

Forest land cover continues to exacerbate freshwater acidification despite decline in sulphate emissions.

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Abstract

Evidence from a multi-date regional-scale analysis of both high-flow and annual-average water quality data from Galloway, south-west Scotland, demonstrates that forest land cover continues to exacerbate freshwater acidification. This is in spite of significant reductions in airborne pollutants. The relationship between freshwater sulphate and forest cover has decreased from 1996 to 2006 indicating a decrease in pollutant scavenging. The relationship between forest cover and freshwater acidity (pH) is, however, still present over the same period, and does not show conclusive signs of having declined. Furthermore, evidence for forest cover contributing to a chlorine bias in marine ion capture suggests that forest scavenging of sea-salts may mean that the forest acidification effect may continue in the absence of anthropogenic pollutant inputs, particularly in coastal areas.

Keywords: Freshwater acidification; Forestry; Diffuse pollution; Regional scale analysis; long-term analysis; Remote Sensing; Galloway; Great Britain; Scavenging; Scotland

Capsule

Relationships between forest land cover and freshwater pH continue to be evident despite declines in anthropogenic pollutant sulphate deposition; sea-salt scavenging may play a role.

Introduction

Diffuse pollution poses a major challenge for environmental management. In the context of the forest environment, the forest acidification effect has long linked forest land cover with increased stream acidity and deleterious impacts on freshwater ecology. This is particularly pertinent when large scale afforestation takes place in acid sensitive areas, as changes of land use to forestry can tip the balance towards acidic freshwaters. The introduction of the Water Framework Directive (WFD; 2000/60/EC) and similar legislation (e.g. US Clean Water Act, 1997) requires diffuse pollution to be managed in a way that promotes good ecological status. However, to effectively manage environmental pollution it is important to have a clear understanding of the form that pollution takes and the mechanisms that drive it.

40 Freshwater acidification occurs when the buffering capacity of a water body is exceeded by
41 acid inputs external to the system. Historically, long-term acidification has resulted where
42 anthropogenic, atmospheric sulphur and nitrogen compounds have tipped the acid-base
43 balance of freshwater systems (Henriksen, 1980). In addition, episodic acidification also
44 occurs in response to individual natural events particularly during high-discharge or sea-salt
45 events, or following droughts (Hindar *et al.*, 2004; Laudon, 2008; Erlandsson, 2010). The role
46 of the forest land use in acidification, the “forest acidification effect”, is *in addition to* these
47 mechanisms. Early paired catchment studies showed that sites under forest land cover were
48 more acid than moorland sites on similar geologies with similar deposition conditions
49 (Harriman and Morrison, 1982; Stoner *et al.*, 1984). The primary mechanism to which this
50 forest acidification effect has been attributed is the enhanced filtration of airborne sulphur and
51 nitrogen compounds as a result of the increased surface roughness of forest canopies: the
52 forest scavenging effect of Fowler *et al.* (1989).

53

54 Since 1990, however, levels of atmospheric pollutants have reduced significantly as a result
55 of international protocols (e.g. CLRTAP, 1979; Gothenburg Protocol, 1999). In the UK, this
56 has corresponded to a reduction in output of both airborne sulphur (91%) and nitrogen
57 (~50%) (ROTAP draft, 2010). These reductions have led many authors suggest that the
58 impact of forestry on acid waters will decline (Nisbet *et al.*, 1995; Neal *et al.*, 2004; Gagkas *et al.*,
59 2007). Conversely, studies looking at the long-term recovery of forest ecosystems have
60 continued to raise the issue of an ongoing impact of forests on freshwaters (Helliwell *et al.*,
61 2001; Harriman *et al.*, 2003; Langan and Hirst, 2004; Neal *et al.*, 2010; Feeley *et al.*, 2010)
62 and despite evidence for recovery at many UK acid waters monitoring sites, three of the five
63 sites with forested catchments show no evidence of recovery and one shows ongoing
64 deterioration (Davies *et al.*, 2005). Part of the difficulty in assessing the impact of forests on
65 acidification is the lack of datasets designed specifically to address diffuse pollution. Paired
66 catchment approaches (Langan and Hirst, 2004; Ormerod and Durance, 2009; Neal *et al.*,
67 2010) are site specific and do not address the regional scale at which the pollution operates.
68 However, regional studies are difficult to implement and are, as a result, rare (Wright and
69 Henriksen, 1980; Harriman *et al.*, 1987; Ormerod *et al.*, 1989, Buffam *et al.*, 2007; Ågren *et al.*,
70 2010). This is particularly true for regional surveys that deliberately target individual
71 high-flow events where forest impacts on episodic acidification are expected to be the greatest
72 (Puhr *et al.* 2000) and none have addressed long-term changes in the forest acidification effect
73 in this manner.

74

This paper aims to address this gap in knowledge directly by quantifying differences in freshwater quality between land uses at the scale of Galloway forest district. Eight regional-scale water quality datasets are collected from 1989 to 2006, three of which specifically target high-flow conditions. These data are then analysed using both simple linear and multiple regression analyses to answer the following questions:

- a) Are there significant differences between water quality between forest and moorland sites under conditions of decreased deposition?
- b) To what extent is sulphate deposition still the driving mechanism behind the forest acidification effect?
- c) What are the implications of these findings for the management of diffuse pollution risks?

Study Area and Regional Context

The study focuses on the seven major catchments of Galloway Forest District in South West Scotland (Figure 1). Galloway Forest District has played an important role in the international research into freshwater acidification and the forest acidification effect since the early years of the acid rain debate (Wright and Henriksen, 1980; Harriman and Morrison, 1982; Battarbee (1984); Helliwell *et al.*, 2001; Puhr *et al.*, 2000; Langan and Hirst, 2004). Afforestation began in the 1940s but peaked 1960-1980; it is now the largest productive forest in the UK boasting 97,000 ha of production forest within a considerably wider forest park. The majority of plantations are still Sitka spruce monocultures (*Picea sitchensis*) or mixtures with lodgepole pine (*Pinus contorta*). Soils are generally thin, and consist primarily of podzols and peaty podzols; a large proportion of the uplands are covered by blanket peat (Bown *et al.*, 1982). Non-forest areas are generally peat moorland, with some small patches of rough and improved grassland in the Galloway lowlands.

The Galloway region receives relatively small inputs of sulphate ($<21 \mu\text{eq l}^{-1} \text{SO}_4$ in rainfall 1997, Figure 2A-B). Nonetheless, the poor buffering capacity of the region's geology makes the area naturally acid sensitive. The most acid-sensitive local lithologies are igneous extrusions of tertiary granite; Ordovician shales, mudstones and greywackes are also shown to be acid-sensitive but local Silurian rocks (also shales, mudstones and greywacke) are relatively well buffered (Puhr *et al.*, 2000; Figure 2C).

Regional pollutant sulphate deposition is greatest in the upland regions of the Cree, Dee and Fleet catchments and decreases towards the coast (Figure 2D-F). All forest cover enhances the "dry deposition" of pollutant directly from the atmosphere, however, this transfer is significantly greater where it is exposed to cloud moisture (Fowler *et al.*, 1989) an effect more

common at altitudes over 300m (Forestry commission, 2009). Nevertheless, the impacts of acidification have been widespread and severe across Galloway, with many rivers losing a significant proportion of their salmon and trout populations even in areas with very small proportions of their catchments over 300m, and distant from the main centre of the pollutant deposition (Galloway Fisheries Trust, 1989). This emphasises the disparity between the upland areas where sulphate scavenging would be expected to play the greatest role in enhancing acidification and the areas where the ecological impacts are most severe.

Materials and Methods

This paper takes a regression-based approach to determine the relationships between land use and water quality variables (Ormerod *et al.* 1989; Kelly-Quinn *et al.*, 1996; Puhr *et al.*, 2000; Buffam *et al.*, 2007; Ågren *et al.*, 2010). Linear regression is used to investigate the relationships between forestry and individual variables; stepwise multiple regression is used to determine the relative influence of forestry amongst other catchment variables. The approach uses eight regional-scale water quality datasets, three collected under high-flow conditions during individual storm events and five drawn from annual averages of records from long-term Scottish Environmental Protection Agency (SEPA) monitoring sites.

Water chemistry data

This paper uses a reanalysis of the data of Puhr *et al.* (2000) as an indication of water quality status in Galloway under conditions of higher deposition; the data were collected on 12th March 1996 for 93 sites during a single storm event. High-flow events were targeted as they commonly promote acid episodes (Welsh and Burns, 1987; Puhr *et al.*, 2000; Laudon *et al.* 1999; Erlandsson *et al.*, 2010). Catchments were selected to represent a range of catchment afforestation (0-100%) and to be as uniform as possible in terms of geology. Two additional datasets were collected during storm events on 16th March 2005 and 8th March 2006. The surveys used the methodology and sites of Puhr *et al.* (2000) with 17 additional sites, a total of 110. In terms of hydrology, the 1996 and 2005 surveys caught the peak of the storm; in 2006 the falling limb was sampled (Figure 3); both the 2005 and 2006 surveys had lower discharges than the 1996 event. In addition, the 1996 and 2005 events have lower mean pH ($pH_{\mu} \approx 4.7$) than the 2006 event ($pH_{\mu} = 5.5$) (Table 1). Furthermore, the 2005 survey shows significant chlorine bias to marine ions ($Na:Cl=0.79$), suggestive of significant sea-salt inputs. Long-term monitoring data from forty-two SEPA monitoring sites were identified and pH data were extracted for analysis. Annual median values were calculated for sites where four or more values were available per year.

Laboratory analysis for the 2005/6 high-flow data used a Dionex DX500 with an EG50 eluent generator with an LC25 chromatography oven to maintain temperature. 2mm AS17 and AG17 columns were used for and both anions and cations analysis. A YSI 556 multi-parameter probe designed for low-ionic strength waters was used to measure pH. The long-term SEPA water quality data used AQUA 800 colorimetric methods for anion analysis and a Varian Vista Pro ICP-OES spectrometer for cations; pH was measured by titration. Both Durham and SEPA labs applied standard methods for Alkalinity and DOC.

The following 13 water quality variables were compiled:

- pH;
- major anions: sulphate (SO_4^{2-}), chloride (Cl^-) and nitrate as nitrogen ($\text{NO}_3\text{-N}$);
- major cations: sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+);
- alkalinity (alk) and
- dissolved organic carbon (DOC).
- sodium:Chloride ratio (Na:Cl),
- charge balance ANC (ANCcb: major cations – major anions / major cations + major anions)
- *Forest and Water Guidelines* Critical Load Exceedance (CLX: following Gagkas, 2007; Nilsson and Grenfelt 1988 using Critical ANC = 0; with 1995 total catchment sulphur deposition)

Forest Cover Data

The height of UK upland forestry plantations can be successfully estimated using optical satellite imagery when matched to contemporary field data (Puhr and Donoghue, 2000; Donoghue *et al.*, 2004; Donoghue and Watt, 2006). The approach of Dunford and Donoghue (2007) was taken whereby a single image:field dataset pair is used to classify a series of radiometrically corrected images. LiDAR forest height data from 2003 was used to generate a model with the shortwave infra-red (SWIR) band of a 2003 spot image ($R^2 = 0.88$, RMSE 1.53m). Five optical satellite images for the years 1989, 1995, 2001, 2003 and 2005 were radiometrically corrected to one another and the SWIR-based height model was applied to each to generate maps of total forest cover for each of the five years; forest was then defined as trees over 2m in height.

Catchment-Based Datasets

Catchment areas were automatically generated for all water survey points using the Ordnance Survey (OS) Panorama 50m Digital Elevation Model (DEM) (OS, 2004) and ArcGIS (ESRI, CA, USA) hydrology tools. These were each verified against OS map data and then used to extract total forest cover for each catchment. Additional datasets were then extracted at the

catchment scale including: Centre for Ecology and Hydrology (CEH) total sulphur deposition; proportions of igneous, Ordovician and Silurian geology (from British Geological Survey (BGS) 1:65,000 digital maps); mean rainfall 1980-2000 (extrapolated from 104 British Atmospheric Data Centre (BADC) sites) and altitude data (mean catchment altitude from the OS Panorama 50m DEM) (Dunford, 2008). The result was a dataset of water quality data linked to catchment variables within the study area. As only five years of forest data were available, only the long-term data for the years 1989, 1995, 2001, 2003 and 2005 were used. For the high-flow data the forest cover from 1995 was used with the 1996 data; forest cover for 2005 was linked to water quality variables of both the 2005 and 2006 surveys. Each water quality site was then classed by its major geology proportion. All high-flow sites had >75% uniform geology. Long-term sites had far greater geological variability and sites with <50% uniform geology were excluded from simple linear regression analysis; this left only the Ordovician geology with sufficient sites for analysis (15-28 sites dependent on the year). However, as many of the 42 sites that had sufficient annual data (>4 records) were included in the multiple regression.

Regression Analysis

For simple linear regression, each geology subset of the eight water chemistry datasets was regressed separately against forest cover (Table 2; Figure 4). The multiple regression approach tried to identify a statistically significant model with total forest cover, total S deposition, rainfall, maximum altitude and the proportion of igneous and Ordovician geology as the predictor variables. A PCA of these variables identifies the main sources of variation within the dataset (Figure 5). The first principal component (PCA1) correlates with increasing altitude, rainfall, sulphate deposition and igneous rock proportion and with decreasing Ordovician rock proportion. The total forest cover variable has very little correlation with PCA1 suggesting it is independent of the main pattern of dataset variation. For multiple regression, a reflexive, stepwise approach was used and variables were added to the regression model in order of the contribution they play to the overall explanation of the variance within data (R^2) using $P < 0.001$, $P < 0.01$, and $P < 0.05$ as significance limits. The final model is the model with the greatest statistical significance (lowest P value) in which Total Forestry played a statistically significant contribution (Table 3). If no model significant at $P < 0.05$ was identified using an additive approach, all variables were included in the model and removed until all model variables played a statistically significant role.

Results and Discussion

Land use differences in a low-deposition climate

Regional-scale freshwater acidity continues to differ between areas of forest and non-forest land cover in Galloway: linear regression identifies statistically significant relationships between forest cover and i) acidic water chemistry in the high-flow surveys 2005/2006 (Table 2) and ii) long-term pH in SEPA datasets for 2003 and 2005 (Figure 4). The differences are identified as positive relationships between forest cover and sulphate, chloride and sodium concentrations and negative relationships with pH, sodium:chloride ratio and charge balance ANC. Multiple regression analyses add support to this (Table 3): total forestry contributes to models significant at $P < 0.001$ for pH in the 2005 and 2006 single-event and 2003 and 2005 long-term surveys. In addition, total forestry contributes to statistically significant models for chlorine, sulphate, charge balance ANC in at least one of the single-event surveys. These relationships are the same as those identified between forest cover and water chemistry in the 1980s and 1990s under high-deposition conditions (Harriman and Morrison, 1981; Harriman and Morrison, 1982; Stoner and Gee, 1985; Ormerod and Edwards, 1985, Kreiser et al., 1990). Moreover, the magnitude of the impacts on pH, reductions of between -0.76 and -1.11 pH units (both geologies), fits well with the results of Ormerod et al. (1989) of an effect between -0.6 and -1.0 units. Furthermore, the findings offer regional-scale support to the interpretation of long-term, single-site studies that have suggested that chemical and biological recovery from acidification may be slower in afforested areas than non-forest ones (Langan and Hirst, 2004; Davies *et al.*, 2005; Ormerod and Durance, 2009).

Although forest cover has a statistically-significant effect on pH, there are a number of other factors to consider when interpreting the results. Firstly, multiple regression identifies geology as the primary driver of Galloway's pH contributing >35% of the explanation of the dataset in both 1996 and 2005 whilst total forest explains 12 and 6% respectively. The Silurian geology appears well buffered with no evidence of relationships with pH, sulphate, marine ions or DOC seen elsewhere. Secondly, differences in the nature of the individual episodes are quite notable: Ordovician sites, which show clear pH trends in 2005, show no statistically significant model for pH during the 2006 event. Furthermore, in 2005 stronger relationships are found with marine ions, as is a statistically significant relationship with DOC that is absent in 1996 and 2006 (Table 2). A number of factors will contribute to these differences, including: impacts of climate change on weather systems (Wright *et al.*, 2006; Wright, 2008); impacts of the North Atlantic Oscillation (NAO) on nitrate and sea salt (Monteith and Evans, 2000; Hindar et al., 2004; Laudon, 2008) as well as the nature of the acid episode (Laudon, 2008; Kroglund et al., 2008; Erlandsson *et al.*, 2010). Finally,

significant scatter remains even following stratification for geology. With the exception of marine ions on igneous sites in 2005, R^2 values are consistently < 0.5 . This is to be expected; interconnected soil, river and rainfall factors will also contribute at the local scale to a site's acidity. This does not diminish the importance of the land use differences as the identified relationships are significant at $P < 0.05$. The forest acidification effect exacerbates existing conditions, with the potential to reduce annual-average pH by -1.19 to -1.81 units and high-flow pH by -0.71 to -1.11 units depending on initial conditions and geology. In addition, the potential to shift local water chemistry over critical thresholds is demonstrated. For igneous sites in 2005, the ANC_{CB} trend (coefficient -0.13 from a y-intercept of 0.05) could change the local system from cation to anion dominant. Similarly, at igneous sites in 2006, a forest-related change in the Na:Cl ratio (-0.13 from a y-intercept of 1.09) shows the potential to change the system from sodium to chloride dominant.

A decline in the land use effect?

The proportion of the pH dataset explained by forest cover in the single-date samples has reduced between 1996 and 2005/6 for both igneous (1996 $R^2=0.36$, 2005 $R^2=0.21$) and Ordovician sites (1996 $R^2=0.19$, 2005 $R^2=0.08$). This may be evidence for a decline in the forest acidification effect, as may the absence of a statistically significant relationship between pH and forestry on Ordovician rocks in 2006. Similar declining R^2 values are seen in all variables with the exception of marine ions on igneous sites between 1996 and the more recent surveys. Furthermore, the proportion of the variation within the pH dataset explained by forestry in multiple regression analyses has decreased from 12% in 1996 to 6% in 2005.

In contrast, the pH records from SEPA's long-term surveys show less evidence for a decrease in the forest acidification (Figure 4). With the exception of 2001 where the relationship was not significant at $P < 0.05$, the relationships between forestry and pH remain relatively consistent: they have similar form, R^2 values in the range $0.25 \leq R^2 \leq 0.39$ and the relationship in 2005 has the highest R^2 of all. Multiple regression analysis of the SEPA data further supports this. Total Forestry is a key explanatory variable for pH in both 2003 and 2005. It is, therefore, difficult to determine the extent to which the decreased R^2 values seen in the high-flow events reflect their individual chemistry or whether the forest acidification effect on overall acidity is in decline.

Mechanisms driving land use differences in acidity

Having identified a significant land use impact on acidity in Galloway it is now necessary to re-evaluate the extent to which sulphate scavenging remains the major mechanism driving the identified trends towards lower pH in forest areas. Many authors have shown that, even in the

absence of sulphate deposition, natural episodic acidification still take place (Kelly-Quinn *et al.*, 1996; Eshleman *et al.*, 2010; Laudon and Norton, 2010). In fact, Laudon and Bishop (1999) estimate that 80% of acid episodes are driven by “natural” factors rather than anthropogenic deposition. Erlandsson *et al.* (2010) studied 258 acid events from 87 Swedish streams (1998-2007) and identified base cation dilution as the major driver for 58% of the episodes studied, followed by increasing sulphate (26%), sea-salt deposition (6%), organic acid (6%) and nitrate (3%). Kline *et al.* (2007) supports this by demonstrating a shift from events driven by increasing inputs of acid anions, to events driven by a dilution of base cations.

We now examine the *role of land use* as a factor with the potential to moderate these drivers either by encouraging additional transfers of sulphate, nitrate, marine or organic anions or by decreasing a water’s ability to mitigate acid transfers that occur due to base cation uptake or flow path modification.

Sulphate

Positive relationships between forest cover and sulphate are identified in all single-date surveys at both igneous and Ordovician sites. These match earlier experimental studies performed within the Galloway region (Harriman and Morrison, 1982; Pühr *et al.*, 2000; Harriman *et al.*, 2003). The continued existence of these trends, found 10 years after the last regional survey, indicate that sulphate transfer to freshwaters is still greater in afforested areas. However, the relationship shows signs of having decreased in strength ($c=15.62^{***}$ in 1996 but $c=5.01^{**}$ and 9.07^{***} in 2005 and 2006 respectively (Ordovician rocks, Table 2). Nonetheless, although the y-intercept is $10 \mu\text{eq l}^{-1}$ lower in 2006 than 1996 and the coefficient in 2006 is half that in 1996, forest cover continues to encourage additional sulphate ions: the coefficient remains positive and significant at $P<0.01$ in both 2005 and 2006. The likely mechanism for the identified decline is the reduction in sulphate scavenging (Mayer and Ulrich, 1974; Fowler, 1989). With 91% less sulphate available (ROTAP draft, 2010) the difference in the magnitude of capture between land uses would be expected to decrease.

Although scavenging of anthropogenic sulphate has long been considered the major driver of additional sulphate in forest waters it is not the only mechanism by which land use may influence sulphate transfer to freshwaters. Forests also scavenge marine sulphate. The multiple regression analysis shows a *negative* relationship between the spatial pattern of sulphate deposition and freshwater sulphate concentration even under the high deposition conditions of 1996. The inverse of this trend reflects a South-Western trend towards coastal

322 areas and may support the thesis of marine-sourced ion capture: an investigation of rainwater
323 chemistry would resolve help to determine the origins of these ions.

324
325 Furthermore, many studies have identified acid episodes as a result of sulphate flushes
326 following droughts (Dillon *et al.*, 1997; Laudon *et al.*, 2004; Laudon and Norton, 2010).
327 Forest drainage and water-uptake by trees can contribute to increased soil drying, particularly
328 immediately following land-use change; additionally, forest floors re-oxidise sulphates which
329 can then be flushed into freshwater systems (Eimers and Dillon, 2002; Eimers *et al.*, 2004).
330 Increased interception and evapotranspiration in forests may also worsen this, particularly in
331 already dry areas (Maitland *et al.*, 1990). However, particularly following droughts, peat bogs
332 are recognised export more sulphate than forests (Eimers *et al.*, 2004). If this were the main
333 mechanism, forest cover would be unlikely to show a positive relationship with sulphate in
334 Galloway. On the other hand, there is potential that catchments with large proportions of
335 waterlogged peat are likely to immobilise sulphate inputs as a result of the prevalence of
336 reducing conditions. A moorland land use effect may result where it is the removal of
337 moorland, rather than the planting of trees, that explains the impacts of afforestation on
338 freshwater sulphate. The Galloway study area includes peat moorlands, mostly in high
339 altitude regions > 600m and the Ordovician Luce, Bladnoch and Cree catchments (Birse and
340 Robertson, 1976). Although rainfall is high (c. 1300 mm yr⁻¹), the extent to which these peats
341 are consistently under reducing conditions is unknown. However, the existence of the
342 sulphate effect on the igneous sites where soils are thin and rock outcrops are common
343 (Welsh and Burns, 1987), suggests that forest-scavenging mechanisms, remain the most likely
344 explanation for the identified sulphate trends.

345
346 Irrespective of the mechanism, it is clear that further conversion of moorland to forest has the
347 potential to transfer additional sulphate anions to rivers. In situations where base cation
348 dilution has made systems sensitive to anion inputs forest-exacerbated acidification may
349 occur. This may be worse still in events directly following long drought periods. To mitigate
350 these impacts more work is needed to determine the source of the ions: Isotope studies
351 (Eimers *et al.*, 2004) would help to determine the relative contribution of anthropogenic to
352 oxidised sulphur from both forest and moorland catchments and help determine whether the
353 effect would be expected to decrease with pollutant levels or increase with climate changes in
354 droughts and storminess. However, for the events presented here, as <10 µeq l⁻¹ of additional
355 anions reach freshwaters at 100% afforested sites in the 2005/2006 surveys sulphate is
356 unlikely to be the sole driver of the differences in pH identified between land uses.

357
358 **Nitrate**

Forest cover contributes to enhanced nitrate leaching as a result of atmospheric NO_x scavenging and following either large-scale felling or tree damage by pests or disease (Neal et al., 1998; Eshleman *et al.*, 1998). In Galloway, however, the lack of any statistically significant relationship with nitrogen in any year, on any rock type, suggests that nitrate leaching is unlikely to be the cause of the differences identified between land uses; any influences of felling or tree damage are localised and short-term or mitigated by good forest management. Forest-enhanced nitrification may however be a more significant in areas with higher nitrogen deposition or greater vegetation disturbance (Eshleman *et al.*, 2004).

Marine ions

Forests capture more marine ions than moorland sites; relationships are positive and highly significant in all surveys. Furthermore they increase with time: chlorine coefficient = 73.87 (1996), 218.38*** (2005) and 132.55*** (2006). Forest-scavenging of sea salts is expected (Fowler, 1989) and identified in other studies (Wright and Henriksen, 1980; Stoner and Gee, 1985; Welsh and Burns, 1987; Ormerod 1989). Furthermore a relationship between Cl:Na ratio and forest cover is identified on Ordovician sites in 2005 and igneous sites in both years and over 60µeq l⁻¹ of additional acid ions are added during the 2005 survey on both sensitive geologies. Additional chloride ions passing through the system will be available to displace additional H⁺ and Alⁿ⁺ anions, encouraging acidity, particularly when base cations have already been diluted. The sea-salt threat to freshwaters has been widely discussed (Welsh and Burns, 1987; Heath *et al.*, 1992; Harriman et al. al, 2003; Neal and Kirchner, 2000; Davies et al., 2005; Laudon, 2008) however, very few studies focus specifically on the role of forest land use in exacerbating these events. Harriman *et al.* (2003) show that for high sulphate deposition catchments with moderate sea salt impacts a 90% forested catchment has the “highest chlorine gradient enhancement of acidity and labile aluminium and also the highest base cation release”. Larsen and Holme (2006) show that afforested spruce catchments encourage larger pH declines and higher Alⁿ⁺ concentrations than natural birch forests even in low sulphate deposition sites in northern Norway. The findings here support the view that the forest scavenging of sea-salts may continue to pose a significant diffuse pollution risk in the absence of any sulphate effects. Furthermore, as sea-salt trends fluctuate with climatic forcing (Hindar *et al.*, 2004; Wright *et al.*, 2006; Laudon, 2008), they are capable of being as strong now as in the past, and are likely to *increase* in significance with climate change (Wright et al., 2006; Whitehead *et al.*, 2009).

Organic acids

Conifer species create humus rich in organic acids with consistently lower pH than both deciduous forest and moorland (Alexander and Cresser, 1995): *Fraxinus excelsior* pH=5.5

Quercus Robor pH=4.4; *Calluna vulgaris* pH=4.5; *Pinus sylvestris* pH=4.0 (Stalfelt, 1972); Sitka spruce (*Picea sitchensis*) pH = 3.6 (Williams, 1983). High-discharge events flushing organic acids from soils to freshwaters, and have led to decreases in pH of more than 1.5 units, particularly where base cations are diluted (Laudon *et al.*, 1999; Serrano *et al.*, 2008). DOC-type also varies dependant on the land use from which it originates; forest-sourced DOC is often lower molecular weight and aliphatic (Ågren *et al.*, 2008), as a result it has higher potential for microbial uptake than peat-sourced carbon leading to both bacterial and photo-degradation which, in turn, also influence pH (Köhler *et al.*, 2008).

The Ordovician forest:DOC relationship in 2005 may show evidence for a greater flushing of organic acids from Galloway forest sites during flood events. Interpretation of this trend is complicated by the controversy over the widespread increases being identified worldwide (Erlandsson *et al.*, 2011). If DOC levels are returning to naturally high levels as a result of recovery from acid deposition (Monteith *et al.*, 2007) the increase in DOC during forest spates may instead reflect greater recovery from acidification taking place under afforested sites in response to the reduction in forest scavenging. Further study is required to determine the exact role of DOC in Galloway, particularly as DOC can reduce negative impacts of aluminium on ecology (Serrano *et al.*, 2008; see below).

Base cation uptake

Forest growth draws base cations, particularly calcium and magnesium, from the soil into the forest matter (Reynolds *et al.*, 2000). The cations taken up are replaced by H⁺ ions which increase pH. In the absence of a strong anion to encourage cation exchange this effect is not expected to influence acidity (Nilsson *et al.*, 1982); however, where mobile anions are input as anthropogenic pollution, organic anions or sea-salts, cation exchange can transfer hydrogen and aluminium ions to freshwaters increasing acidity. In addition forest uptake is likely to exacerbate cation dilution episodes (Erlandsson *et al.*, 2010).

Trends in calcium and magnesium are absent in all surveys on igneous sites, and only a statistically significant *increase* in magnesium is identified at Ordovician sites in 2006 (Table 2); trends are, however, present at Silurian sites in 2005/6. Cation stocks on the base-poor, igneous and Ordovician soils are potentially so depleted that a forest effect is not visible, or base cation dilution may have taken place to such an extent that any trends are hidden. Either way, base-cation removal has the potential to play a part in the land use effect identified in Galloway, but is unlikely to play a large role during acid episodes beyond exacerbating the impacts of external acid inputs.

Hydrological impacts

In addition to chemical impacts, the drainage network under forestry can lead to increased discharge to water courses (Waters and Jenkins, 1992; Kelly-Quinn *et al.*, 1996). This exacerbates base cation dilution for afforested freshwaters and decreases residence times, reducing the potential for buffering. In combination with the additional acid inputs, this leads to H^+ pulses that are longer, more severe and more abrupt at forest rather than moorland sites, particularly where forests are planted on drained peaty catchments (Kelly-Quinn *et al.*, 1996). The Galloway context is similar; land use change has taken place, rainfall is high and forested sites are receiving additional inputs of anions from sulphate, chloride or humic acids. In Galloway, plough furrows are reported to permit rapid transit of storm runoff at the afforested Loch Dee test sites planted in the 1970s (Langan and Hirst, 2004). Contemporary forest management aims to reduce forest impacts on hydrology where possible (Forestry Commission, 2009) and flow analysis can determine the extent to which this policy is effective at reducing forest-drainage enhanced cation dilution in newer plantations.

Critical loadsIn the UK the critical loads model of Nilsson and Grenfeldt (1988) is used to identify where sensitive management is needed to minimise the forest-enhancement of acidification; this includes determining where moorland afforestation is acceptable. The model identifies where sulphate loads are likely to have the greatest impacts on acid-sensitive waters. In a context where sulphate scavenging is far from the only mechanism by which land use change can influence acidification this approach needs to be reconsidered, particularly as the model specifically excludes the influence of marine ions. The fact that pH and acid anions show forest relationships, but no relationship is found between land use and critical load exceedance (CLX) on any geology, in any year, underlines this.

The ecological significance of the forest acidification effect

Fish survival is controlled by levels of pH and aluminium (Levistad and Muniz, 1976; Haya and Waywood, 1981; Havas and Rosseland, 1995). This is modified by the role of DOC as both a source of acidity, and a moderator of the toxicity of aluminium (Laudon *et al.*, 2005). In high DOC waters pH, rather than aluminium, controls fish survival; high brown trout mortality (>40%) can be expected at pH 5.0 for sites with 10mg L^{-1} DOC, but pH 4.7 for areas with 25 mg L^{-1} DOC (Serrano *et al.*, 2008). In the 2005 event Ordovician rocks have mean pH (pH_μ) of 4.8 and DOC_μ of 12.84 whilst igneous rocks have mean $pH_\mu=3.88$ and $DOC_\mu=8.45$. The 2005 land use effect increases DOC by 8.41 mgL^{-1} and decreases pH by -0.76 units on Ordovician sites and by -0.81 units on igneous sites. This suggests that at Ordovician sites any additional ecological tolerance to acidity brought by the forest-derived increase in DOC may not be sufficient to counteract the extremes of decreasing pH. As such, increasing forest cover

on either Ordovician and igneous streams is likely to increase that stream's ecological vulnerability (Feeley *et al.*, 2010).

Conclusion

There is evidence for a continued land use effect on freshwater chemistry in Galloway: statistically significant relationships show a decrease in pH, charge balance ANC and an increase in sulphate and marine ions taking place in proportion to forest cover. There is also evidence that the significance of sulphate scavenging is declining in line with decreasing anthropogenic sulphate emissions. Conversely, sea-salt influences appear to have increased and a number of additional mechanisms have been identified that may exacerbate episodic acidification in afforested areas. As increases in the strength and frequency of both sea-salt events and rainfall-driven acid episodes are expected with climate change (Wright *et al.*, 2006; Whitehead *et al.*, 2009) and levels of DOC are increasing (Worrall *et al.*, 2004; Monteith *et al.*, 2007; Laudon and Buffman, 2008), it is imperative that forest managers consider wider forest acidification effects than sulphate scavenging alone to ensure that impacts on acid-sensitive ecosystems are minimised and international policy targets are met.

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801 Table 1 shows water chemistry differences between surveys and geology All units are in ueq l-1 except pH (units) and DOC (mg l-1). Geol = geology
802 subdivided into I = igneous, O = Ordovician and S = silurian; μ shows all-site mean chemistry for the survey. Alk = alkalinity.
803

		Geol	pH	SO4	Cl	Na	Na:Cl	Ca	Mg	K	ANC _{CB}	alk	CLX	NO ₃ ⁻ N	DOC
High-flow	1996	μ	4.65	42.88	228.17	250.69	1.12	136.16	92.92	10.82	-5.63	0.26	-2.40	10.14	N/A
		I	4.25	41.51	194.23	224.75	1.18	95.70	68.66	7.59	-8.73	0.23	-1.86	14.31	N/A
		O	4.66	40.88	228.84	252.74	1.11	124.51	93.02	10.58	-14.01	0.27	-2.23	7.75	N/A
		S	5.46	53.47	293.18	295.13	1.01	269.38	144.35	19.22	37.63	0.33	-4.29	11.74	N/A
	2005	μ	4.66	24.03	436.43	339.34	0.79	95.36	84.29	10.11	35.09	0.05	0.23	13.18	11.66
		I	3.88	23.41	362.12	290.21	0.81	46.87	46.41	11.09	14.23	0.01	1.20	23.15	8.45
		O	4.80	23.23	465.92	358.82	0.78	92.21	94.47	9.62	24.12	0.06	0.12	9.27	12.84
		S	5.65	30.17	435.34	340.26	0.79	238.25	115.60	11.19	159.29	0.16	-1.46	12.62	12.63
	2006	μ	5.50	27.45	295.48	297.01	1.01	110.57	108.01	12.64	52.73	0.21	-1.64	21.02	15.85
		I	4.78	27.74	266.79	272.34	1.03	65.96	71.85	13.23	16.66	0.13	-0.34	31.62	13.50
		O	5.73	26.06	300.95	305.14	1.02	109.77	118.02	12.44	50.72	0.23	-1.95	16.44	17.55
		S	5.81	34.16	328.60	304.44	0.93	216.73	133.44	12.66	147.57	0.25	-2.73	23.20	11.75
Long-term	1989	O	6.23	121.80	360.20	338.08	0.94	N/A	N/A	13.43	N/A	N/A	N/A	18.11	N/A
	1995	O	6.10	118.95	306.13	289.82	0.94	132.43	126.71	11.97	6.05	0.13	13.51	11.00	N/A

	2001	O	6.01	N/A	281.93	284.56	0.93	122.40	126.02	12.22	10.15	N/A	N/A	14.12	N/A
	2003	O	6.34	N/A	339.48	270.01	0.89	122.50	135.36	10.89	11.29	N/A	N/A	11.73	17.65
	2005	O	5.87	N/A	373.22	309.68	0.79	128.06	125.86	12.02	8.29	N/A	N/A	14.11	13.30

804 Table 2: Regression matrix showing the relationships between Total Forest Cover (% of
805 catchment) and water quality variables. Columns show regression variables from regression in
806 form [Variable] = k + c * [Forest Cover]. N: total number and R²: proportion of data
807 explained by regression model. All units are in ueql-l except pH (units) and DOC (mg l⁻¹).
808 Shaded cells show negative relationships with forestry, unshaded cells show positive
809 relationships. Blank cells indicate no relationship was identified that was significant at
810 P<0.05. CLX = Critical Load Exceedance; ANC_{CB} = charge balance acid neutralising
811 capacity.

		Puhr 1996				UoD 2005				UoD 2006			
		N	C	k	R2	N	c	k	R2	N	c	k	R2
Igneous	pH	27	-0.36**	4.47	0.36	28	-0.81*	4.26	0.21	28	-1.11**	5.30	0.23
	SO ₄	27	20.37***	29.00	0.55	28	6.37**	20.41	0.36	28	8.42***	23.77	0.49
	Cl	27	97.94**	134.06	0.38	28	218.38***	259.23	0.65	28	132.55***	204.34	0.46
	Na	27	82.48**	174.08	0.32	28	131.38***	228.30	0.61	28	105.29***	222.73	0.41
	Na:Cl	27	-0.19**	1.30	0.27	28	-0.13***	0.87	0.56	28	-0.13***	1.09	0.44
	Ca	27				28				28			
	Mg	27				28				28			
	K	27	-7.93*	12.46	0.24	28	-18.11*	19.62	0.16	28			
	Alkalinity	27	15.15*	-18.04	0.2	28				28			
	ANC _{CB}	27	-0.13**	0.31	0.34	28	-0.13***	0.05	0.38	28	-0.08*	0.17	0.16
	CLX	27				26				27			
	NO ₃ -N	27				28				27			
	DOC	0	No Data			28				28			
Ordovician	pH	51	-0.71**	5.08	0.19	70	-0.76*	5.19	0.08	69			
	SO ₄	51	15.62***	31.77	0.49	70	5.01**	20.67	0.1	69	9.07***	21.41	0.17
	Cl	51	73.87***	185.79	0.29	70	170.81*	378.85	0.09	69	118.47**	240.17	0.14
	Na	51	67.19**	213.59	0.2	70	109.29*	303.11	0.07	69	124.93**	241.05	0.15
	Na:Cl	51				70	-0.06**	0.81	0.12	69			
	Ca	51				70				69			
	Mg	51				70				69	36.71*	99.19	0.09
	K	51	-7.96**	15.22	0.2	70	-9.05**	14.23	0.13	69	-8.64**	16.87	0.1
	Alkalinity	51				70	-24.03*	36.37	0.08	69			
	ANC _{CB}	51	-0.12***	0.34	0.22	70	-0.05*	0.08	0.08	69			
	CLX	50				70				68			
	NO ₃ -N	50				70				68			
	DOC	0	No Data			70	8.41***	8.56	0.17	69			
Silurian	pH	12	-1.83*	6.36	0.35	11				12			
	SO ₄	12				11				12			
	Cl	12				11				12			
	Na	12				11				12			
	Na:Cl	12				11				12			

Ca	12				11	-604.68*	516.89	0.39	12	-334.01*	376.37	0.35
Mg	12				11	-221.78*	217.80	0.44	12			
K	12	-18.83*	28.51	0.41	11				12			
Alkalinity	12	-247.03*	159.50	0.33	11	-773.73*	515.84	0.4	12	-402.16*	339.78	0.33
ANC _{CB}	12				11	-0.44*	0.37	0.38	12			
CLX	12				11				12			
NO ₃ -N	12				11				12			
DOC	0	No Data			11				12			

813 **Table 3 Relationships between forestry and water quality variable identified by multiple**
814 **regression. Chlorine is used to represent marine ions, relationships with sodium are very similar.**

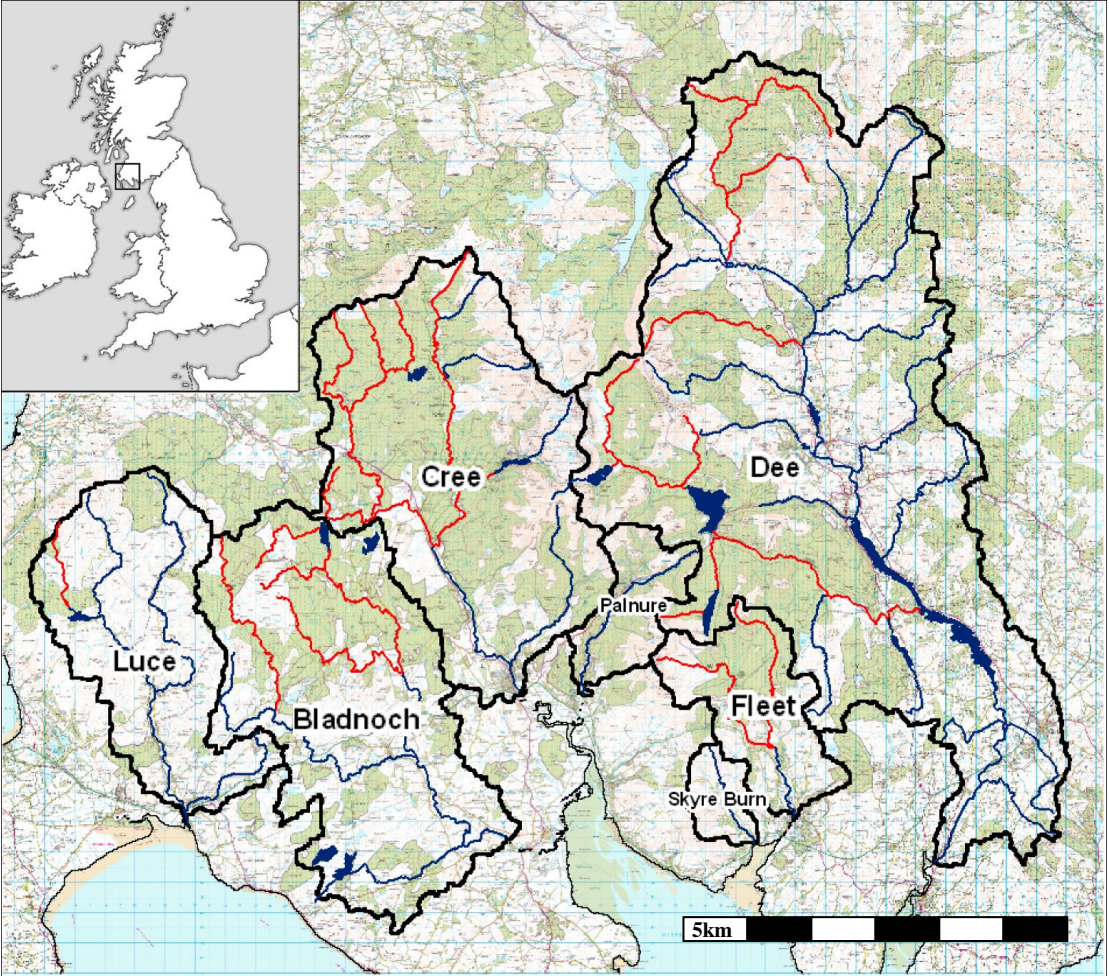
Variable: pH Survey: High-flow 1996 (M***) Model: N=91 R ² =0.481 RMSE=0.4356 0.1749*** Igneous (-) 0.1811*** Ordovician (-) 0.1250*** Total Forestry (-) Variable: pH Survey: High-flow 2005 (M***) Model: N=110 R ² =0.4627 RMSE=0.6070 0.3072*** Igneous (-) 0.0945*** Ordovician (-) 0.0610** Total Forestry (-) Variable: pH Survey: High-flow 2006 (M*) Model: N=110 R ² =0.4317 RMSE=0.5911 0.2722*** Igneous (-) 0.1380*** Max Altitude (+) 0.0215* Ordovician (-)	Variable: SO4 Survey: High-flow 1996 (M***) Model: N=91 R ² =0.6603 RMSE=4.9718 0.3735*** S1995 (-) 0.2138*** Total Forestry (+) 0.0730*** Ordovician (-) Variable: SO4 Survey: High-flow 2005 (M**) Model: N=110 R ² =0.4151 RMSE=3.3364 0.2975*** S1995 (-) 0.0599** Ordovician (-) 0.0577** Total Forestry (+) Variable: SO4 Survey: High-flow 2006 (M***) Model: N=110 R ² =0.4977 RMSE=3.9361 0.2787*** S1995 (-) 0.1090*** Ordovician (-) 0.1100*** Total Forestry (+)	Variable: Na:Cl Survey: High-flow 1996 (M*) Model: N=91 R ² =0.2253 RMSE=0.1115 0.2253*** S1995 (+) Variable: Na:Cl Survey: High-flow 2005 (M***) Model: N=110 R ² =0.2304 RMSE=0.0460 0.2304*** Total Forestry (-) Variable: Na:Cl Survey: High-flow 2006 (M*) Model: N=110 R ² =0.1213 RMSE=0.0688 0.1213*** S1995 (+)
Variable: Cl Survey: High-flow 1996 (M***) Model: N=91 R ² =0.6583 RMSE=32.7413 0.5852*** S1995 (-) 0.0731*** Total Forestry (+) Variable: Cl Survey: High-flow 2005 (M**) Model: N=110 R ² =0.7291 RMSE=68.7187 0.5031*** Max Altitude (-) 0.1239*** Ordovician (+) 0.0322*** S1995 (-) 0.0364*** Igneous (+) 0.0335** Total Forestry (+) Variable: Cl Survey: High-flow 2006 (M***) Model: N=110 R ² =0.6431 RMSE=44.6895 0.5234** Max Altitude (-) 0.0514*** S1995 (-) 0.0683*** Total Forestry (+)	Variable: ANCCb Survey: High-flow 1996 (M***) Model: N=91 R ² =0.2472 RMSE=0.0696 0.2472*** Total Forestry (-) Variable: ANCCb Survey: High-flow 2005 (M***) Model: N=110 R ² =0.419 RMSE=0.0644 0.1821*** Igneous (-) 0.1257*** Ordovician (-) 0.1112*** Total Forestry (-) Variable: ANCCb Survey: High-flow 2006 (M*) Model: N=110 R ² =0.2973 RMSE=0.0717 0.2586*** Igneous (-) 0.0387* Max Altitude (+)	Variable: pH Survey: Long-term 1989 (M*) Model: N=24 R ² =0.5887 RMSE=0.3812 0.3527*** Igneous (-) 0.1242** Ordovician (-) 0.1118* Total Forestry (-) Variable: pH Survey: Long-term 1995 (m*) Model: N=30 R ² =0.4833 RMSE=0.3851 0.1227*** Igneous (-) 0.2274** Ordovician (-) 0.1332* Total Forestry (-) Variable: pH Survey: Long-term 2001 (M*) Model: N=35 R ² =0.5446 RMSE=0.2907 0.1549*** Ordovician (-) 0.3897*** Igneous (-) Variable: pH Survey: Long-term 2003 (M**) Model: N=42 R ² =0.4524 RMSE=0.3824 0.2162*** Total Forestry (-) 0.2362*** S1995 (-) Variable: pH Survey: Long-term 2005 (M**) Model: N=39 R ² =0.172 RMSE=0.4566 0.1720** Total Forestry (-)

815 M = model by addition; m = model by removal; Significance: *** = P<0.001 ** P<0.01

816 *P<0.5; (-) negative relationship (+) positive relationship.

817

Figure 1 The rivers of Galloway Forest District. Reaches were characterised by SEPA using invertebrate data in terms of their likelihood of meeting good ecological status. Those highlighted in red are at risk of failing the directive's requirement of good ecological status as a result of forest enhanced acidification (SEPA classes 1a/1b). The catchments highlighted in the table below have over 50% of their river length affected by forest enhanced acidification.



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Figure 2 Galloway's acid sensitivity in a UK context. A and B show Non-sea salt SO_4^{2-} concentration in rainfall ($\mu\text{eq l}^{-1}$) 1986 and 1997, modified from NEG-TAP (2001). C shows local Geology from British Geological Survey 1:625,000 (BGS, 2011). D-F shows total sulphur deposition ($\text{keq ha}^{-1} \text{ year}^{-1}$) 1970, 1980 and 1995, source: Centre for Ecology and Hydrology.

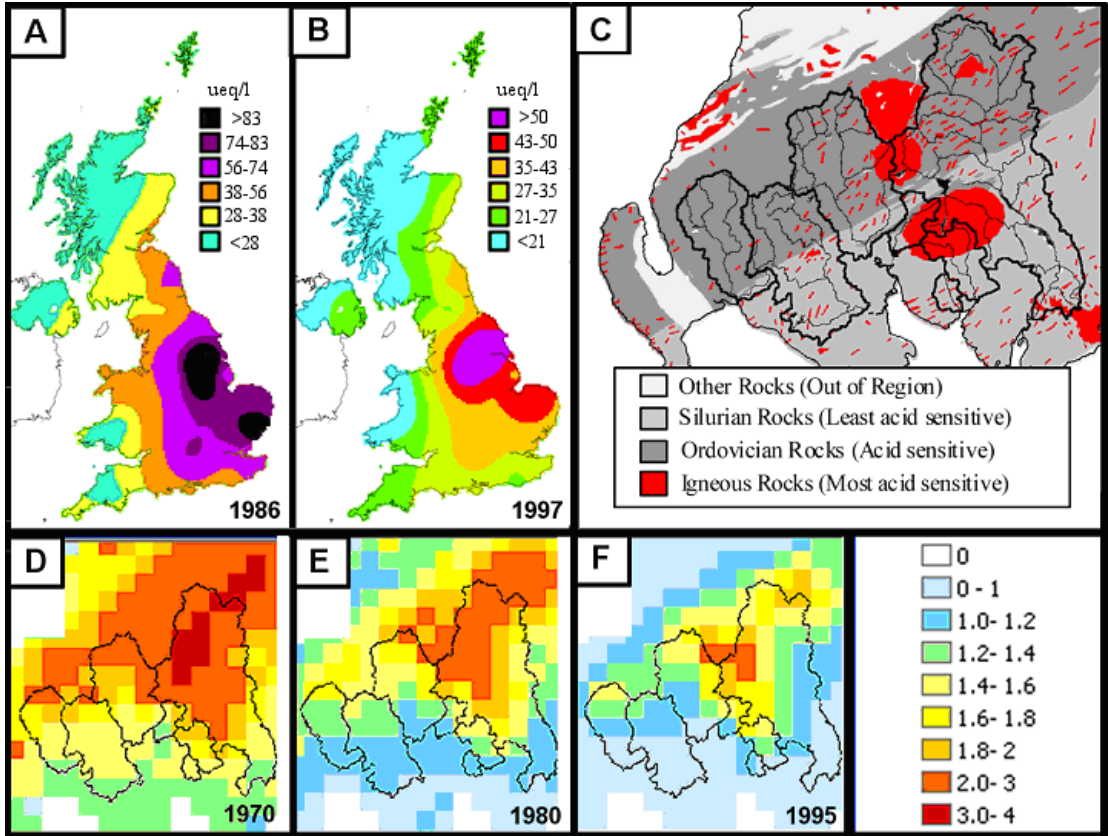
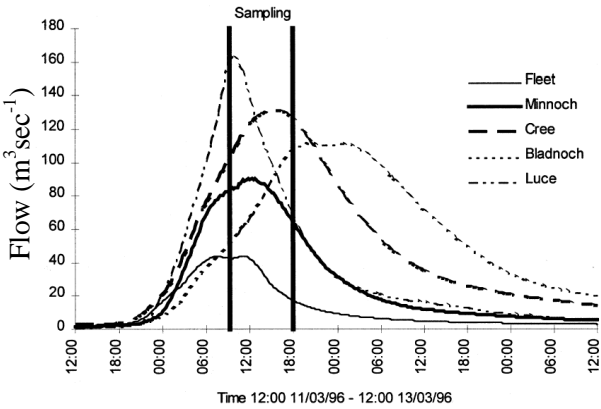
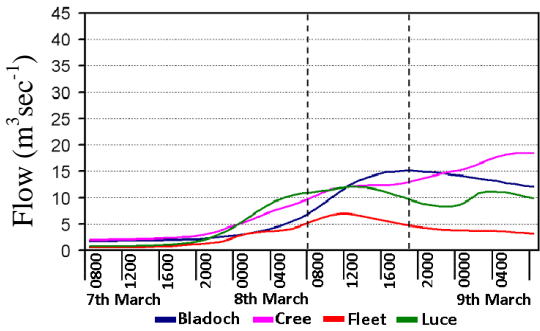


Figure 3 Water quality data: A-C hydrographs comparing storm events for the rivers Fleet, Cree, Bladnoch and Luce and sampling times (within the vertical lines).

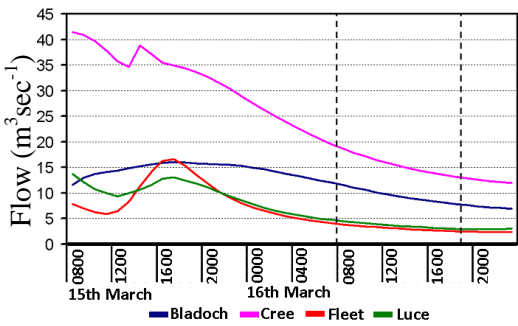
A: 1996



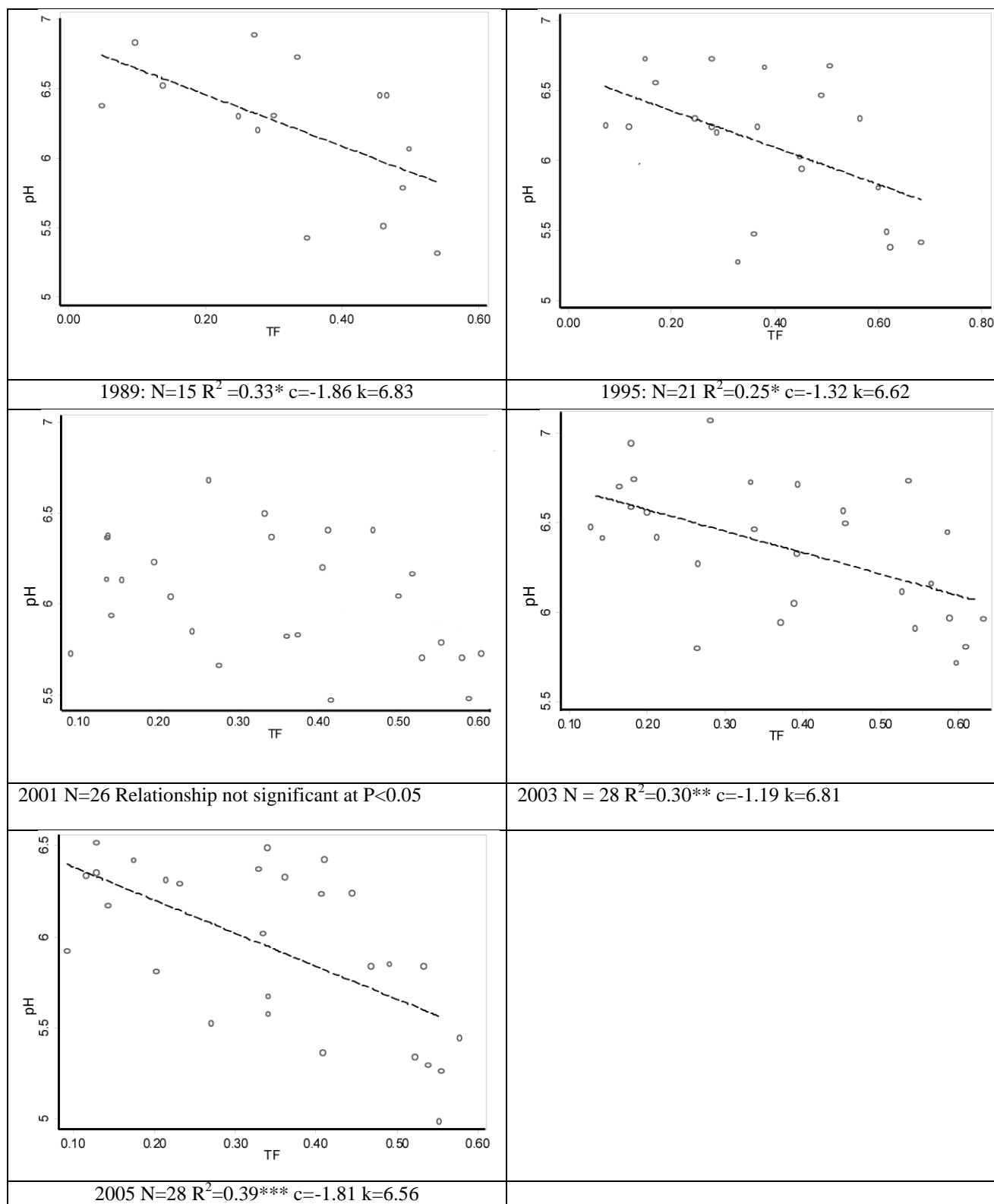
B: 2005



C: 2006



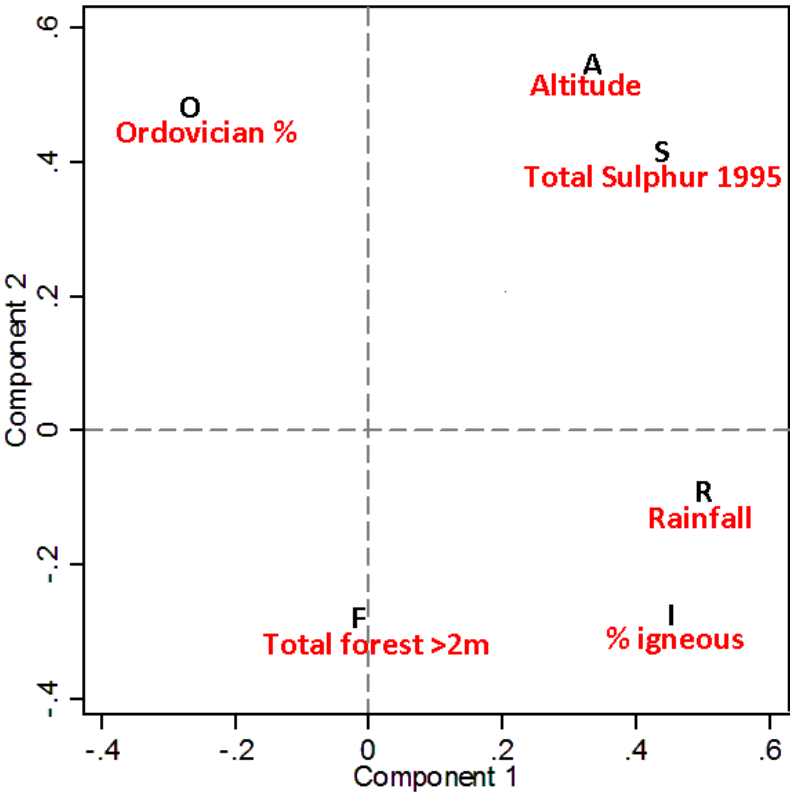
842 Figure 4: Relationship between annual median pH and total forest cover (TF) for the long-term SEPA
843 datasets 1989 -2005 showing data and fitted regression lines of the form $[pH] = k + c * [Forest\ Cover]$.
844 N: total number and R^2 : proportion of data explained by regression model. Statistical Significance * =
845 $P < 0.05$ ** = $P < 0.01$ *** = $P < 0.001$.



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848 Figure 5 PCA loading plot for multiple regression variables showing first and second components.



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