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On the value of long-term, low-frequency water quality sampling: avoiding throwing the baby out with the bathwater

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High-frequency water quality sampling is all the rage, and rightly so. Kirchner *et al.* (2004) show how fine-scale data open up new insights into data structures. They note that new water quality sampling technologies have transformed, and will continue to transform, our view of catchment processes by allowing us to make observations at temporal resolutions that are orders of magnitude finer than before.

High-frequency measurements of chemical behaviour will certainly yield novel insights into many key questions in catchment hydrology and will compel new approaches to data analysis and modelling. This will in turn drive new approaches to field experimentation. While the Kirchner *et al.* (2004) commentary has been highly influential and accelerated interest in new hydrochemical signatures, we fear that one interpretation may be that there is little to be gained from studying past low-frequency data and that we may have been diverted from examining such records.

Here we explore the value of low-frequency water quality data and ask the rhetorical question: are they still useful? We do this because we fear abandonment of many low-frequency long-term datasets and a general attitudinal shift regarding the value of such records. Our purpose here is simply to redress the balance and to point out that examination of long water quality time series remains fruitful. Furthermore, as long records are required to assess long-term changes in catchment response, it would seem negligent to pay no attention to them, especially because recent work has shown that such data may contain evidence of rare events or of very rapid shifts in system behaviour (Burt, 1994; Burt *et al.*, 2010a; Howden *et al.*, 2010), indicate long-term trends (Howden and Burt, 2008, 2009) and set the context within which shorter records can be interpreted (Burt *et al.*, 2008). This last point is crucial because short-term catchment studies (i.e. <10 years) tend to be highly influenced by inter-annual hydroclimatic variability, such that long-term trends are often obscured. However, our main point in this commentary is that we cannot afford to wait years or decades for new types of high-frequency data to accumulate when good scientific use can be made of existing sources. Before the advent of data loggers and field-deployable analytical instrumentation, high-frequency sampling cost much more time and effort in the field, and in laboratory analysis of large numbers of water samples. It is not that high-frequency data were never obtained, but that they were uncommon.

One example to make the point, that is emblematic of many such records around the world, is the 50-year (1957–2007) record of river water nitrate concentrations and flux for the Great Ouse river in eastern England. Gauged daily flows derived from 15-min values are available from 1 January 1933 (NRFA gauge 33002; catchment area 1460 km^2) and, more relevant here, nitrate concentrations are available for the same site from 1957 (first sample 2 January 1957, n = 4250). Sample frequency averages 83 samples per year; however, the record benefits from very frequent sampling during the mid-1980s, with approximately weekly samples for the remainder of the record.

We used the complete daily nitrate concentration record for 1985 (Figure 1) to examine the effect of different sample frequencies on errors in estimated annual flux and flow-weighted concentration (FWC). As a starting point, we assumed that a 'true' nitrate flux could be calculated by multiplying each daily concentration by the gauged daily flow (Method 2, Littlewood *et al*., 1998). The record was then sampled for all possible combinations of 7-day, 14-day and 28-day sampling frequency. Gaps created in the daily nitrate record were interpolated: the nitrate concentration for the nearest sample in time was applied. For weekly sampling, for example, this means that each sample value is allocated to the 3 days without sampling either side of the sampling date. This is the 'stationary interpolation method' of Alewell *et al.* (2004).

The results of our simple analysis are shown in Table I. Note that Method 1 flux is simply the product of annual mean flow and annual mean concentration. FWCs are derived from the flux estimates in all cases except for Method 1 which is simply the annual mean concentration. We quote the coefficient of variation (CV: σ/μ) as a percentage. In terms of precision, assuming a normal distribution of sample values, then 95% will fall within 1·96 standard deviations (σ) of the mean (μ). Seven-day sampling gives a high level of precision with 95% of flux estimates within 2·7% of the mean value. Even 28-day ('monthly') sampling yields 95% of values within 6·5% of the mean; this is a surprisingly high level of precision result given the infrequency of sampling. In terms of accuracy, the mean flux for 7-day sampling is very close to the 'true' flux, but the 14-day and 28-day means slightly underestimate the 'true' load (and also the FWCs therefore), because some periods of higher nitrate concentrations associated with high flows are inevitably missed.

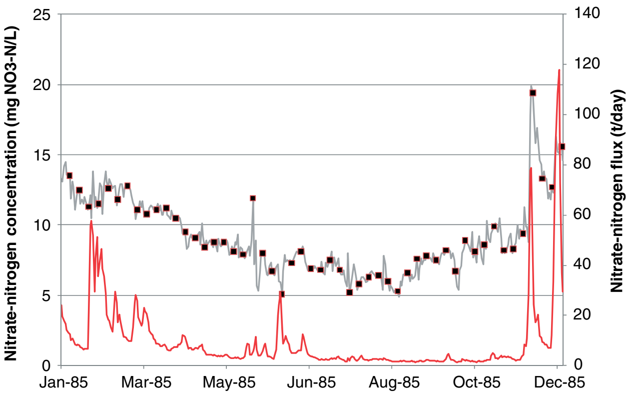

Figure 1. Daily nitrate–nitrogen flux (red line, tonnes) and daily nitrate concentration (grey line, mg NO_3-N l^{-1}) for the Great Ouse, 1985. Black boxes show 7-day ('weekly') samples beginning (arbitrarily) on 7 January

Table I. Mean flux and FWC estimates for the Great Ouse, 1985

	Flux (t)					FWC (mg/l)
Method 2 (daily)	3475·9					10·8
Method 1 (annual)	2945·6					9·2
Sample frequency	Mean flux estimate	σ	CV (%)	1·96σ	CV at 1·96σ (%)	
7-day	3463·3	48·3	1·4	94·7	2·7	10·8
14-day	3424·7	93·4	2·7	183·1	5·3	10·6
28-day	3412·0	113·1	3·3	221·7	6·5	10·6

See text for explanation of sampling procedure. The Method 2 results are assumed to be the 'true' value. Ninety-five percent of sample estimates fall within $\pm 1{\cdot}96\sigma$ of the mean (expressed here as CV%).

The estimated annual nitrate fluxes and FWCs for the Great Ouse 1957–2007 (Figure 2) show the value of long-term low-frequency data. The results show a sharp rise in FWCs from the early 1960s through to the mid-1970s as farming practices intensified in the catchment. FWCs peak in 1977, a very wet year following a severe drought. Thereafter, FWCs fall slowly, despite much effort to reduce nitrate leaching via improved farming practices and government legislation (Burt *et al.*, 2010b). A similar pattern is seen for the neighbouring Thames basin (Howden *et al.*, 2010). Fluxes mirror FWCs to some extent but are also influenced by annual runoff (not shown). Following the late-1970s peak, fluxes too have remained obstinately high. In the 1975 water year (beginning 1 October 1974), annual nitrate-N flux first exceeded the equivalent of 20 kg/ha, the upper threshold for nitrogen flux identified by Hessen (1999) for catchments 'moderately influenced by human activity'. Since 1975, that level has been exceeded in 25 of 33 years.

The explanation of 'reliability' in this case is straightforward. The architecture of the nitrate time

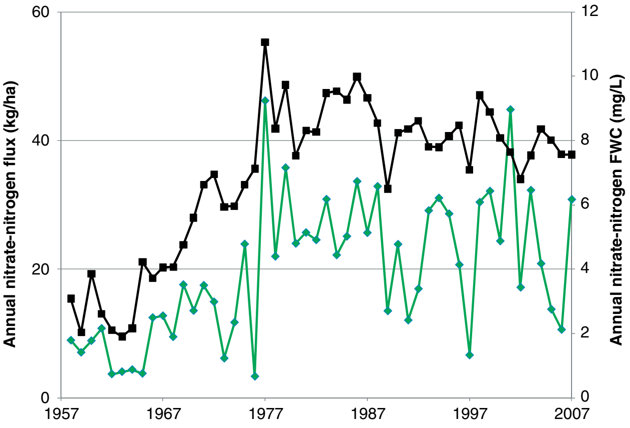

Figure 2. Annual nitrate–nitrogen flux (green line, kg/ha) and FWC (black line, mg NO_3-N l^{-1}) for the Great Ouse for water years 1958–2007

series comprises relatively small variations day to day; the seasonal cycle is the main feature (Figure 1). Storm events affect the record but, given that this is a relatively large river, these perturbations are picked up by weekly sampling if not by less frequent sampling. Variations in discharge are more significant but, as is often the case, the flow record here is reliable, being based on high-frequency observations. It is clear that weekly sampling would be less reliable where concentrations vary more frequently and over a greater range. This is likely to be relevant in small(er) basins and where contaminants are much more discharge-dependent—sediment-related pollutants in particular. Indeed, we note that much of the work on estimating suspended sediment loads from intermittent water sampling (see in particular work by Des Walling and Bruce Webb in the 1980s, such as Walling and Webb, 1981) was driven by the need to cope with concentrations varying over several orders of magnitude in just a few minutes or hours. Under such testing conditions, continuous records provided by turbidity probes have obvious advantages (provided they continue to function properly, of course).

So, what is the value of low-frequency long-term data? Indeed, disagreement exists in the literature on this issue. Alewell *et al.* (2004) found that higher-frequency sampling (of nitrate, chloride and sulphate) brought no additional benefit; while Whyte and Kirchner (2000) concluded that detailed within-storm sampling was the only way to understand highly episodic contaminant transport (particulate mercury fluxes). For phosphorus, a pollutant largely delivered by near-surface and surface quickflow pathways, Johnes (2007) concludes that daily records may fail to capture the full range of P export behaviour in smaller catchments with flashy hydrographs. Our nitrate example shows that, for a large river where there is relatively low variability around the mean concentration, lower-frequency sampling can still produce reliable flux estimates.

We conclude by noting that process studies in small catchments must inevitably benefit from new technologies that can provide near-continuous records of solute concentration. Kirchner *et al.* (2004) were quite right to argue that there is a lot to be learned if we take the time and trouble to monitor catchment hydrochemical behaviour at high frequency over long spans of time; novel insights seem inevitable. However, in taking this agenda forward, we should not neglect other questions which new technology cannot yet address, in particular about already collected data series of long-term change. Low-frequency observations can yield important new insights!

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