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Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/acs.est.6b02155 • Publication Date (Web): 29 Aug 2016

Sensors in the stream: the high-frequency wave of the present

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Abstract

New scientific understanding is catalysed by novel technologies that enhance measurement precision, resolution or type, and that provide new tools to test and develop theory. Over the last 50 years, technology has transformed the hydrologic sciences by enabling direct measurements of watershed fluxes (evapotranspiration, streamflow) at time scales and spatial extents aligned with variation in physical drivers. High frequency water quality measurements, increasingly obtained by *in-situ* water quality sensors, are extending that transformation. Widely available sensors for some physical (temperature) and chemical (conductivity, dissolved oxygen) attributes have become integral to aquatic science, and emerging sensors for nutrients, dissolved CO_2, turbidity, algal pigments, and dissolved organic matter are now enabling observations of watersheds and streams at timescales commensurate with their fundamental hydrological, energetic, elemental, and biological drivers. Here we synthesize insights from emerging technologies across a suite of applications, and envision future advances, enabled by sensors, in our ability to understand, predict, and restore watershed and stream systems.

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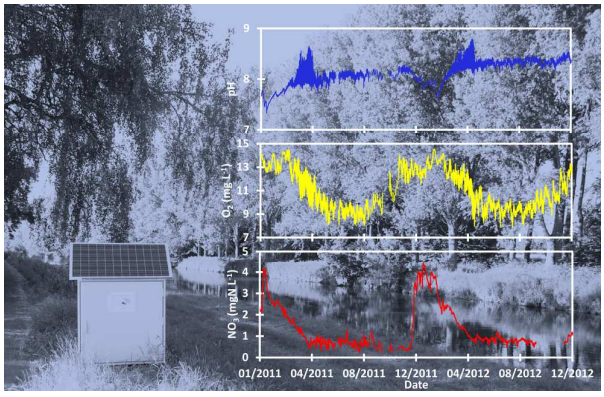


Recent progress in in-situ sensor monitoring

Just over a decade ago, Kirchner et al. [1] envisioned the hydrologic sciences being transformed by the increased availability of stream chemistry measurements at time scales commensurate with hydrologic forcing, a theme echoed in the U.S. National Research Council's "Challenges and Opportunities in the Hydrologic Sciences" in 2012 (http://www.nap.edu/read/13293/chapter/1). At the same time, ecologists were recognizing the transformative potential of sensors that allow ecosystem processes to be measured at time and space scales that match relevant physical, chemical and biological drivers [2-4]. The vision of Kirchner et al. [1] has been realised, in part, with significant progress in estimating solute residence times in watersheds [5], but it is the converging vision across hydrological, biogeochemical, biological and ecological disciplines that highlights the significant intellectual payoff from new sensor technologies in watershed and stream science. Now stream water chemistry data are available every hour, or even every minute across a broad range of analytes, and commensurate biological data are available at fortnightly to daily intervals for sustained periods greater than one year. These advances allow the study of multiple solutes at sub-daily intervals, not just single solute time series, and enable interpretations and hypothesis testing of ideas around river biogeochemistry, biology and ecology, in addition to catchment signals. These novel measurements have revealed complex temporal dynamics that were obscured by traditional sampling frequencies [6-8] and have enabled new insights into the inner-workings of watersheds and streams.

While automated collection and traditional laboratory processing of discrete samples have yielded enormously informative sub-daily data [8-9], the transformation of stream and watershed science will occur primarily in response to increasing availability of automated *in situ* sensors. Indeed, electrode-based measurements of pH, conductivity, temperature, and dissolved oxygen (DO) have been available for over half a century [10] and are now essential tools for stream and watershed studies; however, sensor technology has been extended through the development of other methods

such as optical, wet analytical chemical or flow cytometry techniques (a laser- or impedance-based, biophysical technology employed in cell counting), recent advances in field deployment engineering (anti-fouling, batteries, micropumps), and electronics (detectors, emitters) that have reduced costs. This, in turn, has increased the number of sites at which *in situ* measurements are now made. Among the solutes for which sensors are most widely available is nitrate. Early colorimetric based sensors [11] for nitrate were constrained by performance and reagent wastes, and have largely given way to spectrophotometers [12] enabling very high frequency (0.5 Hz, samples per second) sampling that has proven enormously informative for understanding riverine dynamics [13-15]. For other solutes, wet analytical chemistry remains the most viable approach, with "lab-on-a-chip" sensors lowering power requirements and reducing the interferences that are intrinsic in optical absorbance measurements [16,17]. For example, measurements of orthophosphate using standard reagent-based colorimetry has emerged as a robust field-deployable technology, permitting automated hourly sampling and a host of attendant informative inferences enabled by this increase in temporal resolution [6,18]. Other deployable optical sensors include fluorimeters that can measure chlorophyll-a and other photosynthetic pigments, as well as fluorescent dissolved organic matter[19]; while these sensors have a long history in marine and estuarine settings, their use in streams and small watersheds has revealed a variety of novel insights [20]. Indeed, Fast repetition rate Fluorimetry (FrrF), a technique which measures the variability of light emission from chlorophyll a, can be used to measure photosynthetic rates *in situ* which reduce when algae are stressed due to the prevailing environmental conditions (e.g. drought), and these measurements are supported by weekly (imaging) flow cytometry (that can discriminate and assess abundance among phytoplankton and phytobacterial functional groups) and environmental DNA techniques (that can characterise microbial communities and detect invasive species) [21,22]. In short, the suite of widely used parameters that hydrologists, geochemists, and stream ecologists consider relevant is almost uniformly possible in real time and at high spatial or temporal resolution.

These new data sets have the ability to transform our understanding of a diverse range of fundamental aquatic processes, from watershed dynamics to nutrient spiralling to ecosystem response to disturbance. The potential for sensors to unravel ecosystem functioning and realize improved environmental management was illustrated by the recent commissioning of a "national nutrient sensor challenge" by the White House Office of Science and Technology Policy. This effort seeks to enable the next generation of long-term deployable, high accuracy, high precision *in situ* sensors, and to drive down costs to ensure broad adoption by academic, private and government scientists [23].

Here we present four examples (inferring nutrient sources and transport, measuring *in situ* nutrient processing, detecting ecological effects, and temporal scaling of solute export), spanning continents and time scales, in which recent utilization of sensor technologies have advanced our understanding of stream and watershed systems. While rivers and their watersheds are our focus, the use of novel measurement technologies in other aquatic ecosystems such as lakes, estuaries and oceans has been equally transformative [2-4]. In addition to the insights that have already been made, we highlight ongoing trends in sensor development and suggest areas in which sensors will enable new insights and allow tests of watershed and ecological theory.

Identifying nutrient sources and transport pathways in watersheds

Sub-daily monitoring of nutrient hydrochemistry has traditionally utilized automatic water-samplers, but these are expensive to run in terms of regular sample collection and subsequent laboratory analysis, and can have chemical and biological stability issues during sample storage [24], which usually is in the range of days. Through the deployment of *in situ* sensor and colorimetric based auto-analyser technology, Bowes et al. [25] measured hourly total reactive phosphorus (TRP) and nitrate concentrations and used these to characterise, on a storm-by-storm basis, the nutrient

source changes to a rural river in southern England over a two year period by analysing the hysteresis in the relationship between concentration and flow during storm events when the stream or river flow increases and then recedes. Differences in the hysteresis behavior between storms provide information on nutrient sources and pathways and the findings are summarized in Figure 1. In this case study of the River Enbourne in the UK, the results highlighted the importance of the acute mobilisation of sewage-derived phosphorus in bed sediment and the large diffuse phosphorus inputs entering the stream from manure applications during May storms, thereby helping to target

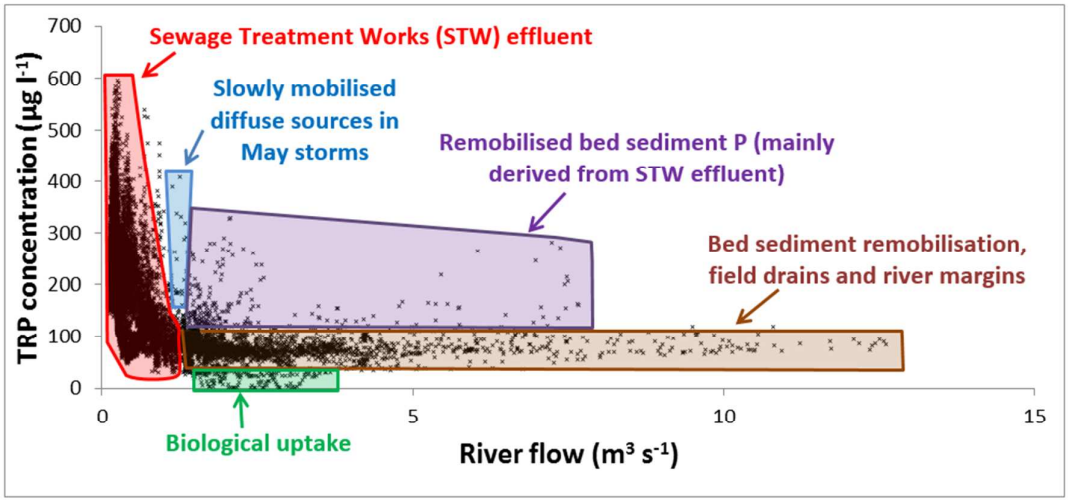


Figure 1: Phosphorus sources to the River Enborne (southern England) identified using two years of hourly total reactive phosphorus (TRP) and flow data. The clusters were derived from storm hysteresis analysis [24].

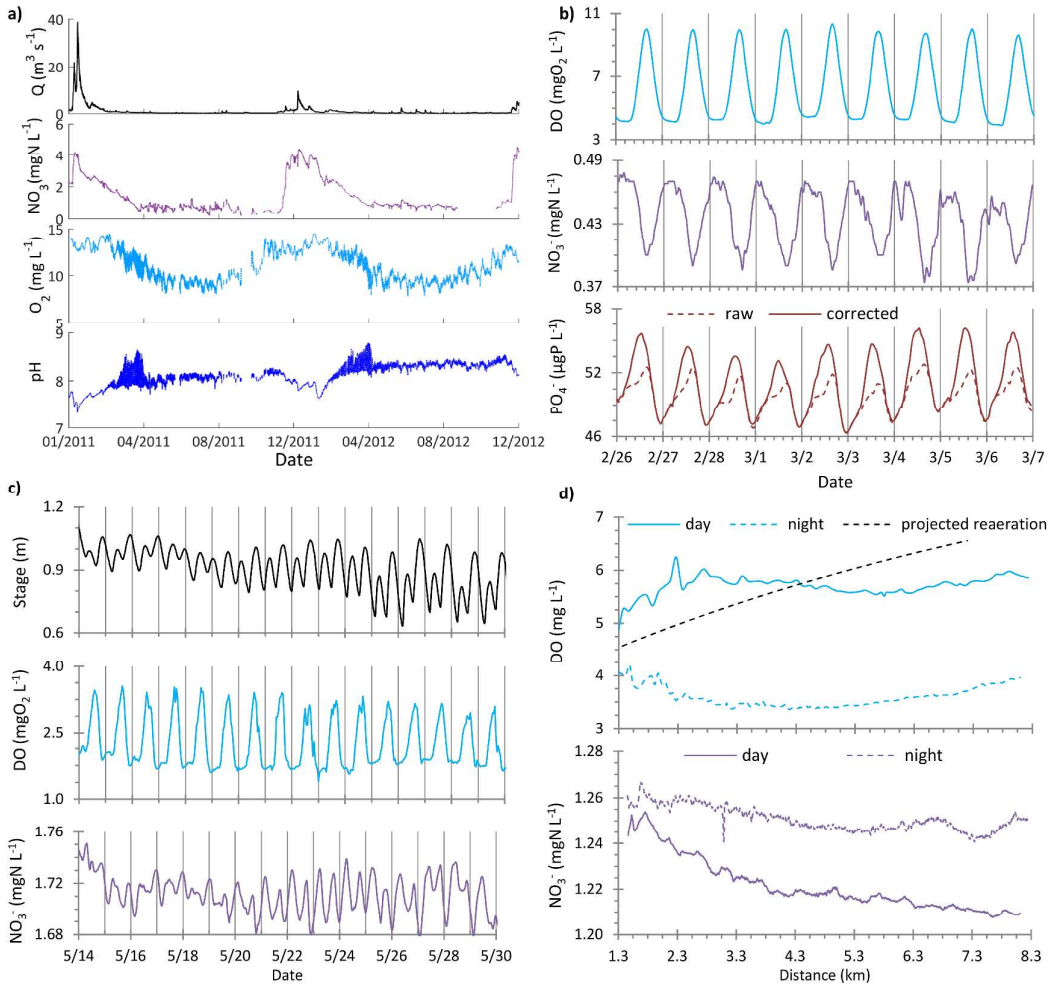
future remediation measures. Additional analysis showed clear double-peaked diel phosphorus and nitrate cycles during low flows, which pointed to chronic pollution related to the daily pattern of effluent discharges from sewage treatment works and septic tank systems [26]. Recently Mellander et al. [27] also used 20 minute phosphorus concentration monitoring to identify that subsurface flows in bedrock cracks were the dominant phosphorus transport pathways in a karst landscape in County Mayo, Ireland, and Mellander et al. [28] demonstrated that phosphorus could predominantly be transferred to streams via groundwater during winter in the south of Ireland using sub daily colorimetric based auto-analyser measurements. Both these studies allowed a deeper

understanding of phosphorus transfer pathways and retention in the aquifer to be developed with advice on location of critical source areas for phosphorus loss in a Karst landscape resultant.

Furthermore, regular sub-daily measurements of dissolved organic matter (DOM) composition (which plays a central role in carbon dynamics and participates in the complexation of trace metals and the mobilization of pollutants) by *in situ* Chromophoric Dissolved Organic Matter (CDOM) fluorescence have revealed a complex short-term variability in DOM composition. This variability is a function of source, flow pathway and instream photochemical and biologically mediated processes [20,29].

Together, these results highlight that sub-daily observations have high potential to accurately make source assignments and that watershed management can greatly benefit from high frequency measurements to identify site specific loss mechanisms and pathways and potential legacy issues [25,28], such as groundwater nitrogen and stream bed phosphorus retention. The development of sensors for an increasing range of water quality constituents, with more widespread deployment, will lead to a greater ability to fingerprint chemical sources through seasons and individual storm events in the future.

158 **Quantifying coupled nutrient processing and metabolism**



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160 Figure 2. Continuous high frequency oxygen, nitrate and pH data reflect the seasonal pattern of primary
161 production and assimilatory N uptake due to flow and light variability (panel a; adapted from Rode et al. [32]).
162 The relative magnitude of diel variation in DO, NO_3^- and PO_4^- (panel b; adapted from Cohen et al. [18]) is strongly
163 correlated with autotroph stoichiometry. The assimilatory P uptake (PO_4^- signal must be corrected for
164 precipitation) notably appears temporally de-coupled from primary production and assimilatory N uptake by
165 several hours. Comparison of day-night profiles can be used to partition assimilatory versus dissimilatory
166 pathways (panel c [33,35]), while high resolution longitudinal profiling (panel d; adapted from Hensley et al. [33])
167 has been used to identify spatial heterogeneity with N processing in a tidal river shown to be strongly
168 influenced by residence time variation.

169 Drainage networks are not passive conduits, but are important for chemical retention and
170 transformation. High frequency data have proven especially useful in quantifying in-stream nutrient

171 processing and understanding the stoichiometric coupling of autotrophic uptake across the periodic
172 table. In addition to seasonal patterns (Fig. 2a), finely resolved time-series have revealed strong diel
173 nitrate variability (Fig. 2b) similar to that observed for DO and interpreted as autotrophic N
174 assimilation [14,15]. Actively measuring nutrient uptake rates (e.g., via isotope or nutrient dosing) is
175 complex and expensive, limiting measurements to short (hours to days) periods [30], typically under
176 steady baseflow conditions, and with a significant bias towards small streams [31]. In Florida's spring
177 fed rivers, autotrophic nitrate uptake amounted to less than 20% of total net N retention[18]. In two
178 central European streams, percentage daily autotrophic N uptake peaked at 47% (agricultural
179 stream) and 75% (forest stream) of the daily N loading input to the stream network of the whole
180 watershed[32]. There were different ranges of autotrophic areal rate of nutrient uptake (U, analogues
181 to the mass of nutrient removed from water per unit area of streambed (m^{-2}) per unit time (d)) with
182 30-160 mg N in the Florida rivers[14] and 0-270 mg N and 0-97 mg N in the central European
183 agricultural and forest stream[32], respectively. Dissimilatory pathways such as denitrification, which
184 account for the balance of net retention, were also coupled with primary productivity through
185 secondary relationships such as the availability of labile carbon [14]. In a separate study, a more
186 complex retention signal (Fig. 2c) arose in a tidal river, representing the convolution of diel
187 assimilatory uptake and tidally varying denitrification based on residence time and benthic surface
188 area [33].

189 While early insights into coupled nutrient processing have focused on nitrate dynamics,
190 sensors for other solutes have proven equally valuable. Cohen et al. [18] used an ortho-phosphate
191 sensor, along with optical nitrate, and electrode based DO and specific conductance sensors. The
192 high frequency signals enabled identification and deconvolution of geochemical P-retention
193 pathways that created overlapping diel P signals. The data also revealed clear coupling of N and C
194 assimilation, and that while also coupled, P uptake was not synchronous with the timing of N and C
195 assimilation. This asynchronous N and P assimilation may represent timing differences in protein and
196 ribosome production in aquatic plants. It has been suggested that temporal nutrient coupling occurs

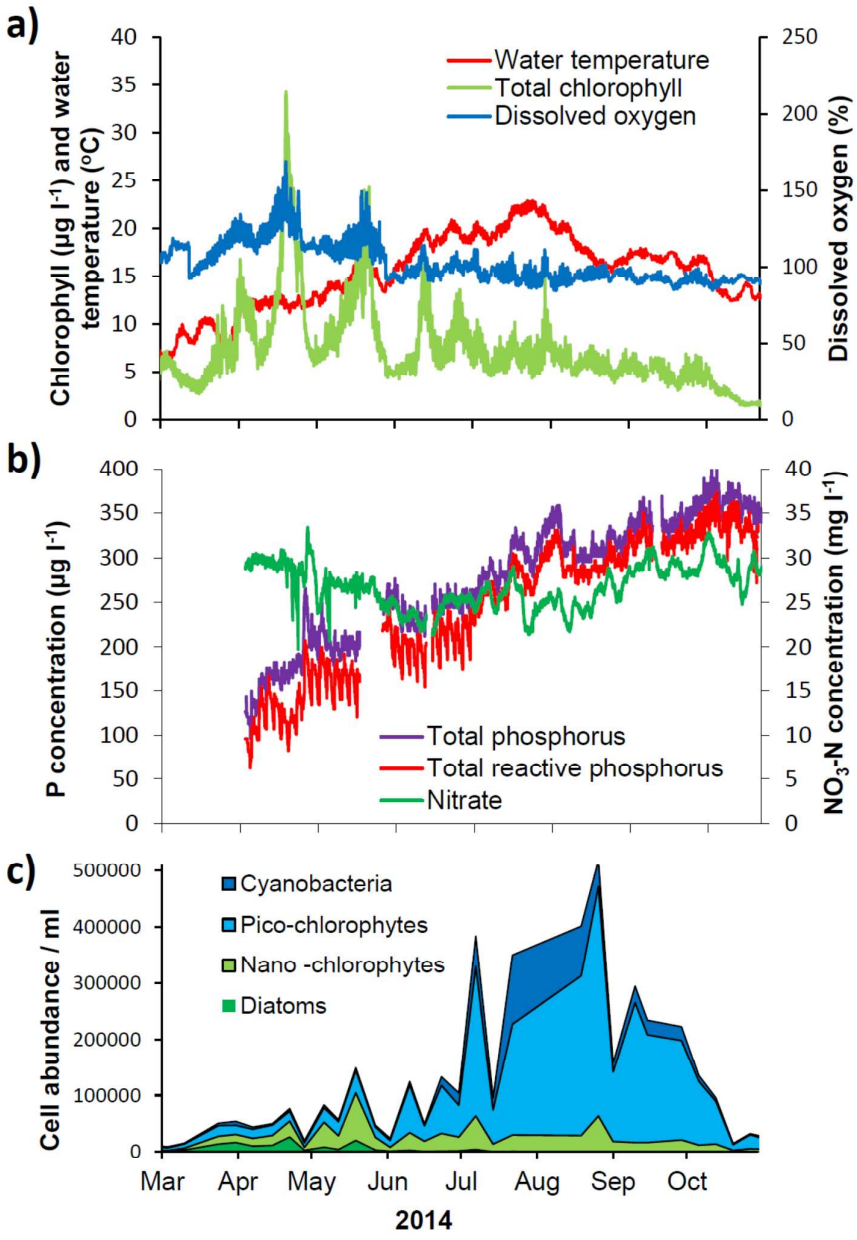
197 only when an input nutrient is limiting and therefore the identification of such temporal coupling,
198 through *in situ* high frequency monitoring, is a useful indicator of ecosystem limitation status [34]. Diel
199 concentration variation for biologically active trace metals (e.g., Ba, Fe, Mn, and U) has similarly
200 been observed in spring systems in Florida, USA, and suggests that aquatic plant metabolism
201 controls diel and seasonal cycling of metals [35]. As sensors emerge for measuring other solutes such
202 as other nutrients (e.g., Si, Fe, Mg), the organic nutrient forms (e.g. DON, DOP), measurements of
203 total concentrations which include the particulate fraction and therefore all the total nutrient
204 potentially available, and organic pollutants, their dynamics can be compared to metabolic, thermal,
205 flow and photolytic forcing, which will enable a rich new arena for understanding aquatic systems.

206 Sensors can also be applied using an alternative Lagrangian approach [36]. Reach-scale
207 nutrient processing rates such as areal rate of nutrient uptake (U) and uptake length (average
208 distance a nutrient molecule, typically nitrate, moves downstream in dissolved form before being
209 assimilated by the biota) have been estimated from longitudinal changes in stream solute
210 concentrations (Fig. 2d), revealing a large degree of spatial heterogeneity in nutrient uptake which
211 appears related to changes in river morphology[33]. Furthermore, estimates of reach-scale metabolism
212 and nutrient processing show diel variations along a continuous gradient from headwaters to mouth,
213 as envisioned in the River Continuum Concept [37,38], and highlight how river regulation disrupts the
214 continuum, for example, in terms of stream metabolism through increased total dissolved N uptake
215 below dams [38,39].

216 These early insights suggest that the emergence of sensor-derived high-frequency time
217 series for multiple solutes will better allow us to observe the stoichiometric coupling of metabolic
218 and geochemical processes and thereby test stoichiometric theory. It will also enable a deeper
219 understanding of variation in retention rates and pathways with flow, temperature and other abiotic
220 drivers across watersheds spanning a gradient of size and geochemical and physical features.

221

222 **Separating the effects of multiple processes on aquatic ecology**



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224 Figure 3: Combined physical (a), chemical (b) and biological monitoring (a, c) of the River Thames at Goring, UK
225 (Unpublished Data, supplied by Centre for Ecology & Hydrology, Wallingford, UK, and the UK Environment
226 Agency). The time axis is the same in the three panels.

227 The effects of multiple pressures on freshwater ecosystems are difficult to separate because
228 of the multiple, interrelated abiotic-biotic interactions. New biological monitoring techniques have

229 been developed that allow the high-frequency characterisation of river plankton composition and
230 function for the first time. Fluorimeters now reliably measure total chlorophyll and other
231 photosynthetic pigments at sub-hourly frequencies to estimate phytoplankton concentrations
232 (Figure 3a). FrrFs are able to monitor changes in the photosynthetic stress of both chlorophyte and
233 cyanobacterial communities at sub-hourly intervals [40]. These *in situ* techniques can be further
234 supplemented by *in situ* flow cytometry (Figure 3c), which provides a rapid and simple methodology
235 to characterise, at high-frequency, the river phytoplankton community by quantifying the cell
236 concentrations of diatoms, chlorophytes, cryptophytes and different classes of cyanobacteria [41]. By
237 combining these new biological data with physico-chemical data of the same high temporal
238 resolution, it has been demonstrated that it is water temperature, flow and light conditions that are
239 controlling the onset and magnitude of phytoplankton blooms in the River Thames, rather than
240 increases in nutrient concentration[42]. However, phosphorus and silicon may ultimately terminate
241 large phytoplankton blooms due to nutrient depletion and limitation[42]. Such insights are only
242 possible through long-term, sub-daily biogeochemical observations that are able to capture the
243 conditions at the precise time points where chlorophyll concentrations begin to increase or
244 decrease. In the coming years, high frequency next generation DNA sequencing will provide an even
245 greater understanding of river microbiological dynamics and their biotic-abiotic interactions [22].

246

Quantifying water quality across multiple time scales

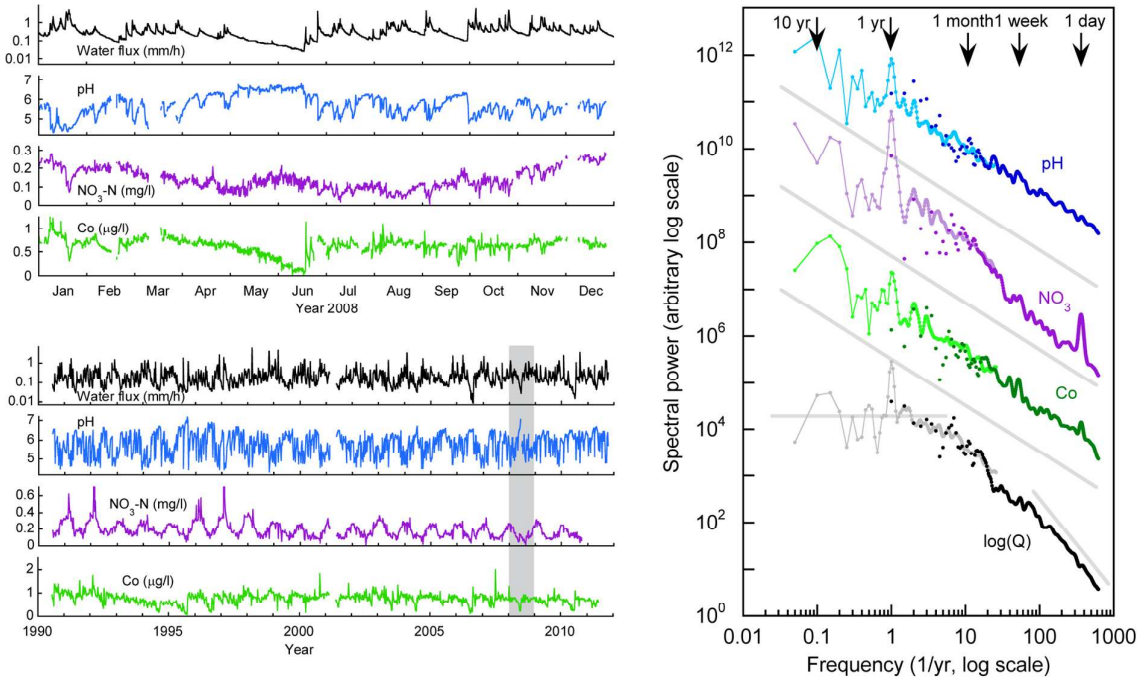

Figure 4. Water quality time series in Upper Hafren streamwater, Plynlimon, Wales, at 7-hour intervals for one year (left upper panel) and weekly intervals for 21 years (left lower panel) (Unpublished Data). Three water quality parameters are shown: pH (an indicator of acid-base status), nitrate (a nutrient that exhibits both diurnal and seasonal cycles) and cobalt (Co). The shaded band in the lower panels shows the time interval covered by the upper panels. The right panel shows power spectra of weekly and 7-hourly time series (light and dark points, respectively), calculated using the methods of Kirchner and Neal [8].

Detecting water quality trends requires an understanding of water quality fluctuations over many time scales, including those that are invisible in typical weekly or monthly sampling [43]. At several small research watersheds, broad suites of chemical parameters have been measured at daily or higher frequency [8,9,44], facilitating chemical dynamic characterization on shorter timescales as well as those captured by typical monitoring programs (weekly or monthly) (Figure 4 – left panels).

Spectral analysis decomposes a time-series into a spectrum of cycles of different wavelengths with the power spectrum defined by the contribution of each frequency, f, to the time series. The combination of high-frequency and long-term chemical analysis has demonstrated that,

on time scales from hours to decades, the power spectrum of mulitple solute time-series, in this case pH (or H^+), NO^-_3 and Co, can be characterised as $1/f^{\alpha}$ noise, where α, the scaling exponent, is approximately equal to 1 (known as "pink noise")[8]. This is shown in Figure 4 (right panel), where the water quality parameters have power-law slopes of -1 (parallel to the long-grey reference lines), indicating that spectral power is inversely proportional to frequency (the 1/f pink noise – which is sometimes referred to as "fractal" noise to emphasise that the scaling exponent, α, can be a non-integer - it does not mean there is self-similarity in the power spectrum). The result implies that three ions do not simply flush through the catchment with the water but that the catchment has a long chemical memory. The stream discharge spectrum, by contrast, has a power-law slope near 0 at low frequencies and -2 at high frequencies (as indicated by the shorter grey reference lines).

Whilst the idea of catchment solute storage is not new, analysis of rainfall and stream water power spectra, for the same solute, allows a transfer function to be derived which can be used to quantify the travel time distribution which is very useful in understanding solute retention in different geographical settings. In addition, the 1/f behaviour of the chemical time series has important implications[45]. Such time series are "non-self-averaging"; they do not converge to stable averages when sampled for longer periods, because their fluctuations do not average out over time. This non-self-averaging behaviour implies that even purely random time series can exhibit spurious trends, on all time scales, which appear to be statistically significant when evaluated by conventional statistics [9,46]. Even more disconcertingly, collecting more data makes this problem worse; non-self-averaging time series exhibit more spuriously "significant" trends (not fewer, as one would expect) when sampled for longer periods, or at higher frequency. Thus, environmental trends should be analysed with more sophisticated statistical methods that are not confounded by the multi-scale correlations that characterize these time series. A recent example of such analysis includes the application of Dynamic Harmonic Regression to use this non-stationary technique to explore stream water nitrate dynamics across decadal to sub-daily timescales and to derive the main cause and effect links at long-term, seasonal and diel time-scales [47,48].

290

291 **Additional advances**

292 Where a particular water constituent cannot yet be measured directly with an *in situ* sensor,
293 it may still be possible to construct a high frequency time-series for that constituent if there is a
294 strong relationship with a water quality parameter that can be readily measured, such as turbidity,
295 dissolved oxygen, temperature and pH. In this way, such sensor measurements have recently been
296 used as proxies for a range of water quality parameters, including total suspended solids [49,50],
297 alkalinity[49], total nitrogen[49], total phosphorus [49,50], sodium[49], chloride[49], fluoride[49], sulfate[49], fecal
298 coliform bacteria[49], fluoranthene and mercury[51], polycyclic aromatic hydrocarbons[52], , and when
299 coupled with discharge measurements allow flux estimation. For example, high resolution *in situ*
300 measurements of turbidity and fluorescence were used to estimate total mercury transport between
301 the San Francisco estuary and an adjacent tidal wetland [53]. High frequency water quality
302 measurements can also be used to reconstruct concentration patterns in combination with other
303 commonly available continuous data, such as precipitation or discharge. In this way, Rozemeijer et
304 al. [54] reduced the bias of total phosphorus load calculations by up to 63% using 20 events sampled at
305 15 minute intervals.

306 Measurements of lake, reservoir, wetland and estuarine diel dynamics help identify internal
307 processing of nutrients and metals. High frequency monitoring in lakes and reservoirs using
308 autonomous vertical profiling systems is increasingly exploited for safeguarding high water quality
309 (e.g., for drinking water abstraction [55]). Such systems detect river intrusions that may quickly reach
310 water abstraction infrastructure [56,57]. High frequency measurements also allow new insights into lake
311 metabolism and help constrain biogeochemical budgets or to differentiate the importance of
312 internal versus external factors[58]. It has been recently shown that monitoring external watershed
313 loading, as well as within lake chemistry, at high frequency, enables separation of carbon
314 accumulation due to internal phytoplankton dynamics versus external inputs of organic carbon from

runoff events[59]. High frequency oxygen measurements revealed that external seasonal forcing plays a key role in determining the extent to which a lake ecosystem is a seasonal carbon sink or source to the atmosphere [60]. Further experimental uses of high-frequency sensors extends to monitoring tracers [6], changes in artificial environments (e.g., benthic chambers) and in process-control systems, for example, to control iron dosing to co-precipitate phosphorus at Wessex Water's Keynsham Sewage Treatment Works in the UK (http://www.worldpumps.com/view/316/control-of-chemical-dosing-in-wastewater-treatment/**)**.

For parameters with a strong diel variation, such as DO, the value obtained, and thus the classification of the European Union Water Framework Directive (WFD), which commits European Union member states to achieve good qualitative and quantitative status of all water bodies, can depend markedly on the frequency of sampling. In lowland UK river-systems, monthly sampling for a year can result in the same water body being assigned to three or four of the WFD classes with 95% confidence, due to random sampling effects, although the specific effect on WFD classification depends on the closeness of the range of measured concentrations to the class boundaries. Where water body status is estimated using parameters, such as water temperature, that are assessed using extreme percentiles in a distribution of measurements, such as the 98th percentile for water temperature as done in the UK, then monthly sampling does not capture the full variance observed and causes an inaccurate estimate of the true value [61].

Implications for environmental modelling

From a modelling perspective, the emerging evidence for excessive nutrient contribution of short-term events puts into question the ubiquitous applications of the data-driven models, such as the water quality balance model SPARROW in North America [62,63]. Underestimating nutrient export by a factor of two or three and missing the timing of greatest nutrient delivery into a waterbody

impedes efforts to delineate watershed "hot-spots" or time periods with increased likelihood of violations of water quality targets [64]. The advent of high resolution data offers a new perspective on process-based model parameterization and our capacity to accommodate threshold-type of behaviours when locating critical source areas of non-point source pollution [65]. In this regard, Wellen et al. [66] presented a Bayesian hierarchical framework which postulated that the watershed response to precipitation occurs in distinct states, depending, for example, on precipitation and catchment storage. The proposed calibration framework enabled the identification of extreme states and the characterization of different watershed behaviours and improved model performance by allowing parameter values to vary between low and high flow conditions. In addition, estimates of instream assimilation and denitrification help to constrain catchment nitrogen delivery and transport models[32], and sub-daily chemistry data coupled with weekly biological monitoring are providing the basis on which to develop a process-based description of aquatic biotic-abiotic interactions, thus enabling an enhanced understanding compared to using ecological indicators alone. Furthermore, development of intelligent water body-specific, cost efficient monitoring schemes combining modelling tools with high frequency monitoring would also help to optimize monitoring schemes and make these technologies accessible for large scale water management.

Limitations of current in situ technologies

In case of conventional *in situ* chemical and biological measurements there are major issues related to calibration (requiring stable reagents and standards) and supporting infrastructure (e.g., of pumped flow systems) and frequency of servicing intervals which in turn affect the scalability of *in situ* deployment. *In situ* optical sensors, such as those for nitrate, require cleaning to remove biofilm. They can also suffer from interferences due to turbidity and from co-absorbing species like humic acids. However, performing multi-parameter sensing, such as monitoring turbidity and nitrate simultaneously, enables the robustness of the nitrate measurements to be assessed. Given the costs,

364 service requirements, the risks of theft and vandalism, and instrument power requirements, which
365 has decreased recently, there is a need for a cost-benefit analysis to assess the utility of *in situ*
366 sensors for widespread operational and regulatory monitoring. Furthermore, "big" data streams
367 from *in situ* measurements pose a challenge to environmental scientists because traditional
368 approaches to data quality assurance and quality control are no longer practical when confronted
369 with the demands of real-time processing. Despite routine maintenance and calibration of sensors,
370 there is a pressing need for the development of automated tools and standards for quality assurance
371 and quality control of sensor data [67].

372

373 **Future directions**

374 The use of high frequency sensors has moved beyond the realm of purely academic
375 research[68] and these sensors are now employed by numerous national, state, and municipal level
376 environmental authorities. In the United States there are over 500 stations with continuous DO
377 sensors, and over 100 stations with continuous nitrate sensors (http://waterdata.usgs.gov/nwis).
378 There are similar levels of deployment in other developed nations.

379 The knowledge gained from new sensor technology has and will continue to stimulate
380 further advancement. Already microfluidic sensors for measuring nutrients based on colormetric
381 techniques have advantages of small size and limited reagent and power requirements [16,17], though
382 further improvements of these devices are necessary to increase robustness and reduce
383 maintenance during permanent deployment. There is still a clear need for further development of
384 new types of sensors, particularly for chemical and organism-based measurements of freshwater
385 ecosystems. Increasing the number of analytes to include redox sensitive elements, micro-nutrients
386 and pesticides would be highly beneficial for more complete environmental assessment. The exciting

prospect of micro-scale inductively coupled plasma spectrometers would allow the measurement of a wide-array of elements in water[69].

The inferences drawn from the examples we present above are broadly applicable, as suggested by their geographic range and variation in temporal scales, and move beyond findings that can be obtained from single experiments. Real time sensor deployment for measuring water quality properties continuously from multi-parameter probes offers new prospects to develop sensor networks for whole river networks, watersheds, and lakes. High frequency measurements will expand from the water column to hot spots of biogeochemical transformation and ecological significance, such as the interfaces between aquatic and terrestrial sites (e.g., hyporheic and riparian zones, wetlands, and river-estuarine transition zones). This would significantly increase our understanding of the interaction between sources, uptake (e.g., primary production) and retention (e.g., denitrification) in whole river networks. The co-location of isotope and dissolved anions and cations measurements will also enable enhanced understanding of pollutant storage and transfer and integration of hydrological and water quality models through better characterisation of water and ion transit times[70].

Current use of real time sensors is still restricted to fundamental aquatic attributes such as DO, pH value, SRP and NO_3 [71], but the field of sensor development is rapidly advancing and we see great potential for developing observational data sets that can substantially improve our ability to understand and predict the causes and consequences of environmental changes of aquatic ecosystems. Furthermore, such high temporal resolution data streams can be complemented by additional data types like satellite products for a synoptic survey of water quality of wetlands, large rivers, and lakes to create new scope for validating ecosystem models across multiple scales [72]. The utility of *in situ* sensor measurements has already begun to transform routine monitoring in the U.S., with federal (e.g., U.S. Geological Survey), and state agencies (e.g., St Johns River Water Management District in Florida) investing heavily in the structural and personnel capacity to deploy

412 and interpret high-resolution solute time series. In Germany, routine high resolution sensor
413 deployments are not restricted to highly sensitive water bodies like drinking water reservoirs and
414 the gain of scientific transport process understanding[65]; German state water authorities (e.g., state
415 environmental agency of Hesse and Baden Wurttemberg) increasingly use high frequency
416 monitoring to quantify matter fluxes (especially at the outlet of large rivers) and for early warning
417 systems for drinking water river bank infiltration facilities (e.g. at the Rhein river). There is also
418 potential to use high frequency monitoring more widely to measure intermittent discharges from
419 Combined Sewer Overflows.

420 Automated sensors that collect novel data, or even traditional data at novel time scales, can
421 enable analyses that inspire new paradigms in aquatic ecology [4]. The susceptibility of an ecosystem
422 to changing drivers or random events depends on the characteristics of critical thresholds, such as in
423 ecosystem metabolism[73] or in the physical drivers of change, such as flow, light and temperature.
424 Fundamental progress in ecology requires better understanding of thresholds and the rate of
425 anthropogenic induced change in aquatic ecosystems. Emerging technology such as FrrF, "lab-on-a-
426 chip", and DNA technology for observing time series data at high temporal resolution will make a
427 growing contribution to this field [74]. High frequency measurements gained by automated sensors
428 will increase our opportunities to better determine the severity of extreme events in terms of water
429 quality and freshwater ecological impacts, and identify the most important variables for assessing
430 the links to environmental change [75] at different spatial scales and for different aquatic ecosystem
431 types[41]. Based on this, we will be in a stronger position to spot early warning signals of critical
432 transitions of watershed biogeochemistry and aquatic ecosystems, and identify and evaluate
433 management options to help mitigate adverse water quality and ecological impacts[76].

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435 **References**

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Biography

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