

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

Colin Neal,<sup>1</sup>  
 Brian Reynolds,<sup>2</sup>  
 James W. Kirchner,<sup>3,4,5\*</sup>  
 Phil Rowland,<sup>6</sup> Dave Norris,<sup>2</sup>  
 Darren Sleep,<sup>6</sup> Alan Lawlor,<sup>6</sup>  
 Clive Woods,<sup>6</sup>  
 Sarah Thacker,<sup>6</sup>  
 Hayley Guyatt,<sup>6</sup>  
 Colin Vincent,<sup>6</sup>  
 Kathryn Lehto,<sup>6</sup>  
 Simon Grant,<sup>2</sup>  
 Jeremy Williams,<sup>7</sup>  
 Margaret Neal,<sup>1</sup>  
 Heather Wickham,<sup>1</sup>  
 Sarah Harman<sup>1</sup> and  
 Linda Armstrong<sup>1</sup>

<sup>1</sup> Centre for Ecology and Hydrology, Crowmarsh Gifford, Wallingford, Oxon OX10 8BB, UK

<sup>2</sup> Centre for Ecology and Hydrology, Bangor University, Environment Centre Wales, Deiniol Road, Bangor, Gwynedd, LL57 2UW, UK

<sup>3</sup> Department of Environmental Systems Science, ETH Zürich, CH-8092 Zürich, Switzerland

<sup>4</sup> Swiss Federal Research Institute WSL, Zürcherstrasse 111, CH-8903, Birmensdorf, Switzerland

<sup>5</sup> Department of Earth & Planetary Science, University of California, Berkeley, California, 94720 USA

<sup>6</sup> Centre for Ecology and Hydrology, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster LA1 4AP, UK

<sup>7</sup> Envirodata-Eryri, Snowdonia, Wales, UK

\*Correspondence to: James W. Kirchner, Department of Environmental Systems Science, ETH Zürich, CH-8092 Zürich, Switzerland

E-mail: kirchner@ethz.ch, kirchner@berkeley.edu

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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 2 years of 7-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<sup>+</sup> 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, the weekly and 7-hourly time series provide a unique data set for studying both long-term trends and short-term dynamics. The data show complex behaviour over a wide range of timescales, challenging our understanding of catchment processes and informing future modelling efforts. Copyright © 2013 John Wiley & Sons, Ltd.

**Key words** catchment hydrology; hydrochemistry; water quality

## 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 2 years, nonstop (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 because of 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 revealed 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 a 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 subdaily 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 that 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 subdaily monitoring would allow an analysis at even higher frequencies and within the timeframe of individual events.
4. Although 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 (Feng *et al.*, 2004b; Kirchner *et al.*, 2000; Neal and Kirchner, 2000). 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 h, 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 nonstandard 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 7-hourly collectors had different geometries and were made of different materials, it cannot 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 (available from Hach Lange Ltd., Manchester, U.K., [www.hach-lange.co.uk](http://www.hach-lange.co.uk)) 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 with 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 protocol, 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 by 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 because of the scope of the



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 the Upper Hafren catchment

effort, the difficulties in monitoring a remote site and the need to assay for a wide array of elements and concentration ranges (Table I). 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 the sampling programme, a database 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 because of the confounding effects of different air mass trajectories and the 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 below 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 a 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  $x$ -axis 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:

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

Analyte	Precipitation mean $\pm$ SD	Upper Hafren mean $\pm$ SD	Lower Hafren mean $\pm$ SD
Water flux mm/h	0.34 $\pm$ 0.77	0.32 $\pm$ 0.39	0.25 $\pm$ 0.38
Conductivity $\mu$ S/cm	27.7 $\pm$ 45.1	28.4 $\pm$ 4.7	41.8 $\pm$ 5.7
pH	4.71 $\pm$ 0.65	5.09 $\pm$ 0.47	4.70 $\pm$ 0.39
Gran alkalinity $\mu$ Eq/l	-27.1 $\pm$ 39.5	-6.4 $\pm$ 26.2	-22.0 $\pm$ 24.9
Nutrients and anions, in order of increasing atomic number			
DOC mg/l	0.72 $\pm$ 1.45	3.35 $\pm$ 2.09	3.38 $\pm$ 1.55
NO <sub>3</sub> <sup>-</sup> mg(N)/l	0.14 $\pm$ 0.26	0.14 $\pm$ 0.07	0.18 $\pm$ 0.06
NO <sub>2</sub> <sup>-</sup> mg(N)/l	0.0031 $\pm$ 0.0026	0.0023 $\pm$ 0.0023	0.0015 $\pm$ 0.0022
NH <sub>4</sub> <sup>+</sup> mg(N)/l	0.177 $\pm$ 0.183	0.028 $\pm$ 0.039	0.026 $\pm$ 0.019
TDN mg/l	0.335 $\pm$ 0.537	0.279 $\pm$ 0.093	0.305 $\pm$ 0.068
DON mg/l	-0.018 $\pm$ 0.029	0.101 $\pm$ 0.081	0.075 $\pm$ 0.045
F <sup>-</sup> mg/l	0.0042 $\pm$ 0.0053	0.0126 $\pm$ 0.0044	0.0159 $\pm$ 0.0027
SO <sub>4</sub> <sup>2-</sup> mg(SO <sub>4</sub> )/l	1.21 $\pm$ 1.36	1.92 $\pm$ 0.30	3.01 $\pm$ 0.40
Cl <sup>-</sup> mg/l	5.69 $\pm$ 11.70	5.29 $\pm$ 1.09	7.19 $\pm$ 1.36
Br <sup>-</sup> $\mu$ g/l	18.1 $\pm$ 45.3	8.7 $\pm$ 3.1	11.8 $\pm$ 3.5
I <sup>-</sup> $\mu$ g/l	n/a	0.84 $\pm$ 0.12	1.00 $\pm$ 0.14
Metals and trace elements, in order of increasing atomic number			
Li $\mu$ g/l	0.04 $\pm$ 0.11	1.49 $\pm$ 0.32	1.90 $\pm$ 0.29
Be $\mu$ g/l	-0.003 $\pm$ 0.004	0.018 $\pm$ 0.009	0.042 $\pm$ 0.017
B $\mu$ g/l	2.49 $\pm$ 3.14	3.39 $\pm$ 0.52	4.10 $\pm$ 0.40
Na mg/l	2.58 $\pm$ 6.23	3.13 $\pm$ 0.50	3.97 $\pm$ 0.50
Mg mg/l	0.31 $\pm$ 0.74	0.51 $\pm$ 0.11	0.66 $\pm$ 0.12
Al $\mu$ g/l	2.9 $\pm$ 10.1	121.6 $\pm$ 63.2	197.8 $\pm$ 81.3
Si mg/l	0.02 $\pm$ 0.02	1.20 $\pm$ 0.45	1.25 $\pm$ 0.37
S mg/l	0.39 $\pm$ 0.57	0.64 $\pm$ 0.09	0.99 $\pm$ 0.13
K mg/l	0.11 $\pm$ 0.22	0.13 $\pm$ 0.08	0.14 $\pm$ 0.04
Ca mg/l	0.29 $\pm$ 0.62	0.41 $\pm$ 0.12	0.62 $\pm$ 0.16
Sc $\mu$ g/l	n/a	0.25 $\pm$ 0.17	0.25 $\pm$ 0.13
Ti $\mu$ g/l	0.02 $\pm$ 0.10	0.32 $\pm$ 0.11	0.27 $\pm$ 0.10
V $\mu$ g/l	0.18 $\pm$ 0.24	0.09 $\pm$ 0.04	0.11 $\pm$ 0.04
Cr $\mu$ g/l	1.01 $\pm$ 8.89	0.14 $\pm$ 0.08	0.24 $\pm$ 0.08
Mn $\mu$ g/l	0.6 $\pm$ 2.1	16.6 $\pm$ 3.2	29.5 $\pm$ 7.4
Fe $\mu$ g/l	3.1 $\pm$ 10.7	123.2 $\pm$ 78.2	116.3 $\pm$ 59.7
Co $\mu$ g/l	0.01 $\pm$ 0.03	0.68 $\pm$ 0.15	1.35 $\pm$ 0.39
Ni $\mu$ g/l	0.12 $\pm$ 0.20	0.69 $\pm$ 0.15	1.31 $\pm$ 0.27
Cu $\mu$ g/l	n/a	5.9 $\pm$ 7.1	1.7 $\pm$ 0.7
Zn $\mu$ g/l	6.6 $\pm$ 9.1	11.0 $\pm$ 5.7	12.0 $\pm$ 3.7
As $\mu$ g/l	0.075 $\pm$ 0.087	0.228 $\pm$ 0.067	0.247 $\pm$ 0.062
Se $\mu$ g/l	0.110 $\pm$ 0.143	0.077 $\pm$ 0.043	0.092 $\pm$ 0.035
Rb $\mu$ g/l	0.042 $\pm$ 0.095	0.222 $\pm$ 0.125	0.260 $\pm$ 0.070
Sr $\mu$ g/l	2.32 $\pm$ 4.43	3.33 $\pm$ 0.74	3.97 $\pm$ 0.78
Mo $\mu$ g/l	0.196 $\pm$ 0.758	0.019 $\pm$ 0.022	0.014 $\pm$ 0.018
Cd $\mu$ g/l	n/a	0.026 $\pm$ 0.011	0.044 $\pm$ 0.014
Sn $\mu$ g/l	0.035 $\pm$ 0.399	0.042 $\pm$ 0.031	0.056 $\pm$ 0.025
Sb $\mu$ g/l	0.306 $\pm$ 1.094	0.067 $\pm$ 0.051	0.047 $\pm$ 0.041
Cs $\mu$ g/l	-0.002 $\pm$ 0.004	0.016 $\pm$ 0.005	0.020 $\pm$ 0.006
Ba $\mu$ g/l	6.73 $\pm$ 11.50	1.67 $\pm$ 0.45	2.34 $\pm$ 0.49
La $\mu$ g/l	0.017 $\pm$ 0.094	0.017 $\pm$ 0.008	0.028 $\pm$ 0.010
Ce $\mu$ g/l	0.018 $\pm$ 0.121	0.049 $\pm$ 0.025	0.083 $\pm$ 0.033
Pr $\mu$ g/l	0.003 $\pm$ 0.015	0.008 $\pm$ 0.004	0.015 $\pm$ 0.006
Pb $\mu$ g/l	n/a	0.29 $\pm$ 0.25	0.55 $\pm$ 0.38
U $\mu$ g/l	-0.0031 $\pm$ 0.0033	0.0024 $\pm$ 0.0027	0.0049 $\pm$ 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 2-year sampling programme, and thus cannot be directly compared to means from Upper Hafren or precipitation. Mean and standard deviation of pH are calculated from H<sup>+</sup>.

DOC, dissolved organic carbon; TDN, total dissolved nitrogen; DON, dissolved organic nitrogen.

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 on the basis of 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 the 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 metadata includes a document that describes the editing that was applied to each analyte and shows all the time series plots, with the edited data in blue and the points that have been culled out in red. Interested users can also directly compare the numerical values in the edited data and the raw data archive.

The data editing principles outlined in the previous text 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, by 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 and raw data archives, are available online as described in the next section.

#### *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.

The Centre for Ecology and Hydrology and its parent organisation, the Natural Environment Research Council, provide a readily accessible data portal, the CEH Information Gateway, at [gateway.ceh.ac.uk](http://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 Information Gateway holding copies of both the weekly and 7-hourly Plynlimon data. The weekly data and metadata (Neal *et al.*, 2013a) can be accessed directly via <http://dx.doi.org/10.5285/44095e17-43b0-45d4-a781-aab4f72da025>, and the 7-hourly data and metadata (Neal *et al.*, 2013b) can be accessed directly via <http://dx.doi.org/10.5285/551a10ae-b8ed-4ebd-ab38-033dd597a374>. Copyright to all our data and associated metadata rests within the Natural Environment Research Council-CEH, and the Information Gateway provides the key link to licencing all of the historical data as well as data 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 on the basis of the 7-h data (Halliday *et al.*, 2012; Neal *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.

We used the edited dataset to provide the time series plots in metadata to illustrate the richness in dynamic response for all the determinands allowing users 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 metadata can be expanded to show more detailed subsets of the full time series.

To provide several specific illustrations in this briefing, time series plots are shown for stream water

concentrations of three elements, arsenic, molybdenum and aluminium, with contrasting hydrochemistry and sources. For example,

1. Arsenic and molybdenum occur predominantly in anionic form, whereas aluminium is mainly in cationic form.
2. Arsenic and aluminium are ecotoxicants, whereas molybdenum is a micronutrient.
3. Arsenic has a strong atmospheric signal, whereas molybdenum and aluminium largely come from within the catchment.
4. Further, aluminium 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 with polluted areas of the UK. 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 dissolved organic carbon 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 on the basis of long-term weekly monitoring. This result was not

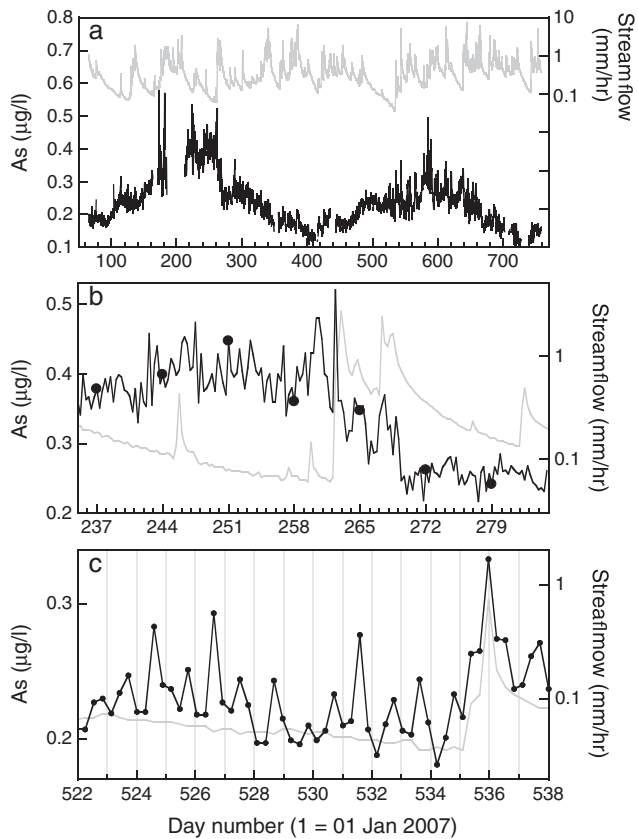


Figure 2. Arsenic time series in the Upper Hafren streamflow, Plynlimon, Wales, showing successively more detail for shorter periods. (a) Complete 7-hourly time series of arsenic concentrations (black), with stream discharge (grey) shown on a logarithmic scale for comparison. (b) Enlarged view of 50-day 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 2 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.

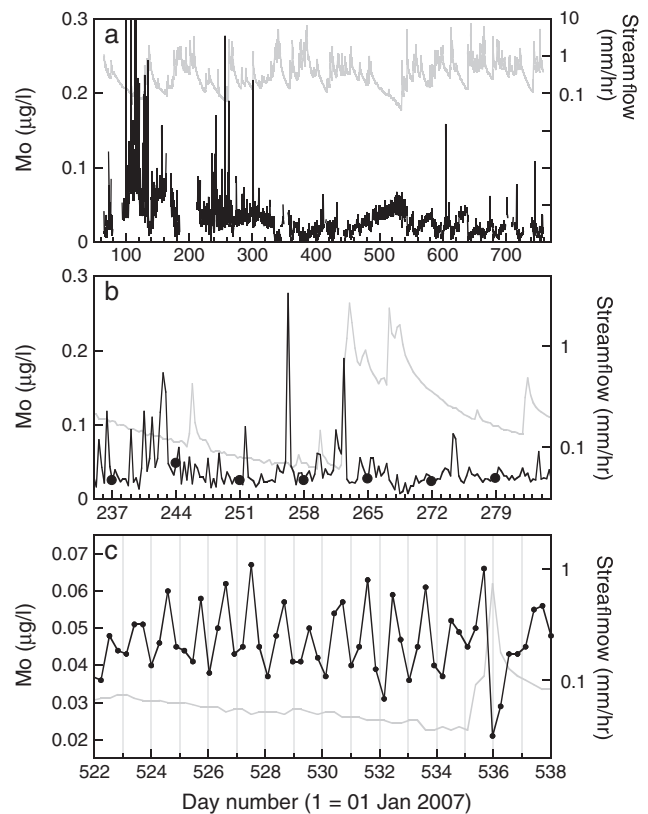


Figure 3. Molybdenum time series in Upper Hafren streamflow, Plynlimon, Wales, showing successively more detail for shorter periods. (a) Complete 7-hourly time series of molybdenum concentrations (black), with stream discharge (grey) shown on a logarithmic scale for comparison. (b) Enlarged view of 50-day 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 2 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.

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 2 years that were intensively sampled, the arsenic concentration range in the regular weekly samples is 0.018 to 0.67  $\mu\text{g/l}$  (with a volume-weighted mean of 0.052  $\mu\text{g/l}$ ), whereas for the 7-h samples, the range is 0.002 to 1.51  $\mu\text{g/l}$  (with a volume-weighted mean of 0.075  $\mu\text{g/l}$ ). 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 the

exchange of arsenic between the water column and the surface coatings on the streambed 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. Molybdenum exhibits diurnal patterns (Figure 3) that are similar to those of arsenic. Under baseflow, molybdenum concentrations average around 0.05  $\mu\text{g/l}$  with a diurnal cycle with an amplitude of about 0.02  $\mu\text{g/l}$ . Peak concentrations during baseflow occur during midday, in contrast to nutrients such as nitrate, which typically peak during nighttime. 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 the rainfall compared with 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. Although there is a nonlinear 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 UK catchments.

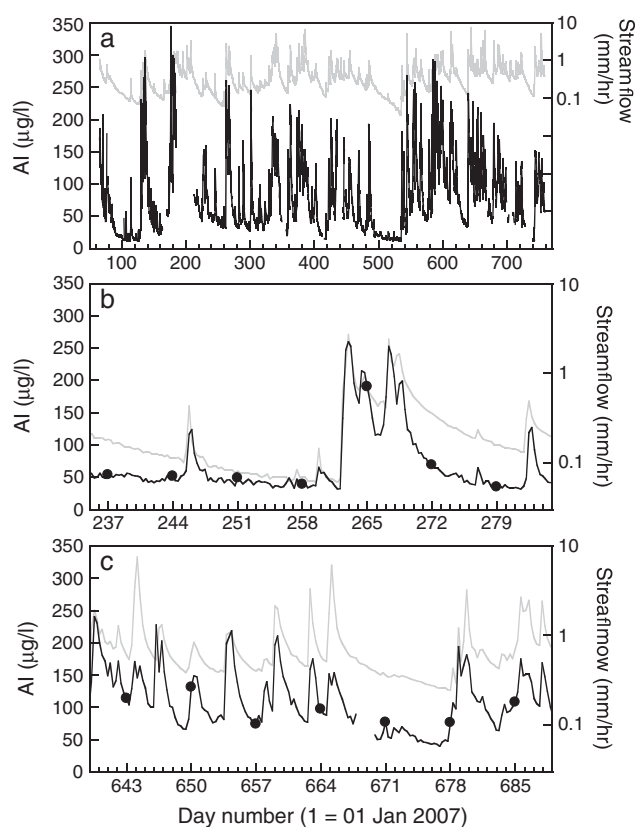


Figure 4. Aluminium time series in Upper Hafren streamflow, Plynlimon, Wales, over the full data record (a) and two shorter periods where there are significant storm events (b,c). (a) Complete 7-hourly time series of aluminium concentrations (black), with stream discharge (grey) shown on a logarithmic scale for comparison. Enlarged views of two 50-day periods (b,c) show responses to individual storms. Although aluminium 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

## 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 links to the online repository containing the data set and complete metadata. 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 edited 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 the 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 performed. For example, censored (‘less than’) values are problematic in statistical analyses (Helsel, 1990). 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 by using conventional visualisation and analysis techniques.

We intensively monitored a wide range of chemical determinands with contrasting hydrobiogeochemical properties (Table I), 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 nonstop, 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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