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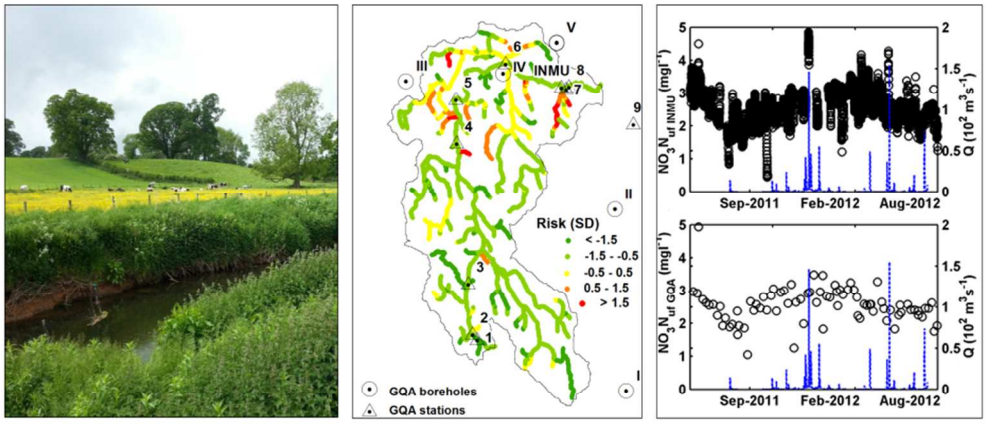

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In this paper we evaluate different nutrient monitoring strategies in providing evidence of diffuse pollution in agricultural catchments. We show that low-frequency nutrient datasets can provide time-integrated information on the spatial distribution of nutrient concentrations, whereas high-frequency datasets provide insights into temporal nutrient dynamics on the time-scales of hydrological responses. Our study highlights the importance of both monitoring strategies in providing unique and complementary insights into catchment biogeochemistry.

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ARTICLE

Understanding nutrient biogeochemistry in agricultural catchments: the challenge of appropriate monitoring frequencies

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We evaluate different frequencies of riverine nutrient concentration measurement to interpret diffuse pollution in agricultural catchments. We focus on three nutrient fractions, nitrate-nitrogen (NO_3-N), total reactive phosphorus (TRP) and total phosphorus (TP) observed using conventional remote laboratory-based, low-frequency sampling and automated, *in situ* high-frequency monitoring. We demonstrate the value of low-frequency routine nutrient monitoring in providing long-term data on changes in surface water and groundwater nutrient concentrations. By contrast, automated high-frequency nutrient observations provide insight into the fine temporal structure of nutrient dynamics in response to a full spectrum of flow dynamics. We found good agreement between concurrent *in situ* and laboratory-based determinations for nitrate-nitrogen (Pearson's R=0.93, p<0.01). For phosphorus fractions: TP (R=0.84, p<0.01) and TRP (R=0.79, p<0.01) the relationships were poorer due to the underestimation of P fractions observed *in situ* and storage-related changes of grab samples. A detailed comparison between concurrent nutrient data obtained by the hourly *in situ* automated monitoring and weekly-to-fortnightly grab sampling reveals a significant information loss at the extreme range of nutrient concentration for low-frequency sampling.

Keywords: Phosphorus, Nitrogen, Diffuse pollution, River Eden, Routine nutrient monitoring, Automated *in situ* nutrient monitoring, SCIMAP

Introduction

Sustained input of N and P in excess can damage the environment through eutrophication, loss of habitat and biological diversity and deterioration of drinking water resources.[1,2] Much scientific effort focuses on quantifying nitrogen and phosphorus export from land to receiving waters, including unravelling the catchment-scale processes controlling nutrient sources, mobilisation and delivery, and the role of human activities in manipulation of these processes.[3-5] Anthropogenic sources of P and N in streams include surface and subsurface runoff from agricultural land, soil erosion, direct (to streams) and indirect (to land) discharges from sewage treatment works and septic tanks, runoff from impervious surfaces like farmyards, roads etc. and other incidental sources such as sewer misconnections and storm overflows.[6-10] To capture the spatial heterogeneity of the sources and pathways of nutrient loss from land to water carefully designed monitoring programmes are needed. Examples include the extensive water quality monitoring programme operated by the Environment Agency (EA) for England.[11,12] The EA routine water quality monitoring is based on analysis of a wide range of biogeochemical determinands including nutrients in streams, lakes and aquifers. The resultant data provide valuable although spatially constrained information on the variability in nutrient concentrations across catchments based on an average of 80 sampling points per catchment.[13] Routine monitoring provides data to meet the statutory requirements as the European Water Framework Directive (WFD) and is used by regulators to assess catchment nutrient status, targeting nutrient control measures and their subsequent evaluation.

Technological advances in the hardware and software to support high-frequency measurement approaches have enabled fine-resolution nutrient dynamics to be captured across a wide spectrum of river flow dynamics relative to conventional grab sampling.[12,14-18] In particular, *in situ* automated nutrient monitoring is important in determination of reactive fractions of P and N because these may undergo a range of physical and biogeochemical transformations during transportation and storage after collection.[19-21] Compared to traditional, low-frequency monitoring, automated nutrient monitoring offers greater temporal resolution of sampling and provides improved characterisation of nutrient dynamics in response to individual

storm events and low flow conditions.[4, 9, 12, 14, 15, 17, 22-26] As the automated nutrient monitoring instruments are becoming more portable and compact with the potential for being powered by rechargeable batteries and renewable energy sources, automated nutrient monitoring offers greater feasibility and applications in remote locations.[17, 27] This flexibility and mobility facilitates selection of sample locations based on scientific and environmental relevance rather than on practicalities of access, power supply or distance to the analytical laboratory.

In this paper we evaluate the efficacy of low and high-frequency nutrient monitoring in providing evidence on spatial and temporal controls of diffuse pollution in agricultural catchments. We focus on the River Eden and its sub-catchment: the River Leith (Figure 1), for which both traditional, low-frequency and automated, high-frequency nutrient monitoring data exist. In particular we: (1) show the value of low-frequency routine monitoring surface and groundwater datasets in understanding catchment-scale variability in nutrient concentrations, (2) compare laboratory-based and *in situ* automated nutrient data and finally, (3) compare simultaneous nutrient determinations from the hourly automated and fortnightly to monthly grab sampling to show how much and what information on nutrient dynamics is lost when sampling frequency is reduced. We evaluate the limitations of both nutrient monitoring approaches and provide recommendations for designing monitoring networks in the future.

Experimental

Study area

The River Eden catchment has been a subject of intensive field and modelling studies evaluating diffuse delivery of nutrients and fine sediments from agricultural land to receiving waters.[28] The River Eden catchment is one of three Defra (Department for Environment, Food and Rural Affairs) Demonstration Test Catchments (DTC) investigating the long-term effects of diffuse pollution on water quality.[28] In particular, intensive research studies facilitating the use of novel high-frequency nutrient monitoring instrumentation are carried out in four River Eden sub-catchments: Leith[27], Moorland, Dacre and Pow[28] covering a wide range of geographical and hydrological settings. In this paper we focus on the River Leith sub-catchment and its lowland reach in Cliburn which has been a subject of intensive hydrogeomorphological and biogeochemical research as a zone of dynamic surface-groundwater interactions.[29] As a result of high spatial variability in sediments lithology and streambed forms, the hyporheic vertical and lateral pathways of nutrients delivery are complex in space and time.[30] The in-stream nutrient concentrations have been monitored in Cliburn since 2009 by an *in situ*, automated laboratory and provide valuable insights into fine temporal structure of P and N responses to hydrological conditions.[27]

The River Leith catchment is sparsely populated (44.4 people per km^2) compared to the River Eden catchment (73 people per km^2) and the UK (256 people per km^2).[31] The majority of the catchment's population is served by the two United Utilities wastewater treatment works in Hackthorpe (425 Population Equivalent (PE) capacity) and Shap (1868 PE capacity) with the final effluent discharging into the River Leith.[32] Recently, significant improvements have been made to the sewerage network including increased capacity of the Shap sewage treatment works and additional treatment installed to reduce P concentrations.[33] Many of the small villages like Great Strickland and Cliburn have been connected to the public sewerage system as a part of the First Time Rural Sewerage programme.[33] No information is available on the number and location of septic tanks in the catchment.

The agricultural land use is dominant in both the River Eden and the River Leith catchments comprising nearly 67% and 85% of the areas (Figure 1). Improved and rough grassland show the largest proportions of 38% and 21% in the River Eden and 63% and 12% in the River Leith catchment. There is a similar proportion of arable land (10%) and built-up areas for both catchments (2%).[34] The River Eden catchment's main aquifers are sustained by the major geological units (Supporting Figure 1) of Permian and Triassic sandstones (Penrith and St Bees Sandstones) in the main Eden valley flanked by the Carboniferous Limestone, Milstone Grit, Ordovician and Silurian sedimentary and volcanic rocks of the Lake District.[35]

Environment Agency routine nutrient monitoring

For the last two decades the EA has been carrying out a comprehensive water quality assessment of surface and groundwaters in terms of chemistry, biology and nutrients (Table 1) known as a General Quality Assessment (GQA). Since 2011 the EA has introduced a new water quality assessment based on requirements of the WFD with the aim to target river reaches of poor ecological status that require mitigating interventions.[36] The new classification focuses on a wider suite of chemical and ecological indicators and is based on a risk assessment of overall ecological status.[36] Under the new WFD classification only reactive phosphorus (RP) is included not nitrate-nitrogen (NO_3-N). Thus we refer to both classifications as appropriate. The threshold P concentrations in the WFD classification are dependent on the characteristics (sampling point altitude) and typology of the water body (mean annual alkalinity measured as mgl^{-1} of $CaCO_3$). For groundwaters, no typology-based classification exists as differences in nitrate concentrations between different environmental (hydrogeological) settings were found to be inconsistent and negligible.[37] A single threshold NO_3-N concentration of 8.5 mgl^{-1} (37.5 mgl^{-1} as NO_3) has been adopted for groundwaters[37] which equals 75% of the Drinking Water Standard and Groundwater Quality Standard (11.3 mgl^{-1} and 50 mgl^{-1} as NO_3^-).[38]

Table 1 Environment Agency Phosphorus and Nitrogen surface water quality classification (grade and mean concentration).[36] For P, WFD classification is given for the type 4n river (the River Leith sampling point 115 m a.s.l and 200 mgl^{-1} $CaCO_3$ 1990-2013, *N*=204)[36] and full WFD classification is give in Supporting Table 1

	Phosphorus (PO_4-P)			Nitrogen (NO_3-N)	
Mean (mgl^{-1})	WFD standard	Mean (mgl^{-1})	GQA grade	Mean (mgl^{-1})	GQA grade
		<0.02	Very low	<1.13	Very low
0.05-0.12	High	0.02-0.06	Low	1.13-2.26	Low
0.12-0.25	Good	0.06-0.10	Moderate	2.26-4.52	Moderately low
0.25-1.00	Moderate	0.10-0.20	High	4.52-6.78	Moderate
>1.00	Poor	0.20-1.00	Very high	6.78-9.04	High
		>1.00	Excessively high	>9.04	Very high

We analysed three nutrient determinands: total phosphorus (TP), total reactive phosphorus (TRP) and NO_3-N routinely measured in 103 surface water and 39 groundwater monitoring points across the River Eden catchment since 1990 (Figure 1, Supporting Tables 2 and 3). TP concentrations are measured at 35% of surface water and 20% of groundwater sites thus we focus mainly on TRP and NO_3-N. The EA routine monitoring TRP measurements, based on the standard colorimetric method[39], are performed on unfiltered water samples and thus TRP concentrations can potentially be higher than soluble reactive phosphorus (SRP) by the amount of easily hydrolysable P leached from suspended sediments in unfiltered samples.[40] Routine monitoring TP measurements facilitate digestion using sulphuric acid and potassium persulphate to convert P fractions to orthophosphate which is then determined colorimetrically.[40] The limits of detection for both methods are 0.008 mgl^{-1} for P and 0.0294 mgl^{-1} for NO_3-N with reporting limits 0.02 mgl^{-1} for P and 0.02 mgl^{-1} for NO_3-N.[41]

To evaluate the changes in the EA monitoring data over time, we calculated simple linear regression for each determinand (Supporting Tables 6 and 7). For linear slopes significant at 0.05 level, a rate of change in concentrations per year was calculated. We analysed rates of concentration change for spatial (land use, bedrock and aquifer depth) and seasonal patterns using analysis of variance.

Hourly *in situ* sampling in the River Leith at Cliburn

The experimental setup of the *in situ*, automated nutrient monitoring laboratory in Cliburn has been described in detail elsewhere[27], thus we present only the key information crucial to understanding the context. An automated and telemetered nutrient laboratory powered by batteries and solar panels is located on the bank of the River Leith. The monitoring unit analyses unfiltered water samples - a simple coarse filter is applied to remove vegetation and debris and prevent the sample line from clogging. The stream water samples are delivered on an hourly basis to the WaterWatch 2610 meter (Partech, UK) which records turbidity (NTU), temperature (ºC), dissolved oxygen (%), conductivity (µScm^{-1}), pH and redox potential (mV). The stream sample is then directed to a Nitratax Plus probe (Hach Lange, DE) measuring NO_3-N and to a sample pot of the two MicroMac C analysers (Systea, IT) facilitating measurements of TP and TRP. The TP analysis is based on the UV/persulphate/acid digestion at high temperature (~97 °C) followed by a modified phosphomolybdenum blue method.[39] *In situ* TP analysis takes 50 minutes and has been optimised for analytical accuracy. *In situ* TRP analysis, based on the phosphomolybdenum blue method[39], takes approximately 10 minutes equates to SRP plus a fraction of particulate P that is reactive to the phosphomolybdenum blue method reagents.[19] Routine lab maintenance takes place on a fortnightly basis including running the reference standards to check the performance of the analysers.

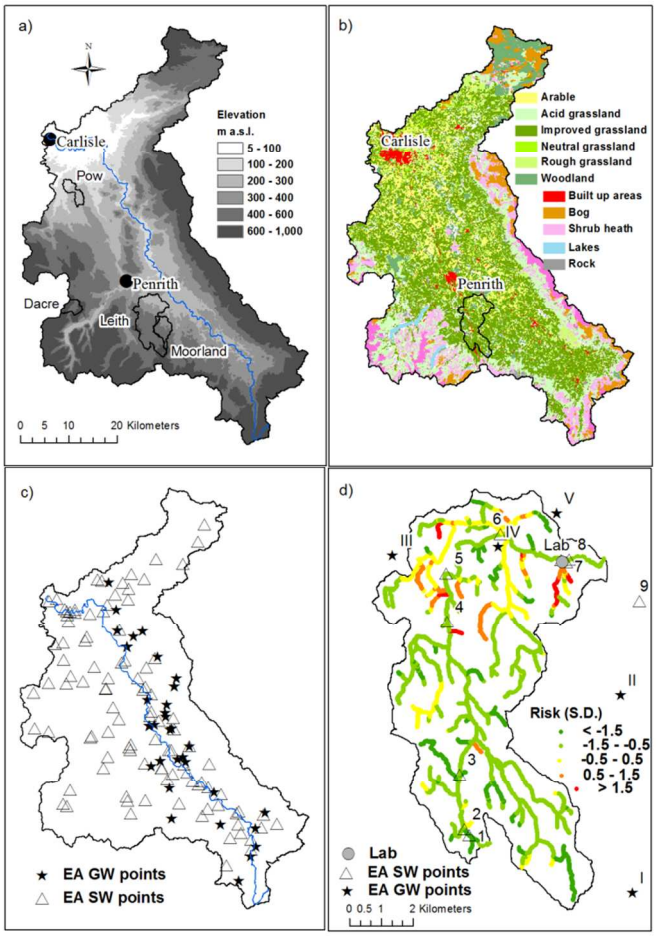

Figure 1 The River Eden catchment: a) DEM[42] and four experimental catchments, b) land cover map[34], c) location of the surface and groundwater EA routine monitoring sampling points, d) the River Leith catchment and the location of the *in situ* nutrient monitoring laboratory. The diffuse pollution risk in channels was modelled with SCIMAP[43] based on the connectivity risk calculated from the DEM, and the erosion risk calculated from the land cover map. The accumulated risk is weighted by the dilution potential of fine sediments delivery in channels. The risk in channels is expressed as a standard deviation of the mean of the risk value. Where the risk is some multiple of the standard deviation greater than the mean, a high risk input to the stream network is identified.[43]

Manual grab sampling in the River Leith at Cliburn

Manual sampling and laboratory analyses are carried out on a weekly to fortnightly basis to provide data for verification of the *in situ* measurements. On each occasion approximately 60 ml unfiltered samples are taken for analysis of TP, TRP and total nitrogen (TN). Samples for analysis of filtered reactive fractions (SRP and NO_3-N) are filtered on site using 0.45 μm cellulose membrane filters to remove bacteria and phytoplankton and to avoid fractionation changes associated with sample storage.[19] All samples are stored in the fridge prior to analysis which is usually carried out on the day of the collection. For all the determinands, samples are run in duplicates and triplicates, with the mean concentration being taken. Intermediate standards and blanks are run every 2-10 samples to check assays reproducibility.

The lab-based and the automated *in situ* nutrient determinations use the same colorimetric basis which enables direct comparison of the concentrations. The colorimetric assays are carried out on an AQ2+ discrete analyser (Seal Analytical, UK) following the manufacturer's recommended methods based on U.S. Environmental Protection Agency method 365.1.[44] Standard errors for each method are calculated as a target concentration of standard solution multiplied by a coefficient of variation of measurements repeated in triplicates and do not exceeded ± 5% for all determinands (TP -2.4%, *S.D.* 8.7%; SRP 0.8%, *S.D.* 6.9%; NO_3-N 0.9%, *S.D.* 8.8%; $N = 101$).

Load estimation

We extracted three sampling periods from the complete datasets to illustrate the nutrient dynamics captured by hourly and EA routine monitoring: 1) May 2011 – Sep 2012, 2) 15 Apr – 19 May 2012 and 3) 26 Aug – 25 Sep 2012 (Figures 5 and 6).

To show the effect of reducing sampling frequency on the annual (from June 2011 to June 2012) load estimation, hourly TRP and NO_3-N time series were resampled in Matlab® to coarser resolution[22, 25, 45]:

- 7-hourly with the first sample collected at 9am and then every sample collected at 7 hour intervals,
- Daily samples collected at 9am and 3pm,
- Weekly sample collected at 9am on Monday,
- Fortnightly sample collected at 9am every second Monday,
- Monthly samples collected at 9am on the 1st, 11th and 21st day of the month.

For all the time series (*in situ* and EA routine monitoring in the three sampling periods and resampled time series) loads were calculated using standard algorithm based on instantaneous concentration (C_i) and flow discharge (Q_i) data[22, 25, 46, 47]:

$$L = \frac{K \sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} Q_\Gamma \quad (1)$$

$$Q_\Gamma = \frac{\sum_{j=1}^{N} Q_j}{N} \quad (2)$$

where L is the load estimate, Q_Γ is the average flow discharge based on 15 minutes data (EA monitoring), Q_j is the 15 minutes flow discharge, K is a constant which accounts for the duration of the record, n is the number of concentration measurements and N is the number of 15 minutes flow measurements.

Nutrient modelling at catchment scale

SCIMAP (http://www.scimap.org.uk/) is a risk based model of diffuse pollution risk in catchments based on high spatial resolution datasets for Digital Elevation Model (DEM), land use and rainfall patterns.[43] SCIMAP embodies the critical source areas (CSAs) paradigm[48] in which the nutrient delivery in the river network is a function of both the distribution of nutrient sources according to land use risk and hydrological connectivity (based on the network index) in the catchment.[49] The relative risk of each location in the catchment generating diffuse pollution is a combined risk of pollution generation (source) and pollution being delivered to the drainage network (delivery). The combined risk is then accumulated along flow paths and diluted to produce a risk concentration.[41, 43] The SCIMAP model for the River Leith catchment was calibrated using readily available spatial datasets resampled to 10 m grids: DEM[42], land cover[34] and rainfall[50] following the procedure described in Reaney *et al.*[43]

Results

N and P concentrations in the River Eden catchment

SURFACE WATERS The EA surface water sampling points are mainly located in the main River Eden valley with a limited spatial coverage for the lower order tributaries and headwaters (Figure 1). The majority of the 103 sites have time series spanning over two decades (1992-2013), however, the temporal resolution is limited to, on average, 6 samples per year (Supporting Tables 4 and 5). Mean surface water TRP concentrations across the catchment are moderate according to the GQA EA classification (Table 1) with the mean value of 0.07 mgl^{-1} and a range between 0.01 mgl^{-1} (N=153, SW_72) and 1.04 mgl^{-1} (N=6, SW_52) (Table 2 and Supporting Table 4). The majority of the sample locations (79%) are of high water quality status in terms of TRP concentrations according to the current WFD classification, with 15% of sites of good, 6% of moderate and a single site of poor quality. Mean NO_3-N concentrations are moderately low with a mean value of 2.2 mgl^{-1} and a range between 0.2 mgl^{-1} (N=7, SW_2) and 8.7 mgl^{-1} (N=206, SW_38). The very low and low GQA EA grades equalling with high WFD quality status (Table 1) dominate for both TRP and NO_3-N comprising over 60% of all sampling points. The highest nutrient concentrations are observed between Penrith and Carlisle for TRP and in the River Eden valley upstream of Carlisle for NO_3-N; the values coincide broadly with the distribution of Penrith and St Bees Sandstones (Figure 1 and Supporting Figure 1).

The land use type at the point of sampling was a significant (p<0.05) discriminator of mean NO_3-N concentrations. The highest values were observed for acid and neutral† (other) grassland class (4.0 mgl^{-1}) and rough grassland (3.5 mgl^{-1}) and

the lowest for the build-up areas (1.5 mgl^{-1}) (Table 2). The mean TRP concentrations were the lowest for the built-up areas (0.04 mgl^{-1}) and improved grassland (0.05 mgl^{-1}) and the highest for rough low-productivity grassland (0.18 mgl^{-1}) and arable land (0.12 mgl^{-1}). Summer TRP concentrations were higher than winter (0.09 vs. 0.05 mgl^{-1}) and winter NO_3-N concentrations were higher than summer (2.67 vs. 1.88 mgl^{-1}). Nearly half of the sampling points showed significant linear trends in concentrations over time, with an average decrease in concentrations between sites; -0.052 mgl^{-1} for NO_3-N and -0.003 mgl^{-1} for TRP per year (Table 2 and Supporting Table 6). The decrease was more pronounced for NO_3-N than for TRP with the highest average decrease for monitoring points on rough grassland (-0.167 mgl^{-1} per year) and arable land (-0.110 mgl^{-1} per year). Similarly to NO_3-N, acid and neutral grassland showed on average an increase in TRP concentrations (0.001 mgl^{-1} per year), whereas built-up areas exhibited the largest average decrease of -0.005 mgl^{-1} per year.

GROUNDWATERS Although both spatial and temporal coverage of the EA routine groundwater sampling points are limited (on average 21 measurements between 1997 and 2013), some clear patterns in groundwater quality were discerned (Table 2 and Supporting Table 5). Mean groundwater TRP (0.7 mgl^{-1}) and NO_3-N (5.7 mgl^{-1}) concentrations were significantly higher relative to surface waters. For over 20% of the sampling boreholes mean concentrations exceeded the drinking water NO_3-N limit of 11.3 mgl^{-1} and 26% exceeded the United Kingdom Technical Advisory Group for the Water Framework Directive (UKTAG) guidance threshold value of 8.5 mgl^{-1}.[37, 38] Significant differences in nutrient concentrations were found between aquifers with concentrations for sandstone (Sherwood, St Bees and Penrith) considerably higher than for the Carboniferous Limestone (Table 2). The differences in mean nutrient concentrations with depth were only significant for NO_3-N (p<0.05) with the highest concentrations at depths of 10-40 m (10.6 mgl^{-1}). The majority of the groundwater sampling points (N=23) showed significant linear slopes over time with the mean decrease in TRP of -0.02 mgl^{-1} per year and in NO_3-N of -0.04 mgl^{-1} per year (Table 2 and Supporting Table 7). The greatest reductions in NO_3-N concentrations were observed for the near surface (0-10 m) aquifer depths.

N and P concentrations in the River Leith catchment

Surface water N and P concentrations in the River Leith catchment exceed those recorded in the River Eden (Supporting Tables 8 and 9) based on 9 surface water EA routine monitoring points: mean TRP 0.28 mgl^{-1} and mean NO_3-N 3.5 mgl^{-1}. However, these average concentrations are highly influenced by the extremely high TRP (1.39 mgl^{-1}) and moderate NO_3-N (5.9 mgl^{-1}) concentrations at monitoring point 2 located 2.5 km downstream of Shap (Figure 1d) affected by the effluent from sewage treatment works. At this point TRP concentrations show a 100-fold decrease in maximum in-stream concentrations from 3.5 mgl^{-1} in 1995 to 0.05 mgl^{-1} in 2012 (SW_84, Supporting Table 6) most likely as a result of significant investments in the public sewerage system.[33]

Table 2 Descriptive statistics of TRP and NO_3-N concentrations in the River Eden catchment measured at the EA surface and groundwater monitoring points (1990-2013). Concentrations are calculated by season and land cover type for surface waters and by aquifer and aquifer depth for groundwaters. Mean value of concentration change per year for significant values (at $\alpha = 0.05$) of linear trend as per Supporting Tables 5 and 6. *N* is the number of monitoring points

	TRP (mgl^{-1})				NO_3-N (mgl^{-1})				
	Mean	**Max**	***S.D.***	**Change per year**	**Mean**	**Max**	***S.D.***	**Change per year**	***N***
Surface waters	0.07	9.37	0.18	-0.003	2.20	51.60	2.39	-0.052	103
Summer	0.09	7.00	0.22	-	1.88	16.30	1.94	-	103
Winter	0.05	1.70	0.08	-	2.67	29.61	2.76	-	103
Improved grassland	0.05	0.15	0.04	-0.001	2.25	8.70	2.46	-0.002	31
Arable	0.12	0.50	0.15	-0.005	2.42	5.20	1.55	-0.110	19
Woodland	0.06	0.16	0.05	-0.003	2.54	5.90	1.72	-0.050	18
Rough grassland	0.18	1.04	0.30	-0.001	3.53	7.40	2.17	-0.167	11
Built-up areas	0.04	0.09	0.03	-0.005	1.46	3.10	0.92	-0.040	8
Other grassland	0.07	0.15	0.05	0.001	4.04	6.80	2.71	0.030	5
Other (bog, shrub heath, montane habitats)	0.08	0.52	0.15	-0.003	1.52	4.30	1.23	-0.004	11
Groundwaters	0.70	17.00	2.17	-0.023	5.70	27.00	1.97	-0.037	39
Sherwood Sandstone	0.87	0.93	0.09	-	13.14	13.24	0.14	-0.180	2
St Bees Sandstone	0.79	1.85	0.47	-0.015	7.96	13.58	4.12	-0.003	11
Carboniferous Limestone	0.37	0.56	0.12	-0.023	2.01	8.73	2.62	-0.092	9
Penrith Sandstone	0.82	1.85	0.45	-0.022	5.51	15.20	3.56	-0.020	16
0-10 m	0.59	1.85	0.55	-0.015	4.52	10.28	3.54	-0.225	9
11-40 m	0.64	0.93	0.27	-0.030	10.63	13.04	2.19	-0.035	3
41-80 m	0.76	1.34	0.34	-0.027	6.58	15.20	4.72	0.011	20
> 81 m	0.70	1.85	0.53	-0.015	2.73	7.16	2.34	-0.025	7

In comparison, the lowland EA monitoring point 7 located 250 m downstream of the *in situ* laboratory shows in the same period a very small negative trend in concentrations with a decrease of 0.025 mgl^{-1} (SW_73, Supporting Table 6). Both points show a similar decrease in NO_3-N concentrations with an average rate of -0.04 mgl^{-1}/year with the lowland location showing a wider range of concentrations (0.2-9.8 mgl^{-1}).

The mean in-stream nutrient concentrations were generally lower than the mean concentrations for groundwaters (Supporting Table 9). Significant differences (p<0.05) in the mean groundwater nutrient concentrations were observed between Carboniferous Limestone and Penrith Sandstone boreholes located in the North, lowland part of the catchment (Figure 1). Carboniferous Limestone points showed very low TRP and NO_3-N concentrations (<0.03 mgl^{-1} and <1 mgl^{-1}) compared to the Penrith Sandstone (>0.10 mgl^{-1} and >4 mgl^{-1} monitoring points; Supporting Table 9). This pattern is consistent with the observations made on the River Eden catchment scale.

Figure 1d shows spatial distribution of the EA routine monitoring points in the River Leith catchment and the distribution of diffuse pollution risk in the river network derived from the SCIMAP risk-based approach.[43, 49] The diffuse pollution risk in the upstream reaches of the River Leith and its tributaries is low-to-medium relative to medium-to-high risks observed in the lowland part of the catchment (Figure 1d). The lowland part of the catchment demonstrates a patchy distribution of high diffuse pollution risk due to a mosaic of high risk land use (arable land and grassland) and variable hydrological connectivity. The high diffuse pollution risk appears typified by short, lowland tributaries draining arable land on hillslopes: such locations have high erosion and connectivity potential. The lowland reaches of the River Leith upstream of the *in situ* laboratory exhibit low-to-medium diffuse pollution risk. The EA monitoring points are located along the main stem of the River Leith and do not target the high risk tributaries controlling the diffuse nutrient pollution in the catchment.

High-frequency nutrient monitoring in the River Leith catchment

Intensive nutrient monitoring of the River Leith provides two temporal datasets. The first dataset is based on manual samples collected on a weekly-to-fortnightly basis and analysed in the laboratory for a range of determinands. Dissolved fractions were found to be dominant P and N forms comprising 81.8% of TP and 97.3% of TN (Table 3). A significant (at α=0.05) relationship was observed between TRP and SRP nutrient fractions with Pearson's correlation coefficient value of R=0.96 and SRP comprising 94% of TRP (Figure 2b).

The second dataset comprises *in situ* hourly determinations of TP, TRP and NO_3-N and provides much larger sampling frequencies and nutrient ranges relative to the grab sampling (Table 4). *In situ* TP and TRP concentrations were an order of magnitude higher than the grab samples collected in the same study period (Figure 2 c and d).

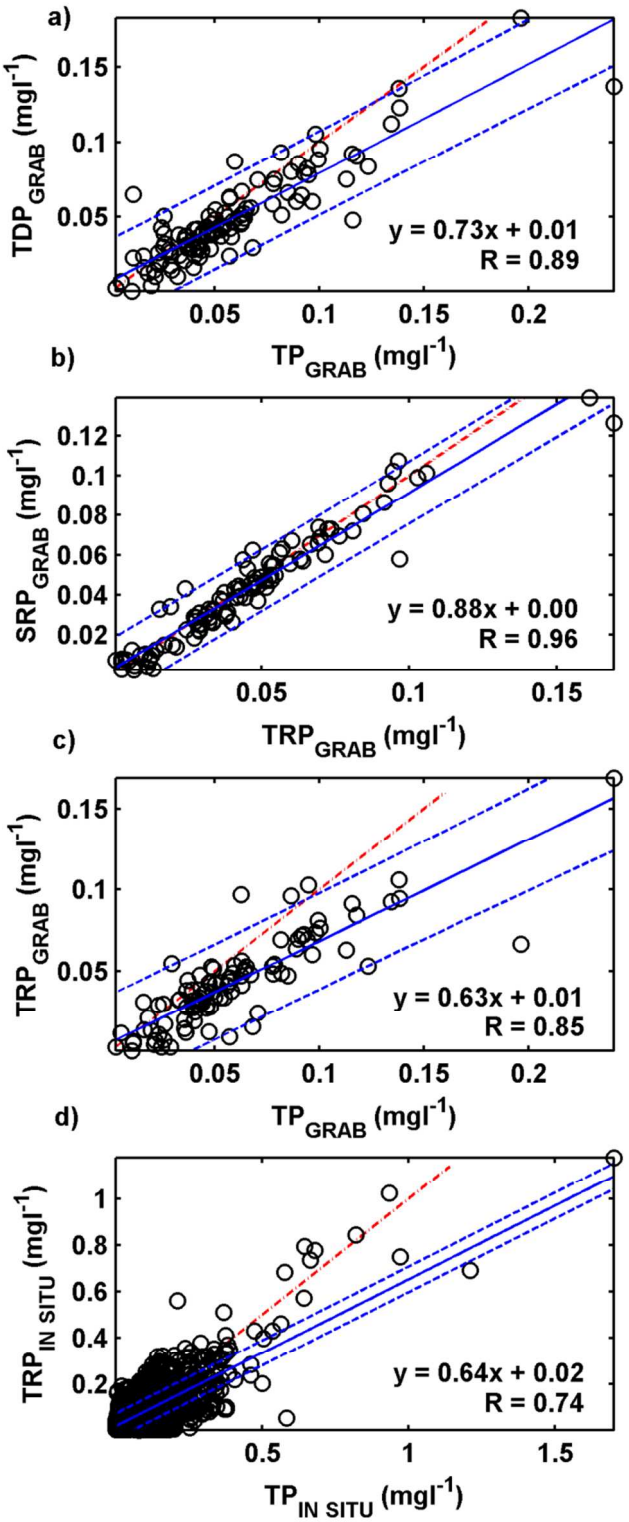

Figure 2 Linear correlations for selected Phosphorus fractions for the spot grab samples (GRAB) and hourly automated *in situ* measurements (IN SITU). The dashed lines indicate 95% confidence limits of the best-fit line (thick blue line) and the red line denotes 1 to 1 relationship

Table 3 Descriptive statistics for the grab samples P and N fractions (2009-2012). Concentrations in mgl^{-1}

mgl^{-1}	*N*	Mean	*S.D.*	Max	% of TP or TN
TP	110	0.06	0.06	0.51	100.0
TDP	113	0.05	0.04	0.25	81.8
TRP	103	0.04	0.03	0.17	70.9
SRP	110	0.04	0.03	0.14	67.0
TN	108	2.94	0.52	4.08	100.0
TDN	104	2.86	0.89	3.99	97.3
NO_3-N	111	2.45	0.56	3.54	83.3

The *in situ* measurements of TP and TRP are carried out independently of each other and are based on distinct methodologies with no inter-analyser calibration. Thus although by definition TRP concentrations cannot be larger than TP concentrations, we observed lower TP than TRP concentrations in 28.8% of cases. We analysed the origins of this phenomenon by comparing two groups of data TRP>TP and TP>TRP. Total phosphorus was generally lower than TRP at low phosphorus concentrations (TP=0.025, *S.D.*=0.022, TRP=0.037, *S.D.*=0.028 mgl^{-1}) and low contribution of suspended sediments approximated by the turbidity measurements (1.4 NTU, *S.D.*=1.5 NTU). Significant differences ($p<0.01$) between the two groups were observed with the TRP>TP occurring at lower stream discharge (Q_{mean}=0.68 vs. 2.15 m^3s^{-1}), lower turbidity concentration ($TURB_{mean}$=1.4 vs. 2.9 NTU) and higher air temperature ($TEMP_{mean}$=10.2 vs. 7.4°C).

High contribution of TRP in TP (70.9% based on grab samples) provides a potential for cross-over between the fractions. This can particularly occur at low TP concentrations (<0.1 mgl^{-1}) at which TP variation was significant. We ran an experiment in which a constant standard solution of 0.1 $mgPl^{-1}$ has been analysed by both TP and TRP analysers for *N*=89 hours. Both analysers showed similar average concentrations TP=0.099 and TRP=0.097 mgl^{-1}, however the TP concentrations varied between 0.058-0.109 mgl^{-1} (*S.D.*=0.0085 mgl^{-1}) compared to a much narrower range for the TRP 0.090-0.109 mgl^{-1} (*S.D.*=0.0038 mgl^{-1}).

Higher degree of variation in TP compared to TRP measurements was also observed during the regular in field calibration of analysers as measured by the mean percentage deviation (-17.8% and -14.6%) and coefficient of variation (30.1% and 14.9%). On average TP and TRP concentrations were 10.2% and 8.4% lower than the calibrant concentration of 0.075 mgl^{-1} (TP_{mean}= 0.067 mgl^{-1}, *S.D.*=0.020 mgl^{-1}, *N*=92, TRP_{mean}=0.069 mgl^{-1}, *S.D.*=0.010 mgl^{-1}, *N*=105). Likewise, NO_3-N concentrations were on average 8.3% lower than the target concentrations of 4.0 mgl^{-1} (NO_3-N_{mean}=3.7 mgl^{-1}, *S.D.*=0.7 mgl^{-1}, *N*=45).

Comparison between low and high-frequency nutrient data

CONCURRENT NUTRIENT DATA Nutrient determinations based on the concurrent water samples were compared between different datasets (*in situ*, grab and EA sampling) to provide an evaluation of the performance of the *in situ* laboratory. The *in situ* and grab water samples were collected at the same location and the EA monitoring station is located 250 m downstream of the *in situ* laboratory (Supporting Tables 8 and 9). The number of concurrent samples varied between the datasets and determinands (Table 4).

Mean *in situ* P concentrations were generally lower than corresponding measurements from laboratory-based sampling by 40% for TP and 3-8% for TRP (Table 4). The *in situ* mean NO_3-N concentrations were consistently higher than both low-frequency datasets by 8% for grab and 2% for the EA data. A regression between concurrent nutrient concentrations determined *in situ* and in the laboratory suggested a reasonably good correlation for all determinands (Figure 3). The *in situ* TP measurements were underestimated with above unity slopes for the grab (α=1.21) and EA samples (α=1.32, Figure 3a).

Table 4 Descriptive statistics of the low and high-frequency nutrient datasets, spot grab sampling (GRAB), EA routine monitoring (EA) and hourly automated *in situ* monitoring (IN SITU). All samples for each monitoring for all data were collected between 2009 and 2012 whereas concurrent samples are samples collected at the same time by *in situ*-grab or *in situ*-EA monitoring

Dataset	TP (mgl^{-1})					TRP (mgl^{-1})					NO_3-N (mgl^{-1})				
	N	Min	Max	Mean	*S.D.*	*N*	Min	Max	Mean	*S.D.*	*N*	Min	Max	Mean	*S.D.*
All samples															
GRAB	108	0.005	0.241	0.058	0.038	103	0.005	0.169	0.044	0.030	111	1.03	3.55	2.43	0.54
EA	226	0.020	1.000	0.072	0.092	252	0.020	0.826	0.049	0.062	252	0.97	4.81	2.58	0.61
IN SITU	15488	0.005	2.683	0.041	0.055	16956	0.005	1.180	0.042	0.039	9228	0.19	5.33	2.57	0.48
Concurrent samples															
IN SITU	56	0.005	0.092	0.034	0.022	58	0.008	0.081	0.038	0.016	33	1.48	3.47	2.62	0.52
GRAB	56	0.005	0.138	0.051	0.029	58	0.005	0.106	0.039	0.026	33	1.03	3.25	2.42	0.50
IN SITU	74	0.005	0.178	0.031	0.027	91	0.008	0.121	0.033	0.021	47	1.68	3.56	2.56	0.44
EA	74	0.020	0.320	0.050	0.042	91	0.020	0.143	0.036	0.022	47	1.76	3.27	2.52	0.39

Regression slopes for TRP were close to 1:1 ratio and suggested an overall underestimation in both grab (α=0.95) and EA samples (α=0.85; Figure 3b). In general, the TRP regression was strong (R=0.90, p<0.01) at moderate concentrations but there was a poor agreement in both the lower (<0.02 mgl^{-1}) and higher concentration ranges (>0.07 mgl^{-1}). The EA samples at the lower detection limit (0.02 mgl^{-1}) were excluded from the regression; both *in situ* and grab methods have similar limits of detection (0.005 mgl^{-1}). Of the three determinands the strongest linear correlations were found for NO_3-N with slopes indicating overall underestimation of low-frequency datasets: grab α=0.75 and EA α=0.81 (Figure 3c).

To further quantify the differences between fractions measured *in situ* and their laboratory-based equivalents a mean percentage deviation was calculated. The overall percentage error for *in situ* TP determinations was -25.4% (*S.D.*=43.8%) compared to grab samples with significantly lower mean underestimation for the concentrations <0.03 mgl^{-1} (-0.3% *S.D.*=58.4%) compared to the concentrations >0.03 mgl^{-1} (-35.0% *S.D.*=32.9%). The corresponding error was similar for the *in situ* TP when compared to the EA samples (-38.8% *S.D.*=33.4%) for the concentrations >0.02 mgl^{-1}. The *in situ* TRP concentrations were on average 19.4% (*S.D.*=90.5%) higher than the laboratory-measured concentrations. However, a positive error was typical in the <0.02 mgl^{-1} range (124.6%, *S.D.*=154.7%) and a negative in the >0.02 mgl^{-1} range for both grab (-9.2%, *S.D.*=20.7%) and EA samples (-8.1%, *S.D.*=31.3%). For NO_3-N a small mean error of 5.4% (*S.D.*=14.1%) for grab and 1.8% (*S.D.*=7.5%) for EA samples was found.

ALL NUTRIENT DATA To evaluate the range of nutrient concentrations captured by each monitoring regime we compared all data collected in the study period (Table 4). The *in situ* monitoring showed the greatest range of concentrations for all determinands and lower mean concentrations compared to low-frequency sampling. The TP-TRP relationship showed similar slope and intercept values of 0.63 for the *in situ*, 0.64 for the grab and 0.60 for the EA routine monitoring (Figure 2 cd, EA data not shown here).

To show the difference in sampling frequency we used a simple Kernel smoothing function to estimate the probability density distribution for the complete time series of *in situ*, grab and EA nutrients concentrations (Figure 4). All determinands showed unimodal distribution with a positive skew (right-hand side) for P time series and a normal-like distribution for the NO_3-N time series. The concentration frequency distribution can be linked to the relationship between nutrient concentration and flow. Both P fractions show increases in concentrations with flow (Figure 5), whereas for NO_3-N high flows can lead to both concentration (increase in concentrations) and dilution (decrease in concentrations) effects (Figure 6). Both the flow discharge and P concentrations show a positive skew which suggests the predominance of the concentration effect with increasing flow discharge indicative of diffuse inputs. For the NO_3-N time series a normal-like distribution suggests uniform importance of both dilution and concentration effects.

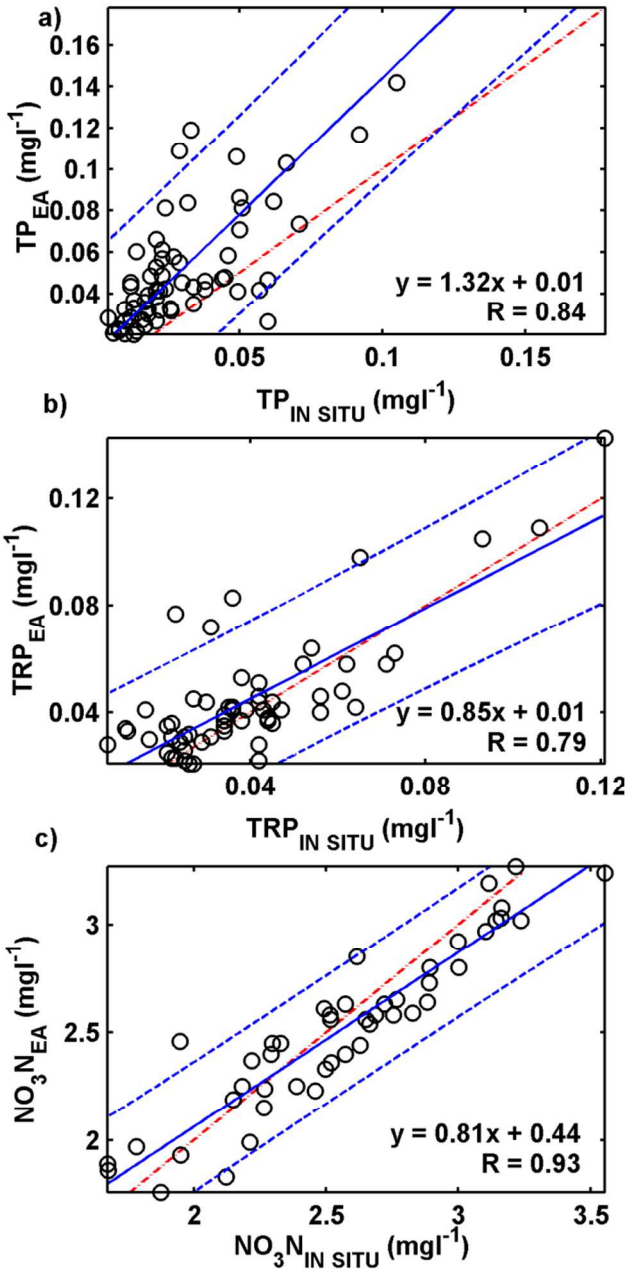

Figure 3 Linear correlations for TP (a), TRP (b) and NO_3-N (c) between EA routine monitoring and hourly automated *in situ* measurements. The dashed lines indicate 95% confidence limits of the best-fit line (thick blue line) and the red line denotes 1 to 1 relationship

For all three determinands the *in situ* sampling showed the widest range of concentrations, especially compared to spot grab sampling that significantly undersampled both low and high concentrations. The *in situ* monitoring sampled the widest range of flows (0.045-176 m^3s^{-1}) compard to both the EA (0.051-138 m^3s^{-1}) and manual sampling (0.055-87 m^3s^{-1}). Although the mean P concentrations indicate high quality status (Table 1) according to the WFD classification, the absolute

range of P concentrations captured by the high-frequency data spans all water quality classes (from high to poor). For the NO_3-N concentrations a much narrower chemical range is observed as the concentrations change in the range between low to moderate GQA classes (Table 1). The good agreement between TRP *in situ* and EA time series for the highest concentrations resulted from the EA targeting the storm event on 10-12th of August 2011 when the highest TRP concentration in the study period (0.88 mgl^{-1} EA and 1.18 mgl^{-1} IN SITU) was recorded.

The maximum density estimates for *in situ* determinations of TP appear at considerably lower concentrations (0.022 mgl^{-1}) compared to grab (0.040 mgl^{-1}) and EA routine monitoring (0.041 mgl^{-1}) samples. For TRP there is a good agreement between *in situ* and EA routine monitoring maximum density (0.020 and 0.022 mgl^{-1}) with grab samples showing maximum density concentration of 0.040 mgl^{-1}. The NO_3-N distribution is generally consistent between the three sampling approaches with the maximum probability density estimate for concentration value of 2.5 mgl^{-1} (Figure 4c).

To highlight the main advantages and limitations of both low and high-frequency nutrient monitoring, both automated *in situ* and EA routine monitoring TRP and NO_3-N time series were plotted in Figures 5 and 6.

The high-frequency TRP and NO_3-N time series exhibit a much wider range of concentrations compared to EA routine monitoring data and responses to individual storm events are apparent (Figures 5a and 6a). Although the EA time series does not provide insights into storm-event nutrient dynamics, the general concentration trends are preserved for both TRP and NO_3-N, including the seasonal variation in NO_3-N of low summer (~2.0 mgl^{-1}) and high winter (~3.5 mgl^{-1}) concentrations. The load estimation based on instantaneous concentration and discharge in the sampling period shows significant underestimation of NO_3-N load for both low-frequency datasets relative to hourly data: -29.2% for EA and -30.1% for grab samples (Table 6). The TRP loads are overestimated by 7.1% for the EA and underestimated for the grab samples by-17.8% (Table 6). On a storm event-basis (Figures 5b and 6b) the value of high-frequency over low-frequency nutrient monitoring becomes evident. High-frequency monitoring provides detailed information on nutrient responses to increased flow discharge from which further insights can be gained on the potential nutrient sources. The in storm nutrient dynamics can be complex as shown on the example of the storm event on 25th of September (Figures 5c and 6c). The storm event followed dry summer with potentially significant accumulation of nutrients in near and within- stream sources. For both TRP and NO_3-N the first-flush effect can be observed with a rapid increase in concentrations on the rising limb of the hydrograph. The double-peak hydrograph produced two different nutrient behaviours, concentration for TRP and dilution for NO_3-N as captured by the *in situ* laboratory. A delayed response in TRP concentrations (anticlockwise behaviour) to the second flow peak and the presence of an exhaustion effect (lower concentration for consecutive storm flow peaks) can be observed. EA routine monitoring does not capture the individual storm events unless they are specifically targeted (Figure 6c, storm event on the 25th of September). The storm event targeting improves the measured nutrient range of sampling and load estimation (Table 6) but offers very limited information on the chemical behaviour of the system. Similarly, during baseflow conditions (Figure 6c) high-frequency monitoring shows strong diurnal signal in NO_3-N concentrations which is not replicated by the low-frequency monitoring. During high flow conditions (Figures 5b and 6b) the underestimation of loads calculated from the low-frequency data is evident: -65.4% for TRP and -22.7% for NO_3-N (Table 6). During baseflow conditions (Figures 5c) TRP EA loads are overestimated as the concentrations reach the EA detection limit of 0.02 mgl^{-1}. Finally, the effect of reducing the sampling frequency on load estimation can be observed for hourly data resampled to lower frequencies (Table 6). There is a clear difference between TRP and NO_3-N load estimates with TRP load underestimation significantly increasing for coarser datasets and lower, both positive and negative errors associated with the NO_3-N estimates (Table 6).

Table 6 TRP and NO_3-N load estimation for the *in situ* and EA routine monitoring time series in Figures 5 and 6 and artificially resampled *in situ* time series to coarser resolution

Dataset	Load estimate		Difference from hourly load estimate	
	TRP (kg Pyr^{-1})	NO_3-N (kg Nyr^{-1})	TRP (%)	NO_3-N (%)
May 2011-Sep 2012 Figures 5-6 a				
IN SITU	5790	143200	-	-
EA	6200	101400	7.1	-29.2
GRAB	4760	100100	-17.8	-30.1
15 Apr – 19 May 2012 Figures 5-6 b				
IN SITU	260	13100	-	-
EA	90	10100	-65.4	-22.7
GRAB	50	8700	-80.8	-33.7
26 Aug – 25 Sep 2012 Figures 5-6 c				
IN SITU	530	11400	-	-
EA	770	9900	45.3	-13.2
GRAB	350	13200	-36.0	15.8
Resampled time series				
Hourly	3720	96700	-	-
7h	3470	95700	-6.7	-1.0
Daily (9am)	4240	93900	14.0	-3.0
Daily (3pm)	5530	101000	49.0	4.4
Weekly	1330	97400	-64.2	0.7
Fortnightly	1350	102500	-63.8	6.0
Monthly (1st)	2040	92200	-45.2	-4.7
Monthly (11th)	1170	94700	-68.6	-2.1
Monthly (21st)	1630	93100	-56.2	-3.7

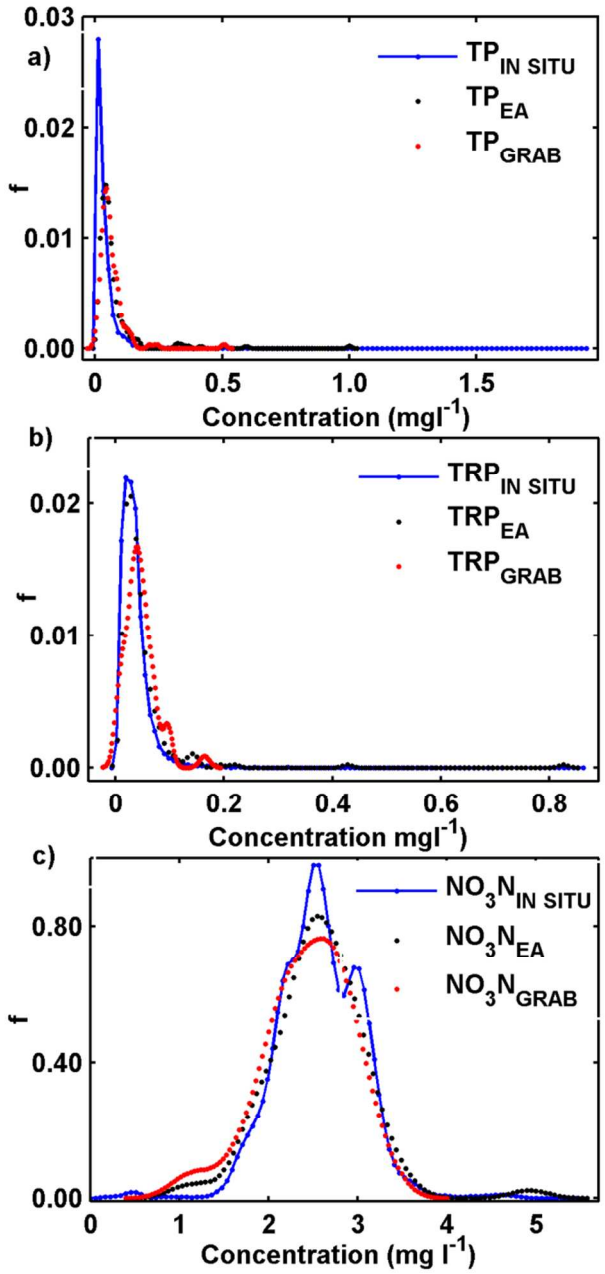

Figure 4 Probability density estimates (f) for *in situ*, grab and EA routine monitoring for a) TP, b) TRP and c) NO_3-N time series. The distributions are calculated from the complete time series collected in the same period: May 2009 - Oct 2012 for TP and TRP and May 2011 – Oct 2012 for NO_3-N (Table 4). Calculated as the kernel smoothing function estimate evaluated at 100 equally spaced points

Discussion

Spatial and temporal patterns in nutrient concentrations

Although the River Eden EA monitoring record comprises only a few samples per monitoring site, as the complete dataset spans over twenty years it provides basic evidence of the distribution of catchment nutrient sources and their effect on the in-stream nutrient concentrations over time.[40,51,52] We observed spatial patterns of high NO_3-N concentrations correlated with agricultural land uses that are consistent with the findings of other studies relating catchment characteristics to nutrient concentrations.[51,53] Spatial correlation of TRP concentrations with the land use at the sampling point was poorer compared to NO_3-N. Other studies showed that the presence of point P sources[51] and in-stream processing[53] can affect the relationship and stressed the importance of hydrological connectivity as nutrient sources can potentially be distant in space and time from the locations in the stream network where their negative impact is observable or measurable.[41,55]

Both determinands showed significant temporal trends with a mean annual decrease of -0.003 mgl^{-1} for TRP and -0.052 mgl^{-1} for NO_3-N. These substantial reductions in nutrient concentrations in recent years can potentially be linked with a number of factors including ongoing improvements in the public sewerage system[33], reductions in atmospheric deposition[56], changing fertiliser and land use practices[57] and the introduction of mitigation measures e.g. Catchment Sensitive Faming (CSF) scheme introduced in 2006.[33,58]

On a sub-catchment level, we observed a two orders of magnitude decrease in the River Leith mean TRP concentrations over a relatively short distance of 15 km between site 2 with known sewage effluent[32] and a lowland site 7. Rothwell *et al*.[51] showed that for agricultural catchments with no major point sources TRP concentrations do not exceed 0.06 mgl^{-1} and they can be characterised by high in-stream nutrient attenuation capacity. Intensive in-stream processing including biological uptake, sediment binding.[25,59] and nutrient attenuation along the subsurface pathways can play an important role in controlling nutrient concentrations in groundwater-dominated catchments.[60,61] The lowland part of the River Leith catchment has been shown to sustain intensive surface-groundwater interactions that control transformations of soluble fractions of N and P in the hyporheic zone including denitrification, microbial uptake and transient storage.[30,62]

An important consideration in analysing current and future trends in surface water nutrient concentrations is the role of groundwaters. The aquifers consistently show higher nutrient concentrations compared to surface waters. The biogeochemical time lags associated with subsurface pathways can potentially delay nutrient concentration responses to best management practices and mitigation strategies and make meeting the demands of the WFD problematic.[57,63,64] Wang *et al*.[65] estimated that the peak nitrate loading for Penrith Sandstone in several areas of the Eden catchment including Cliburn will arrive in around 34 years. Thus in the next decades surface water nitrate concentrations might continue to rise despite the best efforts to minimise the catchment-scale nitrate exports to aquatic systems.

Uncertainty in low and high-frequency nutrient data

The number of studies evaluating the analytical uncertainty of the *in situ* sampling are limited[17, 18]. Our evaluation shows that the *in situ* 'wet chemistry'-based determination of P, at near

detection limit, is more challenging compared with much simpler spectroscopic determination of NO_3-N. The underestimation of the TP fraction (-25% relative to grab and -39% relative to EA sampling) was much larger than TRP (-9% compared to grab and -8% compared to EA sampling). Similar results were reported by Jordan *et al.*[18] who showed that *in situ* TP readings were consistently 20% lower than the laboratory tests. However, a direct comparison in performance can be difficult as different types of *in situ* analysers were used in the two studies, Systea's MicroMac here and Lange's Phosphax in the study of Jordan *et al.*[18] The analysers can potentially differ in terms of analytical sensitivity and utilised methodologies and the baseflow TP concentrations (~0.03 mgl^{-1}) in the River Leith are lower and closer to the lower detection limit (0.005 mgl^{-1}) than those reported by Jordan *et al.*[18] (~0.06 mgl^{-1}). At this concentration range we observed a high degree of variation *in situ* TP concentrations and occasionally lower TP than TRP concentrations. As both measurements are taken from the same sample, this phenomenon can be a combination of several factors including 1) low analytical sensitivity of the TP analyser at low P concentrations, 2) incomplete *in situ* digestion resulting in lower TP concentrations and 3) a high contribution of TRP in the total P pool and low difference in TP and TRP concentrations. The Systea's MicroMac analyser was originally designed to monitor TP concentrations in waste activated sludge and effluents from sewage treatment works that typically show much higher phosphorus concentrations than observed in the River Leith[66].

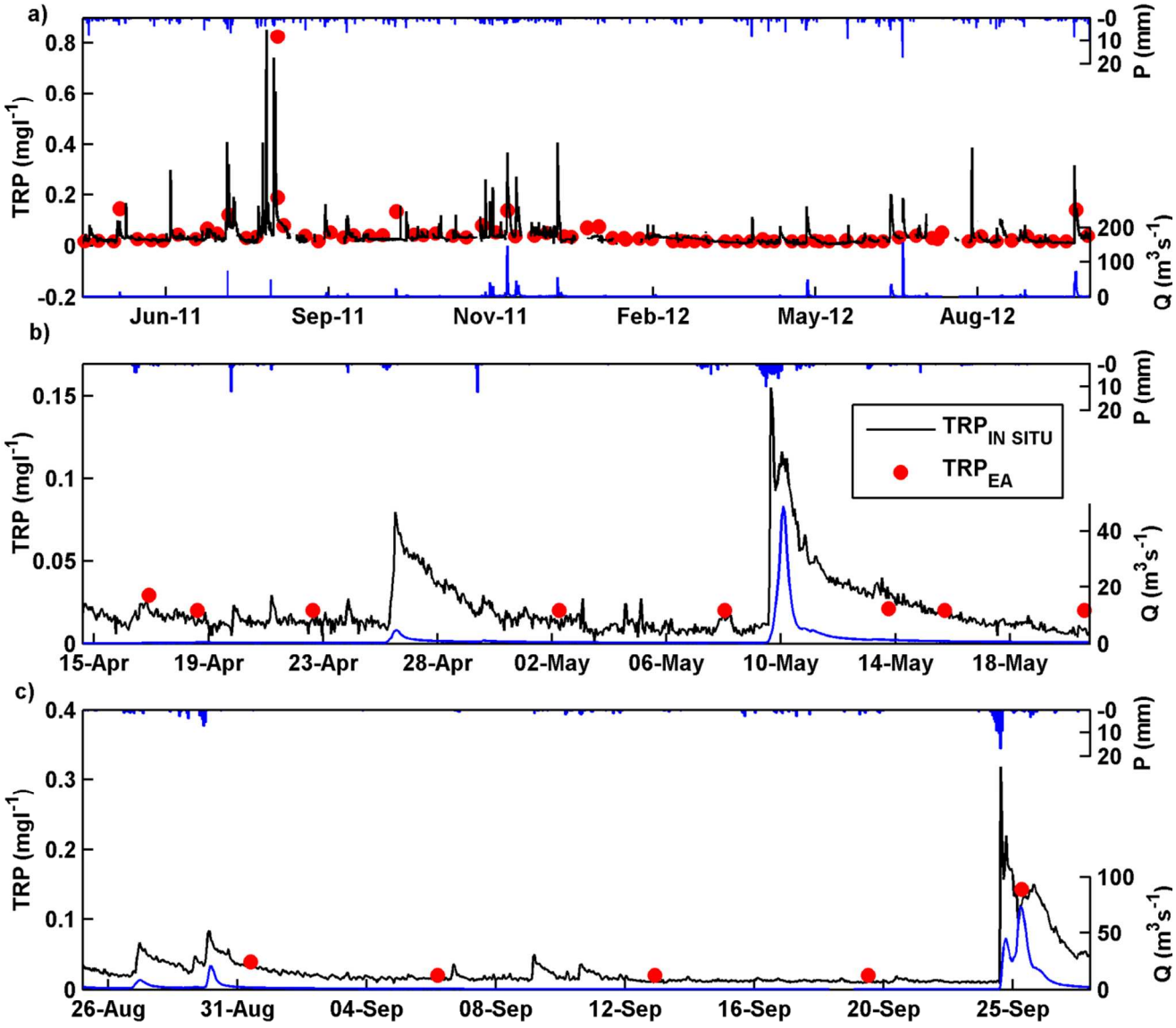

Figure 5 Time series of hourly automated *in situ* TRP and EA routine monitoring TRP measurements for the EA sampling point 7 in Figure 4. Flow discharge in blue (the right-hand vertical axis) and rainfall in blue (the top axis). a) May 2011-Sep 2012, b) 15 Apr – 19 May 2012, c) 26 Aug – 25 Sep 2012

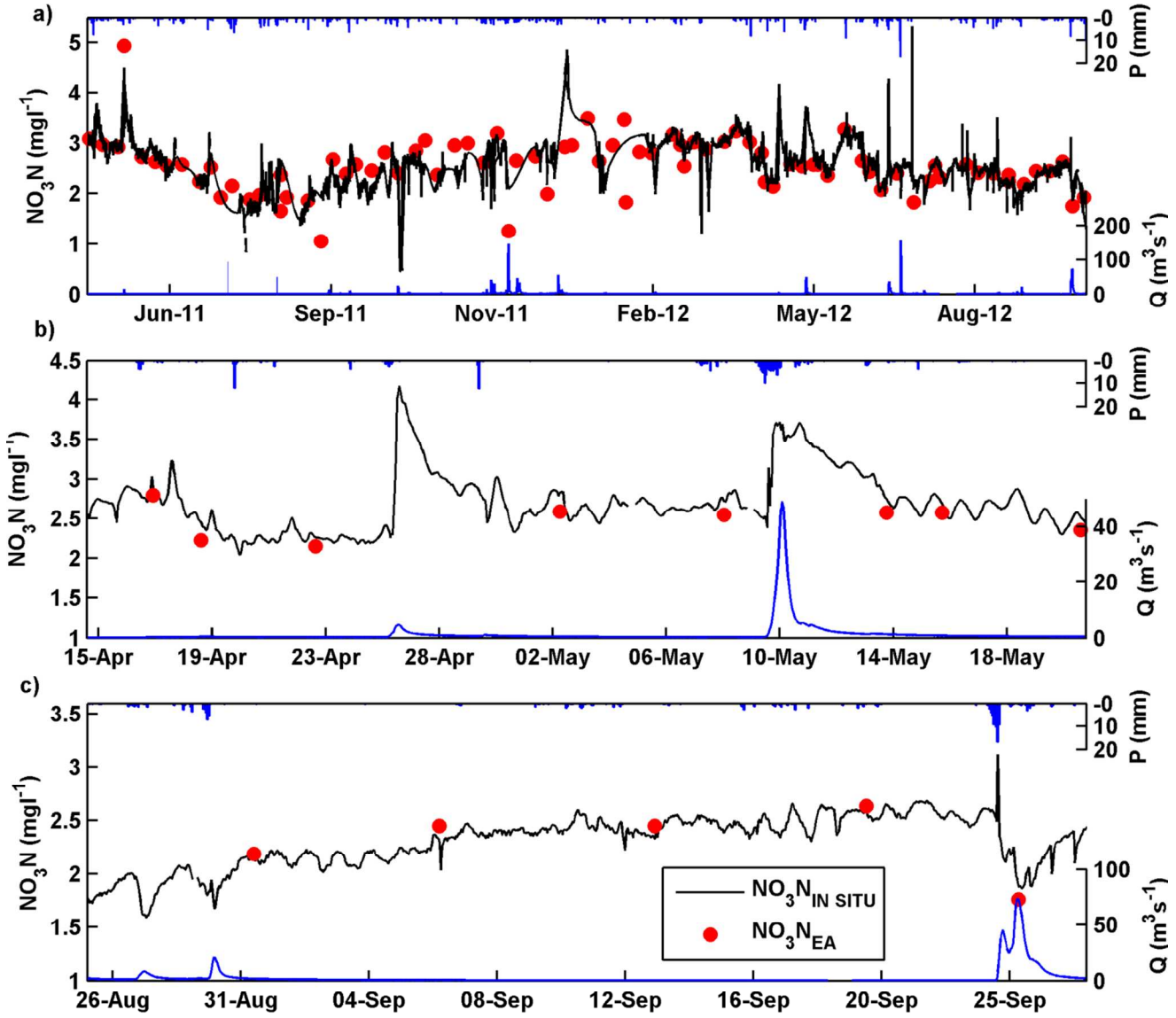

Figure 6 Time series of hourly automated *in situ* NO_3-N and EA routine monitoring NO_3-N measurements for the EA sampling point 7 in Figure 4. Flow discharge in blue (the right-hand vertical axis) and rainfall in blue (the top axis). a) May 2011-Sep 2012, b) 15 Apr – 19 May 2012, c) 26 Aug – 25 Sep 2012

The errors associated with *in situ* facilitation of TP chemical determination can also result from several factors affecting the effectiveness of the digestion including change in oxidant concentration, digestion temperature, sample matrix and the amount of suspended solids.[19] In our study, the TP measurements were temperature-independent in the range of ambient temperatures recorded at the site (from -6 to 28ºC) and the digestion temperature was found stable between measurements controlled by a large coiled-tube heater (data not shown here). Jordan *et al.*[18] suggested that underestimation of the *in situ* TP measurements can also be caused by lower extraction of particulates by the *in situ* sampling unit rather than inefficient digestion. Jarvie *et al.*[19] showed that the incomplete recovery of TP can occur at high suspended solids concentration as a result of failure of acid-persulphate digestion to fully release P contained in oxides.

The slopes of linear TRP and NO_3-N correlations suggest that the laboratory-based determinations are lower compared to *in situ* concentrations and can potentially suggest underestimation of the reactive forms of P and N. Although laboratory analysis of the grab samples in our study was usually performed on the day of collection, a minimum of four hours passed from sample collection to commencing the laboratory analyses. The time delay between collection and analysis can lead to storage-related transformation of reactive fractions in water sample.[20] For refrigerated water samples analysed within 54 hours post collection storage-related errors can be significant: TP -7 to 92%, SRP -14 to 22% and NO_3-N -47 to 14%.[20, 21] The

occurrence of the storage-related losses of dissolved P in grab samples is generally the highest for the low concentration samples[19-21,67]; this is consistent with observations from our study as the differences in TRP between grab, EA and *in situ* samples were the largest for P concentrations <0.03 mgl^{-1}. The potential decreases in the TRP fraction in grab samples can result from P readsorption to sediment particles, microbial uptake and chemical precipitation.[19] At a higher concentration range we observed higher grab sample TRP concentrations compared to *in situ* measurements that can potentially result from 1) underestimation of *in situ* measurements and/or 2) the overestimation in grab samples due to hydrolysis of organic and polymeric P, phosphorus desorption from sediment particles and mineralisation in unfiltered water samples.[19]

Implications for nutrient monitoring

High-frequency monitoring reveals patterns of nutrients concentration changes that are not captured by the infrequent routine monitoring. These patterns include the presence of hysteretic behaviour during storm events[23,26,68,69], diurnal cycling[4,17,23,25,70-72] and non-storm transfers of P.[10,18,23] High-frequency nutrient responses have also been explained in the context of seasonal variation in nutrient source, mobilisation and delivery.[3, 23] For the River Leith, high-frequency monitoring reveals complex nutrient behaviour during both baseflow and high flow conditions, including concentration-discharge hysteresis and switches between dilution and concentration flow patterns. Other studies showed that the presence of both dilution and concentration effects of NO_3-N concentrations during storm events suggest the presence of different delivery mechanisms and differences in dominant hydrological pathways.[23,26] Patterns of decreasing concentrations with flow were shown to indicate a groundwater source that becomes diluted at high flows[73], whereas a concentration effect was linked with mobilisation of nitrate from soil horizons.[26] A seasonal pattern of low summer and high winter NO_3-N concentrations, observed for both the River Leith and the River Eden catchments, potentially reflects seasonal processes in the catchment: increased soil mineralisation, flushing of nitrogen from agricultural land, fertiliser runoff and increased groundwater inputs to the stream during autumn and winter and intensive in-stream processing including biological uptake during spring and summer.[25,73,74] Low TRP (0.05 mgl^{-1}) mean concentrations observed in the lowland part of the River Leith catchment suggest a lack of major point sources and a predominance of diffuse agricultural nutrient sources as might be expected by the low population density.[6,7,64,75] Diffuse delivery of TRP has been shown to occur along both surface and subsurface delivery pathways.[25,61]

This important temporal information on nutrient dynamics is lost when the sampling frequency is reduced to weekly-to-monthly measurements.[4,12,20,24,25] Harmel *et al.*[20] showed that less intensive manual sampling can introduce substantial uncertainty in measured nutrient data as it does not capture the temporal variability in constituent concentrations. The low-frequency strategies tend to under-sample nutrient concentrations occurring at the extreme hydrological conditions resulting in a narrower range of nutrient concentrations and leading to significant errors in nutrient load estimation[12,17,27,69,76] The annual nutrient loads (0.69 kg TRP $ha^{-1}yr^{-1}$ and 17.9 kg NO_3-N $ha^{-1}yr^{-1}$) in the River Leith are comparable with similar small rural catchments.[7,22,25,77] However many of these catchments have a higher population density and are affected by point sources and as a result, exhibit dilution of P concentrations during high flows. The effect of reducing sampling frequency on load estimation in our study was more pronounced for TRP than NO_3-N, unlike in other studies where a similar effect was observed for both determinands[25]. The underestimation of TRP load increased dramatically from -7% for every 7h sampling to -70% for frequencies lower than weekly. A similar uncertainty in load estimation (up to 60%) was observed in the study of a small flashy catchment by Cassidy and Jordan[15] who concluded that only hourly and sub-hourly sampling sufficiently captures P export during storm events. The errors in the NO_3-N loads overall did not exceed 6% and were similar for different sampling frequencies, e.g. daily load estimates were as accurate as monthly ones. The observed differences in uncertainty of load estimation result from differences in dominant nutrient sources and delivery pathways between TRP and NO_3-N. The P delivery is episodic as it occurs during storm events and the concentrations can change dramatically, from high to poor chemical status over a very short period (hours). The NO_3-N concentrations show a much narrower chemical range due to the presence of internal sources (groundwaters) of solute to buffer the periodicity in episodic inputs.[78] The chemostatic behaviour for NO_3-N and resultant consistency in load estimation for different sampling frequencies was also observed by Wade *et al.*[25] in a groundwater-dominated catchment of the River Enborne.

As the goal of the routine monitoring is to capture current and future ecological and chemical status, the underrepresentation of extreme nutrient concentrations can lead to misclassification of nutrient status[17]. We show that for P low-frequency sampling potentially overestimates the nutrient concentrations during baseflow conditions and the 0.02 mgl^{-1} analytical limit of detection makes it impossible to detect very low phosphorus concentrations observed in the River Leith. Therefore, the routine sampling can underestimate the importance of baseflow nutrient concentrations, when the in-stream biogeochemical processing of nutrients and their implications to stream ecology are potentially the most critical.[9,72,79] Targeting high flows specifically can extend the range of concentrations captured by low-frequency sampling, improve nutrient load estimation[23] and evaluation of water quality against chemical thresholds[25]. However, as we show here, concentration-discharge relationship can be complex with considerable temporal lags between peak discharge and peak concentrations. Other studies[23,26] showed also that similar nutrient peaks are produced by different magnitude storm events as function of the antecedent hydro-meteorological conditions, transient nutrient sources and in-stream processing.[25,68,76]

The EA routine monitoring points are typically located around point sources e.g. sewage effluent discharges[40] and on high order rivers[41], whereas high diffuse pollution risk is typified by short, headwater tributaries draining 'risky' land uses outside of the network of surveillance monitoring points. To address this limitation the EA is introducing operational monitoring outside of the fixed surveillance sites network with the aim to target aquatic bodies under threat of not meeting the WFD objectives.[11] We suggest that high-frequency *in situ* nutrient sampling should become an operational tool in future monitoring networks to provide improved scientific understanding of the sources and pathways of diffuse pollution in catchments. An example of such operational monitoring is funded by the Defra DTC project with the River Eden being one of the three test catchments.[28,80] High-frequency *in situ* infrastructure monitors nutrient responses to on-farm mitigation measures including streamside fencing, storage ponds and active-buffer zones on a sub-catchment scale.[73] The implementation allows specific temporal targeting of the monitoring with a remote control to capture nutrient responses to particular hydrological events. To target hot-spots of diffuse pollution in catchment a simple risk-based model like SCIMAP with explicit representation of surface hydrological pathways could be used.

Conclusions

Recognising the advantages and limitations of both low and high-frequency nutrient sampling, we suggest that there is a need for a more holistic, long-term strategy to nutrient monitoring incorporating both approaches as they offer complementary pieces of information on nutrient pollution in agricultural catchments. We show that low-frequency nutrient datasets can provide time-integrated information on the spatial distribution of nutrient concentrations, whereas high-frequency datasets provide insights into temporal nutrient dynamics on the time-scales of hydrological responses. We also demonstrate analytical uncertainties in both approaches: potential storage-related errors and underestimation of reactive forms of N and P for low-frequency sampling and underestimation of the *in situ* time series due to likely loss of particulate material in the sampling system. We show that the choice of sampling regime has important implications for accurate quantification of water quality status and nutrient loads. The different biogeochemical export regimes for TRP (episodic) and NO_3-N (chemostatic), revealed by high-frequency data, determine that TRP a minimum of hourly sampling is required whereas for NO_3-N weekly and monthly sampling is adequate.

A potential limitation in the wide application of high-frequency nutrient monitoring can be a high cost of such infrastructure and high energy consumption.[17,25] However, as we show for the River Leith, the *in situ* technology can be contained in a mobile unit and easily transported to another monitoring location in the future. The laboratory also facilitates the use of renewable energy in form of solar panels and wind turbines which significantly reduces the environmental footprint. Further technological advances are expected to reduce the cost, size and energy consumption of the sensors and will make the facilitation of the *in situ* automated nutrient monitoring easier. An example of such innovation is the lab-on-a-chip based on ion chromatography that will measure a wide range of ions in stream water.[17]

Further research is needed to link the distribution of critical nutrient source areas in the catchment with the in-stream nutrient dynamics inferred from high-frequency sampling. Ultimately, high resolution nutrient monitoring data could provide a crucial link between small scale studies of nutrient sources and mobilisation and basin scale patterns of nutrient delivery and impact.

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Notes and references

† Acid and neutral grasslands are separate Land Cover Map 2007 classes for semi-natural grassland dominated by grasses and herbs differing in terms of soils acidity (pH <4.5 for acid and pH 4.5-6.5 for neutral grassland).[34]

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