

The fine structure of water-quality dynamics: the (high-frequency) wave of the future

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Science is often driven forward by the emergence of new measurements. Whenever one makes observations at a scale, precision, or frequency that was previously unattainable, one is almost guaranteed to learn something new and interesting. Our purpose in this commentary is to argue that catchment hydrochemistry is on the verge of just such a major new advance, driven by automated, online continuous analysis for many chemical constituents in natural waters.

To date, most catchment hydrochemical studies have been based on hourly or sub-hourly measurements of water fluxes, and weekly or monthly samples of rainfall and streamflow chemistry. This stark mismatch in measurement time scales springs from the measurement technologies involved. Water flux measurements are easily automated, and can be logged at any interval that is desired. Conventional laboratory measurements of water chemistry, by contrast, are time consuming and expensive, and at high sampling frequencies the sample bottles pile up fast. For this reason, high-frequency chemical monitoring has typically been restricted to intensive studies of individual storm events.

That is now changing. Field-deployable autoanalysers are now a reality, and ion-specific electrodes continue to improve. These technological developments promise to provide measurements of rainfall and streamflow chemistry at hourly or sub-hourly intervals (similar to the time scales at which hydrometric data have long been available) and to provide these measurements for long spans of time, not just for intensive field campaigns associated with individual storms.

These technologies are likely to transform our view of catchment processes, by allowing us to observe their hydrochemical evolution at temporal resolutions that are orders of magnitude finer than before. Continuous online measurements of pH and electrical conductivity have been available for years, and they provide a preview of the high-frequency hydrochemical behaviour that will become observable through automated online chemical analysis (e.g. Robson, 1993; Robson *et al.*, 1993, 1995; Jarvie *et al.*, 2001). Figure 1 shows part of a year-long time series of hourly measurements of electrical conductivity at Plynlimon, Wales (Robson *et al.*, 1992, 1993), along with daily, weekly, and monthly subsamples of the same record to illustrate the dramatic loss of information that occurs at lower sampling

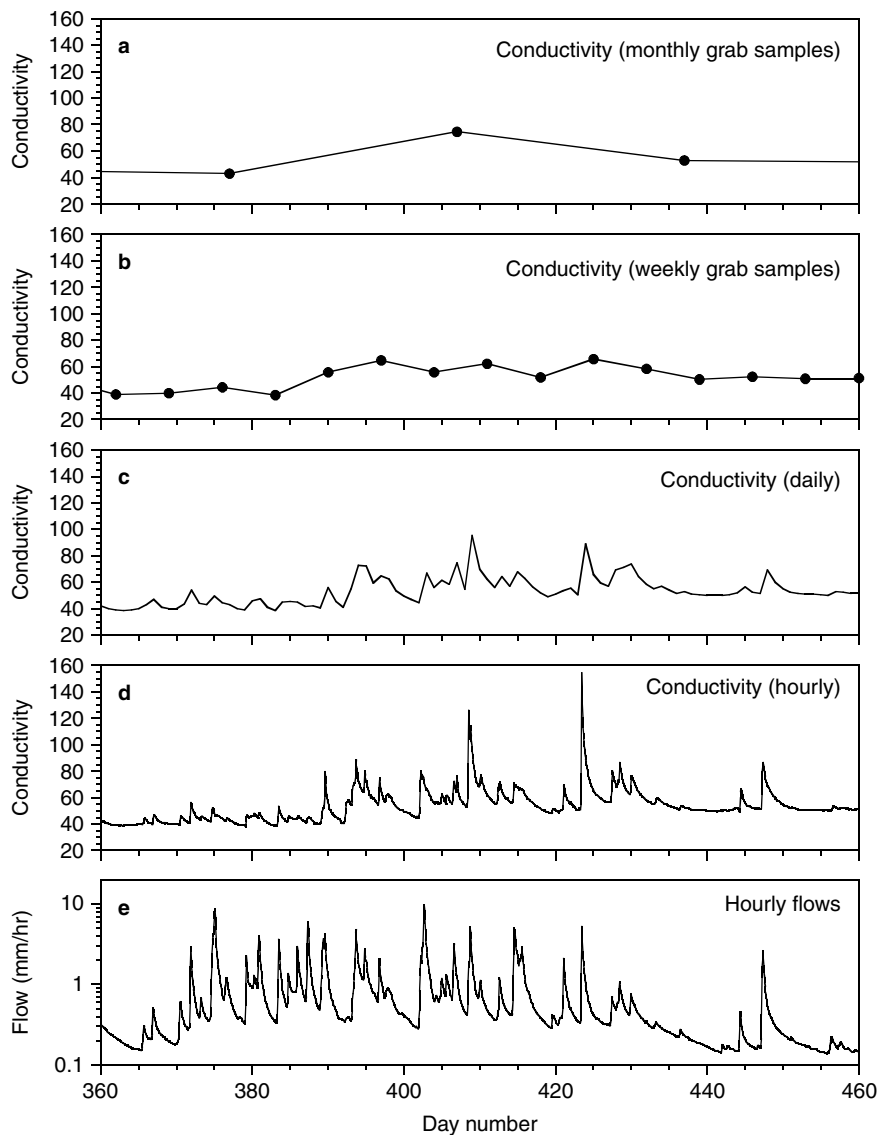


Figure 1. Electrical conductivity measured monthly, weekly, daily, and hourly from 27 December 1989 to 6 April 1990 at Hore stream, Plynlimon, Wales, with discharge record for comparison. Monthly, weekly, and daily measurements conceal the rapid response of conductivity to hydrologic episodes. Note also that the coupling of conductivity and hydrology is variable over the period shown here; between days 360 and 390, conductivity does not respond strongly to changes in flow, whereas from day 390 onward it is much more sensitive to hydrologic variations

frequencies. From samples collected at monthly or weekly intervals (Figure 1a and b), one could hardly imagine the highly dynamic, information-rich behaviour that is readily observable at hourly time scales. Chemical measurements taken weekly (the typical sampling interval for catchment hydrochemistry studies) miss almost all the storm events,

and thus fail to reveal the very close coupling between the hydrological and chemical dynamics (Figure 1b). Even daily measurements (Figure 1c) fail to convey the fine structure of the hydrochemical behaviour of this catchment.

Weekly or monthly chemical monitoring data have been widely used for catchment input–output

mass balances, or for detecting and measuring long-term trends in water quality. For these purposes, weekly or monthly sampling may or may not be adequate (for two contrasting examples, see Alewell *et al.* (2004) and Whyte and Kirchner (2000)). But in any case, relying only on weekly or monthly chemical measurements restricts one's scientific worldview to the questions that those data can address. The emergence of long-term, high-frequency chemical monitoring data promises to open up new lines of inquiry that have previously been largely inaccessible.

In particular, understanding the process linkages between catchment hydrology and streamwater chemistry requires chemical measurements on the time scale of hydrologic response in small catchments, and that time scale is on the order of minutes or hours, not weeks or months. We have every reason to believe that high-frequency measurements of chemical behaviour will yield novel insights into many key questions in catchment hydrology, including:

1. How long do catchments store water in the subsurface, and by what combination of flowpaths does this water reach the stream?
2. What are the mechanisms connecting catchments' (relatively long) time scales of water storage and their (much shorter) time scales of hydrological response to rainfall inputs?
3. How do the time scales and flowpaths of subsurface transport change with flow regime and antecedent conditions?
4. How do hydrological conditions, and thus flowpath routing, affect the chemical interaction of porewaters with soils, bedrock, and biological processes within the catchment?
5. How should models aggregate catchments' intrinsic complexity and heterogeneity, in order to represent catchment behaviour adequately across a range of time scales?

These are important questions in catchment research, and high-frequency chemical monitoring promises to shed new light on them. To understand how hydrological flowpaths affect stream chemistry (and conversely, to use stream chemistry to decipher hydrological processes) we need chemical

measurements at time scales that correspond to hydrological dynamics.

Our own recent experience illustrates our view that higher-frequency chemical monitoring will lead to new insights into the structure and function of catchments. We recently found that conventional catchment 'box' models were inconsistent with daily measurements of chloride (a naturally occurring chemical tracer) in rainfall and streamflow at Plynlimon (Kirchner *et al.*, 2000; Figure 2). Instead, the Plynlimon data implied that subsurface flowpaths are highly heterogeneous, resulting in strong dispersion of chemical tracers (Kirchner *et al.*, 2001). These results also have important implications for the longer-term dynamics of catchment response to contaminant inputs: in the long term, a highly dispersive transport system will be slower to flush itself of residual contamination than a well-mixed 'box' would be (Kirchner *et al.*, 2000).

This view of subsurface transport could not have been developed without the daily chloride measurements from Plynlimon. As Figure 2 shows, the daily chloride data from Plynlimon clearly exhibit both long-term persistence and short-term transient response to storm events. This superficially paradoxical pattern of behaviour (a long-term persistence that implies a long residence time, combined with a short-term transience that implies a short residence time) is essential for understanding subsurface transport in these catchments, and it is invisible in the weekly and monthly time series at Plynlimon. It is sobering to consider that even the daily chloride measurements in Figure 2 may be concealing yet another level of fine structure in the hydrochemical dynamics, just as the daily conductivity record in Figure 1c conceals the much greater hydrochemical complexity that is revealed in the hourly record in Figure 1d.

High-frequency chemical measurements are also essential for testing hydrological models. Hydrological data alone are rarely sufficient to test the process assumptions embedded in typical hydrological models. Instead, both hydrological and geochemical time-series data are needed to identify appropriate model structures and constrain their parameters (e.g. Mroczkowski *et al.*, 1997). But typical weekly or monthly monitoring programmes cannot capture the short-term chemical dynamics

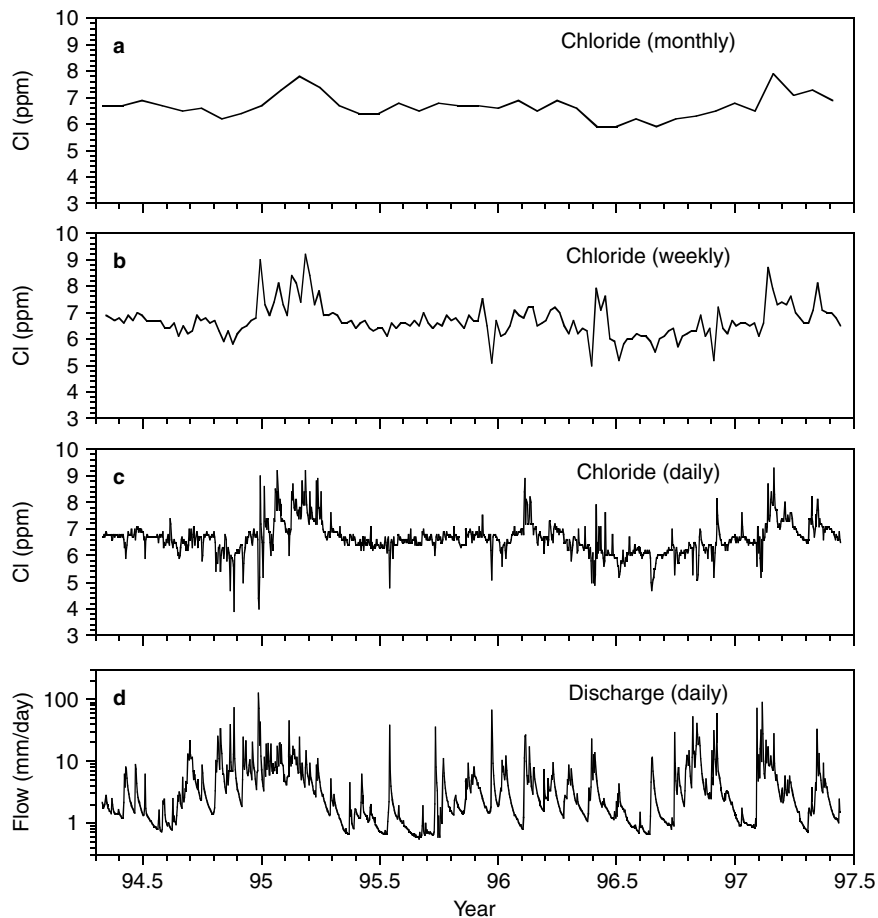


Figure 2. Streamflow chloride concentrations measured monthly, weekly, and daily for three years at Hafren stream, Plynlimon, Wales, with daily discharge record for comparison. The daily chloride record clearly shows short-term transient response during hydrologic episodes and long-term persistence between episodes; the weekly and monthly records conceal this pattern of behaviour

that most closely reflect hydrological processes. Thus high-frequency chemical observations will be essential in developing, calibrating, and validating the next generation of catchment models.

High-frequency chemical sampling has been almost exclusively employed in intensive studies of individual storm events, but a lot will be learned by extending these high-frequency measurements over much longer spans of time. Long records are needed to capture a wide range of hydrological regimes, as well as episodes with unusual chemical inputs; these provide natural manipulation experiments that provide new clues concerning the dynamics of catchment processes. One might assume that nothing interesting would be observed

during the hydrologically boring periods between storm events. But, as Figure 3 illustrates, it is during just such periods that interesting biogeochemical signals may emerge, precisely because they are not obscured by large hydrological fluctuations. The marked diurnal cycle shown in Figure 3 probably results from the combined effects of evapotranspiration and in-stream respiration (e.g. Jarvie *et al.*, 2001). Under daily, weekly, or monthly sampling, this distinct daily oscillation would have remained undiscovered. As this example indicates, studying the interaction between hydrological and biological processes requires detailed chemical monitoring under a wide range of hydrological conditions.

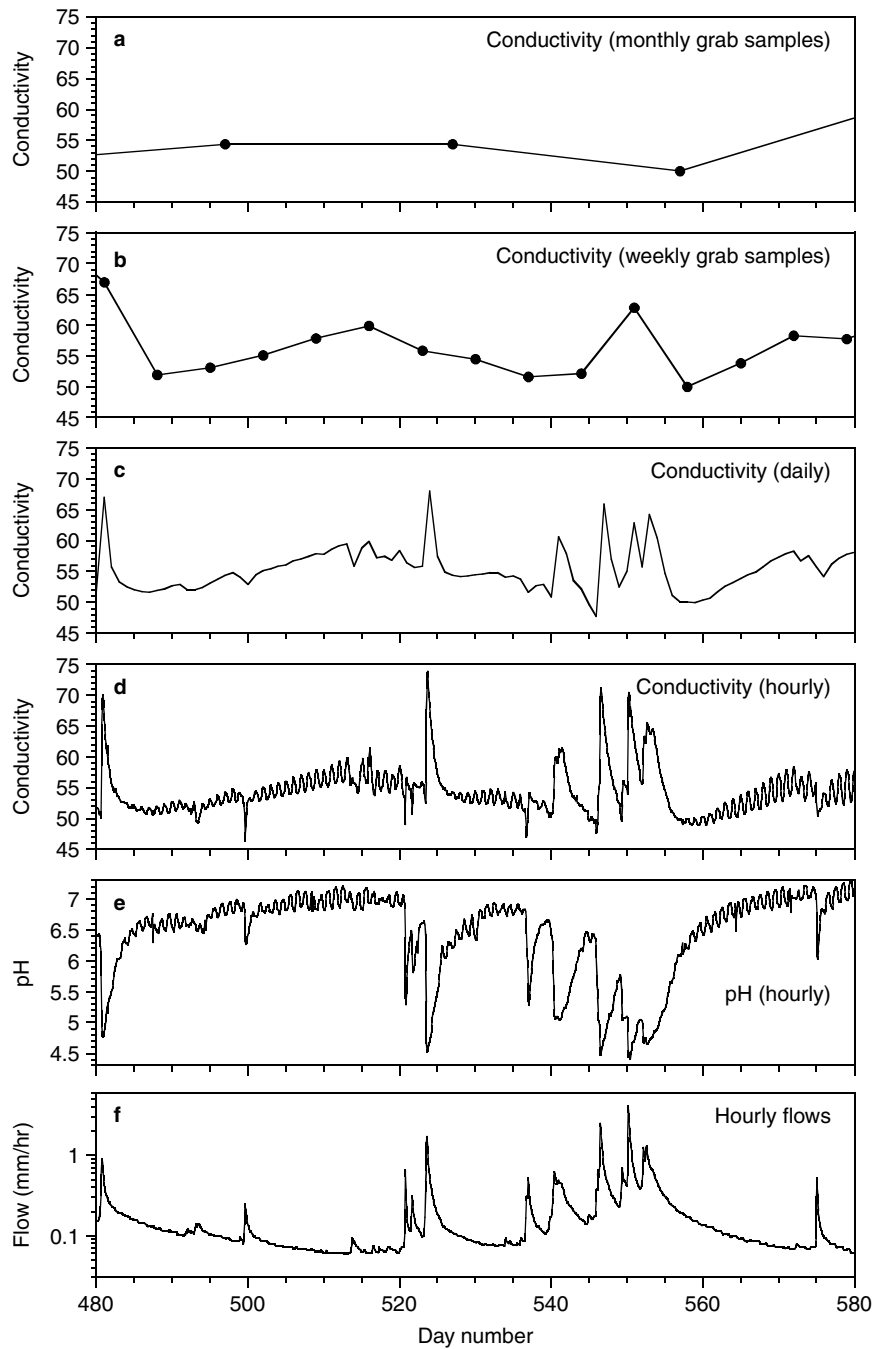


Figure 3. Electrical conductivity measured monthly, weekly, daily, and hourly, with hourly pH and discharge, at Hore stream, Plynlimon, Wales. The time span shown is 26 April to 4 August 1990, a relatively dry period with few storm events. Hourly sampling reveals pronounced daily cycles in conductivity and pH, which are concealed in daily, weekly, and monthly sampling

Figures 1 and 3 jointly illustrate the value of sustaining high-frequency chemical measurements over long spans of time. The time series shown in Figure 3 begins only 20 days after Figure 1 ends, but the behaviour of the catchment system is distinctly different. If the time series had been discontinued at the end of the 100-day record shown in Figure 1, then the very different pattern shown in Figure 3 would never have been detected. Monitoring catchment hydrochemistry for long periods of time, under diverse hydrologic regimes, maximizes the chances for serendipitous discoveries.

Long-term, high-frequency measurements are also needed because hydrochemical response to rainfall events can vary greatly, even within a single catchment, depending on precipitation intensity, antecedent conditions, and seasonal changes in catchment biogeochemistry (e.g. Robson *et al.*, 1993; Elsenbeer *et al.*, 1994). In Figure 1, for example, conductivity responds weakly to storm events for the first 30 days, and then abruptly becomes much more sensitive to variations in flow. Observations of an individual storm, no matter how detailed, would give an incomplete picture of the diverse hydrochemical behaviours that this catchment can exhibit. Long-term monitoring is also required to maximize the chances of catching extreme hydrological or chemical events (such as severe storms, acid pulses, or seasalt episodes), which can be particularly informative both hydrologically and biogeochemically. Thus, a comprehensive view of catchment hydrochemistry will require systematic observations, at sub-storm time scales, for diverse storm events under a wide range of hydrological conditions.

Long-term, quasi-continuous records of catchment hydrochemistry will both compel, and invite, new methods of data analysis and modelling. High-frequency chemical records will open the door to methods such as spectral analysis, wavelet techniques, and cross-spectral and cross-correlation analysis, which have only rarely found application in hydrochemical studies to date. Conversely, the sheer volumes of data involved will make casual 'eyeball analysis' problematic, so new tools for data reduction and pattern detection will be needed.

How frequent must chemical measurements be, to create a virtually continuous record of

catchment hydrochemistry? When one can verify that additional measurements will merely 'connect the dots' between the existing observations, the hydrochemical record can be considered continuous for all practical purposes. Figures 1 and 3, for example, are created from 15 min measurements, but the 15 min data do not reveal any behaviour that is not already captured in the hourly measurements; thus, hourly observations can be considered virtually continuous for this particular catchment. Hydrometric data can probably give a first indication of the necessary measurement frequency; Robson (1993) notes that, at Plynlimon, additional pH and conductivity measurements become redundant at about the same sampling frequency as additional discharge measurements do. This implies that the necessary measurement frequency is likely to be higher in smaller catchments.

Systematically collecting high-frequency hydrochemical data presents technical and logistical challenges. At present, the two major technologies for continuous field measurements of individual chemical constituents are ion-specific electrodes and field-deployable autoanalysers. Neither of these methods has yet come into widespread use in catchment hydrochemistry, and each has its drawbacks; ion-specific electrodes can be prone to drift, instability, and fouling when used in the field, and field-deployable autoanalysers are costly and require significant ongoing maintenance. All of these devices have been primarily designed for wastewater monitoring and industrial process control, and are not optimally configured for hydrochemical research. Heretofore, off-the-shelf systems have been widely used for field measurements of only a few parameters, notably pH, conductivity, temperature and dissolved oxygen. Attempts have been made to interpret continuous pH and conductivity data as proxies for other chemical parameters, such as alkalinity or seasalt (e.g. Jarvie *et al.*, 2001), but such efforts require that the relationships between the various chemical constituents are both simple and stable through time, and this is often in doubt.

Thus, we will need to expand our view beyond turnkey systems that can simply be picked out of a catalogue, and we will need to invest effort to adapt the available online analysis technologies to

meet the requirements of catchment hydrochemical research. The reliability of online chemical analysis continues to improve, but it will probably never match the dependability of laboratory analyses on bottled samples. Thus, it will be necessary to collect bottled samples periodically (perhaps even daily), to provide benchmarks against instrument drift, to provide cross-checks to detect unreliable readings, and to provide backup measurements for when the online analysis systems break down. Ongoing data analysis will be needed to catch equipment malfunctions promptly. Where continuous unbroken time series are required, duplicate or triplicate measuring systems may be necessary. Measuring rainfall chemistry at high frequencies presents its own special challenges; automated analysis systems must be kept in calibration over long intervals without any rainfall to analyse, and at typical rainfall rates, large precipitation collectors will be needed to generate suitable volumes of water at hourly or sub-hourly intervals.

In our view, overcoming these technical and logistical obstacles will be well worth the effort. If we 'make do' with weekly or monthly water-quality sampling, then we are viewing the catchments behaviour through a blurry telescope that can only see its largest and most persistent features. If we 'make do' with high-frequency sampling of an individual storm event, then we are peering at the catchment through a pinhole, with a sharp view of only a small part of its overall behaviour. Our point is not that there is anything wrong with either of these conventional sampling schemes, but 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.

Imagine trying to understand a Beethoven symphony if one could only hear one note every minute or two! That is what we are trying to do when we infer the hydrochemical functioning of a catchment from weekly or monthly grab samples. Or imagine trying to understand a symphony from a high-fidelity recording of just one of its crashing crescendos. That is what we are trying to do when we analyse high-frequency samples of an individual storm event. Continuous high-frequency monitoring of catchment hydrochemistry will require

significant resources and tenacity. In our view, however, what we stand to learn is well worth the effort. If we want to understand the full symphony of catchment hydrochemical behaviour, then we need to be able to hear every note.

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