation, and the simulation runs until the velocity field is stable.

The predicted velocity field around a cartridge in a channel is shown in Fig. 3.3. The cartridge is to scale in a channel that is 150 mm wide, with velocities given in lattice units per time step (LU/t), where a lattice unit for this model is ~ 0.3 mm. The interior of the cartridge has been simplified to a high-porosity matrix of solid dots to allow open channels through the interior that would be present in three-dimensional packing configurations at lower porosities. Although stylised, the simulation highlights the issue with flow divergence around the cartridge and low-flow velocities within the pore space. High velocities are necessary to produce throughflow in the cartridges, and this corresponds to the company's findings that velocities below 0.2 m s^{-1} are ineffective.

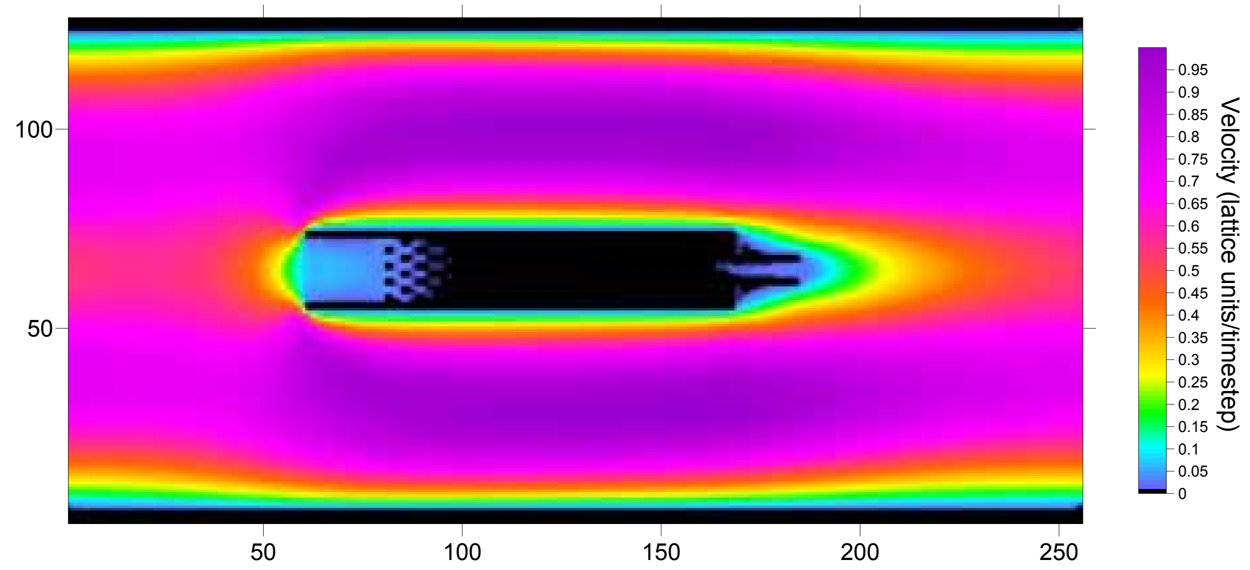


Figure 3.3. Simulated velocity field in a channel (150 mm wide) containing a stylised Sorbicell cartridge (outer diameter 12.8 mm) generated using a lattice Boltzmann discrete element model in two dimensions. Flow divergence around the cartridge results in low throughflow.

In response to this, Sorbisense evaluated mounting the cartridges in a Venturi tube (Fig. 3.4a) to increase velocities around and through the cartridge. In an open channel, however, the Venturi tube itself causes flow divergence, so the increase in velocity is only proportional to the slower entry velocities at the opening (Fig. 3.4b).

Nevertheless, the tests did indicate that laminar flow conditions within the tube reduced the variation in concentrations between duplicates compared with those in an open channel. In terms of increasing flow velocities, the results indicate that the channel at the deployment site would have to be confined in an effort to increase velocities where they are generally lower than 0.2 m s^{-1}. In the catchments, the channel either side of the rack was restricted to increase flow velocities during low-flow periods where deemed necessary.

A final set of simulations were undertaken to test different cartridge designs and porosities, and the results were passed to Sorbisense. Further development of the cartridge design constituted part of Sorbisense's research and development, and was ultimately not

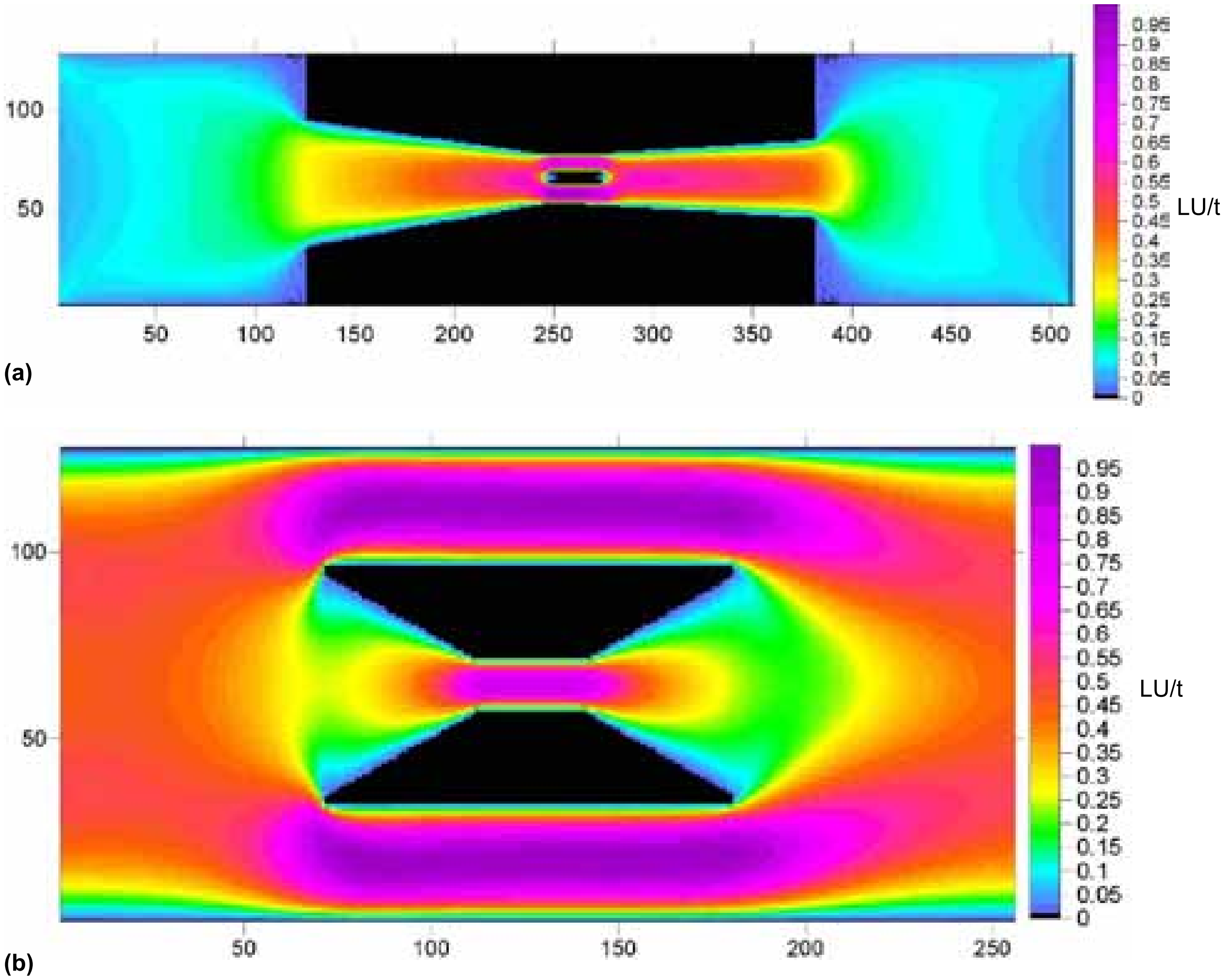


Figure 3.4. (a) Simulated velocity field (in lattice units per time step – LU/t) through a Venturi tube with the cartridge mounted mid-channel. The field tests of this design were undertaken by Sorbisense. (b) Positioning the Venturi tube in an open channel also caused issues with flow divergence, so the increased velocities in the constricted part of the tube were not significantly increased.

part of this research project. In light of these tests, the company modified the cartridge porosity and packing to lower resistance. These modified cartridges were subsequently used in the frit size tests and subsequent deployments.

3.2.3 *Frit Size Trials*

Three deployments were conducted to establish the influence of frit size on adsorption, while simultaneously evaluating the extent to which the passive sensors were flow-proportional. Table 3.2 details cartridge deployment period and both TWMC and FWMC as calculated from the continuous analysers at the high-resolution monitoring stations.

P, N and discharge time series are shown for the deployment periods in Figs 3.5 and 3.6. Four different frit sizes were tested in duplicate during each deployment. Frit sizes were 20 µm, 40–100 µm, 100–160 µm and 160–250 µm. Cartridges were retrieved when examination revealed significant staining of the gel adsorbent and tracer loss was clearly visible in the downstream end of the cartridges.

Concentrations recovered from Sorbisense analysis of InStream cartridges for the deployments are illustrated in Figs 3.7 to 3.9. Time- and flow-weighted mean concentrations for P and N are overlain for comparison.

Table 3.2. Time- and flow-weighted mean concentrations (TWMC and FWMC) for N (as total oxidisable nitrogen – TON) and P (total phosphorus – TP) from high-resolution monitoring stations for frit size test deployments.

Catchment	Deployment	Retrieval	Duration	TWMC (mg l^{-1})		FWMC (mg l^{-1})	
				TON	TP	TON	TP
Co. Tyrone (1)	19/05/09	10/06/09	22 days	0.550	0.134	0.547	0.153
Co. Monaghan (2)	25/06/09	16/07/09	21 days	1.585	0.249	2.222	0.553
Co. Tyrone (3)	25/06/09	30/07/09	35 days	0.731	0.155	1.077	0.204

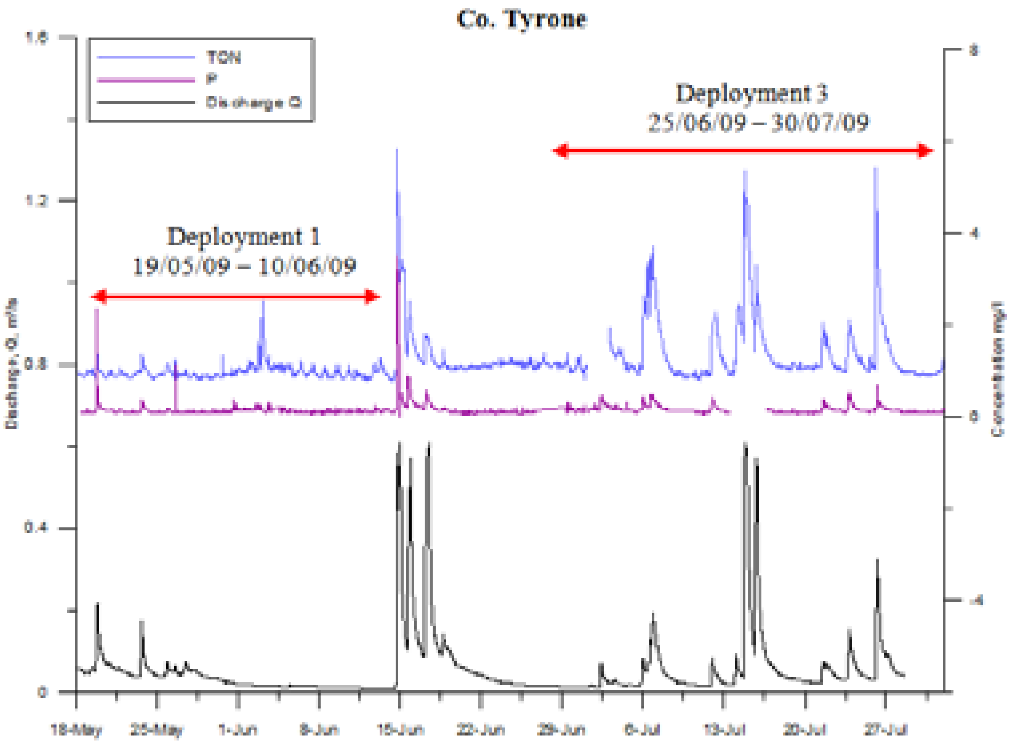


Figure 3.5. Total oxidisable nitrogen (TON), total phosphorus (TP) and discharge (Q) time series for the Co. Tyrone catchment for the period 18/05/09 to 31/07/09. TON concentrations were adjusted using the calibration relationships from Fig. 3.1.

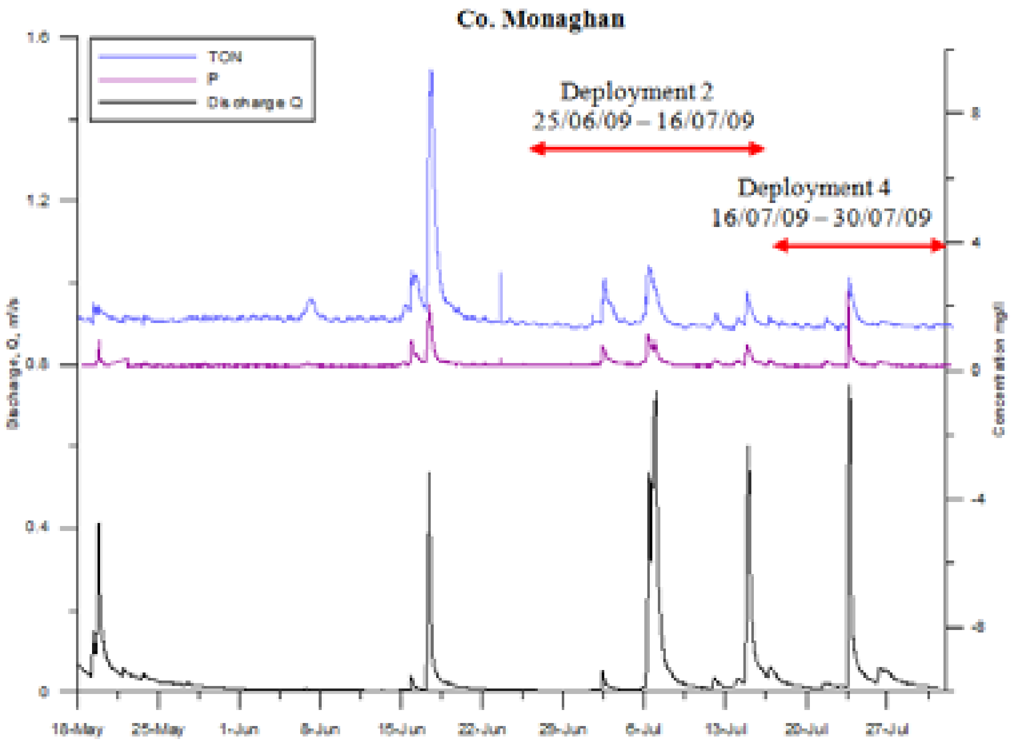


Figure 3.6. Total oxidisable nitrogen (TON), total phosphorus (TP) and discharge (Q) time series for the Co. Monaghan catchment for the period 18/05/09 to 31/07/09. Concentrations have been adjusted using the calibration relationships from Fig. 3.1.

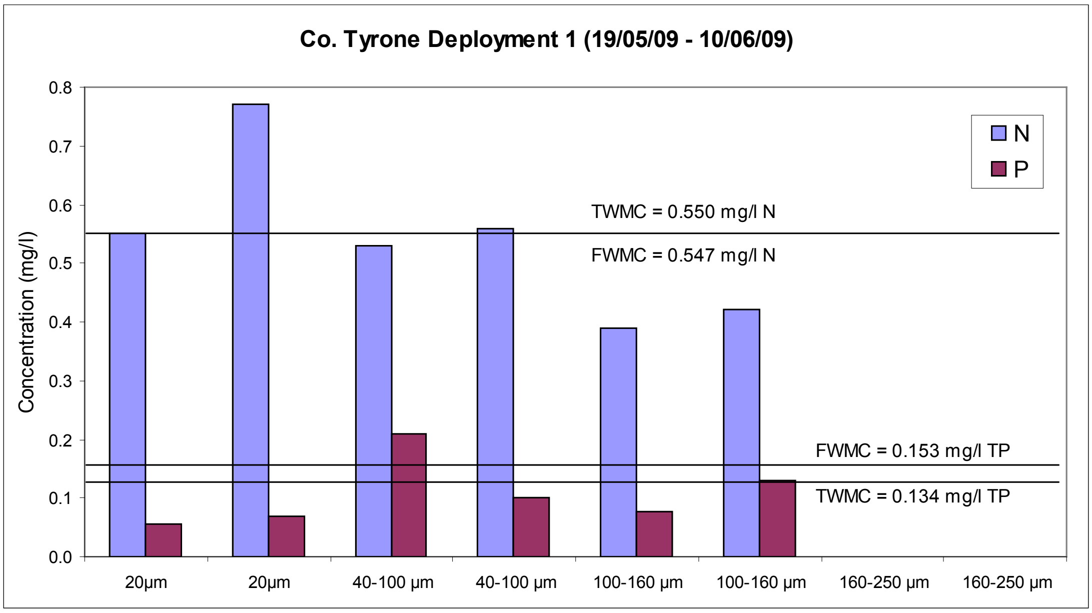


Figure 3.7. Results from Deployment 1 at the Co. Tyrone monitoring station. Flow- and time-weighted mean concentrations (FWMC and TWMC) for N and P (as total phosphorus – TP) are indicated.

Deployment 1 (Fig. 3.5) coincided with a period of low flow in the river. Fine scale measurements of velocity around the rack and cartridges indicated that minimum velocities immediately upstream of the cartridges were between 0.19 and 0.20 m s^{-1} during the lowest flow, which is the minimum velocity advised by Sorbisense.

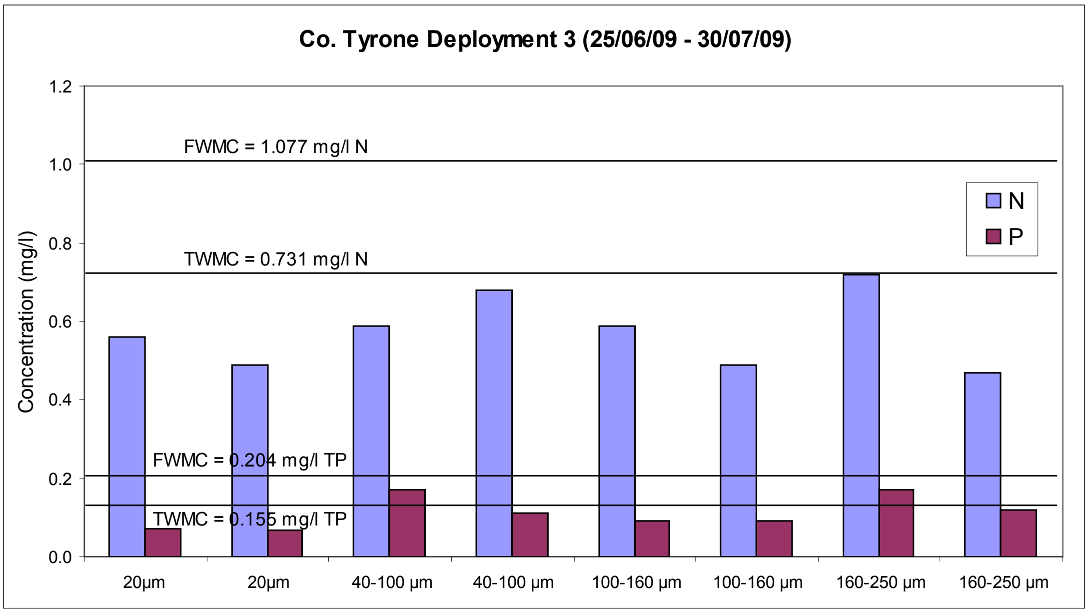


Figure 3.8. Results from Deployment 3 at the Co. Tyrone monitoring station. Flow- and time-weighted mean concentrations (FWMC and TWMC) for N and P (as total phosphorus – TP) are indicated.

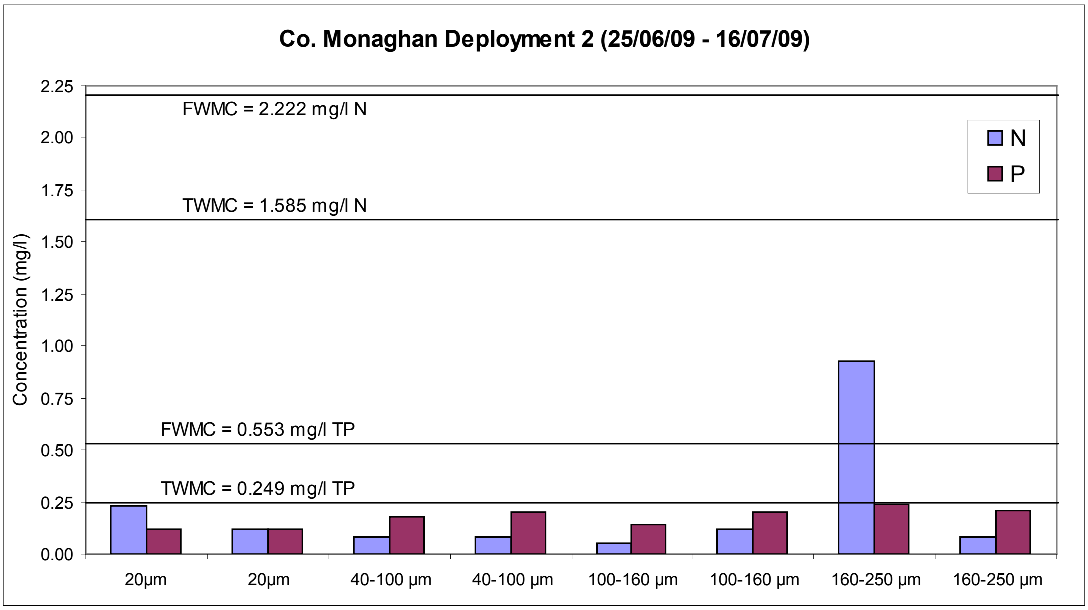


Figure 3.9. Deployment 2 at the Co. Monaghan monitoring station. Flow- and time-weighted mean concentrations (FWMC and TWMC) for N and P (as total phosphorus – TP) are indicated. Recovery of N is an order of magnitude lower than expected.

Of the frit sizes deployed, the 40–100 µm frit extractions yielded concentrations in the range of the continuous samplers for FWMC TP and nitrate (and the 20 µm PE frits were also optimum for nitrate) (Fig. 3.7). The 160–250 µm frit size could not be analysed as there was no significant loss of tracer salt. However, there was significant recovery of P and N in these cartridges, which indicates that at least nutrient adsorbance was occurring. There was no notable reason for this anomaly, although if particulate material entered and blocked the cartridge pore space, some circulation and adsorption could occur at the upstream end of the cartridge.

Deployments 2 and 3 occurred at the Co. Monaghan and Co. Tyrone monitoring stations, respectively.

Storm events took place during both deployments, as illustrated by the hydrographs (Figs 3.5 and 3.6) and the difference between the TWMC and FWMC. Higher flow velocities (0.25–0.40 m s^{-1} upstream of the cartridges at low flow) and low turbidity at the Co. Monaghan station resulted in a noticeable loss in tracer salt and colouration in the adsorbent resin over the first weeks of the deployment. After 20–80% of tracer salt had been lost, the cartridges were retrieved and shipped to Sorbisense in Denmark for analysis. The rate of tracer salt dissolution was slower in the Co. Tyrone catchment due to lower velocities, and as a consequence this deployment was extended to five weeks before retrieval.

Results from the three deployments differed considerably. Cartridge concentrations recovered from Co. Monaghan (Fig. 3.9) were all lower than the TWMC and FWMC as recorded by the continuous samplers. N recovery, in particular, was an order of magnitude lower than expected. At the Co. Tyrone site, extracted concentrations for the 40–100 µm cartridges were close to the TWMCs for both P (0.249 mg l^{-1}) and N (1.585 mg l^{-1}), but not the FWMCs (0.553 mg l^{-1} and 2.222 mg l^{-1}, respectively). Identification of the optimum frit size from the deployments was not wholly satisfactory, but on balance and following discussion with Sorbisense it was decided, at this stage of the study, that the 40–100 µm frits yielded marginally better estimates of P and N concentrations.

3.2.4 Comparison of Sealed and Unsealed Cartridges

Disparity between Sorbisense passive samplers and FWMCs, and the variation in concentrations between duplicate cartridge measures, prompted a further test to investigate the extent to which throughflow controls adsorption and salt loss. Three cartridges were prepared and deployed at the Co. Monaghan site; two were sealed at the downstream end to prevent throughflow. After three weeks (Fig. 3.6 – Deployment 4) the cartridges were retrieved and sent to Sorbisense for analysis. The deployment period included both low and high flows. Concentrations of P and N were detected in all cartridges at levels comparable with the FWMCs for the deployment period (Fig. 3.10).

Elevated concentrations present within the closed cartridges were the result of significant adsorption and limited tracer loss. (Measured extractions and tracer loss are shown in Fig. 3.11.) There was no appreciable

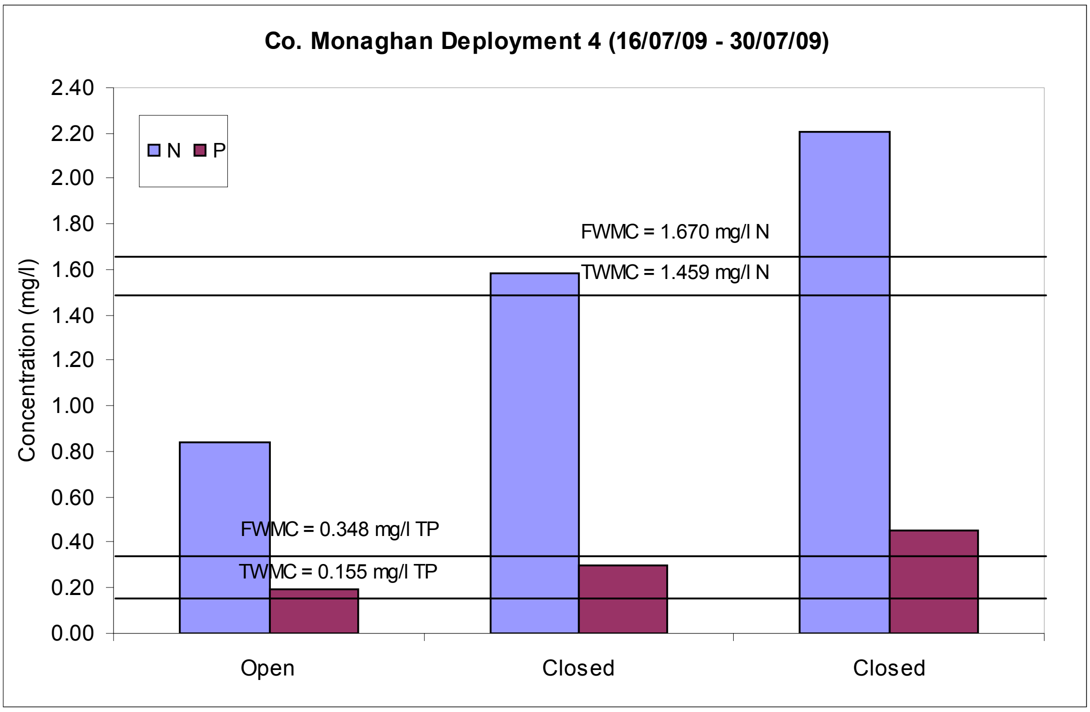


Figure 3.10. Deployment 4 at the Co. Monaghan monitoring station. Flow- and time-weighted mean concentrations (FWMC and TWMC) for N and P (as total phosphorus – TP) are indicated. Two cartridges were sealed at the downstream end to prevent throughflow.

difference in adsorption recoveries between the open and closed cartridges, which suggested that a combination of advection and diffusion was operating within the upstream sections of the cartridges, independent of throughflow, possibly resulting in salt flushing from the front of the sealed cartridges.

Deployments 5 and 6 were then conducted to further explore if advection and/or diffusion was more influential than throughflow in the loss of tracer salt. These were executed at the Co. Tyrone and Co. Monaghan sites, using open and closed cartridges for a period of approximately five weeks. Frit sizes were 20 µm, 40–100 µm and 100–160 µm. A range of frit sizes was used to establish the extent to which aperture influences circulation in the upstream section of the cartridge when throughflow is prohibited. Four cartridges of each frit size were deployed to allow duplicate measures for open and closed cartridges. As before, closed cartridges were sealed at the downstream end to prevent throughflow. P, N and discharge time series are shown in Figs 3.12 and 3.13; deployment periods are also indicated. Note that UV nitrate probe data were not available at the Co. Tyrone site between 20/09/09 and 26/09/09. Low flow prevented any appreciable variance in concentrations during this time.

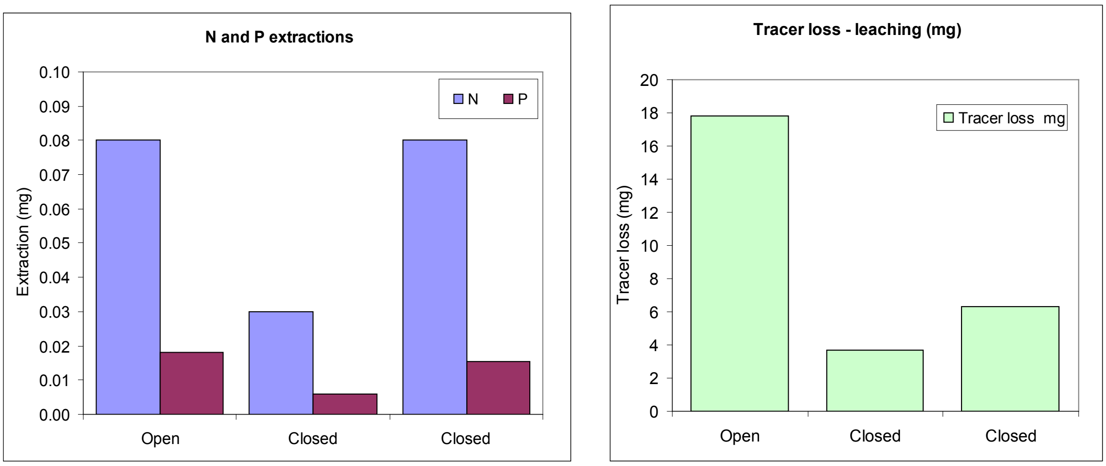


Figure 3.11. P and N extractions and dissolution of tracer salt for sealed and open cartridges. Tracer losses from the sealed cells were less than 10% of initial volume and are indicative only.

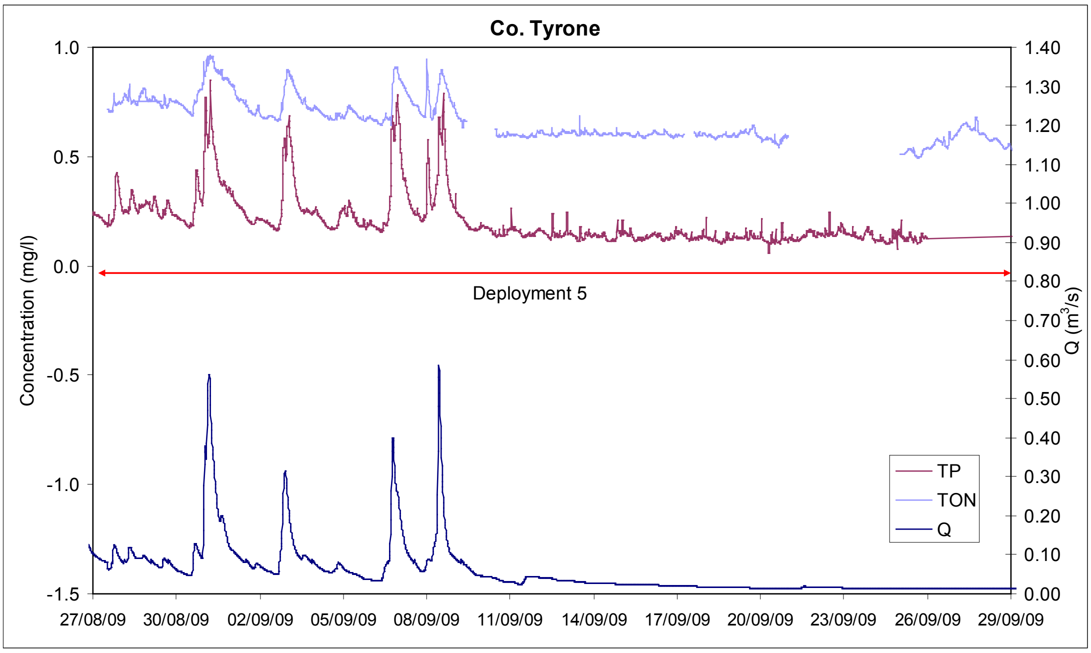


Figure 3.12. Total oxidisable nitrogen (TON), total phosphorus (TP) and discharge (Q) time series for the Co. Tyrone catchment for the period 27/08/09 to 29/09/09.

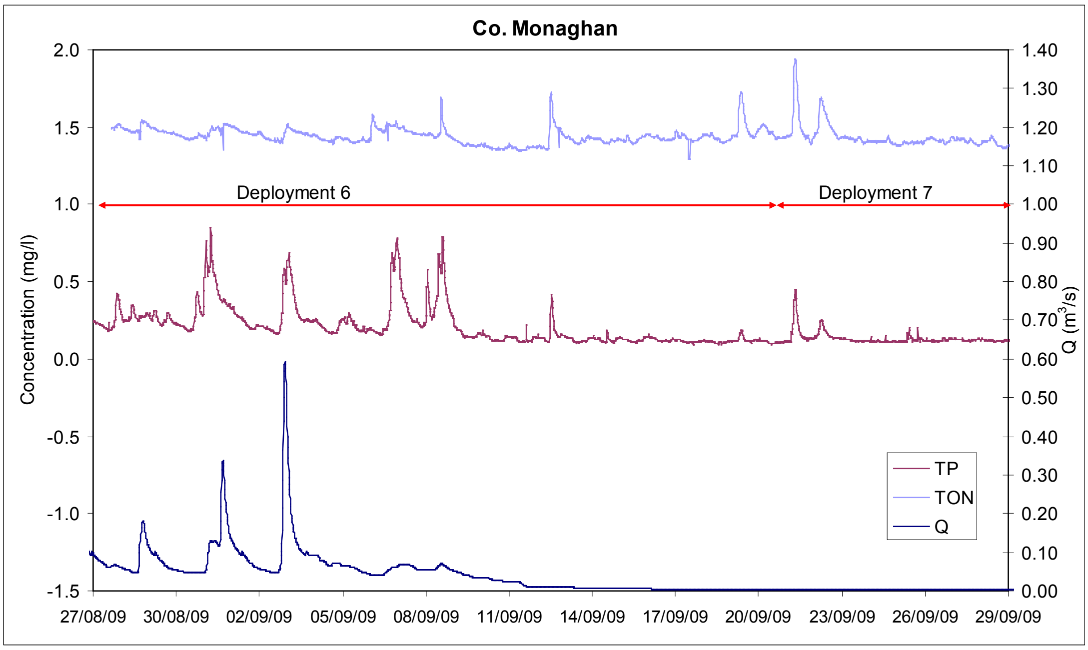


Figure 3.13. Total oxidisable nitrogen (TON), total phosphorus (TP) and discharge (Q) time series for the Co. Monaghan catchment for the period 27/08/09 to 29/09/09.

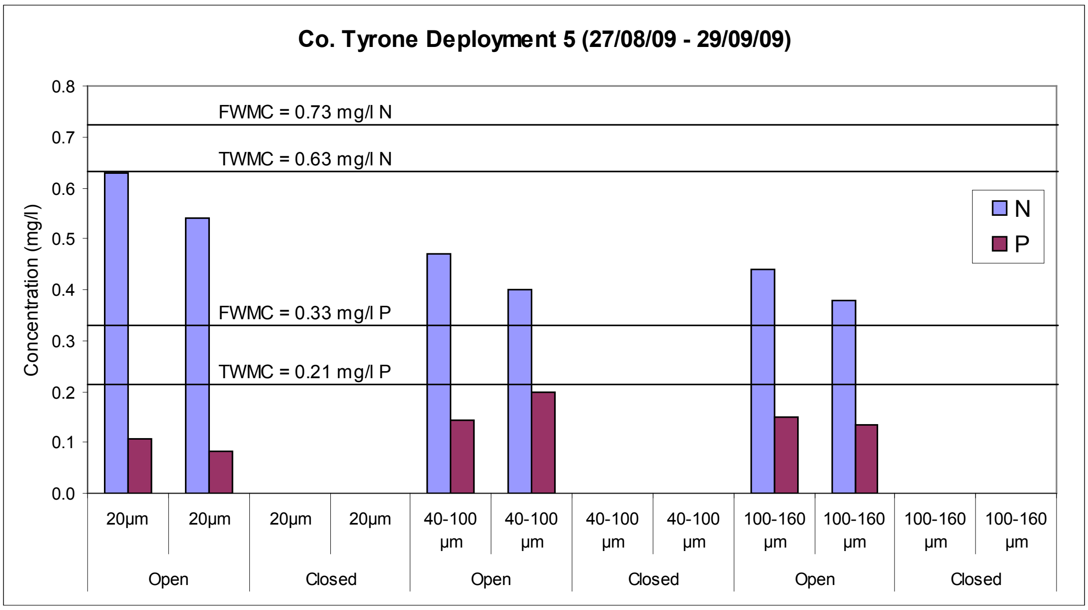


Figure 3.14. Results from Deployment 5 at the Co. Tyrone site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for N and P are indicated.

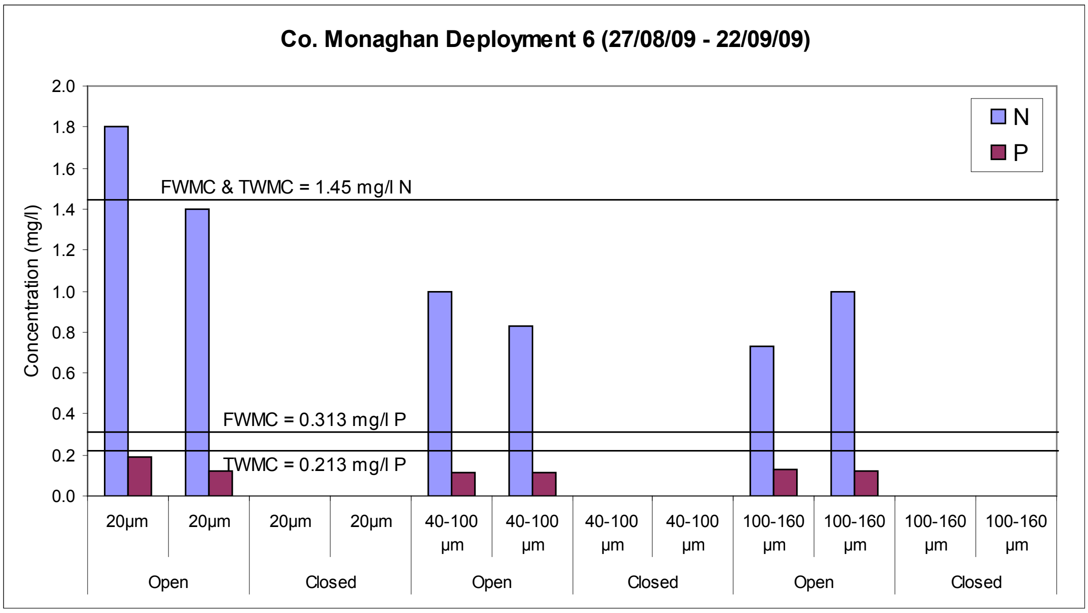


Figure 3.15. Results from Deployment 6 at the Co. Monaghan site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for N and P are indicated.

Concentrations recovered from Sorbisense analysis of instream cartridges for Deployments 5 and 6 are illustrated in Figs 3.14 and 3.15. Time- and flow-weighted mean concentrations for P and N are overlain for comparison.

Hydrological conditions during the trial of open and closed cartridges at the Co. Monaghan and Co. Tyrone sites consisted of a series of storm events at the beginning of the deployment followed by a period of low flow (Figs 3.12 and 3.13). At both sites, all sealed cartridges returned P and N concentrations that would have been below the detectable limit in normal water samples. The results suggested that the advection and/or diffusion theory (their being more influential than throughflow in relation to salt loss) was unsound, and that the adsorption of P and N, and the dissolution of tracer salt, were governed by the rate of influent water that passed through the cartridge.

Open cartridges delivered P and N concentrations that were lower than both the TWMC and FWMC, as recorded by the high-resolution equipment and similar to previous results. Cartridges containing the 20 µm frit did, however, return N concentrations that were in the range of the TWMC. Nevertheless, this pattern was not replicated by the other frit sizes. Using analysis of variance (ANOVA), P and N concentrations returned for Co. Tyrone showed no statistical difference in relation to frit size ($F_{2,3} = 4.449$, $p > 0.05$; $F_{2,3} = 6.476$, $p > 0.05$). The same was also true for Co. Monaghan in relation to P and N concentrations ($F_{2,3} = 0.976$, $p > 0.05$; $F_{2,3} = 7.731$, $p > 0.05$). Frit size, therefore, appears to have a limited influence on N and P concentrations. Cartridge reproducibility, as with previous deployments, was acceptable in relation to P concentrations. A greater range in recoveries existed in relation to N concentrations.

3.2.5 *Development of the Multi-frit Cartridge*

In response to the issues flagged regarding possible throughflow interference, Sorbisense manufactured a new multi-frit cartridge using the 40–100 µm and 100–160 µm sintered glass frits. In the former single-frit cartridge there was only one glass frit, located at the entrance to the cartridge. The other internal filters separating the resin and salt compartments were made of glass fibre filters. The purpose of sintered glass frits was to generate a high hydraulic conductivity and therefore lower resistance within the cartridge. With the new multi-frit cartridge, all internal filters were replaced with sintered glass frits in an effort to further improve hydraulic conductivity.

Four of the new multi-frit cartridges, two open and closed, were deployed at the Co. Monaghan site between 22/09/09 and 29/09/09 (Deployment 7 – see

Fig. 3.16). The deployment occurred during a period of low flow. Concentrations recovered from the cartridges and the high-resolution data are illustrated in Fig. 3.16. Closed cartridges returned N and P concentrations that would have been below the limit of detection in normal water samples, which was consistent with the previous deployment. Open cartridges delivered measurements that were lower than both the TWMC and FWMC. The degree of under-estimation was greatest for nitrate. Reproducibility between the two open cartridges showed minimal variation in relation to N and P. Initial trials of the multi-frit cartridge showed limited improvement as concentrations were still lower than expected.

3.2.6 Co. Wexford Deployment in October 2009

Cartridges were deployed (Deployment 8) at the Co. Wexford site from 06/10/09 to 24/10/09 to further investigate the influence of frit size on cartridge adsorption. This site was typified by high N and low P concentrations during low-flow conditions, with increases in P during high flow. Four cartridges of the 20 µm, 40–100 µm and 100–160 µm frit size were deployed (Figs 3.17–3.19).

Cartridge recoveries revealed very high irregularities within the data for P, N and tracer salt loss. High P concentrations were indicated in cartridges 627, 644 and 646 (Fig. 3.17). Results also showed high nitrate concentrations in cartridges 644 and 646 (Fig. 3.18). Tracer salt loss from the cartridges was also inconsistent, and in cartridges 625 and 626 salt loss was negligible (Fig. 3.19). Despite this, some of the recovered FWMCs were close to the data from the high-resolution station and especially in the 100–160 µm multi-frit range.

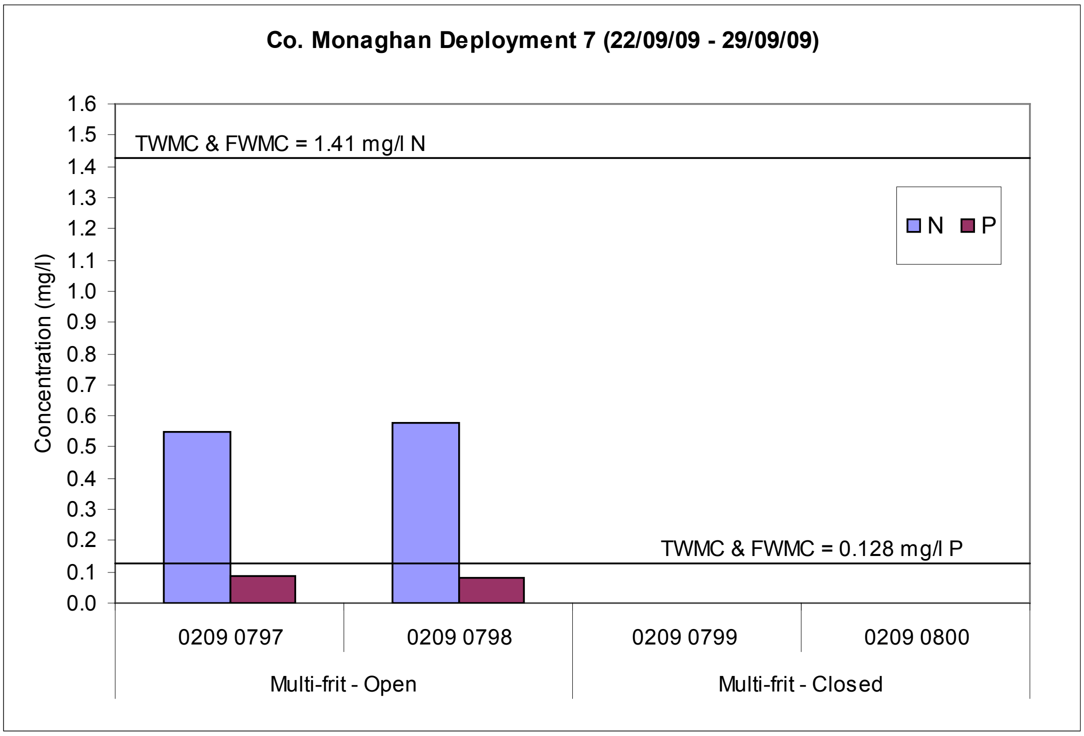


Figure 3.16. Deployment 7 at the Co. Monaghan site of open and closed (40–100 µm) multi-frit cartridges. Flow- and time-weighted mean concentrations (FWMC and TWMC) for N and P are indicated. Numbers on the *x*-axis refer to cartridge numbers.

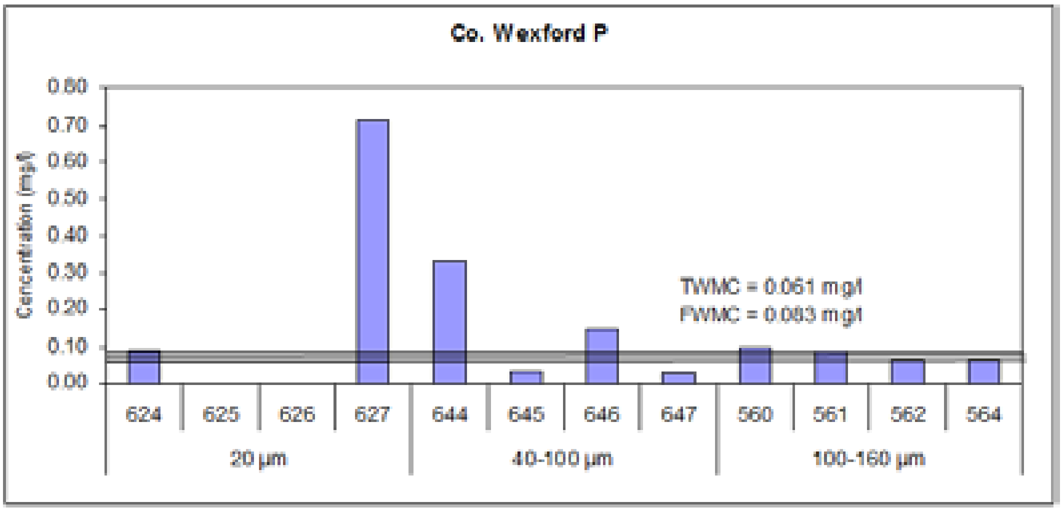


Figure 3.17. Deployment 8, of 3 ml cartridges at the Co. Wexford site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for total phosphorus (TP) are indicated. Numbers on the *x*-axis refer to cartridge numbers.

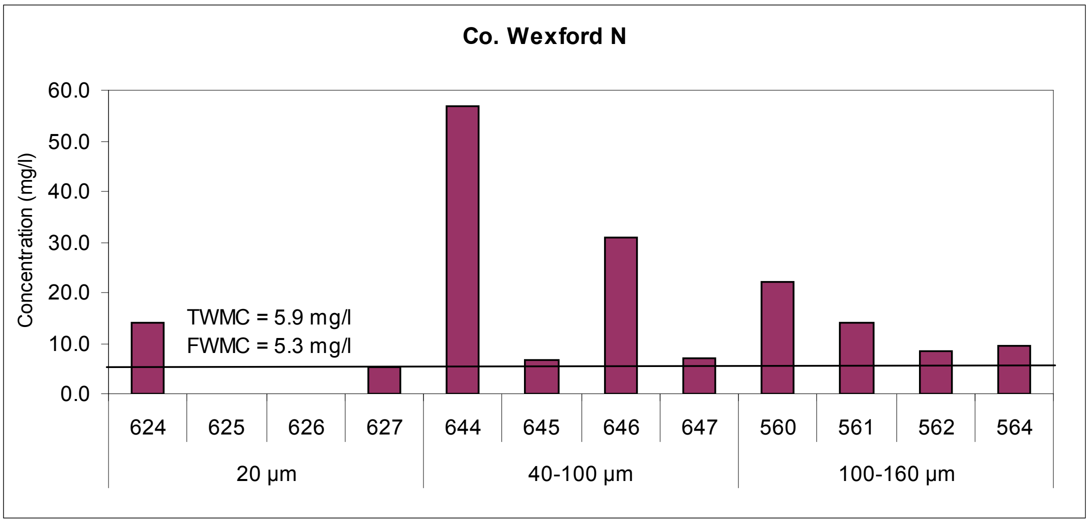


Figure 3.18. Deployment 8, of 3 ml cartridges at the Co. Wexford site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for N are indicated. Numbers on the *x*-axis refer to cartridge numbers.

In response to the poor recoveries of P and N from the October 2009 Co. Wexford deployment, Sorbisense conducted a re-run of the N and P measurements delivered from their subcontractor, and results demonstrated a discrepancy that existed between the subcontractor and Sorbisense laboratories. Cartridge results returned by Sorbisense laboratories were used in the generation of Figs 3.17–3.19.

Analysis of the Co. Wexford deployment highlighted two issues. The first concerned the problems surrounding subcontractor analysis, which appeared to manifest only on very high nutrient concentrations (this laboratory was accredited). The second concerned damage sustained to some of the cartridges, which cracked during deployment (Fig. 3.20); this is likely to have influenced the first issue. In an effort to resolve both issues, Sorbisense advised

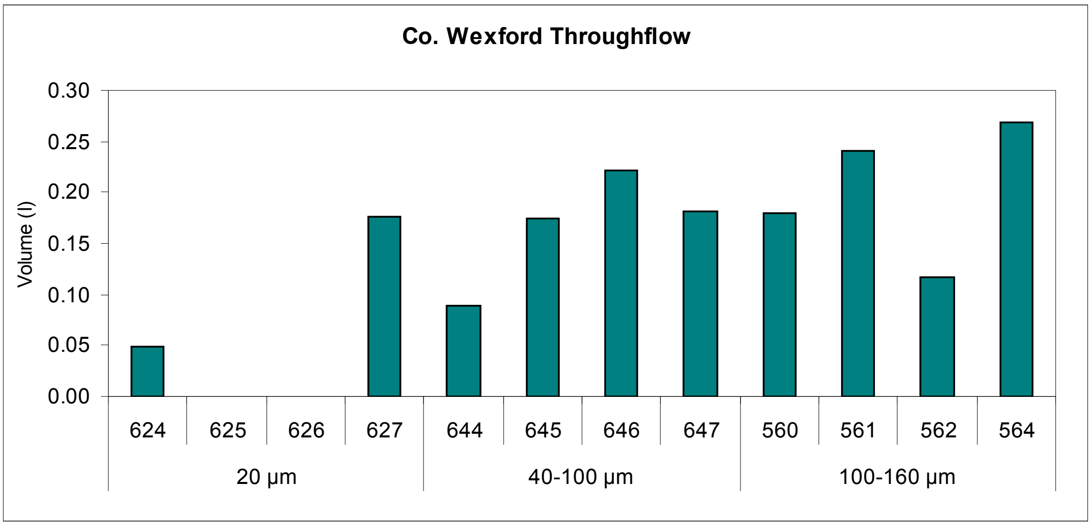


Figure 3.19. Tracer salt estimation of cartridge throughflow during deployment at the Co. Wexford site. Numbers on the *x*-axis refer to cartridge numbers.

Figure 3.20. The red arrow points to the crack on a cartridge sustained during the Co. Wexford deployment.

that care must be taken when deploying cartridges to ensure that they are fitted carefully into the clip holder to avoid damage and resin contamination. Also, Sorbisense decided to perform all the remaining analysis for the project in-house, in preference to using an external subcontractor, to mitigate any possibility that recovered high concentrations were suspect. (Note that no further concentrations in the ranges of, for example, cartridges 627 and 644 were observed.)

3.2.7 March 2010 Deployment

To account for possible issues concerning adsorbance capacity, cartridges were deployed at sites located in Co. Monaghan (Deployment 9), Co. Mayo (10), Co. Wexford (11) and Co. Louth (12), for a period of three weeks between 8/9 and 29/30 March 2010. Two capacities, of the 40–100 µm multi-frit cartridges, were used in triplicate at each site. Capacities consisted of the existing 3 ml cartridge and a new 10 ml design; see Fig. 2.3. Two capacities were deployed per site in order to investigate possible saturation of the adsorbent resin contained within the 3 ml cartridge with N and P. Saturation of the resin may begin to explain the discrepancy between cartridge recoveries and high-resolution data. The issue of saturation was highlighted in previous deployments as the recovery of N and P from the cartridges was an order of magnitude lower than that measured by the high-resolution monitoring equipment. Table 3.3 lists deployment details and associated TWMC and FWMC. However, the issue of salt throughflow was also highlighted as a possibility, and the 10 ml cartridges were deployed with a larger volume of calcium citrate.

3.2.7.1 Co. Monaghan

Hydrometric station data

Deployment 9 at the Co. Monaghan site was dominated by stable low flow, with a single storm event (Fig. 3.21). Concentrations of TP, TRP and TON remained relatively constant until the storm event occurred. Increased surface runoff, due to the high flow gradient in the catchment, caused a rapid increase in nutrient concentrations (Fig. 3.22).

Table 3.3. Time- and flow-weighted mean concentrations (TWMC and FWMC) for N (as total oxidisable nitrogen – TON), TP (total phosphorus) and TRP (total reactive phosphorus) from high-resolution monitoring stations for March 2010 deployment.

Catchment	Deployment	Retrieval	Duration	TWMC (mg l⁻¹)			FWMC (mg l⁻¹)		
				N	TP	TRP	N	TP	TRP
Co. Monaghan	08/03/10	28/03/10	20 days	1.386	0.096	0.070	2.087	0.334	0.197
Co. Mayo	08/03/10	29/03/10	21 days	0.095	0.025	0.013	0.095	0.025	0.013
Co. Wexford	09/03/10	30/03/10	20 days	5.330	0.044	0.023	5.850	0.062	0.023
Co. Louth	09/03/10	30/03/10	21 days	4.660	0.138	0.096	5.150	0.311	0.164

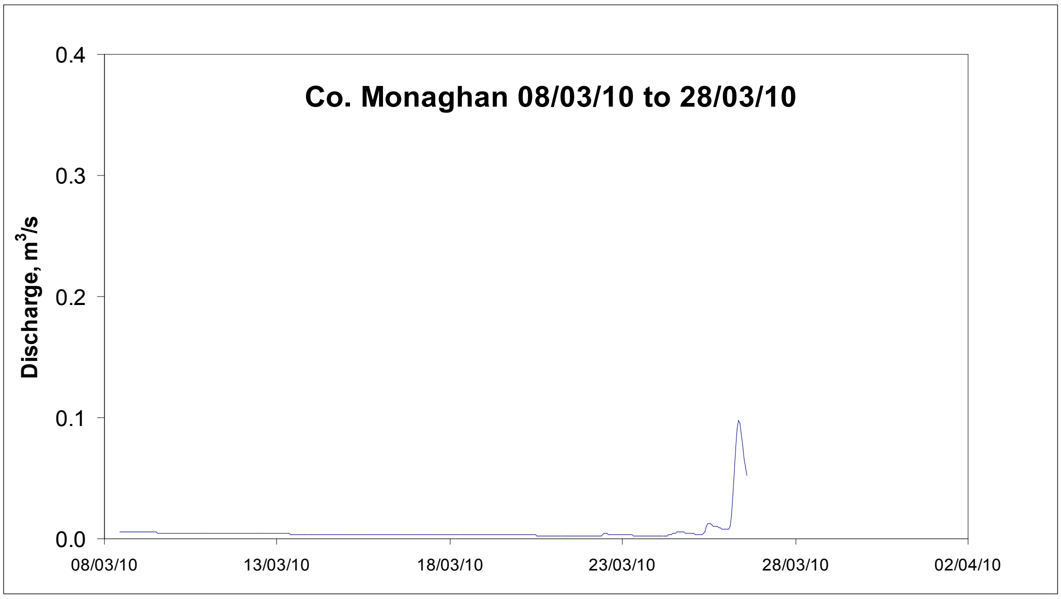


Figure 3.21. Discharge time series for Co. Monaghan for the period 08/03/10 to 28/03/10.

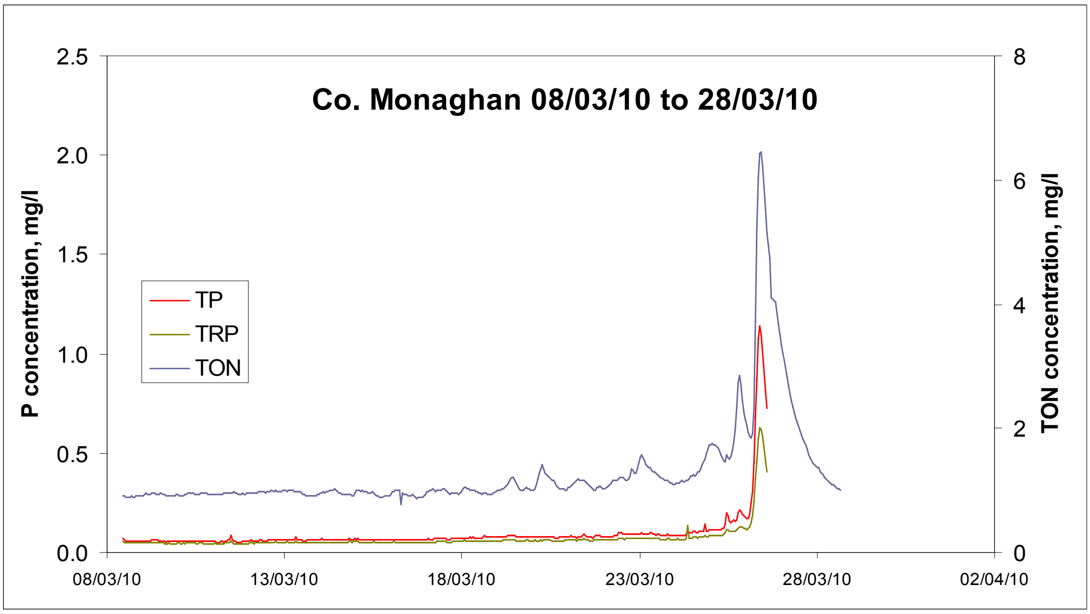


Figure 3.22. Total oxidisable nitrogen (TON), total phosphorus (TP) and total reactive phosphorus (TRP) series for Co. Monaghan for the period 08/03/10 to 28/03/10.

Cartridge recoveries

P concentrations returned by Sorbisense cartridges were more consistent with TWMC for both TP and TRP (Figs 3.23 and 3.24). However, for TRP, the results were just marginally lower than the FWMC, with the exception of one 3 ml cartridge. In general, the 10 ml capacity cartridges performed better than the 3 ml ones, both in terms of accuracy and repeatability. In relation to nitrate, the 3 ml and 10 ml cartridges were considerably lower than both the TWMC and FWMC (Fig. 3.25). In terms of tracer salt loss, there was less variation with the 3 ml cartridges (but the P results were less variable with the 10 ml cartridges) (Fig. 3.26). The recoveries from the 3 ml cartridges were highly variable, with TP ranging from 0.08 mg l^{-1} to 0.70 mg l^{-1}, with cartridge 0909 0367 much higher (also for TRP) than the others. This cartridge did not deliver a comparably high N or throughflow reading, so there appears to be no obvious reason for this high concentration.

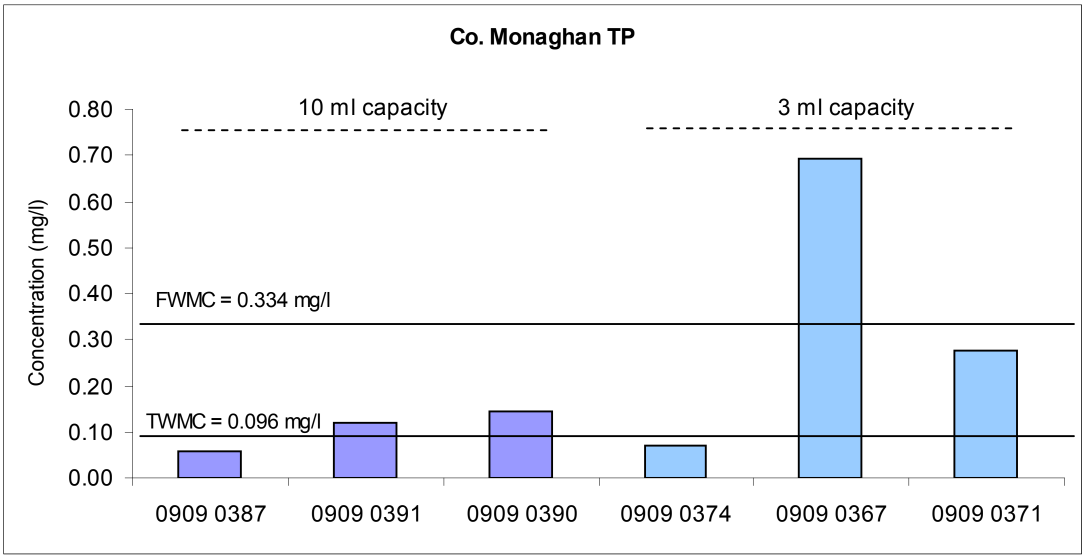


Figure 3.23. Deployment of 3 ml and 10 ml cartridges at the Co. Monaghan site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for total phosphorus (TP) are indicated. Numbers on the *x*-axis refer to cartridge numbers.

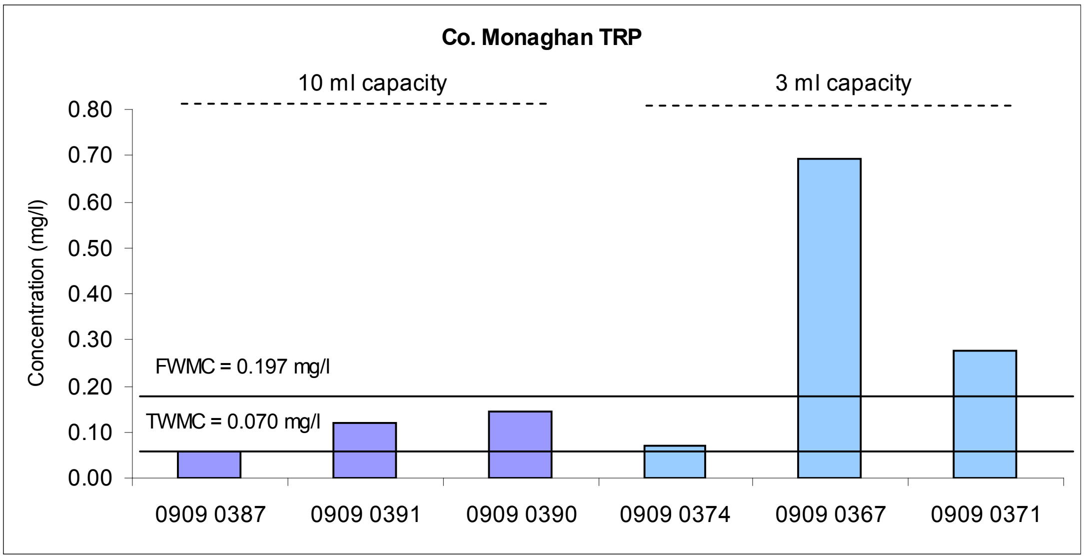


Figure 3.24. Deployment of 3 ml and 10 ml cartridges at the Co. Monaghan site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for total reactive phosphorus (TRP) are indicated. Numbers on the *x*-axis refer to cartridge numbers.

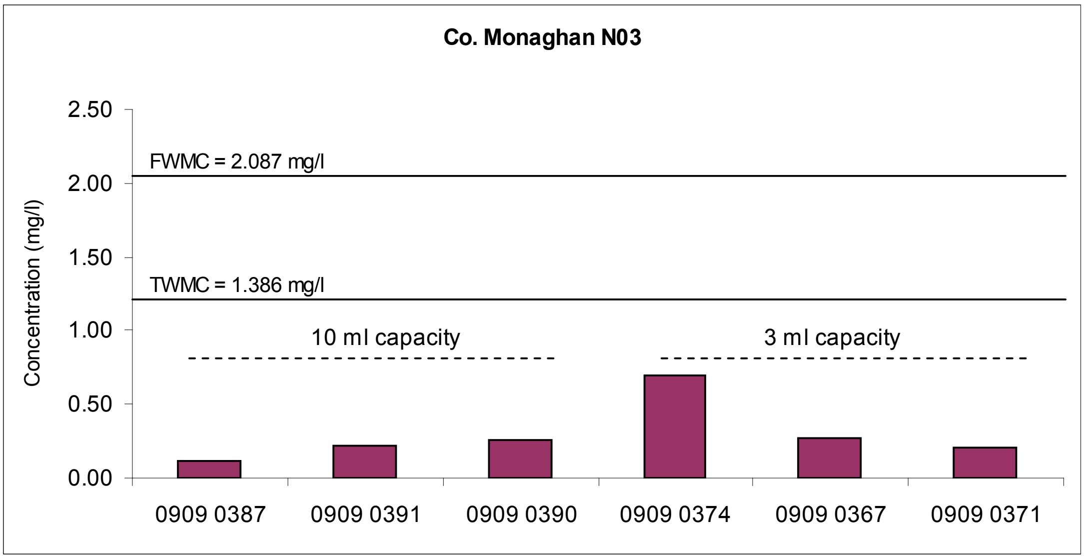


Figure 3.25. Deployment of 3 ml and 10 ml cartridges at the Co. Monaghan site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for nitrate are indicated. Numbers on the *x*-axis refer to cartridge numbers.

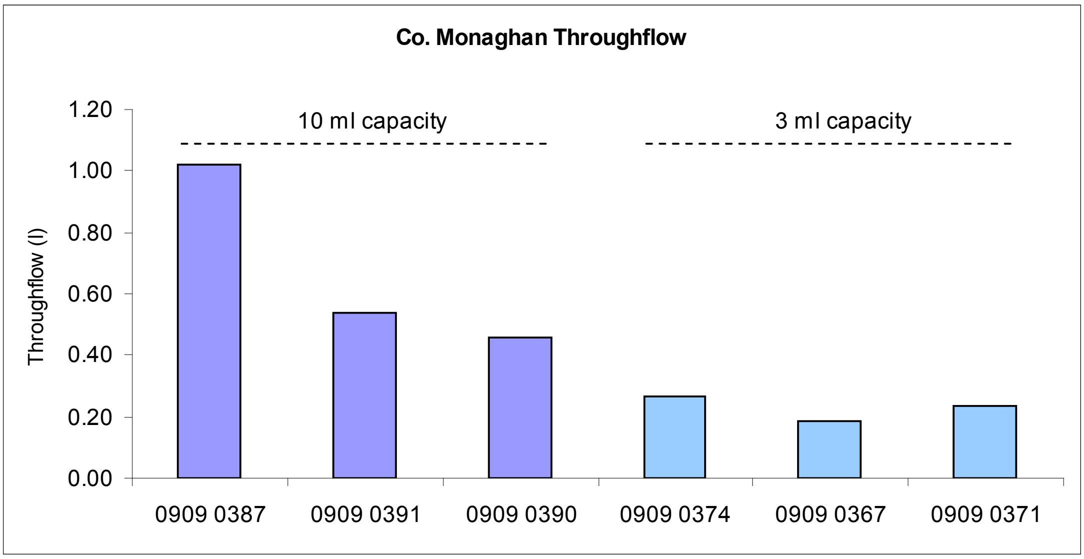


Figure 3.26. Tracer salt estimation of cartridge throughflow during March 2010 deployment of 3 ml and 10 ml cartridges at the Co. Monaghan site. Numbers on the *x*-axis refer to cartridge numbers.

3.2.7.2 Co. Mayo

Hydrometric station data

Deployment 10 at the Co. Mayo site consisted of a constant, low-flow discharge rate from the emergent spring, with a single storm event (Fig. 3.27). The increase in discharge resulting from the storm event was modest due to the fact that the aquifer helps to regulate the release of water from the spring. As a consequence, there was no rapid change in nutrient levels relative to discharge (Fig. 3.28). The water emerging from this spring had very low concentrations of both P and N. This site is an example of a very low flow gradient.

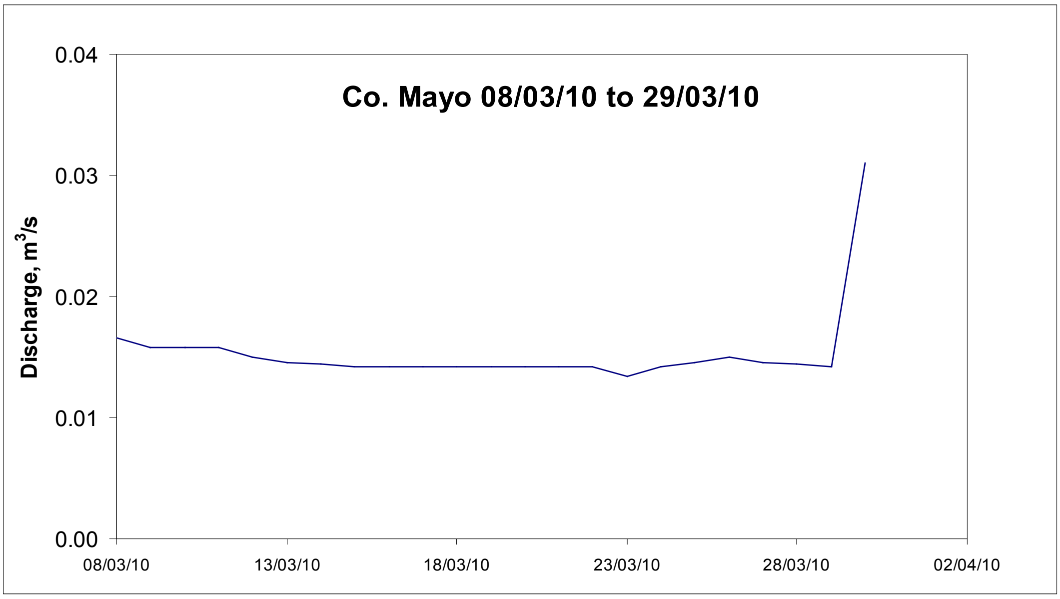


Figure 3.27. Discharge time series for Co. Mayo for the period 08/03/10 to 29/03/10.

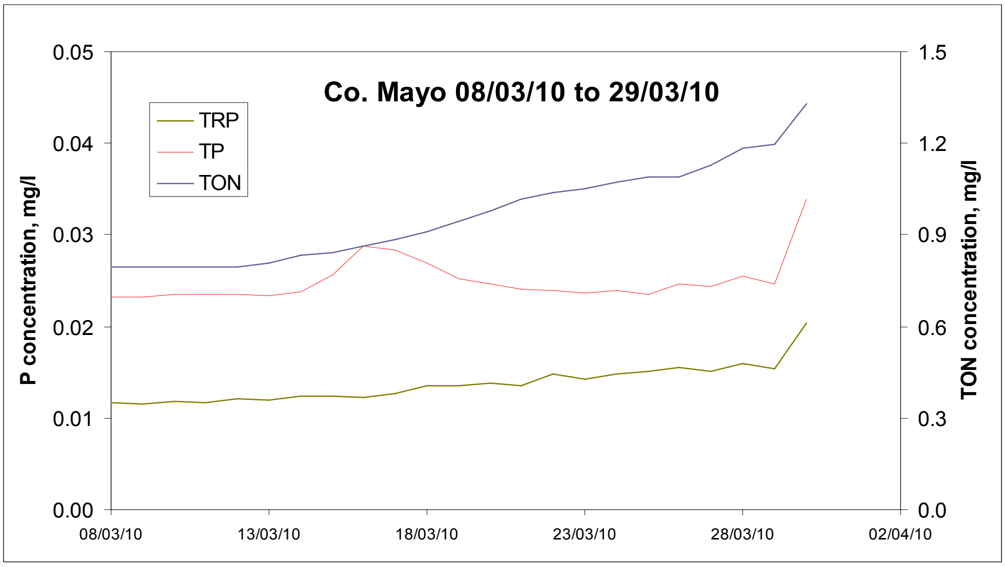


Figure 3.28. Total oxidisable nitrogen (TON), total phosphorus (TP) and total reactive phosphorus (TRP) series for Co. Mayo for the period 08/03/10 to 29/03/10.

Cartridge recoveries

P recoveries from the 3 ml and 10 ml cartridges were in excess of both the TWMC and FWMC (Figs 3.29 and 3.30). However, recoveries from the 10 ml cartridges were marginally closer to the TP measurements as recorded by the high-resolution equipment. This may be due to the low levels of particulate matter contained within the spring water. As noted at Co. Monaghan, the 10 ml cartridges were more accurate for P recovery than the 3 ml cartridges. In relation to nitrate, the 10 ml cartridges were more accurate than the 3 ml cartridges (Fig. 3.31); nevertheless, all cartridges did under-estimate nitrate levels. Limited variation existed between TWMC and FWMC at this site as it is an emergent spring and the aquifer is able to buffer the effects of storm events. Salt loss from the 3 ml and 10 ml cartridges was reasonably consistent (Fig. 3.32). One point worthy of note is that the 3 ml cartridges experienced less throughflow but delivered higher P concentrations than the 10 ml cartridges, and this is likely to be a result of more efficient routing of water through the cartridge, dissolving a greater mass of salt and so influencing the calculation of the concentrations relative to the mass of P adsorbed.

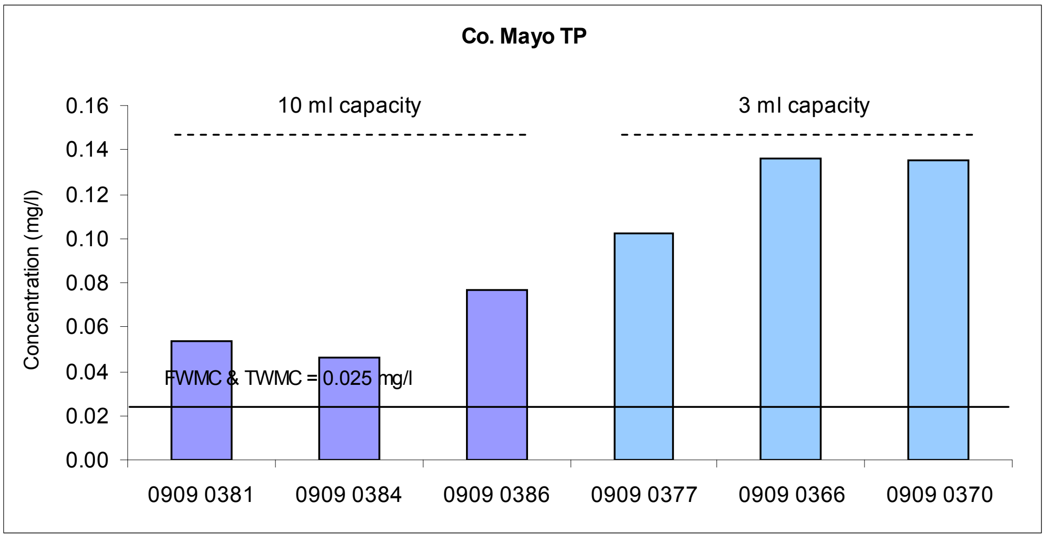


Figure 3.29. Deployment of 3 ml and 10 ml cartridges at the Co. Mayo site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for total phosphorus (TP) are indicated. Numbers on the *x*-axis refer to cartridge numbers.

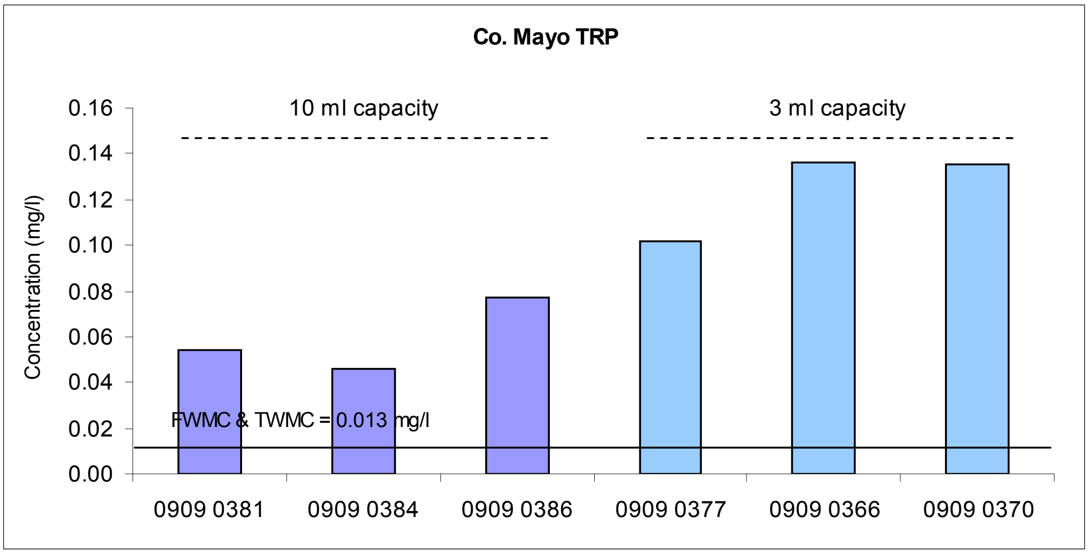


Figure 3.30. Deployment of 3 ml and 10 ml cartridges at the Co. Mayo site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for total reactive phosphorus (TRP) are indicated. Numbers on the *x*-axis refer to cartridge numbers.

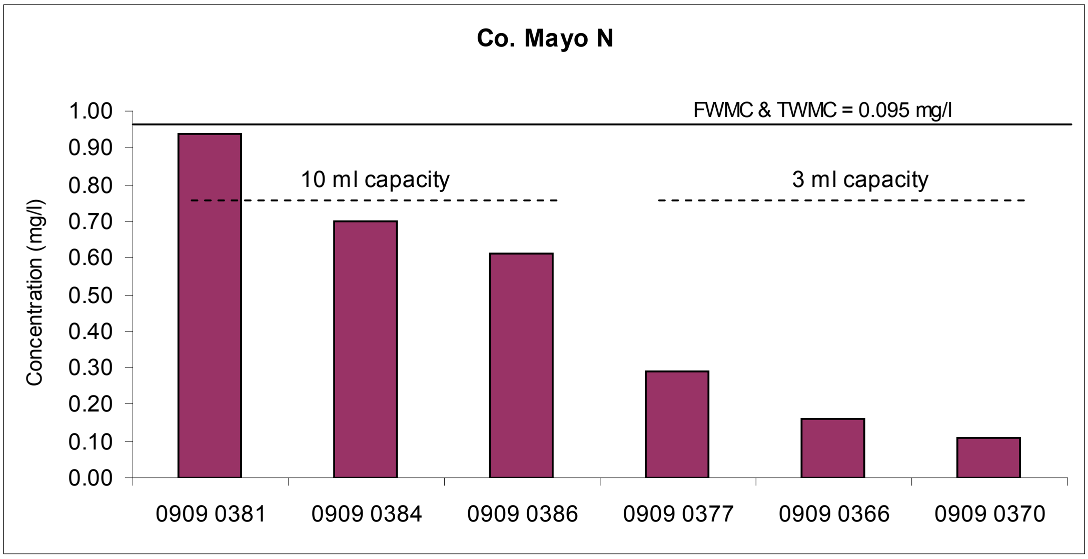


Figure 3.31. Deployment of 3 ml and 10 ml cartridges at the Co. Mayo site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for nitrate are indicated. Numbers on the *x*-axis refer to cartridge numbers.

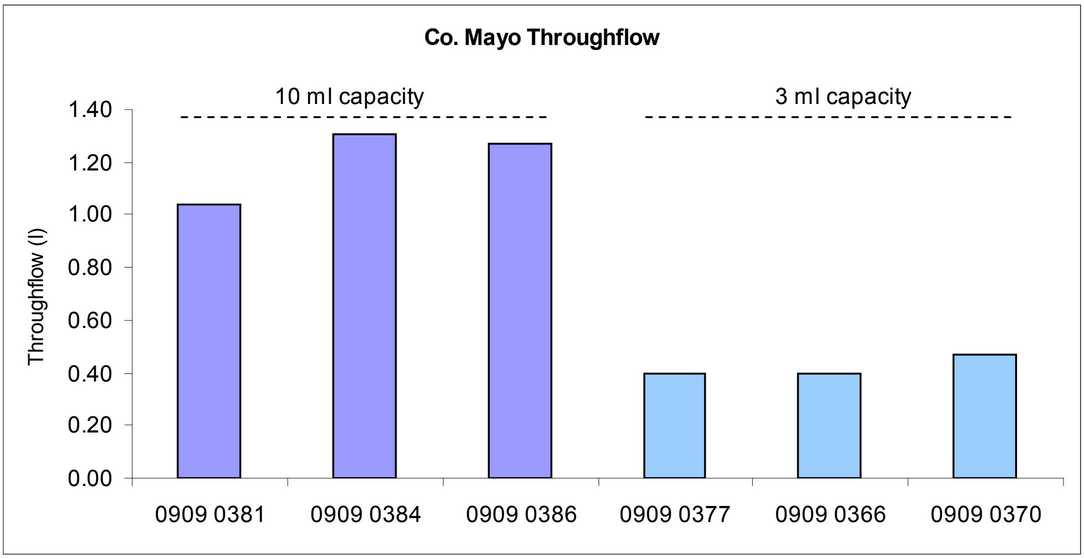


Figure 3.32. Tracer salt estimation of cartridge throughflow during March 2010 deployment of 3 ml and 10 ml cartridges at the Co. Mayo site. Numbers on the *x*-axis refer to cartridge numbers.

3.2.7.3 Co. Wexford

Hydrometric station data

Deployment 11 in Co. Wexford consisted predominantly of low flow, with a series of low-intensity storm events and one high-intensity event on 29/03/10 (Fig. 3.33). TP and TRP concentrations increased, with increasing discharge due to near-surface flow. N concentrations within the catchment are groundwater fed, hence the decline in TON level with increasing discharge (Fig. 3.34).

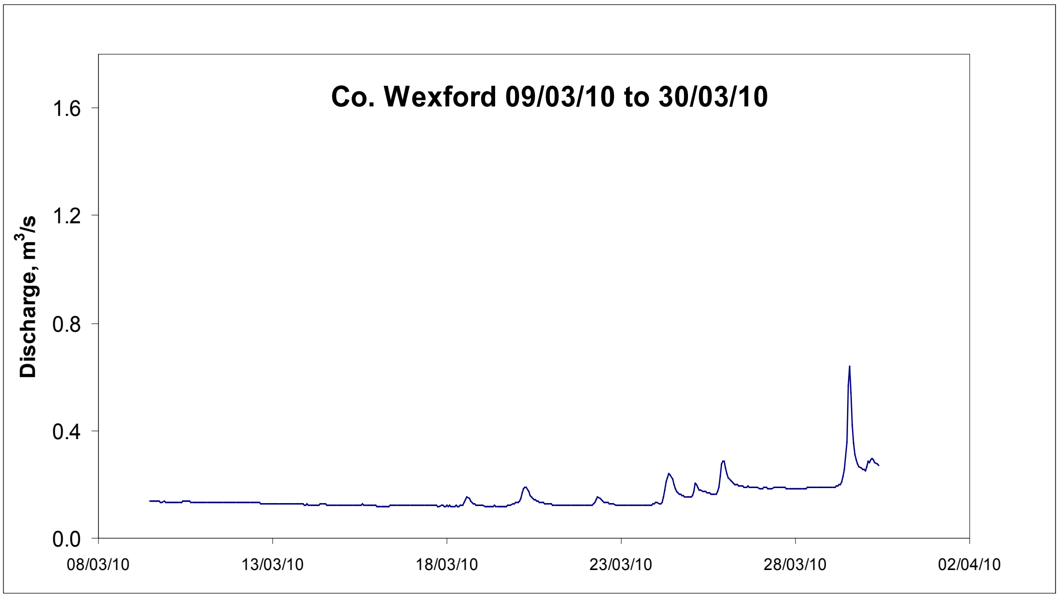


Figure 3.33. Discharge time series for Co. Wexford for the period 09/03/10 to 30/03/10.

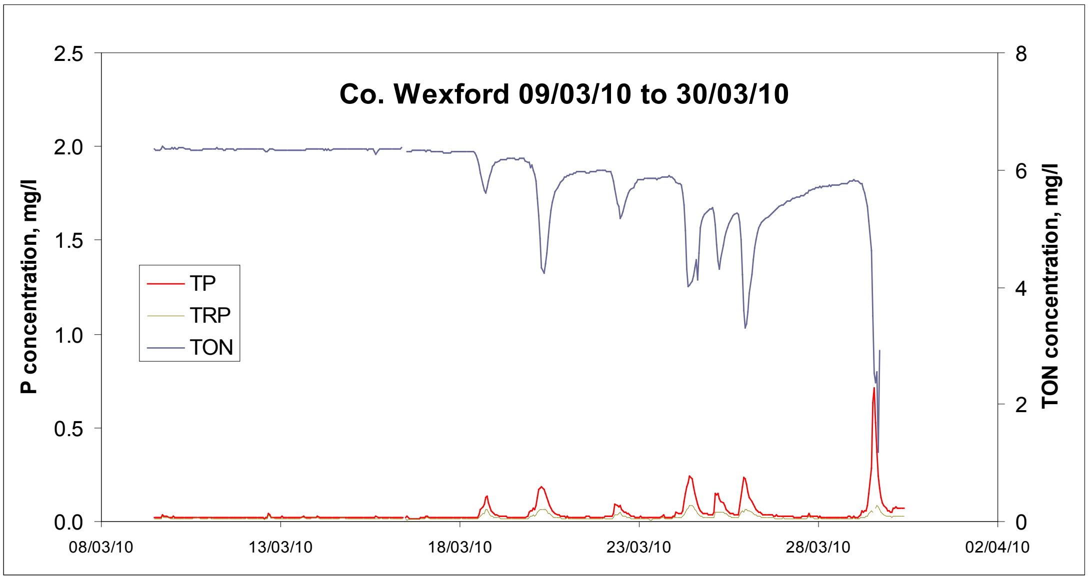


Figure 3.34. Total oxidisable nitrogen (TON), total phosphorus (TP) and total reactive phosphorus (TRP) series for Co. Wexford for the period 09/03/10 to 30/03/10.

Cartridge recoveries

P concentrations returned by Sorbisense cartridges were consistent with both the TWMC and FWMC for TP (Fig. 3.35). For TRP, cartridge results were all in excess of the TWMC and FWMC (Fig. 3.36). The 10 ml capacity cartridges performed better that the 3 ml ones in terms of accuracy. In relation to nitrate, both the 3 ml and the 10 ml cartridges were notably higher than both the TWMC and FWMC (Fig. 3.37). This is the first set of cartridges to have consistently over-estimated nitrate levels. In previous deployments, nitrate recoveries were normally lower than expected (see Sections 3.2.3 and 3.2.4). Traces of nitrite were present in all deployed cartridges at the Co. Wexford site. In terms of tracer salt loss, there was less variation with the 3 ml cartridges, but the P results were more accurate with the 10 ml cartridges (Fig. 3.38).

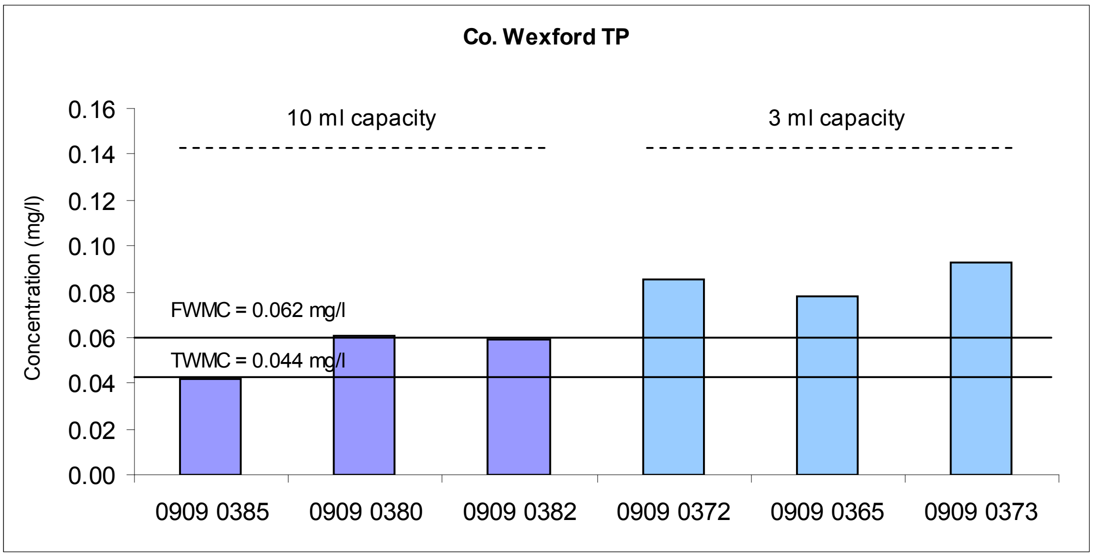


Figure 3.35. Deployment of 3 ml and 10 ml cartridges at the Co. Wexford site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for total phosphorus (TP) are indicated. Numbers on the *x*-axis refer to cartridge numbers.

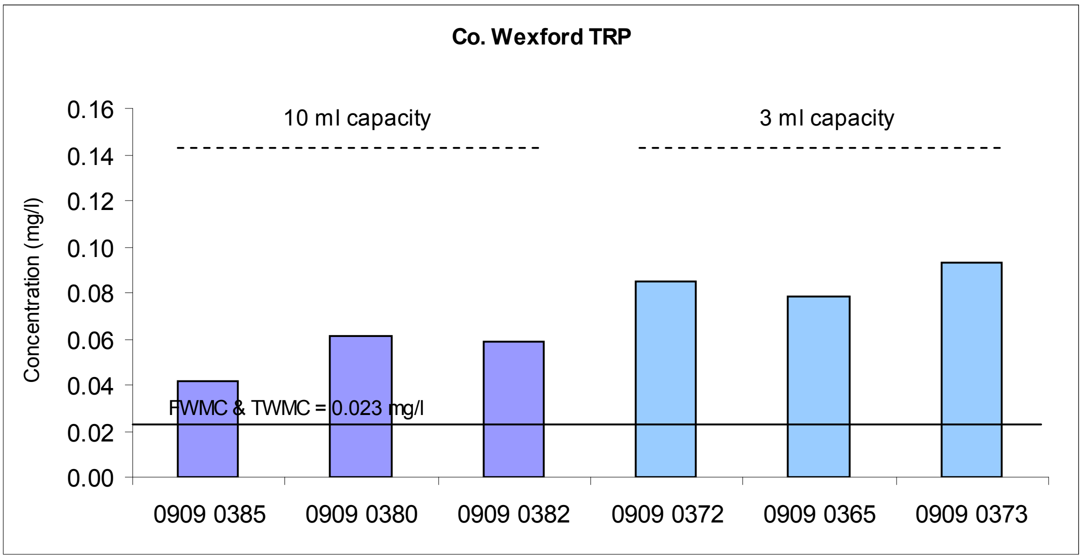


Figure 3.36. Deployment of 3 ml and 10 ml cartridges at the Co. Wexford site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for total reactive phosphorus (TRP) are indicated. Numbers on the *x*-axis refer to cartridge numbers.

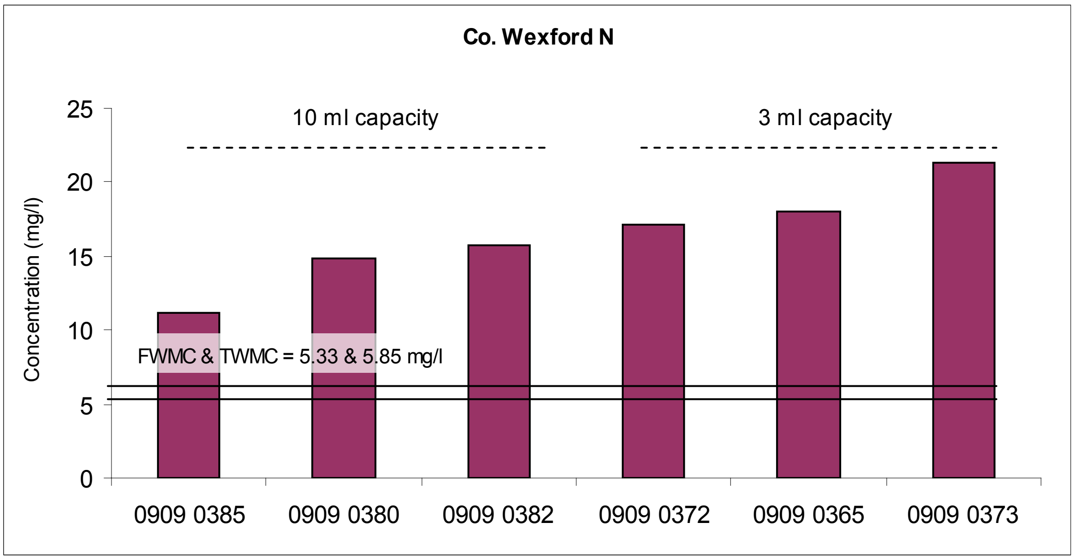


Figure 3.37. Deployment of 3 ml and 10 ml cartridges at the Co. Wexford site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for nitrate are indicated. Numbers on the *x*-axis refer to cartridge numbers.

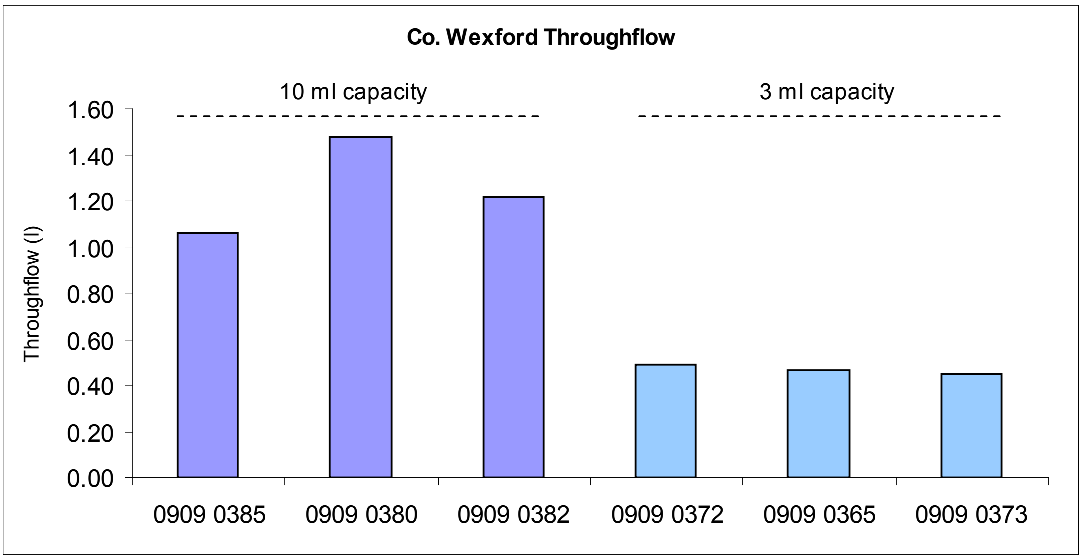


Figure 3.38. Tracer salt estimation of cartridge throughflow during March 2010 deployment of 3 ml and 10 ml cartridges at the Co. Wexford site. Numbers on the *x*-axis refer to cartridge numbers.

3.2.7.4 Co. Louth

Hydrometric station data

Deployment 12, in Co. Louth, was also dominated by low flow, with a series of low-intensity storm events and one extremely high-intensity event towards the end (Fig. 3.39). As with the Co. Wexford site, TP and TRP concentrations increased, with increasing discharge due to near-surface flow. N concentrations within the catchment are groundwater fed, hence the decline in TON level with increasing discharge (Fig. 3.40).

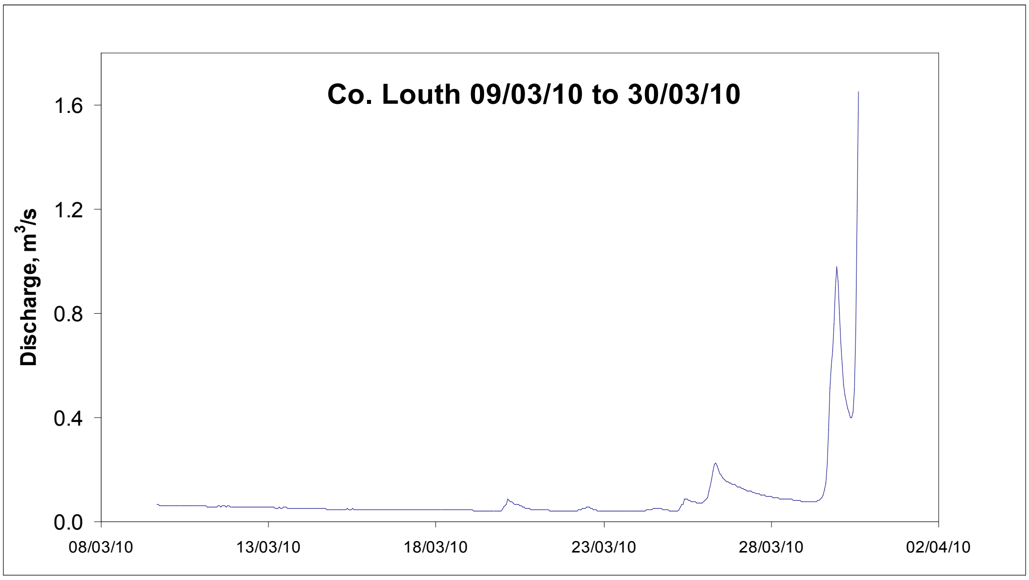


Figure 3.39. Discharge time series for Co. Louth for the period 09/03/10 to 30/03/10.

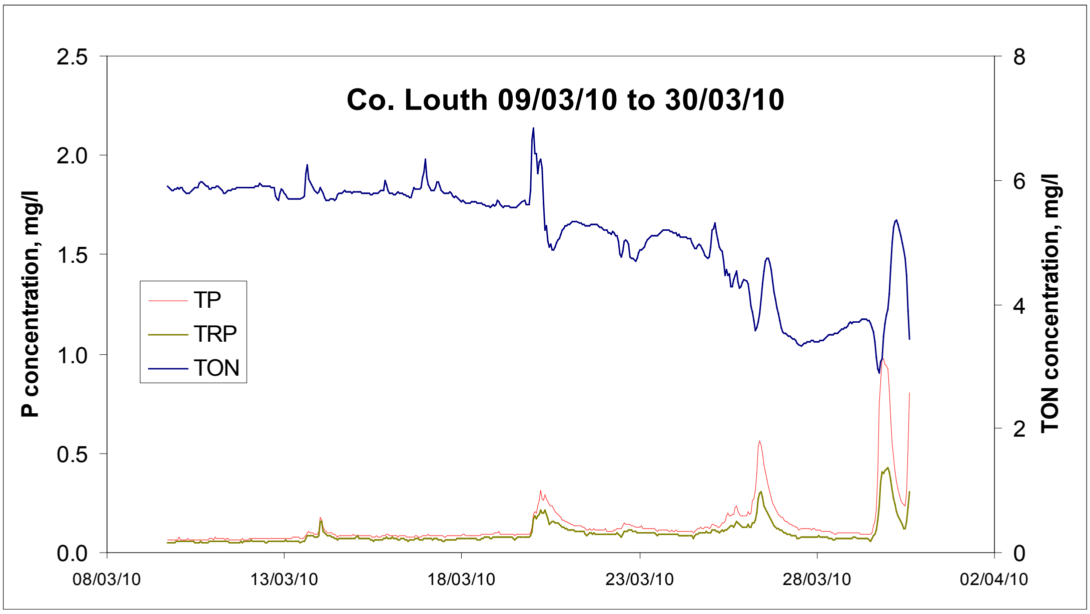


Figure 3.40. Total oxidisable nitrogen (TON), total phosphorus (TP) and total reactive phosphorus (TRP) series for Co. Louth for the period 09/03/10 to 30/03/10.

Cartridge recoveries

P concentrations returned by the 10 ml Sorbisense cartridges were more consistent with the TWMC for TP, whereas the 3 ml cartridges were closer to the FWMC (Fig. 3.41). However, for TRP the 10 ml cartridges were more accurate in relation to the FWMC, and the 3 ml cartridges were in excess of both the TWMC and FWMC (Fig. 3.42). The 10 ml capacity cartridges performed better than the 3 ml ones in relation to TRP, but the 3 ml cartridges were more accurate for TP (Figs 3.41 and 3.42). In relation to nitrate the 10 ml cartridges were more accurate than the 3 ml ones, which tended to over-estimate (Fig. 3.43). In terms of tracer salt loss, there is less variation with the 3 ml cartridges compared to the 10 ml ones (Fig. 3.44).

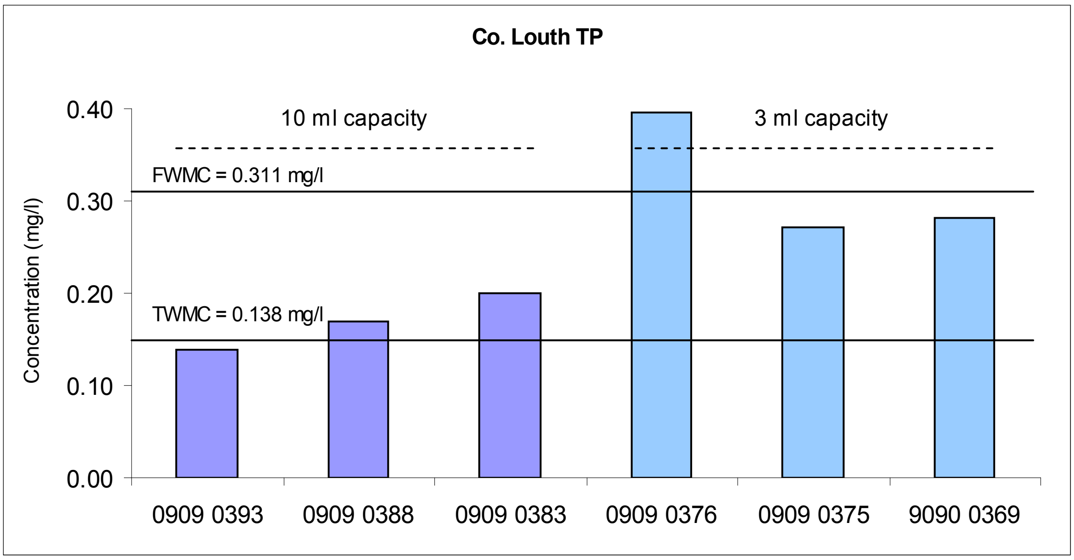


Figure 3.41. Deployment of 3 ml and 10 ml cartridges at the Co. Louth site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for total phosphorus (TP) are indicated. Numbers on the *x*-axis refer to cartridge numbers.

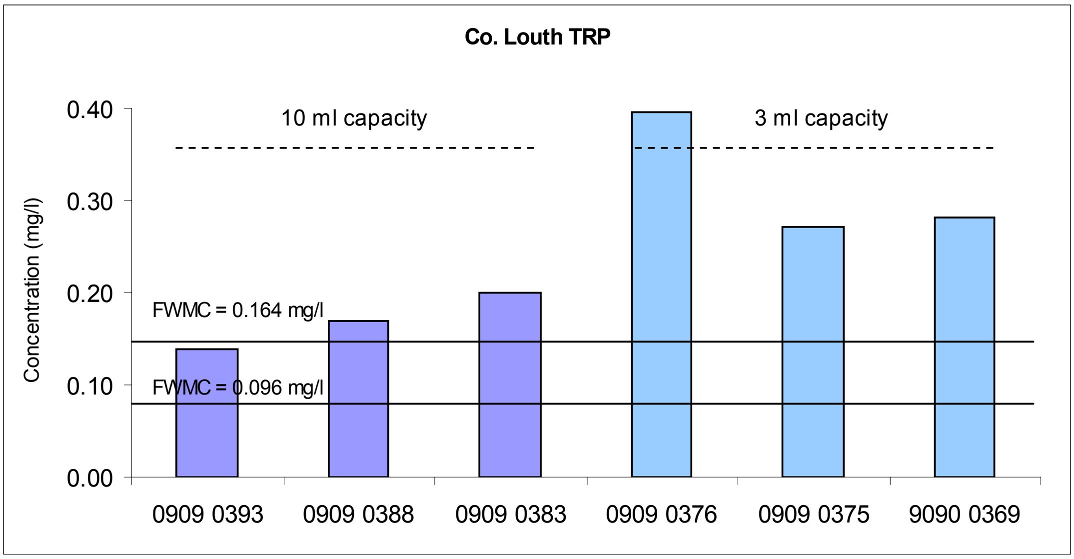


Figure 3.42. Deployment of 3 ml and 10 ml cartridges at the Co. Louth site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for total reactive phosphorus (TRP) are indicated. Numbers on the *x*-axis refer to cartridge numbers.

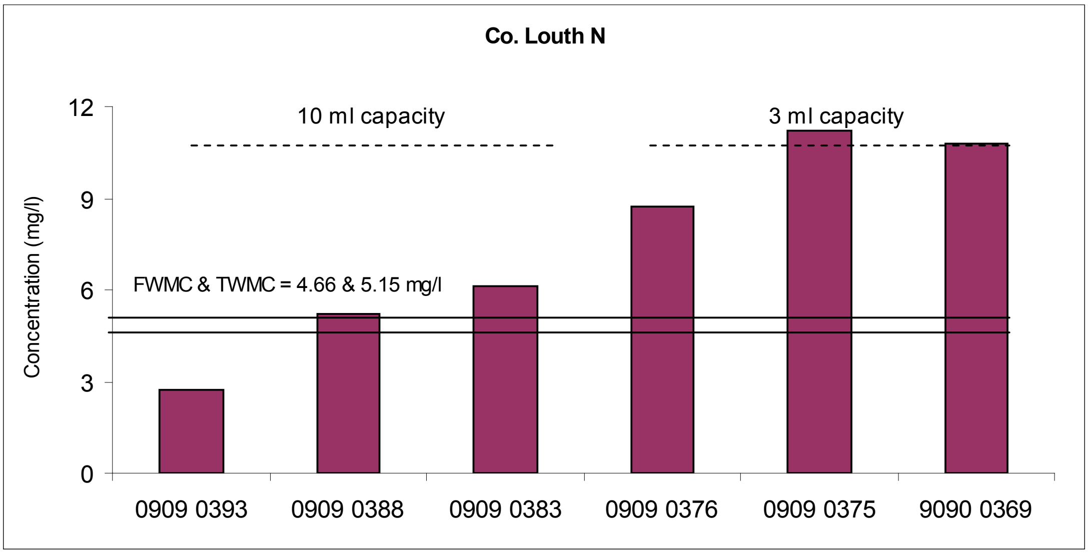


Figure 3.43. Deployment of 3 ml and 10 ml cartridges at the Co. Mayo site. Flow- and time-weighted mean concentrations (FWMC and TWMC) for nitrate are indicated. Numbers on the *x*-axis refer to cartridge numbers.

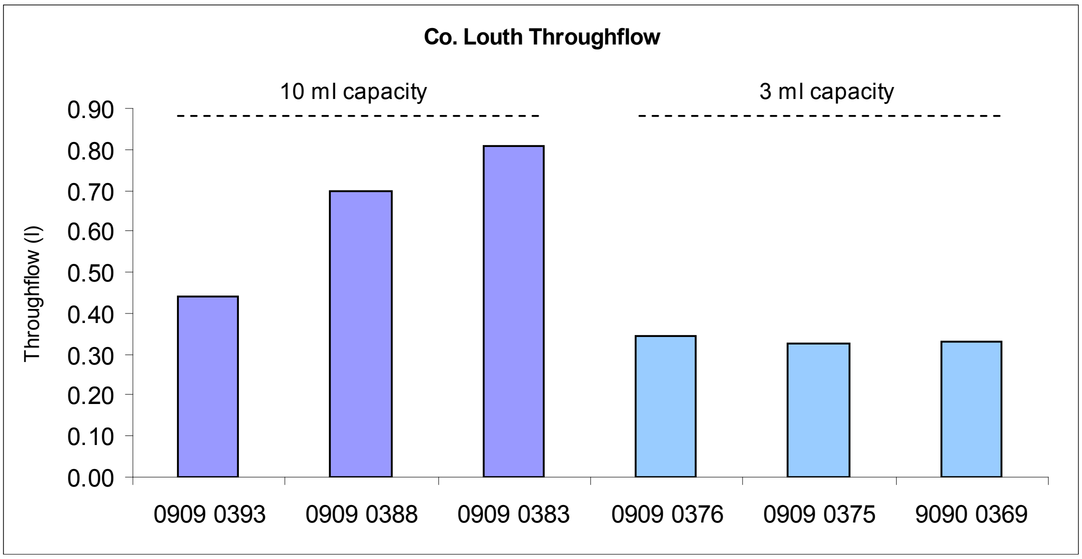


Figure 3.44. Tracer salt estimation of cartridge throughflow during March 2010 deployment of 3 ml and 10 ml cartridges at the Co. Louth site. Numbers on the *x*-axis refer to cartridge numbers.

3.2.7.5 Summary of March 2010 deployment

P results recovered from the Sorbisense InStream cartridges were more satisfactory for these deployments. The 10 ml cartridges appeared to out-perform the 3 ml ones in terms of P recovery. However, it remained unclear as to the exact fraction of P that the cartridges were measuring within the stream environment, with variability in terms of recovered magnitudes in both TP and TRP fractions. The fraction recovered by the cartridges may be dependent on specific instream characteristics such as turbidity. This was further investigated in the in-house pump tests using river water samples (see Section 3.2.9.2).

In relation to nitrate recoveries there were no visible patterns for either the 10 ml or the 3 ml capacity cartridges. Nevertheless, tracer salt estimations of cartridge throughflow were reasonably consistent across both cartridge capacities. As anticipated, the 10 ml cartridges had a greater throughflow volume than the 3 ml ones.

3.2.8 Low-flow Deployment at Co. Louth and Co. Wexford During May/June 2010

Two final deployments of cartridges took place in Co. Louth (Deployment 13) and Co. Wexford (14) during May/June 2010. The 10 ml cartridges were deployed at each site, in triplicate, to test the use of the InStream cartridge during a period of stable low flow. Discharge and nutrient transfers for Co. Louth and Co. Wexford are shown in Figs 3.45–3.48. Deployment details and the associated TWMC and FWMC are in Table 3.4. Although this was chosen as a low-flow period, a small storm on 01/06/10 transferred high nutrient concentrations in both catchments.

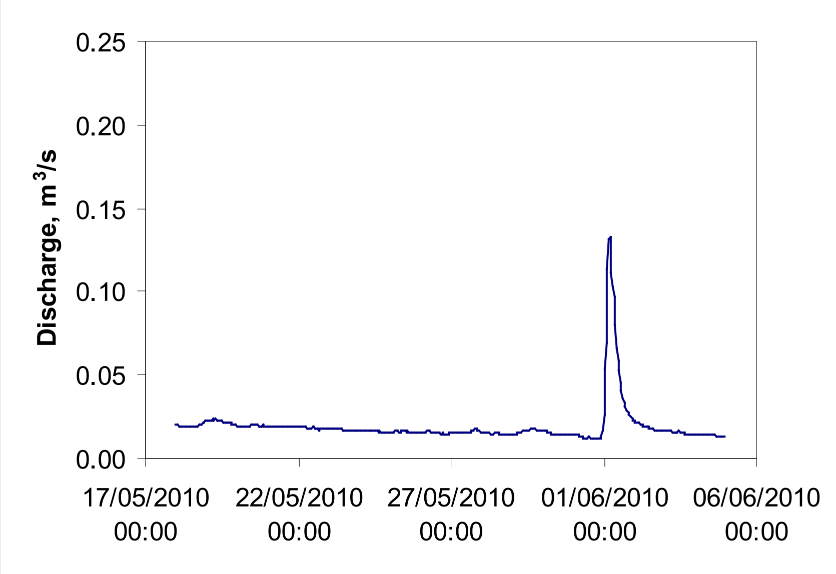


Figure 3.45. Discharge time series in Co. Louth from 18/05/10 to 04/06/10.

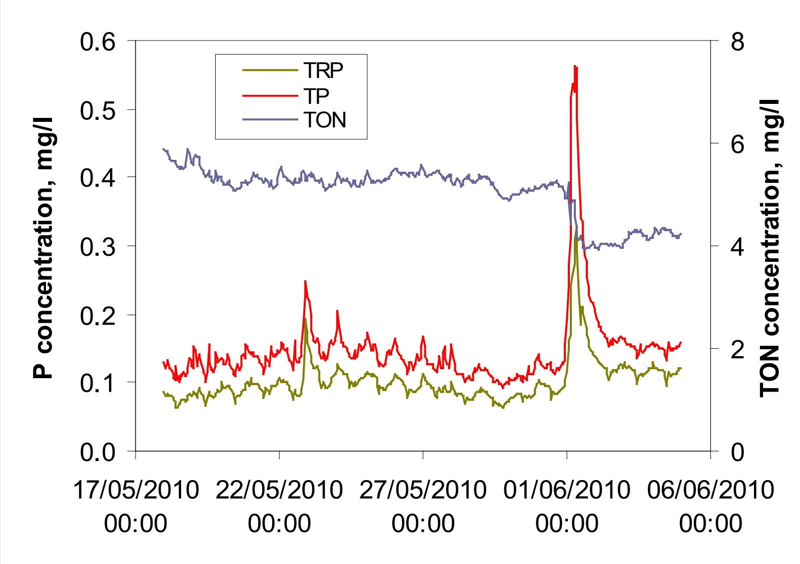


Figure 3.46. Total oxidisable nitrogen (TON) and P time series in Co. Louth from 18/05/10 to 04/06/10.

Table 3.4. Time- and flow-weighted mean concentrations (TWMC and FWMC) for N (as total oxidisable nitrogen – TON), total phosphorus (TP) and total reactive phosphorus (TRP) from high-resolution monitoring stations.

Catchment	Deployment	Retrieval	Duration	TWMC (mg l^{-1})			FWMC (mg l^{-1})		
				N	TP	TRP	N	TP	TRP
Co. Louth	18/05/10	04/06/10	17 days	5.05	0.148	0.102	5.00	0.182	0.118
Co. Wexford	18/05/10	04/06/10	17 days	6.51	0.046	0.027	6.23	0.051	0.029

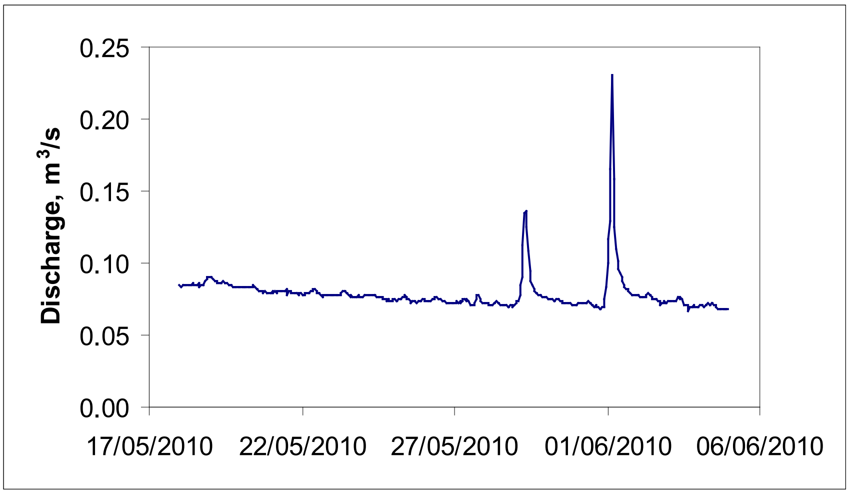


Figure 3.47. Discharge time series in Co. Wexford from 18/05/10 to 04/06/10.

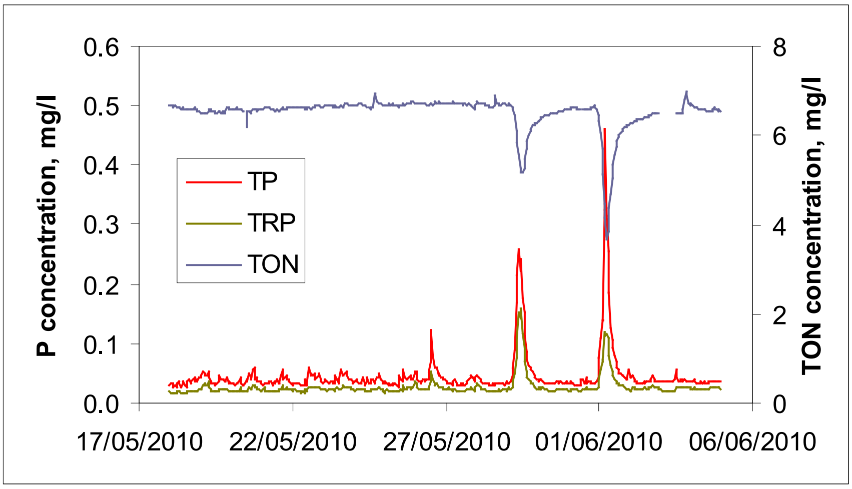


Figure 3.48. Total oxidisable nitrogen (TON) and P time series in Co. Wexford from 18/05/10 to 04/06/10.

Of note during this period were the differences in background P concentration between the two catchments, with much higher TP concentrations in Co. Louth (> 0.1 mg l^{-1}) than in Co. Wexford (< 0.05 mg l^{-1}). The storm event in Co. Louth yielded lower peak flows on 01/06/10, and the P concentrations peaked at a similar level in both catchments. TON concentrations were of the same order in both catchments. Table 3.4 shows how these relate to TWMC and FWMC, with Co. Louth having much higher P concentration for the period and TON broadly similar. Table 3.5 details P and N concentrations and throughflow volumes returned by the deployed cartridges.

Table 3.5. P, N and throughflow recoveries returned by the 10 ml cartridges during low-flow deployment (where * denotes less than 10% loss of tracer salt).

Catchment	Cartridge ID	Throughflow (l)	P concentration (mg l^{-1})	N concentration (mg l^{-1})
Co. Louth	0909 0713	0.290	0.047	1.0
	0909 0714	0.058	0.235	5.5
	0909 0715	0.220	0.088	0.7
Co. Wexford	0909 0716	0.904	0.014	1.3
	0909 0717	0.141	0.100	10.0
	0909 0718	*	*	*

Cartridges deployed during low flow in Co. Louth and Co. Wexford demonstrated apparent variation in throughflow volumes between replicates. In the case of cartridge 0909 0718, there was insufficient throughflow to leach more than 10% of the tracer salt, thus preventing the accurate determination of P and N concentrations. Cartridges did not recover P and N concentrations comparable to the levels measured by the high-resolution monitoring stations (Table 3.4). Only cartridge 0909 0714 returned a nitrate concentration that was accurate in relation to TWMC and FWMC. It can be suggested, therefore, that at low flow the velocity of stream water is not of sufficient magnitude to induce cartridge throughflow, hence the variability in the Sorbisense results.

3.2.9 Laboratory Tests Using Sorbisense InStream Samplers

In response to the variable comparisons between cartridge concentrations and high-resolution data, it was decided to conduct in-house laboratory tests at the University of Ulster. Cartridges were attached, via tubing, to a peristaltic pump (Fig. 3.49). The pump was fed from a conical flask containing known concentrations of P and N. The use of a peristaltic pump allowed the movement of known concentrations of standard solutions through the cartridges at constant and variable flow rates.

The first laboratory test was conducted to investigate the impact of high- and low-flow events on cartridge performance. This was performed by pumping known concentrations through the cartridges at different flow rates comparable to instream conditions. A standard solution containing 1.2 mg l^{-1} N and 0.159 mg l^{-1} P was passed through a single frit and a multi-frit cartridge at a variable flow rate. The same standard solution was then passed though a multi-frit cartridge at a constant flow rate. Cartridge analysis for this first laboratory test was conducted by the Sorbisense external subcontractor.

N and P concentrations recovered from the laboratory test of the cartridges were lower than the concentrations contained within the standard solution (Table 3.6). This was consistent with previous stream deployments (see Sections 3.2.3 and 3.2.4), where cartridge measurements were less than those recorded by the

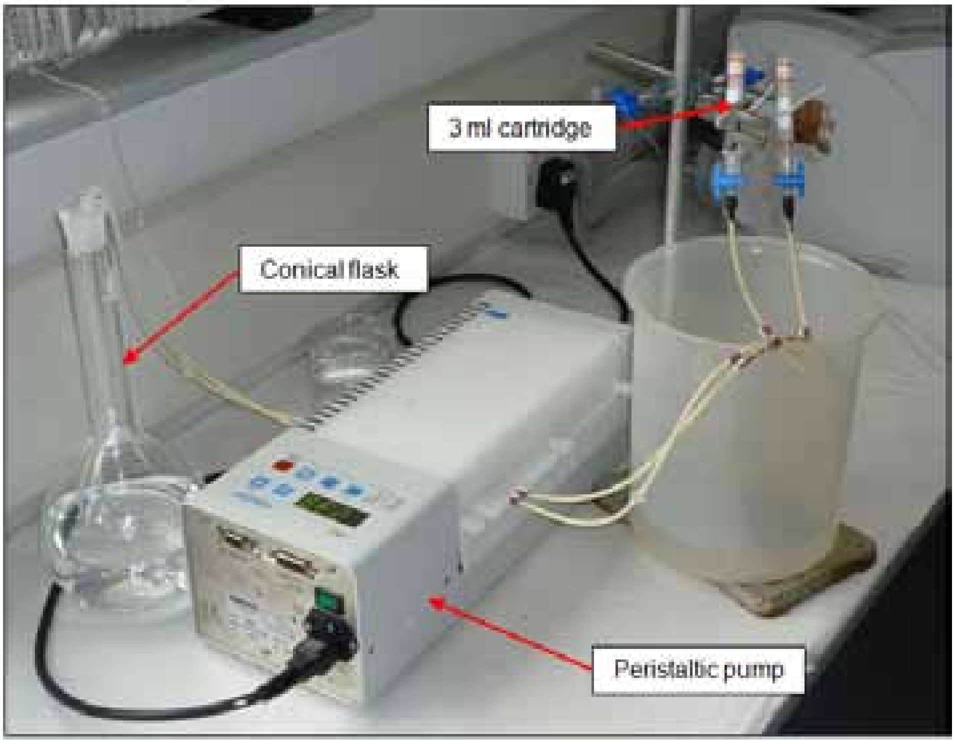


Figure 3.49. Equipment to conduct laboratory testing using Sorbisense InStream cartridges.

high-resolution equipment. Estimation of cartridge throughflow using the tracer salt mechanism appeared, from this controlled test, to be a satisfactory method (Table 3.6).

3.2.9.1 *Quality assurance using spiked cartridges*

In light of the issues raised by the October 2009 Co. Wexford deployment (Section 3.2.6) and the unsatisfactory recovery of N and P concentrations from Sorbisense cartridges, the following two decisions were made. First, it was agreed that all future analysis by Sorbisense was to be performed by their laboratory in preference to an external subcontractor. Second, it was agreed (also with the project steering committee) that all subsequent shipments of deployed cartridges should include spiked reference samples of known concentrations.

Spiked reference cartridges were included for analysis with the March 2010 deployment. A total volume of 0.281 l of standard solution, containing 1.50 mg l^{-1} of N and 0.120 mg l^{-1} of P, was passed through two 3 ml cartridges at a constant rate, using the peristaltic pump. Concentrations returned by Sorbisense for the spiked cartridges are detailed in Table 3.7.

Analysis of spiked cartridges in the Sorbisense laboratory returned satisfactory recoveries for both N and P concentrations, and the volume of throughflow. This helped to generate confidence in the Sorbisense methodology for eluting and calculating nutrient concentrations adsorbed by the resin. As with the previous pump test experiment, the tracer salt methodology for estimating throughflow appeared to be consistently accurate.

The final deployments of cartridges and river pump tests (Section 3.2.8) were conducted in May/June 2010. A further three spiked cartridges were sent to Sorbisense with this shipment. A total volume of 0.843 l of standard solution, containing 7.50 mg l^{-1} of N and 0.200 mg l^{-1} of P, was passed through three 10 ml cartridges at a constant rate, using the peristaltic pump. Table 3.8 details the P and N concentrations and throughflow volumes returned by the cartridges.

Table 3.6. Concentration and volume of standard solution passed through cartridges, and the recoveries returned by the cartridges.

Cartridge	Rate	Pump throughflow (l)	Solution concentration (mg l^{-1})	Cartridge throughflow (l)	Cartridge Concentration (mg l^{-1})
Multi-frit	Variable flow	0.281	1.200 N	0.278	0.840 N
			0.159 P		0.101 P
Single-frit	Variable flow	0.281	1.200 N	0.295	0.760 N
			0.159 P		0.092 P
Multi-frit	Constant flow	0.281	1.200 N	0.291	0.670 N
			0.159 P		0.089 P

Table 3.7. Concentration and volume of standard solution passed through 3 ml cartridges, and the recoveries returned by the cartridges.

Cartridge	Rate	Pump throughflow (l)	Solution concentration (mg l^{-1})	Cartridge throughflow (l)	Cartridge concentration (mg l^{-1})
Multi-frit	Constant flow	0.281	1.500 N	0.290	1.400 N
			0.120 P		0.142 P
Multi-frit	Constant flow	0.281	1.500 N	0.260	1.410 N
			0.120 P		0.152 P

Table 3.8. Concentration and volume of standard solution passed through 10 ml cartridges, and the recoveries returned by the cartridges.

Cartridge	Rate	Pump throughflow (l)	Solution concentration (mg l^{-1})	Cartridge throughflow (l)	Cartridge concentration (mg l^{-1})
Multi-frit	Constant flow	0.843	7.500 N 0.200 P	1.015	3.600 N 0.146 P
Multi-frit	Constant flow	0.843	7.500 N 0.200 P	0.949	4.200 N 0.166 P
Multi-frit	Constant flow	0.843	7.500 N 0.200 P	0.954	3.900 N 0.159 P

Recoveries from this set of spiked reference samples were not as accurate as the previous set (see Table 3.7). The volume of throughflow was slightly over-estimated, yet the concentrations of N and P were under-estimated; this was particularly true of N. Discrepancies may be due to the fact that the previous spiked cartridges were 3 ml in capacity in preference to 10 ml. However, on both occasions all cartridges had visibly lost adequate tracer salt to ensure accurate determinations of N and P concentration. Further to this, Sorbisense actually advocates the deployment of two or more capacities in river sites due to the fact that flow conditions cannot be pre-empted (see Rozemeijer et al., 2010, which was published after the experimental period in this project) and suggests that 'at the end of the installation period, the sampler with the best sampling volume can be selected for laboratory analysis'. Thus, it would be fair to assume that the rate of nutrient adsorption to the resin and the dissolution of tracer salt should be the same for both the 3 ml and the 10 ml cartridges. The two cartridges should behave in exactly the same way when deployed in the riverine environment. The only difference is that the 10 ml cartridge contains more resin and tracer salt than the 3 ml cartridge, to allow for greater throughflow volumes.

3.2.9.2 Laboratory pump test using low-flow river water samples

As a final in-house experiment at the University of Ulster, the peristaltic pump was used to pass river water samples through the 10 ml cartridges. Samples were collected at low flow during May 2010. The purpose of the pump test was to determine under controlled conditions:

- The exact P fraction adsorbed by the resin;
- The role of riverine suspended material;
- The efficiency of the adsorbent resin.

Five rivers were selected, to ensure a range of P and N concentrations. Water samples were collected from the Co. Louth and Co. Wexford sites, and the remaining three were taken in Co. Derry. The three rivers sampled in Co. Derry were the Mettican, Macosquin and Ballysally. Triplicate cartridges per sample were attached, via tubing, to a peristaltic pump (Fig. 3.50). The pump was fed from two conical flasks containing the river water samples. The conical flasks were placed on a magnetic stirrer plate for the duration of the experiment, to ensure sample homogeneity. To preserve the longevity of the river water samples, the experiment was conducted in the dark and the samples were kept refrigerated until the conical flasks needed to be replenished.

Water samples were analysed colorimetrically for P fractions at the University of Ulster, using the molybdate antimony method of Murphy and Riley (1958,1962). Fractions determined were TP, TRP, total soluble phosphorus (TSP) and soluble reactive phosphorus (SRP). Nitrate concentrations were determined at Dundalk Institute of Technology. Filtrate expelled from the cartridges during the pump test was collected and analysed for P.

P and N concentrations and throughflow volumes recovered from the triplicate cartridges, for the five river water samples, are shown in Table 3.9. In all five river samples, the cartridges returned P concentrations that

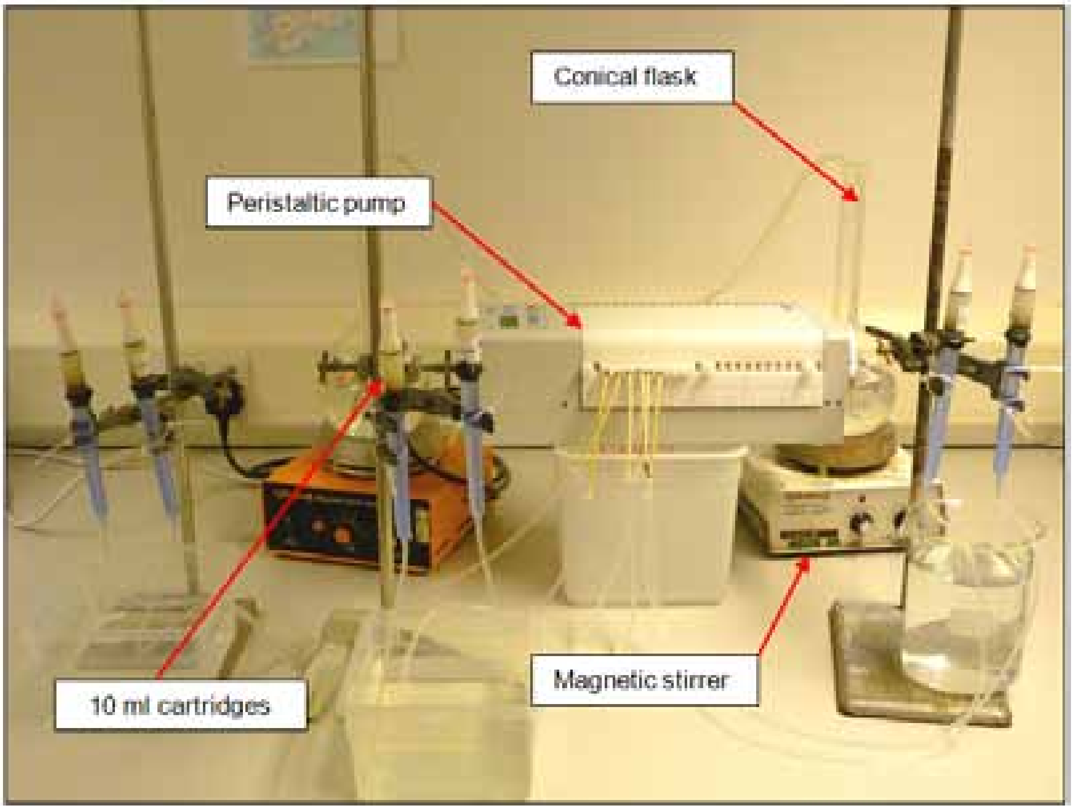


Figure 3.50. Equipment used to conduct laboratory tests using Sorbisense InStream cartridges and river water samples.

were lower than the actual concentrations present in the water sample. As a result of this, it was not possible to determine the exact P fraction being adsorbed by the cartridges. However, the concentration returned by the cartridges for the River Mettican, Co. Derry, was comparable to both TRP and SRP. Reproducibility of the triplicate cartridges was satisfactory, but the concentrations were under-estimated. Nitrate concentrations returned from the cartridges were also lower than the actual concentrations present in the water samples. Nevertheless, nitrate recoveries were more accurate in comparison to the P results, particularly for the Co. Louth site. Reproducibility of the triplicate cartridges was again satisfactory.

Filtrate exiting the cartridges was analysed for P at the end of the each pump test. On each occasion, the concentration of SRP measured was below the limit of detection (< 0.003 mg l^{-1}). It appeared that the adsorbent resin was capable of removing P from the water as it passed through the cartridge, but concentrations recovered from the cartridges suggests that not all P was being eluted from the cartridge resin.

Table 3.9. P, N and throughflow recoveries returned by the 10 ml cartridges during river water pump test.

Catchment	Cartridge ID	Throughflow (l)	Cartridge concentration (mg l^{-1})		Actual concentration (mg l^{-1})				
			P	N	TP	TSP	TRP	SRP	N
Co. Louth	0909 0711	0.723	0.026	5.2	0.125	0.101	0.095	0.086	5.449
	0909 0707	0.763	0.024	5.0					
	0909 0709	0.775	0.025	4.6					
Co. Wexford	0909 0710	1.119	0.015	4.2	0.032	0.029	0.027	0.023	6.436
	0909 0712	0.902	0.014	5.3					
	0909 0708	0.941	0.013	5.0					
R. Mettican	0909 0719	0.781	0.016	0.4	0.030	0.024	0.013	0.011	0.534
	0909 0720	0.886	0.014	0.3					
	0909 0721	1.006	0.012	0.3					
R. Macosquin	0909 0722	1.016	0.012	1.0	0.081	0.070	0.060	0.056	1.682
	0909 0723	0.950	0.013	1.1					
	0909 0724	1.603	0.008	0.5					
R. Ballysally	0909 0726	0.947	0.013	1.8	0.084	0.064	0.054	0.046	3.736
	0909 0727	0.735	0.017	2.1					
	0909 0730	0.809	0.015	2.1					

Throughflow

Passing river water samples through the cartridges, under controlled laboratory conditions, further validated the estimation of throughflow using tracer salt as a satisfactory method (Fig. 3.51). The standard deviation of throughflow volume for the river samples was 0.220 l.

Particulate matter present within the water samples did not appear to inhibit cartridge throughflow; however, a brown accumulation was visible on the adsorbent resin (Fig. 3.52). Throughflow volumes returned by the cartridges were comparable to the 0.843 l delivered by the peristaltic pump, with the exception of cartridge 724.

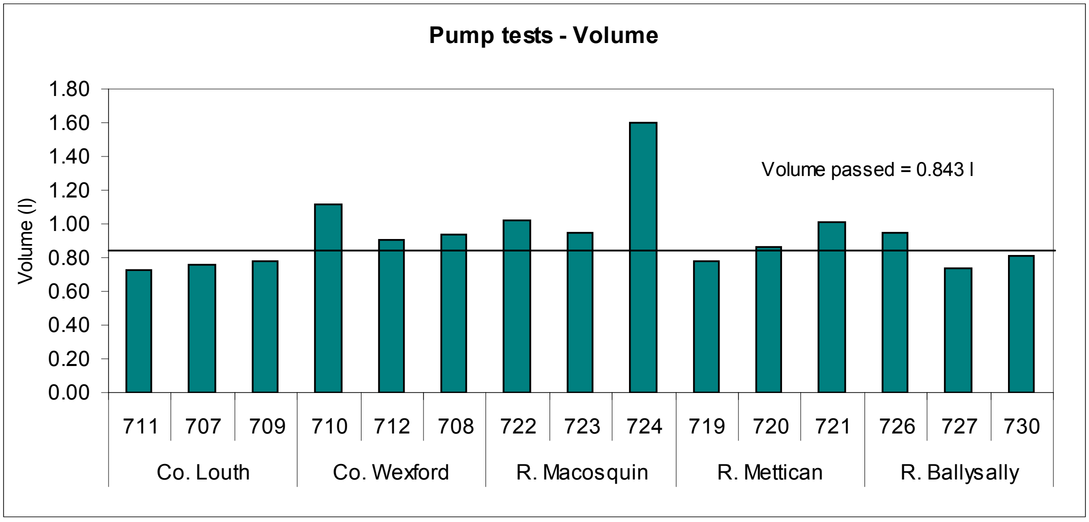


Figure 3.51. Volume of cartridge throughflow during laboratory pump test as determined by tracer salt loss. Actual throughflow volume of 0.843 l is indicated. Numbers on the *x*-axis refer to cartridge numbers.

River samples were taken at low flow, and turbidity values ranged between 1.827 and 3.940 nephelometric turbidity units (NTU). It is therefore feasible that particulate matter may be less influential in constricting the cartridge frits during low flow. To substantiate this, it would be necessary to repeat the pump test during a high-flow storm event, when samples would be increasingly turbid due to overland flow.

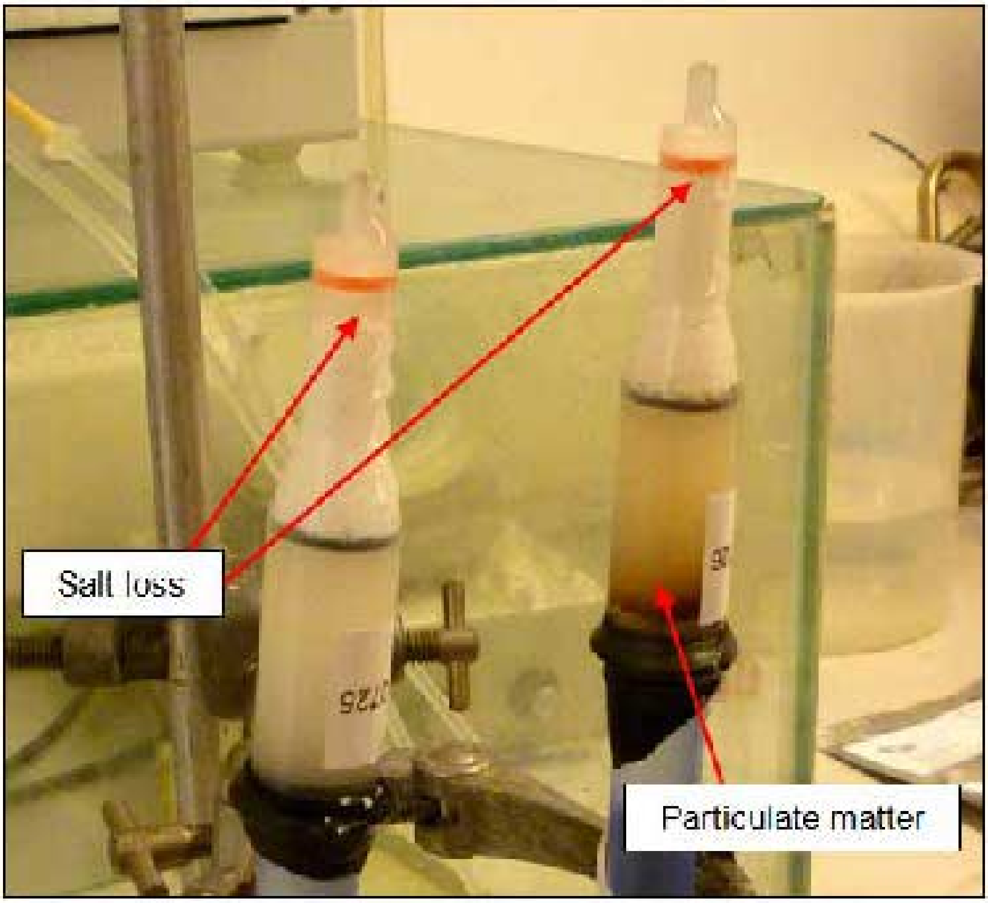


Figure 3.52. Cartridge 725 after pumping standard solution, and cartridge 726 after pumping water from the River Ballysally. Note the accumulation of particulate matter in the resin.

4 Conclusions and Recommendations

4.1 Overall Conclusions

Flow-proportional passive sampling of nutrients in rivers remains an attractive solution for optimising the under-representation of grab sampling and avoiding the technological constraints and expense of high-resolution sampling. Research questions concerning spatial and temporal variability of point and diffuse nutrient transfers from catchments, and routine WFD river monitoring campaigns by government, would both benefit. Results from this study that used high-resolution data sets to compare with passive sampler deployments were, however, variable with regard to nutrient recovery. Overall, many of the 14 deployments had recoveries that were less than the TWMC and/or FWMC of P and N. Those recoveries that were less than the TWMC can be regarded as being of less utility than individual grab samples for the period of deployment.

The approach to providing an FWMC for nutrients was based on a number of assumptions. The two key assumptions were first that water would enter and exit cartridges, and deposit nutrient ions at a rate proportional to velocity, and second that throughflow of water was closely approximated by the loss of tracer salt. In terms of the first assumption, hydraulic fluid simulations demonstrated that fluid will inevitably take the path of least resistance, and as a result flow will tend to diverge round the cartridge rather than enter into it. It is therefore highly likely that in ambient environments, stream flow will diverge preferentially around deployed cartridges. It is speculated that this will be exacerbated during high storm flows. High-flow events also tend to transport stream debris, and this is particularly prevalent during autumn due to the transportation of fallen leaves during a period of high nutrient transfers due to storm runoff. Figure 4.1 illustrates the problems that arise during storm events in relation to the accumulation of detritus around the cartridges and the instream rack. It is also possible that a large enough quantity of stream debris could further dislodge and/or damage cartridges. Flow-proportional passive sampling was designed to reduce the labour-intensiveness of grab sampling, yet the system requires frequent visitations throughout the deployment to ensure that cartridges are free from obstruction – and this would be prohibitively expensive during periods of high flow.

In terms of the second assumption, loss of throughflow potential could also occur due to hydraulic resistance and/or the accumulation of material. Variable responses were observed during the 14 deployments that were also influenced by some lower flows, a known constraint of the cell system. Throughflow estimates using the calcium citrate dissolution method were, however,

Figure 4.1. Debris collection on the rack during high-flow events.

found to be a satisfactory proxy during laboratory pump tests with known volumes recovered in blind trials. Again, the ambiguity with field trials perhaps points to conditions in ambient river deployments being unsuited to throughflow in the cartridge as highlighted above, especially where large flow gradients exist, despite some reasonable recoveries in deployments of porous media and controlled flow environments.

Within the cartridges, internal constriction of the frit apertures and resin with particulate organic matter was also of concern during field deployments (see Fig. 3.52). In an effort to improve throughflow and reduce the passage of particulate matter into the resin, trials were conducted using cartridges manufactured with varying frit sizes. Results demonstrated that there was no statistical difference in P and N concentrations in relation to frit size. To further address the issue of cartridge throughflow, a new multi-frit cartridge was designed in an effort to improve hydraulic conductivity. Trials of the multi-frit cartridge again showed limited improvement in relation to P and N recoveries.

Further to the issues concerning velocity-proportional adsorbance of P and N ions, questions on elution recoveries were also unresolved. The laboratory pump trials sought to test both P and N recovery and throughflow, and found lower than expected P recoveries in the trials with ambient water, despite good throughflow. The tests measured very low residual P concentrations exiting the cartridges in the laboratory tests, reported as below the limit of detection in normally analysed water samples. Despite this, recovery of eluted P was only 16–53% of the TP pumped through the cartridges. It remains unclear why these controlled pump trial P recoveries were low (i.e. there were reasonable nitrate recoveries and the exact chemical interaction with P fractions in the resin may require investigation), but this adds to the uncertainty in providing a reliable solution for river deployment.

Apart from the hydrodynamic issues pertaining to the InStream passive sampler, the cartridges may also have biological limitations. It is widely acknowledged that unprotected surfaces, in riverine environments, become rapidly colonised with algal and bacterial communities (Vrana et al., 2005). The implications of algae and particulate accumulations on passive sampling membranes are widely accepted within the literature (Pichette et al., 2007, 2009; Vrana et al., 2005). Biofouling of diffusive membranes restricts the ‘free movement’ of solutes onto the adsorbing resin. Research undertaken by Pichette et al. (2007) suggested that pre-treatment of the membrane filter with a metal, such as silver or copper iodide, was effective at preventing biofouling on DGT deployments for the analysis of P. Figures 4.2 and 4.3 illustrate the biological implications of invertebrate and algal colonisation on the InStream cartridges. The occurrence of *Simuliidae* sp. (blackfly) larvae and pupae at the cartridge entrance may have further impeded the passage of water into the resin.

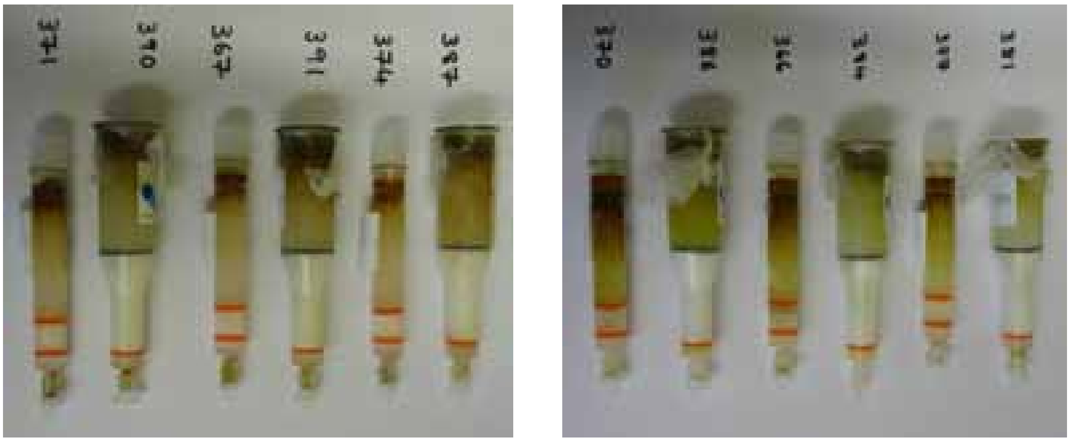
Figure 4.2. *Simuliidae* (blackfly) larvae and pupae located at a cartridge entrance in June 2010.

Green pigmentation on the adsorbent resin in the cartridges was noticed during the March 2010 deployment (Fig. 4.3). The presence of algal communities within the cartridge may have implications for P and N recoveries as photosynthetic cells utilise nutrients for growth (Stevenson et al., 1996). The green colouration was particularly noticeable at the Co. Mayo site. Cartridges deployed in Co. Mayo may offer a 'ready-made' sink of P and N for biological activity in a stream system characterised by very low nutrient concentrations.

Two further elements of this research study were to trial a reagentless TON probe and to maintain the data run of an *in situ* bankside P analyser for sampler comparisons. Despite a degree of technical sophistication, both monitoring devices appear capable of providing a long-term high-resolution data set of nutrient transfers in Irish rivers. There are issues pertaining to data hiatus, and these are more related to the sustained delivery of water to the sampling apparatus that will require troubleshooting. P recoveries from the Hach Lange P suite appear reasonable and are reported in Jordan et al. (2007). The Hach Lange TON probe appears to require a site-specific calibration curve, especially where there is evidence of high amounts of dissolved humic matter.

Co. Monaghan

Co. Mayo



Co. Wexford

Co. Louth

Figure 4.3. Green pigmentation on the adsorbent resin suggests the colonisation of algal cells.

4.2 Recommendations

The passive sampling systems would be extremely useful to research and statutory agencies monitoring water quality for P and N transfers. Recommendations arising from this project are that further research and development are required to fully address the issues raised in this report regarding the use of flow-proportional passive samplers in Irish rivers. Multiple factors have been highlighted regarding the performance of the cartridges that appear not to perform in a flow-proportional manner and therefore do not return appropriate recoveries of P and N concentrations as compared with high-resolution data sets. These interacting factors are:

- Flow divergence;
- Loss of flow/velocity-proportional nutrient adsorbance;
- Loss of throughflow;
- Debris build-up at cartridge interface due to deployment methodology;
- Speculated biological interference on a physical and chemical level;
- Laboratory elution and recovery of nutrients (possibly also influenced by laboratory methods).

Further investigation into these factors would allow the effectiveness of the cartridges to be quantified in Irish river systems and informed adaptations made to the cartridge design to improve function, including deployment to ensure unobstructed throughflow and anti-biofouling. However, research into the developmental issues surrounding the InStream passive system was not part of this project outline or within the remit of the EPA Science, Technology, Research and Innovation for the Environment (STRIVE) funding.

Although outside the remit of this study, a cost–benefit analysis of all sampling systems, including passive sampling, would be an essential element in defining future needs based on richness and necessity of data, and economic cost of resources. Although passive sampling has the potential to increase the data richness of a high spatial network of monitoring sites (compared, for instance, with time-discrete grab sampling), it may, for example, be more scientifically defensible and economically parsimonious to deploy fewer but higher-resolution (and more accurate) systems, as also highlighted in this study. At present, the national monitoring programme fails to capture diffuse nutrient transfers during storm events, and the interpretation of these data for, for example, monitoring the recovery of agricultural soil nutrient pressures, is open to question. While successful passive sampling may increase data richness by integrating concentrations over deployment periods, the problems associated with the samplers in this study are found more in those (flashy) catchments where diffuse storm-associated nutrient risk is highest.

Despite these findings, the role of passive sampling systems such as the Sorbisense cartridges is not without merit in the Irish environment. Previous work with sampling cells in the groundwater and soil water environments – these samplers were embedded in porous media and therefore subject to different flow mechanisms, e.g. capillary action in soils and Darcy’s Law in groundwater – has demonstrated good recoveries (de Jonge and Rothenberg, 2005). This is perhaps evidence for very low water velocities and samplers acting in equilibrium with those solid–water interfaces that recoveries have been good and that TWMC and FWMC will be similar. Other results show reasonable recoveries, especially for nitrate in surface water controlled flumes (Rozemeijer et al., 2010) where both nutrient and flow gradients are low. Again, this would be consistent with the findings in this report. These two examples are environments where the use of passive samplers may be utilised in the Irish environment.

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Acronyms and Annotations

AA	Atomic adsorption
ANCOVA	Analysis of covariance
ANOVA	Analysis of variance
DET	Diffusive equilibrium in thin-film
DGT	Diffusive gradient in thin-film
EPA	Environmental Protection Agency (Ireland)
EU	European Union
FWMC	Flow-weighted mean concentration
GRP	Glass reinforced plastic
ICP	Inductively coupled plasma
LU/t	Lattice units per time step
NIEA	Northern Ireland Environment Agency
NTU	Nephelometric turbidity units
PE	Polyethylene
POM	Programme of measures
RBD	River Basin District
SRP	Soluble reactive phosphorus
STRIVE	Science, Technology, Research and Innovation for the Environment
TON	Total oxidisable nitrogen
TP	Total phosphorus
TRACE	Trans-boundary River-basin Action for Community and Environment
TRP	Total reactive phosphorus
TSP	Total soluble phosphorus
TWMC	Time-weighted mean concentration
UV	Ultraviolet
WFD	Water Framework Directive (*OJEC*, 2000)

An Ghníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomhnithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Ghníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil, Pobal agus Rialtais Áitiúil.

ÁR bhFREAGRACHTAÍ

CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreail;
- scardadh dramhuisce.

FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain.
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisce agus caighdeán uisce.
- Obair le húdaráis áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí comhordú a dhéanamh ar líonra forfheidhmithe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a ngníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOL

- Monatóireacht ar chaighdeán aeir agus caighdeáin aibhneacha, locha, uiscí taoide agus uiscí talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntí a dhéanamh.

RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

TAIGHDE AGUS FORBAIRT COMHSHAOIL

- Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdéan aeir agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

MEASÚNÚ STRAITÉISEACH COMHSHAOIL

- Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le pleananna bainistíochta dramhaíola agus forbartha).

PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Ghníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstiúrthóir agus ceithre Stiúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmiúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.

Science, Technology, Research and Innovation for the Environment (STRIVE) 2007-2013

The Science, Technology, Research and Innovation for the Environment (STRIVE) programme covers the period 2007 to 2013.

The programme comprises three key measures: Sustainable Development, Cleaner Production and Environmental Technologies, and A Healthy Environment; together with two supporting measures: EPA Environmental Research Centre (ERC) and Capacity & Capability Building. The seven principal thematic areas for the programme are Climate Change; Waste, Resource Management and Chemicals; Water Quality and the Aquatic Environment; Air Quality, Atmospheric Deposition and Noise; Impacts on Biodiversity; Soils and Land-use; and Socio-economic Considerations. In addition, other emerging issues will be addressed as the need arises.

The funding for the programme (approximately €100 million) comes from the Environmental Research Sub-Programme of the National Development Plan (NDP), the Inter-Departmental Committee for the Strategy for Science, Technology and Innovation (IDC-SSTI); and EPA core funding and co-funding by economic sectors.

The EPA has a statutory role to co-ordinate environmental research in Ireland and is organising and administering the STRIVE programme on behalf of the Department of the Environment, Heritage and Local Government.

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