

Technical Note: Assessing a 24/7 solution for monitoring water quality loads in small river catchments

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Abstract. Quantifying nutrient and sediment loads in catchments is difficult owing to diffuse controls related to storm hydrology. Coarse sampling and interpolation methods are prone to very high uncertainties due to under-representation of high discharge, short duration events. Additionally, important low-flow processes such as diurnal signals linked to point source impacts are missed. Here we demonstrate a solution based on a time-integrated approach to sampling with a standard 24 bottle autosampler configured to take a sample every 7 h over a week according to a Plynlimon design. This is evaluated with a number of other sampling strategies using a two-year dataset of sub-hourly discharge and phosphorus concentration data. The 24/7 solution is shown to be among the least uncertain in estimating load (inter-quartile range: 96 % to 110 % of actual load in year 1 and 97 % to 104 % in year 2) due to the increased frequency raising the probability of sampling storm events and point source signals. The 24/7 solution would appear to be most parsimonious in terms of data coverage and certainty, process signal representation, potential laboratory commitment, technology requirements and the ability to be widely deployed in complex catchments.

1 Introduction

Quantifying river transfers of chemical parameters, especially those relating to suspended sediments and/or higher discharges, remains a challenge to research and regulatory bodies owing to dependencies on storm hydrology (Bowes et al., 2009; Wall et al., 2011). Phosphorus (P) and sediment, for example, tend to be removed from land in rapid diffuse transfer events, via surface and near-surface hydrological pathways (Heathwaite and Dils, 2000; Deasy et al., 2009) and the magnitude and rate of change of transfer is particularly influenced by land use (urban and agricultural intensities) and landscape permeability (soil permeability, geology and prevalence of hard surfaces). Highest risk is often when these factors coincide with critical source areas for diffuse transfer (Gburek et al., 2002). Transfers of P are also observed in rivers during lower flows, due to municipal and domestic waste water discharges that may exhibit a diurnal pattern linked to the timing of discharge cycles (Palmer-Felgate et al., 2010).

Regulatory monitoring of P is considered especially important as this is generally considered to be the limiting nutrient in freshwater systems. There are exceptions, but for the most part, considerable additional efforts have been placed in national policies in many countries to deal with P from municipal and domestic effluents and from diffuse agricultural sources (e.g. OJEC, 1991a, b; OJEC, 2000). This monitoring is often spatially rich in terms of river network coverage but temporally poor and, as storm driven diffuse P transfers from agricultural land tend to form very significant contributions



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to annual loads in rivers (Greene et al., 2011), low frequency monitoring may be insufficient to monitor these transfers. This has potentially serious implications as competent authorities are charged with implementing agricultural mitigation measures within legislation and monitoring the benefits at catchment scale (Mainstone et al., 2008). Expectations of change from these national programmes, which in many countries are based on descriptive means of (up to) monthly sampling in rivers, may then be unrealised due to sampling strategies which are inadequate to identify change associated with mitigation effects.

Johnes (2007) clearly demonstrates the uncertainties in trying to collate sparse data into annual metrics of P load by deconstructing daily sampling from large catchments in the UK into less frequent datasets and applying interpolation and extrapolation algorithms. Moatar and Meybeck (2007) also quantified the ranges in uncertainty associated with sub-sampling daily records at up to monthly frequencies for a range of chemical and particulate contaminants, including P, in six large catchments in both France and the US (Moatar and Meybeck, 2007).

Several methods have been used to overcome issues of sparse data samples with automatic water sampling used to target storm events or composite sampling to include a flow weighted element to account for higher flows (Lennox et al., 1997; Jordan et al., 2001). However, targeted storm and composite sampling tends to avoid interim periods where process and chemical-biological interactions may be greatest (Hilton et al., 2006). More recently, automated bankside spectrophotometric equipment has been used to monitor P on a near continuous basis (Jordan et al., 2007; Palmer-Felgate et al., 2010; Wall et al., 2011) but, while giving temporally rich data, these systems are never likely to be spatially rich owing to capital and maintenance costs.

There is, therefore, a requirement to add complimentary monitoring to national programmes that is sufficient to monitor all flow regimes in rivers. Such monitoring should account for the influences of point and diffuse P transfers, where these are likely, provide process information such as diurnal cycling and hysteresis patterns, respectively, and enable trajectories of change for all transfer types to be audited.

Recent work in the Plynlimon experimental catchment has used an alternative strategy based on the use of an automatic water sampler with a 24 bottle configuration set to sample on a 7 h basis (Neal et al., 2011; Halliday et al., 2011). This “24/7” configuration can be used for total chemical species and conservative solutes if the sampler is retrieved on a weekly basis.

In this paper, we evaluate the 24/7 sampling and other configurations, which are feasible using standard field autosampling equipment, by deconstructing and sampling a two-year sub-hourly time series of discharge and P chemistry. Loads are estimated for all sample sets and the aggregated results compared across all sampling configurations.

2 Methods

Data were used from a hydrometric and hydrochemical monitoring station in Co. Monaghan, Ireland. The station set-up is described in detail elsewhere (Jordan et al., 2005, 2007; Cassidy and Jordan, 2011). In summary, discharge was monitored at a rated station at 5 km² in a catchment draining grassland agriculture on drumlin soils. This landscape type is predisposed to high P transfers during storm events (Douglas et al., 2007) and high background P concentrations during low flows from scattered point sources (Arnscheidt et al., 2007). These transfers were monitored by a Dr. Lange Sigmatax-Phosphax suite of instruments that samples river water and analyses TP on a 20 min time-step (3 samples each every hour). Data were extracted over two hydrological years, quality controlled and assessed for completeness. During 2006–2007 and 2007–2008, discharge/TP data were 100%/94% and 100%/98% complete, respectively. Loads were calculated from discharge and TP concentration by interpolation of the 20 min time series (Eq. 3).

Sampling was simulated by applying a numerical algorithm to generate all possible sample sets from the sub-hourly time series, based on a set of caveats for each sampling strategy, and combining both systematic and Monte-Carlo approaches. For the 24 weekly samples a random and 7 h interval were assessed:

1. 24 samples at 7 h intervals
 - Sampling to be initiated between 8 a.m. and 6 p.m., and restricted to Monday to Friday to correspond to normal working hours during which an autosampler would be deployed and initiated.
2. 24 samples at random times over 7 days
 - The autosampler would be programmed to take samples at 24 random times during the week, with each set of time stamps generated weekly and uploaded to the autosampler.

For comparison, sample sets were also generated for monthly, weekly, daily and random sampling frequencies as described in Cassidy and Jordan (2011) and also at sub-daily frequencies less than and greater than the 7 h sampling frequency (Table 1).

Loads were estimated for each sample set using a standard flux-based approach (Method 5 in Littlewood et al., 1998), also known as the first-choice Paris Commission algorithm (PARCOM, 1992), to estimate load L_E (kg) as:

$$L_E = \frac{K \sum_{i=1}^n (C_i Q_i)}{\sum_{i=1}^n Q_i} \cdot Q_r \quad (1)$$

with

$$Q_r = \frac{\sum_{k=1}^N Q_k}{N} \quad (2)$$

Table 1. Series of sampling solutions used to estimate TP load based on the PARCOM algorithm (Eq. 1) showing the number of sample sets and samples per set used in each estimate.

	Sampling Strategy	Number of sample sets	Number of samples per set
1	Random 10 (10 random samples annually)	100	10
2	Monthly	180	12
3	Weekly (during normal working hours, 08:00–18:00)	120	52
4	Weekly (any time- assumes pre-set autosampler)	300	52
5	Weekly + sampling when $Q < 10$ th Percentile ¹	180	117
6	Random 60 (60 random samples annually)	100	60
7	24 hourly samples on a day each week (autosampler)	14	1248
8	Random 360 (360 random samples annually)	100	360
9	Daily Sampling (08:00–18:00)	181	365
10	Nightly Sampling (18:00–08:00)	181	365
11	12 h sampling intervals	151	730
12	24 samples per week – random intervals	151	1248
13	24 samples per week – uniform intervals	151	1248
14	24 samples per week + hourly samples when $Q < 10$ th percentile	151	1508
15	6 h sampling intervals	151	1428
16	3 h sampling intervals	151	2846

¹ Autosampler triggered when stage height exceeds pre-set limit.

where C_i is the instantaneous TP concentration (mg l^{-1}), Q_i is the instantaneous discharge ($\text{m}^3 \text{s}^{-1}$), and Q_r is the average discharge, based on higher frequency discharge records over that sampling duration. K is a constant which accounts for the duration of the record. Q_k is the recorded discharge at 20 min intervals.

The load was estimated for each sample set from each sampling strategy and aggregated for comparison with the “20 min interpolated load”, L_T , based on the sub-hourly data, which was calculated as:

$$L_T = \int_{t_{\text{start}}}^{t_{\text{end}}} Q(t)C(t)dt \quad (3)$$

where, over a sampling period (t_{start} to t_{end}), Q is the instantaneous discharge and C the instantaneous concentration at sample time t .

3 Results and discussion

The several hundred datasets generated by simulation and applied to the flux-based load algorithm (Eq. 1) were plotted as loads in box whisker plots and compared with the 20 min interpolated load of high resolution data (Eq. 3) (Fig. 1a and b).

The 20 min interpolated load was calculated as 1608 kg in 2006–2007 and 1880 kg in 2007–2008. In general, all sampling strategies gave variable estimates of TP load when used with the algorithm. However, as might be anticipated, the distribution in this variation was greater with decreased initial sample frequency and less so with increased frequency.

Random (10 samples) and monthly sample estimates were highly inaccurate with 25th and 75th interquartile ranges well below the 20 min interpolated load calculations and only maximum estimates within the datasets being over-estimates and excessively so in 2006–2007. Accounting for storm events through additional triggered sampling when $Q < 10$ th percentile increased the median load and produced an improvement on the standard weekly strategies, with greatest effect in 2006–2007. Random sampling (360 samples) performed well by comparison with other lower frequency approaches (median = 97.2 % in 2006–2007; median = 104.8 % in 2007–2008). This is attributed to the clustering inherent in randomly distributed points (sample times) providing a good likelihood of investigating the full spectrum of TP variability in the annual data set without bias, while the sample number (the average frequency is approximately equivalent to daily sampling) increases the probability of sampling a broad range of event sizes.

Daily sampling, while resulting in a smaller range of estimated loads compared with the lower frequency approaches, still underestimated load with the interquartile range (IQR) for both years ranging between 72 and 88 % of the 20 min interpolated load for 2006–2007 and 91 to 95 % for 2007–2008. This strategy was based on operational considerations where samples could only be collected during a working day between 08:00 and 18:00. However, when this strategy was changed to sample during overnight periods (18:00 to 08:00), the resulting sample sets tended to over-estimate annual load due to higher TP concentrations as observed with the 20 min data during non-storm periods

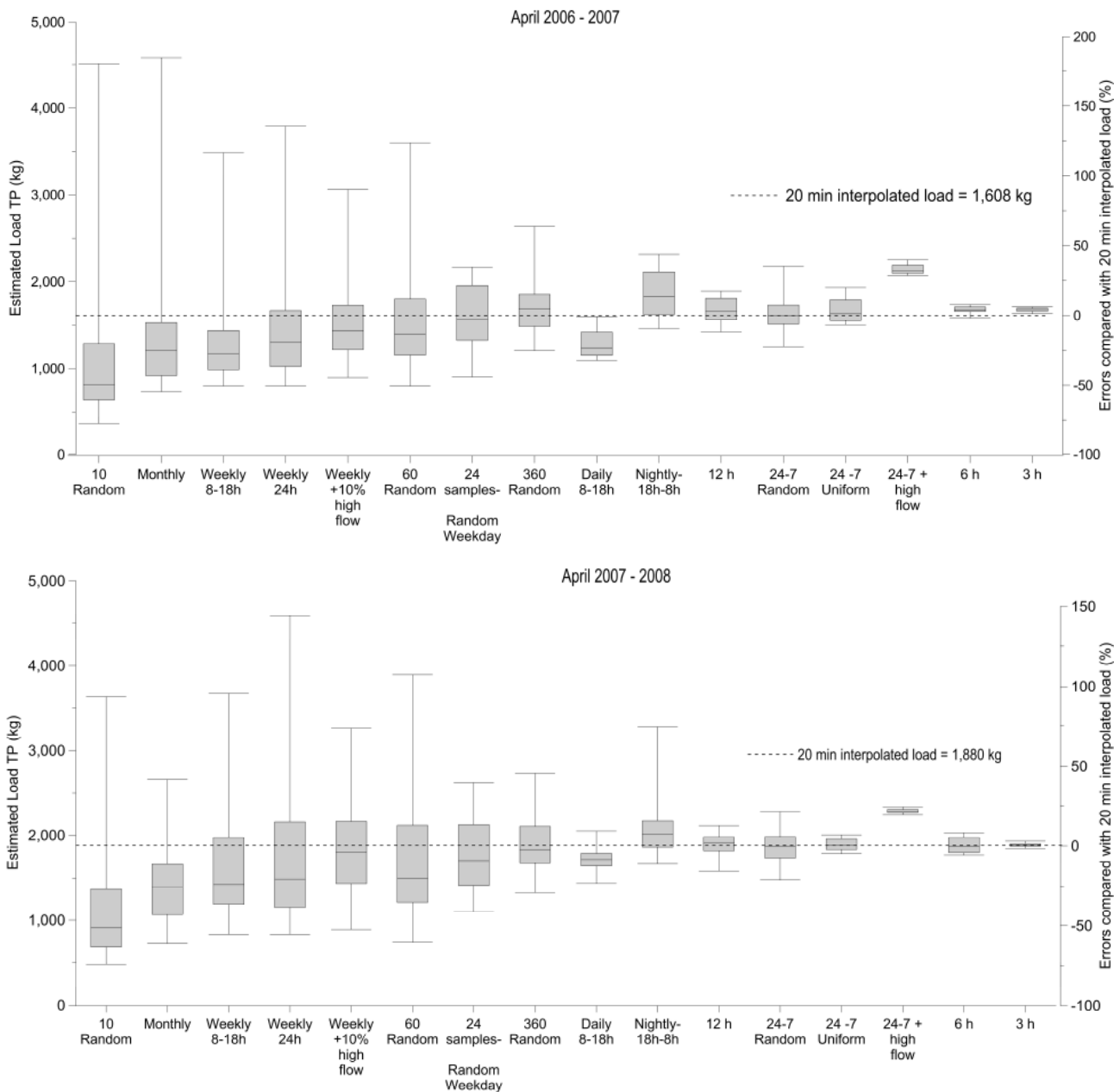


Fig. 1. Box whisker plots showing development of estimated loads (25th, 50th, 75th percentiles, maximum and minimum) using systematic and random sample sets from a decimated sub-hourly dataset of P concentration and discharge in 2006–2007 (a) and 2007–2008 (b).

(median = 114 %, IQR = 101–131 % of 20 min interpolated load for 2006–2007; median = 107 %, IQR = 99–115 % for 2007–2008). The diurnal variation in concentration, with an increase during evening and at night, is evident in the low flow time series shown in Fig. 2b and may be attributed both to a decline in biological activity at night leading to reduced uptake of P and (more likely – Arnscheidt et al., 2007) an increase in household activity either side of the working day and hence a peak in point source pressures. A compromise was shown to be a 12 h sampling

regime that was able to capture both day and night time samples (median = 103 %, IQR = 97–112 % of 20 min interpolated load for 2006–2007; median = 102 %, IQR = 97–105 % for 2007–2008).

Good estimates to the 20 min interpolated load were also generated by the 24 samples (at 7 h intervals) per 7 days (24/7) approach (median = 106.2 %, IQR = 96.6–110 % of 20 min interpolated load for 2006–2007; median = 101.4 %, IQR = 97.3–104.3 % for 2007–2008). The random sampling 24/7 approach gave a similar result, though with

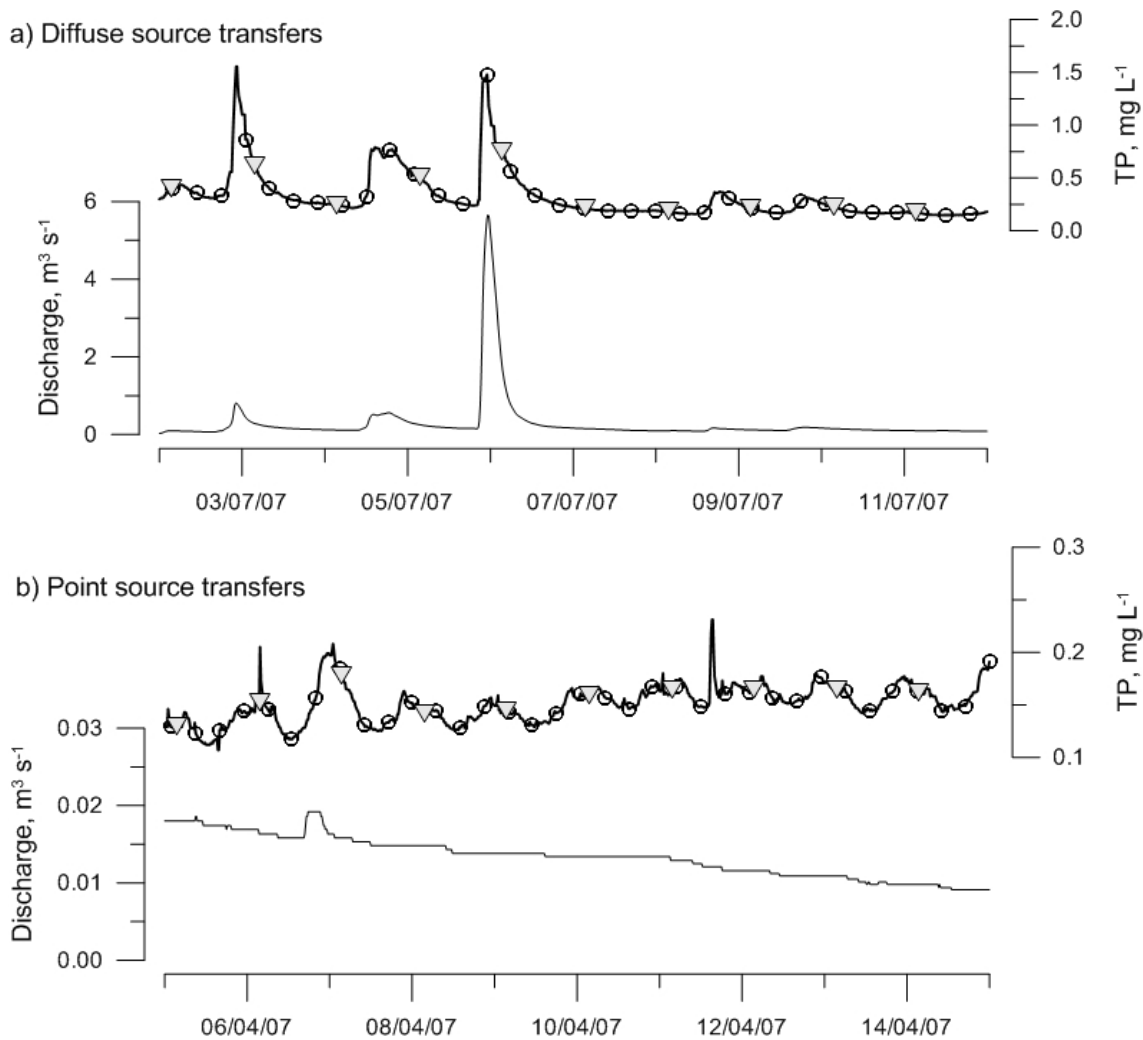


Fig. 2. Representation of a period of discharge and diffuse P transfer during a diffuse storm event (a) with sub-hourly data (solid line), 7 hourly sampling (open circles) and daily sampling (closed triangles). Seven hourly sampling is more likely to capture important times of hydrograph and chemograph development. Also, (b) important diurnal signals during point source P transfers are better represented using the 7 hourly sampling and are missed with daily sampling which, by coinciding with a daily peak in the cycle, may overestimate mean daily low flow concentrations (and similarly underestimate if sampled 12 h previously).

a larger range (median = 100.1 %, IQR = 94.2–107.5 % of 20 min interpolated load for 2006–2007; median = 99.5 %, IQR = 92.4–105.4 % for 2007–2008). Similarly, sample sets for sampling intervals less than 7 h generated estimates of annual load that were close to the 20 min interpolated load and with low variability (e.g. 6 h interval: median = 104.4 %, IQR = 103.1–106.2 % of 20 min interpolated load for 2006–2007; median = 99.5 %, IQR = 95.6–104.8 % for 2007–2008; 3 h interval: median = 104.5 %, IQR = 103.2–105.4 % of 20 min interpolated load for 2006–2007; median = 100.3 %, IQR = 99.6–100.9 % for 2007–2008). However, increasing the sample frequency from 7 h to include samples when $Q < 10$ th percentile flow biased the loads to over-estimate compared with the 20 min interpolated load (median = 132.0 %, IQR = 130.4–136.2 % of 20 min interpo-

lated load for 2006–2007; median = 121.2 %, IQR = 120.4–122.6 % for 2007–2008).

The improved load estimates using the sub-daily approaches are directly attributable to the increased probability of capturing short term fluctuations in concentration. Storm events and diffuse P transfers are often of hours rather than days duration and have a much increased sampling probability at lower intervals (Fig. 2a). The close agreement between 12 h and 24/7 estimated loads indicates that these regimes may be desirable in terms of parsimony of cost, effort and data coverage. The 24/7 approach, for one extra sample per day compared with the 12 h regime, also has the advantage of sampling each hour of the day during a 7 day period (Halliday et al., 2011) for more representative coverage. Apparent also in the 24/7 sub-sample datasets were the representation

of non-storm discharge periods with important diurnal processes represented possibly relating to point P transfers, as noted above, that were absent in the daily sampling (Fig. 2b). Inherent with sampling at the same time daily is the risk of coinciding with diurnal discharges from agricultural or wastewater treatment works and, therefore, either under or overestimating the low flow concentration by coinciding with either a peak or trough in the cycle.

The scale of the river catchment and landscape type used in this study (flashy hydrology with a low baseflow index, high magnitude diffuse P transfers and high frequency point source signals) is typically a challenge for most sampling strategies not based on near continuous data collection. Most of the total annual load can result from higher concentration, short duration events for which sampling probabilities decrease as a power-law with increasing concentration (see Cassidy and Jordan, 2011 for a discussion). Sampling as much of the concentration range as possible is desirable and the improved coverage provided by 24/7 sampling, compared with daily sampling, is demonstrated by examining the proportion coverage of the concentration range by the sample sets for each strategy (Fig. 3). It is a scale, however, that is useful in monitoring the influences of changed policy expediencies towards catchment management such as the Nitrates Directive and other programmes of measures linked to the EU Water Framework Directive (Wall et al., 2011). This landscape type is again a useful benchmark to demonstrate that TP patterns linked specifically to source, viz. point, diffuse and incidental (Jordan et al., 2007) and where these patterns, independent of annual load, change according to specific mitigation measures.

The attractiveness of using the 24/7 approach, for conservative analytes at least, is that it can be achieved using low-technology and off-the-shelf autosampling equipment at existing hydrometric stations, and the pump-type samplers with a 24-bottle configuration are ubiquitous items of monitoring equipment. Personnel requirements and laboratory resources are also easily timetabled on a once per week basis (C. Neal, personal communication, 2011) and if TP load is preferred over pattern then the 24 samples can be composited in the laboratory according to flow-weighted volumes using weekly hydrometric data.

There are, however, some issues related to extreme events and non-conservative analytes. The 24/7 approach only gives scope for 3 samples every 24 h and this, in some very small catchments, may not be enough to sample extreme storm events that can dominate the annual transfers of P and sediment. It is here, even for less extreme events, that uncertainty in the box whisker plots in Fig. 1 is generated during the higher flow events. Again, this may not be so much of an issue as scale and catchment buffering increases at larger national monitoring sites. The non-conservative nature of some analytes is, however, not so readily accommodated. Depending on what the objectives of the monitoring are will be important as, for example, chemical-ecological relation-

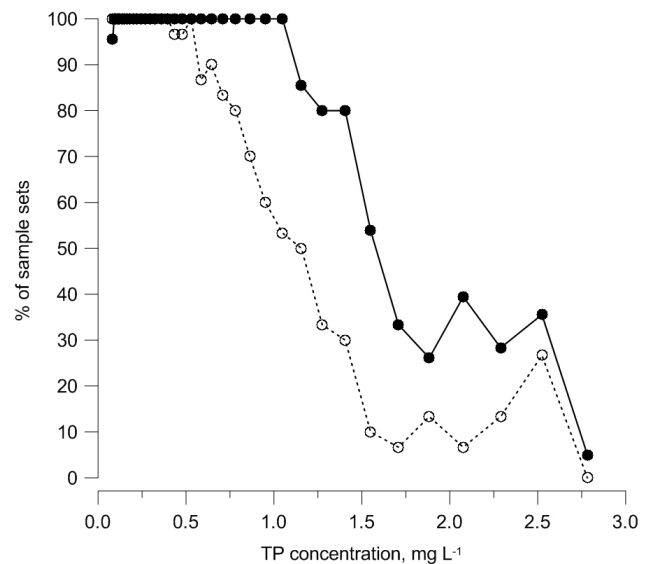


Fig. 3. Percentage coverage of the TP concentration range by the sample sets using the 24/7 sampling solution (closed symbols) and daily sampling solution (open symbols). The 24/7 solution is approximately twice as likely to sample higher TP concentrations, with for example, 100% of the 24/7 sample sets containing samples in the 1 mg l⁻¹ range while only 50% of the daily sample sets contain values in the same range.

ships are more likely to be linked to soluble nutrient status of water bodies. Total reactive P and other soluble P fractions may not be amenable to being left in sample bottles for up to 7 days (Haygarth et al., 1995) and possibly the best that can be achieved is for samples taken from the last three bottles for immediate processing on return to the laboratory. Other conservative solutes and sediments are easily accommodated (Neal et al., 2011).

In other, larger catchments, where hydrological buffering due to scale, soil type and geology may decrease runoff flashiness and possibly where there is a stronger diffuse pollution signal (or this is the most important signal to monitor in very small catchments), it may not be necessary to increase sample resolution during non-storm periods. Here, other workers have shown that the variation in non-storm transfers is small enough for the emphasis to be on storm events (e.g. Kronvang and Bruhn, 1996). Additionally, variability in flux for a range of chemical and particulate contaminants (in catchments > 1000 km²) may be predictable based on the percentage of long-term flux transported in a small percent of the time (Moatar and Meybeck, 2007). However, in many catchments, there is an increasing recognition of the interaction between nutrient sources related to flow regime (e.g. Hilton et al., 2006). For example, in river base flows Cassidy and Jordan (2011), indicate that data from monthly sampling are likely to be useful in capturing low flow signals from the high probability of sampling these high frequency flows (and their point source impacts – if present) and this

is also indicated by Foy (2007) in large river systems. This creates a conundrum for agencies that are required to monitor the benefits accruing from both diffuse and point source mitigation measures and especially relationships with ecological metrics in flowing and standing waters and it may be that a moderate to high degree of empiricism is required before looking to reduce to a coarser sampling regime. In the analysis in the current study, the different resolution sampling regimes have at least been tested with a much higher resolution dataset to resolve these important signals and which is likely to provide a richer dataset at larger scales – this could then be subsequently tested for further parsimony if required.

4 Conclusions

A two year, sub-hourly data-set of synchronous discharge and P concentration from a flashy 5 km² catchment was deconstructed into artificial data-sets of coarser resolution, and a numerical algorithm was used to generate sample sets both systematically and with a Monte-Carlo approach. Sample sets were collated into annual P loads using a standard flux-based algorithm based on metrics of instantaneous discharge and concentration with findings that:

- In this catchment, with examples of point and diffuse P transfer, daily sampling tended to underestimate load with an IQR between 72 and 88 % of the 20 min interpolated load and failed to reveal important sub-daily transport patterns.
- A 24/7 sampling solution based on a Plynlimon design and modelled on an auto-sampler generating 24 samples per week on a 7 h cycle improved the estimated load variability (IQR = 96.6–110 % for 2006–2007; IQR = 97.3–104.3 % for 2007–2008) and also revealed sub-daily patterns related to point and diffuse P transfers which can be used to monitor trajectories of change from both signals.
- Sub-7 h samples showed small reductions in load estimate variability but the 24/7 design is more easily implemented and is likely to improve the coverage of all metrics (annual load, sub-daily patterns, etc) as catchment scale increases; with, for example, hydrological buffering increasing to higher baseflow indices (due to soil and geology influences on runoff) and the interaction of multiple P sources diminishing.
- Implemented as a complimentary part of forward national WFD monitoring, the 24/7 solution is likely to be a parsimonious and cost effective compromise between spatially rich routine monthly sampling and temporally rich fully automated bankside analysis and could form the basis of further reductions in sample resolution when used as a comparative dataset at larger scales.

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