Catchment Similarity Concepts for Understanding Dynamic Biogeochemical Behaviour of River Basins

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Quantitative assessment of the effectiveness of water quality mitigation measures such as Nitrate Vulnerable Zones (NVZ) and Agricultural Stewardship Programmes (*Worrall et al*., 2009; *Deasy et al.,* 2010; *Mian et al.,* 2010; *Kay et al.,* 2012) is impeded by the current limitations of both process-based models (*Rode et al.,* 2010; *Guber et al.,* 2011) and empirical models (*Rothwell et al.,* 2010) at catchment and regional scales. The current failure of models to provide accurate water quality predictions at catchment scales and beyond is founded in significant observational uncertainties of water quality parameters (*McMillan et al.,* 2012) linked to our partial understanding of temporally dynamic source area contributions to water quality responses at the catchment outlet (*Kirchner et al.,* 2000, 2004; *Jordan et al.,* 2005; *Harris & Heathwaite*, 2005; *Haygarth et al.,* 2005; *Jarvie et al.,* 2010). These limitations critically restrict the predictive capacity of risk assessment frameworks for scientists and practitioners to forecast variable catchment scale water quality response and, in turn, to assess the resilience to environmental change, including human impacts (*McIntyre et al.,* 2003). As a consequence, quantifications of the likelihood of exceedance of critical thresholds as well as identification of dynamic source area activation that may be used to target amelioration measures or adaptation and mitigation strategies are inhibited.

Therefore, the challenge is to improve predictions of chemical catchment behaviour in response to dynamic hydrological conditions at management relevant scales.

1. Current limitations in predicting dynamic chemical behaviour of river basins:

A major reason for the limited understanding of dynamic catchment hydrochemical behaviour is the current lack of appropriate monitoring data to derive mechanistic process understanding addressing the aforementioned challenges (Howden et al., 2011a). If catchments may be understood as diverse chemical reactors, characterised by spatially heterogeneous patterns of chemical reactivities, residence time distributions and flow proportioning, observations are usually limited to chemical conditions at the catchment outlets or, at its best, sub-catchment level. In contrast, most detailed biogeochemical process studies naturally range from small plot to hillslope scales, causing a paucity of overarching concepts that integrate small-scale process information and large-scale biogeochemical behaviour at the catchment outlet. This lack of large-scale perspectives on water quality variation inhibits a detailed quantitative analysis of complex spatio-temporal dynamics in chemical cycling required to underpin setting of environmental standards, development of assessment tools and evaluation of management options (*Beck*, 1987; *Zheng & Keller,* 2006, 2007a, b; *Chin,* 2009; *Rode et al.,* 2010).

Substantial progress has been made in high-frequency in-situ water quality sampling *(Jordan et al.,* 2007, *Cassidy & Jordan,* 2011, *Mellander et al*., 2012; *Neal et al*., 2013) as well as statistical data analysis and signal processing to learn about intrinsic system behaviour (*Neal et al*., 2012; *Kirchner et al.,* 2000, 2004; *Kirchner & Neal*, 2013). However, improvements in signal disaggregation for identifying process inference including interlinked spatial and temporal dynamics of source area contributions remain a challenge, limiting the quantification of catchment-scale implications of biogeochemical hotspots (McClain et al., 2003; Lautz & Fanelli, 2008). Certainly, novel distributed sensor network technologies and advancements in remote sensing will continue to improve the spatial and temporal resolution of monitoring networks for both hydrological and hydrochemical parameters, but observations of everything, everywhere will surely remain a dream. Hence, there is continued demand for improvement in the intelligent design of observational networks and the key question remains: "How to best design experimental networks that are capable of utilising spatially and temporally unsatisfying data?".

In comparison to discharge observation networks (reviewed by Hannah et al., 2011), monitoring networks of water quality parameters are even more sparsely distributed; e.g. the National River Flow Archive (http://www.ceh.ac.uk/data/nrfa/) of England and Wales covers > 1400 river flow stations with average record length ~25 yrs for at least daily time series while water quality parameters are usually monitored on a monthly basis at best. These spatially and temporally constrained water quality monitoring intervals limit the assessment of reactive transport at the catchment-scale, critically affecting in particular the interpretation of event-based transport and transformation of diffuse pollutants (*Jordan et al.,* 2005, *Cassidy & Jordan*, 2011).

Answers to this practically relevant question require improving the understanding of underlying mechanistic organisational principles that shape the distributions of observational data at the catchment scale. The International Association of Hydrological Sciences (IAHS) decade (2003-2012) on Predictions in Ungauged Basins (PUB) finished in 2012. This global initiative aimed to reduce uncertainties in hydrological predictions in poorly monitored river basins *(Sivapalan*, 2003, *Hrachowitz et al*., 2013). Although many open questions remain, significant advances have been made in conceptualisation of catchment hydrological behaviour, including spatially and temporally dynamic runoff generation and streamflow contributions, resulting in subsequent improvements in the capacity of predictions of catchment scale hydrological behaviour (*Blöschl et al.,* 2013).

2. Utilising PUB knowledge to learn about catchment biogeochemistry:

We propose that lessons learned from *PUB*, and in particular the developed catchment similarity schemes can help to improve the understanding of catchment biogeochemical behaviour. Transfer of *PUB* type thinking and concepts of catchment comparison to water quality predictions in poorly monitored basins has the potential to improve mechanistic process understanding, including the conceptualisation of process transferability between and across catchments. Comparative hydrology is based on the principle of investigating the specific event, seasonal or management related hydrological responses of catchments and analysing for similarity in other places in order to understand the complexity of process drivers and controls (*Wagener et al.,* 2007; *Blöschl et al.,* 2013). As Figure 1 indicates, this concept could be extended with adequate water quality data to better understand catchment biogeochemical responses to variable source area contributions, catchment physical properties, land use and land management practice or climatic forcing. This would improve capabilities not only for analysis and prediction of current conditions but also for projections of scenarios of environmental change, thus, linking to *Panta Rhei*, the ongoing IAHS Scientific Decade on “Change in Hydrology and Society” (http://distart119.ing.unibo.it/pantarhei/).

To date, a range of catchment classification schemes have been developed in order to improve the understanding of hydrological process dynamics and conceptualise hydrological behaviour at catchment scales and across catchments (*McDonnell & Woods*, 2004, *Wagener et al*., 2007; *McDonnell* et al., 2007; *Ali et al*., 2012). Such schemes find application for predicting similarities in specific hydrologic signatures [e.g. flood frequency indices (*Acreman& Sinclair*, 1986*; Castellarin et al.,* 2001; *Sauquet & Catalogne*, 2011) or subsurface and baseflow responses (*Lyon & Troch.,* 2010, *Kirkby et al*., 2011)], or use combinations of hydrologic signatures for a more generic large scale organization of catchments (*Hannah et al*., 2005; *Sawicz et al*., 2011).

The general objective of catchment classification schemes is the organization of catchments into groups of similar hydrologic behaviour. The analysis is often based on observable physical catchment properties, assuming that these can be linked to hydrological behaviour, e.g. variability in streamflow (*Yadav et al*., 2007). This link can be implicit or explicit depending on the classification strategy followed. There have also been attempts to directly link the grouping of catchments to the parameters of specific models. There has, however, been evidence that the assumed relationship between "apparent similarity" as defined by the analysed catchment properties, and the expected "behavioural similarity" as output of hydrological model application, does not always coincide (*Bower et al.,* 2004; *Oudin et al.,* 2010). The mismatch between apparent and behavioural similarity seems to be most pronounced across regions with similar catchment properties but marked variability in climatic forcing (*Bower et al.,* 2004), or when the role of subsurface properties on catchment hydrological behaviour was poorly defined, or when such properties are simply unknown (*Oudin et al.,* 2010). This highlights the important role of adequately selected physical properties as descriptors of hydrological behaviour. Although generally all classification schemes focus on identification and analysis of different types of similarity indices, usually based on catchment specific hydrological responses, there are open questions about appropriate metrics (*Ali et al*., 2012).

The last couple of years have seen the development of a wide range of classification metrics, comprising catchment typology, topography and topology. Classifications are based on measures of fluxes, storages, mean transient times and response timescale as well as combinations thereof and include approaches that combine static catchment properties and dynamic catchment response (see *Ali et al*., 2012; *Carrillo et al.*, 2011; *Hrachowitz et al*., 2010; *Patil& Stieglitz,* 2011; *Bouma et al*., 2011; *Capell et al.,* 2012; *Sawicz et al*., 2011). Conceptually, significant progress has been made in the synthesis of catchment hydrological behaviour by learning from other disciplines about the functioning of organisational principles and resulting spatial patterns and temporal response dynamics (e.g. *Schroeder*, 2006).

While the chemical signature of catchment discharge has been used partly to explain the hydrological behaviour of catchments, very few attempts have been made to apply recent catchment classification methods and similarity analysis approaches for the analysis of catchment biogeochemical behaviour (e.g. *Poor et al.,* 2008). This seems rather surprising given the continuing high demand for improved conceptualisation of scale and time dependent catchment chemical behaviour for the efficient implementation of regulatory frameworks such as the European Water Framework and Nitrate Directives (WFD; 2000/60/EU) that struggle in prioritising target areas for management and mitigation measures.

3. Strategies for comparison of catchment biogeochemical behaviour:

There has been a long history of catchment and river comparison studies aiming to improve understanding of controlling process dynamics of up-land export of dissolved organic carbon, and lowland and riparian nitrogen turnover. For example, the LINX (Lotic Intersite Nitrogen eXperiments) experiments provided valuable comparison of the nitrogen removal potential across biomes (*Mulholland et al*., 2008; 2009). Recently, there has furthermore been an increase in the development and application of quantitative approaches to estimate nitrogen or carbon delivery at catchment to national scales (*Helliwell et al*., 2007, *Worrall et al.*, 2012a,b,c). The later are based on the development of export coefficient models using physical catchment characteristics to explain observed process dynamics and behaviour at the catchment outlet. Although these studies yield promising results, in particular with regard to the understanding of average, long term system dynamics, they mainly focus on analysing mean annual or seasonal behaviour, and thus do not usually consider event based nutrient transport phenomena. These annual and seasonal metrics obscure important spatio-temporal heterogeneity, notably “hot spots” or “hot zones” of biogeochemical cycling that may have a disproportionally important impact (compared to their space-time scale) on nutrient turnover at catchment scales relevant for water and land resource management (*Peterjohn & Correll*, 1984; *Johnston et al.,* 1990; *McClain et al*., 2004). Furthermore, the focus on long-term averages of system dynamics limits potential for assessment of intermediate system behaviour including system memory at seasonal and sub-seasonal scales.

If catchment comparison approaches are to be deployed to support an adequate design of adaptation and mitigation strategies then these have to synthesise the complexity and high resolution of biogeochemical catchment responses to variable loading terms, source zone activation and heterogeneous biogeochemical reactivity at definitely sub-annual scale, probably even sub-seasonal to event scale (Figure 1). They have to be able to incorporate potentially fast dynamics and turnover but also account for long-term residence-time controlled memory effects of the system. Building on a successful UK example, we propose that current regional to national scale Export Coefficient Models (ECM, see *Worrall et al*., 2012 a, b, c) can be adapted to inform the development of similarity frameworks that account for dynamic biochemical catchment behaviour and responses.

Incorporation of short-term system dynamics into current ECM at management relevant catchment scales would ideally require long-term datasets of high temporal resolution. Most existing datasets are either high resolution and short-term or lower resolution (often with variable sampling frequency) and longer term. However, long-term high resolution archives are rare. Hence, the implementation of new types of ECM for comparison of catchment chemical responses will require creative approaches and innovative strategies to combine spatially and temporally “unsatisfying” data. There are several possible ways of bridging the gap between what we would like and what we have. Firstly, while most data from monitoring programmes is of low temporal frequency (e.g. monthly) we often have long series of it. In an extreme case the longest monitoring record in the World (River Thames, UK) goes back to 1868 (*Howden et al.,* 2010, 2011a) and 30 years of monthly spot samples, representing the numeric equivalent to a year's worth of daily spot. However, although similar in numbers, the coverage of characteristic flow conditions would obviously be likely to differ between daily and monthly spot sampling. The problem with comparing long-term spot sampling to high frequency spot sampling is to ensure that the long term record can be made stationary with respect to time (Howden et al., 2011b). Secondly, many water quality monitoring sites are co-located with streamflow gauging stations and so the context of each water quality data point can be known. Therefore, one issue for this research is the development of statistical techniques that can contextualise data in order to reconstruct data distributions of interest (e.g. removal of systematic bias diurnal variations (*Worrall et al*., 2013)) and can handle situations where water quality and gauging stations are not co-located. Thirdly, many monitoring programmes have reasonable spatial coverage, e.g. in the UK there are 272 monitoring points used as part of the *Harmonised Monitoring Scheme* (*Simpson*, 1980). With this third possibility in mind there is a great potential for applying concepts developed during the PUB initiative for the analysis of similarity in catchment hydrological behaviour resolution. This will help to strengthen mechanistic understanding of the conceptual relationship between observed apparent similarity based on observations of chemical dynamics at the catchment outlet and inferred behavioural similarity.

In addition, the development of new, high-frequency sampling schemes has promising potential for improved conceptualisation of high-resolution chemical responses to hydrological dynamics. In the UK, high frequency (sub hourly) monitoring of nutrient speciation at the DEFRA DTCs (Demonstration Test Catchments) are providing first insights into selected management implications on water quality at sub-daily and sub-catchment scales (*Owen et al.,* 2012). Further efforts will be required to conceptualise the knowledge gained from the generally rather small-scale, impact oriented studies in order to support transferability to unmonitored and larger scales. Furthermore, the nearly 30 year time series of sub-daily sampling of discharge and water quality parameters of the Plynlimon study (*Neal et al.,* 2012; 2013) provide suitable data for identifying catchment chemical responses to dynamic hydrological behaviour. Even though the unique dataset with observations of up to 7-hour intervals provides mainly information on major element dynamics and does not include redox-sensitive speciation of nutrients for instance, the application of fractal scaling technologies for the analysis of water quality trends (*Kirchner et al.,* 2000; 2013) highlights the enormous potential for the inference of process behaviour from high-resolution chemical data. Such high frequency datasets can not only be examined to understand hydrological behaviour but also to develop methods for improved handling of low frequency data [e.g. assessing bias in low frequency methods (Cassidy and Jordan, 2011)] and for improving our approaches to low frequency data (Worrall et al., in press).

Future investigations may focus in particular on the comparison of the trend behaviour of reactive and rather conservative species with variable transport properties and chemical kinetics to deduce chemical behaviour of different systems. The identification and comparison of lag time variance and response functions provides the potential to learn about the compound specific “system memory” resulting from flow path dependent chemical turnover and residence time distributions (Figure 1).

In addition to improved sampling frequencies at a limited number of selected monitoring locations, the increasing application of novel distributed sensor networks such as Fibre-Optic Distributed Temperature Sensing (*Selker et al., 2006*; *Tyler et al., 2009; Krause et al.,* 2012; *Krause & Blume,* 2013) or such in-situ analysis technologies as ion selective electrodes (*Le Goff et al.,* 2003; *Scholefield et al.,* 2005) and real-time fluorometry (*Carstea et al.,* 2009;

2010) will improve the current toolkit for analysing dynamic catchment responses. In addition to improving spatial and temporal data resolution in support of catchment chemical similarity studies, the developed classification schemes provide the potential for identifying trade-offs between spatially and temporally limited data in order to help to improve future designs of intelligent and adaptive monitoring networks.

Hence, we encourage the scientific community to seek further integration of applications of advanced real time sensing technologies and novel distributed sensor networks to enhance the data base of improved comparative analyses of catchment similarity. We would, therefore, like to stimulate a discussion that uses the legacy of PUB and other initiatives as an inspiration for a continued community effort advancing these investigations from a rather observational character towards predictions of catchment chemical responses and behaviour.

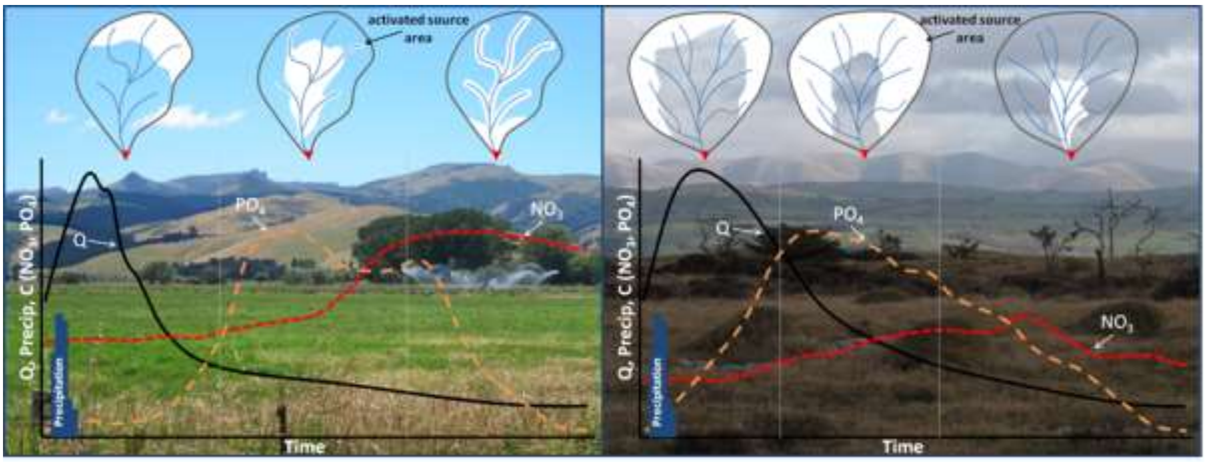

Figure 1: Comparison of variable catchment responses to similar precipitation events with example hydrographs and phosphate, nitrate response functions (bottom) in relation to catchment properties and source area activation (top) of an example upland catchment with extensive moorland and shallow soil depth (right, Southern Cumbria, UK) and a catchment

with extensive, agricultural floodplain sections and deep soils surrounded by partly deforested foothills (left, Canterbury Plains, NZ)

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