Journal of Hydrology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Hydrology

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

Research papers

Chemical regulation of alpine headwater streams during a storm event (Bogong High Plains, Victoria, Australia)

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ARTICLE INFO

Article history:
Received 19 January 2016
Received in revised form 26 August 2016
Accepted 3 September 2016
Available online xxxx
This manuscript was handled by L. Charlet, Editor-in-Chief, with the assistance of Joshua Larsen, Associate Editor

Keywords:
Peatland
Storm response
Chemostasis
Alkalinity
Dissolved organic carbon
Buffering

ABSTRACT

The headwater streams originating in the Australian Alps are the highest water yielding landscape in South-Eastern Australia and are projected to be impacted by climate change through longer dry periods and more episodic rainfall. In this work we studied the major ion and DOC responses of three alpine peatlands (and the broader catchment containing these systems) to a high intensity (summer) storm event. Despite the high volume of rainfall, major ions in stream waters remained strongly chemostatic throughout the event. This was particularly the case for Ca^{2+} and Mg^{2+}, as well as the alkalinity by association, and suggests that chemical regulation of these particular cations occurs through rapid equilibration processes. DOC concentrations increased during the storm pulse, leading to a shift in alkalinity partitioning from bicarbonate to organic anions and a decrease in pH, mediated by the CO_2 saturation levels in the stream water. Our results suggest that alkalinity generation (Ca^{2+} and Mg^{2+} acquisition) and partitioning (DOC export) are decoupled processes that may respond differently to repeat storm events depending on the capacity of these systems to provide these constituents. Under extreme case scenarios depletion of DOC (at constant alkalinity) would lead to a smaller pH dip during a storm pulse, while depletion of alkalinity would lead to a larger pH dip, with buffering controlled by free acid. We have not identified the mechanism for the chemostasis of Ca^{2+} and Mg^{2+} (and therefore alkalinity) in this work, but this will be critical to understanding the capacity of these peatlands to respond to repeat and more intense storm events.

1. Introduction

On the Australian mainland peatlands are largely restricted to the alpine and subalpine landscapes and are the source of high yielding headwater streams. These systems represent one of very few permanently water-rich environments in Australia, and the water yield from this landscape is extremely important to the base flows of major rivers in the Murray-Darling basin (Good and Worboys, 2011). Due to their limited extent and high vulnerability, these alpine peatlands are listed under Australian environmental legislation (Department of Environment, 2016) as endangered, as are all of the biological species and processes that occur in these peatlands. Climate change projections for the Australian Alps are for decreased winter snowpacks and more frequent storm events (Laurance et al., 2011; Pickering et al., 2004). Changing precipitation patterns are likely to impact on groundwater recharge processes that are critical to peatland hydrology in extended summer periods (Silvester, 2009; Western et al., 2008). As a consequence, these systems are likely to experience longer periods of drying and more episodic rainfall. In light of this, the response of these peatlands to storm events is likely important in the longer term functioning of these systems, and has not been studied previously.

Peatlands generally are important carbon (C) reservoirs (Reichstein et al., 2013) and the potential mobilisation of this stored C has significant implications for the global C budget (Freeman et al., 2001; Hope et al., 1994). For this reason a number of studies have investigated dissolved organic carbon (DOC) mobilisation from peatlands during storm pulses (Austnes et al., 2010; Bishop et al., 1990; Clark et al., 2007; Morel et al., 2009; Stutter et al., 2012; Worrall et al., 2002). These studies show that DOC export is a product of the catchment water sources, flow paths and biogeochemical processing. Consequently, DOC concentrations in a storm pulse can increase due to mobilisation of decomposed organic material from the hydraulically active part of the peat profile (the 'acrotelm') (Austnes et al., 2010) or the soil profile of the catchment more generally (Stutter et al., 2012). Conversely, DOC

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http://dx.doi.org/10.1016/j.jhydrol.2016.09.014
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decreases can occur due to exhaustion of acrotelm DOC or dominance of direct overland flows (Worrall et al., 2002). Consistent with this, the magnitude of the DOC pulse has been shown to be controlled in part by the condition of the catchment (e.g. soil moisture) prior to the storm event, influencing organic carbon oxidation, and therefore mobility of DOC (Stutter et al., 2012). The export of DOC exerts a strong control on stream pH, through the action of organic acids, with the magnitude of the associated pH drop ('acid episode') mediated by the stream buffering capacity (Bishop et al., 1990; Driscoll et al., 1989; Lövgren et al., 1987).

The concentrations of the major ions in stream waters are also perturbed during storm events (typically diluted), however, changes in concentrations are often strongly damped and do not reflect changes in discharge through simple dilution (Bishop et al., 2004; Clow and Mast, 2010; Godsey et al., 2009; Kirchner, 2003). This apparent 'chemostasis' has been attributed to a range of processes, including mobilisation of stored (old) water, mineral dissolution processes, vertical movement of water tables through variable porewater-depth profiles and diffusion controlled release. It is likely that combinations of these mechanisms control individual component responses to storm pulses.

While alpine peatlands in the Australian Alps are a minor part of the world-wide peat reserves, they are extremely important in the context of Australian water resources due to their intimate association with high yielding headwater streams (Good and Worboys, 2011). Moreover, these peatlands are discrete (confined in valleys) wetlands and their relatively simple hydrology likely provides an ideal environment to understand the response of these systems to storm events. In this work we have monitored the physicochemical responses of three isolated sub-catchment peatlands as well as the wider catchment containing these peatlands during a high-intensity storm event. We show that during this event the total alkalinity remains effectively constant and apparently linked with the acquisition of Ca (and Mg) in an example of 'rapid response' chemostasis. Export of DOC from the peatlands partitions the alkalinity strongly towards organic anions, leading to a pH drop, the magnitude of which is mediated by CO_2 saturation.

2. Experimental methods

2.1. Site description

The study area was the Watchbed Creek catchment, part of the Bogong High Plains, near Falls Creek, Victoria, Australia. (Fig. 1). This sub-alpine landscape is entirely contained within the Alpine National Park, a contiguous protected area of 6460 km^2. Cattle, horse and sheep grazing occurred in the Australian Alps for over 100 years, ceasing in the study area in 1994 (Lawrence, 1995). The catchment area of Watchbed Creek is 3.35 km^2 (Lawrence, 1995) as defined by a gauging station near where Watchbed Creek drains into Rocky Valley storage dam (Fig. 2). The altitude of the catchment ranges from a maximum of 1810–1625 m at the gauging station. The geology of the Watchbed Creek catchment consists of Ordovician sedimentary rocks that have undergone metamorphism to a form of foliated granite (Cobungra granite) (Morand, 2005) and gneiss (High Plains gneiss) (Beavis, 1962). Typical of these rock types, the dominant minerals are quartz, orthoclase, plagioclase (andesine) and biotite (Beavis, 1962). The surface rocks are highly fractured and have a vertically oriented foliation that likely facilitates groundwater recharge. Vegetation in this landscape includes closed and open heathlands, Snow Gum forest, tussock grassland, and peatlands (McDougall, 1986). The peatland vegetation is typically closed heath, composed of *Sphagnum* moss in association with candle heath (*Richea continentis*), alpine baeckea (*Baeckea gunniana*) and rope rush (*Empodisma minus*) (Wahren et al., 1999).

Four stream sampling locations were used in this work, shown as sites A, B, C and D in Fig. 2. Sites A, B and C were located at drainage points of discrete peatlands (sub-catchments) within the Watchbed Creek catchment while site D was the gauging station. The peatland associated with site B is also known as 'Heathy Spur 1' and has been the subject of a previous study (Silvester, 2009). The location details of the four sampling sites as well as their estimated peatland and catchment areas are provided in Table 1.

Groundwater composition data was from samples collected at a groundwater source located at site B. This groundwater source is a long-term monitoring site and previous work has shown that it is representative of the local groundwater (McCartney et al., 2013; Silvester, 2009); the site was sampled immediately prior to the storm event as part of the long-term monitoring program. There were no similar sources adjacent to sites A or C, so the groundwater collected at site B was taken to be representative for all peatlands in this work. It is assumed that the groundwater composition did not change appreciably during the storm event studied.

2.2. Instrumentation

At each of the sampling sites a gauging weir (v-notch) was used to measure stream flow. At sites A, B and C these were 300 mm high 90° v-notch weir plates, fabricated from 15 mm recycled plastic board. The weir at Site D is a permanent 120° v-notch design of height 1120 mm. At sites A, B and C a Trutrack water height logger (WT-HR 500; TruTrack Ltd, Christchurch, New Zealand) was installed. Loggers were contained in a 32 mm peizometer tube held with a stainless steel stay connected to the weir. These loggers were configured to record water height (stage), water temperature and logger (atmospheric) temperature at 30 min intervals (Fig. A1). The loggers were calibrated in the month prior to the storm study described here (calibration plots shown in Fig. A2). Static rain gauges were installed at each of sites A, B and C immediately (less than 12 h) prior to the storm event. The receiving vessels were acid washed prior to deployment to allow analysis of the rain composition. A tipping bucket rain gauge (HOBO S-RGB-M002) linked to a HOBO weather station (H21-001) was also installed at Site B, with the rainfall binned in 30 min intervals. The water table response at the peatland associated with site B was measured using a (linear) array of piezometers, spaced at 50 m intervals, longitudinally between the major groundwater source for this peatland and the gauging weir (see: Fig. 2). These piezometers were constructed of perforated 32 mm PVC tubing with 1 m Trutrack loggers (WT-HR 1000). Data transfer from field deployed devices was carried out using a HOBO shuttle (U-DT-1; Onset, Masschusetts) for the tipping bucket and Omni7 (Trutrack loggers; Trutrack Ltd, Christchurch) for water level sensors.

2.3. The storm event

This work describes the chemical and hydrologic response of alpine headwater streams (draining peatlands) to a high intensity rainfall event. The rain event chosen occurred on the 30th January 2012 and lasted for approximately 15 h. All sites (A–D) were sampled on the day prior to the rain event to provide a measure of base flow composition. Sites A and B were additionally sampled 4 days prior, as part of a separate study, but with the data included in this work. Rainfall commenced at 3am on the 30th of January (taken as zero 'storm time'), with samples collected every 4 h for the first 24 h, and then less frequently in subsequent days.