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A regional examination of episodic acidification response to reduced acidic deposition and the influence of plantation forests in Irish headwater streams

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HIGHLIGHTS

- ► We re-examined the status of episodic acidity in headwater streams in Ireland after 20 years.
- ► We examined the drivers of episodic acidification across different geologies and forest cover.
- ► Provided a unique opportunity to examine acidification drivers in a region with low atmospheric deposition
- ► Results indicated increasing organic acidity and reductions in anthropogenic pollutants.
- ► Forest cover found to be exacerbating the contribution of organic acidity to storm-water

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ABSTRACT

Episodic surface water acidification is common in many regions worldwide; the driving processes are dependent on a variety of physicochemical and climatic characteristics, and acid deposition pressures, which have changed significantly over the last two decades. This study provided a unique opportunity to re-examine the drivers of acidity in an environment of low anthropogenic input. In three geologically distinct acid-sensitive regions of Ireland during 2009–2010, 34 headwater streams were evaluated in peat-dominated catchments draining moorlands without forest, 20–50% (low) forest cover and >50% (high) forest cover. Results indicated episodic acidity/alkalinity loss in headwater streams, despite significant reductions in acid deposition. Both the differences in pH between base and storm-flow (ΔpH) and the number of pH events ≤ 5.5 were higher in forested streams. Dissolved organic carbon and inorganic aluminium concentrations were also higher in forested catchments. The primary driver of acidity was strong organic anions, which generally increased with increasing forest cover. Base-cation dilution was also prominent in west and southern regions, while surprisingly chlorine anion acidity from sea-salts had little or no influence on stream acidity. The contributions of excess non-marine sulphate (xSO_4) and nitrate (NO_3) to storm-water were low, with no observed increases in xSO_4 with increasing forest cover, although contributions of NO_3 were higher in forested catchments in the east. The results suggest that episodic acidification in Ireland is primarily driven by organic acids. However in peat dominant catchments, plantation forest, climate change and/or reductions in xSO_4 appear to also be having an effect on stream pH from increased DOC, with some forested streams previously unaffected by deposition now showing low pH (<5.5) during storm-flow. As quantified from this study, observed changes in stream acidification in Ireland may provide a better understanding of future chemical responses to declining acid deposition and climate change elsewhere.

1. Introduction

The acidification of freshwater systems is among the most extensively researched topics in environmental science (Kowalik et al., 2007). Over the last twenty years a considerable number of studies have highlighted the acidic nature of lotic systems in acid-sensitive regions throughout the northern hemisphere (e.g. Aherne et al., 2002; Bishop et al., 2000; Burton and Aherne, 2012; Dangles et al., 2004; Deyton et al., 2009; Evans et al., 1995; Fowler et al., 1989; Harriman and Morrison, 1982; Kelly-Quinn et al., 1996; Laudon et al., 2001; Lepori et al., 2003; Ormerod et al., 1989; Puhr et al., 2000; Soulsby, 1995). Surface water acidification has been predominantly associated with deposition of acid pollutants (e.g. sulphate and nitrate) and further enhanced by canopy interception in conifer plantations, influencing the potential for,

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and magnitude of, freshwater acidification downstream (e.g. Fowler et al., 1989; Kreutzer et al., 1998; Neal et al., 2010; Ormerod et al., 1989; Ormerod and Wade, 1990; Reynolds et al., 1994; Stevens et al., 1997; Waters and Jenkins, 1992; Wilkinson et al., 1997). Catchment characteristics including geology, soils and land use, together with stream discharge, influence the capacity of freshwater systems to buffer against such induced acidification (Edmunds and Kinniburgh, 1986; Jenkins et al., 1990; Ormerod et al., 1991). Similarly, climatic conditions, such as the frequency and amount of rainfall, prevailing wind direction and air mass circulation patterns, may influence the frequency, magnitude, duration and nature of acidification events in surface waters (e.g. Battarbee et al., 2005; Evans et al., 2008b; Kelly-Quinn et al., 1996; Soulsby, 1995).

Episodic acidity in streams throughout Ireland has been reported in forested and moorland (NF) headwater catchments in regions with low buffering/acid neutralising capacity (ANC) (Allott et al., 1990, 1997; Cruikshanks et al., 2008; Kelly-Quinn et al., 1996); although the south of Ireland is considered to generally have higher buffering capacity (Clenaghan et al., 1998; Giller et al., 1997). In the 1990s, excess sulphate and nitrates were identified as the main drivers of episodic acidity within forested catchment systems, although dissolved organic carbon (DOC) and sea-salt spray were also contributing factors, especially in western Ireland (Allott et al., 1990, 1997; Kelly-Quinn et al., 1996, 1997). The higher levels of sulphate and nitrate deposition that occurred in the east of Ireland, in comparison to the west, were attributed to easterly air flow carrying atmospheric pollution from the United Kingdom (UK) and the European mainland (Aherne et al., 2000; Bowman, 1991; Bowman and McGettigan, 1994). However, Ireland's westerly location at the periphery of Europe keeps atmospheric pollution levels relatively low (Giller and O'Halloran, 2004; Burton and Aherne, 2012). The reduction in anthropogenic sulphur and nitrogen oxide emissions across Europe in recent times, as highlighted by a growing body of literature, has seen a corresponding decrease in anthropogenic acidification of surface waters, draining both forested and non-forested moorlands (e.g. Bashir et al., 2006a, 2006b; Burton and Aherne, 2012; Curtis and Simpson, 2010; Davies et al., 2005; Evans et al., 2001, 2008b; Evans and Monteith, 2001, 2002; Fowler et al., 2005; Monteith et al., 2010; Skjelkvåle et al., 2001, 2003, 2005; Stoddard et al., 1999). For example, recent observations in the UK suggest that upland headwater streams and rivers have shown improvement in pH as a result of reductions in anthropogenic sulphur dioxide (SO_2) emissions which decreased by 71% and nitrogen oxides which fell by 40% between 1986 and 2001 (Curtis and Simpson, 2010; Fowler et al., 2005; Monteith et al., 2010; Ormerod and Durance, 2009). This was directly associated with changes in industrial practices in response to legislation controlling emissions (e.g. the Clean Air Act 1986, Gothenburg Protocol 1999 and the Large Combustion Plant Directive (DIRECTIVE 2001/80/EC)) (Mason, 2002; Review Group on Acid Rain, 1997; UN-ECE, 1999). However, in the UK, forest cover is still a factor contributing to episodic surface water acidification in acid-sensitive catchments through the scavenging and interception of sulphates (Evans et al., 2008b; Kowalik et al., 2007; Ormerod and Durance, 2009).

Similar trends in reduced atmospheric deposition, especially in sulphur, were highlighted in Ireland (Aherne and Farrell, 2002; Bashir et al., 2006a, 2006b; Burton and Aherne, 2012). For example, Bashir et al. (2006a, 2006b) reported that ambient SO_2 and excess (non-marine) SO_4 levels decreased by about 60 and 40%, respectively, during the period 1980 to 2004. No such trends were apparent for total nitrogen deposition (Bashir et al., 2006b); although a 13% reduction in nitrate (NO_3^-) was recorded during the period 1994 to 1998 across a wider set of recording stations (Aherne and Farrell, 2002).

Recent studies on Irish upland lakes indicated no significant threat from anthropogenically-derived sources of acidification; although measurable amounts still occur and potentially pose a threat to acid-sensitive catchments, especially with forest plantations (Aherne and Curtis, 2003; Aherne and Farrell, 2000; Burton and Aherne, 2012; Farrell et al., 2001). However, studies quantifying the regional frequency of streams still affected by acidification are uncommon (Kowalik et al., 2007), especially in Ireland, and studies assessing the influence of forestry under current environmental conditions where atmospheric deposition has decreased are rare (Malcolm et al., in press). Regional studies are essential for the formulation of locally applicable management plans to minimise the effects of catchment afforestation on freshwater ecosystems (Puhr et al., 2000). Therefore, given the importance of surface water quality in maintaining the ecological health of freshwater systems and requirements of the Water Framework Directive (European Parliament and Council, 2000) to achieve and maintain at least 'good status' for all waters, it is imperative that the complex interaction between plantation forestry and surface water quality is investigated and reassessed in the light of changes to potential drivers. Thus, the aim of this study was to examine and describe the current chemistry of Irish headwater streams in the acid-sensitive regions of the west, east and south of the country and characterise the drivers of episodic acidity (estimated as alkalinity loss) with respect to the effect of conifer forest cover. From an international perspective this study provided a unique opportunity to examine acidification drivers in an area that has relatively low levels of atmospheric pollution and may provide further evidence for potential responses of stream chemistry elsewhere to declining acidic deposition and climate change into the future.

2. Methods

2.1. Study sites

Thirty-four streams in three regions of Ireland were selected; in the east in County Wicklow, the west in County Mayo and the south in counties Cork and Kerry (Fig. 1) in known acid-sensitive areas (see Aherne et al. (2002) or Burton and Aherne (2012) for a map of Irish surface water sensitivity). Sites were second or third order streams draining 0.40–6.99 km^2 catchments (Table 1). Streams in the west drain mixed metamorphic geology consisting of schist/gneiss or quartzite, streams in the east drain igneous (granite/felsite) geology and streams in the south overlie sedimentary Old Red Sandstone (Table 1). Catchment soils are either blanket peat or poorly drained, peaty lithosolic/podzolic soils (Table 1). Land cover consists of open non-forested semi-natural moorland (see Feeley et al., 2011, 2012a for more details) and/or plantation conifer forest only (Table 1). For the purposes of this study the extent of forest cover in each catchment was grouped into three bands: no forest cover (NF: moorland controls), low forest catchment cover (LF: ~20 to 50%) and high forest catchment cover (HF: >50%) after Kelly-Quinn et al. (2008) who showed evidence of differing susceptibility to surface water acidification within these bands. All three regions had reasonable replication in each band, with the exception of the east where only one HF site was available (Table 1). Much of the plantation forest in this region has reached harvesting age and there were no large expanses of mature forest without areas of harvesting activity. Therefore, in the east the forested streams were categorised together into a single forest cover band (F).

2.2. Water sampling and analysis

A total of 155 base-flow samples and 173 storm event samples were collected over a period of 14 months from October 2009 to November 2010 across all three regions (see Table 2), during both westerly and easterly airflow conditions. All were grab samples taken at centre-stream with low-density, polyethylene plastic bottles. The bottles were labelled with site codes and only used at that site thereafter. The bottles were triple rinsed in the laboratory with de-ionized water and triple rinsed again in the field with sample water to ensure that no contamination occurred. Storm-flow samples were collected within 24 h of >20 mm rainfall,