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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,

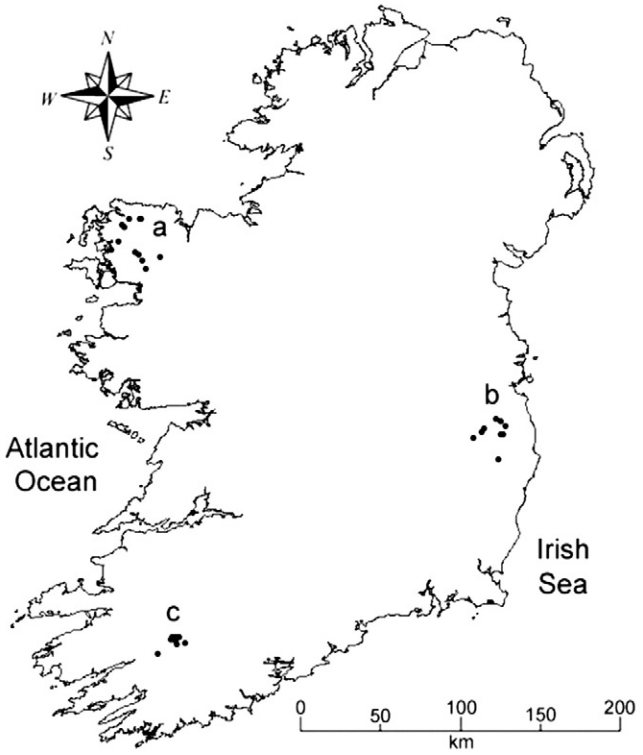

Fig. 1. Geographic locations of the 34 streams sampled in (a) the west (County Mayo), (b) the east (County Wicklow) and (c) the south (County Cork/Kerry) of Ireland from October 2009 to November 2010.

which is known to result in increased stream-flow (e.g. Feeley et al., 2012b). Consequently, storm sample values are not necessarily peak flow values but generally represent storm-flow conditions at the time of sampling. It was not possible to sample all storms at all sites at their peak, although all efforts were made to sample as close to the peak as possible.

All samples were analysed for pH (Wissenschaftlich-Technische-Werkstätten (WTW) pH meter 330I), alkalinity (Gran titration), the base cations; sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}) and total monomeric aluminium (Al^{n+}, filtered at 45 μm) (Varian SpectrAA 300), ammonia/ammonium (NH_4^+, FIA method following 0.45 μm filtration), and acid anions; nitrate (NO_3^-), chloride (Cl^-) and sulphate (SO_4^{2-}) (Lachat QuikChem 800 FIA) using standard methods (Clesceri et al., 2001). Dissolved organic carbon (DOC) concentrations were determined using high temperature combustion at 680 °C (Shimadzu TOC-VCPH Total Organic Carbon Analyzer) (see Gadmar et al., 2002). The difference in pH between the mean base-flow and each storm-flow event (ΔpH) and the number of pH values recorded below the biologically sensitive threshold (pH_{BT}) of 5.5 (e.g. Sutcliffe and Hildrew, 1989) were calculated. Alkalinity, the cations NH_4^+, Na^+, K^+ Ca^{2+}, Mg^{2+}, and Al^{n+}, and the anions Cl^-, NO_3^- and SO_4^{2-} were converted to μeq L^{-1} for analysis. Mean alkalinity, and Cl^-, NA^+, K^+, Ca^{2+} and Mg^{2+} values for each forest band in each region can be found in Table 3. Due to uncertainty, Al^{n+} was given a valence of 2^+ for calculations (after Sullivan et al., 1989).

The approximate contributions of strong organic acids (OA) expected were estimated for each region using the methodology based on pH and DOC developed by Oliver et al. (1983). Hruška et al. (2003) noted strong similarities in the amount of carboxylic groups per milligramme of DOC across temperate regions. However, the OA contribution to storm-water within the three study regions were found to vary and were estimated at 4.4 (±0.47) μeq mg^{-1} DOC for sites in the west, 7.9 (±0.26) μeq mg^{-1} DOC for sites in the east and 6.8 (±0.31) μeq mg^{-1} DOC for sites in the south. Slight regional differences may be expected due to the variation in the humic content of soils and variability in stream pH (Hruška et al., 2003; Kortelainen, 1993; Munson and Gherini, 1993). Excess, or non-marine, sulphate (xSO_4) for each sample was calculated by subtracting the marine equivalent (mSO_4), based on the ratio of SO_4^{2-} to Cl^- in seawater (0.104 in μeq), from the total SO_4^{2-} measured and multiplying it by the amount of Cl^- in μeq (i.e. $xSO_4 = SO_4^{2-} - 0.104 * Cl^-$). The acid neutralising capacity (ANC) was calculated by subtracting the sum of acid anions ($SO_4^{2-} + NO_3^- + Cl^-$ in μeq) from the sum of base cations ($Ca^{2+} + Mg^{2+} + K^+ + Na^+$ in μeq) (e.g. Hemond, 1990; Evans et al., 2008a).

The loss in alkalinity due to base-cation dilution was calculated for each storm flow sample relative to the mean base flow using the methodology developed by Kahl et al. (1992) as follows:

$$\text{Dilution} = \frac{((\sum BC_b - \sum BC_s)/\sum BC_b)Alk_b}{(Alk_b - Alk_s)} \times 100$$

where $\sum$BC is the sum of base cations, Alk is the Gran alkalinity in μeq, subscript 'b' is base flow and subscript 's' is storm flow. This method assumes that the sum of base cations should dilute in proportion to alkalinity (which is likely to be predominantly bicarbonate) (Kahl et al., 1992; Kowalik et al., 2007; Lepori et al., 2003). However, small discrepancies are possible due to desorption of base cations in the uppermost layers of soils during storm events (Bishop et al., 2000; Kahl et al., 1992). Dilution values<100% indicate the addition of strong acids to the surface water titrated from elsewhere, either through precipitation, deposition and/or catchment processes (Kahl et al., 1992). To calculate the importance of titrated strong acids, where base-cation dilution was not the sole contributor of alkalinity loss, the proportional contribution of strong acid anions to the sum of strong acid anions ($\sum$AA: xSO_4, mSO_4, NO_3, Cl^- and OA) was calculated for each storm event (anion/$\sum$AA) (e.g. Kowalik et al., 2007). A substantial loss in the ratio alkalinity/$\sum$cations, set with a lower limit of zero, indicates evidence for the titration effect, and therefore, must be accompanied by increases in one or more acid anions (Kahl et al., 1992). The sum of the ratio alkalinity/$\sum$cations plus all anion/$\sum$AA should be equal to 1.0, although small discrepancies in the analytical precision may occur due to the omission of minor ionic contributors (Kahl et al., 1992; Kowalik et al., 2007; Lepori et al., 2003). Given that $\sum$cations is theoretically equal to $\sum$AA, $\sum$cations was substituted for $\sum$AA as the latter can be determined with less certainty (Kahl et al., 1992; Kowalik et al., 2007; Lepori et al., 2003).

Additional losses in ANC may occur due to the contribution of excess Cl^- relative to Na^+ from marine sources, otherwise known as the 'sea-salt' effect (e.g. Sullivan et al., 1988). Of the acid anions, Cl^- is the most mobile, usually following water through the soil from precipitation to runoff (Lydersen and Henriksen, 1995). If Na^+ is adsorbed in the soil, Cl^- moves through the system leading to H^+ and Al^{n+} enrichment owing to ion exchange, lowering the ANC (Harriamn and Wells, 1985; Heath et al., 1992; Hindar et al., 1995; Kowalik et al., 2007; Sullivan et al., 1988). Therefore, the regional importance of Na^+ retention is an important consideration given the coastal proximity of the three study areas (Fig. 1). The Na:Cl ratio of seawater and coastal precipitation is assumed to be identical at ~0.86 (e.g. Evans et al., 2001; Heath et al., 1992; Hindar et al., 1995; Sullivan et al., 1988). Therefore, the contribution of 'sea-salt' acidification in each region was determined by calculating the relative change in ionic concentrations of Cl^- and Na^+ between mean base- and individual storm-flow samples (i.e. $\Delta Cl^- - \Delta Na^+$), with ANC loss occurring when there were substantially higher concentrations of Cl^- relative to Na^+ (Evans et al., 2008b; Kowalik et al., 2007).

2.3. Statistical analysis

Differences in pH, ANC, Al^{n+}, DOC and base-cation dilution across the three regions and forest cover class during base and storm-flow

Table 1
Stream sites sampled during the period October 2009 to November 2010, site code, location and physical characteristics.

Region	Stream name	Site code	Latitude	Longitude	Order	Mature forest[a] (%)	Forest cover class	Mean slope (degrees)	Elevation (m a.s.l.)	Catchment size (km^2)	Soil[b]	Geology[b]
West	Croaghaun Str	MM1	54° 6′ 33.1″ N	−9° 46′ 5.5″ W	3	44.9	LF	4.94	20	4.93	BktPt	S/Gn
West	Srahnamanragh Str	MM2	54° 4′ 1.6″ N	−9° 49′ 24.6″ W	2	0.0	NF	4.45	15	5.43	BktPt	S/Gn
West	T of Glenturk Beg	MM3	54° 11′ 18.3″ N	−9° 42′ 58.5″ W	2	23.2	LF	7.48	30	1.27	BktPt	Quartz
West	Glenturk More	MM4	54° 12′ 7.2″ N	−9° 44′ 8.6″ W	2	53.1	HF	6.92	29	2.56	BktPt	Quartz
West	T of Glenamoy Rv	MM5	54° 14′ 6.9″ N	−9° 40′ 22.3″ W	2	0.0	NF	5.57	10	3.16	BktPt	S/Gn
West	Fiddaunuganass Str	MM6	54° 14′ 4.7″ N	−9° 33′ 58.9″ W	2	68.1	HF	3.62	116	2.28	BktPt	S/Gn
West	Fiddauntuckletaun Str	MM7	54° 14′ 4.1″ N	−9° 34′ 24.4″ W	2	47.6	LF	4.30	102	1.72	BktPt	S/Gn
West	Hw of Skerdagh Rv	MM8	53° 58′ 5.8″ N	−9° 30′ 46.7″ W	3	0.0	NF	16.53	152	2.03	SRPT	S/Gn
West	Hw of Bar Deela Rv	MM9	54° 2′ 36.7″ N	−9° 34′ 50.0″ W	2	69.1	HF	6.24	100	1.52	BktPt	Quartz
West	Hw of Oweniny Rv	MM10	54° 3′ 10.9″ N	−9° 36′ 17.3″ W	2	18.5	LF	9.67	128	6.35	BktPt	Quartz
West	T of Goulan Rv	MM11	54° 0′ 39.3″ N	−9° 32′ 50.7″ W	2	21.3	LF	8.48	109	1.51	BktPt	S/Gn
West	T of Castlehill Rv	MM12	54° 2′ 7.4″ N	−9° 22′ 59.2″ W	2	0.0	NF	13.19	85	1.57	SRPT	S/Gn
East	Cransilliagh Bk	WM1	53° 10′ 5.2″ N	−6° 22′ 19.2″ W	2	31.1	LF	9.72	339	0.41	BktPt	Gr/F
East	T of Rv Liffey	WM2	53° 9′ 4.8″ N	−6° 19′ 59.4″ W	3	0.0	NF	5.04	377	1.93	BktPt	Gr/F
East	T of Cloghoge Rv	WM3	53° 7′ 41.5″ N	−6° 17′ 31.9″ W	2	0.0	NF	4.30	411	2.94	BktPt	Gr/F
East	Inchavore Rv 1	WM7	53° 4′ 59.6″ N	−6° 18′ 43.0″ W	2	23.6	LF	5.88	233	1.99	BktPt	Gr/F
East	Inchavore Rv 2	WM8	53° 5′ 3.2″ N	−6° 19′ 57.4″ W	2	38.1	LF	6.53	299	0.95	BktPt	Gr/F
East	Clohernagh Bk	WM9	52° 57′ 2.7″ N	−6° 21′ 51.6″ W	2	61.2	HF	9.94	312	3.67	SRPT	Gr/F
East	Ballyknocken Bk	WM10	53° 5′ 52.1″ N	−6° 30′ 15.9″ W	2	36.1	LF	12.08	221	1.13	SRPT	Gr/F
East	Fraughan Bk	WM11	53° 6′ 55.5″ N	−6° 28′ 44.8″ W	2	0.0	NF	11.17	227	0.84	SRPT	Gr/F
East	Toor Bk	WM12	53° 3′ 49.9″ N	−6° 34′ 36.7″ W	2	33.0	LF	10.13	277	1.87	BktPt	Gr/F
South	Foherish Rv	KM1	51° 58′ 25.2″ N	−9° 6′ 1.9″ W	2	65.8	HF	11.35	246	5.49	SRPT	ORS
South	Boohill Rv	KM2	51° 58′ 8.1″ N	−9° 10′ 26.9″ W	2	0.0	NF	12.01	219	2.37	SRPT	ORS
South	Cummeenabuddoge Str	KM3	52° 0′ 17.9″ N	−9° 9′ 34.9″ W	2	53.9	HF	9.02	343	3.77	BktPt	ORS
South	T of Clydagh 2	KM4	51° 59′ 58.0″ N	−9° 10′ 18.7″ W	2	85.6	HF	7.30	259	0.56	BktPt	ORS
South	T of Clydagh 3	KM5	51° 59′ 56.3″ N	−9° 10′ 28.0″ W	2	22.8	LF	6.14	333	1.17	BktPt	ORS
South	Clydaghroe Str	KM6	51° 59′ 52.1″ N	−9° 11′ 27.8″ W	2	83.6	HF	5.12	307	1.32	BktPt	ORS
South	T of Clydagh 5	KM7	51° 59′ 44.0″ N	−9° 11′ 52.6″ W	2	89.1	HF	13.36	298	0.77	BktPt	ORS
South	T of Clydagh 6	KM8	51° 59′ 43.1″ N	−9° 13′ 12.5″ W	2	80.0	HF	6.38	264	3.03	BktPt	ORS
South	Glashacormick Str	KM9	51° 59′ 43.5″ N	−9° 13′ 30.8″ W	2	0.0	NF	9.39	256	3.70	BktPt	ORS
South	Glashnasharragh Str	KM10	52° 0′ 21.3″ N	−9° 11′ 59.2″ W	2	0.0	NF	9.07	332	1.51	BktPt	ORS
South	Knocknagowen Str	KM11	52° 0′ 21.6″ N	−9° 9′ 41.2″ W	2	34.0	LF	7.38	342	6.99	SRPT	ORS
South	Glanlee Rv	KM12	51° 55′ 10.1″ N	−9° 20′ 23.6″ W	3	0.0	NF	10.51	210	1.73	BktPt	ORS
South	Knocknabro Str	KM13	52° 0′ 16.3″ N	−9° 12′ 57.3″ W	2	44.7	LF	4.94	330	1.41	BktPt	ORS

[a] Plantation conifer forest only, 0.0 = moorland.
[b] Predominant within catchment. NF = no forest cover, LF = low forest cover, HF = high forest cover, BktPt = blanket peat, SRPT = peaty lithosolic–podzolic soils, ORS = Old Red Sandstone, T = tributary, Hw = headwater, Rv = river, Str = stream, Bk = brook, S/Gn = schist/gneiss, Quartz = quartzite, Gr/F = granite/felsite.

conditions in the west and south were examined using non-parametric Kruskal–Wallis tests, while the difference between NF and F sites during base and storm-flow conditions in the east was tested using non-parametric Mann–Whitney U-test. Differences between pooled base-flow and pooled storm-flow pH, ANC, Al^{n+} and DOC recorded were examined using non-parametric Mann–Whitney U-test. Regional differences and within region forest cover differences in ΔpH and proportional anion contributions within the west and south with respect to forest cover were examined using Kruskal–Wallis tests, while the difference between NF and F sites in the east was tested using Mann–Whitney U-tests as above. For all statistical tests calculated $P<0.05$ was assumed to indicate statistical significance for the sites in question. All statistics were calculated using PASW Statistics 18 (IBM SPSS Inc., 2010).

3. Results

3.1. Regional pH, ANC, Al^{n+} and DOC

In all three regions, storm-flow pH values dropped significantly (Mann–Whitney: west $Z=-6.44$, $P<0.001$, east $Z=-7.71$, $P<0.001$ and south $Z=-9.31$, $P<0.001$) compared to base-flow conditions (Table 4). Regional differences were also evident, with the east having significantly lower pH values (Kruskal–Wallis: $H_{2,316}=89.62$, $P<0.001$) than both the west and south, irrespective of flow conditions for the sites examined (Table 4). The number of pH_{BT} values recorded was highest in the east at both base-flow (9) and storm-flow (52) compared to both the west and south, which had 2 and 0 pH_{BT} values recorded during base-flow, respectively, and 15 values each during storm-flow conditions (Table 4). The mean regional change in pH (ΔpH) was significantly greater in the east (1.41) compared to the western (1.13) and southern regions (1.17) (Kruskal–Wallis: $H_{2,172}=11.91$, $P<0.01$) (Table 4).

Episodic acidity is indicative of periods of ANC loss, with significant reductions in ANC between base-flow and storm-flow conditions in all three regions (Mann–Whitney: west $Z=-5.43$, $P<0.001$, east $Z=-2.77$, $P<0.01$, and south $Z=-6.06$, $P<0.001$) (Table 4). Regionally, irrespective of flow conditions, sites in the west and the south had significantly higher ANC values than the east (Kruskal–Wallis: $H_{2,316}=104.13$, $P<0.001$) (Table 4). Measured inorganic aluminium concentrations increased substantially during storm-flow conditions in all three regions, with the increase being statistically significant in the west (Mann–Whitney: $Z=-4.27$, $P<0.001$), east (Mann–Whitney: $Z=-5.41$, $P<0.001$) and south (Mann–Whitney: $Z=-6.81$, $P<0.001$) (Table 4). During base-flow conditions Al^{n+} concentrations were significantly higher in the order east > west > south (Kruskal–Wallis: $H_{2,316}=95.61$, $P<0.001$) (Table 4). Dissolved organic carbon concentrations during storm-flow were substantially higher than base-flow conditions, with the differences found to be statistically significant in all three regions (Mann–Whitney: west $Z=-4.56$, $P<0.001$, east $Z=-6.82$, $P<0.001$ and south $Z=-7.45$, $P<0.001$) (Table 4). Overall, DOC concentrations were significantly lower in the south compared to the west and east (Kruskal–Wallis: $H_{2,316}=19.62$, $P<0.001$) (Table 4).

3.2. Forest effects on pH, ANC, Al^{n+} and DOC

3.2.1. The west and metamorphic geology

No forest cover effects on stream-water pH were recorded during base-flow conditions (Kruskal–Wallis: $H_{2,48}=3.71$, $P=0.157$). However,

Table 2
Dates and number of base- and storm-flow samples taken in each region during the study period from October 2009 to November 2010.

	Region	West			East		South		
	Land use	NF	LF	HF	NF	F	NF	LF	HF
	No of sites	4	5	3	3	6	4	3	6
Flow	Sampling month								
Base	October 2009	–	–	–	3	5	3	3	6
	Feb/Mar 2010	4	5	3	3	6	4	3	6
	May 2010	4	5	3	3	6	4	3	6
	July 2010	4	5	3	3	6	4	3	6
	October 2010	4	5	3	3	6	4	2	6
	13-month total (n)	16	20	12	15	29	19	14	30
Storm	Oct/Nov 2009	–	–	–	6	8	–	–	–
	Feb/Mar 2010	4	5	3	2	4	4	3	6
	Jun/Jul 2010	7	7	5	10	15	7	6	10
	Oct/Nov 2010	8	10	4	5	8	8	6	12
	14-month total (n)	19	22	12	23	35	19	15	28

NF = no forest cover, LF = low forest cover, HF = high forest cover, F = pooled low and high forest cover, n = number of samples.

the storm-flow pH in LF sites were significantly higher than NF and HF sites (Kruskal–Wallis: west $H_{2,53}=8.65$, $P<0.05$) (Table 4, Fig 2b). Similarly, the highest number of pH_{BT} values was recorded in the LF streams (11) compared to the HF (4) and the NF (0) streams during storm-flow (Table 4). The mean ΔpH was greater with increasing forest cover, although the differences were not statistically significant (Kruskal–Wallis: $H_{2,53}=3.34$, $P>0.05$) (Table 4). Likewise, no significant forest cover differences in ANC values were measured during base-flow or storm-flow conditions ($P>0.05$). Inorganic Al concentrations during base- and storm-flow were higher in both low and HF sites compared to the NF streams (Kruskal–Wallis: base-flow $H_{2,48}=11.45$, $P<0.001$, storm-flow $H_{2,53}=24.32$, $P<0.001$) (Table 4). Both LF and HF sites also had higher DOC concentrations than NF sites (Kruskal–Wallis: $H_{2,48}=17.74$, $P<0.01$) (Table 4). However, during storm-flow DOC increased significantly in the order NF (5.4 mg l^{-1})<LF (11.6 mg l^{-1})<HF (14.2 mg l^{-1}) (Kruskal–Wallis: $H_{2,53}=15.07$, $P<0.001$) (Table 4).

3.2.2. The east and igneous geology

Stream-water pH recorded during base-flow conditions were similar regardless of forest cover (Mann–Whitney: $Z=-0.80$, $P=0.421$). Similarly, pH during storm-flow did not differ with forest cover (Mann–Whitney: $Z=-0.95$, $P=0.340$) (Table 4, Fig. 2d). The change in pH (ΔpH) was greater with forest within the catchment, although the differences were not significant (Mann–Whitney: $Z=-1.32$, $P=0.185$), while the number of pH_{BT} values recorded also increased with forest cover (Table 4). ANC values were slightly lower in F catchments compared to NF catchments in both base-flow and storm-flow conditions, however no significant differences were recorded ($P>0.05$) (Table 4). Concentrations of Al^{n+} were similar during base-flow irrespective of forest cover (Mann–Whitney: $Z=0.00$, $P=1.0$), while F sites (359.5 μg l^{-1}) recorded significantly higher concentrations of Al^{n+} compared to NF sites (180.8 μg l^{-1}) (Mann–Whitney: $Z=-0.84$, $P<0.001$) during episodic storm-flow conditions (Table 4). In contrast, base-flow DOC was significantly higher in NF sites (10.13 mg l^{-1}) compared to the F sites (6.3 mg l^{-1}) (Mann–Whitney: $Z=-2.32$, $P<0.05$), while during episodic storm-flow events no forest cover differences in DOC concentrations were observed (Mann–Whitney: $Z=-0.84$, $P=0.84$) (Table 4).

3.2.3. The south and sedimentary geology

Again no forest cover effects on stream-water pH were recorded during base-flow conditions (Kruskal–Wallis: $H_{2,63}=1.19$, $P=0.551$). However, during storm-flow pH values were significantly lower when forest was present (Kruskal–Wallis: west $H_{2,62}=14.30$, $P=0.001$), although the amount of forest cover was not significant (Table 4, Fig. 2f). Similarly, the mean ΔpH increased with increasing forest cover, with significantly greater changes observed when forest cover was present (Kruskal–Wallis: $H_{2,62}=10.63$, $P<0.01$), although again the amount of forest cover was not significant (Table 4). The number of pH_{BT} also increased with forest cover during in storm-flow conditions, with a 2, 3 and 10 pH values equal to or below 5.5 recorded in the NF, LF and HF streams, respectively (Table 4). Again, no significant forest cover differences in ANC values were measured during base-flow or storm-flow conditions ($P>0.05$). Base-flow Al^{n+} concentrations were significantly higher in the order NF (14.3 μg l^{-1})<LF (42.0 μg l^{-1})<HF (56.6 μg l^{-1}) (Kruskal–Wallis: $H_{2,63}=37.79$, $P<0.001$) (Table 4). Similar trends were seen during storm-flows, with Al^{n+} concentrations increasing in the order NF (70.9 μg l^{-1})<LF (93.4 μg l^{-1})<HF (120.0 μg l^{-1}) (Kruskal–Wallis: $H_{2,62}=15.42$, $P<0.001$) (Table 4). Both LF and HF sites had higher DOC concentrations than NF (Kruskal–Wallis: $H_{2,63}=37.79$, $P<0.001$) during base-flow conditions, while mean storm-flow concentrations of DOC increased in the order NF<LF<HF, with means of 9.7, 12.9 and 17.3 mg l^{-1}, respectively, with significantly higher concentrations in the HF sites (Kruskal–Wallis: $H_{2,62}=12.06$, $P<0.01$) (Table 4).

Table 3
The mean and standard deviation (SD in parenthesis) of alkalinity, Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+} and sum of base-cations (∑BC) in μeq l^{-1} at base-flow and storm-flow within each region and across forest cover within each region. For n see Table 2.

Region	Forest cover	Flow	Alkalinity		Cl^-		Na^+		K^+		Mg^{2+}		Ca^{2+}		∑BC	
			Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
West	NF	Base	355.3	(124)	219.3	(19)	565.3	(209)	22.7	(9)	356.9	(143)	514.0	(186)	1458.8	(491)
		Storm	156.0	(174)	173.7	(45)	420.6	(157)	27.5	(14)	155.7	(83)	178.0	(88)	781.7	(312)
	LF	Base	321.7	(113)	212.2	(30)	579.5	(168)	16.2	(7)	232.8	(122)	485.5	(531)	1313.9	(622)
		Storm	117.3	(188)	187.6	(54)	459.6	(145)	16.0	(7)	129.7	(46)	155.4	(116)	760.7	(220)
	HF	Base	335.7	(193)	259.5	(29)	591.9	(174)	18.8	(10)	248.1	(114)	564.7	(476)	1423.6	(683)
		Storm	81.6	(110)	220.3	(48)	526.1	(84)	15.2	(7)	136.9	(30)	197.2	(128)	875.5	(207)
East	NF	Base	71.7	(54)	129.8	(19)	169.6	(30)	5.7	(2)	46.5	(14)	61.6	(21)	283.4	(59)
		Storm	−21.9	(33)	101.7	(24)	124.3	(23)	7.8	(3)	42.7	(16)	44.4	(31)	219.2	(61)
	F	Base	82.3	(185)	185.0	(31)	206.9	(27)	6.7	(2)	54.1	(17)	83.7	(40)	351.5	(77)
		Storm	−14.9	(27)	127.1	(33)	147.6	(27)	8.8	(5)	42.4	(12)	49.5	(20)	248.3	(52)
South	NF	Base	801.9	(320)	219.3	(19)	234.4	(22)	6.2	(1)	121.1	(39)	279.5	(76)	641.1	(124)
		Storm	199.9	(160)	173.7	(45)	189.5	(44)	8.9	(4)	75.9	(19)	167.7	(80)	441.9	(129)
	LF	Base	593.0	(635)	212.2	(30)	241.9	(27)	7.1	(2)	115.3	(27)	245.0	(77)	609.3	(122)
		Storm	11.3	(141)	187.6	(54)	212.1	(38)	9.1	(3)	72.6	(28)	147.8	(67)	441.5	(109)
	HF	Base	688.8	(576)	259.5	(29)	285.6	(41)	6.5	(2)	142.9	(58)	222.8	(108)	657.8	(196)
		Storm	124.7	(150)	220.3	(48)	256.0	(48)	5.9	(4)	84.2	(26)	115.6	(80)	461.7	(120)

NF = no forest cover, LF = low forest cover, HF = high forest cover, F = pooled low and high forest cover.

Table 4
The mean and ranges of recorded pH, the number of pH ≤ the biological threshold of 5.5 (pH_{BT}), ANC (μeq l^{-1}), Al^{n+} (μg l^{-1}) and DOC (mg l^{-1}) at base-flow and storm-flow within each region and across forest cover within each region, and mean ΔpH and ranges within each region and across forest cover within each region. For *n* see Table 2.

Region	Forest cover	Flow	pH		pH_{BT}	ΔpH		ANC		Al^{n+}		DOC	
			Mean	Range		Mean	Range	Mean	Range	Mean	Range	Mean	Range
West	All	Base	7.13	4.43–7.91	2	–	–	676.7	37–2155	66.0	1–219	10.2	2–33
		Storm	6.01	4.00–7.22	15	1.13	0.22–2.50	195.1	0–540	121.4	14–388	16.4	6–34
	NF	Base	7.44	7.19–7.85	0	–	–	761.6	331–1494	22.9	5–48	5.4	2–11
		Storm	6.48	5.80–7.22	0	0.76	0.02–2.33	210.9	56–506	77.4	14–211	11.4	6–17
	LF	Base	6.92	5.42–7.91	1	–		590.3	37–2155	91.9	11–219	11.6	2–21
		Storm	5.74	4.56–7.15	11	1.13	0.40–2.51	176.2	0–540	142.8	85–313	17.1	7–31
	HF	Base	7.05	4.43–7.89	1	–		707.6	121–1733	80.3	1–184	14.2	5–33
		Storm	5.78	4.00–6.99	4	1.48	0.28–3.10	204.7	31–435	152.0	47–338	23.2	14–34
East	All	Base	6.12	5.03–6.94	9	–	–	106.8	8–254	135.8	43–278	7.6	2–25
		Storm	4.66	3.93–6.09	52	1.41	0.07–2.17	73.6	−49–204	287.3	63–581	18.6	9–34
	NF	Base	6.05	5.12–6.94	3	–	–	111.4	37–219	139.8	43–268	10.1	3–25
		Storm	4.63	4.09–6.09	20	1.34	0.07–2.07	78.4	−1–128	180.8	63–348	19.0	9–34
	F	Base	6.16	5.03–6.91	6	–	–	104.4	8–254	133.6	43–348	6.3	2–34
		Storm	4.68	3.93–5.59	32	1.45	0.46–2.17	70.3	−49–167	359.5	118–581	18.3	10–30
South	All	Base	7.19	6.61–7.82	0	–	–	348.9	78–770	40.6	5–143	5.6	1–15
		Storm	6.03	4.06–7.05	15	1.17	0.02–3.10	190.3	56–549	98.5	15–218	13.9	3–26
	NF	Base	7.21	6.73–7.82	0	–	–	361.1	174–512	14.3	5–27	2.6	1–7
		Storm	6.45	5.02–7.05	2	0.96	0.22–1.55	207.7	66–548	70.9	27–137	9.7	3–17
	LF	Base	7.23	6.84–7.61	0	–	–	343.2	171–534	42.0	17–95	6.9	3–12
		Storm	6.10	4.86–6.70	3	1.15	0.51–2.33	189.5	72–431	93.4	16–199	12.9	5–18
	HF	Base	7.16	6.61–7.67	0	–	–	343.9	18–770	56.6	21–143	6.8	2–15
		Storm	5.70	4.06–6.80	10	1.38	0.50–2.50	178.8	56–549	120.0	15–218	17.3	5–26

All = all sites, NF = no forest cover, LF = low forest cover, HF = high forest cover, F = pooled low and high forest cover.

3.3. Causes of episodic acidification

3.3.1. Regional differences

The percentage loss of alkalinity during acidic episodes attributable to base-cation dilution varied between the three regions. The west (median: 46.9%, range: 6–82%) and south (median: 53.5%, range: 1–97%) had significantly greater (Kruskal–Wallis test: $H_{2,150} = 53.76$, $P<0.001$) base-cation dilution than that in the east (median: 20.5%, range: 0–42%). When strong acid anions were examined most of the anion contribution to the storm-flow chemistry in all three regions was due to Cl^- during storm-flow. Contributions were significantly higher (Kruskal–Wallis test: $H_{2,163} = 55.93$, $P<0.001$) in the order west (mean: 61%, range: 24–86%) > south (mean: 44%, range 17–63%) > east (mean: 40%, range: 22–56%). However, for the most part, all increases in Cl^- were balanced by Na^+ at all sites in the south and the east, with the exception of one storm event recorded at WM9 (10 November 2010). Conversely, in the west six possible sea-salt effects were recorded during episodic storm-flow events. Four sites had one possible sea-salt event (MM5, MM8 and MM12 on 26 March 2010 and MM10 on 26 November 2010), while MM2 had two (on 11 and 26 November 2010).

The contribution of other acid anions differed spatially between regions with strong organic acids (OA) significantly higher (Kruskal–Wallis test: $H_{2,163} = 116.43$, $P<0.001$) in the order east > south > west (Table 5). Excess sulphate (xSO_4) was significantly higher in the order east > west > south (Kruskal–Wallis test: $H_{2,163} = 33.29$, $P<0.001$). Marine derived sulphate (mSO_4) contributions were significantly higher (Kruskal–Wallis test: $H_{2,163} = 55.93$, $P<0.001$) in the order west > south > east, while the proportional contribution of nitrate (NO_3) in the east was significantly higher (Kruskal–Wallis test: $H_{2,163} = 18.85$, $P<0.001$) than that observed in the west and south (Table 5).

3.3.2. Effect of forest plantations

In the west, base-cation dilution was significantly greater (Kruskal–Wallis test: $H_{2,52} = 8.73$, $P = 0.01$) in non-forested streams (median: 62.4%) than in either the LF or HF streams (LF median: 35.6%, HF median: 50.7%). In the east, the opposite occurred with the F streams (median: 20.1%) which had a significantly greater base-cation dilution (Mann–Whitney: $Z = -2.69$, $P<0.001$) compared to the NF streams (median: 13.1%). However, in the south, base-cation dilution in NF streams (median: 59.2%) was significantly greater (Kruskal–Wallis test: $H_{2,59} = 12.16$, $P<0.01$) than that in both the LF streams (median: 42.1%) and the HF streams (median: 34.5%).

Differences in Cl^- contributions with respect to forest cover in any of the three regions were not significantly different ($P>0.05$). Other strong anion contributions across forest cover within each region varied (Fig. 3). In the west, only OA contributions to episodic storm water (Kruskal–Wallis test: $H_{2,53} = 13.37$, $P = 0.001$) was significantly higher with the presence of conifer forest compared to the NF streams, although the amount of forest cover was not significant (Table 5, Fig. 3a). Contributions of mSO_4, xSO_4 and NO_3 to alkalinity loss during storm-flow events did not change significantly ($P>0.05$) across forest cover (Table 5, Fig. 3a). In the east, only NO_3 contributions to episodic storm-water were significantly higher (Mann–Whitney test: $Z = -2.71$, $P<0.01$) with the presence of forest within the catchment (Table 5, Fig. 3b), while in the southern sites, the only significant forest cover differences in acid anion contributions during episodic storm events were recorded for OA (Kruskal–Wallis test: $H_{2,62} = 8.59$, $P<0.05$), with higher contributions in HF streams compared to NF streams (Table 5, Fig. 3c).

4. Discussion

The study of episodic acidification across Europe and North America suggests widespread geographical variation in its magnitude, nature and drivers (Evans et al., 1995; Lepori et al., 2003). Episodic acidity has previously been typical of peat-covered, low-order catchments in Ireland, with plantation forests previously found to exacerbate the levels of acidity due to enhanced scavenging of acidic sulphur and nitrogen compounds (Allott et al., 1997; Cruikshanks et al., 2008; Kelly-Quinn et al., 1996, 2008). During this study almost all sites examined recorded circumneutral pH values in base-flow conditions, while the majority of NF sites in the west on metamorphic geology and south on sedimentary geology maintained pH values above 5.5 for the most part during episodic storm-flow events. However, despite low anthropogenic deposition, forest cover had an effect on pH with values generally decreasing with increasing forest cover in storm-flow conditions in both these regions. In contrast, both NF and F streams in the east became episodically acidic (pH<5.5) during storm-flow. Similar results were reported previously

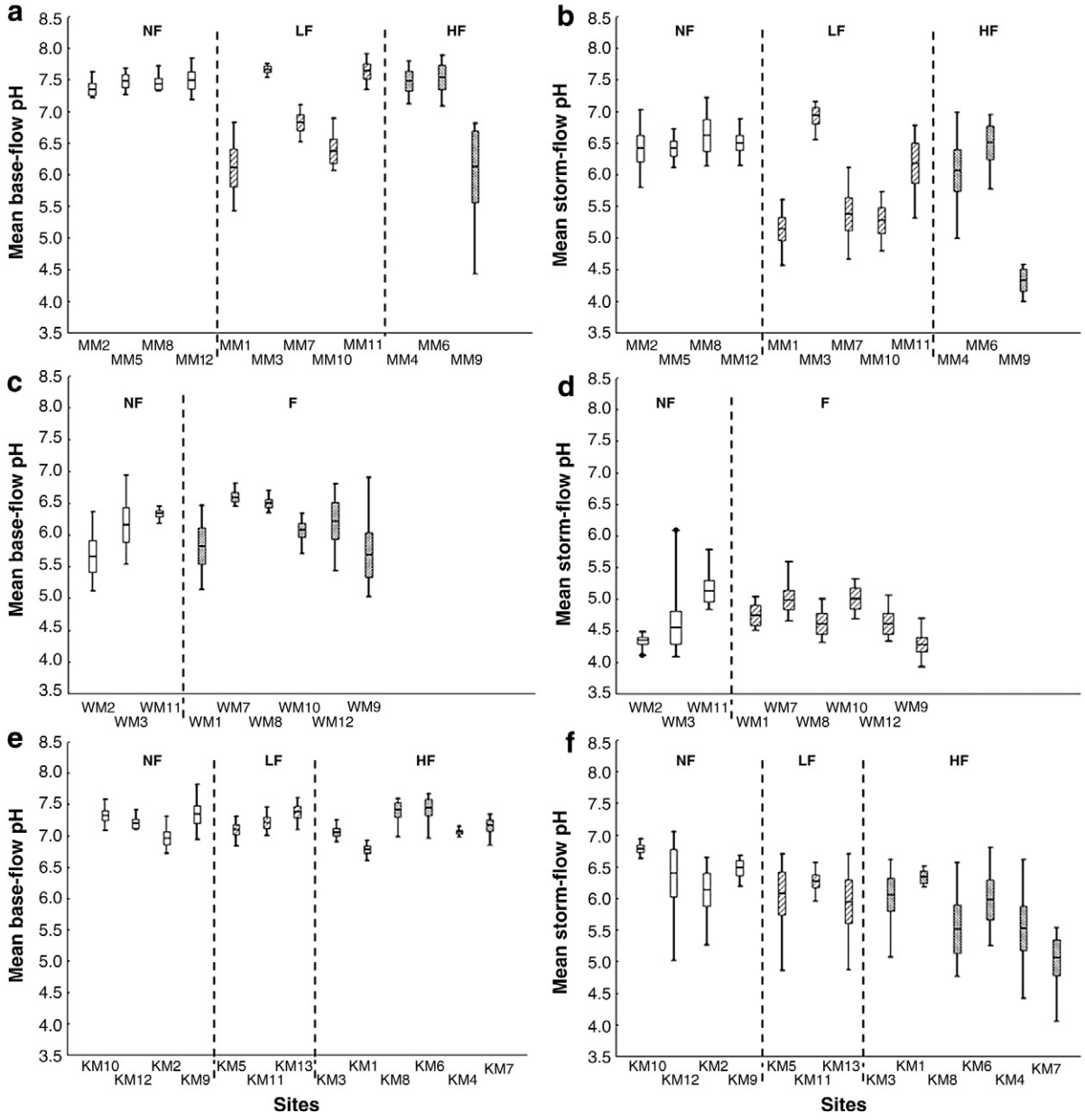

Fig. 2. Mean pH (box: ±SE, error bars: min–max) of base- and storm-flow for all sites; the west (a, b), the east (c, d) and south (e, f). Closed black circles represent outliers. Streams are ordered and separated by forest cover: NF = no forest cover, LF = low forest cover, HF = high forest cover, F = pooled low and high forest cover.

for the eastern regions and are most likely related to extremely base-poor catchments associated with igneous geology and peaty soils found in the east (Aherne et al., 2002; Kelly-Quinn et al., 1996).

The mean pH difference between base to storm-flow (ΔpH) reflected catchment buffering capacity, with sites in the east on base-poor igneous geology recording greater changes than those in the west and south on more alkaline metamorphic and sedimentary geologies. Within all three regions the mean ΔpH was greater with increasing forest cover, although forest cover differences in the west and east were not statistically significant. This is contrary to previous studies in the south of the country where forest cover was found to have little or no effect on stream water chemistry (Clenaghan et al., 1998; Giller et al., 1997; Giller and O'Halloran, 2004) during a period of higher anthropogenic deposition. The numbers of acidic events with a pH below 5.5 (pH_{BT}), known to be the lower threshold for acid-sensitive biota (e.g. Sutcliffe and Hildrew, 1989; Kowalik and Ormerod, 2006), were significantly higher in the east compared to the west and south. However, the number of pH_{BT} events increased when plantation forest was present in all three regions.

In the present study the majority of acidic events involved titrated anions, of which strong organic acids (OA) predominated and mirrored changes in pH observed across the three regions. This is not unusual; in Scandinavia, for example, organic acidity may episodically depress pH by up to 2 pH units (Laudon et al., 2001) while OA was the dominant source of acidity in 56% of Irish upland lakes sampled in 1997 (Aherne et al., 2002). The influence of OA was seen particularly in the east and south. In the west, both xSO_4 and OA contributions were generally similar, but pH only dropped when OA increased and tended to be in association with increasing forest cover. This is supported by the fact that xSO_4 concentrations changed relatively little across forest cover classes. This trend was also observed in the south, with increasing OA and decreasing pH when plantation forest was present, while xSO_4 concentrations remained similar. No significant forest cover effects were seen for OA in the east. Comparable

Table 5
Percentage contributions (mean with ranges in parentheses) of selected strong acid anion fractions to the total ionic content of episodic storm-flow water across land-use in all three regions. For *n* see Table 2.

Region	AA	All	NF	LF	HF
West	OA	9 (0–21)	7 (4–14)	10 (3–17)	12 (6–21)
	xSO_4	6 (0–8)	7 (1–23)	6 (1–16)	6 (0–14)
	mSO_4	6 (2–9)	6 (4–8)	7 (2–9)	6 (5–8)
	NO_3	1 (0–13)	1 (0–13)	1 (0–6)	1 (0–4)
East	OA	49 (27–81)	54 (32–81)	46 (27–70)[a]	–
	xSO_4	10 (4–19)	10 (4–19)	10 (5–17)[a]	–
	mSO_4	4 (2–6)	4 (2–5)	4 (2–6)[a]	–
	NO_3	2 (0–5)	1 (0–3)	2 (0–5)[a]	–
South	OA	21 (5–46)	16 (5–30)	21 (8–44)	25 (8–46)
	xSO_4	8 (4–17)	9 (4–16)	8 (5–17)	8 (5–14)
	mSO_4	5 (2–7)	4 (2–6)	4 (2–6)	5 (2–7)
	NO_3	2 (0–7)	2 (0–7)	2 (0–7)	1 (0–5)

AA = acid anion, All = all sites, NF = no forest cover, LF = low forest cover, HF = high forest cover, OA = organic acids, xSO_4 = excess non-marine sulphate, mSO_4 = marine sulphate, NO_3 = nitrate.
[a] Pooled low and high forest sites in east.

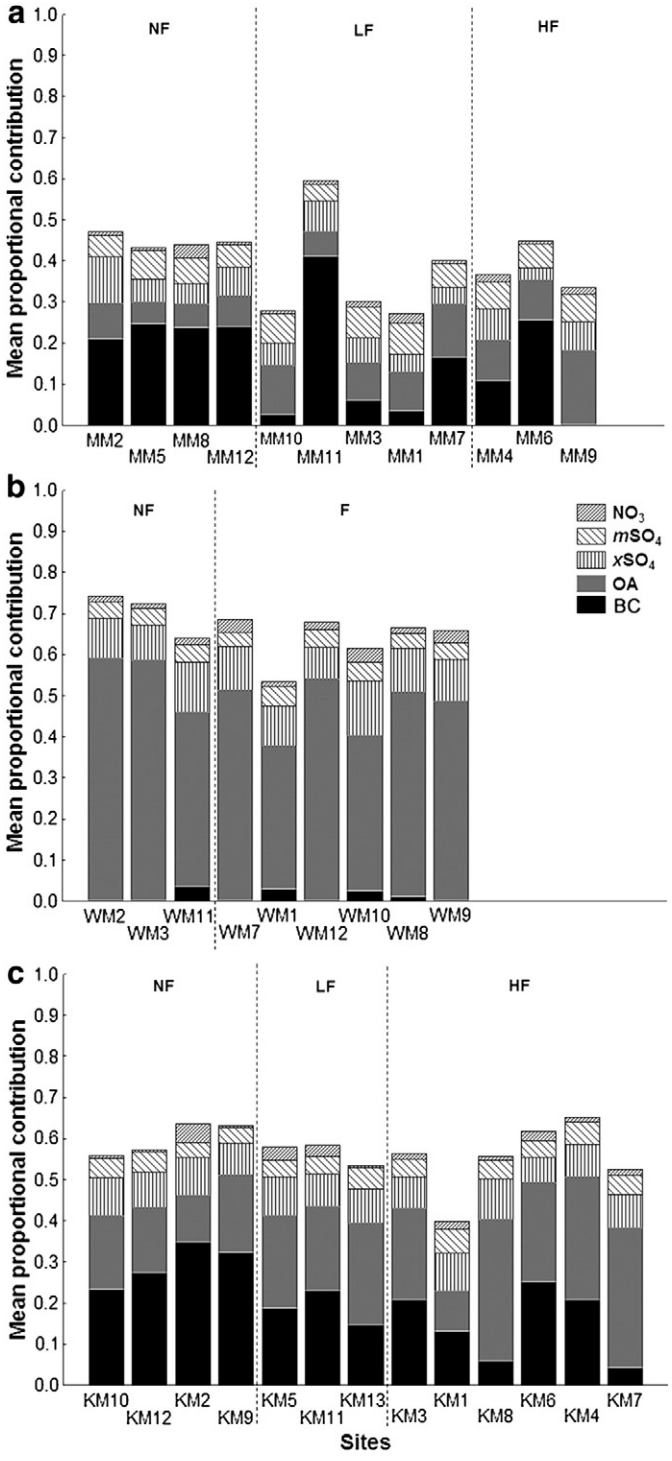

Fig. 3. Mean proportional contributions of base-cations (Alk/$\sum$cations) and acid anion fractions (anion/$\sum$AA) to storm-flow water in (a) the west (n = 12 sites, 53 storm samples), (b) the east (n = 9, 48 storm samples) and (c) the south (n = 13, 62 storm samples). Legend applies to all three plots: NO_3 = nitrate, mSO_4 = marine sulphate, xSO_4 = excess non-marine sulphate, OA = organic acids, BC = base-cations. Streams are ordered and separated by forest cover: NF = no forest cover, LF = low forest cover, HF = high forest cover, F = pooled low and high forest cover. Alk = alkalinity, $\sum$AA = sum of NO_3, mSO_4, xSO_4, Cl^- and OA.

NF/F contributions in this region may reflect historical land practices (e.g. peat extraction) within some NF areas examined, although Kelly-Quinn et al. (1996) previously found that OA largely accounted for the pH changes during storm-flows in NF catchments during the early 1990s, with the exception of prolonged easterly airflows when xSO_4 and NO_3 predominated. In the west, during the same period, OA contributed to 75% of the acidic events recorded in peaty catchments and in some instances the contribution of OA in forested streams was twice that of comparative NF catchments (Allott et al., 1997). Interestingly, Giller and O'Halloran (2004) state that no forest-related chemical differences were recorded in the south of Ireland during studies in the 1990s, in contrast to observed OA concentrations during this study. Internationally, these results are contrary to many recent studies in the UK and elsewhere (e.g. Kowalik et al., 2007; Lepori et al., 2003; Laudon and Norton, 2010; Malcolm et al., in press; Monteith et al., 2010; Ormerod and Durance, 2009) where OA is relatively low and inorganic acidity still predominates.

Generally, mean concentrations of DOC seem to have increased across all three regions since the 1990s, irrespective of forest cover, with ~35% increase in the east for example (see Kelly-Quinn et al., 1996 for 1990s values). Similarly, a recent study on Irish upland lakes reported increases in DOC concentrations (although not statistically significant) over a ten year period from 1997 to 2007 (Burton and Aherne, 2012). Such trends are consistent with long-term trends seen elsewhere, with continual monitoring of surface waters in the UK and Europe showing a strong trend in increasing DOC concentrations since the early 2000s (e.g. Davies et al., 2005; Harriman et al., 2001, 2003; Monteith et al., 2010; Skjelkvåle et al., 2003). Many explanations from climatic changes (e.g. Clark et al., 2005; Evans et al., 2005; Freeman et al., 2001; Tipping et al., 1999), to persistent and increased nitrogen interception (Findlay, 2005; Harriman et al., 1998; Pregitzer et al., 2004), reductions in sulphate inputs, and sea-salt events (Chapman et al., 2008; Dawson et al., 2009; Evans et al., 2006, 2008b; Moldan et al., 2012; Monteith et al., 2007, 2010), as well as changes in hydrology and changes in land-use have been suggested as possible reasons (Evans et al., 2005).

Base-cation dilution was a stronger driver of alkalinity loss during episodic storm events and was higher in the west and south regions compared to that of the east; with up to 82 and 97% dilution recorded in the west and south, respectively, in comparison to a maximum of 42% in the east. Small headwater catchments in base-poor regions are naturally dilute and acidic owing to heavy rainfall and the limited capacity of the soils and bedrock to neutralise acidity (Neal et al., 2010; Waters and Jenkins, 1992). Forest cover differences in the west and south reflected higher dilution in non-forested streams. This may be due to the lower water yields in forested catchments (e.g. Nutter, 1979; Robinson et al., 1998). However, higher dilution occurred in the forested catchments in the east most likely related to higher slopes

and increased and modified drainage networks within the forest plantations (Kelly-Quinn et al., 1996; Robinson, 1998). Many studies throughout Europe and North America have indicated dilution related acidification (e.g. DeWalle and Swistock, 1994; Kline et al., 2007; Laudon et al., 2001, 2004; Laudon and Norton, 2010; Lepori et al., 2003). Nonetheless, dilution events rarely cause acid episodes with alkalinity or ANC below zero in the absence of elevated strong acid anion concentrations (Evans et al., 2008a).

Most of the anion contributions to episodic storm water chemistry in this study were Cl^-. However, Cl^- anion acidity from sea-salt events was rare during our study period, and was site specific, generally associated with streams in the west. No statistically significant forest cover differences were found in this study, although Cl^- increased slightly with increasing forest cover. Previous studies have indicated that sea-salt effects in forests (both deciduous stands and conifer plantations) in maritime regions are likely to be relatively common for a variety of reasons, including increased interception, generally base-poor soils and higher base-cation uptake (e.g. Farrell et al., 1998; Hindar et al., 1995). Burton and Aherne (2012) recently observed high inter-annual variation in sea-salt inputs in an examination of upland lakes in Ireland, while sea-salt events in acid-sensitive regions of the UK vary with climate and seem to be cyclical (e.g. Evans et al., 2008b; Kowalik et al., 2007; Monteith et al., 2007, 2010).

The contributions of xSO_4 and NO_3 to alkalinity loss in storm water in the east were higher than in the west and south. Similar trends were found in the 1990s, and were associated with easterly air flow carrying atmospheric pollution from the UK and the European mainland (Aherne et al., 2000; Allott et al., 1997; Bowman, 1991; Bowman and McGettigan, 1994; Giller et al., 1997; Kelly-Quinn et al., 1996). However, in this study neither pollutant was found to act as a dominant driver of acidity/alkalinity loss as in the 1990s when xSO_4 and NO_3 explained >59% of the change in H^+ during storm-flow conditions in studied streams and rivers (Kelly-Quinn et al., 1996) and approximately 25% in upland lakes (Aherne et al., 2002). This supports the evidence for reductions in the interception and deposition of these anthropogenic air pollutants since the 1990s, as found in upland lakes in Ireland (Burton and Aherne, 2012). While xSO_4 and NO_3 dominated events are likely to occur, evidence from this study suggests that they are now uncommon in Irish headwaters. However, elsewhere in many regions of the northern hemisphere, deposition and interception of xSO_4 and NO_3 continue to predominate in episodic acid events, even though concentrations of xSO_4 and NO_3 have generally decreased over the past 20-years (e.g. Deyton et al., 2009; Kowalik et al., 2007; Lepori et al., 2003; Laudon and Norton, 2010; Malcolm et al., in press; Monteith et al., 2010).

Inorganic aluminium concentrations increased with increasing forest cover in all three regions with highest values seen in streams draining HF. This has consequences for the ecological health of streams due to the known toxic effects on biota (e.g. Driscoll et al., 1980; Ormerod et al., 1993). Previous research in Ireland found that Al^{n+} concentrations increased with increasing forest cover, with up to 587 $\mu g\ l^{-1}$ observed (Allott et al., 1997; Kelly-Quinn et al., 1997). Similar results were found in the UK, although maximum ranges were often higher (up to and above 700 $\mu g\ l^{-1}$) (e.g. Grieve, 1991; Grieve and Marsden, 2001; Harriman and Morrison, 1982; Kowalik et al., 2007; Neal et al., 1990; Ormerod et al., 1987; Puhr et al., 2000). The current range of Al^{n+} concentrations recorded during storm-flow is lower than that recorded during the 1990s, (see Allott et al., 1997; Giller et al., 1997; Kelly-Quinn et al., 1996, 1997), with comparable results reported in the UK, although plantation forest still seems to be associated with higher concentrations (e.g. Monteith et al., 2010). The higher concentrations observed in HF catchments are most-likely a result of two possibilities; the slow reduction of historically higher Al^{n+} concentrations in forested catchments compared to NF streams, and/or the larger reductions in xSO_4 inputs in forested catchments, although it must be noted that some increases in Al^{n+} are poorly understood to date (Monteith et al., 2010).

5. Conclusions

This study indicates that episodic acidification of Irish headwater streams is predominantly driven by organic acidity, followed by base-cation dilution demonstrating that the mechanisms and drivers have changed substantially, with reductions in the influence of both xSO_4 and NO_3. Interestingly, only organic anion concentrations increased with the amount of forest cover, with many HF streams in the south, previously unaffected by episodic acidification (e.g. Giller et al., 1997), now regularly recording pH values ≤5.5. Although, the estimation of OA concentrations from DOC is subject to uncertainties (see Evans et al., 2008b for more details), the increase in DOC concentrations is having a direct effect on the pH of headwater streams draining peaty soils in Ireland. International evidence (e.g. Davies et al., 2005; Deyton et al., 2009; Evans et al., 1995, 2008a, 2008b; Kowalik et al., 2007; Laudon et al., 2004; Laudon and Norton, 2010; Lepori et al., 2003; Ormerod and Durance, 2009; Stendera and Johnson, 2006; Soulsby, 1995; Wellington and Driscoll, 2004) suggests that reductions in xSO_4 deposition, varying sea-salts effects and changing climate are influencing DOC concentrations in episodic storm-water. However, altered land cover may also be influencing the increased loss of DOC in catchments through alterations to the hydrological regime, and other processes such as soil/peat disturbance as seen in both moorlands and forested catchments in the east of Ireland.

The increases in OA have partially offset the effects of declining xSO_4 deposition in surface waters in the UK and Ireland, reducing the magnitude of recovery from acidification in terms of rising alkalinity and pH, and declining inorganic aluminium concentrations (Chapman et al., 2008; Dawson et al., 2009; Evans et al., 2008b; Monteith et al., 2007; Posch et al., 2008). Although counter intuitive, such responses by OA are essential in our understanding of the chemical response to declining acid deposition and recovery from acidification (Evans et al., 2008b), especially in the east where xSO_4 deposition was historically higher (see Kelly-Quinn et al., 1996, 1997). On the other hand, the increases in DOC in the historically lower-deposition regions, as in the west and south, indicate that other factors, such as land cover change from moor to forest, declining sea-salt deposition and/or climatic change, may in fact be resulting in greater stream acidification at present (Evans et al., 2008b; Moldan et al., 2012) compared to previous findings in these regions. The difference in DOC drivers is an important factor in our understanding of recovery from acidification as OA increases resulting from changes not related to changing acid deposition can be considered to have delayed chemical recovery (Evans et al., 2008b), and potentially result in stream acidification in regions previously unaffected by acid deposition as in the south of Ireland.

Indeed, the presence of subtle but potentially relevant variations caused by catchment characteristics among the regions as discussed above may warrant further investigation as further potential decreases in acidic deposition, and greater variation in climate, highlighted by several studies (e.g. Butler et al., 2007; McElwain and Sweeney, 2007; Sweeney et al., 2003, 2008), are likely to increase the variability in the nature and drivers of episodic stream acidification across different land types, especially regarding DOC concentrations and sea-salt episodes, potentially confounding any positive responses to future reductions in acid deposition (Burton and Aherne, 2012) or measures targeted at forest practices. As such, the continuation of studies such as this one will become increasingly important to address surface water acidification in the future.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2012.10.074. These data include Google maps of the most important areas described in this article.

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