Science of the Total Environment 434 (2012) 186–200

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

An analysis of long-term trends, seasonality and short-term dynamics in water quality data from Plynlimon, Wales

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ARTICLE INFO

Article history:
Received 24 May 2011
Received in revised form 4 July 2011
Accepted 20 October 2011
Available online 25 November 2011

Keywords:
High frequency monitoring
Carbon
Nitrogen
Plynlimon
Time-series analysis
Diurnal cycles

ABSTRACT

This paper examines two hydrochemical time-series derived from stream samples taken in the Upper Hafren catchment, Plynlimon, Wales. One time-series comprises data collected at 7-hour intervals over 22 months (Neal et al., 2012-this issue), while the other is based on weekly sampling over 20 years. A subset of determinands: aluminium, calcium, chloride, conductivity, dissolved organic carbon, iron, nitrate, pH, silicon and sulphate are examined within a framework of non-stationary time-series analysis to identify determinand trends, seasonality and short-term dynamics. The results demonstrate that both long-term and high-frequency monitoring provide valuable and unique insights into the hydrochemistry of a catchment. The long-term data allowed analysis of long-term trends, demonstrating continued increases in DOC concentrations accompanied by declining SO_4 concentrations within the stream, and provided new insights into the changing amplitude and phase of the seasonality of the determinands such as DOC and Al. Additionally, these data proved invaluable for placing the short-term variability demonstrated within the high-frequency data within context. The 7-hour data highlighted complex diurnal cycles for NO_3, Ca and Fe with cycles displaying changes in phase and amplitude on a seasonal basis. The high-frequency data also demonstrated the need to consider the impact that the time of sample collection can have on the summary statistics of the data and also that sampling during the hours of darkness provides additional hydrochemical information for determinands which exhibit pronounced diurnal variability. Moving forward, this research demonstrates the need for both long-term and high-frequency monitoring to facilitate a full and accurate understanding of catchment hydrochemical dynamics.

1. Introduction

Catchment hydrochemical monitoring programmes continue to be based largely on low-frequency sampling regimes, with grab samples collected on a weekly to monthly basis and analysed in a laboratory. Although certain studies have employed in-situ analytical equipment to facilitate high-frequency monitoring, intensive sampling has primarily been limited to either individual storm events, to a limited number of determinands measured by sondes (e.g. pH) or to determinands such as specific conductance and turbidity which can be utilised as water quality surrogates (Cassidy and Jordan, 2011; Hart and Martinez, 2006; Horsburgh et al., 2010; Jones et al., 2011; Jordan et al., 2005; Jordan et al., 2007; Kirchner, 2005, 2006; Kirchner et al., 2004; Madrid and Zayas, 2007; Neal and Kirchner, 2000; Palmer-Felgate et al., 2008; Robson et al., 1992a,b; Rozemeijer et al., 2010; Rücker and Schrautzer, 2010). Water quality parameter values vary widely over a range of scales in space and time and therefore, short-term, infrequent, fixed-interval sampling does not capture system extremes and can obscure complex hydrochemical patterns (Kirchner et al., 2000,2004; Madrid and Zayas, 2007; Montgomery et al., 2007; Neal et al., 2006; Palmer-Felgate et al., 2008; Prien, 2007; Robson and Neal, 1991). To fully understand the processes which link catchment hydrology and hydrochemistry, measurement frequencies should be based on the timescale of the catchment's hydrological response, which is often on the order of minutes or hours (Horsburgh et al., 2010; Kirchner, 2006; Kirchner et al., 2004; Moraetis et al., 2010; Scholefield et al., 2005; Tomlinson and De Carlo, 2003). Recent research has demonstrated the benefits of employing high-frequency data to better resolve storm-event dynamics, to quantify stream temporal variability, to increase the accuracy of load estimates and nutrient retention, to improve the understanding of groundwater–surface water interactions in the hyporheic zone and to better constrain hydrological and hydrochemical model parameters (Birkel et al., 2010; Bowes et al., 2009; Jarvie et al., 2001; Leecaster and Weisberg, 2001;

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doi:10.1016/j.scitotenv.2011.10.052

Malcolm et al., 2006, Rücker and Schrautzer, 2010; Soulsby, 1995; Soulsby et al., 2007).

A robust hydrological/hydrochemical model by definition offers the best possible approximation of reality given the constraints of the data upon which it was based and current knowledge of the processes involved (Dunn et al., 2008; Hughes, 1995). As such the success and validity of a model are dependent on the accuracy of the data used in its development and how well the data represent the spatio-temporal heterogeneity of hydrological processes, as well as the range of timescales over which they vary. This makes system modelling extremely complex (Kirchner, 2006, 2009). Many of the problems associated with hydrological modelling such as nonlinearity, scale, non-uniqueness of parameter sets, equifinality, the identification of model structure, overparameterisation and limited predictive capability have been well documented (Bergström and Graham, 1998; Beven, 2001, 2006a, 2006b, 2007; Beven and Binley, 1992; Bronstert, 2004; Dean et al., 2009; Kirchner, 2006; Vrugt et al., 2001). As a consequence of these problems the field of hydrochemistry has seen the development of a larger number of different hydrochemical models and no single agreed model structure. In recognition of these limitations there is an increasing focus on the utilisation of high-frequency data to test and advance the system representations being adopted within hydrochemical models (Beven, 2007; Kirchner, 2006).

While the limitations of current hydrochemical models and datasets are increasingly recognised, in-situ automated analytical equipment capable of analysing a range of water quality parameters at high-frequency are also being developed. This is leading to an emerging focus within hydrochemistry on high-frequency monitoring (Moraetis et al., 2010). Despite these advances, high-frequency monitoring remains challenging. Unless in-situ analytical equipment is available, samples have to be collected either manually or using automated equipment and returned periodically to the laboratory for analysis. This is laborious, exacting, subject to issues of sample stability and integrity and unsustainable over long periods both in terms of physical and financial resources (Horsburgh et al., 2010; Palmer-Felgate et al., 2008). Even when in-situ analytical devices are available, these suffer their own drawbacks as they are vulnerable to damage and breakdown and may experience problems such as biofouling and temperature drift. Where the system relies on loggers for data capture, such problems may not be detected immediately (Prien, 2007; Scholefield et al., 2005). Ideally some form of telemetry to transmit data to the user in real time should be used, but this may be limited by lack of a reliable communication network coverage in remote areas. Monitoring equipment also needs to be sited in secure locations, often requiring mains power to run effectively and manual grab samples are still required to provide validation for the automated data (Capelo et al., 2007; Hart and Martinez, 2006; Jordan et al., 2005; Palmer-Felgate et al., 2008; Scholefield et al., 2005).

Running concurrently with the move towards high-frequency monitoring is the argument that true system understanding can only be fully achieved through long-term monitoring. This is required to place system variability within the context of long-term changes such as decadal climatic oscillations (Evans et al., 2001a; Neal, 2002; Robson and Neal, 1996). To justify the large resources required with both high-frequency and long-term monitoring it is essential to demonstrate the worth of both types of data by showing that the insights provided by each are unattainable in the two or three year period typical of most water quality research programmes with weekly sample collection (Kirchner, 2006; Neal et al., 2012-this issue).

In this paper, data collected from the Upper Hafren headwater catchment of the River Severn at Plynlimon, mid-Wales are examined based on long-term monitoring and the results of an innovative and intensive sampling programme (Neal et al., 1997, 2010, submitted, this issue). This enables us to compare the hydrochemical information content and value of both long-term and high-frequency sampling. This is achieved through time-series analysis of 20 years of weekly hydrochemical data (1990–2010), referred to hereafter as the low-frequency dataset (LF), and a two year, 7-hour dataset (2007–2009), referred to hereafter as the high-frequency dataset (HF) (Table 1). The period between March 2007 and January 2009 is common to both datasets.

2. Study area and data resources

2.1. Study area

All the data presented in this paper were collected by the Centre for Ecology and Hydrology (CEH) in the upper River Severn, Plynlimon, mid-Wales (Fig. 1). This catchment has been studied extensively both in terms of hydrology and hydrochemistry over the last 40 years (Green and Marsh, 1997; Marc and Robinson, 2007; Neal, 1997, 2004). The Upper Hafren is a sub-catchment of the Plynlimon research catchments and contains the source of the River Severn (Fig. 1) (Hodgson and Evans, 1997; Neal et al., 2010; Page et al., 2007). Situated on the upper slopes of Pumlumon Fawr, 24 km inland from the Irish Sea, the catchment has a temperate maritime climate with the weather dominated by westerly frontal systems. Annual precipitation is approximately 2650 mm and the majority of rainfall, around 65%, occurs between September and February. The catchment area is 117 ha and has an altitude range of 546–635 m AOD. The flow responds rapidly to rainfall events, varying over two orders of magnitude from $<0.01\ \mathrm{m^3\ s^{-1}}$ to $1.9\ \mathrm{m^3\ s^{-1}}$ (the highest flow recorded since 2005).

The bedrock geology is base-poor and comprises of fractured Lower Palaeozoic slates, mudstones and sandstones (Foster et al., 2001; Godsey et al., 2010). The landscape has been influenced by Quaternary glaciation, with peri-glacial activity leaving remnants of locally derived overlying boulder clay and till (Neal et al., 2010). The soils consist of acidic peat, stagnopodzols, acid brown earths and stagnogleys, which exceed 40 cm in depth in certain areas (Foster et al., 2001; Neal et al., 2005a). Peat erosion has also resulted in significant hag formation (Neal et al., 2010). The catchment is largely semi-natural moorland with land-use limited to low intensity sheep grazing (Neal et al., 2010). The vegetation cover is predominantly a dwarf shrub heath community, *Calluna vulgaris* and *Eriophorum* spp., with acid grass species, *Nardus–Festuca*, on steeper slopes and *Juncus* spp. in gullies. The whole catchment has been designated as a Site of Special Scientific Interest (Fig.1).

2.2. Data resources

Water quality in the Upper Hafren is monitored at a location 25 m upstream of the edge of Hafren forest at an altitude of 552 m (Fig.1). In 1990, there was only one discharge gauging station within the Hafren catchment and this was located at the bottom of the Lower Hafren. A second flume was constructed within the catchment at the upstream boundary of the Hafren forest, 533 m AOD and 150 m downstream of the Upper Hafren water quality monitoring point. Flows have been recorded at this location since 2005. There is a strong linear correlation between flows recorded at the Lower and Upper Hafren sites ($r^2 = 0.968$) (Neal et al., 2010). Consequently, the flows for the Upper Hafren site, for the period between 1990 and 2005, have been estimated

Table 1
Sampling period for the Upper Hafren catchment.

	Low-frequency dataset	High-frequency dataset
Dataset duration	20 years	1.9 years
Sampling period	17 - July - 1990– 26 - October - 2010	6 - March - 2007– 27 - January - 2009
Sampling frequency	Weekly	7 h