Rode, Michael; Wade, Andrew J.; Cohen, Matthew J.; Hensley, Robert T.; Bowes, Michael J.; Kirchner, James W.; Arhonditsis, George B.; Jordan, Phil; Kronvang, Brian; Halliday, Sarah J.; Skeffington, Richard A.; Rozemeijer, Joachim C.; Aubert, Alice H.; Rinke, Karsten; Jomaa, Seifeddine. 2016
Sensors in the stream: the high-frequency wave of the present.
Environmental Science & Technology, 50 (19). 10297-10307.
10.1021/acs.est.6b02155

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

Michael Rode [1,13*], Andrew J. Wade [2,13], Matthew J. Cohen [3], Robert T. Hensley [4], Michael J. Bowes [5], James W. Kirchner [6], George B. Arhonditsis [7], Phil Jordan [8], Brian Kronvang [9], Sarah J. Halliday [2], Richard A. Skeffington[2], Joachim C. Rozemeijer [10], Alice H. Aubert [11], Karsten Rinke [12], Seifeddine Jomaa [1]

[1] Department of Aquatic Ecosystem Analysis and Management, Helmholtz Centre for Environmental Research-UFZ, Brueckstrasse 3a, D-39114 Magdeburg, Germany, *(michael.rode@ufz.de)

[2] Department of Geography and Environmental Sciences, University of Reading, Whiteknights, Reading, United Kingdom (a.j.wade@reading.ac.uk)

[3] School of Natural Resources and Environment, University of Florida, Gainesville, Florida

[4] School of Forest Resources and Conservation, University of Florida, Gainesville, Florida

[5] Centre for Ecology and Hydrology, Wallingford, Oxon. OX10 8BB, United Kingdom

[6] Department of Environmental Sciences, Swiss Federal Institute of Technology-ETH, Zürich, Switzerland; Swiss Federal Research Institute, WSL, Birmensdorf, Switzerland

[7] Ecological Modelling Laboratory, Department of Physical and Environmental Sciences, University of Toronto, Toronto, Ontario, Canada

[8] School of Environmental Sciences, Ulster University, Coleraine, N. Ireland, United Kingdom,

[9] Department of Bioscience and DCE–National Centre of Environment and Energy, Aarhus University, Vejlsøvej 25, DK-8600 Silkeborg, Denmark

[10] Deltares, P.O. Box 85467, NL-3508TA, Utrecht, The Netherlands

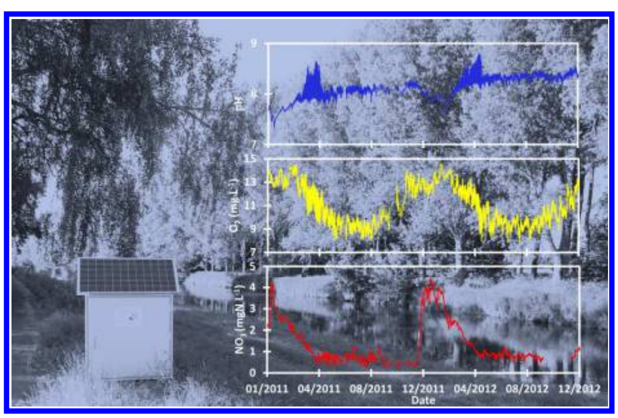
[11] Department of Environmental Social Sciences, Eawag, Überlandstrasse 133, 8600 Dübendorf, Switzerland

[12] Department of Lake Research, Helmholtz Centre for Environmental Research-UFZ, Brueckstrasse 3a, D-39114 Magdeburg, Germany

[13] Both authors contributed equally to this work

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.



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

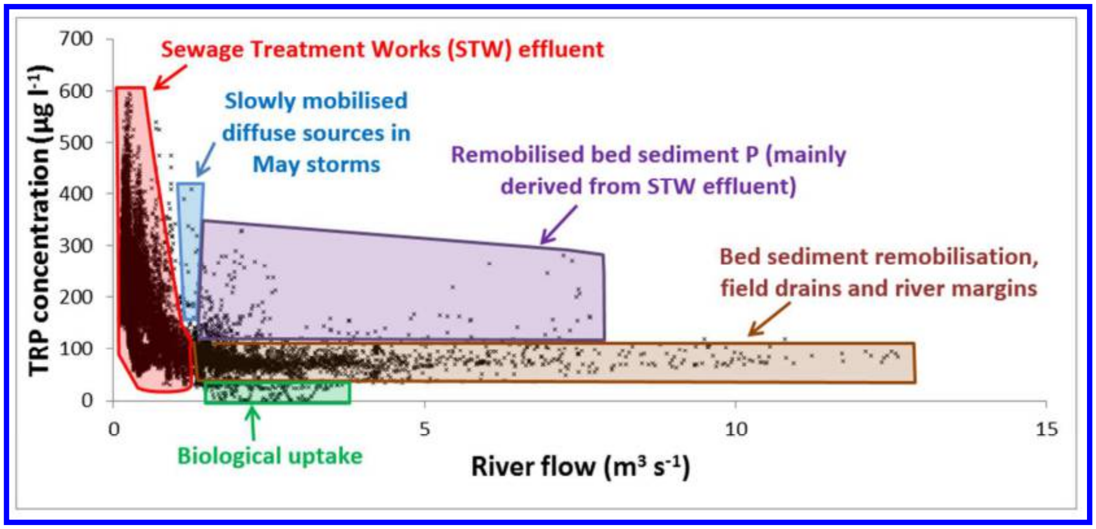


Figure 1: Phosphorus sources to the River Enborne (southern England) identified using two years of hourly total reactive phosphorus (TRP) and flow data. The clusters were derived from storm hysteresis analysis [24].

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.

Quantifying coupled nutrient processing and metabolism

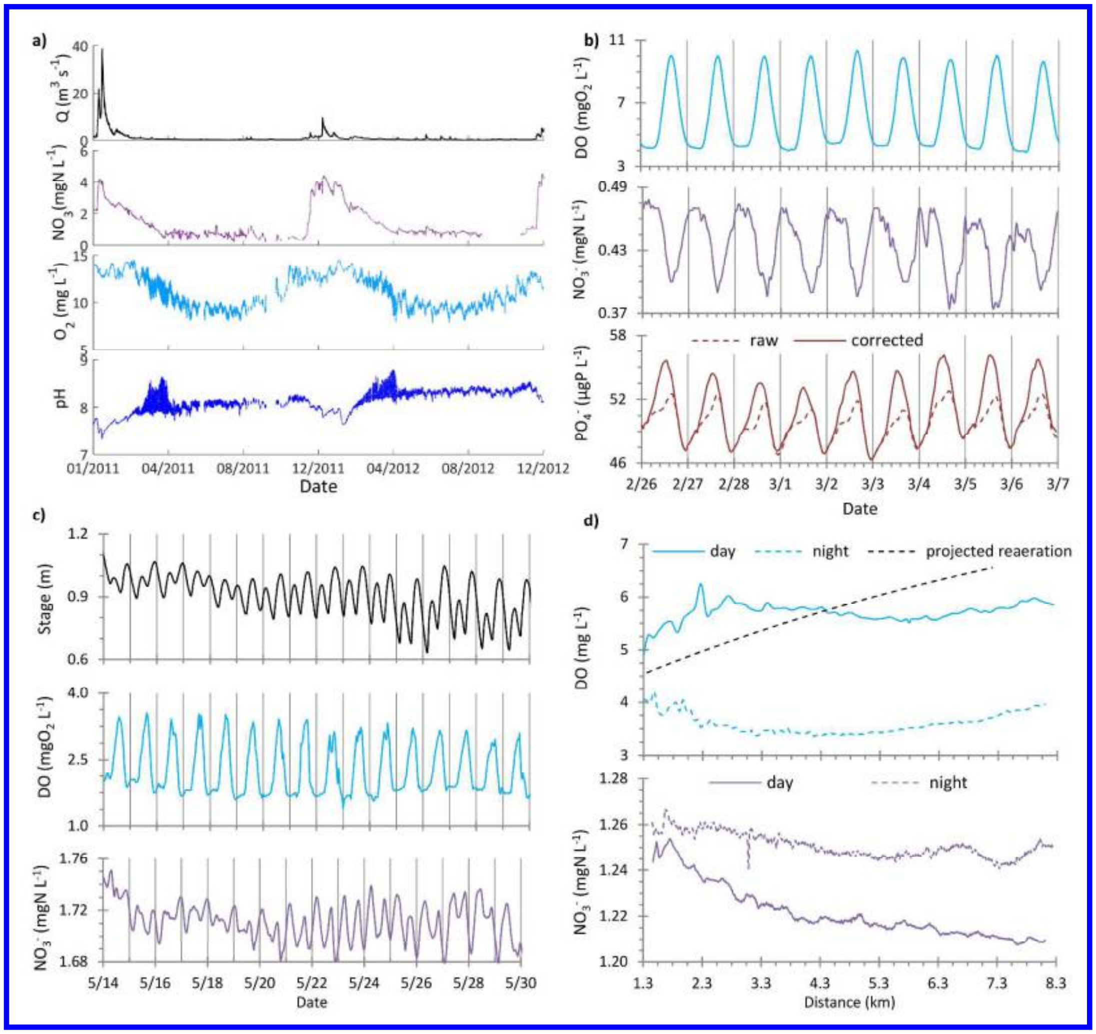


Figure 2. Continuous high frequency oxygen, nitrate and pH data reflect the seasonal pattern of primary production and assimilatory N uptake due to flow and light variability (panel a; adapted from Rode et al. [32]). The relative magnitude of diel variation in DO, NO_3^- and PO_4^- (panel b; adapted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

Drainage networks are not passive conduits, but are important for chemical retention and transformation. High frequency data have proven especially useful in quantifying in-stream nutrient processing and understanding the stoichiometric coupling of autotrophic uptake across the periodic table. In addition to seasonal patterns (Fig. 2a), finely resolved time-series have revealed strong diel nitrate variability (Fig. 2b) similar to that observed for DO and interpreted as autotrophic N assimilation [14,15]. Actively measuring nutrient uptake rates (e.g., via isotope or nutrient dosing) is complex and expensive, limiting measurements to short (hours to days) periods [30], typically under steady baseflow conditions, and with a significant bias towards small streams [31]. In Florida's spring fed rivers, autotrophic nitrate uptake amounted to less than 20% of total net N retention[18]. In two central European streams, percentage daily autotrophic N uptake peaked at 47% (agricultural stream) and 75% (forest stream) of the daily N loading input to the stream network of the whole watershed[32]. There were different ranges of autotrophic areal rate of nutrient uptake (U, analogues to the mass of nutrient removed from water per unit area of streambed (m^{-2}) per unit time (d)) with 30-160 mg N in the Florida rivers[14] and 0-270 mg N and 0-97 mg N in the central European agricultural and forest stream[32], respectively. Dissimilatory pathways such as denitrification, which account for the balance of net retention, were also coupled with primary productivity through secondary relationships such as the availability of labile carbon [14]. In a separate study, a more complex retention signal (Fig. 2c) arose in a tidal river, representing the convolution of diel assimilatory uptake and tidally varying denitrification based on residence time and benthic surface area [33].

While early insights into coupled nutrient processing have focused on nitrate dynamics, sensors for other solutes have proven equally valuable. Cohen et al. [18] used an ortho-phosphate sensor, along with optical nitrate, and electrode based DO and specific conductance sensors. The high frequency signals enabled identification and deconvolution of geochemical P-retention pathways that created overlapping diel P signals. The data also revealed clear coupling of N and C assimilation, and that while also coupled, P uptake was not synchronous with the timing of N and C assimilation. This asynchronous N and P assimilation may represent timing differences in protein and ribosome production in aquatic plants. It has been suggested that temporal nutrient coupling occurs only when an input nutrient is limiting and therefore the identification of such temporal coupling, through *in situ* high frequency monitoring, is a useful indicator of ecosystem limitation status [34]. Diel concentration variation for biologically active trace metals (e.g., Ba, Fe, Mn, and U) has similarly been observed in spring systems in Florida, USA, and suggests that aquatic plant metabolism controls diel and seasonal cycling of metals [35]. As sensors emerge for measuring other solutes such as other nutrients (e.g., Si, Fe, Mg), the organic nutrient forms (e.g. DON, DOP), measurements of total concentrations which include the particulate fraction and therefore all the total nutrient potentially available, and organic pollutants, their dynamics can be compared to metabolic, thermal, flow and photolytic forcing, which will enable a rich new arena for understanding aquatic systems.

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

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

Separating the effects of multiple processes on aquatic ecology

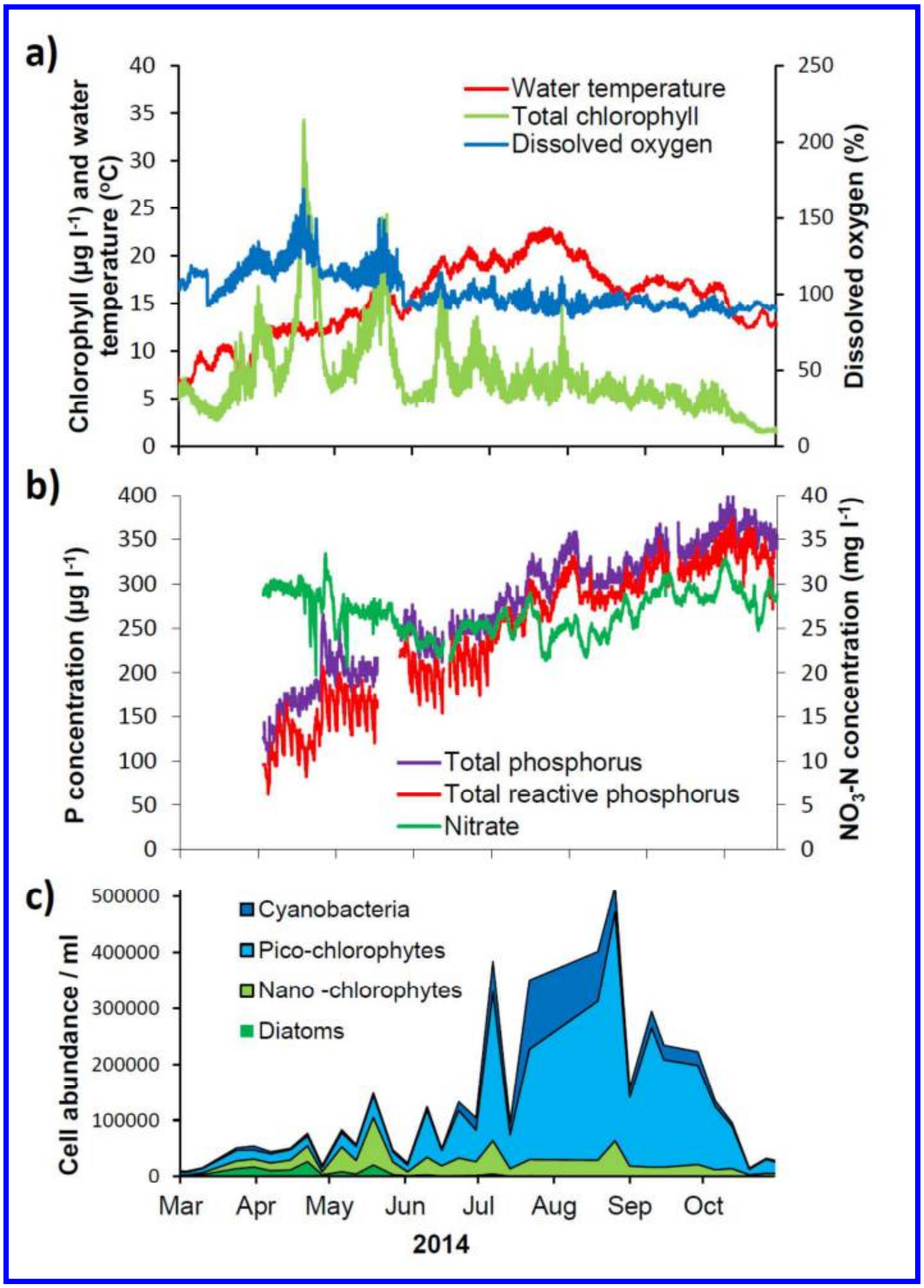


Figure 3: Combined physical (a), chemical (b) and biological monitoring (a, c) of the River Thames at Goring, UK (Unpublished Data, supplied by Centre for Ecology & Hydrology, Wallingford, UK, and the UK Environment Agency). The time axis is the same in the three panels.

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

Quantifying water quality across multiple time scales

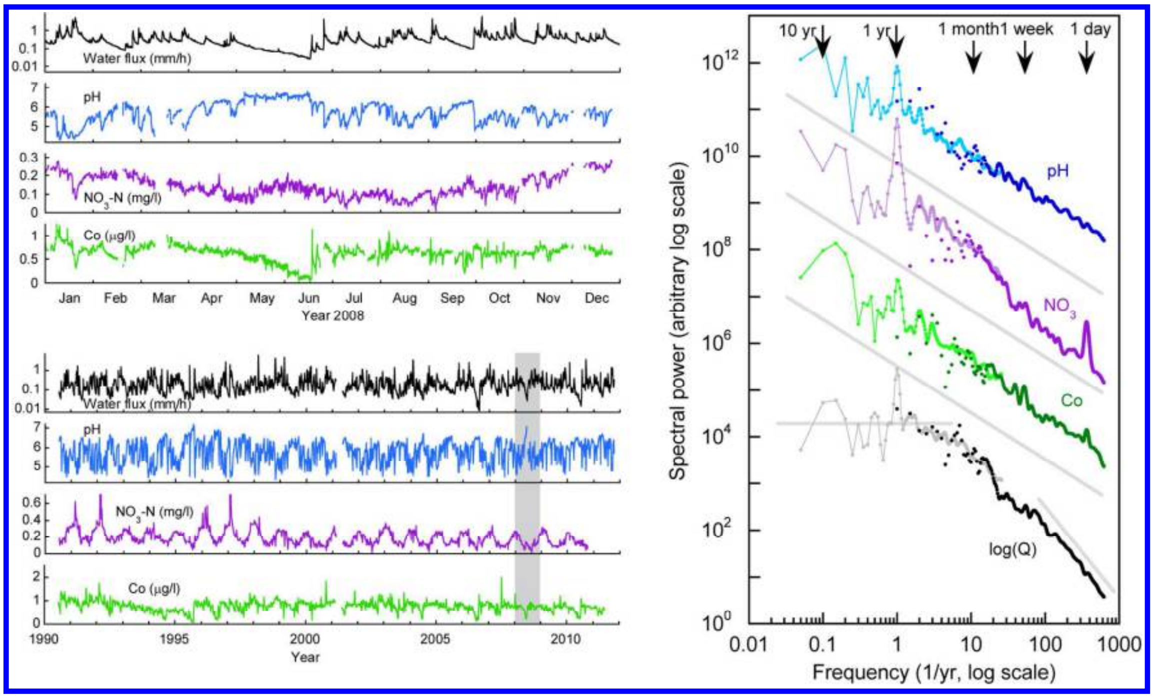


Figure 4. Water quality time series in Upper Hafren streamwater, Plynlimon, Wales, at 7-hour intervals for one year (left upper panel) and weekly intervals for 21 years (left lower panel) (Unpublished Data). Three water quality parameters are shown: pH (an indicator of acid-base status), nitrate (a nutrient 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].

Additional advances

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

Measurements of lake, reservoir, wetland and estuarine diel dynamics help identify internal processing of nutrients and metals. High frequency monitoring in lakes and reservoirs using autonomous vertical profiling systems is increasingly exploited for safeguarding high water quality (e.g., for drinking water abstraction [55]). Such systems detect river intrusions that may quickly reach water abstraction infrastructure [56,57]. High frequency measurements also allow new insights into lake metabolism and help constrain biogeochemical budgets or to differentiate the importance of internal versus external factors[58]. It has been recently shown that monitoring external watershed loading, as well as within lake chemistry, at high frequency, enables separation of carbon 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, service requirements, the risks of theft and vandalism, and instrument power requirements, which has decreased recently, there is a need for a cost-benefit analysis to assess the utility of *in situ* sensors for widespread operational and regulatory monitoring. Furthermore, “big” data streams from *in situ* measurements pose a challenge to environmental scientists because traditional approaches to data quality assurance and quality control are no longer practical when confronted with the demands of real-time processing. Despite routine maintenance and calibration of sensors, there is a pressing need for the development of automated tools and standards for quality assurance and quality control of sensor data [67].

Future directions

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

The knowledge gained from new sensor technology has and will continue to stimulate further advancement. Already microfluidic sensors for measuring nutrients based on colormetric techniques have advantages of small size and limited reagent and power requirements [16,17], though further improvements of these devices are necessary to increase robustness and reduce maintenance during permanent deployment. There is still a clear need for further development of new types of sensors, particularly for chemical and organism-based measurements of freshwater ecosystems. Increasing the number of analytes to include redox sensitive elements, micro-nutrients 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 and interpret high-resolution solute time series. In Germany, routine high resolution sensor deployments are not restricted to highly sensitive water bodies like drinking water reservoirs and the gain of scientific transport process understanding[65]; German state water authorities (e.g., state environmental agency of Hesse and Baden Wurttemberg) increasingly use high frequency monitoring to quantify matter fluxes (especially at the outlet of large rivers) and for early warning systems for drinking water river bank infiltration facilities (e.g. at the Rhein river). There is also potential to use high frequency monitoring more widely to measure intermittent discharges from Combined Sewer Overflows.

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

References

(1) Kirchner, J.W.; Feng, X.H.; Neal, C. et al. The fine structure of water-quality dynamics: the (high-frequency) wave of the future. *Hydrol. Process*. **2004**, 18:1353-1359.

(2) Porter, J.; Arzberger, P.; Braun, H. W.; Bryant, P.; Gage, S.; Hansen, T.; Hanson, P.; Lin, C. C.; Lin, F. P.; Kratz, T.; Michener, W.; Shapiro, S.; Williams, T., Wireless sensor networks for ecology. *Bioscience* **2005**, 55, (7), 561-572.

(3) Johnson, K. S.; Needoba, J. A.; Riser, S. C.; Showers, W. J., Chemical sensor networks for the aquatic environment. *Chemical Reviews* **2007**, 107, (2), 623-640.

(4) Porter, J. H.; Nagy, E.; Kratz, T. K.; Hanson, P.; Collins, S. L.; Arzberger, P., New Eyes on the World: Advanced Sensors for Ecology. *Bioscience* 2009, 59, (5), 385-397.

(5) Godsey, S. E.; Aas, W.; Clair, T. A.; de Wit, H. A.; Fernandez, I. J.; Kahl, J. S.; Malcolm, I. A.; Neal, C.; Neal, M.; Nelson, S. J.; Norton, S. A.; Palucis, M. C.; Skjelkvale, B. L.; Soulsby, C.; Tetzlaff, D.; Kirchner, J. W., Generality of fractal 1/f scaling in catchment tracer time series, and its implications for catchment travel time distributions. *Hydrol. Process*. **2010**, 24, (12), 1660-1671.

(6) Cassidy, R.; Jordan, P., Limitations of instantaneous water quality sampling in surface-water catchments: Comparison with near-continuous phosphorus time-series data. *J. Hydrol*. **2011**, 405, (1-2), 182-193.

(7) Wade, A. J.; Palmer-Felgate, E. J.; Halliday, S. J.; Skeffington, R. A.; Loewenthal, M.; Jarvie, H. P.; Bowes, M. J.; Greenway, G. M.; Haswell, S. J.; Bell, I. M.; Joly, E.; Fallatah, A.; Neal, C.; Williams, R. J.; Gozzard, E.; Newman, J. R., Hydrochemical processes in lowland rivers: insights from in situ, high-resolution monitoring. *Hydrol. Earth Syst. Sci.* **2012**, 16, (11), 4323-4342.

(8) Neal, C.; Reynolds, B.; Kirchner, J. W.; Rowland, P.; Norris, D.; Sleep, D.; Lawlor, A.; Woods, C.; Thacker, S.; Guyatt, H.; Vincent, C.; Lehto, K.; Grant, S.; Williams, J.; Neal, M.; Wickham, H.; Harman, S.; Armstrong, L., High-frequency precipitation and stream water quality time series from Plynlimon, Wales: an openly accessible data resource spanning the periodic table. *Hydrol. Process*. **2013**, 27, (17), 2531-2539.

(9) Kirchner, J. W.; Neal, C., Universal fractal scaling in stream chemistry and its implications for solute transport and water quality trend detection. Proc. Natl. Acad. Sci. U. S. A. **2013**, 110, (30), 12213-12218.

(10) Carrit, D. E.; Kanwisher, J. W., An electrode system for measuring dissolved oxygen. Analytical Chemistry **1959**, 31, 5-9.

(11) Jannasch, H. W.; Johnson, K. S.; Sakamoto, C. M., Submersible, osmotically pumped analyzers for continuous determination of nitrate in situ. Analytical Chemistry **1994**, 66, (20), 3352-3361.

(12) Johnson, K. S.; Coletti, L. J., In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean. Deep-Sea Research Part I-Oceanographic Research Papers **2002**, 49, (7), 1291-1305.

(13) Pellerin, B. A.; Downing, B. D.; Kendall, C.; Dahlgren, R. A.; Kraus, T. E. C.; Saraceno, J.; Spencer, R. G. M.; Bergamaschi, B. A., Assessing the sources and magnitude of diurnal nitrate variability in the San Joaquin River (California) with an in situ optical nitrate sensor and dual nitrate isotopes. *Freshwater Biol*. **2009**, 54, (2), 376-387.

(14) Heffernan, J. B.; Cohen, M. J.; Frazer, T. K.; Thomas, R. G.; Rayfield, T. J.; Gulley, J.; Martin, J. B.; Delfino, J. J.; Graham, W. D., Hydrologic and biotic influences on nitrate removal in a subtropical spring-fed river. *Limnol. Oceanogr*. **2010**, 55, (1), 249-263.

(15) Heffernan, J. B.; Cohen, M. J., Direct and indirect coupling of primary production and diel nitrate dynamics in a subtropical spring-fed river. *Limnol. Oceanogr*. **2010**, 55, (2), 677-688.

(16) Beaton, A. D.; Cardwell, C. L.; Thomas, R. S.; Sieben, V. J.; Legiret, F. E.; Waugh, E. M.; Statham, P. J.; Mowlem, M. C.; Morgan, H., Lab-on-Chip Measurement of Nitrate and Nitrite for In Situ Analysis of Natural Waters. *Environ. Sci. Technol*. **2012**, 46, (17), 9548-9556.

(17) Nightingale, A. M.; Beaton, A. D.; Mowlem, M. C., Trends in microfluidic systems for in situ chemical analysis of natural waters. *Sensors and Actuators B-Chemical* **2015**, 221, 1398-1405.

(18) Cohen, M. J.; Kurz, M. J.; Heffernan, J. B.; Martin, J. B.; Douglass, R. L.; Foster, C. R.; Thomas, R. G., Diel phosphorus variation and the stoichiometry of ecosystem metabolism in a large spring-fed river. *Ecological Monographs* **2013**, 83, (2), 155-176.

(19) Lorenzen, C. J., A method for the continuous measurement of in vivo chlorophyll concentrations. *Deep-Sea Research Part I-Oceanographic Research Papers* **1966**, 13, 223-227.

(20) Pellerin, B. A.; Saraceno, J. F.; Shanley, J. B.; Sebestyen, S. D.; Aiken, G. R.; Wollheim, W. M.; Bergamaschi, B. A., Taking the pulse of snowmelt: in situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. *Biogeochemistry* **2012**, 108, (1-3), 183-198.

(21) Robinson, J. P.; Roederer, M., Flow cytometry strikes gold. *Science* **2015**, 350, (6262), 739-740.

(22) Read, D. S.; Gweon, H. S.; Bowes, M. J.; Newbold, L. K.; Field, D.; Bailey, M. J.; Griffiths, R. I., Catchment-scale biogeography of riverine bacterioplankton. *Isme Journal* **2015**, 9, (2), 516-526.

(23) Alliance for Coastal Technologies Nutrient Sensor Challenge. http://www.act-us.info/nutrients-challenge/ (07 February 2016),

(24) Harmel, R. D.; Cooper, R. J. ; Slade, R. M.; Haney, R. L.; Arnold, J. G., Cumulative uncertainty in measured streamflow and water quality data for small watersheds. *Trans. ASABE* **2006**, 49, 689-701.

(25) Bowes, M. J.; Jarvie, H. P.; Halliday, S. J.; Skeffington, R. A.; Wade, A. J.; Loewenthal, M.; Gozzard, E.; Newman, J. R.; Palmer-Felgate, E. J., Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration-flow relationships. *Sci. Tot. Environ.* **2015**, 511, 608-620.

(26) Halliday, S. J.; Skeffington, R. A.; Bowes, M. J.; Gozzard, E.; Newman, J. R.; Loewenthal, M.; Palmer-Felgate, E. J.; Jarvie, H. P.; Wade, A. J., The Water Quality of the River Enborne, UK: Observations from High-Frequency Monitoring in a Rural, Lowland River System. *Water* **2014**, 6, (1), 150-180.

(27) Mellander, P.-E.; Jordan, P.; Melland, A. R.; Murphy, P. N. C.; Wall, D. P.; Mechan, S.; Meehan, R.; Kelly, C.; Shine, O.; Shortle, G., Quantification of Phosphorus Transport from a Karstic Agricultural Watershed to Emerging Spring Water. *Environ. Sci. & Technol*. **2013**, 47, (12), 6111-6119.

(28) Mellander, P. E.; Jordan, P.; Shore, M.; McDonald, N. T.; Wall, D. P.; Shortle, G.; Daly, K., Identifying contrasting influences and surface water signals for specific groundwater phosphorus vulnerability. *Sci. Tot. Environ*. **2016**, 541, 292-302.

(29) Spencer, R. G. M.; Pellerin, B. A.; Bergamaschi, B. A.; Downing, B. D.; Kraus, T. E. C.; Smart, D. R.; Dahgren, R. A.; Hernes, P. J., Diurnal variability in riverine dissolved organic matter composition determined by in situ optical measurement in the San Joaquin River (California, USA). *Hydrol. Process.* **2007**, 21, (23), 3181-3189.

(30) Ensign, S. H.; Doyle, M. W., Nutrient spiraling in streams and river networks. *J. Geophys. Res.-Biogeosci.* **2006**, 111, (G4).

(31) Hall, R. O.; Baker, M. A.; Rosi-Marshall, E. J.; Tank, J. L.; Newbold, J. D., Solute-specific scaling of inorganic nitrogen and phosphorus uptake in streams. *Biogeosciences* **2013**, 10, (11), 7323-7331.

(32) Rode, M.; Halbedel S. (née Angelstein), Anis M.R., Borchardt D., Weitere M., Continuous In-Stream Assimilatory Nitrate Uptake from High Frequency Sensor Measurements. *Environ. Sci. Technol.*, 50 (11), pp 5685–5694
(33) Hensley, R. T.; Cohen, M. J.; Korhnak, L. V., Inferring nitrogen removal in large rivers from high-resolution longitudinal profiling. *Limnol. and Oceanogr*. **2014**, 59, (4), 1152-1170.
(34) Appling, A.P.; Heffernan, J.B., Nutrient limitation and physiology mediate the fine-scale (de)coupling of biogeochemical cycles. *American Naturalist* **2014**, 184: 384-406.
(35) Kurz, M. J.; de Montety, V.; Martin, J. B.; Cohen, M. J.; Foster, C. R., Controls on diel metal cycles in a biologically productive carbonate-dominated river. *Chemical Geology* **2013**, 358, 61-74.
(36) Doyle, M. W.; Ensign, S. H., Alternative Reference Frames in River System Science. *Bioscience* **2009**, 59, (6), 499-510.
(37) Vannote, R. L.; Minshall, G. W.; Cummins, K. W.; Sedell, J. R.; Cushing, C. E., River Continuum Concept. *Canadian Journal of Fisheries and Aquatic Sciences* **1980**, 37, (1), 130-137.
(38) Ward, J. V.; Standford, J. A., The serial discontinuity concept of lotic ecosystems. In: Dynamics of Lotic Ecosystems, Fontaine, T. D.; Bartell, S. M., Eds. Ann Arbor Science: Ann Arbor, **1983**; pp 29-42.
(39) von Schiller, D.; Aristi, I.; Ponsati, L.; Arroita, M.; Acuna, V.; Elosegi, A.; Sabater, S., Regulation causes nitrogen cycling discontinuities in Mediterranean rivers. Sci. Tot. Environ. **2016**, 540, 168-177.
(40) Twiss, M.; MacLeod, I., Phytoplankton community assessment in eight Lake Ontario tributaries made using fluorimetric methods. Aquatic Ecosystem Health & Management **2008**, 11, (4), 422-431.
(41) Read, D. S.; Bowes, M. J.; Newbold, L. K.; Whiteley, A. S., Weekly flow cytometric analysis of riverine phytoplankton to determine seasonal bloom dynamics. *Environ. Sci.-Process. & Impacts* **2014**, 16, (3), 594-603.
(42) Bowes, M. J.; Loewenthal, M.; Read, D. S.; Hutchins, M. G.; Prudhomme, C.; Armstrong, L. K.; Harman, S. A.; Wickham, H. D.; Gozzard, E.; and Carvalho, L., Identifying multiple stressor controls on phytoplankton dynamics in the River Thames (UK) using high-frequency water quality data, *Sci. Tot. Environ.* **2016**, 569–570, 1489-1499.
(43) Halliday, S. J.; Wade, A. J.; Skeffington, R. A.; Neal, C.; Reynolds, B.; Rowland, P.; Neal, M.; Norris, D., An analysis of long-term trends, seasonality and short-term dynamics in water quality data from Plynlimon, Wales. *Sci. Tot. Environ*. **2012**, 434, 186-200.
(44) Aubert, A. H.; Kirchner, J. W.; Gascuel-Odoux, C.; Faucheux, M.; Gruau, G.; Merot, P., Fractal Water Quality Fluctuations Spanning the Periodic Table in an Intensively Farmed Watershed. *Environ. Sci. Technol*. **2014**, 48, (2), 930-937.
(45) Godsey, S. E.; Aas, W.; Clair, T. A.; de Wit, H. A.; Fernandez, I. J.; Kahl, J. S.; Malcolm, I. A.; Neal, C.; Neal, M.; Nelson, S. J.; Norton, S. A.; Palucis, M. C.; Skjelkvåle, B. L.; Soulsby, C.; Tetzlaff, D.; Kirchner, J. W., Generality of fractal 1/f scaling in catchment tracer time series, and its implications for catchment travel time distributions. Hydrol. Process. 2010, 24, 1660–1671.
(46) Gisiger, T., Scale invariance in biology: coincidence or footprint of a universal mechanism? *Biological Reviews* **2001**, 76, (2), 161-209.
(47) Halliday, S. J.; Skeffington, R. A.; Wade, A. J.; Neal, C.; Reynolds, B.; Norris, D.; Kirchner, J. W., Upland streamwater nitrate dynamics across decadal to sub-daily timescales: a case study of Plynlimon, Wales. *Biogeosciences* **2013**, 10, (12), 8013-8038.
(48) Dupas, R., Jomaa, S., Musolff, S., Borchardt, D., Rode, M., Disentangling the influence of hydroclimatic patterns and agricultural management on river nitrate dynamics from sub-hourly to decadal time scales. *Sci. Total Environ*. **2016,** doi:10.1016/j.scitotenv.2016.07.053

(49) Horsburgh, J. S.; Jones, A. S.; Stevens, D. K.; Tarboton, D. G.; Mesner, N. O., A sensor network for high frequency estimation of water quality constituent fluxes using surrogates. *Environ. Model. Software* **2010**, 25, (9), 1031-1044.
(50) Jones, A. S.; Stevens, D. K.; Horsburgh, J. S.; Mesner, N. O., Surrogate Measures for Providing High Frequency Estimates of Total Suspended Solids and Total Phosphorus Concentrations. *J. Am. Water Resour. Ass*. **2011**, 47, (2), 239-253.
(51) Kirchner, J. W.; Austin, C. M.; Myers, A.; Whyte, D. C., Quantifying Remediation Effectiveness under Variable External Forcing Using Contaminant Rating Curves. *Environ. Sci. Technol*. **2011**, 45, (18), 7874-7881.
(52) Rugner, H.; Schwientek, M.; Beckingham, B.; Kuch, B.; Grathwohl, P., Turbidity as a proxy for total suspended solids (TSS) and particle facilitated pollutant transport in catchments. *Environ. Earth Sci*. **2013**, 69, (2), 373-380.
(53) Bergamaschi, B. A.; Fleck, J. A.; Downing, B. D.; Boss, E.; Pellerin, B. A.; Ganju, N. K.; Schoellhamer, D. H.; Byington, A. A.; Heim, W. A.; Stephenson, M.; Fujii, R., Mercury Dynamics in a San Francisco Estuary Tidal Wetland: Assessing Dynamics Using In Situ Measurements. *Estuaries and Coasts* **2012**, 35, (4), 1036-1048.
(54) Rozemeijer, J. C.; Van der Velde, Y.; Van Geer, F. C.; De Rooij, G. H.; Torfs, P.; Broers, H. P., Improving Load Estimates for NO3 and P in Surface Waters by Characterizing the Concentration Response to Rainfall Events. *Environ. Sci. Technol*. **2010**, 44, (16), 6305-6312.
(55) Effler, S. W.; O'Donnell, S. M.; Prestigiacomo, A. R.; O'Donnell, D. M.; Matthews, D. A.; Owens, E. M.; Effler, A. J. P., Tributary Plunging in an Urban Lake (Onondaga Lake): Drivers, Signatures, and Implications. *J. Am. Water Res. Ass*. **2009**, 45, (5), 1127-1141.
(56) Chung, S. W.; Hipsey, M. R.; Imberger, J., Modelling the propagation of turbid density inflows into a stratified lake: Daecheong Reservoir, Korea. *Environ. Model. Software* **2009**, 24, (12), 1467-1482.
(57) Bertone, E.; Stewart, R. A.; Zhang, H.; O'Halloran, K., Intelligent data mining of vertical profiler readings to predict manganese concentrations in water reservoirs. *Journal of Water Supply Research and Technology-Aqua* 2014, 63, (7), 541-552.
(58) Powers, S. M.; Tank, J. L.; Robertson, D. M., Control of nitrogen and phosphorus transport by reservoirs in agricultural landscapes. *Biogeochemistry* **2015**, 124, (1-3), 417-439.
(59) Rinke, K.; Kuehn, B.; Bocaniov, S.; Wendt-Potthoff, K.; Buettner, O.; Tittel, J.; Schultze, M.; Herzsprung, P.; Roenicke, H.; Rink, K.; Rinke, K.; Dietze, M.; Matthes, M.; Paul, L.; Friese, K., Reservoirs as sentinels of catchments: the Rappbode Reservoir Observatory (Harz Mountains, Germany). *Environ. Earth Sci*. **2013**, 69, (2), 523-536.
(60) Tsai, J.-W.; Kratz, T. K.; Hanson, P. C.; Wu, J.-T.; Chang, W. Y. B.; Arzberger, P. W.; Lin, B.-S.; Lin, F.-P.; Chou, H.-M. & Chiu, C.-Y., Seasonal dynamics, typhoons and the regulation of lake metabolism in a subtropical humic lake. Freshwater Biol., 2008, 53, 1929-1941.
(61) Skeffington, R. A.; Halliday, S. J.; Wade, A. J.; Bowes, M. J.; Loewenthal, M., Using high-frequency water quality data to assess sampling strategies for the EU Water Framework Directive. *Hydrol. Earth Syst. Sci*. **2015**, 19, (5), 2491-2504.
(62) Pellerin, B. A.; Bergamaschi, B. A.; Gilliom, R. J.; Crawford, C. G.; Saraceno, J.; Frederick, C. P.; Downing, B. D.; Murphy, J. C., Mississippi River Nitrate Loads from High Frequency Sensor Measurements and Regression-Based Load Estimation. *Environ. Sci. Technol*. **2014**, 48, (21), 12612-12619.

(63) Alexander, R. B.; Smith, R. A.; Schwarz, G. E.; Boyer, E. W.; Nolan, J. V.; Brakebill, J. W., Differences in phosphorus and nitrogen delivery to the gulf of Mexico from the Mississippi river basin. *Environ. Sci. Technol.* **2008**, 42, (3), 822-830.
(64) Wellen, C.; Arhonditsis, G. B.; Labencki, T.; Boyd, D., Application of the SPARROW model in watersheds with limited information: a Bayesian assessment of the model uncertainty and the value of additional monitoring. *Hydrol. Processes* **2014**, 28, (3), 1260-1283.
(65) Hesser, F. B.; Franko, U.; Rode, M., Spatially Distributed Lateral Nitrate Transport at the Catchment Scale. Journal of Environmental Quality **2010**, 39, (1), 193-203.
(66) Wellen, C.; Arhonditsis, G. B.; Long, T.; Boyd, D., Quantifying the uncertainty of nonpoint source attribution in distributed water quality models: A Bayesian assessment of SWAT's sediment export predictions. J. Hydrol. **2014**, 519, 3353-3368.
(67) Campbell, J. L.; Rustad, L. E.; Porter, J. H.; Taylor, J. R.; Dereszynski, E. W.; Shanley, J. B.; Gries, C.; Henshaw, D. L.; Martin, M. E.; Sheldon, W. M.; Boose, E. R., Quantity is Nothing without Quality: Automated QA/QC for Streaming Environmental Sensor Data. *Bioscience* **2013**, 63, (7), 574-585.
(68) von der Geest KB, Hyvonen J, Laurila T . Real-time determination of metal concentrations in liquid flows using microplasma emission spectroscopy . IEEE Photonics Global Conference (PGC), Singapore, DEC 13-16, **2012.**
(69) Hrachowitz M, Benettin P, van Breukelen BM, Fovet O, Howden NJK, Ruiz L, van der Velde Y, Wade AJ. Transit times – the link between hydrology and water quality at the catchment scale. *WIREs Water*. **2016**, Doi: 10.1002/wat2.1155.
(70) Zacharias, S.; Bogena, H.; Samaniego, L.; Mauder, M.; Fuss, R.; Putz, T.; Frenzel, M.; Schwank, M.; Baessler, C.; Butterbach-Bahl, K.; Bens, O.; Borg, E.; Brauer, A.; Dietrich, P.; Hajnsek, I.; Helle, G.; Kiese, R.; Kunstmann, H.; Klotz, S.; Munch, J. C.; Papen, H.; Priesack, E.; Schmid, H. P.; Steinbrecher, R.; Rosenbaum, U.; Teutsch, G.; Vereecken, H., A Network of Terrestrial Environmental Observatories in Germany. *Vadose Zone J.* **2011**, 10, (3), 955-973.
(71) Carpenter, S. R.; Cole, J. J.; Pace, M. L.; Batt, R.; Brock, W. A.; Cline, T.; Coloso, J.; Hodgson, J. R.; Kitchell, J. F.; Seekell, D. A.; Smith, L.; Weidel, B., Early Warnings of Regime Shifts: A Whole-Ecosystem Experiment. *Science* **2011**, 332, (6033), 1079-1082.
(72) Hipsey, M. R.; Hamilton, D. P.; Hanson, P. C.; Carey, C. C.; Coletti, J. Z.; Read, J. S.; Ibelings, B. W.; Valesini, F. J.; Brookes, J. D., Predicting the resilience and recovery of aquatic systems: A framework for model evolution within environmental observatories. *Water Resour. Res.* **2015**, 51, (9), 7023-7043.
(73) Scheffer, M.; Bascompte, J.; Brock, W. A.; Brovkin, V.; Carpenter, S. R.; Dakos, V.; Held, H.; van Nes, E. H.; Rietkerk, M.; Sugihara, G., Early-warning signals for critical transitions. *Nature* **2009**, 461, (7260), 53-59.
(74) Batt, R. D.; Carpenter, S. R.; Cole, J. J.; Pace, M. L.; Johnson, R. A., Changes in ecosystem resilience detected in automated measures of ecosystem metabolism during a whole-lake manipulation. Proc. Natl. Acad. Sci. U. S. A. **2013**, 110, (43), 17398-17403.
(75) Michalak AM. 2016. Study role of climate change in extreme threats to water quality. *Nature* 535, 349-350.
(76) Halliday, S. J., Skeffington, R. A., Wade, A. J., Bowes, M. J., Reed, D. S., Jarvie, H. P. and Loewenthal, M. Riparian shading controls instream spring phytoplankton and benthic diatom growth. *Environmental Science: Process and Impacts* **2016**, 18 (6). pp. 677-689. ISSN 2050-7895 doi: 10.1039/C6EM00179C

Biography

Dr. Michael Rode is Deputy Head of the Department of Aquatic Ecosystem Analysis at Helmholtz Centre for Environmental Research-UFZ in Magdeburg; he leads a research team on new water quality monitoring techniques and modelling of matter fluxes at watershed scale. Andrew J Wade is a Professor of Hydrology in the Department of Geography and Environmental Science at the University of Reading. His research focuses on catchment hydrology, water quality and the links to ecology. Dr. Cohen is a professor in the School of Forest Resources and Conservation at the University of Florida in Gainesville, Florida. He works on a variety of watershed and aquatic systems research. Dr. Hensley is a post-doctoral associate in the Ecohydrology Lab at the University of Florida. He is part of a research team using in-situ sensors to better understand riverine metabolism and nutrient spiraling. Dr. Bowes leads the Water Quality Processes Group at the Centre for Ecology & Hydrology. His research investigates the sources and fates of phosphorus and nitrogen in river catchments, and how they impact on river ecology. James Kirchner is the Professor of the Physics of Environmental Systems at ETH Zurich and the former Director of the Swiss Federal Research Institute WSL; his group conducts research at the interfaces between hydrology, geomorphology, and watershed geochemistry. Professor Arhonditsis is the Chair of the Department of Physical and Environmental Sciences at the University of Toronto. He leads the Ecological Modelling Laboratory that has developed integrated biogeochemical models to guide the policy making process in several impaired systems in North America over the past decade. Phil Jordan is Professor of Catchment Science, Ulster University, Northern Ireland. His research focuses on the dynamics and fate of nutrients and sediment in catchments with an emphasis on the capture and analysis of high resolution water quality data. Professor Brian Kronvang is Head of Section of Catchment Science and Environmental Management at Department of Bioscience, Aarhus University. Dr. Sarah Halliday works as a researcher at the Department of Geography and Environmental Science, University of Reading, UK; her research focuses on the new insights into catchment biogeochemical processing attainable from high-frequency hydrochemical data. Dr. Richard Skeffington is Professor of Geography at the University of Reading, with research interests in water quality monitoring and modelling and understanding biogeochemical processes. Dr. Joachim Rozemeijer coordinates the Environmental Monitoring and Modeling research program at Deltares, The Netherlands; he is scientific researcher and advisor in the Groundwater and Soil Quality department and holds a PhD in Dynamics in Groundwater and Surface water Quality. Dr. Aubert was a post-doctoral fellow at Justus Liebig University in Giessen working on high-frequency nitrate time series analysis ; now she is a fellow at Eawag (the Swiss federal institute of aquatic science and technology) in Dübendorf studying how water quality can be considered as part of structured decision making. Karsten Rinke is heading the Department of Lake Research at the Helmholtz Centre for Environmental Research-UFZ in Magdeburg, Germany; he is a limnologist working on lake modelling and the application of online water quality monitoring in lake and reservoir management. Dr. Seifeddine Jomaa is a research scientist at the Helmholtz Centre for Environmental Research-UFZ in Magdeburg. He leads a research effort on hydrological water quality monitoring and modelling at the watershed scale.