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High-frequency precipitation and stream water quality time series from Plynlimon, Wales: an openly accessible data resource spanning the periodic table

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Abstract

This scientific briefing announces the availability of a new multi-element high-frequency water quality data set that is openly accessible to the research community. The data set comprises up to two years of seven-hourly water quality data for two streams and one rainfall site in the Upper Severn catchment at Plynlimon in mid-Wales. The measurements cover 50 analytes ranging from H^+ to U and spanning six orders of magnitude in concentration**,** including major, minor, and trace elements as well as nutrients, and they complement decades of weekly measurements of the same analytes at the Upper Severn. Together they provide a unique data set for studying both long-term trends and short-term dynamics. Archives and metadata for both the seven-hourly and weekly measurements accompany this scientific briefing as supplementary online information. The data show complex behaviour over a wide range of timescales, challenging our understanding of catchment processes and informing future modelling efforts.

Background

In 2007, the management of the Centre for Ecology and Hydrology (CEH) launched a major exploratory study at the Plynlimon experimental catchments of the Upper Severn in mid-Wales, examining the high-frequency dynamics of stream water quality for two years, non-stop (Neal et al., 2012). This initiative was bold in that the measurements constituted an act of discovery that would not normally be supported within conventional grant applications due to the enormous financial cost. The initiative was also bold in that it was decided from the beginning that this unique dataset would be made fully available to the research community soon after the initial publication of the findings.

The study posed a fundamental question: “What components of stream water quality dynamics do we miss with conventional weekly or monthly monitoring and ad hoc, event-based high-frequency measurement campaigns?” This question was raised for five reasons:

1) Continuous monitoring of pH and conductivity started to reveal highly complex dynamics within the streams of the Plynlimon experimental catchments (Kirchner et al., 2004) that were not observed within the corresponding weekly water quality monitoring programme. As pointed out by Kirchner et al. (2004), “If we want to understand the full symphony of catchment hydrochemical behaviour, then we need to be able to hear every note”.

2) Under different hydrometeorological or pollution climates the notes of the hydrochemical "symphony" may follow a different score. Hence, there was a need to extend the high-frequency monitoring to encompass seasonal time scales and the long intervals between hydrologic events. Sustained monitoring over such long periods inevitably limits the temporal detail that can be resolved during brief storm hydrographs. However, monitoring focused only on very detailed documentation of a few storm periods would risk missing a series of events that may show different chemical responses to flow variations. Furthermore, there may be many hydrochemical behaviours that arise independently of flow variations, and therefore would be missed if intensive sampling were focused solely on hydrologic events. For example, biogeochemical processes within the streams would not be fully examined as their chemical consequences are most obvious during steady low-flow periods. Hence, the need was recognised to measure a wide range of determinands at sufficiently high frequency, and over a sufficiently long time frame, to encompass the range of responses to hydrological, abiotic and biological drivers operating at seasonal, daily and sub-daily timescales.

3) Previous measurements of chloride at both weekly and daily time steps over a sufficiently long period allowed the identification of a fractal pattern that could not be resolved so clearly with fewer and less frequent measurements (Kirchner et al., 2000, 2001; Feng et al., 2004a). By examining a wider range of determinands which have not previously been measured below a weekly time step, similar analyses can be conducted across the periodic table. Indeed, even for chloride there would be additional information as sub-daily monitoring would allow an analysis at even higher frequencies, and within the time-frame of individual events.

4) While the fractal signal for chloride was originally found for the Plynlimon study, it is not a phenomenon restricted to these catchments. Rather, it seems to be a general phenomenon that applies to a wide range of catchments (Kirchner et al., 2001; Godsey et al., 2010). Hence, the Plynlimon study provides an exemplary case.

5) This work is required because even for simple elements such as chloride and sodium, the time-series behaviour challenges the conventional view of hydrologists and geochemists about how catchments function (Kirchner et al., 2000; Neal and Kirchner, 2000; Feng et al., 2004b). Furthermore, high-frequency chemical measurements are particularly valuable in quantifying the distributions of residence times that determine the rates of mass transfer. This is critical for example in reliably determining the rates of long-term changes within the system in response to external drivers.

Data resource

Rainfall samples were collected from a site adjacent to the CEH hydrometric station in moorland near the top of the Hafren catchment (Figure 1). River water samples were collected near the routine water quality monitoring sites just upstream of the Upper and Lower Hafren flow gauging structures (Figure 1). Automated systems containing 24 sample bottles were used. Sampling was on a regular 7-hourly basis from March of 2007 through January of 2009. Rainfall was sampled using a sequential, continuously open collector of 57.5 cm diameter, 42 cm above short grass vegetation, whereas rainfall volumes were measured with a ground-level rain gauge of 12.5 cm diameter and long-term weekly precipitation was sampled with a collector of 15 cm diameter approximately 1.5 m above ground-level (Figure 1). Because samples were collected every 7 hours, the rain collector had to be large enough to provide (in most cases) a sufficient volume for analysis in that short time interval. Therefore a non-standard collector was employed. As with all continuously open collectors, the samples will include dry-deposited material that has accumulated since the last rainfall event (i.e. the dry deposited material is not washed into the sample bottle until the next rainfall event occurs). Because the weekly and seven-hourly collectors had different geometries and were made of different materials, it can not be assumed that they sample the same rain drop size spectrum or collect the same amount of aerosol. Stream water samples were collected using Xian automatic samplers that collected instantaneous samples (Figure 1). Both rainfall and stream samplers were emptied/reloaded and cleaned once a week.

For the streams, the main focus is on the Upper Hafren as this drains a relatively undisturbed moorland catchment compared to the Lower Hafren which is afforested with plantation Sitka spruce. Although the long-term weekly records show that the phased forest felling that has taken place in the Lower Hafren has had only limited effects on water quality (Neal et al., 2010), these effects can be excluded entirely in the moorland Upper Hafren. For this reason, when the very high level of activity required for the collection and analysis of samples from rainfall plus two streams proved unsustainable, it was decided to discontinue intensive sampling of the Lower Hafren after the first year so that sampling could continue at the Upper Hafren for the second year. Details of the sampling sites, analytical protocols, and the broader hydrochemistry based on weekly monitoring are contained in Neal et al. (1997, 2010, 2012) together with the metadata attached to the data sets accompanying this paper.

The measurement programme was logistically complex and required a huge field and laboratory resource. Contamination in the field was minimised as best we could using equipment prepared for low-level measurement. Rigorous laboratory calibration and quality control procedures were employed for all analytes. The work was undertaken by well-trained and experienced field workers and analysts, with over 35 years of continuous experience among them. Multi-element analytical instrumentation was optimised so that the full range of elements could be measured simultaneously. We could not undertake ultra-clean sampling and analysis for low-level analytes. This was due to the scope of the effort, the difficulties in monitoring a remote site, and the need to assay for a wide array of elements and concentration ranges (Table 1). Furthermore, the exploratory nature of the study and sheer volume of information being generated meant that there were no "gold standard" reference points for rigorous assessment of the quality and representativeness of the data in real time. Therefore at the end of sampling programme, a data base was constructed that included both an archive of the raw data, as well as a retrospectively edited data set that was extensively checked for likely field sampling, contamination and analytical errors. Comprehensive consistency checks could only be applied to the stream water. For rainfall, the patterns exhibited much wider and erratic variability due to the confounding effects of different air mass trajectories and varying amounts of catch (and dry deposition), as well as incomplete analysis when sample volumes were low. The rainfall data were checked by comparing the weekly catch with a volume-weighted integration of the 7-hourly catch for the same weekly period, as well as by inter-element comparisons.

Archive data set. The raw data archive provides all of the measurements taken so that subsequent data manipulations are fully transparent. The only changes made to the raw data were to correct clear transcription errors which could be traced back to the original field, laboratory and database records. Note that in the raw data set values less than zero appear for some determinands as conventional detection limits have not been applied and data have not been rounded to a small number of significant figures. To compensate for this, the metadata provide all the relevant analytical qualifiers.

Edited data set. The edited data set is based on the expert judgement of all the lead researchers (hydrogeochemists, analytical chemists and physicists) following lively and sustained discussion. An interactive database and analysis package (JMP, SAS Institute) allowed the time series to be displayed simply, interactively and rapidly with scrollable and scalable x and y axis ranges. It also had the ability to track individual data points or groups of data-points easily across a range of determinands. For the streams, data were edited out for several reasons:

1) Outliers. These were identified by close visual inspection of the time series and a comparison with markers such as geochemically similar elements and flow. If a data point departed significantly from the time series and there was no clear change in the other parameters, then it was excluded.

2) Step changes in the reported concentrations at the start and end of a weekly monitoring / analytical batch of 24 samples. These clearly indicated issues of background contamination or instrument calibration. Erroneous data blocks were excluded based on an examination of several consecutive blocks and comparison with the independently collected weekly data.

3) Values consistently close to and below the detection limit. For a very limited number of elements such as uranium and tungsten, all reported data were very low, the data were grainy and many of the values were less than zero owing to very small differences in background correction. Where useful data could be preserved by careful editing (e.g., uranium), we have done so; where this was not possible (e.g., tungsten) we have omitted the analyte entirely from the edited data.

4) Step changes within a batch. These occurred very rarely, and where they occurred they indicated that the labelling of two successive batches of samples had been transposed or that the column headings within a batch of raw data had been transposed. Where this was blatantly the case (even if the paper record could not confirm it), the data were interchanged.

5) Abrupt changes in concentration at the start of a sample batch followed by a sequential change within the batch. These data were only rejected if there was no clear accompanying geochemical or hydrological marker.

6*) Sampler failure*. With instrument malfunction the time stamp and sample identifier were maintained and a “null” value recorded. This was also the case in the raw data set. For rainfall, the same protocol was applied for periods with no rainfall or insufficient catch to provide a sample for analysis.

In all cases, great care was taken to minimise potential editing bias. For transparency, the editing applied to each analyte is documented and the changes are all shown as time series plots in the metadata accompanying the data set. Interested users can also directly compare the values in the edited data and the raw data archive.

The data editing principles outlined above have also been applied to the long-term weekly hydrochemical data set, described in Neal et al. (2011a). Both data sets were edited by the same authors, at the same time, using the same approach, to ensure that they were treated as consistently as possible. Both the 7-hourly and weekly data sets, along with their metadata, are provided as online supplementary information accompanying this paper.

Referencing and data availability

This technical briefing provides the primary citation for the 7-hourly dataset and the related paper by Neal et al. (2012) provides the primary citation for the study. Users of the 7-hourly data should cite this present contribution as well as Neal et al. (2012) in any resulting publications. The paper by Neal et al. (2011a) is the primary citation for the weekly hydrochemical data set, and provides references to a wider body of published work describing that long-term research effort and its major findings. Although the other main authors are now retired, the corresponding author (Kirchner) is available for consultation and collaboration, as appropriate, in subsequent analyses of the data.

CEH and its parent organisation, the Natural Environment Research Council (NERC), aim to provide a readily accessible data portal, the CEH Information Gateway (CIG), at gateway.ceh.ac.uk, to make freely available its wealth of environmental information. We strongly support this approach and wish to lead the way with the CIG holding copies of both the weekly and 7-hourly Plynlimon data. Copyright to all our data and associated metadata rests within NERC-CEH and the CIG provides the key link to licensing all of the data collected and currently being collected.

The data, a brief overview with illustrations

There are two publications that illustrate the wide range of dynamic behaviour of stream water quality based on the 7-hour data (Neal et al., 2012; Halliday et al., 2012). The dynamics include hydrological responses that follow the flow hydrograph, and biological variations as indicated by diurnal fluctuations during periods of low flows and high biological activity.

To illustrate the richness in dynamic response for all the determinands, time series plots using the edited dataset are provided in the online supplementary information for the readers to judge for themselves. The time series plots of the edited data provide a master set to show the range and complexity of dynamic responses. Although a great deal of detail is lost when an entire time series is plotted on a single page, the digital versions of the figures in the supplementary information can be expanded to show more detailed subsets of the full time series.

To add several specific illustrations in the main body of the text, time series plots are provided for streamwater concentrations of three elements, arsenic, molybdenum, and aluminium, with contrasting hydrochemistry and sources. For example:
(1) Arsenic and molybdenum occur predominantly in anionic form while aluminium is mainly in cationic form.
(2) Arsenic and aluminum are ecotoxicants, while molybdenum is a micro-nutrient.
(3) Arsenic has a strong atmospheric signal, while molybdenum and aluminum largely come from within the catchment.
(4) Further, aluminum is also of major concern with surface water acidification because it is mobilised within acid soils, and this is highly significant for the uplands reported on here. In contrast, arsenic and molybdenum have very low concentrations at Plynlimon compared to polluted areas of the U.K. Note that in the case of rainfall, the temporal dynamics are far too complex to describe in any detail here, but we note, for example, that small events result in unusual chemistries such as dilute hydrochloric acid (pH 3.7) enriched in DOC that represent pollution that cannot be detected in the weekly rainfall samples.

Arsenic

Decadal-scale reductions in arsenic concentrations in rainfall and stream water have been demonstrated based on long-term weekly monitoring. This result was not anticipated at the outset of the long-term monitoring and illustrates the value of less intensive monitoring for a wide range of elements. The long-term changes match global reductions in anthropogenic emissions to the atmosphere. However, it is only with the 7-hourly measurements that the full range in concentration in rainfall is picked up. For example, during the two years that were intensively sampled, the arsenic concentration range in the regular weekly samples is 0.018 to 0.67 μg/l (with a volume-weighted mean of 0.052 μg/l) while for the 7-hour samples the range is 0.002 to 1.51 μg/l (with a volume-weighted mean of 0.075 μg/l). In the stream waters, weekly sampling would show the broad seasonal cycle in arsenic (Figure 2a), but higher-frequency sampling is needed to see the clear diurnal cycling that emerges during spring and summer baseflow periods (Figure 2b,c). This diurnal variation may arise from exchange of arsenic between the water column and surface coatings on the stream bed that are both biologically and chemically active. Indeed, it is only with both accurate and precise measurements that we have been able to detect small changes for a relatively clean catchment system. There may be a hint of a flow-related increase in arsenic concentration on the rising limb of the hydrograph, but in general there is no clear relationship with flow. The biogeochemistry and dynamics of arsenic at Plynlimon have been explored in more detail by Rowland et al. (2011).

Molybdenum

Molybdenum is rarely monitored in rivers and we observe very low concentrations at Plynlimon, probably reflecting the absence of obvious pollutant sources within the region. Molydenum exhibits diurnal patterns (Figure 3) that are similar to those of arsenic. Under baseflow, molybdenum concentrations average around 0.05 µg/l with a diurnal cycle with an amplitude of about 0.02 µg/l. Peak concentrations during baseflow occur during mid-day, in contrast to nutrients such as nitrate, which typically peak during night-time. Molybdenum is biologically linked to nitrogen fixation by bacteria and there may well be complex relationships involved (Greenwood and Earnshaw, 1997). Molybdenum concentrations generally decrease with increasing flows, but concentration spikes can also occur during low-flow conditions (Figure 3). Several mechanisms may well be operating to influence the diurnal and other behaviour. However, the main point is that the results illustrate just one of the many “discovery” elements in these high-frequency time series.

Aluminium

Aluminium concentrations are relatively low in rainfall compared to stream waters due to the dominance of within-catchment sources. As aluminium is mobilised within the acidic soils, high concentrations are observed in the stream under high-flow conditions (Figure 4). The weekly monitoring picks up this variability. However, the timings in peaks with the rising limb and decays in the falling limb of the hydrograph are much more clearly shown within the 7-hourly data. This is because the 7-hourly sampling interval lies within the timeframe of individual hydrological events. While there is non-linear correlation of aluminium concentration and flow, in detail the relationship changes through the monitoring period. This means that there is significant scatter within the concentration-flow relationship for the 7-hourly data. The scatter that has been previously observed in the weekly data is thus not an artefact of sampling or analysis; instead it is representative of more complex behaviour that can only be detected with higher resolution measurements. Neal et al. (2011b) have explored mechanisms controlling aluminium concentrations in diverse U.K. catchments.

Conclusion

The purposes of this scientific briefing are to alert the research community to the availability of the Plynlimon 7-hourly hydrochemistry data, to briefly illustrate the rich behaviour of these high frequency time series using examples of just three elements, and, last but not least, to provide an archival copy of the data set, including metadata and a complete set of time-series plots, as supplementary information. The data provide a remarkable resource for the environmental research community in fields as diverse as hydrology, aquatic chemistry, statistical analysis, and dynamic modelling

The 7-hourly and weekly data complement each other as they provide different insights into catchment functioning and controls on water quality. Given the wide range of elements examined, the data resource provides perhaps the most comprehensive hydrochemical dataset currently available for examining the dynamics of water quality functioning of an acidic and acid-sensitive upland catchment across a range of timescales, typologies and environmental drivers.

The data have been generated under rigorous field and analytical protocols that go well beyond those often used in routine water quality studies of freshwater systems. We have used the best analytical techniques and quality assurance protocols we could draw on for river waters. Detailed scrutiny can now be made of the degree of success achieved by comparing the raw and modified datasets for the wide range of elements. The raw data archive shows a "warts and all" view of the anomalous results that can sometimes arise even when highly rigorous protocols are being followed. Thus, pointers can be drawn for future surveys where environmental measurements require high degrees of accuracy and precision across the concentration range.

Critically, there is a need to provide raw uncensored data (e.g. providing data below lowest quotable detection levels and with sufficient decimal points) to avoid producing too grainy a view of the natural dynamics and thereby limiting the analysis that can be done. For example, censored (“less than”) values are problematic in statistical analyses. And for spectral analysis in particular, small concentration step sizes are required to avoid spurious results when detecting low-amplitude fluctuations.

It is unlikely that a similar monitoring study will be undertaken in the foreseeable future given the labour-intensiveness of the exercise, the high financial costs, and the ongoing shift in funding away from sustained long-term investments in data collection. We hope that this trend will be offset somewhat by emerging technologies that enable continuous in-stream measurements, complementing long-term studies. These technologies will be needed to better capture the influence of the rising limb of the hydrograph and the full cycle of diurnal response. For previously unmonitored catchments, the new technologies may rapidly capture the short-term dynamics and provide sufficient data for statistical analysis of short-term hydrochemical behaviour. Nonetheless, these new technologies still have to overcome issues of reliability, substantial field maintenance costs, and the limited range of determinands available. These issues may well take some time to overcome, particularly in remote rural locations with no mains electricity and a harsh climate. Thus we are confident that this data set represents a valuable resource that would be extremely difficult for other research teams in the community to generate on their own. It is for this reason that we are publicly releasing it as a community resource.

To return to the question that launched this study: **What components of stream water quality dynamics do we miss with conventional weekly or monthly monitoring and ad hoc, event-based high-frequency measurement campaigns?** The answer is that we have been astonished by both the complexity of the dynamic responses and the difficulty in capturing them using conventional visualization and analysis techniques.

We intensively monitored a wide range of chemical determinands with contrasting hydrobiogeochemical properties (Table 1), on a regular time step that could capture hydrochemical behaviour on seasonal, diurnal, and storm-event time scales. Rather than focusing on particular periods of interest, we sampled regularly and non-stop, in order to minimise any bias associated with our preconceptions of how the system functions. We hope that, where feasible, future intensive monitoring efforts will adopt a similar rationale to ours in which “all the notes of the symphony” are heard, and in which water quality determinands with contrasting hydrochemistry are examined to properly test conceptual models of catchment functioning.

We hope that this research will stimulate novel lines of inquiry and new thinking about how catchments function, and we strongly encourage the development of the emerging hydrochemical analysis technologies for which our study provides the proof of concept.

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Table 1. Volume-weighted mean concentrations (± standard deviations) in 7-hourly samples of precipitation and Upper and Lower Hafren streamflow, Plynlimon, Wales

Analyte	Precipitation mean±s.d.	Upper Hafren mean±s.d.	Lower Hafren mean±s.d.
Water flux mm/hr	0.34±0.77	0.32±0.39	0.25±0.38
Conductivity µS/cm	27.7±45.1	28.4±4.7	41.8±5.7
pH	4.71±0.65	5.09±0.47	4.70±0.39
Gran alkalinity µEq/l	-27.1±39.5	-6.4±26.2	-22.0±24.9
Nutrients and anions, in order of increasing atomic number			
DOC mg/l	0.72±1.45	3.35±2.09	3.38±1.55
NO_3^- mg(N)/l	0.14±0.26	0.14±0.07	0.18±0.06
NO_2^- mg(N)/l	0.0031±0.0026	0.0023±0.0023	0.0015±0.0022
NH_4^+ mg(N)/l	0.177±0.183	0.028±0.039	0.026±0.019
TDN mg/l	0.335±0.537	0.279±0.093	0.305±0.068
DON mg/l	-0.018±0.029	0.101±0.081	0.075±0.045
F^- mg/l	0.0042±0.0053	0.0126±0.0044	0.0159±0.0027
SO_4^{-2} mg(SO_4)/l	1.21±1.36	1.92±0.30	3.01±0.40
Cl^- mg/l	5.69±11.70	5.29±1.09	7.19±1.36
Br^- µg/l	18.1±45.3	8.7±3.1	11.8±3.5
I^- µg/l	n/a	0.84±0.12	1.00±0.14
Metals and trace elements, in order of increasing atomic number			
Li µg/l	0.04±0.11	1.49±0.32	1.90±0.29
Be µg/l	-0.003±0.004	0.018±0.009	0.042±0.017
B µg/l	2.49±3.14	3.39±0.52	4.10±0.40
Na mg/l	2.58±6.23	3.13±0.50	3.97±0.50
Mg mg/l	0.31±0.74	0.51±0.11	0.66±0.12
Al µg/l	2.9±10.1	121.6±63.2	197.8±81.3
Si mg/l	0.02±0.02	1.20±0.45	1.25±0.37
S mg/l	0.39±0.57	0.64±0.09	0.99±0.13
K mg/l	0.11±0.22	0.13±0.08	0.14±0.04
Ca mg/l	0.29±0.62	0.41±0.12	0.62±0.16
Sc µg/l	n/a	0.25±0.17	0.25±0.13
Ti µg/l	0.02±0.10	0.32±0.11	0.27±0.10
V µg/l	0.18±0.24	0.09±0.04	0.11±0.04
Cr µg/l	1.01±8.89	0.14±0.08	0.24±0.08
Mn µg/l	0.6±2.1	16.6±3.2	29.5±7.4
Fe µg/l	3.1±10.7	123.2±78.2	116.3±59.7
Co µg/l	0.01±0.03	0.68±0.15	1.35±0.39
Ni µg/l	0.12±0.20	0.69±0.15	1.31±0.27
Cu µg/l	n/a	5.9±7.1	1.7±0.7
Zn µg/l	6.6±9.1	11.0±5.7	12.0±3.7
As µg/l	0.075±0.087	0.228±0.067	0.247±0.062
Se µg/l	0.110±0.143	0.077±0.043	0.092±0.035
Rb µg/l	0.042±0.095	0.222±0.125	0.260±0.070
Sr µg/l	2.32±4.43	3.33±0.74	3.97±0.78
Mo µg/l	0.196±0.758	0.019±0.022	0.014±0.018
Cd µg/l	n/a	0.026±0.011	0.044±0.014
Sn µg/l	0.035±0.399	0.042±0.031	0.056±0.025
Sb µg/l	0.306±1.094	0.067±0.051	0.047±0.041
Cs µg/l	-0.002±0.004	0.016±0.005	0.020±0.006
Ba µg/l	6.73±11.50	1.67±0.45	2.34±0.49
La µg/l	0.017±0.094	0.017±0.008	0.028±0.010
Ce µg/l	0.018±0.121	0.049±0.025	0.083±0.033
Pr µg/l	0.003±0.015	0.008±0.004	0.015±0.006
Pb µg/l	n/a	0.29±0.25	0.55±0.38
U µg/l	-0.0031±0.0033	0.0024±0.0027	0.0049±0.0041

Analytes marked "n/a" were not measured in precipitation, or yielded suspect values. Lower Hafren means cover only the first year of the two-year sampling program, and thus cannot be directly compared to means from Upper Hafren or precipitation. Mean and standard deviation of pH are calculated from H^+.

Figure 1. Photographs of sampling sites and instrumentation. Clockwise from upper left: (a) Sampling point on the Upper Hafren with protective housing for sampling tube; (b) sampling point on the Lower Hafren, just upstream from the flow gauging structure; (c) duplicate Xian automatic samplers and protective enclosure at the Upper Hafren sampling site; and (d) continuously open 7-hourly rainfall collector (57.5 cm diameter) in short grass vegetation near Upper Hafren catchment.

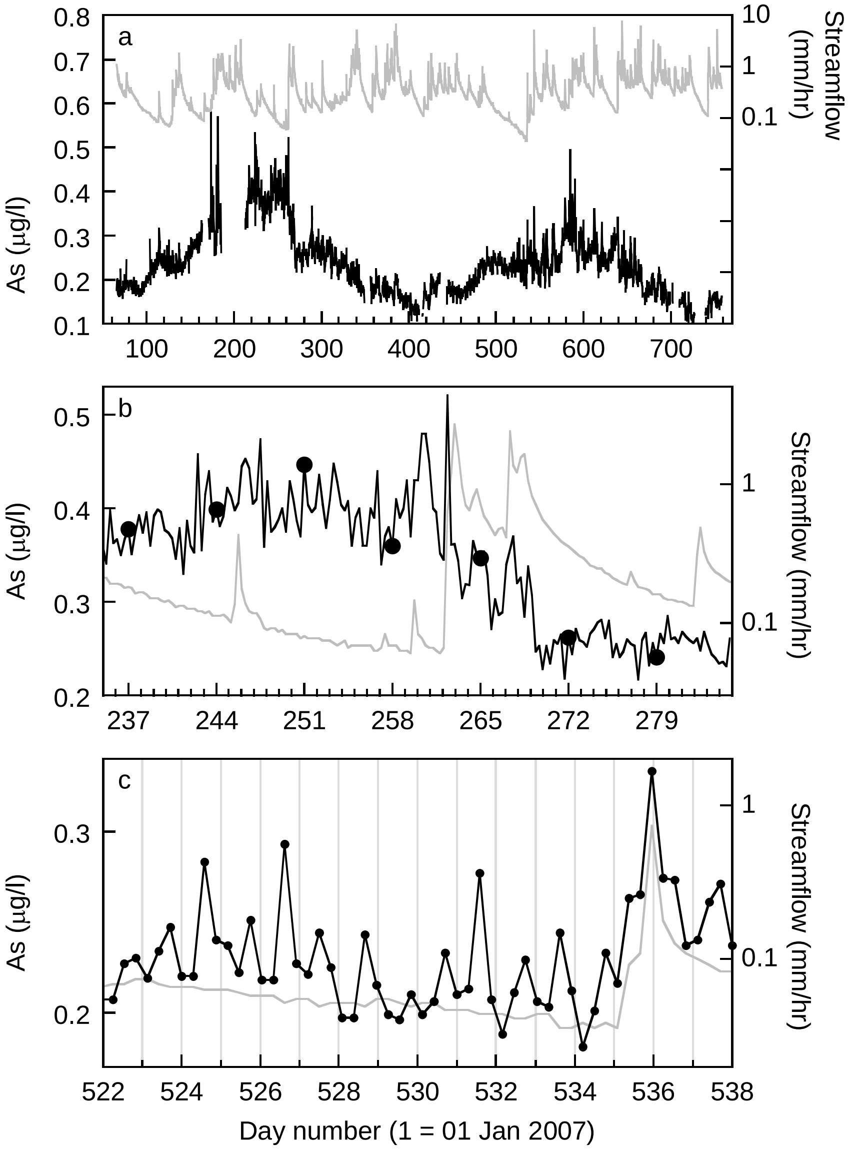

Figure 2. Arsenic time series in Upper Hafren streamflow, Plynlimon, Wales, showing successively more detail for shorter periods of time. (a) Complete 7-hourly time series of arsenic concentrations (black), with stream discharge (grey) shown on a logarithmic scale for comparison. (b) Enlarged view of 50-day period from late August to early October 2007. Large black dots illustrate values that would result from typical once-a-week sampling; the rest of the dynamics would be invisible. Note that the sharp arsenic peak on Day 262 occurs just before streamflow starts to rise. Detecting such coupling between hydrology and chemistry requires high-frequency chemical sampling. (c) Detailed view of two weeks in June 2008, with vertical lines indicating midnight between successive days. Dots indicate individual 7-hourly samples. During the long period of low flow, a diurnal cycle in arsenic emerges. Also note that unlike in (b), the large arsenic peak is synchronous with the peak in flow, showing that the relationship between arsenic and discharge varies between storm events.

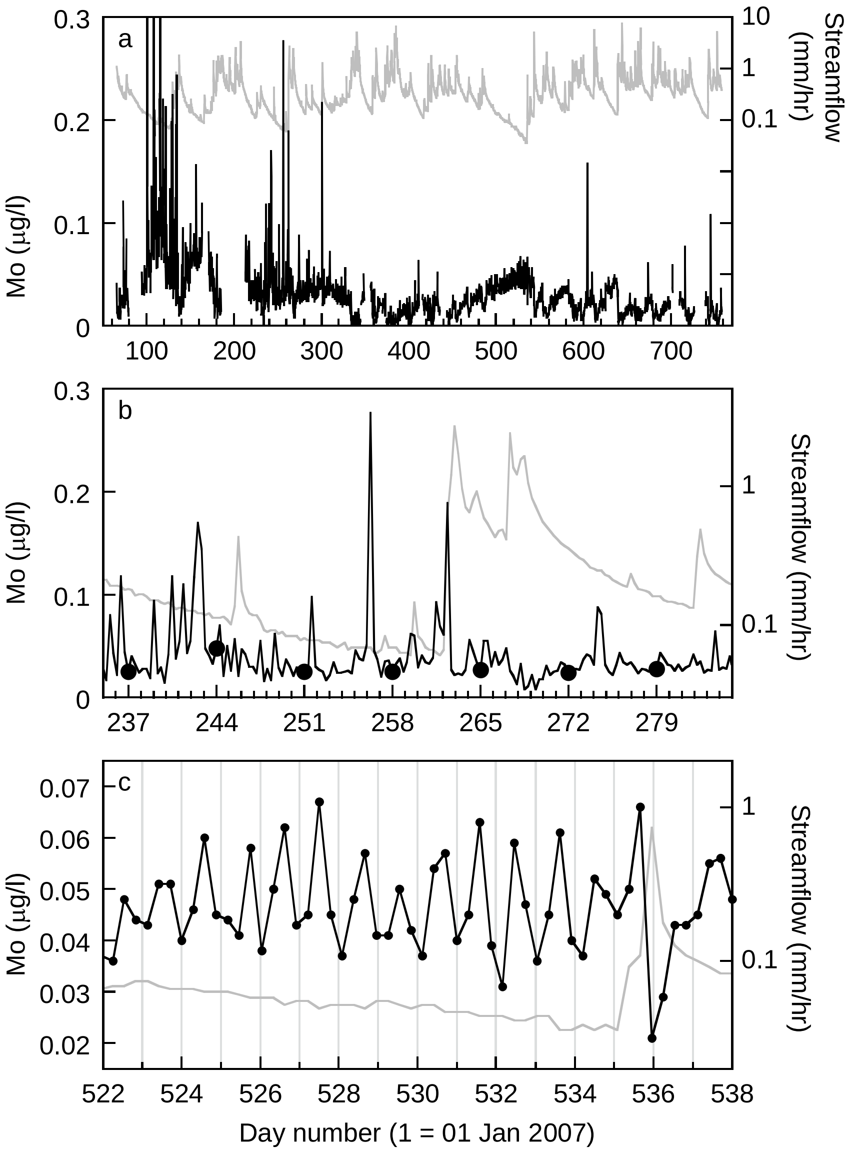

Figure 3. Molybdenum time series in Upper Hafren streamflow, Plynlimon, Wales, showing successively more detail for shorter periods of time. (a) Complete 7-hourly time series of molybdenum concentrations (black), with stream discharge (grey) shown on a logarithmic scale for comparison. (b) Enlarged view of 50-day period from late August to early October 2007. Large black dots illustrate values that would result from typical once-a-week sampling; the rest of the dynamics would be invisible. Note that the largest molybdenum peak occurs without any change in streamflow, but the second-largest occurs on the rising limb of the flow event on Day 262. (c) Detailed view of two weeks in June 2008, with vertical lines indicating midnight between successive days. Dots indicate individual 7-hourly samples. During the long period of low flow, a clear diurnal cycle in molybdenum emerges. There is a molybdenum peak on the rising limb of the flow event on Day 535, but the peak flow is associated with a marked dip in molybdenum concentrations. Detecting such chemical dynamics requires high-frequency sampling.

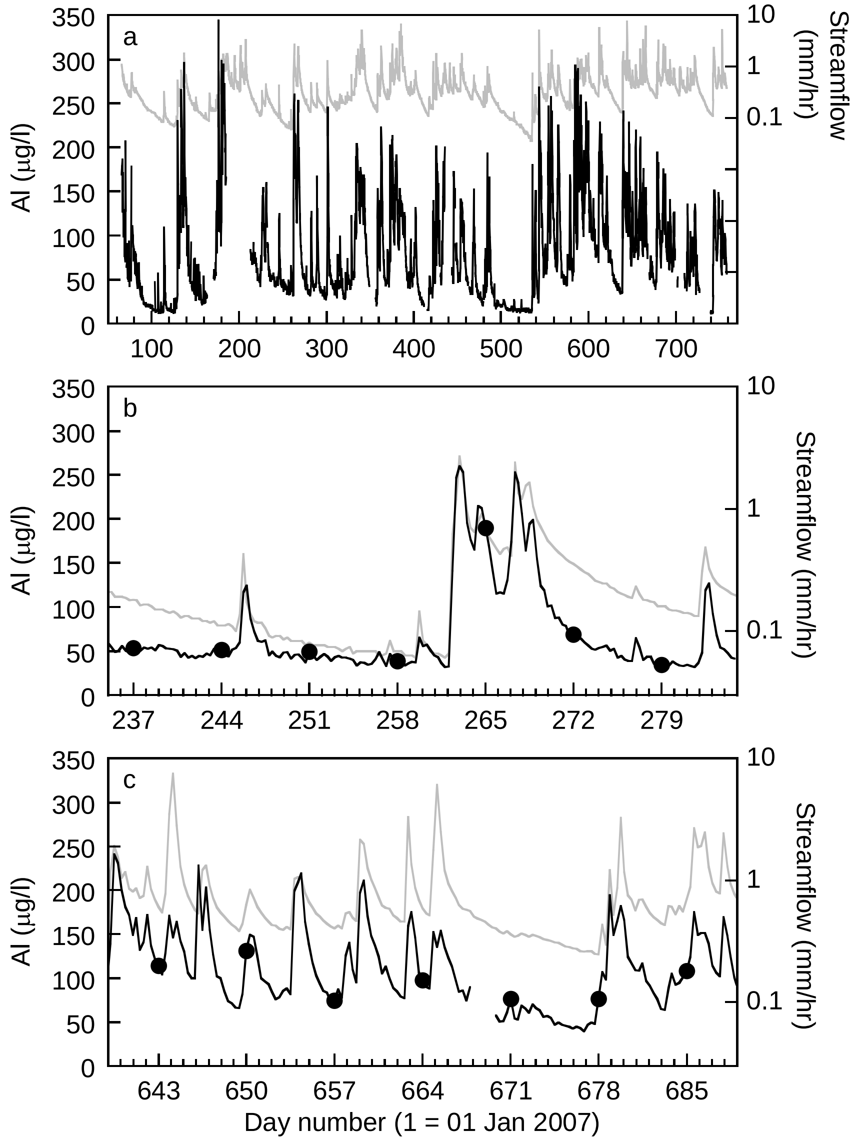

Figure 4. Aluminium time series in Upper Hafren streamflow, Plynlimon, Wales, over the full data record (a) and two shorter periods where there are significant storm events (b,c). (a) Complete 7-hourly time series of aluminum concentrations (black), with stream discharge (grey) shown on a logarithmic scale for comparison. Enlarged views of two 50-day periods (b, c) show responses to individual storms. Although aluminum concentrations generally increase with discharge, the relationship shifts from one event to the next, with different concentrations at the same flows; the relative timing between concentration peaks and flow peaks also varies from storm to storm. Detecting such coupling between hydrology and chemistry requires high-frequency chemical sampling. Large black dots in (b) and (c) illustrate values that would result from typical once-a-week sampling; the rest of the dynamics would be invisible.