Science of the Total Environment 543 (2016) 388–404

Contents lists available at ScienceDirect

Science of the Total Environment

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

Using hysteresis analysis of high-resolution water quality monitoring data, including uncertainty, to infer controls on nutrient and sediment transfer in catchments

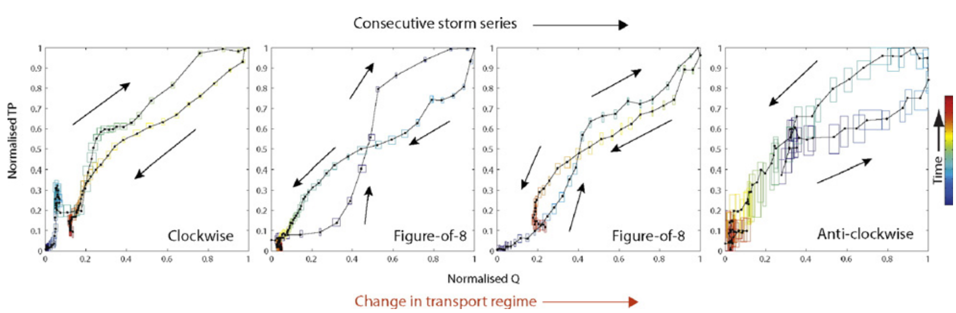
C.E.M. Lloyd [a,b,*], J.E. Freer [b], P.J. Johnes [b], A.L. Collins [c]

[a] School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK
[b] School of Geographical Sciences, University of Bristol, University Road, Bristol BS8 1SS, UK
[c] Sustainable Soils and Grassland Systems Department, Rothamsted Research, North Wyke, Okehampton EX20 2SB, UK

HIGHLIGHTS

- Hysteretic storm behaviour was analysed in 3 water quality parameters at 2 sites
- Storms were analysed within an observational uncertainty framework
- Range of metrics were used, including a new index, to quantify storm hysteresis
- Differences in transport mechanisms shown between nitrate and TP in chalk system.
- Behaviour was complex but provides insight into catchment processes in landscapes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 September 2015
Received in revised form 5 November 2015
Accepted 5 November 2015
Available online 18 November 2015

Editor: D. Barcelo

Keywords:
Nutrient transport
Storm behaviour
Turbidity
Rivers
Uncertainty
Catchment processes

ABSTRACT

A large proportion of nutrients and sediment is mobilised in catchments during storm events. Therefore understanding a catchment's hydrological behaviour during storms and how this acts to mobilise and transport nutrients and sediment to nearby watercourses is extremely important for effective catchment management. The expansion of available in-situ sensors is allowing a wider range of water quality parameters to be monitored and at higher temporal resolution, meaning that the investigation of hydrochemical behaviours during storms is increasingly feasible. Studying the relationship between discharge and water quality parameters in storm events can provide a valuable research tool to infer the likely source areas and flow pathways contributing to nutrient and sediment transport. Therefore, this paper uses 2 years of high temporal resolution (15/30 min) discharge and water quality (nitrate-N, total phosphorus (TP) and turbidity) data to examine hysteretic behaviour during storm events in two contrasting catchments, in the Hampshire Avon catchment, UK. This paper provides one of the first examples of a study which comprehensively examines storm behaviours for up to 76 storm events and three water quality parameters. It also examines the observational uncertainties using a non-parametric approach. A range of metrics was used, such as loop direction, loop area and a hysteresis index (HI) to characterise and quantify the storm behaviour. With two years of high resolution information it was possible to see how transport mechanisms varied between parameters and through time. This study has also clearly shown the different transport regimes operating between a groundwater dominated chalk catchment versus a surface-water dominated clay catchment. This information, set within an uncertainty framework, means that confidence can be derived that the patterns and relationships thus identified are statistically robust. These

* Corresponding author at: School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK.
E-mail address: charlotte.lloyd@bristol.ac.uk (C.E.M. Lloyd).

http://dx.doi.org/10.1016/j.scitotenv.2015.11.028

insights can thus be used to provide information regarding transport processes and biogeochemical processing within river catchments.

1. Introduction

Storm events generate significant transport of nutrient fractions and sediment in catchments. A range of publications report that a large proportion of a catchment's annual total phosphorus (TP) load can be transported by a small number of large storm events (Bowes et al., 2003; Evans and Johnes, 2004; Jarvie et al., 2002; Jordan et al., 2007; Verhoff et al., 1979). These are key transport events in which both nutrient and sediment sources are mobilised, releasing pollutants which are transported along flow pathways (surface and subsurface) and delivered to adjacent waters (Beschta, 1987; Evans et al., 2003; Meade and Parker, 1985; Walling and Webb, 1987). Therefore, understanding the role of hydrological activity in storms as a mechanism for the delivery of contaminants to streams is essential for producing effective agricultural land management strategies to support compliance with water quality legislation such as the Water Framework Directive (WFD) (European Parliament, 2000).

The recent expansion of the use of in-situ sensors to monitor nutrient parameters routinely at high temporal resolution is making detailed analysis of catchment behaviours in response to storm flow activation more feasible. Traditionally, parameters such as turbidity have been used to investigate storm behaviours as it can be measured at high frequency and has been shown to be a reasonable surrogate for the transport of sediment and sediment-associated contaminants such as phosphorus (as particulate P), ammonium and particulate organic nitrogen fractions which cannot be measured directly with existing sensor technologies (Grayson et al., 1996; Kronvang et al., 1997; Stubblefield et al., 2007). The more recent introduction of novel sensors systems and bankside automated photometers means that parameters such as nitrate-N and total phosphorus can be investigated at higher temporal resolutions than previously possible.

Understanding of the catchment transport pathways activated during storm events can be enhanced by studying the changing relationship between discharge and water quality parameters during an individual storm event. The relationship often exhibits a cyclical form known as hysteresis. Hysteresis between discharge and suspended sediment or dissolved solids during storm events was first observed by Hendrickson and Krieger (1964) and Toler and Ocala (1965) and since has been noted in many other water quality parameters such as turbidity, nitrate, TP, Total Reactive P (TRP) and conductivity (e.g. Bowes et al., 2009; Carey et al., 2014; House and Warwick, 1998; Lawler et al., 2006).

A paper by Williams (1989) was one of the first studies which described the most common shapes of hysteresis loops and provided possible explanations for why they occur, with respect to suspended sediment concentrations during storm events. Williams (1989) classified hysteresis loops into five classes. Class I was described as a single-valued line, where the increase and decrease in discharge and sediment concentrations are synchronised and suggests this can occur when sediment is plentiful. Class II was a clockwise loop, where the suspended sediment peak concentration occurs early in the discharge event. This is suggested to be caused by quick flushing of sediment which may become exhausted by the end of the storm event. On the other hand, anti-clockwise loops (class III) are also common, signifying the sediment peak lagging the discharge. This could provide evidence of differing transit times of water and sediment. Class IV was classified as a mixture of classes I and II, a single-line plus a loop and is described as resulting from a change in the form of the relationship during a storm event, possibly due to sediment availability, storage and transportability. The final class (V) was a figure-of-eight configuration, which combines classes II and III, again caused by a shift in the form of the relationship between discharge and suspended sediment concentration during a single event. It is important to note that many hysteresis loops maybe difficult to classify easily into these classes, and care should be taken with interpretation as the same type of loop could occur for different reasons. Nevertheless, the study of discharge-water quality hysteresis in storm events can provide a valuable research tool to infer the likely contributing source areas and flow pathways contributing to nutrient and sediment transport in catchments.

The examination of hysteresis loops can provide information regarding the time-lags between discharge and contaminants (Drewry et al., 2009; Langlois et al., 2005; Littlewood, 1992). The technique has been widely used over the past two decades in an attempt to increase understanding of how catchments are functioning, for example, Bowes et al. (2005) used the size of hysteresis loops to investigate the TP storage and mobilisation capability of storm events across a reach in the River Swale, Yorkshire during a succession of 10 storms. In addition, Chen et al. (2012) examined hysteresis in inorganic N fraction transport (ammonium, NH_4^+ and nitrate, NO_3^-) for two storms and showed that the transport mechanisms were different between the two parameters. These papers illustrate how catchment responses to storm events are complex and vary between and within catchments, as well as being parameter dependent.

To date, research has generally focussed on a small number of storm events for a particular catchment and often on just one water quality parameter. Against that background, this study is one of the first investigations to examine the storm responses of a range of water quality parameters over a two year period (up to 75 storms), allowing the comparison of storms between catchments with contrasting environmental characteristics, and between differing antecedent conditions and water years. Outram et al. (2014) used hysteresis as a tool to compare one country-wide storm event across three contrasting UK catchments monitored as part of the Demonstration Test Catchment project (McGonigle et al., 2014). The analysis showed interesting differences between catchment behaviours even during similar storm conditions and highlighted the need for a study which directly compares catchments over a broader range of storm events. The second novel aspect of this work is that it examines storm hysteresis accounting for the observational uncertainties in the data records. Krueger et al. (2009) examined uncertainty of storm hysteresis from a modelling perspective and considered four storm events. This study develops this research further and provides a non-parametric approach to quantifying observational uncertainties in both the discharge and water quality parameters and the storm analysis is completed within this uncertainty framework. Previous research has shown that observational uncertainties in these types of data can have implications for routine data analyses to produce data products to underpin catchment management and policy, such as load estimation, even when high temporal resolution data is used (Lloyd et al., 2015b). As a result, using an uncertainty framework in such analyses allows more robust conclusions to be drawn from these complex data sets particularly for when hysteresis behaviour between storms is non-overlapping across uncertainty limits.

This paper uses data from two field sites with contrasting hydrogeology, land use and management in the Hampshire Avon catchment, UK. The Wylye at Brixton Deverill has a groundwater dominated chalk catchment, while the Sem at Prior's Farm has a surface water dominated clay catchment. The catchments lie within 20 km of each other, and both form part of the wider drainage network of the Hampshire Avon catchment. The data were collected as part of the Defra funded