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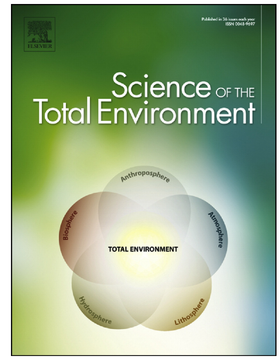

Interpretation of river water quality data is strongly controlled by measurement time and frequency

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Interpretation of river water quality data is strongly controlled by measurement time and frequency

Inge Elfferich[1]*, Elizabeth. A. Bagshaw[2]*, Rupert G. Perkins[1], Penny J. Johnes[2], Christopher A. Yates[2,3], Charlotte E. M. Lloyd[2,4], Michael J. Bowes[5], Sarah J. Halliday[6,7]

1. School of Earth and Environmental Sciences, Cardiff University, Park Place, Cardiff, CF10 3AT, UK

2. School of Geographical Sciences, University of Bristol, University Road, Bristol, BS8 1SS, UK

3. AtkinsRéalis, The Hub, 500 Park Avenue, Aztec West, Bristol, BS32 4RZ, UK

4. School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

5. UK Centre for Ecology and Hydrology, Benson Lane, Crowmarsh Gifford, Wallingford, Oxfordshire, OX10 8BB, UK

6. School of Humanities, Social Sciences and Law, University of Dundee, Nethergate, Dundee, DD1 4HN, UK

7. UNESCO Centre for Water Law, Policy and Science, University of Dundee, Perth Road, Dundee, DD1 4HN, UK

*Corresponding authors: elfferichi@cardiff.ac.uk (I. Elfferich) and liz.bagshaw@bristol.ac.uk (E. Bagshaw)

Abstract

Water quality monitoring at high temporal frequency provides a detailed picture of environmental stressors and ecosystem response, which is essential to protect and restore lake and river health. An effective monitoring network requires knowledge on optimal monitoring frequency and data variability. Here, high-frequency hydrochemical datasets (dissolved oxygen, pH, electrical conductivity, turbidity, water temperature, total reactive phosphorus, total phosphorus and nitrate) from six UK catchments were analysed to 1) understand the lowest measurement frequency needed to fully capture the variation in the datasets; and 2) investigate bias caused by sampling at different times of the day. The study found that reducing the measurement frequency increasingly changed the interpretation of the data by altering the calculated median and data range. From 45 individual parameter-catchment combinations (six to eight parameters in six catchments), four-hourly data captured most of the hourly range (>90%) for 37 combinations, while 41 had limited impact on the median (<0.5% change). Twelve-hourly and daily data captured >90% of the range with limited impact on the median in approximately half of the combinations, whereas weekly and monthly data captured this in <6 combinations. Generally, reducing sampling frequency had most impact on the median for parameters showing strong diurnal cycles, whilst parameters showing rapid responses to extreme flow conditions had most impact on the range. Diurnal cycles resulted in year-round intra-daily variation in most of the parameters, apart from nutrient concentrations, where daily variation depended on both seasonal flow patterns and anthropogenic influences. To design an optimised monitoring programme, key catchment characteristics and required data resolution for the monitoring purpose should be considered. Ideally a pilot study with high-frequency monitoring, at least four-hourly, should be used to determine the minimum frequency regime needed to capture temporal behaviours in the intended focus water quality parameters by revealing their biogeochemical response patterns.

Keywords

Water quality, high-resolution data, monitoring frequency, sampling bias, diurnal cycling, river basins

1. Introduction

Water quality monitoring programmes must strike a balance between resource efficiency (cost) and representation of changes in water conditions required to fulfil the monitoring purpose. Traditional water quality sampling relies on periodic sample collection and subsequent laboratory analysis but such manual sampling regimes cannot capture all events, and indeed biases in data can be caused by changing day and time of the week (Johnes, 2007; Skeffington et al., 2015), weather conditions (Rand et al., 2022) and extreme high or low flow conditions (Lloyd et al., 2015). Rand et al. (2022) compared manual and automated sensor data from the Belgrade Lakes, USA, where they found that manual lake sampling showed a significant likelihood to take place during “fair weather”, with lower windspeeds and rainfall intensity and higher air temperature than the mean. Infrequent manual sampling of water chemistry, which most likely occurs during standard working hours at regular intervals (weekly, monthly etc.), can bias the calculation of annual average concentration, annual nutrient load and environmental quality standards (Cassidy and Jordan, 2011; Halliday et al., 2015; Johnes, 2007; Jordan et al., 2007; Skeffington et al., 2015). Extreme high or low flow conditions are important for nutrient transport; they can contribute to most of the total nutrient load in rivers with a flashy hydrology (Cassidy and Jordan, 2011). These conditions are often short-lived, only occur infrequently (Johnes, 2007; Lloyd et al., 2014) and will not be captured fully by infrequent manual sampling. High flows can promote transport of sediment-bound nutrient fractions from land to water or via in-channel remobilisation, whilst low flow conditions are dominated by nutrient inputs from sewage effluent, due to low dilution capacity (Halliday et al., 2015), as well as nutrient delivery along throughflow pathways including from waterlogged soils when there is drizzle (Collins et al., 2010; Durand et al., 2011; Evans and Johnes, 2004; Lloyd et al., 2014; Yates and Johnes, 2013). Thus, sampling regimes that capture such conditions are critical to reflect nutrient transport processes and estimate nutrient loads accurately.

Advances in in situ sensing technologies have the potential to reduce bias associated with sampling periodicity. Continuous or high temporal resolution hydrochemical sampling therefore can enable an enhanced understanding of catchment processes (Bieroza et al., 2023; Blaen et al., 2017; Bowes et al., 2015b; Kirchner et al., 2004; Lloyd et al., 2015; Rode et al., 2016). This is especially relevant for transient events and short-term biogeochemical dynamics, including diurnal or other cyclic patterns that are closely linked to hydrological and biological processes (Khalil and Ouarda, 2009) such as pollutant load estimates (Johnes, 2007) and response to storm events (Chappell et al., 2017; Jordan et al., 2007), as they are based on representative measured concentrations and the discharge rate. In the UK, increased interest in high-resolution water quality monitoring is partly driven by the recent implementation (April 2023) of Section 82 of the Environment Act 2021, which requires water companies to deploy continuous water quality monitoring up and down stream of all sewage effluent discharges to a water course (DEFRA, 2023; Hanson, 2023). Simultaneously, drinking water production is moving towards smart catchment monitoring and management with high-resolution sensor technologies in source waters; for example for anoxia (Wentzky et al., 2019), iron and manganese concentrations (Hammond et al., 2023) and algal bloom related issues (Carey et al., 2021; Painter et al., 2023; Zamyadi et al., 2016).

An important consideration in monitoring, however, is that more data are not always better (Coraggio et al., 2022). The optimal sampling regime must balance the minimum frequency needed to capture fluctuations, particularly in flashy streams, and the maximum frequency that can be collected sustainably (considering power demands and data costs) without returning redundant information and increasing potential noise in the data that masks the information required (Coraggio et al., 2022; Khalil and Ouarda, 2009). The objectives of the monitoring network, for example meeting certain environmental quality standards, detecting sources of pollution or measuring a change before or after a mitigation, will determine the required data analysis, which in turn sets requirements for the temporal resolution of the data. Determining the temporal frequency of measurement is not a static process. Measurement intervals can be optimised over time or in response to external stressors (Coraggio et al., 2022), for example adaptive monitoring (Blaen et al., 2016) aims to optimise the intervals in real-time when a threshold is met, like an extreme event. This study provides a systematic assessment of high resolution hydrochemical data from six different UK catchments to: 1) understand the lowest measurement frequency that can fully capture variation in different parameters; and 2) investigate bias induced by manual sampling at different times of the day.

2. Materials and methods

2.1 Catchment characteristics

High-frequency water quality data were collected at least every hour using in situ sensors, in six different UK rivers (Figure 1): the Wylye (Hampshire Avon catchment), Enborne (Kennet catchment), Blackwater drain (Wensum catchment), Thames (Thames catchment), Hiraethlyn (Conwy catchment) and Newby Beck (Eden catchment).

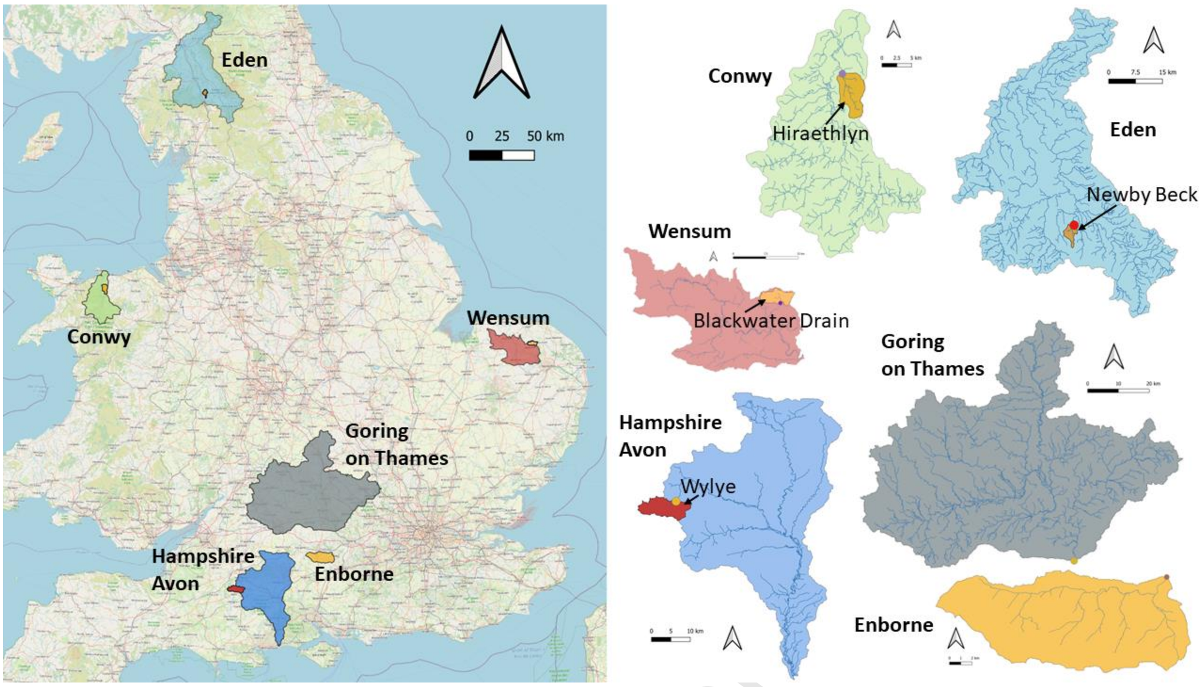
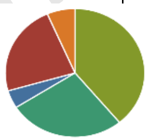
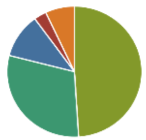
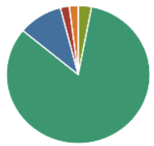


Figure 1: Catchments in the UK that were used for this study.

The monitoring stations in the Hampshire Avon (Lloyd et al., 2015; Lloyd et al., 2019; Outram et al., 2014), Wensum (Cooper et al., 2018; Outram et al., 2014) and Eden (Outram et al., 2014; Owen et al., 2012; Perks et al., 2015) catchments were part of the DEFRA funded Demonstration Test Catchments (DTC). The Enborne monitoring station was part of the LIMPIDS programme and UKCEH Thames Initiative (Bowes et al., 2018; Bowes et al., 2015a; Halliday et al., 2014; Wade et al., 2012) and the Conwy catchment was monitored as part of the DOMAINE programme (supplied by Chris Yates and Penny Johnes, University of Bristol, Bristol, UK; underpinning data set as referenced by Mackay et al. (2020) and Yates et al. (2023)). The Thames monitoring station at Goring-on-Thames was part of UKCEH Thames Initiative monitoring (unpublished data, supplied by Mike Bowes, UK Centre for Ecology & Hydrology, Wallingford, UK, and the UK Environment Agency; referenced in Rode et al. (2016) and Moorhouse et al. (2018)). The studied catchments cover a wide range of catchment characteristics related to geology and climate, like the base flow index (BFI) and mean flow (Table 1). Moreover, they vary significantly from 13 to 4634 km^2 in area, and there is a marked difference in land use (Table 1). Further details about the catchments can be found in the papers referenced in Table 1. The list of monitored parameters varied slightly per site, but all included temperature, water level or discharge, pH, electrical conductivity (EC), dissolved oxygen (DO), turbidity, chlorophyll-a

(Chl-a), nitrate (as N) and total reactive phosphorus (TRP). At some sites, total phosphorus (TP) and ammonium (as N) were also measured. Full details of all equipment and sampling regimes, including monitoring frequency (Table S1 in supplementary materials), as well as details on required data conversions can be found in the supplementary materials.

Table 1: Catchment characteristics of the six UK catchments studied and the exact period of high-frequency monitoring.

River	Hiraethlyn	Enborne	Wylye	Thames	Blackwater Drain	Newby Beck
Catchment	Conwy	Kennet	Hampshire Avon	Thames	Wensum	Eden
Monitored location	Bodnant	Brimpton	Brixton Deverill	Goring-on-Thames	Kiosk F - Park Farm	Newby
Latitude	53.2260	51.3803	51.1600	51.5235	52.7771	54.5853
Longitude	-3.7990	-1.1838	-2.1901	-1.1435	1.1491	-2.6202
Size of catchment (km^2)	20.5 (g)	148.0	50.2	4633.7 (h)	19.7	12.5
Elevation of sampling point (m a.s.l.)	11 (f)	62	189 (a)	30	43 (a)	233 (i)
Annual average rainfall (mm)	1200 (f)	810 (d)	967 (d)	680 (d)	655 (a)	1167 (a)
Baseflow Index (BFI)	0.46 (f)	0.54 (d)	0.93 (a)	0.64 (d)	0.66 (c)	0.39 (a)
Mean flow (m^3/s)	0.54 (l)	1.06 (l)	0.47 (l)	23.0 (l)	0.094 (c)	0.33 (l)
Dominant land use	Improved grassland (g)	Arable and grassland	Livestock and cereals	Arable/horticulture, improved grassland (h)	Intensive arable cultivation	Livestock (dairy and meat)
% Urban	0.3 (g)	6.5	7.0	7.3	1.0	2.0 (d)
Land use distribution						
Monitoring start date	19/06/2015	01/11/2009	13/03/2012	29/12/2013	08/03/2011	14/09/2011
Monitoring end date	30/09/2017	29/02/2012	05/03/2014	13/10/2015	31/12/2014	01/01/2016

a: Robson and Reed (1999); b: https://www.landis.org.uk/soilscapes/ (accessed: 24/06/2021); c: Cooper et al. (2018); d: Marsh and Hannaford (2008); e: https://en-gb.topographic-map.com/maps/iu/United-Kingdom/ (accessed: 24/06/2021); f: Estimate based on Yates et al. (2023) and Marsh and Hannaford (2008); g: Yates et al. (2019a); h: Gauging station Thames at Reading https://nrfa.ceh.ac.uk/ (accessed: 24/06/2021); i: Outram et al. (2014); j : Lloyd et al. (2019); k : Bowes et al. (2015b); l: Calculated from dataset. Legend for land use distribution pie-charts:

■ Arable (%) ■ Improved pasture (%) ■ Rough grazing (%) ■ Woodland (%) ■ Urban (%)

2.2 Analysis

2.2.1 Data manipulation – artificial decimation

At each site, the sensors logged data at time intervals ranging from 15 minutes to one hour (Table S1). The high-resolution datasets were sub-sampled at predefined intervals to create a subset of smaller datasets. This artificial decimation (Johnes, 2007) process was executed in two different ways, to test a) the influence of reduced sampling frequency on median and range, and b) the influence of intra-daily variation. Methods are described below:

2.2.2 Temporal frequency effects (a)

Some data in this study were collected every 15-min, but for consistency the lowest available frequency in all catchments was used for this comparison, which was *hourly* data. Artificial decimation was used to create one version of an *hourly* (every day at every whole hour), *four-hourly* (every day at 00:00, 04:00, 08:00, 12:00, 16:00 and 20:00), *twelve-hourly* (every day at 00:00 and 12:00), *daily* (every day at 12:00), *weekly* (every Wednesday at 12:00), and *monthly* dataset (every second week of the month, on Wednesday at 12:00). Artificially created datasets with *four-hourly, twelve-hourly, daily, weekly,* and *monthly* data were compared to the *hourly* data, to assess the influence of a reduced frequency on the percentage of the total *hourly* range captured in the data set and the percentage change in the median.

Percentage of the total range captured was calculated for each parameter accordingly (Equation 1):

Equation 1: $$\frac{MAX(x)-MIN(x)}{MAX(hourly)-MIN(hourly)} * 100$$

where x is the artificially created datasets e.g. four-hourly, twelve-hourly, daily, weekly and monthly data. Parameter behaviour is determined by the median, 25% and 75% interval and data distribution, which can be visualised by the width of a violin boxplot (the width of the boxplot depends on the number of datapoints at each value).

Percentage change in the median was calculated for each parameter accordingly (Equation 2):

Equation 2: $$\frac{Median\ (x) - Median\ (hourly)}{Median\ (hourly)} * 100$$

where x is the artificially created datasets e.g. four-hourly, twelve-hourly, daily, weekly and monthly data.

2.2.3 Intra-daily variation (b)

Artificial decimation was repeated for multiple initial conditions to create different versions of a daily dataset (Halliday et al., 2015; Johnes, 2007); Daily with different times of the day: *every day at 00:00, 04:00, 08:00, 12:00, 16:00, 20:00*, resulting in six different *daily* datasets.

To determine intra-daily variation, for each of these timeframes a new dataset was created which included the median for each day. The difference between the median and the corresponding datapoints in the six artificially decimated daily datasets was calculated and compiled in one dataset (Figure 2). For example, the intra-daily variation data consisted of a calculated difference for each of the six times of day (00:00, 04:00, 08:00, 12:00, 16:00, 20:00) for every day in the multi-year dataset. The outcome was tested for significant differences using Kruskall-Wallis analysis of variance and Dunn's post-hoc test (Rstudio version 2023.06.2+561, R version 4.2.1 (2022-06-23 ucrt)). Each dataset was then banded by significance, with data that showed no significant differences grouped together (denoted by the same colour). Variation for the multi-year datasets was plotted as boxplots (with significant outliers removed to enable better visualisation on the y-axis).

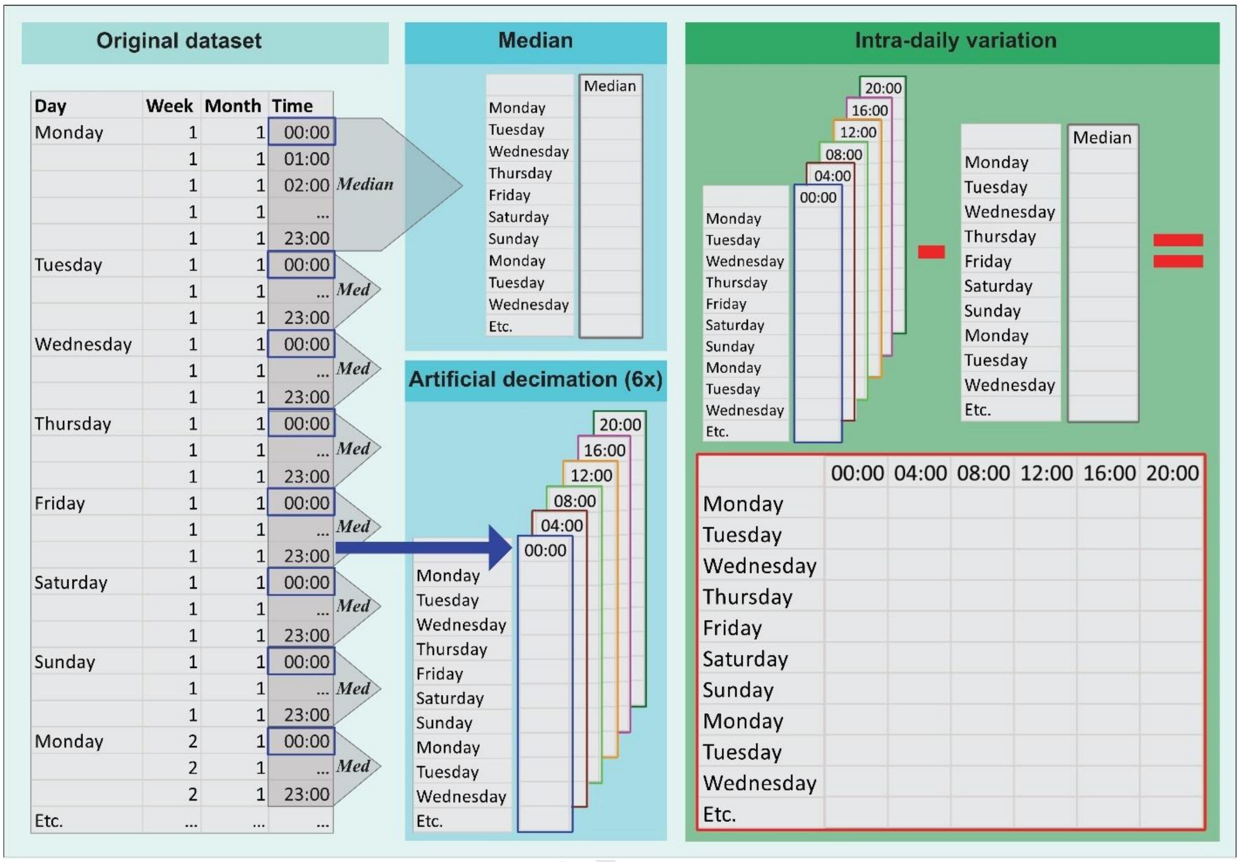


Figure 2: Artificial decimation process to calculate intra-daily variation. Daily median and six new daily datasets from six selected times of day were created to calculate intra-daily variation for the whole dataset.

3. Results

3.1 Seasonality

Variation in all parameters recorded in the full datasets from each site prior to artificial decimation (Figure 3) indicated a considerable temporal and spatial difference in range, median as well as 25% and 75% interval. The seasonal effect depended on the catchment and varied by parameter (Figure 3). Median nitrate, total phosphorus and total reactive phosphorus concentrations calculated per month (in multi-year datasets) highlight important biogeochemical processes and dominant transport mechanisms that occur throughout the year, which are catchment dependent (Figure S2 in supplementary materials).

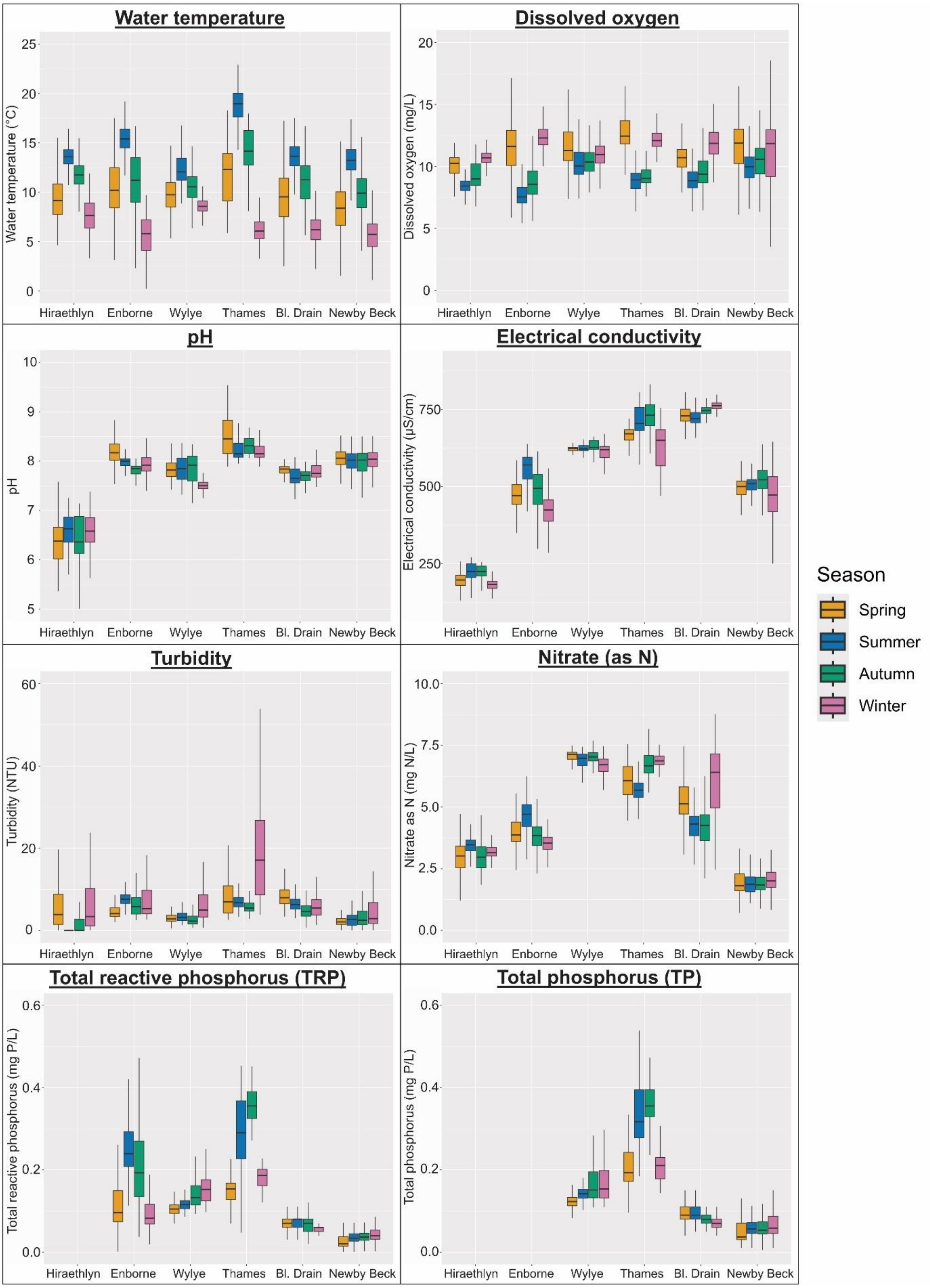


Figure 3: Boxplots (without outliers) for water quality data from the six study catchments. Bl. Drain = Blackwater Drain. Seasons are defined as follows; spring: March, April, May; summer: June, July, Augustus; autumn: September, October, November; winter: December, January, February.

3.2 Temporal frequency effects

Reducing the temporal frequency had a different impact on the captured range (Table 2), median (Table 2) and data distribution (histogram; the width of the violin boxplot visualises the number of datapoints at that value, Figure S3 in supplementary materials), depending on the parameter and catchment. Reduced frequency showed the largest percentage change in median for turbidity, dissolved oxygen, temperature, TP and TRP, and had the largest overall impact on total range of turbidity captured (Table 2), but there are many nuances dependent on the catchment. Monthly frequency impacted dissolved oxygen concentrations in the Wylye and turbidity in Blackwater Drain, changing the median by >13% whilst capturing 53% and 8% of total range, respectively (Table 2). In general, reducing frequency had the least impact on median and range for nitrate and electrical conductivity, followed by dissolved oxygen, temperature, and pH, although this was largely catchment dependent. Reducing to monthly frequency had a relatively small impact on nitrate concentration observations in Newby Beck and electrical conductivity in the Hiraethlyn, where the median changed by <2% whilst 88% and 90% of the total range was recorded, respectively (Table 2).

The percentage of the total range captured and percentage change in the median were not always similarly affected by a reduction in frequency. For example, daily data for dissolved oxygen in the Wylye almost captured the total range of the hourly data variation (99%) but had a large impact (>10% change) on the calculated median (Table 2). The opposite pattern, with a large impact on total range captured and relatively small impact on median, was also present in some catchments (Table 2), for example in weekly observations of EC in Blackwater Drain (28% of total range captured, 0% change in median).

In the six catchments, the change in median for turbidity was most consistent, decreasing (negative) at monthly compared to hourly data, but this was not the case for every temporal frequency studied (Table 2). There was no consistent direction (increase or decrease) of change in the median with reduced temporal frequency for any of the studied catchments (Table 2).

Table 2: Percentage of total range captured and percent median change, comparing reduced frequencies to hourly data. Reduced temporal frequency datasets were artificially created at: four-hourly, twelve-hourly, daily, weekly and monthly frequency. Figure S3 violin boxplots visualise this data and the data distribution. Colours in the percentage of total range table are added to clarify the trend, with a continuous green-yellow-red scale to indicate 100-50-0 percent of total range captured by the reduced frequency datasets.

		% Total range captured					Median % change				
River	**Parameter**	**4 Hourly (%)**	**12 Hourly (%)**	**Daily (%)**	**Weekly (%)**	**Monthly (%)**	**4 Hourly (%)**	**12 Hourly (%)**	**Daily (%)**	**Weekly (%)**	**Monthly (%)**
Hiraethlyn	**Temperature**	100	88	82	74	62	0.00	-0.18	-0.18	-0.26	-0.62
	DO (mg/L)	80	73	64	44	38	0.11	0.43	2.46	1.98	4.98
	pH	94	94	94	92	54	-0.15	0.00	0.31	0.62	-0.77
	EC	98	98	96	95	90	0.00	0.00	0.00	-0.73	-0.97
	Turbidity	100	19	19	3	1	33.33	100.00	200.00	0.00	-33.33
	NO_3-N	82	80	79	59	36	0.00	0.31	-0.62	-2.15	0.31
	TRP	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	TP	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Enborne	**Temperature**	97	93	93	87	74	0.00	0.97	0.97	-4.85	-7.28
	DO (mg/L)	99	81	80	74	65	0.06	2.02	5.03	9.74	10.60
	pH	100	88	74	65	47	0.00	0.13	0.25	0.13	0.13
	EC	83	83	75	52	48	0.00	0.00	0.63	0.95	0.95
	Turbidity	83	48	48	8	6	0.85	1.69	-1.69	-6.78	-0.85
	NO_3-N	93	90	79	67	54	0.00	0.18	0.18	0.55	-0.36
	TRP	97	85	80	80	53	0.61	0.00	-5.32	1.23	-9.20
	TP	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Wylye	**Temperature**	100	81	80	69	64	0.00	1.28	7.95	7.70	5.99
	DO (mg/L)	99	99	99	88	53	0.00	1.49	10.55	10.18	14.38
	pH	99	96	95	83	73	0.00	0.13	1.29	1.23	1.94
	EC	98	85	85	58	11	0.00	0.00	-0.32	-0.16	0.32
	Turbidity	100	52	51	33	3	0.00	-3.13	-9.38	-6.25	-12.50
	NO_3-N	95	95	95	55	17	-0.06	-0.05	0.12	-0.10	1.43

	TRP	93	84	52	48	11	0.00	0.00	0.00	0.00	-3.92
	TP	98	60	42	38	9	0.21	0.00	0.00	-0.22	-7.29
Thames	**Temperature**	99	97	97	95	78	0.07	0.07	0.59	0.63	3.97
	DO (mg/L)	97	96	75	74	68	0.00	0.27	0.27	2.71	-2.58
	pH	100	67	67	65	59	0.00	0.00	0.12	-0.12	-0.49
	EC	100	96	94	94	84	0.00	-0.04	-0.03	-0.34	-0.94
	Turbidity	68	68	68	12	12	-0.57	0.85	1.70	6.75	-12.00
	NO_3-N	99	99	99	39	31	0.00	-0.11	-0.11	-0.79	-0.07
	TRP	87	85	82	82	71	0.00	1.46	1.46	1.46	-6.58
	TP	71	69	66	59	48	0.00	0.00	1.88	1.61	-0.27
Blackwater Drain	**Temperature**	98	89	88	80	57	-0.19	0.84	6.00	2.44	3.61
	DO (mg/L)	98	95	91	80	73	0.00	0.60	2.05	3.50	6.70
	pH	98	77	77	55	41	0.00	0.00	0.26	0.26	0.26
	EC	100	67	66	28	19	0.00	0.00	0.00	0.00	-0.13
	Turbidity	100	89	89	15	8	0.00	-1.64	-9.84	-11.48	-13.11
	NO_3-N	99	98	98	90	39	0.00	0.21	0.64	0.64	4.06
	TRP	92	89	87	29	18	0.00	0.00	0.00	0.00	0.00
	TP	96	57	57	17	11	0.00	0.00	0.00	0.00	-12.50
Newby Beck	**Temperature**	99	89	87	85	71	-0.11	-0.21	0.96	0.53	0.85
	DO (mg/L)	59	59	59	43	23	0.09	0.83	4.86	4.95	6.42
	pH	97	92	92	87	73	0.00	0.12	0.87	1.00	1.06
	EC	98	96	73	72	51	0.00	0.20	0.39	0.39	-0.99
	Turbidity	100	100	100	36	11	0.00	0.00	-4.17	-6.25	-12.50
	NO_3-N	98	97	97	91	88	-0.11	0.11	0.11	0.44	-1.31
	TRP	100	82	56	44	43	0.00	0.90	1.74	-0.41	1.74
	TP	100	100	99	67	42	0.00	2.86	4.57	0.56	4.01

Four-hourly data captured most of the parameter behaviour (Figure S3, supplementary materials), as well as the percentage of total range captured and percentage change in median compared to hourly data (Table 2). From all 45 individual parameter-catchment combinations (six to eight parameters in six catchments), four-hourly data captured most of the hourly range (>90%) for 37 combinations, and 41 had limited impact on the median (<0.5% change). The Wylye and Blackwater Drain four-hourly datasets captured 92%-100% of the total range for all parameters in the hourly data, which is a higher overall range captured than the other four catchments at four-hourly frequency (Table 2). The Newby Beck four-hourly dataset captured 95-100% of the total range apart from for DO, where only 59% was recorded (Table 2). The other catchments captured >90% for most parameters at four-hourly measurement frequency, except for DO and nitrate at the Hiraethlyn; turbidity and EC at the Enborne; and turbidity, TP and TRP at the Thames (Table 2). Twelve-hourly and daily data represented >90% of the range with limited impact on the median (<0.5% change) in approximately half of the combinations. Daily measurements captured >90% of total range for certain parameters; nitrate (4 of 6 catchments), pH (3 of 6 catchments), EC (2 of 6 catchments) and DO (2 of 6 catchments). Most parameters at weekly frequency did not cover >90% of total range, except for the pH and EC at the Hiraethlyn; EC and temperature at the Thames; nitrate at the Blackwater Drain and nitrate at Newby Beck (Table 2), which all had <1% change in median. Monthly data frequency resulted in generally low percentages of range captured for all catchments, with some exceptions (Table 2). Monthly data from the Hiraethlyn revealed the lowest percentage of range captured; 1% of the hourly range in turbidity, but also the highest percentage of range captured; 90% of the hourly range in EC (Table 2).

3.3 Intra-daily variation

Most parameters and catchments displayed significant differences in variation between the six different times of day (denoted by differing colour bands in Figure 4).

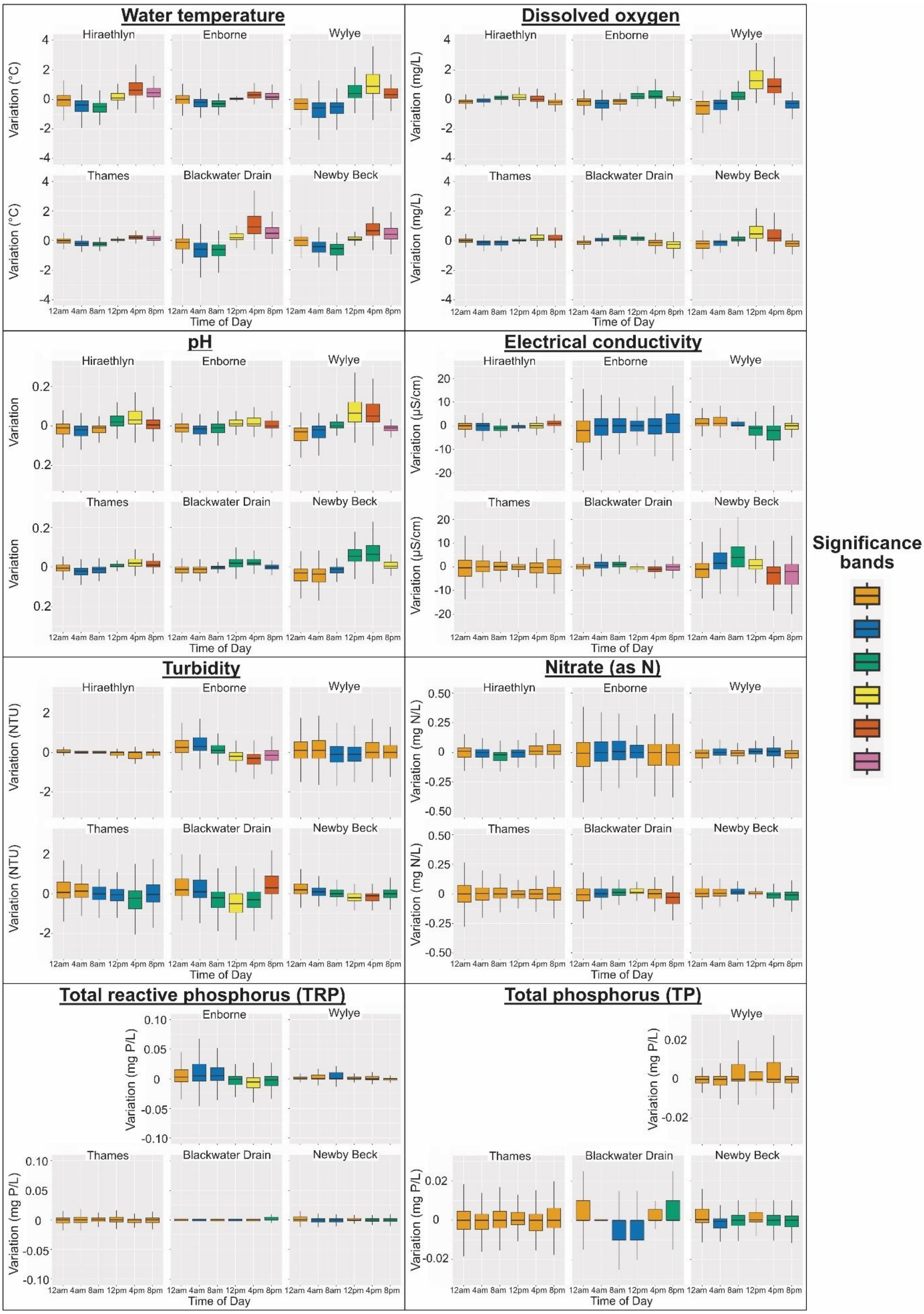


Figure 4: Intra-daily variation for all study catchments based on six versions of a daily dataset. Datapoints were selected from different times of day; 00:00, 04:00, 08:00, 12:00, 16:00, 20:00. Significance bands bar colours indicate for each individual plot (each catchment within each parameter) the significance between the six different times of day from the

Kruskall-Wallis analysis of variance and Dunn's post-hoc test; bars with the same colour are not significantly different from each other, whilst different colours denote significant difference.

3.1.2 Physico-chemical parameters

The intra-daily variation in water temperature can be used to interrogate the patterns of significance shown, as this parameter has a predictable cyclic pattern throughout the day, with cooler temperatures at night and warming throughout daylight hours. This physical process persists throughout different seasons and is expected to reveal a strongly significant intra-daily variation pattern for this multi-year analysis. The variation is calculated as the parameter value at one of the six selected times of day minus the parameter median of the whole day, collated for each day in the dataset. The outcome plotted for the six selected times of day allows a comparison of variation within a day (intra-daily). Throughout the dataset there are cooler temperatures at night-time, which result in a more negative variation value (for all days in the dataset, the value at that time is lower than the daily median), and warmer temperatures at daytime which cause a more positive variation (higher values than the daily median) (Figure 4). The variation for the water temperature was significantly different for every time of day in almost all catchments, which means the described pattern was consistent throughout the whole dataset and all seasons (denoted by differing colours in Figure 4). Relative to the median temperature each day, 04:00 or 08:00 was the coldest and 16:00 was the warmest in every catchment. The Thames had the smallest range in variation, followed by the Enborne.

A cyclical day-night pattern for DO and pH was also visible in all catchments, albeit more pronounced in some, such as the River Wylye and Newby Beck (Figure 4). In most of the catchments there was a strong connection between DO and pH, where they both followed the same day-night trend. However, in the Blackwater Drain and Hiraethlyn, DO had maximum positive variation four hours earlier than pH. Electrical conductivity (EC) revealed a significant diurnal trend in most catchments, apart from the Enborne and Thames. The variation in EC followed the opposite trend of pH and DO in the Wylye and Newby Beck, DO in the Hiraethlyn and pH in the Blackwater Drain. Intra-daily variation for turbidity in the Enborne, Thames, Blackwater Drain and Newby Beck showed significantly more positive variation at night and significantly more negative variation during the day (Figure 4), whilst the Hiraethlyn and Wylye didn't show any trends.

3.1.4 Total reactive phosphorus, total phosphorus and nitrate

Intra-daily variation in nutrients revealed less clear significant patterns than the physico-chemical parameters, and these patterns were catchment dependent (Figure 4). Nitrate had significant intra-daily variation in most catchments, apart from the Thames, with the clearest diurnal cycle (most significant differences between the timesteps) in the Blackwater Drain. There was a general trend towards more positive variation (higher values compared to the median for each day) from early morning until mid-day and more negative variation (lower values compared to the daily median) from late afternoon until midnight (Figure 4), except for the Hiraethlyn in which this pattern seemed to be reversed. Total reactive phosphorus (TRP) and total phosphorus (TP) showed significant intra-daily variation in some catchments, but there was often no clear diurnal trend. The Enborne showed the clearest diurnal cycle in TRP with most positive variation in early morning and most negative variation in the afternoon. Newby Beck and the Blackwater Drain had similar patterns for TRP and TP and revealed a general tendency for more negative variation in the morning. TRP in the Enborne and TP in the Blackwater Drain followed similar intra-daily variation patterns to turbidity (Figure 4).

Differences in intra-daily variation depending on the season will not be visible in Figure 4, as the datasets consisted of multiple whole years which would even out any intra-daily variation pattern that only existed seasonally. Examples for the Enborne and Newby Beck are presented here to show intra-daily variations by season (Figure 5), while all other results are visualised in supplementary materials, Figure S4. Nitrate and TRP concentrations for the Enborne and Newby Beck, with intra-daily variation separated by season (Figure 5), illustrate the influence of season on intra-daily variation patterns in nutrients. Nitrate concentrations in the Enborne didn't show an impact of season on intra-daily variation, but Newby Beck had a much clearer diurnal cycle in spring, summer and autumn compared to winter (Figure 5). TRP concentrations in the Enborne had clear diurnal cycle in spring, summer, and autumn but not in winter, whereas Newby Beck had only minor diurnal fluctuations in summer (Figure 5).

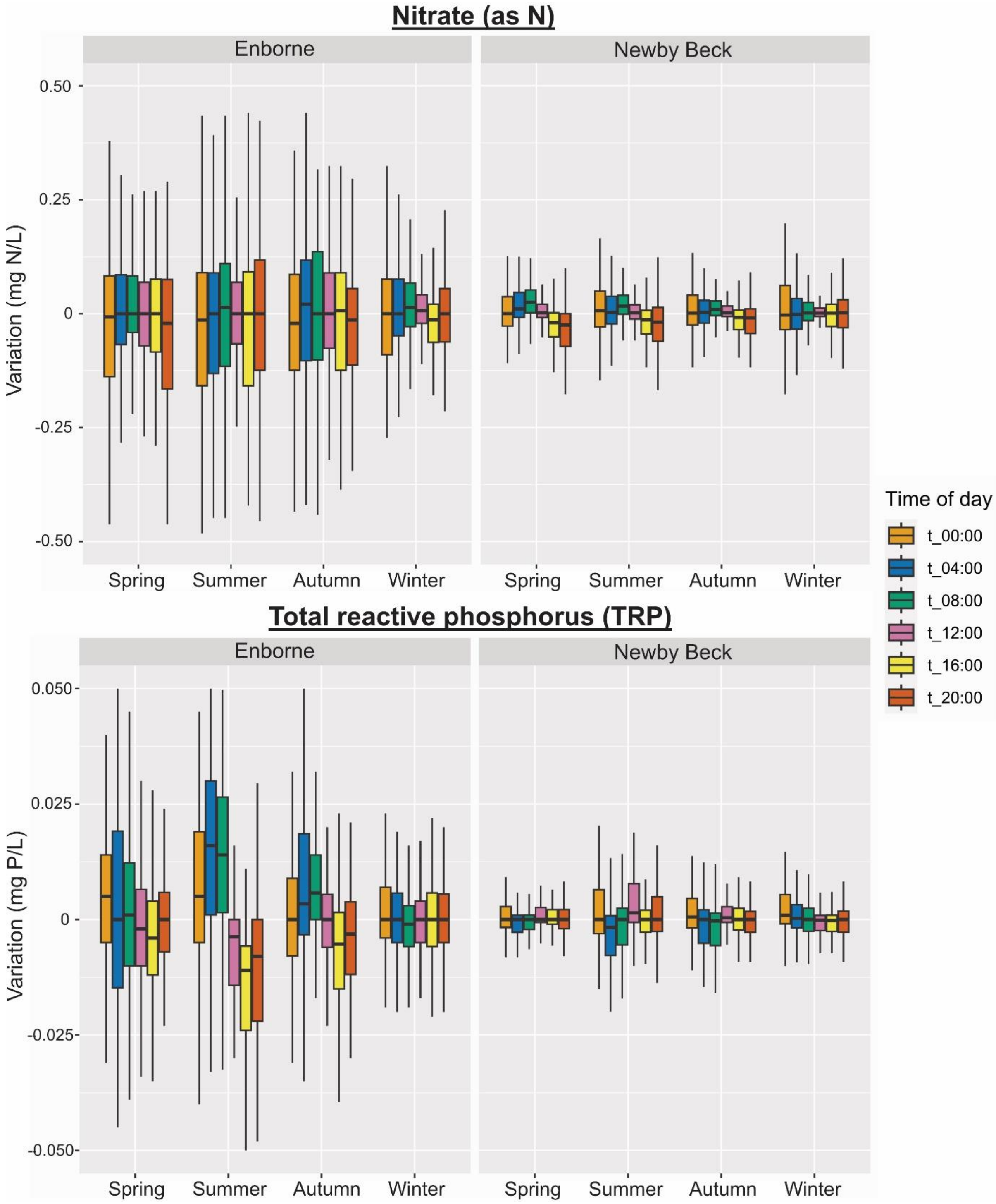


Figure 5: Nitrate (as N) and total reactive phosphorus (TRP) intra-daily variation separated by season for the Enborne and Newby Beck. Datapoints were selected from different times of the day; 00:00, 04:00, 08:00, 12:00, 16:00, 20:00, which are indicated by different colours.

4. Discussion

Catchment characteristics such as size, land use (urban and agriculture) and dominant flow paths (groundwater, throughflow or overland flow) which are primarily controlled by catchment geology, are a first order control of variation in these datasets. Previous assessments have demonstrated that monthly sampling cannot capture the full variation of physical and biogeochemical parameters, and even that monitoring at less than daily frequency can alter nutrient load assessments (Wade et al., 2012). Infrequent sampling and random sampling effects may result in the same water body being misclassified under legislation such as the Water Framework Directive (Halliday et al., 2015; Skeffington et al., 2015), with multiple classes possible depending on sampling frequency for the determinand of interest. However, different parameters display different patterns in different catchments, seasons and times of the day, so exploring high-resolution data and signposting when, where and what frequency observation is necessary is critical for optimising sampling regimes.

4.1 Reduced temporal frequency effects

Reducing temporal frequency creates the risk that the data will not capture the “real” median and range, a phenomenon termed ‘aliasing’ (Chappell et al., 2017). Reducing measurement frequency from hourly to four-hourly, twelve-hourly, daily, weekly, and monthly in this study increasingly changed the interpretation of the data by altering data distribution, median and range, with catchment- and parameter-specific effects. In general, turbidity, dissolved oxygen, temperature, TP and TRP showed the largest percentage change in median with reduced frequency of observation, whilst the greatest overall impact on total range was for turbidity, although this effect was catchment dependent. These parameters, where reduced frequency has the largest impact, are expected to have a large data variability due to rapid rainfall response (turbidity which is controlled by sediment mobilisation and transport, and overland flow-generated phosphorus transfers such as for TP) or strong diurnal cycles (temperature and dissolved oxygen).

Reduced temporal frequency did not always affect the captured range and the median simultaneously, since the range could be impacted without any changes in the median and vice versa. Data variability for each parameter in every catchment can be influenced by some or all of; time of day (diurnal cycle), season (seasonal cycle) and extreme weather (rainfall-response and flow pathway activation and separation) (Figure 6). Parameters which are less strongly controlled by the latter, and in particularly with overland flow or near-surface throughflow pathways, such as nitrate and electrical conductivity in some study catchments, can potentially be measured at lower temporal frequencies without compromising the median and range, but this depends on the monitoring purpose and the catchment flow activation regime.

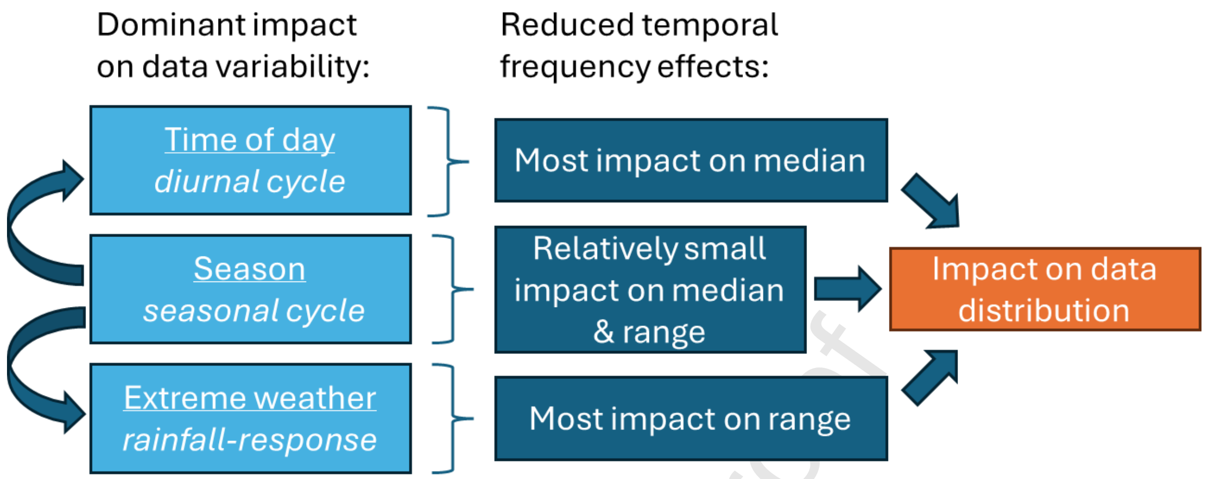


Figure 6: Processes that can impact data variability and their effect on median, range and data distribution.

Variability caused by time of day has the largest impact on the median, as diurnal cycles cause intra-daily variation in some parameters, which won't be fully represented in the data set (Figure 6). Variability caused by seasonality alone will have relatively little effect on median and range at reduced frequency. However, in nutrient load calculations by Williams et al. (2015), the summer season was more biased and less precise for nitrate (as N) and dissolved reactive phosphorus (DRP). Moreover, seasonality can influence the diurnal cycle, illustrated by the nitrate and total reactive phosphorus concentration presented in this study (Figure 5). Variability caused by extreme weather responses will have the largest impact on range, because reduced frequency will not fully capture high concentration flux responses to short-term extreme events (Figure 6), unless the sample happens to accidentally capture the peak of such an event, which can then positively bias annual load estimates (Johnes, 2007; Jordan et al., 2007). Variability caused by all three factors will have an impact on data distribution (histogram), by not capturing the full width of the data variation.

Reducing the measurement frequency not only impacts the range and variability of the data, but also the distribution (Figure S3 in supplementary materials), as demonstrated by Cassidy and Jordan (2011) for TP, Johnes (2007) for total dissolved phosphorus (TDP) and TP and Lloyd et al. (2014) for these same fractions plus for nitrate. This result indicates that monthly or weekly sampling fails to capture important extreme events, and potentially underestimate (or overestimate) median and subsequent annual load calculations (Johnes, 2007). While the median did change in this study, our data showed no consistent under- or over-estimation. This can be partially attributed to the nature of the analysis, as sub-sampling was done at only one selected time of day (daily), day of the week (weekly) and week of the month (monthly), based on common manual sampling regimes. These conditions, however, would have had an impact on the direction of percentage change in the median, as the time of day would have skewed the results, especially for parameters with strong diurnal cycles like dissolved oxygen (Rand et al., 2022).

4.2 Optimal frequency

From all 45 analysed parameter-catchment combinations (six to eight parameters in six catchments), four-hourly data captured most of the hourly range (>90%) for 37 combinations, and 41 out of 45 had limited impact on the median (<0.5% change). Twelve-hourly and daily data captured >90% of the range in 17 and 15 combinations respectively, with limited impact on the median in 30 and 19 combinations, respectively. Weekly data captured >90% of the hourly range in 6 combinations and 16 had limited impact on the median. Monthly data didn't capture >90% of the hourly range in any combination, whilst 10 had limited impact on the median. The individual parameters that were most affected by reducing frequency depended on the catchment.

Mathematical methods can define an optimum sampling frequency for any water quality parameter by calculating the point at which an increase in frequency does not provide an increase in information. Coraggio et al. (2022), for example, used high-frequency monitoring data from Bristol Harbour and mathematically determined the optimum sampling frequency for water temperature, electrical conductivity, dissolved oxygen, and turbidity as 9 hours, 6 hours, 5 hours, and 3 hours, respectively. Parameters with a rapid response to extreme events, such as turbidity and total or particulate phosphorus fractions, need to be monitored at a higher frequency to capture full data variability. Parameters with a diurnal cycle, like pH, dissolved oxygen and electrical conductivity need to be monitored frequently enough to capture these cycles or could be monitored at an appropriate, but standardised time on each day to calculate an average, depending on the monitoring purpose. Changing the time of day at which observations are captured, within any monitoring programme could bias the resulting data sets.

To determine the optimal monitoring frequency for a parameter, which captures sufficient data without using excess resources, the following factors need to be considered; (I) Parameter & catchment and (II) Monitoring purpose.

I) Parameter & catchment

Parameter and catchment interaction determined the effect of reduced temporal frequency on the range, median and data distribution. No parameter in this study was found to behave consistently for the six different catchments, hence parameter behaviour was largely dependent on catchment specific characteristics that define its response to biogeochemical cycling processes and hydrological regime (Figure 6).

Catchment characteristics

As observed in previous work on P fractions alone (Johnes, 2007; Jordan et al., 2007) catchment characteristics such as the contribution of groundwater to river flow (base flow index), land use (urban and agriculture) and size have a strong impact on water quality data variability (Table 1). Catchment size can strongly influence data distribution, with biogeochemical changes damped or subject to lag times (Creed et al., 2015). Year-round high flows in the Thames (Table 1) were found to mask local biogeochemical effects, which is possibly a result of the large catchment size and subsequently large river flow volume (Williams et al., 2000). Diurnal biogeochemical patterns in rivers are often stronger during stable, non-turbid, low flow conditions as riverine biological processes are more prominent (Bowes et al., 2016; Scholefield et al., 2005).

Catchments with a high base flow index (BFI) have notable groundwater contributions which influence temperature and nutrient concentrations. This is illustrated in the Wylye, where groundwater nitrate inputs vary inversely with overland flow inputs (Outram et al., 2014; Yates and Johnes, 2013). Nutrient concentrations are also strongly influenced by agriculture and urban land use (Salvia-Castellví et al., 2005). Intensive livestock farming and urban wastewater discharges cause a similar biogeochemical reaction as their effluents are both rich in ammonium (Donald et al., 2011). Rivers with a more urbanised catchment will receive a larger proportion of wastewater discharges, from sewage treatment works (STW) or septic tanks, especially during low flow conditions (Macintosh et al., 2011; Yates et al., 2019b). STW discharges are often related to increased turbidity, EC, temperature and ammonium and phosphorus, whilst triggering microbial activity; nitrification (production of nitrate) and the decomposition of organic material, which can in turn reduce dissolved oxygen (Halliday et al., 2015) and change the composition of the nutrient pool instream (Yates et al., 2019b).

Dominant impact on data variability

Temporal effects

Our analyses show that all catchments had a clear intra-daily water temperature pattern, coldest in the early morning and warmest late afternoon. Dissolved oxygen and pH also showed intra-daily variation in every catchment, positive in the afternoon and negative in the early morning as a result of photosynthesis-respiration cycles. Driven by diurnal water temperature and solar energy cycles, daytime photosynthesis removes (acidic) carbon fractions and produces oxygen, whilst night-time respiration does the opposite (House, 2003; Scholefield et al., 2005). The amplitude of this biological diurnal cycling depends on the temperature, light availability, and the relative contribution of autotrophic and heterotrophic organisms (Nimick et al., 2011). More abundant submergent plant communities in certain catchments, particularly chalk streams like the Wylye (Evans and Johnes, 2004; Lloyd et al., 2019; Yates and Johnes, 2013), would explain its more prominent diurnal cycle for DO and pH. Electrical conductivity had intra-daily variation, negative in the afternoon and positive in the early morning, in most catchments apart from urbanised rivers Enborne and Thames, which is most likely due to uptake and release (or lack of uptake) of free ions with diurnal biological activity. Intra-daily variation for turbidity, negative (lower values than the daily median) in the afternoon and positive (higher values than the daily median) in the early morning, occurred in most catchments apart from the Wylye and Hiraethlyn, which might be a result of night-time bioturbation: sediment resuspension caused by the feeding and movement of fish and invertebrates like crayfish (Cooper et al., 2020; Cooper et al., 2016; Halliday et al., 2015). These natural biogeochemical patterns can be masked by, for example, the volume of flow, shading from bankside growth, a large groundwater influx with lower temperatures or a large influx of non-natural water such as sewage outflows.

Nitrate as (N), total reactive phosphorus and total phosphorus can also follow diurnal cycles as a response to nutrient uptake by biological activity in the river, which results in a typical diurnal cycle of lowest concentrations in the late afternoon and highest in the early morning (Cooper et al., 2020; Nimick et al., 2011; Palmer-Felgate et al., 2008; Scholefield et al., 2005). However, in most rivers, this is not the dominant process all year round, because of minimal biological activity in the winter months and the alteration of natural cycles by anthropogenic influences (agriculture or wastewater discharges) (Jordan et al., 2007; Nimick et al., 2011; Pellerin et al., 2009). In urbanised catchments, electrical conductivity, turbidity, nitrate (as N) and phosphorus fractions (TRP, TP) can also exhibit diurnal cycles because of consistent daily patterns in wastewater effluent discharges to these rivers (Halliday et al., 2014; Palmer-Felgate et al., 2008; Withers and Jarvie, 2008). High-frequency data from the River Cut, of which 36%-90% of flow consists of STW effluent, revealed a double-peak daily EC signal, during midday and late evening, a delayed response to peak domestic water usage in the morning and evening (Palmer-Felgate et al., 2008; Withers and Jarvie, 2008), though such effects will become less evident in larger rivers with greater dilution capacity. The same parameters can exhibit diurnal signals in agricultural catchments because of consistent daily discharges from dairy farm operations (milking) (Foy and Kirk, 1995), which might also have a delayed response.

Diurnal cycles can also be influenced by seasons, so although seasonal cycles themselves will most likely be captured with a reduced temporal monitoring frequency (monthly), it is critical to understand the influence of seasonal signals on daily, and sub-daily (for example, extreme weather) events. In certain catchments, episodic short-lived extreme events can play a major role in biogeochemical processes, and it is important to fully capture their data variability.

II) Monitoring purpose

Optimal temporal frequency depends on the purpose of monitoring; long-term trend analysis, load calculations and storm-induced solute transport modelling require different inputs and therefore have unique data frequency demands (Coraggio et al., 2022). Sub-sampling high-frequency data to predetermined lower frequencies can be done iteratively to contain multiple initial conditions, and determine the optimal monitoring frequency for specific purposes (Chappell et al., 2017; Coraggio et al., 2022; Crockford et al., 2017; Johnes, 2007; Reynolds et al., 2016; Skeffington et al., 2015; Williams et al., 2015). Previous analyses have suggested that seasonal variation or long-term trends can be captured with monthly or up to half-yearly frequency (Coraggio et al., 2022). For basic statistical calculations, for example to assign Water Framework Directive classifications, for phosphorus fractions, dissolved oxygen, pH and temperature (Skeffington et al., 2015), or to detect trends in nitrate data such as mean concentration, peak concentration, drinking water standard exceedance and flux (Reynolds et al., 2016), weekly or daily sampling is recommended. In annual load estimates (Bowes et al., 2009; Crockford et al., 2017; Johnes, 2007; Williams et al., 2015) daily sampling gives the more robust and reliable results but weekly is also acceptable provided the uncertainties associated with load estimates are also reported (Lloyd et al., 2014). This largely depends on the nutrient fraction, the season and catchment characteristics as those influence reaction time and variability. Williams et al. (2015) found optimal frequency for dissolved reactive phosphorus (DRP) was every 13-26 hours and nitrate (as N) every 2.7-17.5 days. When modelling biogeochemical response during storm events (Chappell et al., 2017; Lloyd et al., 2015; Outram et al., 2014), a higher measurement frequency is required to capture this accurately, with Chappell et al. (2017) arguing for sampling rates of less than 120 minutes to greater than 600 minutes. However, these studies, and our data demonstrate that minimum temporal frequency can change over time, and between catchments and parameters, with a higher frequency needed when there is more variation and depending on the variable of interest and its environmental behaviour in each catchment.

4.4 Sensor uncertainty implications for monitoring design

The data variability captured by any monitoring campaign is subject to the limitations of the equipment used for measurement. Where data fluctuations are within the uncertainty bounds of a technique, or when measurements are subject to bias, limiting the availability of data points by reducing measurement frequency can be problematic. It is therefore critical that uncertainty bounds are known to ensure relevant fluctuations can be captured. The uncertainty of the sensor measurements used in this study is well-quantified, by comparison between laboratory samples for TP and nitrate (as N) and the sensor data at Brixton Deverill on the Wylye (Lloyd et al., 2015). The headline uncertainty bounds of ±0.15 mg/L for TP and ±0.75 mg/L for nitrate (as N) calculated by Lloyd et al. (2015) suggest that the daily variation patterns that we have identified could fall within the range of uncertainty. The maximum daily variation without outliers that we identified in the six studied catchments is ±0.05 mg/L for TP and ±0.5 mg/L for nitrate (as N). However, where the sensor data display daily variation, the uncertainty bounds of the data also vary according to the antecedent conditions, so the signal is unlikely to fluctuate between the highest and lowest bounds at adjacent time points. This temporal autocorrelation effect means that the variations revealed in our data are likely to be a real signal, even if they fall within the overall sensor uncertainty. It is therefore imperative that data users have a strong understanding of the measurement capabilities of the chosen device.

4.5 Recommendations

Reliance on weekly or monthly data means the likelihood of capturing total data variability (range and median) is small for most catchments. A balance is therefore required to determine the most cost-effective yet representative sampling regimes for different catchments. High-frequency sensor data cannot be captured everywhere, so instrumentation should be selected and deployed for the target chemistries of interest. It is also important to note that sensors cannot currently measure all parameters of interest, so optimal sampling programmes are likely to combine both high resolution sensor networks with manual or automated sample collection paired with laboratory analyses where tighter quality assurance and quality control can reduce uncertainties, albeit at a lower temporal sampling resolution. Jordan and Cassidy (2022) created an overview with important considerations to select a fit-for-purpose monitoring strategy, for example stakeholder engagement and evidence for policy or land-use management changes.

Our analysis of sensor datasets here shows that the size of the catchment, land use, baseflow index and the degree of urbanisation with associated sewage discharges to rivers will determine the most important biogeochemical cycles for each parameter in each season, and hence the required sampling frequency when relying on sensor-derived observations. An additional challenge is that the minimum temporal frequency is not static but can vary per season and per year. This variability might also increase in the future, with warmer, wetter years and a greater frequency of sudden, intense rainfall are predicted (Ockenden et al., 2016). Optimising the measurement frequency over time or in real-time as a response to external stressors (extreme events) with adaptive monitoring strategies (Blaen et al., 2016; Coraggio et al., 2022), can improve data collection for extreme weather driven parameters. For parameters affected by diurnal cycles, possible methods to prevent bias are to sample at standardised times of the day or taking 24 samples every seven hours (the 24/7 sampling approach), which samples every hour of the day over the course of a week (Halliday et al., 2012). The 24/7 approach was designed for the use of auto-samplers which require samples to be returned to the lab for analysis, but has the potential to be a cost-effective measurement frequency regime for sensor optimisation to capture dynamic river conditions (Halliday et al., 2012; Jordan and Cassidy, 2022).

In general, when deciding a minimum measurement frequency for a sensor suite, the median, 25% and 75% intervals and the data distribution as well as the range should be investigated relative to hourly data. The minimum required sampling frequency can only be determined with high-frequency observations at that location, which are often unavailable when a monitoring programme is designed. As a result, sampling frequency recommendations are typically done retrospectively, as with our analyses that suggested a minimum of four-hourly frequency. We therefore recommend flexible high-frequency monitoring installations, including sensors or autosamplers, that can be deployed for trial periods to understand the behaviour of the catchment before the long-term sampling regime commences, so this can be optimised to reduce resource expenditure which capturing representative environmental behaviours for the determinands of interest. We also caution that the data should be captured with a clear focus on understanding what questions will be asked, whether the sensors selected have uncertainty bounds beyond the expected variability, and whether capturing the full range of behaviour of all parameters is indeed necessary.

5. Conclusions

Variation in water quality data is strongly controlled by measurement frequency, but also time of day and time of year. Different catchments have different responses to biogeochemical and hydrological events, thus the measurement regime required to capture the true range of variation will itself be variable. Nutrient concentrations, flow regimes and temperature drive much of the in-stream biological activity and their temporal variations can in turn affect variability in other water quality parameters, such as DO and pH. Most catchments included in this study showed significant intra-daily trends in physico-chemical parameters, often clearly defined diurnal cycles, highlighting the importance of considering which time of day to monitor. If the data variation is small, fluctuations are harder to capture with a sensor that has a large uncertainty, hence an understanding of the sensor response is required before deployment for data capture. All catchments in this study showed that for almost every parameter, a four-hourly data frequency was required to capture most of the variation across all determinands monitored, although for some parameters most variation could be captured with twelve-hourly or daily frequency. In many cases, particularly in routine national monitoring programmes, manual sample collection cannot physically be done more than weekly or monthly, unless increased resources are made available. For these situations calculating, reporting, and minimising sampling bias is critical, while reporting data with resultant uncertainty bands is essential, to inform the user of the uncertainties in the evidence base thus generated. Before a monitoring regime is established, the purpose must be truly considered to effectively direct resource. In research-driven research, or where greater certainty is required to produce a robust and reliable evidence base to support a programme of action, pre-monitoring optimisation periods are recommended. These will allow researchers to understand how an individual catchment responds and should include high-frequency (<twelve-hourly, ideally four-hourly) measurements, and a combination of periodic (same time every day) and random samples to assess the frequency required to capture the necessary information. Lastly, it is crucial to re-assess the monitoring network periodically in case of changes in the catchment and the environment as well as changes in sensor performance, and differences in management priorities as they emerge.

CRediT author contribution statement

Inge Elfferich: Writing – original draft, writing – review & editing, data curation, investigation, methodology, formal analysis, conceptualization, visualization. Elizabeth Bagshaw: Writing – review & editing, supervision, funding acquisition, methodology, conceptualization. Rupert Perkins: Writing – review & editing, supervision, methodology, conceptualization. Penny Johnes: Writing – review & editing, methodology, resources (access to unpublished data), supervision. Christopher Yates: Writing – review & editing, supervision, resources (access to unpublished data). Charlotte Lloyd: Writing – review & editing. Michael Bowes: Writing – review & editing, resources (access to unpublished data). Sarah Halliday: Writing – review & editing. This is Cardiff EARTH CRediT Contribution 32.

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Data availability

Hiraethlyn (DOMAINE) and Enborne (LIMPIDS) data and contact details for data requests are available on the Environmental Information Data Centre (UK Centre for Ecology and Hydrology): https://eidc.ac.uk/. Wylye, Blackwater Drain and Newby Beck (Demonstration Test Catchments) data and contact details for data requests are available on the Agricultural and Environmental Data Archive: http://www.environmentdata.org/.

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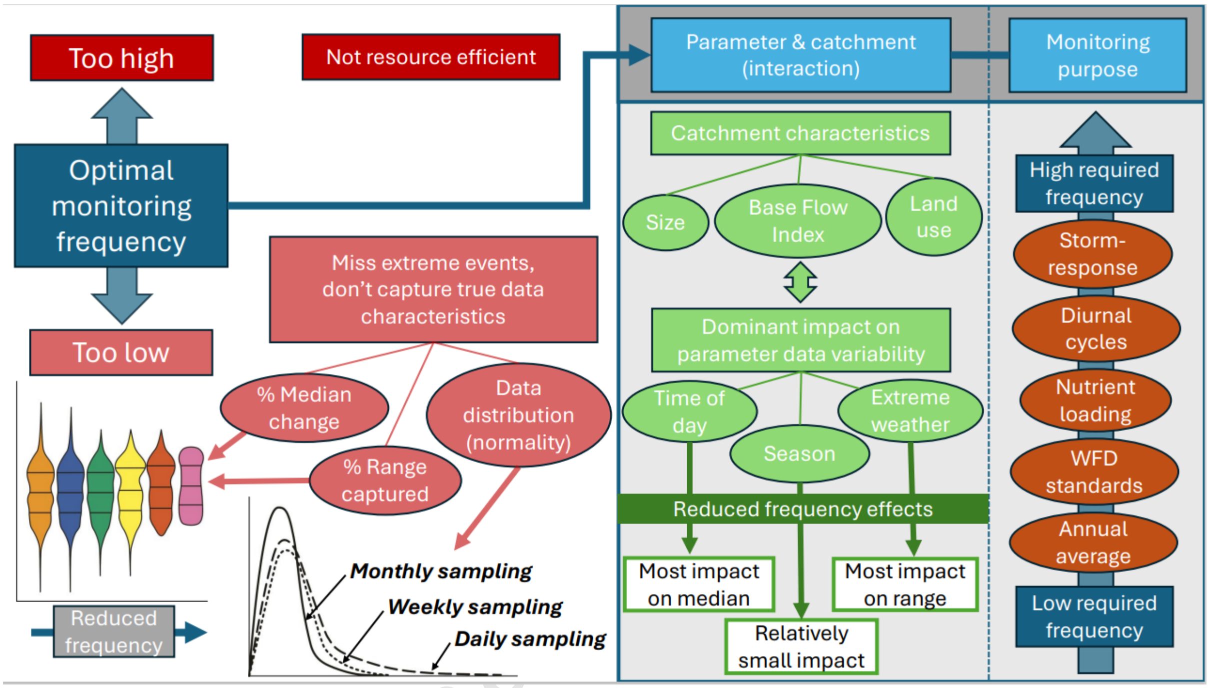
Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract



Highlights

- Measurement timing and frequency influenced water quality data interpretation.
- Four-hourly monitoring was the lowest frequency that captured data variation.
- Diurnal data patterns alter the median, response to extreme weather alters the range.
- Sampling at specific times of day can introduce bias, due to intra-daily variation.
- Identify catchment characteristics and required data resolution for optimised monitoring.