Modelling the long-term response of stream water chemistry to atmospheric pollution and forestry practices in Galloway, SW Scotland

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Executive Summary

The primary cause of soil and water acidification is the deposition of acidifying sulphur and nitrogen pollutants mainly from the combustion of fossil fuels. Acid deposition is known to acidify soils and surface waters in areas where the soils and geology are unable to neutralise acid inputs.

Whilst international agreements to limit emissions of sulphur and nitrogen have been very effective in reducing acid deposition, there has been significant debate as to the role of forest management in acidification and recovery processes and its impact on aquatic ecology. It is well documented that forestry has the potential to exacerbate acidification, principally by forest canopies enhancing the deposition of acid pollutants.

This report assesses the long term role of forestry in relation to the acidification and recovery of soil and surface water. It is driven by the need to inform discussions between the forestry sector, SEPA, fisheries groups and other interested stakeholders on the case for future reductions in forest cover to aid the recovery process in affected areas.

The report targets some of the most acid impacted head waters in the Galloway region of southwest Scotland, including three sub-catchments in the Black Water of Dee (Dargall Lane, Green Burn and Cuttie Shallow); Cardoon Burn in the Big Water of Fleet and Waterside on the River Bladnoch. All catchments have a history of forest management with the exception of Dargall Lane, which is 100% moorland. This site was included as a paired catchment control, having similar characteristics in terms of slope, soils, geology, size, and climate to the nearby forested Green Burn.

The long term (1860-2100) response of soil and surface water chemistry to changes in acidic deposition and forest management practices were assessed using the dynamic model MAGIC (Model of Acidification of Groundwater in Catchments), and uncertainties in the parameters and data are explicitly quantified. To try and disentangle the relative effects of forestry and acid deposition a scenario of ‘no forestry’ was compared to future Forest Design Plans provided by the Forestry Commission.

The report identifies surface water Acid Neutralising Capacity (ANC) as a general indicator of acidification status and the annual mean ANC value of >20 μeql^{-1} (‘ANC 20’ is used as the lower limit to define good ecological status for standing water bodies under the Water Framework Directive) was adopted as a critical threshold for damage. However the report acknowledges that there is continuing debate over ANC standards and whether ANC is the best chemical indicator for assessing the ecological health of rivers. Reference is also made to a higher ANC threshold of 50 μeql^{-1} that is applied in some countries.

Acidification phase

Prior to the onset of industrialisation in the mid 19th century, the modelled ANC at all sites was above the selected threshold for acid sensitive aquatic organisms (ANC 20), suggesting that stream waters were unaffected by acidification at that time. From the Industrial Revolution to 1970, uncontrolled emissions of sulphur and nitrogen seriously impacted soil and water quality. During this period, acid deposition stripped base cations from the soil resulting in soil acidification with a simulated average decrease in the soil base saturation of 6.2% across all sites. In response, surface water ANC declined by an average of 47 μeql^{-1}. Notably, simulated surface water pH approached minimum values prior to the start of conifer afforestation in the 1960's and 1970's. By the time when acid deposition peaked (1970), modelling indicated that the decline in ANC breached the critical ANC threshold (ANC 20) at only one of the five sites, the moorland site, Dargall Lane. It is unclear whether this breach resulted in a loss of brown trout since records only began in 1980, when low densities of fry and parr were observed.

Recovery phase

Widespread chemical recovery of surface waters has been observed from the mid 1980s to present in response to a c.80% reduction in UK SO_2 emissions and associated decreases in S deposition and SO_4 concentrations. Unexpectedly, the rate of decline in surface water SO_4 appeared to be unrelated to the extent of forest cover in the catchments. Surface water NO_3 concentrations have responded slower to a significant declining trend in N deposition (1990 to present).

Annual mean ANC values are now above the critical ANC 20 threshold in all five sites and exceed the higher threshold of ANC 50 in three of the four forested sites. Continued recovery is predicted in response to agreed reductions in acid deposition to 2020 and planned reductions in forest cover to 2050, with chemical conditions eventually reaching close to or above the ANC 50 threshold in both the Green Burn (ANC 48.5 μeql^{-1}) and Dargall Lane (50.4 μeql^{-1}) sites. However, recovery proceeds at a much slower rate post 2020 and no site is expected to return to the original pristine chemical conditions of 1860 by 2100.

Despite clear evidence of chemical recovery to date, recent ecological surveys show that the response of fish and aquatic invertebrates has generally been small. The authors acknowledge that the presence and absence of aquatic species is dependant on many complex factors and ANC may not be the best predictor of fish status. Indeed new evidence suggests that labile aluminium may provide a better predictor of the sensitivity of brown trout to acidification, although it does not contradict the use of ANC 20 as an appropriate threshold for protecting this species - providing that the considerable uncertainty over the value is recognised.

Implications for forestry

Differences in the ANC response post 2010 under the planned forest scenario and the 'no forest' scenario were relatively small, ranging from 0.7-6.3 μeql^{-1} between all sites. Whilst there was a weak relationship between the extent of forest area and ANC recovery in the longer term predictions, the difference between scenarios was unlikely to be biologically significant in terms of ANC thresholds. The subtle improvements in water quality simulated following the complete removal of forestry suggest that future changes in forest cover are likely to have a relatively minor effect on the recovery process.

1. Aim

This study aims to assess the role of forestry in acidification and recovery of soils and surface waters under historical and contemporary acid deposition conditions through the use of a process based biogeochemical model (MAGIC). The findings of the study are intended to inform future discussions between the forestry industry, fishery groups, Scottish Environment Protection Agency (SEPA) and other interested stakeholders as to future land-use management in order to secure the recovery of acid sensitive waters in Scotland. This study is directly relevant to the setting and achievement of Water Framework Directive (WFD) objectives, on which SEPA leads.

2. Background

Sulphur pollution has been, historically, the main component of 'acid rain', which has caused acidification of soils and waters, leading to biological damage in acid sensitive areas (Harriman et al*.,* 1987). Although sulphur deposition (mainly from fossil fuel burning) has decreased greatly from its 1970s peak (Harriman et al*.,* 2001), damaged ecosystems have been slow to recover, and some of the most sensitive waters may remain acidified even under reduced loadings (Monteith et al*.,* 2005). At the same time, levels of atmospheric nitrogen pollution (mainly from fossil fuel burning and agriculture) have increased (Fowler et al*.,* 2004). Excess nitrogen can also contribute to acidification, and as a key nutrient for plant growth, can cause nutrient enrichment (eutrophication) of semi-natural ecosystems.

Forestry is acknowledged to be an exacerbating factor in the acidification of surface waters in acid sensitive parts of the UK (Harriman et al*.,* 2003). Research has shown the main mechanism to be the enhanced interception of acidic sulphur and nitrogen pollutants from the atmosphere by aerodynamically-rough forest canopies (Forestry Commission, 2003; Miller et al., 1991). An additional, but in general less important mechanism is the loss of neutralising capacity in forest soils as a result of tree uptake and subsequent removal of base cations by harvesting (Department of Environment and Forestry Commission 1991; Kirchner and Lydersen, 1995). The influence of forestry on water quality therefore depends not only on trends in acid deposition but also on the stage of the forest cycle from planting and growth to felling and re-planting. There has been significant debate as to the role of forest management in acidification and recovery processes, and much scepticism from the fisheries sector regarding the suitability of critical load thresholds for evaluating the sensitivity of waters to a forestry acidification effect.

The critical loads approach has been broadly accepted by the scientific community and policy makers to guide emission control for water protection at UK and European levels. However, the application of the approach at the local catchment level has been disputed, particularly the selection of appropriate chemical thresholds for the protection of freshwater ecology, especially salmonid fish (McCartney et al*.,* 2003; Bridcut et al*.,* 2004).

The critical load concept takes a static view, which assumes steady state conditions between acid deposition, water chemistry and biological effects. In this sense it invokes a precautionary principle. In reality of course the response of water chemistry to changes in acid deposition is not instantaneous but, rather, entails lag times of years to decades, depending upon the processes involved and the natural characteristics of vegetation, soils and waters. Neither is the response of biological components to changes in water chemistry instantaneous, with lag times associated with rates of recruitment and re-colonisation(e.g. distance to nearest refuge population).

Predicting the future dynamics of biogeochemical processes in acidification/recovery of soils and freshwater ecosystems requires the use of models. Process orientated models have been developed over the past 20 years to explain observed trends in water quality and to predict future changes in response to emission reductions and land use management. Such models are time dynamic, such that they can be used to estimate the lag between simultaneous changes in deposition and forest management, and the response of water chemistry

3. **Approach**

The newly enhanced biogeochemical model MAGIC (Model of Acidification of Groundwater in Catchments) with an improved representation of dynamic forestry processes was applied to five headwater catchments in the Galloway region. The long term response of soil and surface water chemistry to changes in acid deposition and forestry management according to past and future forest plans was investigated.

Such model predictions are inherently fraught with uncertainty and here we propose to quantify the degree of uncertainty so that this can be taken into account in interpretation and decision-making. The method used for this task combines the deterministic model MAGIC with a stochastic model for the observed output data, and to estimate all unknown parameters by Bayesian computations using Markov Chain Monte Carlo (MCMC) techniques (Larssen et al., 2006). This approach allows a formal management of uncertainties in both parameters and data, and the impact of the uncertainty on model results to be explicitly shown.

4. Site selection

The success of any model application relies on the suitability of the selected site to address the issue; in this case the impact of forestry on surface water acidification, and the quality of the data used to parameterise the model. To ensure appropriate site selection, key interested parties were consulted, including the Galloway Fisheries Trust, Forest Research (and the Forestry Commission), the Scottish Environment Protection Agency (SEPA) and Marine Scotland Freshwater Laboratory. Sites were selected according to the following agreed criteria:

- Headwaters of acid sensitive catchments, with a focus on the River Cree, Bladnoch and the Black Water of Dee
- Availability of high quality, long-term hydrochemical data
- History of forest management practices plus one moorland (control) site that shares similar soil, geological and topographic characteristics to the forested sites
- Sites that currently fail to achieve WFD good status because of acidification
- Contrasting forested sites with evidence of a) poor and b) good biological recovery.

Spatial data including forest area, past and future management practice, the distribution of soil types (and physico-chemical parameters) and site physiography (from a Digital Elevation Model) were available for the entire Galloway region and therefore did not constrain site selection. The challenge was the identification of sites with high quality hydrochemical records with supporting information on WFD designations for acidification and ecological status. In the first instance these data were sought from SEPA given their long term monitoring programmes for regulatory jurisdiction. However, with closer scrutiny of the SO_4 record it became apparent that SEPA's data, whilst fit for regulatory purposes, were generally not suitable for acidification modelling due to methodological changes and a generally low level of measurement precision and accuracy. An alternative source of better quality data was sought from Marine Scotland's Freshwater Laboratory, who operate a network of research focused monitoring sites with the specific aim of detecting long term environmental change in this acid sensitive region (Harriman et al*.,* 2001, 2003; McCartney et al*.,* 2003). The fine scale precision and accuracy of these data met the requirements of this study.

A list of the selected sites with their location, catchment size and forest area is shown in Table 1. The sites are distributed across a 1200 km^2 area of the acid sensitive region of south west Scotland and range in size from the largest, Waterside on the River Bladnoch (35.30 km^2) to the smallest, Cuttie Shallow (1.91 km^2), draining to Loch Grannoch. All catchments are forested with the exception of Dargall Lane, which is 100% moorland. This site was included as a paired catchment control, having similar characteristics in terms of slope, soils, geology, size, and climate to the nearby forested Green Burn.

Table 1: Site characteristics (The moorland control site, Dargall Lane, is highlighted in grey)

Monitoring site (code)	River	Grid Reference	Altitude of outflow (m)	Catchment size (km^2)	Forest area (%)	Dominant soil type
Waterside (BW)	Bladnoch	NX290723	106	35.30	63	Peaty podzol
Green Burn (GB)	Black Water of Dee	NX480789	225	2.60	48	Peaty podzol
Dargall Lane (DL)	Black Water of Dee	NX449786	225	2.02	0	Sub-alpine podzol
Cuttie Shallow (CS)	Black Water of Dee	NX543708	215	1.91	89	Peat
Cardoon Burn (CB)	Big Water of Fleet	NX547660	130	6.55	20	Peat

The sites largely meet the selection criteria listed above. Headwater tributaries of acid sensitive river systems in Galloway were selected, although it was not possible to find a site on the River Cree because of a lack of suitable data. While an earlier unpublished study by Welsh et al. (1986) of the Solway River Purification Board ((RPB), predecessor to SEPA) on the relationship between water chemistry and solid geology in south-west Scotland, found the most acid waters in the region to be in the River Cree system, the selected sites were nevertheless considered to be representative of acid impacted waters. Cardoon Burn on the Black Water of Fleet was selected as an alternative site. It was not possible to select a first order river on the Bladnoch due to data constraints. This was unfortunate since it is recognised that catchment size can influence the susceptibility of surface waters to acidification, with rivers draining larger catchments tending to have a greater contribution of groundwater with higher base cation concentrations compared to first order upland rivers. Nonetheless the Bladnoch at Waterside is recognised as an acidified headwater river system.

Strict data quality control procedures were followed and the environmental data at all sites were deemed to be of the highest quality for a study of this nature. The Forestry Commission provided details on past and future forest management and the present day forest area ranged from 20-89%. Dargall Lane was a suitable control as described previously. It was also important to include sites that currently fail to achieve WFD good status because of acidification. Of the five sites selected only two (River Bladnoch at Waterside and Dargall Lane) are classified for WFD. The Bladnoch site failed to achieve good status on pH (poor classification); however, a moderate classification was determined from the macroinvertebrate acid tool and fish ecology. Dargall Lane achieved good status on pH, but failed on the macroinvertebrate acid tool (moderate classification) and fish ecology was not classified. It should be noted that hydrochemical and ecological records used for the WFD classification are based on SEPA's data, whilst the data used for modelling was collected and analysed by Marine Scotland's Freshwater Laboratory.

Since the primary objective of this report was to assess the past and future influence of forestry on surface water acidification and recovery, a detailed assessment of the ecological status of the study sites is beyond the scope of the commissioned report. However, to address the final site selection criteria, a summary of existing information on the extent of biological recovery at the study sites is described. Without dedicated long term monitoring and analysis of ecological records it is difficult to draw concrete conclusions about biological recovery. For this reason the section below on biological response should be interpreted with extreme caution as statements are based mainly on observations, not robust trend analysis, unless the evidence is supported by published references.

The Bladnoch at Waterside has been monitored by the Solway RPB and SEPA since 1994. It has always supported at least one acid-sensitive macroinvertebrate taxon, the number of taxa in any one sample varying from one to six. Over the period 1994–2006 there was a significant positive correlation between percent abundance of acid sensitive taxa and year, suggesting some recovery (Rendall & Bell, 2008). Since 2006 there has been little further change.

The Bladnoch at Waterside is accessible to migratory fish and has good habitats upstream and downstream of this location. Very low numbers of juvenile salmonids have been counted at Waterside, but are well below expected levels. The site has been surveyed annually for many years but data is only readily accessible from 1997 onwards (Appendix 1a). In the early 1990s salmon were observed spawning at Waterside but electrofishing surveys found no or very few juvenile salmon. Historically Waterside was known to support spawning salmon and their progeny. The Bladnoch at Waterside is not the most impacted site in the catchment and whilst salmon egg survival is reduced here (42% and 66% of salmon egg survived in 2010 and 2011 respectively), in the lower order tributaries such as Dargoal Burn, there was no egg survival (unpublished data from Galloway Fisheries trust).

The Green Burn has been monitored by SEPA since 1998. A few acid-sensitive taxa were present most years between 1998 and 2006. A significant positive correlation between percent abundance of acid-sensitive taxa and year suggests some recovery (Rendall & Bell, 2008). Since 2006 there has been little further change. Previous monitoring by the former Freshwater Fisheries Laboratory, Pitlochry showed no evidence of any trend in the abundance of acid-sensitive mayflies over the period 1980-89 (Morrison & Collen, 1993). In August 1980, trout density in the Green Burn was estimated at 9 per 100 m^2 and despite stocking in April 1981, the population showed only a small increase to 16 per 100 m^2. In June 1983, trout density was recorded as 54 per 100 m^2, and the majority of fish caught were fry, indicating successful spawning (Burns at al, 1984). In a survey carried out in 1984, trout densities were estimated at 23 per 100 m^2 and 16 0+ fish were caught, indicating successful spawning (Harriman et al., 1987). In 1989, the fry population collapsed, and this event was also observed in the nearby Black and White Laggan tributaries. During the winter of 1984-85, boxes of trout eggs were planted in each of the Loch Dee tributaries. Mean survival (live alevins) was only 14% in the Green Burn, compared with 48% in the Dargall Lane (Morrison & Collen, 1993). In summary trout (including fry and parr), pike and minnow were present at various stages between 1984 and 2003 at Green Burn (Malcolm Pers. Comms.)

The ecology at Dargall Lane has been monitored as part of the UKAWMN since 1988 and by SEPA since 1998. Acid-sensitive macroinvertebrate taxa occurred sporadically between 1998 and 2006, and at best, this stream may be regarded as being in the very early stages of recovery (Rendall & Bell, 2008). Since 2006 there has been little further change. Evidence for limited recovery is supported by UKAWMN data which shows a significantly increasing temporal trend in the AWICsp index since 1988, indicating some recovery, but it was noted again that recovery is still in the early stages (Kernan et al., 2010). Considerable changes in epilithic diatoms were observed since 1988 which are consistent with recovery from acidification. Aquatic macrophytes also show an increase in new species since 2003. Before this date, the macroflora was exclusively dominated by acid-tolerant liverworts (Kernan et al., 2010).

Detailed quantitative electrofishing data from three 50m reaches of stream, carried out over the period 1988–2006 as part of the UKAWMN showed that both trout fry and parr were present, but there was substantial inter-annual variability and no significant overall trends in fish presence (Malcolm et al., 2010). In another survey of Dargall Lane carried out in August 1980, trout densities were very low (3 per 100 m^2) and remained the same in August 1981 and June 1983, even though the burn was stocked with fry in April 1981 (Burns et al., 1984). In a 1984 survey, trout densities were estimated at 12 per 100 m^2, but only a single 0+ fish was found, indicating poor spawning success (Harriman et al., 1987). In surveys carried out annually over the period 1983-91, trout densities in the Dargall Lane were lower than those found in the other Loch Dee tributaries (Morrison & Collen, 1993). During the winter of 1984–85, boxes of trout eggs were planted in each of the Loch Dee tributaries. Mean survival (live alevins) was 48% in the Dargall Lane, compared with 68% in the neighbouring tributaries, White and Black Laggan (Morrison & Collen, 1993). Whilst trout egg boxes give an indication of water quality, more recent evidence has shown that there are many other controls that influence in-redd mortality (Malcolm Pers. Comms.).

There are few published ecological records for Cuttie Shallow, however, after a long period of absence, trout were observed in 1997, 1999 and 2009 and although the densities were very low (2, 3, 3 trout for the respective years) for a relatively large area ($83m^2$) these data provide evidence of some biological recovery (McCartney et al., 2003; Malcolm pers. comms.).

According to the GFT, Cardoon burn is accessible to migratory fish and has excellent and varied habitats throughout its length with important sea trout nursery reaches. Cardoon Burn was fished in 1978-9, 1984, 1991 and 1992 by Marine Scotland, formerly the Freshwater Fisheries Laboratory and low densities of trout and eels were detected. It is noted that during the survey in 1984 trout densities were low (<5 per $100m^2$) (Harriman et al., 1987). Numbers of salmon and trout increased significantly in 1999 and 2002 but it is not clear if these data supplied by GFT are directly comparable with those supplied by Marine Scotland.

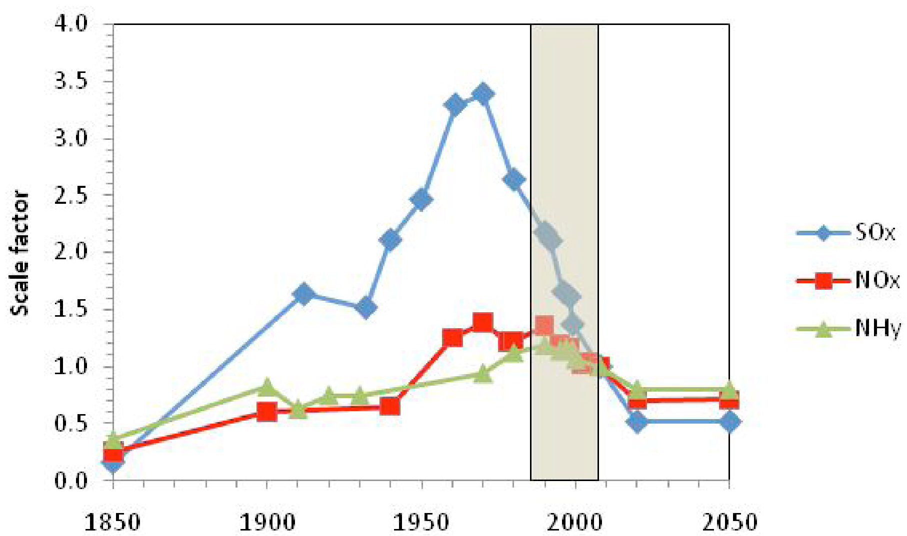
5. Data Sources

A Geographic Information System (GIS) and 50 km^2 resolution Digital Elevation Model (DEM) were used to identify catchment boundaries for the drainage areas of the five sites and generate catchment area and minimum/maximum/average altitude figures.

5.1. Deposition chemistry

For the period 1988 to 2008, observed deposition chemistry for Loch Dee, south-west Scotland (part of the UK Acid Deposition Monitoring Network (UKADMN), Grid reference NX 468779)) was used to estimate annual pollutant deposition loads of S, NOx and NHy to the sites. Longer term historic trends of these pollutants were modelled by scaling current deposition for Loch Dee to reconstructed emission sequences using established techniques (Bettelheim and Littler 1979; Warren Spring Laboratory 1987; Simpson et al., 1997). Looking to the future, sulphur and nitrogen deposition forecasts were based on projections from the FRAME model and represent current legislation (CLE) using the Updated Energy Projections (UEP30) scenario (Malgorzata et al., 2009). CLE is based on the Gothenburg protocol (Multi-Pollutant Multi Effects Protocol), which aims to reduce emissions of sulphur, nitrogen and ozone to achieve critical load targets for acid sensitive areas (Figure 1). Unlike emission sources of S and N compounds, which are predominantly anthropogenic and can be effectively controlled and realistic projections made, the same is not the case for sea salt deposition. Predictions of future trends are fraught with uncertainty due to the magnitude and frequency of sea-salt events. Given this huge uncertainty, deposition sequences for sea salts and all other ions were assumed to remain constant at 2008 levels throughout the simulation period. Base cation deposition was also assumed to remain constant irrespective of forestry activities due to data limitations and a lack of current understanding of the dynamics of these processes in forested systems.

Figure 1: Historic and future sulphate and nitrogen (oxidised and reduced) deposition sequence (scale factor: 2008 deposition is equivalent to a factor of 1.0) for the period 1850–2050. The shaded area delineates the period with observed deposition data.



5.2. **Rainfall**

Rainfall quantity data was sourced primarily from the bulk deposition rainfall collector at Loch Dee as part of the UKADMN. Following quality control checks and analysis of rainfall records from Eskdalmuir (to the east of the region) it was obvious that rainfall amounts in 2001 and 2005 were underestimated due to the under catch of snow during the harsh winters, and rainfall in 2003 was overestimated. In addition rainfall estimates at Loch Dee were compared with calculated catchment rainfall time series and statistics prepared by the National River Flow Archive (NRFA). Since NRFA calculates hydrological budgets for the local river gauging sites in our catchments it was clear that rainfall amounts in this study during 2001, 2003 and 2005 were erroneous. A regression model was used to rectify this problem. The datasets from Loch Dee and Eskdalemuir were first converted to daily time series by dividing each rainfall volume equally across its collection interval. This was necessary as rainfall volumes were collected at approximately weekly or fortnightly intervals. Simple linear regression of the Loch Dee rainfall volumes on the corresponding Eskdalemuir measurements yielded an equation which enabled patching of expected data gaps in the Loch Dee data. The Eskdalemuir data were also used to correct the 2003 record for Loch Dee, which appeared highly spurious compared to rainfall volumes measured at other localities nearby. The hydrological budgets were assessed and, for all sites except Dargall Lane, the budget looked credible. In some instances at Dargall Lane, flow volumes exceeded rainfall volumes possibly as a consequence of reduced evaporation at Dargall Lane compared to the forested sites. In such circumstances a correction factor was applied to the rainfall data.

Bulk deposition samples, collected at weekly or fortnightly intervals, represent average bulk deposition and rainfall volumes for the collection interval. The data were standardised by dividing the rainfall volume equally between each day in the collection interval (a constant chemical concentration was assumed per sample period). In general, for a collection interval lasting T days, associated with a rainfall of R mm with an average chemical concentration of X mg/l, estimated daily rainfall values for this interval were calculated as R/T mm/day, each with a concentration of X mg/l. This gives a standardised daily series which can then be compared with the other datasets.

Finally, daily time series for the Loch Dee rainfall chemistry was converted to an average monthly series, and weighted according to rainfall volume. The resulting series of chemical concentrations were then aligned with monthly rainfall volumes for the rainfall collectors listed in Table 2. Each site therefore uses the same time series of rainfall chemistry, but a different series for rainfall volume. These monthly series were then processed to yield total annual rainfall volume and average, volume-weighted, annual rainfall chemical loads.

5.3. Discharge

Discharge data was provided by the NRFA (CEH Wallingord) for the nearest river gauging station downstream of each site (Table 2). Daily mean flow values (cumecs) were converted to a total daily discharge depth and checked against SEPA's own discharge records. In some instances where the nearest gauging station was a significant distance down river, the discharge data was downscaled to match site catchment drainage areas:

$Q_{\text{Key site}} = Q_{\text{Flow site}} * \left(\frac{A_{\text{Key site}}}{A_{\text{Flow site}}}\right)$ where Q is the flow rate and A is the upstream area.

Monthly chemical fluxes were calculated using monthly measured concentrations in sampled river water and scaled daily discharges summed to give monthly total volumes. The resulting time series pairs were then processed to give the total annual flow volume and the average, volume-weighted, annual river chemical concentrations for each site. Gaps in the flow records for Dargall Lane and Cuttie Shallow during 2002 complicated this process. The gap at Dargall Lane was patched using scaled data from the nearby Green Burn site, while the missing date for Cuttie Shallow was in-filled using the mean of the scaled estimates for the Green Burn and Rusko flow stations (both of which are similarly distant from the Cuttie Shallow site).

Table 2: Location of the river gauging stations and rainfall collectors

Site code	Rainfall/river gauge	Grid Reference of river gauge	Drainage area (km^2)	Additional notes
BW	Low Malzie	NX382545	344	Natural flow to within 10% of 95 centile
GB	Green Burn	NX481791	2	Natural flow to within 10% of 95 centile
DL	Dargall Lane	NX451787	2	Natural flow to within 10% of 95 centile
CS	Dee at Glenlochar	NX733641	809	Regulation for HEP
CB	Water of Fleet –Rusko	NX529590	77	Natural flow to within 10% of 95 centile

HEP Hydro Electric Power

5.4. **Forestry**

Forest information was extracted from Forestry Commission spatial databases, including the current extent of the plantations, proportion of open ground within the forest (Table 3), tree species composition, and yield class of the crop. Historic Ordnance Survey maps were used to determine changes in forest cover since 1940. The Forestry Commission provided information on future forest management according to Forest Design Plans, including details of planned felling, thinning and restocking until 2050. For modelling purposes the extent of forestry in 2050 was assumed to remain constant to 2100.

Forest management can influence soil and water chemical status, in particular through the removal of base cations and nitrogen (N) from catchment soils in harvested biomass. Typically the stem wood and bark are removed from the catchment (net loss) whereas the brash is left on site so that their higher nutrient content is ultimately returned to the soil. The long-term average annual net uptake of major nutrients including base cations (Ca, Mg, Na, K) and N by forests in the study catchments was calculated from the average annual volume growth and estimated nutrient concentrations in the removed (harvested) biomass (Aherne et al., 2008).

For each compartment of the forest plantation the area, species, planting year, yield class and age at planned felling were known. It was therefore possible to determine the mean annual increment of harvested stem wood for the duration of the rotation using published species specific management tables (Hamilton and Christie, 1971). Annual stem wood growth in each stand was calculated by dividing the cumulative stem wood volume at felling (main harvest plus thinnings) by the rotation length, rather than creating a time-series of nutrient uptake using allometric growth curves, i.e. for each stand annual uptake is constant. The harvested volume was converted to biomass using nominal specific gravity values for each species (McKay et al., 2003).

The nutrient removal associated with the harvested biomass was calculated using published nutrient concentration data. Nutrient uptake for each stand was estimated as a long-term average annual value rather than a dynamic time-series, i.e. annual uptake was assumed to be constant. Nutrient losses due to forest management were estimated up to 2050 based on planned felling and restocking dates. Long-term sustainable soil management depends on base cation losses from harvesting being balanced by inputs from atmospheric deposition and weathering; it was therefore important that these processes were included in the model framework.

Forest management can also influence the amount of runoff from a catchment. Evapotranspiration is assumed to vary between 10 % of rainfall for a moorland catchment and 20 % for a fully forested catchment, these values were scaled linearly to the percentage of forestry (Robson et al., 1991).

Table 3: Present day forest areas at the study sites

Bladnoch Waterside	Forested area within FC estate =	879.5 ha	(FC forest 83% forest cover)
	Open/unplantable area within FC estate =	176.5 ha	
	Non FC forest within catchment =	1331 ha*	
	catchment area =	3532 ha	63% forest cover
Cardoon Burn	Forested area within FC estate =	131 ha	
	Open/unplantable area within FC estate =	4 ha	
	catchment area =	655 ha	20% forest cover
Cuttie Shallow	Forested area within FC estate =	169 ha	
	Open/unplantable area within FC estate =	22 ha	
	catchment area =	191 ha	88% forest cover
Green Burn	Forested area within FC estate =	126 ha	
	Open/unplantable area within FC estate =	165 ha	
	catchment area =	260 ha	48% forest cover

*Note: assume tree cover within NIWT is approximately 1108ha
Rate of uptake/removal/loss across FC 'forested' area (880 ha)

5.5. Soil Physico-Chemical Properties

Soil physico-chemical data for each catchment were derived by weighting soil data vertically (by horizon) and spatially according to the methodology of Helliwell et al. (1998). The proportion of each catchment occupied by different soil map units was derived from the national Soil Map of Scotland (1:250 000). For individual soil map units, the proportion of each component soil series was determined along with typical sequences of soil horizons (with typical depths). For each of these soil horizons, values for corresponding soil chemistry parameters were derived from the Scottish Soils Knowledge and Information Base (SSKIB, Smith et al., 2010). This represents an improvement on previous UK model applications, which generally only considered the dominant soil series within each map unit.

5.6. Surface water chemistry

Surface water samples were collected at monthly intervals, although for some periods the sampling intensity increased to fortnightly. The model was calibrated to data representing the period 1988-2008 for Green Burn and Dargall Lane; 1993-2008 for Cuttie Shallow; 1991-2007 for Cardoon Burn; and 1998-2008 for Waterside. Chemical records for these sites were analysed at Marine Scotland Freshwater Laboratory. Chemical analysis was carried out using standard analytical procedures. Importantly, temporal consistency of analysis was ensured through participation in analytical quality control programmes (AQC) appropriate to the range of analytes and concentrations found in upland Scottish streams (Gardner, 2008). Surface water chemistry records for Waterside (Bladnoch) were collected and analysed by the Scottish Environment Protection Agency (SEPA). Sulphate records were omitted from the latter dataset due to quality control issues and instead summaries of monthly data for 1998 and 2009 were used from a complementary set of data analysed by the Freshwater Laboratory (Faskally) for this site.

6. The MAGIC model and uncertainty analysis

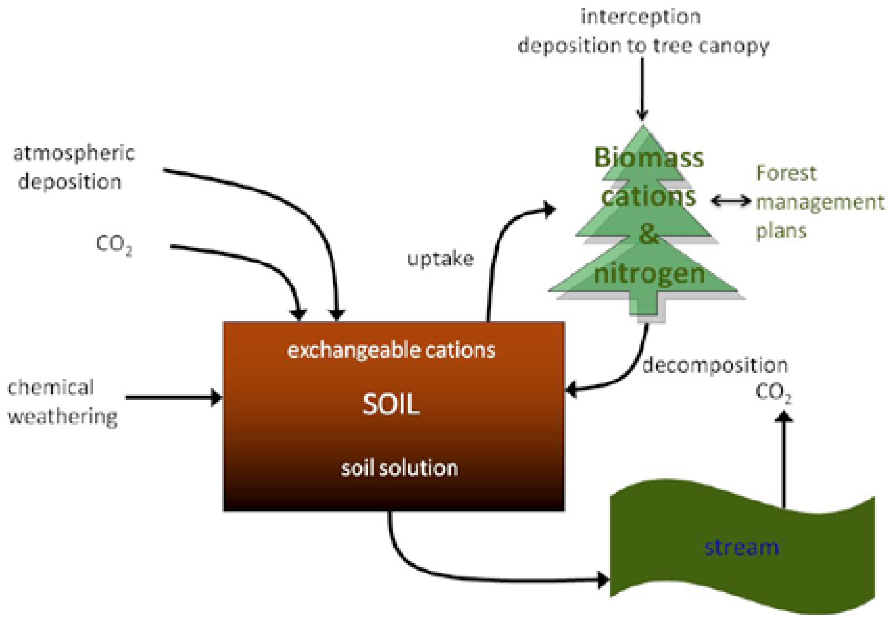
MAGIC is a process-orientated model, developed to predict the long-term effects of acidic deposition on soil and surface water chemistry (Cosby et al., 2001). The model consists of: (i) soil-soil solution equilibrium equations in which the chemical composition of the soil solution is assumed to be governed by simultaneous reactions involving cation exchange, dissolution and speciation of inorganic and organic carbon; and (ii) mass balance equations in which fluxes of major ions to and from the soil and surface water are assumed to be governed by atmospheric inputs, mineral weathering, net uptake by biomass and loss in runoff (Figure 2).

Previous work on UK upland lakes (Cooper and Jenkins, 2003) has demonstrated a strongly synchronous response between S input and output fluxes, suggesting that SO_4 behaves conservatively and in-catchment below-ground processes have a relatively minor impact, especially in hard rock catchments, where soils are shallow and responsive and mean catchment residence times are short. Such characteristics are typical of the Galloway catchments (Hrachowitz et al., 2010). Therefore, SO_4 was treated as 'pseudo-conservative', with surface water outputs equal to deposition inputs on an annual basis.

Nitrogen dynamics within the model embrace the N saturation concept (Stoddard, 1994) with the inclusion of dynamic equations for N cycling. The introduction of a soil organic matter compartment that controls NO_3^- leakage from the soil is based conceptually on an empirical model described by Gundersen et al. (1998). Major processes affecting NO_3^- and NH_4^+ concentrations in surface water have been represented in the model, the most significant being nitrification (biological conversion of NH_4^+ to NO_3^-), immobilisation and uptake (Gundersen et al., 1998; Jenkins et al., 2001).

For this study, MAGIC was applied on an annual time-step. Soil physico-chemical parameters were represented as a single soil box (by weighting soil data vertically and spatially within the catchment), with a number of simplifying assumptions. Note that, in the model and throughout this report, ANC is calculated using the charge balance definition, as the sum of base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+ and NH_4^+) minus the sum of acid anions (Cl^-, SO_4^{2-} and NO_3^-).

Figure 2: Schematic of the MAGIC model



To quantify the uncertainty in model outputs, we combined the deterministic model MAGIC, as described above, with a stochastic model for the observed output data, to estimate all unknown parameters by Bayesian computations using Markov Chain Monte Carlo (MCMC) techniques. This involves specifying prior probability distributions for the input parameters (based on the input data if available) and the likelihood functions for the output data (again based on data if available, Table 4). The prior distributions for the input parameters implicitly define corresponding prior distributions for the output parameters, which, when combined with the data likelihood functions, give posterior conditional distributions for all parameters. The posterior distributions are calculated by running the deterministic model repeatedly with parameters suggested by an MCMC scheme. The results are analysed after the algorithm has converged. This approach allows a formal management of uncertainties in both parameters and data and the impact of the uncertainty on model results to be explicitly shown. The calibration year was 2008, and 15,000 iterations were made at all sites except Dargall Lane where 25,000 iterations were performed. Since all statistics were based on 1000 runs between 5,000 and 15,000 iterations; the last 10,000 iteration at Dargall Lane were omitted from the study to allow for consistency in the method and model output for all sites.

Table 4: Model input parameters and uncertainty ranges used in the Monte Carlo Markov Chain Bayesian calibration. Input parameters were derived from site specific observations (SSO), site specific estimates (SSE: parameters derived from other observations) or default values specified.
*All distributions are rectangular

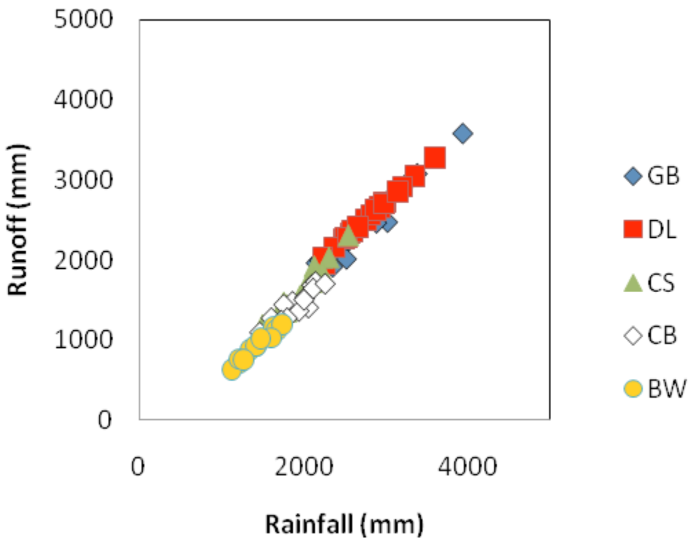
		Prior Distributions*		
Parameters	Initial	Min	Max	Description
Soil depth (m)	SSO	–	–	Site specific observation (fixed)
Soil porosity (%)	SSO	–	–	Site specific observation (fixed)
Bulk density (kg/m^3)	SSO	–	–	Site specific observation (fixed)
CEC (meq/kg)	SSO	SSO – 35%	SSO + 35%	Min/max range based on uncertainty around observations
Sulphate adsorption half saturation ($mmol_c/m^3$)	100	–	–	Regional default value
Sulphate adsorption maximum capacity ($mmol_c/kg$)	0.1	–	–	Regional default value
Soil K aluminium (Log10)	–	4	14	Regional default value
Temperature (°C)	5	–	–	Regional default value
Partial pressure CO_2 (% atm)	SSE	0	SSE + 40%	Site specific estimate
Soil DOC (µmol/L)	SSE	0	SSE + 200%	Site specific estimate
Soil nitrification (%)	100	–	–	Regional default value
Ca^{2+} weathering ($meq/m^2/yr$)	–	0	400	Minimum set to zero. Maximum set to highest reasonable value for all study sites.
Mg^{2+} weathering ($meq/m^2/yr$)	–	0	50	
Na^+ weathering ($meq/m^2/yr$)	–	0	100	
K^+ weathering ($meq/m^2/yr$)	–	0	20	
Initial exchangeable Ca^{2+} (%)	–	0	20	Minimum set to zero. Maximum set to highest reasonable value for all study sites.
Initial exchangeable Mg^{2+} (%)	–	0	20	
Initial exchangeable Na^+ (%)	–	0	10	
Initial exchangeable K^+ (%)	–	0	10	
Lake relative area (%)	SSO	–	–	Site specific observation (fixed)
Lake retention time (yr)	SSO	–	–	Site specific observation (fixed)
Lake K aluminium (Log10)	SSE	SSE – 40%	SSE + 40%	Site specific estimates
Lake temperature (°C)	5	–	–	Regional default value
Partial pressure CO_2 (% atm)	–	0.015	0.09	Maximum reasonable range for region.
Lake DOC (µmol/l)	SSE	0	SSE × 2	Site specific estimate
Lake nitrification (%)	100	–	–	Regional default value
Retention C/N Upper (mol/mol)	SSE	SSE – 20%	SSE + 20%	Site specific estimate
Retention C/N Range (mol/mol)	SSE	SSE – 20%	SSE + 20%	Site specific estimate
Initial carbon pool (mol/m^2)	SSE	SSE – 40%	SSE + 40%	Site specific estimate
Initial C/N ratio (mol/m^2)	SSO	SSO – 10%	SSO + 10%	Site specific observations

7. Results

7.1. Hydrological budgets

MAGIC is a flux based model and requires specification of the annual hydrological budget in terms of rainfall, runoff and evapotranspiration. Figure 3 shows the variability in the hydrological budgets between sites. Waterside (Bladnoch) has the lowest annual average rainfall of 1400 mm whilst the highest rainfall and discharge was observed at Green Burn and Dargall Lane, the two highest altitude catchments in the study.

Figure 3: Annual hydrological budgets for the study sites



Data source: National River Flow Archive

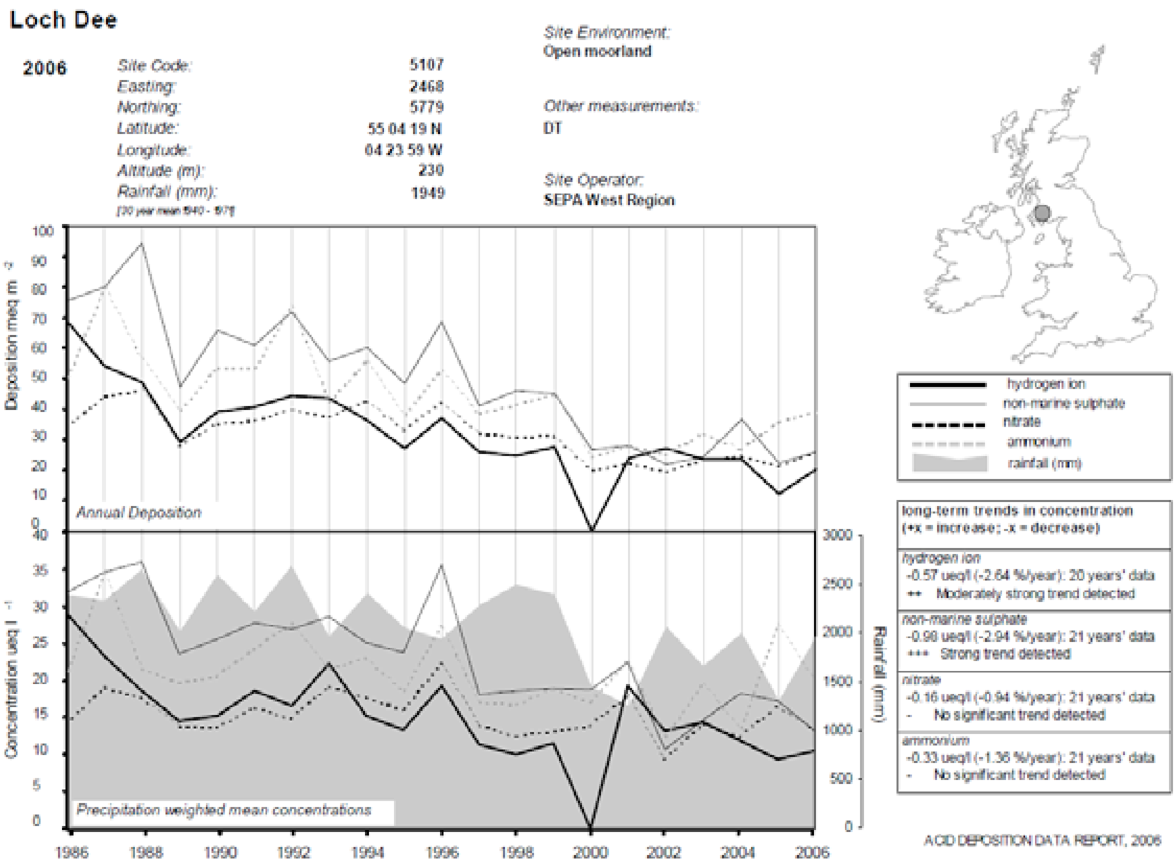
7.2. Deposition

Measurements of precipitation composition from the bulk collector at Loch Dee are presented in Figure 4 (Lawrence et al., 2006). Chemical analysis was carried out using standard analytical procedures (Griffin et al., 2009). In the current study the raw data from Loch Dee, including more recent data to 2008, were screened for contamination by bird strike. A phosphate concentration >0.01 mg P l^{-1} (or >1.0 μeq l^{-1}) and NO_3 and NH_4 concentrations in excess of 2 mgl^{-1} were taken as evidence of contamination. Trend analysis on the non-sea salt sulphate and nitrate concentrations for the period 1986-2006, exhibited a statistically significant ($p<0.001$) decline in non marine SO_4^{2-} of 0.52 μeql^{-1} yr^{-1} (change per year of -2.74%) and in nitrate of -0.06 μeql^{-1} yr^{-1} (change per year of -0.61%).

Sulphate deposition data from Loch Dee were modified to account for dry deposition processes to the forest canopy and to ensure that this conservative ion is in balance with the amount observed in the rivers as discussed in section 6. These volume weighted concentrations of SO_4 are shown in Figure 5a (note, these concentrations do not represent deposition inputs through enhancement mechanisms, these are

presented in section 7.3). Although interception deposition was not accounted for in Figure 5a, the higher volume weighted SO_4 concentrations at Dargall Lane were the result of a correction factor being applied to the rainfall data (Section 5.2).
On the whole, the rate of change and the magnitude of the change in the observed S deposition trend compared well to the FRAME scaler. However, all sites show a slight deviation from the FRAME deposition in the early record, thereafter the observed data corresponds well to the FRAME deposition trend (Figure 5b).

Figure 4: Long term trends in mean annual deposition chemistry at Loch Dee



Source: Lawrence et al., 2006

Figure 5a: Volume weighted sulphate deposition for the 5 study sites (note observed SO_4 concentrations were volume weighted using estimated rainfall data as described in section 5.2)

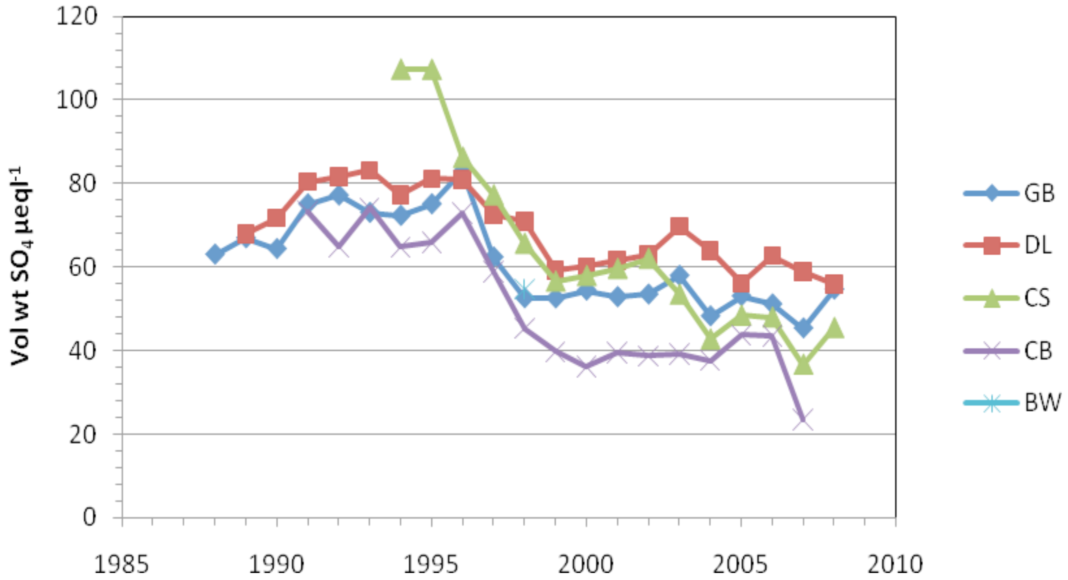
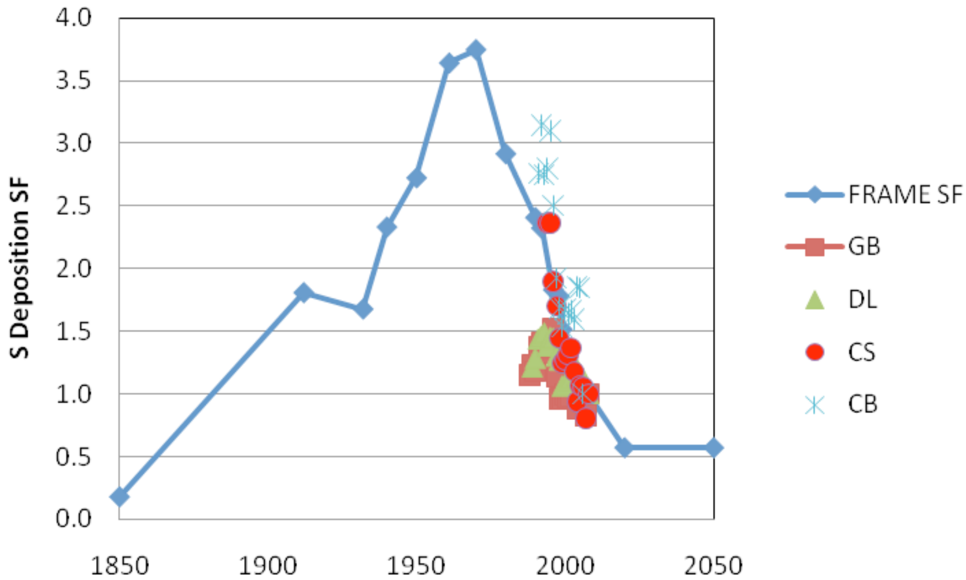


Figure 5b: Observed S deposition and FRAME predicted deposition trends scaled to 1 for present day



Data source: UK Acid Deposition Monitoring Network (http://www.airquality.co.uk/)

7.3. Forestry

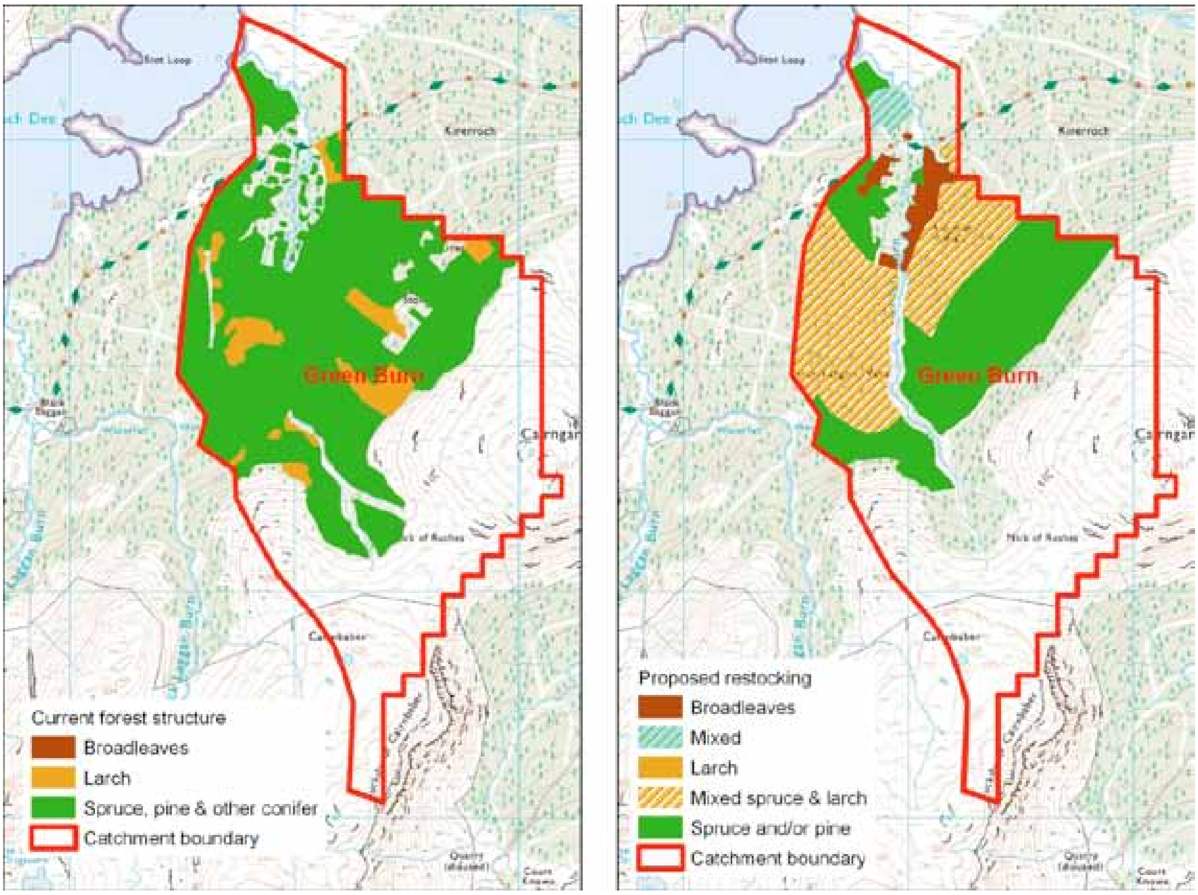
Forestry is acknowledged to be a contributing factor in the acidification of surface waters in acid sensitive parts of the UK principally through the increased capture or 'scavenging' of acidic sulphur and nitrogen pollutants from the atmosphere by their aerodynamically rough canopies (Forestry Commission, 2003; Miller et al., 1991).

Current forestry policy addresses the acidification issue and aims to promote recovery through improvements to the design and diversity of upland plantations. Sustainable forest management is resulting in major restructuring of plantations, involving a shift from forests dominated by single species, even aged stands to more diverse forests with greater open space, a higher proportion of native broadleaves, an increased variety of conifer species, and a broader range of tree age. The net effect of these changes is to reduce the area of conifer forest, usually the higher altitude stands, and lower the proportion of closed canopy forest at any given time, which can be expected to decrease the overall scavenging effect and thus the additional acidification pressure exerted by forestry.

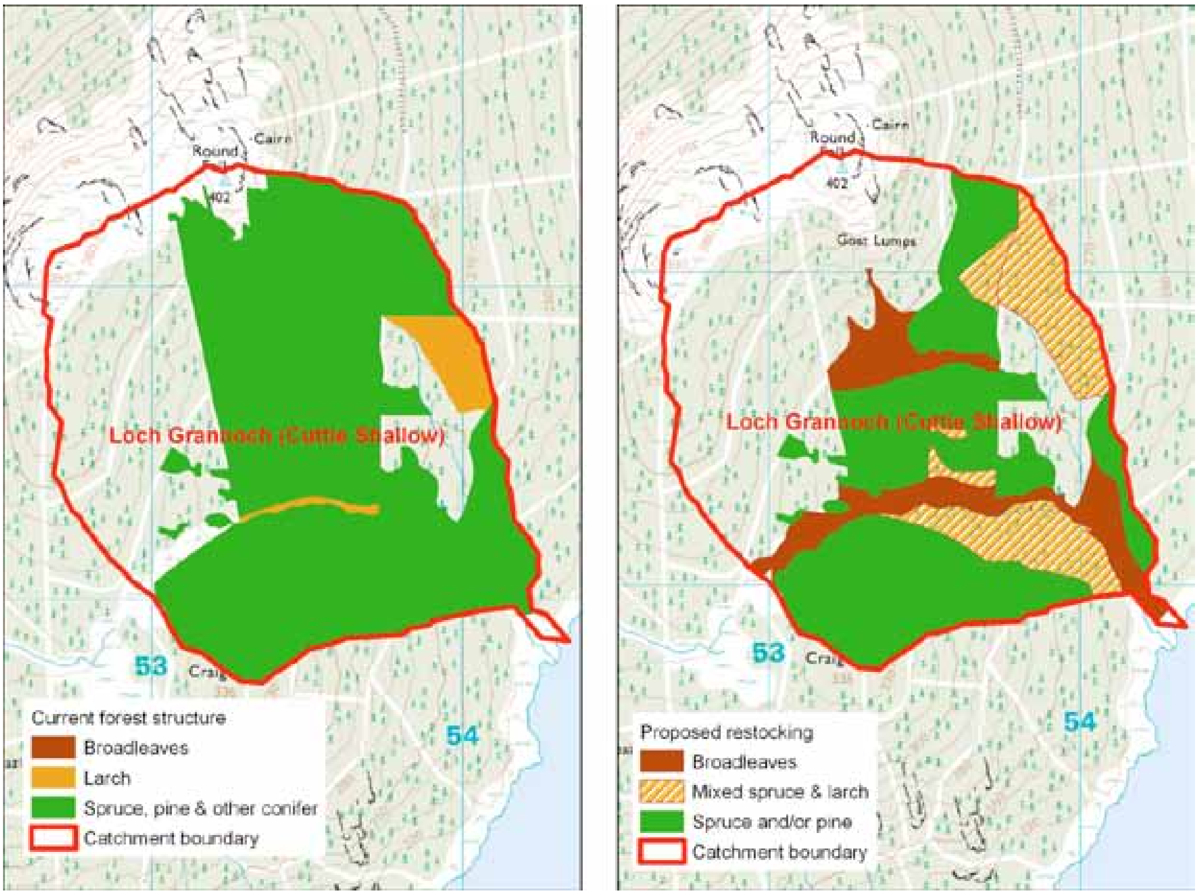
Forest plans are a set of maps and documents that outline the felling, thinning and restocking work to be carried out over a period of 20 years or more. They are reviewed at regular intervals and subject to a period of consultation and application for approval by the Forestry Commission. All public sector owned forests and most large private forests are covered by a forest plan. The plans for each of the four forested catchments used in the study are shown in Figure 6.

Figure 6: Current forest design (left panel) and proposed future restocking (right panel) at the study sites (Panel 1 Green Burn, Panel 2 Cuttie Shallow, Panel 3 Cardon Burn, Panel 4 Waterside)

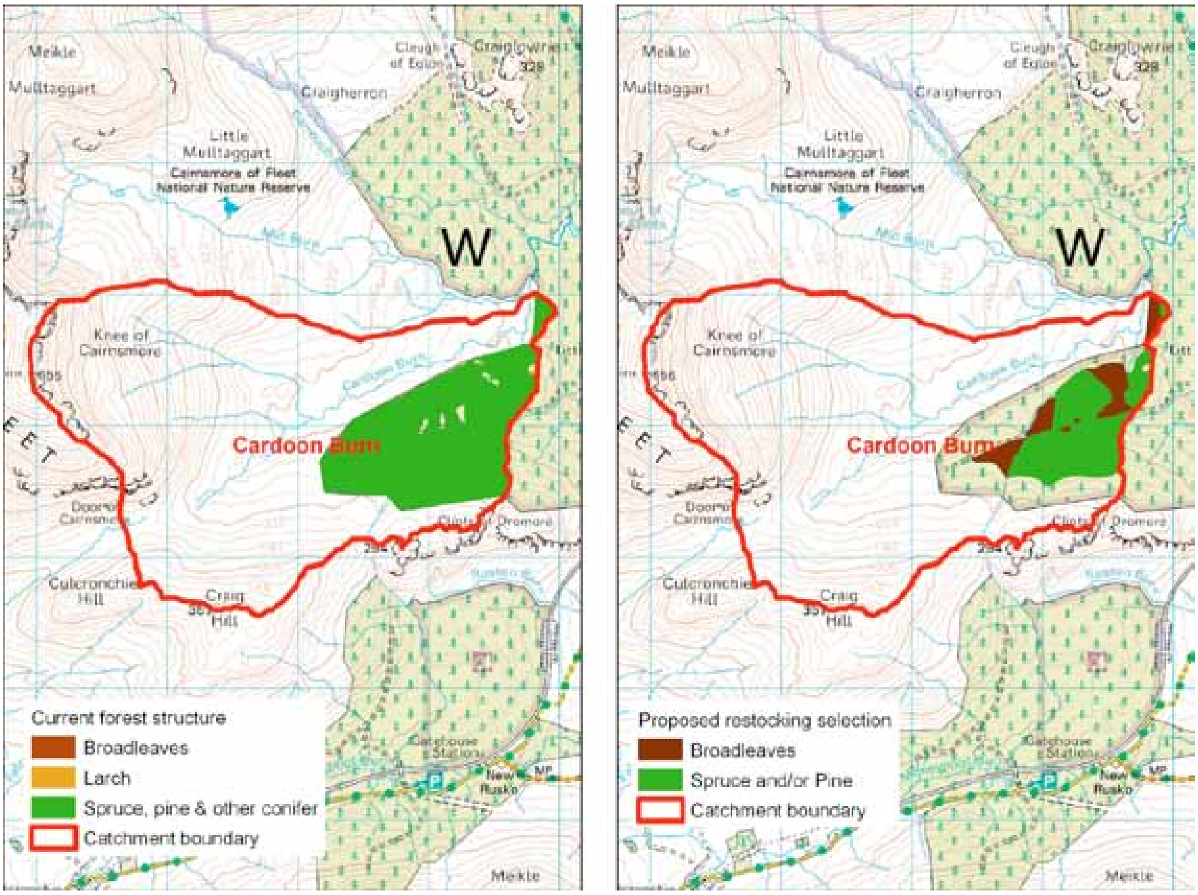
Panel 1 Green Burn



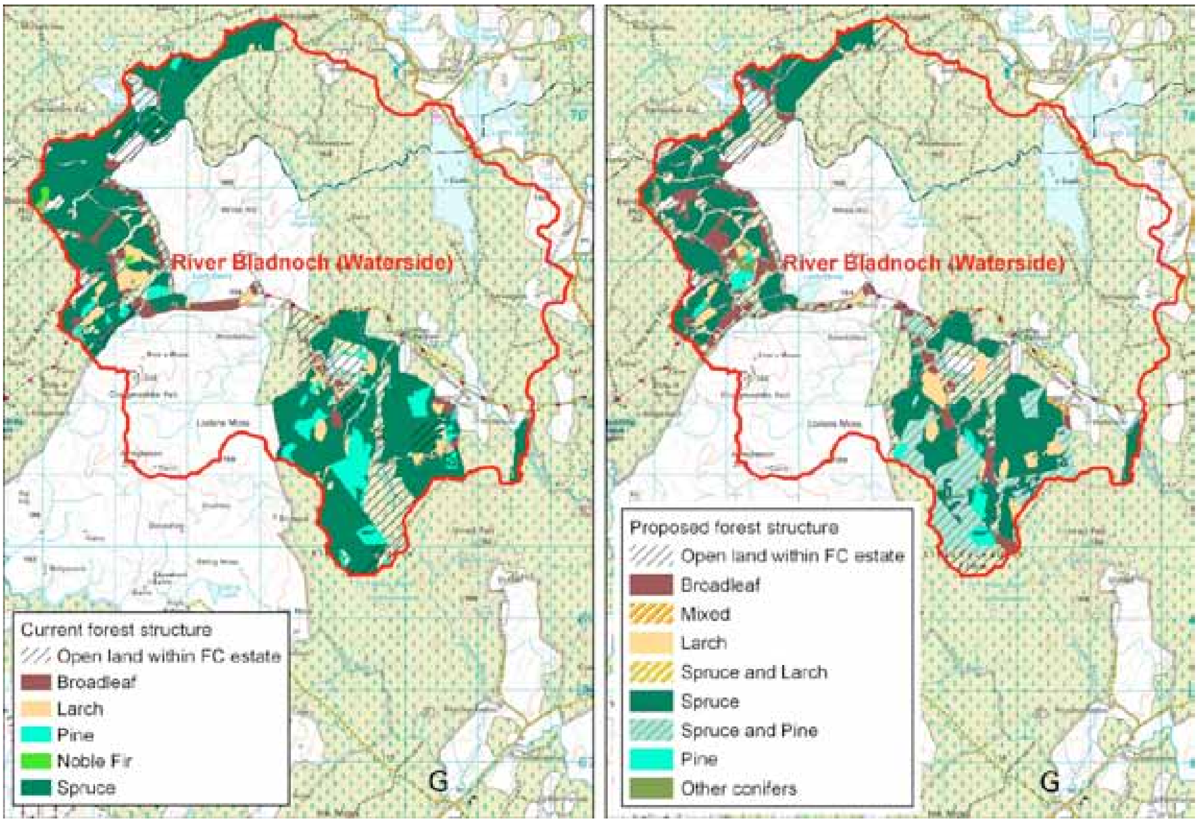
Panel 2 Cuttie Shallow



Panel 3 Cardoon Burn



Panel 4 Bladnoch Waterside



Forest management (described in section 5.4) as practiced in the past and planned into the future were summarised into periods of significant forestry activity (i.e. tree planting/felling) to capture the dynamics of nutrient uptake through time (Table 5). Nutrient uptake was scaled to 1 for present day (calculated as nutrient uptake from the past & future /present day uptake) and the sequences produced represented the relative historical and future change in nutrient uptake to present day for the simulation period (Table 5). Base cation and nitrogen uptake was greatest at Green Burn in 2021 reaching 18.0 and 18.7 meq $m^{-2}yr^{-1}$ respectively. The lowest uptake of nutrients from tree uptake and removal was calculated at the Cardoon catchment (Table 5)

Table 5: Catchment losses of nitrogen and base cations through conventional harvesting of timber (stem and bark) for the simulation period (Units meq $m^{-2}yr^{-1}$)

	Green Burn			Cuttie Shallow			Cardoon Burn			Waterside	
	Base cations	Nitrogen		Base cations	Nitrogen		Base cations	Nitrogen		Base cations	Nitrogen
1973	5.1	4.9	1962	1.4	1.2	1976	3.7	3.0	1965	1.2	1.1
1974	15.0	15.2	1963	9.0	7.6	2013	3.7	3.0	1970	2.8	2.7
2004	17.4	17.3	1978	9.0	7.6	2015	3.5	2.9	1975	8.9	8.2
2015	14.5	14.3	2003	13.3	11.2	2016	3.0	2.5	1984	9.8	9.0
2017	17.8	18.2	2010	14.2	12.2	2017	3.0	2.5	1987	10.1	9.3
2021	18.0	18.7	2012	12.2	10.5	2023	2.3	2.0	1999	10.4	9.8
2022	10.8	11.0	2014	7.1	6.3	2025	0.9	0.8	2005	11.5	11.2
2028	14.0	14.0	2021	10.8	9.3	2026	1.7	1.7	2010	11.9	11.0
2029	9.1	9.8	2022	5.8	5.2	2027	1.7	1.7	2020	10.9	10.8
2035	14.0	14.8	2032	10.4	9.6	2028	1.3	1.3	2030	11.2	11.0
2036	13.8	14.4	2049	9.5	8.5	2029	1.5	1.5	2040	10.9	10.7
2050	13.8	14.4	2050	8.9	8.0	2050	1.5	1.5	2050	10.2	10.8

It is well established that decreased canopy cover will result in decreased atmospheric scavenging and consequently reduced total deposition to the forests and vice versa (Neal et al., 1992; Ormerod et al., 1989). These processes have been incorporated in MAGIC assuming that the reduction in the proportion of coniferous species will result in a proportional reduction in dry deposition of anthropogenic air pollutants (Table 6). Dry deposition sequences were calculated using a similar method to the forest nitrogen and base cations uptake sequences but a dry deposition factor of 1.3 for SO_4, 1.8 NO_3, and 1.4 NH_4 for 100% forest cover was scaled to the forested area through time relative to present day.

To assess the relative effects of afforestation and acid deposition on past and future changes in soil and surface water chemistry a scenario of ‘no forestry’ was implemented.

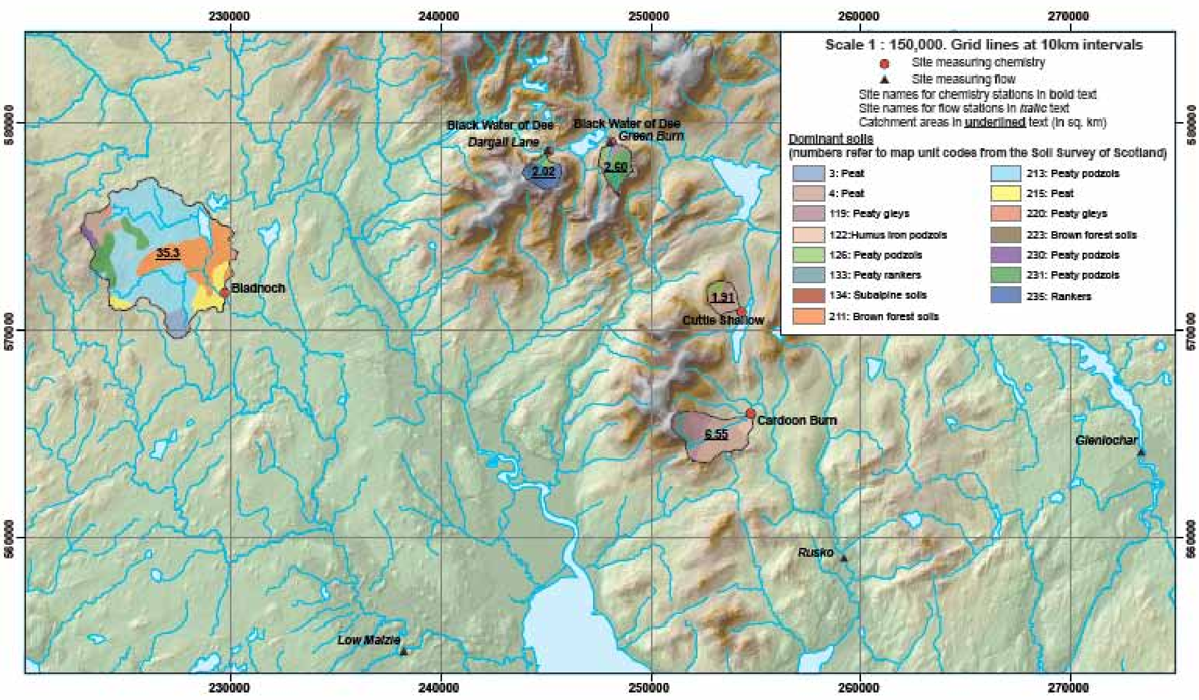
Table 6: Dry deposition factors applied to the study sites (Scaled to 1 for present day)

	GB SO_4	GB NH_4	GB NO_3		CS SO_4	CS NH_4	CS NO_3		CB SO_4	CB NH_4	CB NO_3		BW SO_4	BW NH_4	BW NO_3
1973	0.91	0.88	0.80	1962	0.81	0.77	0.63	1975	0.95	0.94	0.89	1964	0.91	0.89	0.80
1974	0.98	0.97	0.95	1963	0.92	0.91	0.85	1976	1.00	1.00	1.00	1965	0.92	0.90	0.82
1975	1.00	0.99	0.99	1978	0.92	0.91	0.85	2013	1.00	1.00	1.00	1968	0.93	0.92	0.85
2005	1.00	0.99	0.99	1979	1.00	1.00	0.99	2014	0.99	0.99	0.98	1974	0.96	0.94	0.89
2006	1.00	0.99	0.99	2001	1.00	1.00	0.99	2015	1.00	1.00	0.99	1977	0.98	0.98	0.96
2007	1.00	1.00	1.00	2003	0.99	0.98	0.97	2016	0.99	0.99	0.98	1984	0.99	0.98	0.97
2008	1.00	1.00	1.00	2004	1.00	1.00	1.00	2017	0.99	0.99	0.98	2004	0.99	0.99	0.98
2013	1.00	1.00	1.00	2010	1.00	1.00	1.00	2023	0.98	0.97	0.95	2007	1.00	1.00	1.00
2014	0.98	0.97	0.95	2011	0.96	0.95	0.93	2024	0.98	0.97	0.95	2008	1.00	1.00	1.00
2016	1.00	1.00	1.00	2012	0.97	0.96	0.94	2025	0.96	0.94	0.90	2012	0.99	0.99	0.98
2019	1.00	1.00	1.00	2014	0.90	0.87	0.79	2026	0.97	0.96	0.93	2017	1.00	1.00	1.00
2022	0.95	0.94	0.89	2015	0.95	0.94	0.90	2027	0.97	0.96	0.93	2020	0.99	0.99	0.98
2023	0.97	0.96	0.94	2021	0.95	0.94	0.90	2028	0.96	0.95	0.91	2025	1.00	1.00	1.00
2027	0.97	0.96	0.94	2022	0.88	0.85	0.76	2029	0.97	0.96	0.92	2027	0.99	0.99	0.97
2028	0.97	0.96	0.94	2023	0.94	0.93	0.89	2050	0.97	0.96	0.92	2029	1.00	0.99	0.99
2029	0.94	0.92	0.86	2032	0.94	0.93	0.89					2040	0.99	0.99	0.98
2030	0.97	0.96	0.94	2034	0.94	0.93	0.89					2042	1.00	0.99	0.99
2036	0.97	0.96	0.94	2035	0.93	0.91	0.86					2048	0.99	0.99	0.97
2050	0.97	0.96	0.94	2050	0.92	0.90	0.85								

7.4. Soil and Geology

The soil parent materials and the underlying geology of Dargall Lane, Green Burn, Cardoon Burn and Cuttie Shallow comprise predominantly granite (Countesswells, Dalbeattie and Priestlaw Associations: Soil map units 119, 122, 126, 133, 134), while the Waterside catchment is underlain by metamorphosed greywackes (Ettrick Association: Soil map units 211, 213, 215, 220, 223, 230, 231, 235, Figure 7). Soils derived from granitic bedrock are inherently more acid sensitive than those developed on greywackes parent material. The soils of Waterside, Cuttie Shallow and Cardoon Burn are highly organic compared to Dargall Lane and Green Burn as indicated by the area of peat and organic dominated soils (Table 7), low bulk densities, high cation exchange capacity, carbon/nitrogen pools and soil water dissolved organic carbon (DOC) (Table 8). These soil traits influence the rate of soil acidification and recovery, making soils very responsive to increases in acid deposition but slow to recover as base cation replenishment is predominantly from atmospheric sources rather than from mineral weathering. In terms of the susceptibility of soils to acidification, the more mineral soils at Green Burn and Dargall Lane have the lowest present day soil base saturation (7.22% and 4.81% respectively), have fewer cation exchange sites than the more organic rich soils at the other sites; making the soils more prone to the effects of acidification. Recovery of these soils is slow as replenishment of the base status is dependant on weathering processes. In addition, the main sources of pCO_2 in soil air are respiration from plant roots and decaying organic matter and as a consequence pCO_2 emissions from mineral rich soils are low, as observed at Dargall Lane (Table 8). Soil information is mapped to the major soil 'subgroup' for clarity in Figure 7 and summarised to the 'major' soil group in Table 7.

Figure 7: Distribution of soil types (major soil subgroups) within the study sites



For further details regarding soil map units please refer to the sheet "QMUnit codes explained" in the accompanying spreadsheet.

Table 7: Spatial extent of soils (major soil groups) in the study sites

Monitoring site (code)	P		PP		PG		PR		HIP		SAP		BFS		Peat as MSG	
	km^2	%	km^2	%	km^2	%	km^2	%	km^2	%	km^2	%	km^2	%	km^2	%
Waterside (BW)	5	16	21	62	0	1	0	0	0	0	0	0	8	22	27	78
Green Burn (GB)	0	15	2	73	0	12	0	0	0	0	0	0	0	0	3	100
Dargall Lane (DL)	0	0	0	20	0	0	0	0	0	0	2	80	0	0	0	20
Cuttie Shallow (CS)	1	74	0	21	0	5	0	0	0	0	0	0	0	0	2	100
Cardoon Burn (CB)	3	52	0	0	2	27	1	12	1	8	0	2	0	0	6	91

Abbreviations			
P	Peat	**HIP**	Humus Iron Podzol
PP	Peaty Podzol	**SAP**	Sub Alpine Soil
PG	Peaty Gley	**BFS**	Brown Forest Soil
PR	Peaty Ranker	**MSG**	Major Soil Group

Soil input data were determined as described by Helliwell et al., 1998. The area of each soil map unit represented in the national Soil Map of Scotland (1:250 000) was derived for each catchment. The proportion of the component soil series in the soil map unit was determined along with typical sequences of soil horizons (with typical depths) as established by Smith et al (2010). For each of these soil horizons, corresponding soil chemistry parameters were derived from observation in the Scottish Soils Database (The James Hutton Institute). Soil input data were determined by vertically (horizon) and spatially (soil series proportion) weighting of soil physico-chemical properties for each catchment. The main physico-chemical parameters are reported in Table 8.

Table 8: Soil physico-chemical characteristics for the study sites (Control site highlighted in grey)

	Units	GB	DL	CS	CB	BW
Depth	m	1.00	0.40	1.00	0.90	0.96
Bulk density	kg m^{-3}	956	1326	357	362	460
Cation exchange capacity (CEC)	$mmol_c\ kg^{-1}$	154	215	348	351	310
Exchangeable calcium	% CEC	3.11	1.59	3.30	3.68	4.20
Exchangeable magnesium	% CEC	2.75	1.20	5.04	5.62	4.55
Exchangeable sodium	% CEC	0.68	0.64	0.79	0.83	0.78
Exchangeable potassium	% CEC	0.68	1.38	0.42	0.47	0.52
Base saturation	%	7.22	4.81	9.55	10.60	10.05
Soil pH	pH unit	4.2	4.6	3.9	4.0	4.0
Carbon pool	mol m^{-2}	2814	2250	4369	4003	4229
Nitrogen pool	mol m^{-2}	104	139	116	110	125
Carbon:Nitrogen		27	16	38	36	34
Carbon dioxide partial pressure	%atm	1.532	0.650	2.763	2.684	2.621
Gibbsite coefficient	-log10	7.36	7.50	6.78	7.05	6.59
DOC	µmol l^{-1}	37	32	56	49	62

7.5. Surface water chemistry

The concentration of SO_4 in all rivers declined over the 20-year period (Figure 8a), largely in line with reductions observed in bulk deposition at Loch Dee. The greatest decline occurred in Cuttie Shallow (0.4 $\mu eql^{-1}\ yr^{-1}$). Following the initial declining trend in observed surface water SO_4 concentrations at Dargall Lane, the trend plateaus from the late 1990's onwards, which is broadly consistent with observed deposition during this time. Compared to the afforested catchments (Green Burn and Cardoon Burn), concentrations in Dargall Lane are generally higher, yet the mechanisms behind this response in surface waters are unclear. It is unlikely that SO_4 desorption from the soil during drought/rewetting cycles is responsible due to the high rainfall in the region and the fact that this mechanism could be expected to be more evident at the forested sites due to their increased water demand. Uncertainties with the hydrological budgets may be the cause, as described in section 5.2.

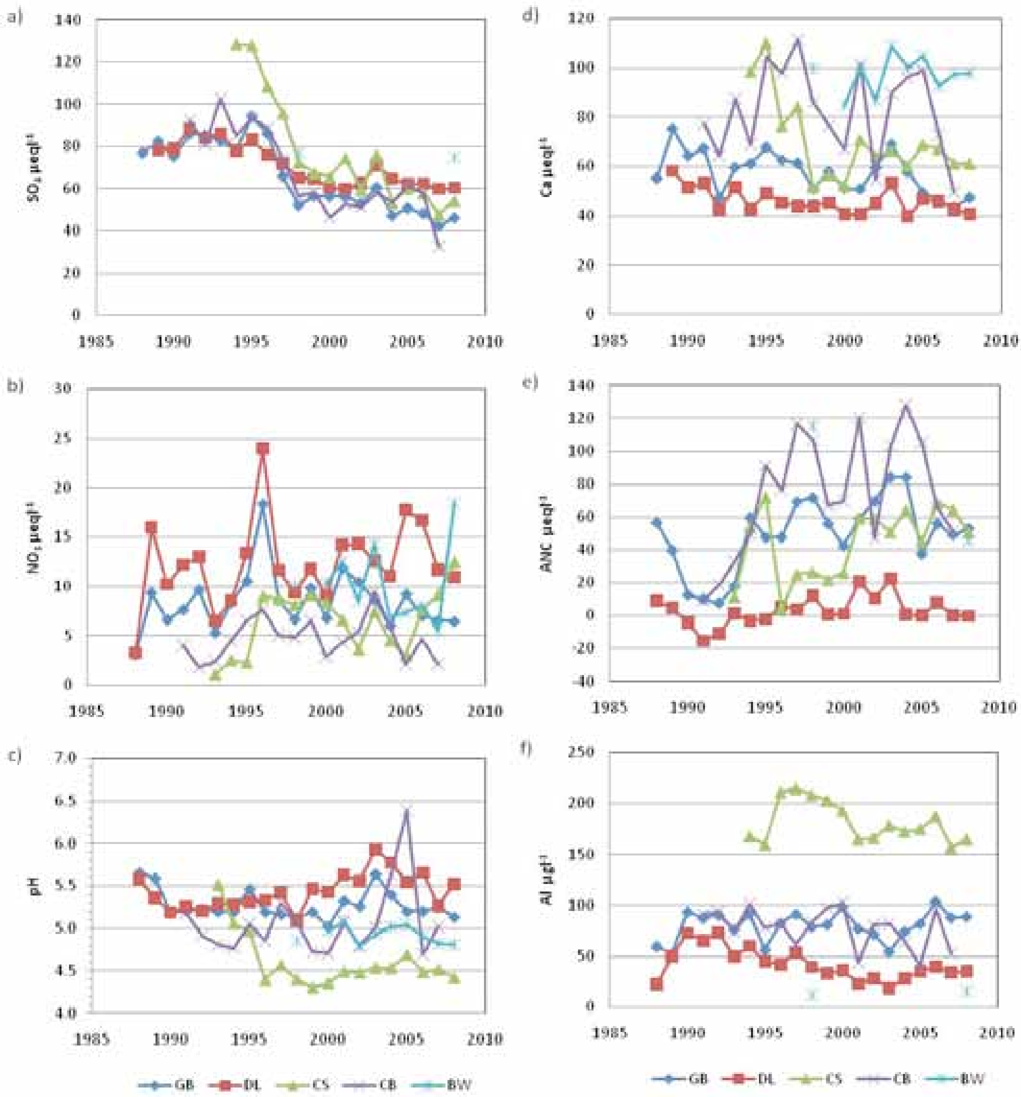
The concentration of NO_3 shows substantial inter-annual variability at all sites but whilst no obvious trends are observed at most sites a slight increasing trend was apparent at Dargall lane ((0.17 $\mu eql^{-1}\ yr^{-1}$), although this was not statistically significant Figure 8b). No consistent trends were observed for surface water pH and inter site comparisons demonstrate a mixed response to the clear reduction in SO_4 that was observed at all sites (Figure 8c). No trends were observed for Ca although clear differences in the inter year variability of Ca concentrations are apparent. For example Cardoon Burn exhibits substantially greater inter-annual variability than Dargall Lane (Figure 8d).

Acid Neutralising Capacity (ANC) describes the ability of water to buffer acidification by a strong acid. As such it is a useful indicator of acidification status. Waters with negative ANC are almost certainly in an acidified condition as a consequence of anthropogenic pollution (i.e. Dargall Lane). However, the determination of precise ANC thresholds and whether ANC is the best indicator to use is still subject to debate (McCartney et al., 2003, Neal et al., 1992). ANC, as determined from the difference between the concentration of base cations (i.e. Ca, Mg, Na, K and NH_4) and strong acid anions (SO_4, NO_3 and Cl) in units of equivalence, is the calculation used in MAGIC. Analysis of the uncertainty in this measure of ANC has highlighted a broad range of predicted outcomes that represent the sum or aggregation of all the slight errors or misfits in the component ions that contribute to the simulated ANC. In regions with high sea-salt inputs such as Galloway, there is a tendency for a slight imbalance of ions in waters with high seasalt concentrations and this can influence the predicted range of ANC. Whilst it could be argued that the alternative way of calculating ANC using acid-base estimates should be applied to such surface waters with high conductivity, rather than the charge balance method, there are no dynamic biogeochemical models available at the present time that are capable of simulating the forest dynamics and surface water acidification in this way. The acid-base approach is based on pH, Al and organic acidity. All sites show increases in ANC to varying degrees, the most significant recovery being observed for forested Green Burn, Cardoon Burn and Cuttie Shallow catchments, primarily as a result of the declining trend in anthropogenic deposition of S and N in the mid 1990s, but also in response to the reduction in sea-salt deposition in the early years of monitoring (data not shown) (Figure 8e).

Concentrations of labile Al generally reflect the acidification status of soils and reductions were observed at Dargall Lane and to some extent Cuttie Shallow, particularly in response to the period of recovery post 1990 (Figure 8f). Labile Al was inversely related to pH during this period. It is also noteworthy that labile Al concentrations at Cuttie Shallow are almost double those at the other sites. Inter-site differences in observed surface water chemistry result from a range of catchment specific factors including acid and sea salt deposition, geological characteristics and land use.

The hydrochemistry of river systems are complex, and long term datasets such as those presented here should be analysed using statistical approaches such as non-linear models (i.e. General Additive Models) which can handle temporally complex data. Detailed statistical analysis was not possible in this contract.

Figure 8: Flow weighted surface water chemistry a) non-marine SO_4, b) NO_3, c) pH, d) Ca, e) ANC, f) Labile Al



Data source: Marine Scotland Freshwater Laboratory

7.6. MAGIC calibration

The model was calibrated to the longest possible period with available data (section 5.6). For the majority of ions, the predicted output parameters from the Bayesian calibration are in reasonable agreement with the corresponding observations (Figures 9-13). Surface water observations are generally simulated between the 5% and 95% pointwise credible intervals as shown by the red dashed line in Figures 9-13. The observed decline in SO_4 concentration is reproduced well, but MAGIC under predicts the significant decline in SO_4 in the first part of the simulation (1989-96) at Green Burn (Figure 9) and Cuttie Shallow (Figure 11). At Dargall Lane (Figure 10) MAGIC slightly over predicts SO_4 concentrations during the first 5 years of the simulation but captures the general trend. While concentrations of NO_3 are significantly lower than SO_4, and hence more of a challenge to model, MAGIC on the whole reproduces the subtle inter year variability. The peaks in NO_3 are not well replicated by MAGIC particularly where they result from climate induced events such as in 1996 (Green Burn and Dargall Lane, Figures 9 and 10 respectively). A strong correspondence between observed and simulated surface water Ca, Mg, Na, and Cl further demonstrates the suitability of the model and the datasets used in the calibration procedure. Relative to Ca, Mg, and Na, the K concentrations are very low but whilst there are some outlying observations, the majority are within the 95% confidence interval.

Figure 9 Hydrochemical predictions of output parameters for Green Burn (blue solid line-median calibration from 15000 runs) with corresponding observations (black circles). The red dashed lines show the 95% credible intervals for the output parameters (Units $\mu eq l^{-1}$ except Al $\mu g l^{-1}$).

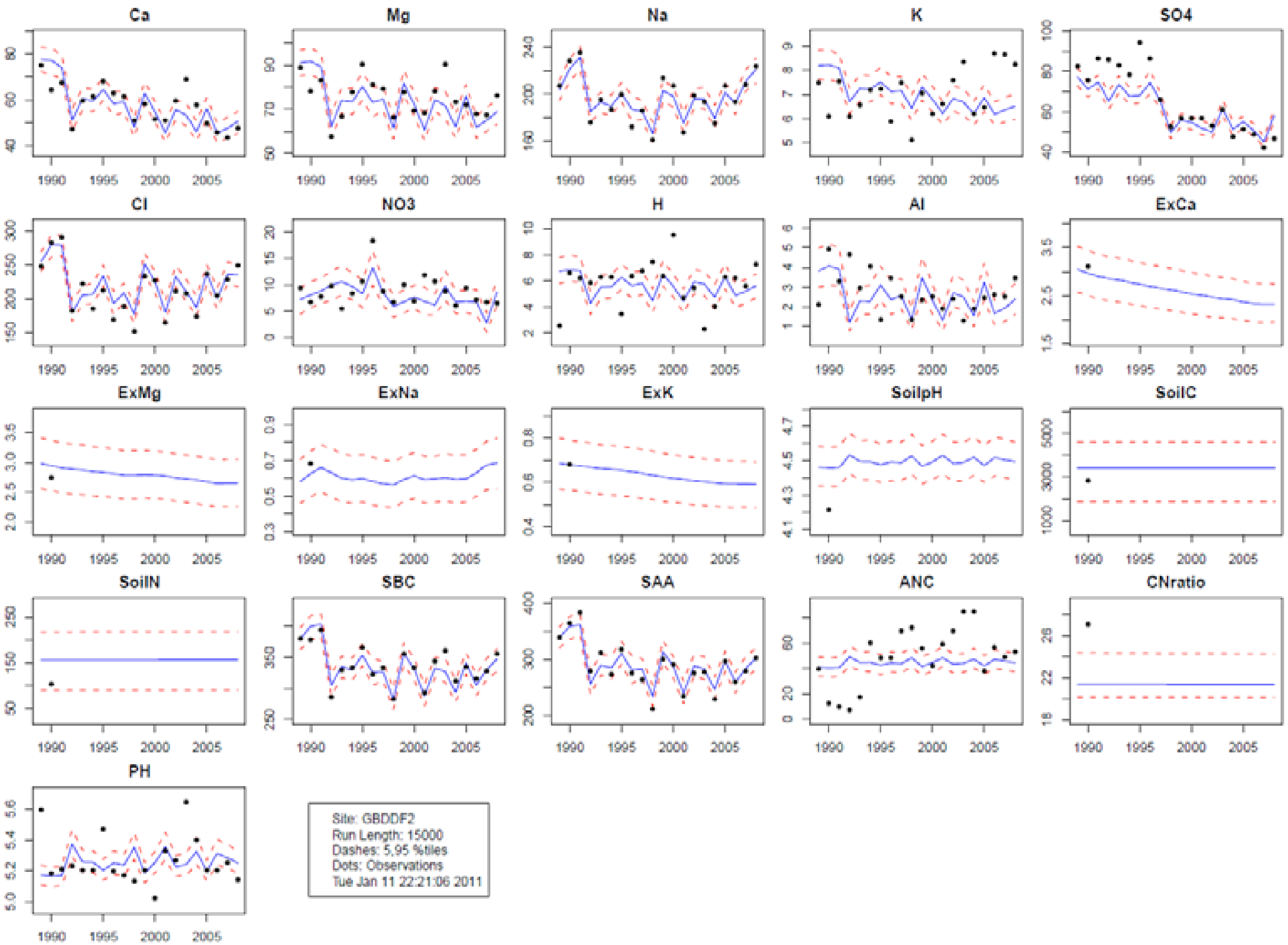


Figure 10 Hydrochemical predictions of output parameters for Dargall Lane (blue solid line-median calibration from25000 runs) with corresponding observations (black circles). The red dashed lines show the 95% credible intervals for the output parameters (Units µeql^{-1} except Al µgl^{-1}).

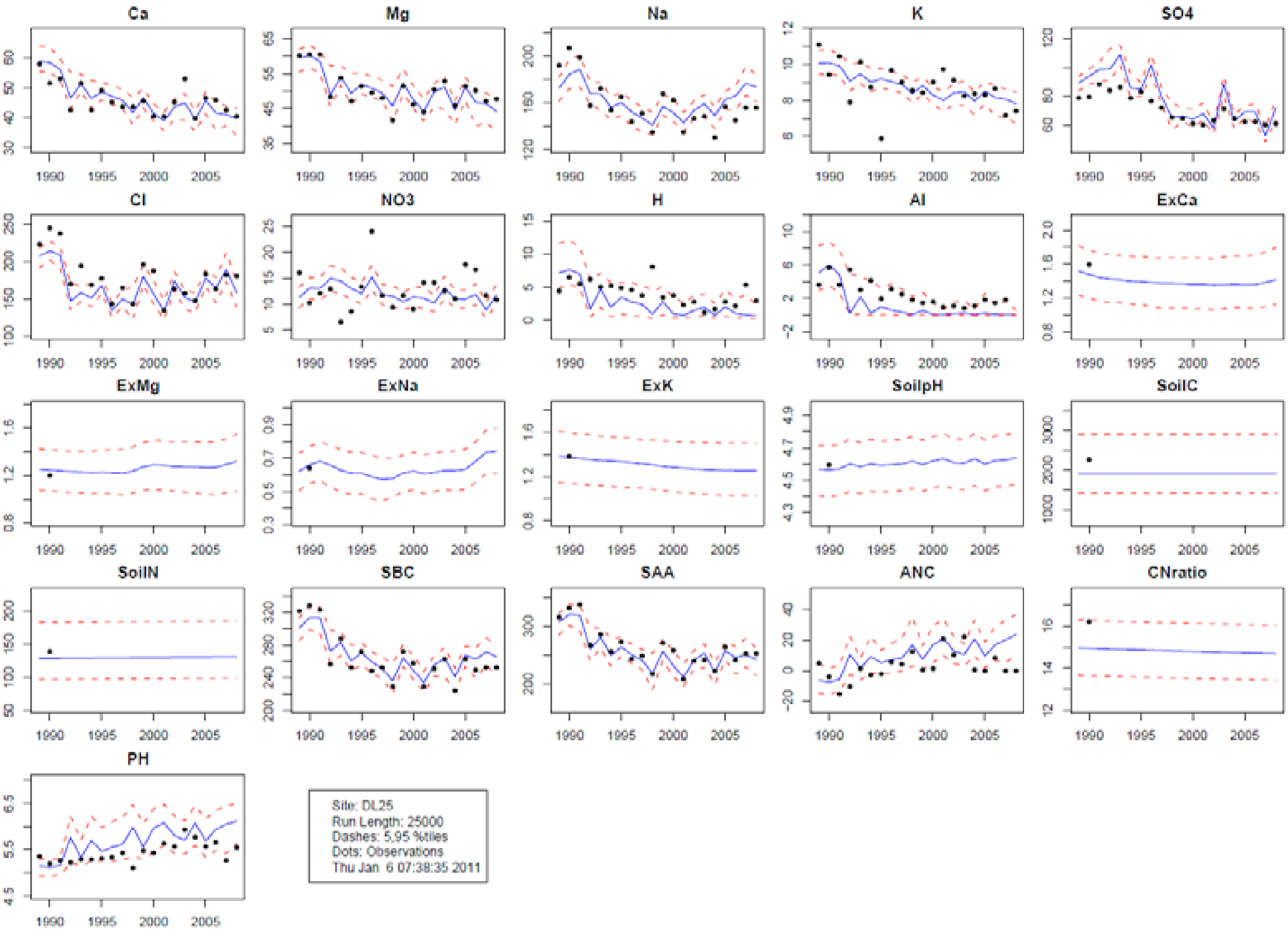


Figure 11: Hydrochemical predictions of output parameters for Cuttie Shallow (blue solid line-median calibration from 15000 runs) with corresponding observations (black circles). The red dashed lines show the 95% credible intervals for the output parameters (Units $\mu eq l^{-1}$ except Al $\mu g l^{-1}$).

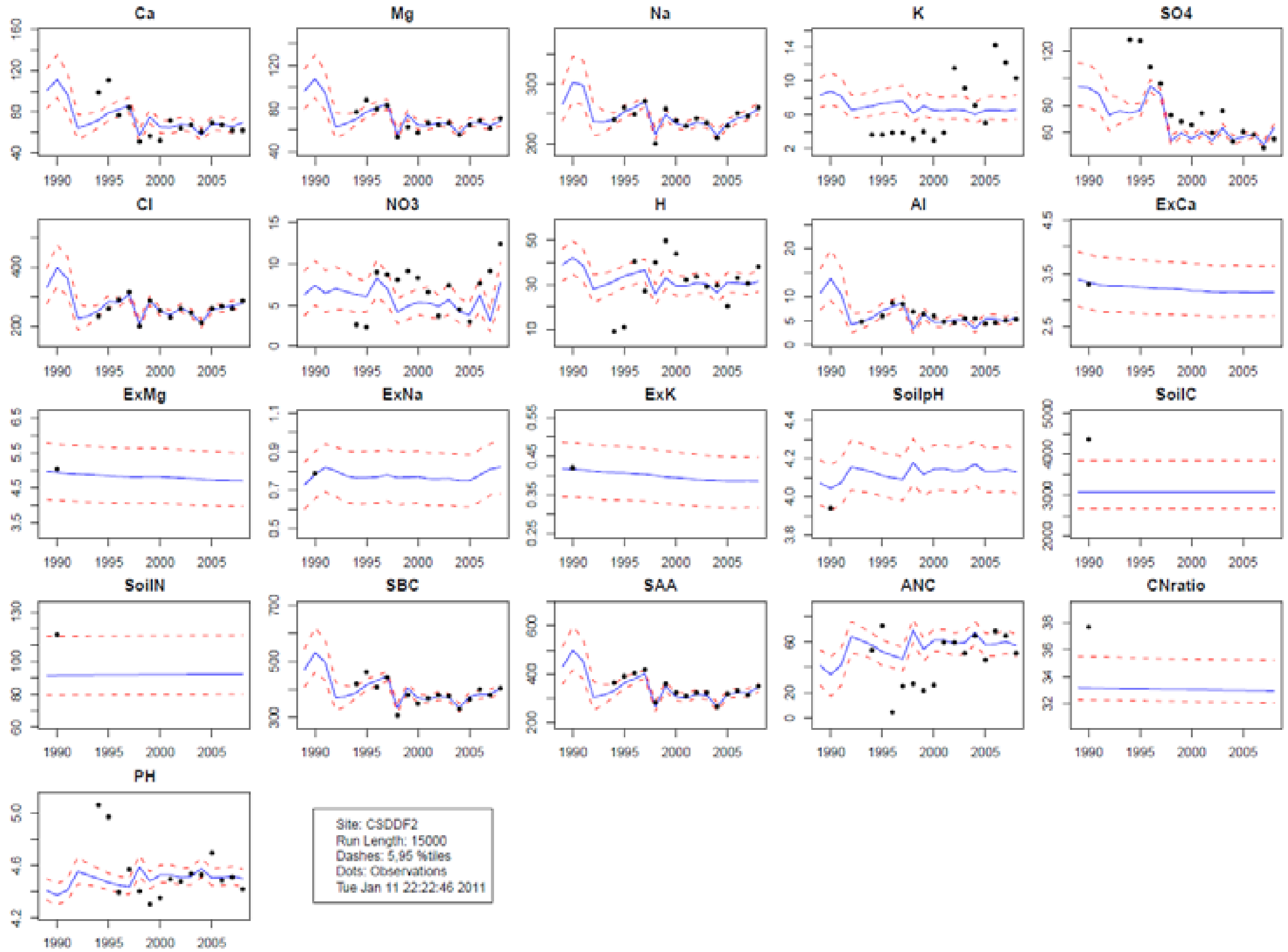


Figure 12: Hydrochemical predictions of output parameters for Cardoon Burn (blue solid line-median calibration from 15000 runs) with corresponding observations (black circles). The red dashed lines show the 95% credible intervals for the output parameters (Units μeql^{-1} except Al μgl^{-1}).

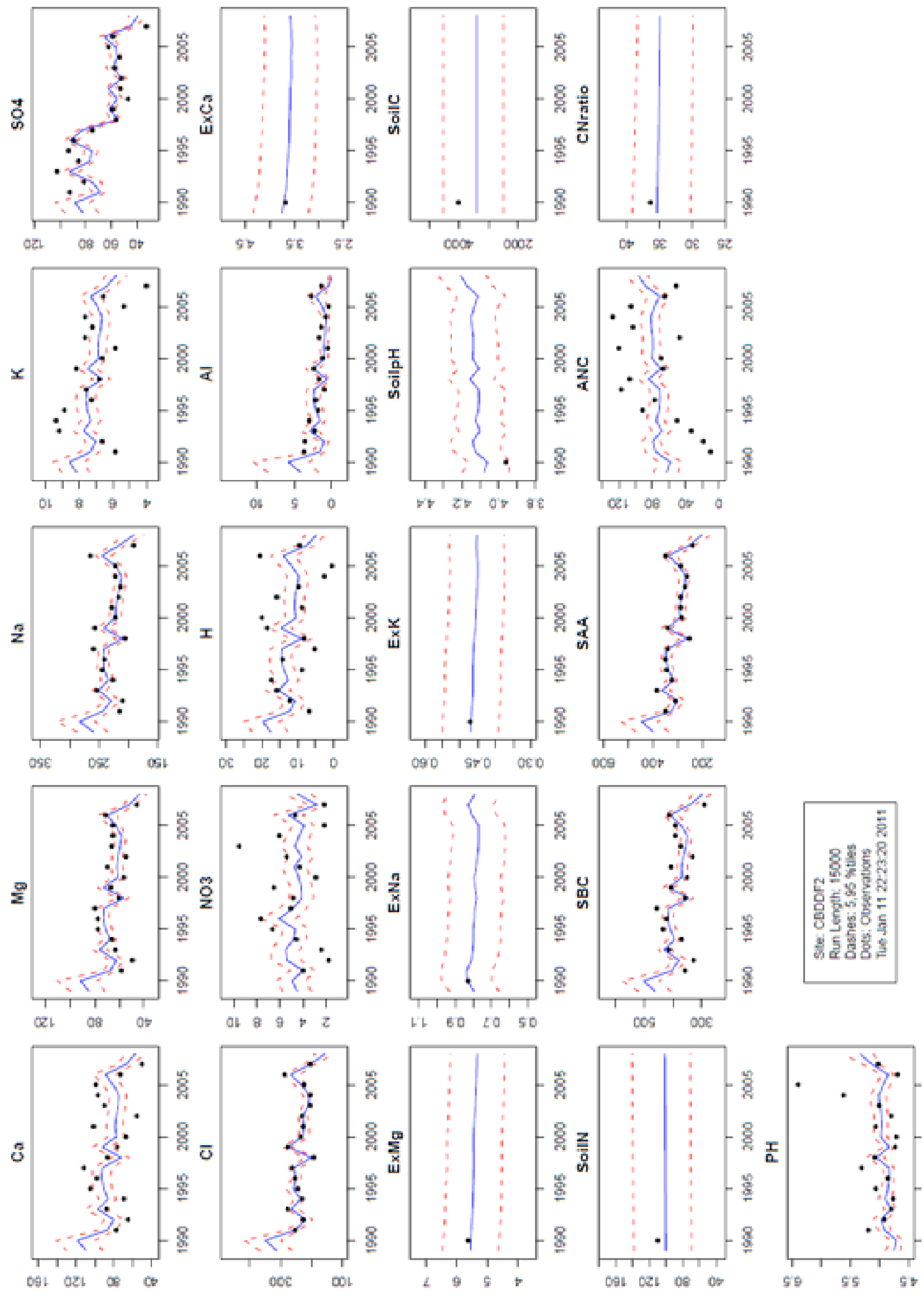
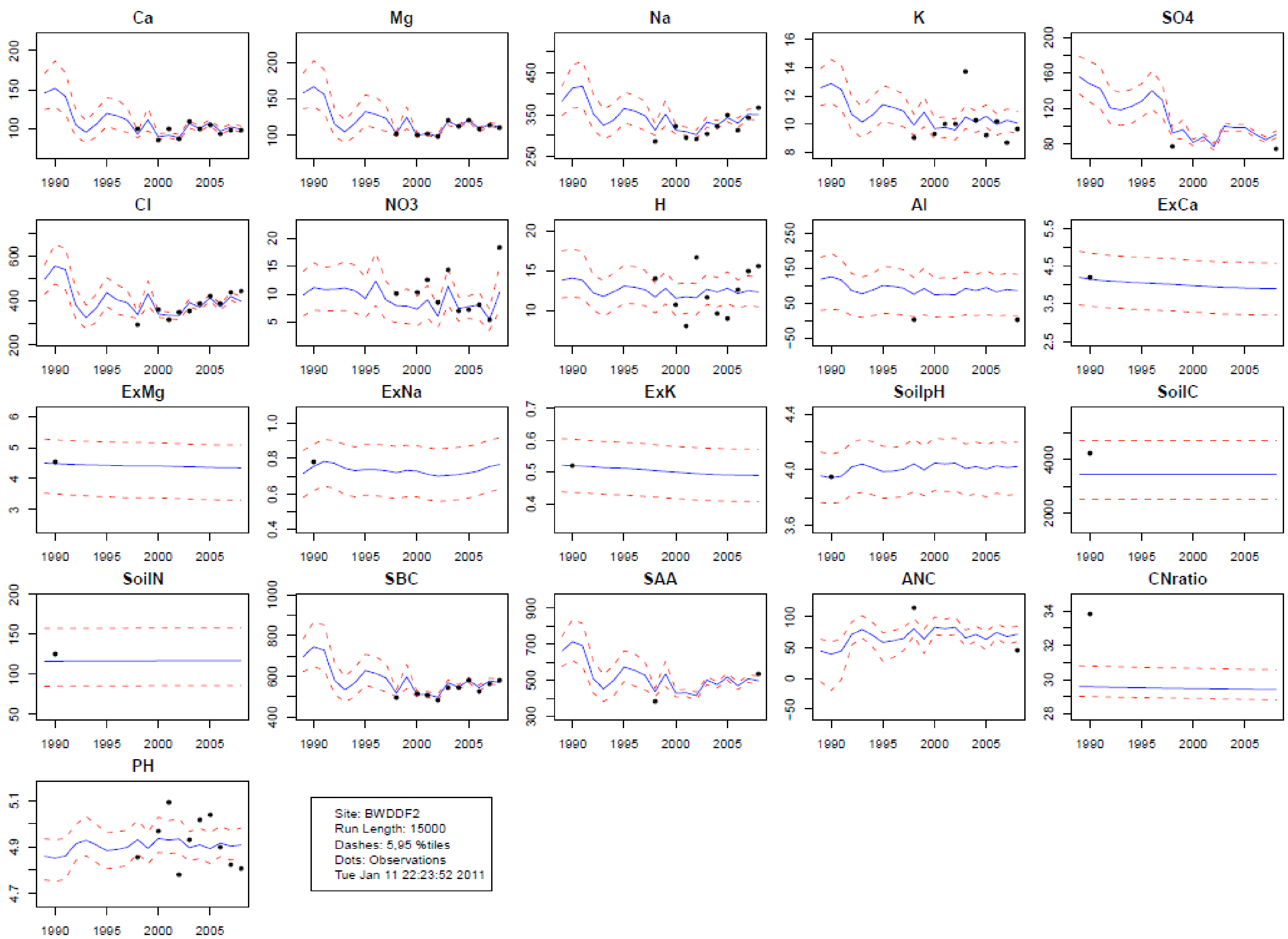


Figure 13: Hydrochemical predictions of output parameters for Bladnoch (Waterside) (blue solid line-median calibration from 15000 runs) with corresponding observations (black circles). The red dashed lines show the 95% credible intervals for the output parameters (Units µeql^{-1} except Al µgl^{-1}).



7.7. Long term assessment of surface water acidification and recovery

a) 1860-1970

Note: Unless otherwise stated, all statistics in this section are based on median data calculated from 1000 model iterations.

The results presented cover the period from assumed 'pristine' water quality conditions in 1860 through to 1970, a time when acid deposition and its impacts were most severe. Simulated ANC for 1860 represents the hydrochemical reference condition prior to the Industrial Revolution. In 1860 all sites are above the annual mean critical threshold for acid sensitive aquatic organisms (>20 μeql^{-1}) that is adopted by the UK under the Gothenburg Protocol and is used to define good ecological status for lake water bodies under the Water Framework Directive. Lien et al. (1992) reported that where ANC lies above 20 μeql^{-1}, 90% of sites within their study of 1095 lakes and 30 rivers in Norway were un-impacted in terms of their brown trout populations, while 100% of sites were un-impacted in terms of their salmon populations. However, there are a number of limitations with the Lien study which give rise to uncertainty over the reported relationships between fish status and ANC. Specifically, chemical sampling of lakes was limited to once a year in the autumn, more than one method was used to calculate ANC, there was no formal statistical analysis of the relationships between ANC and fish status, and fish impacts in lakes were primarily assessed from questionnaires, albeit often supported by extensive historic records and occasionally test fishing. Therefore, while the Lien study offers considerable value in terms of overall sample size, these limitations need to be recognised when setting critical ANC limits for protecting fish. It is important to note that ANC does not have a direct toxic effect and the use of an annual mean value to represent a critical ANC threshold hides significant episodic variation in this parameter (McCartney et al*.,* 2003; Bridcut et al*.,* 2004). There are also issues over the method of calculating ANC and variability in the critical threshold value between fish species and different life stages in relation to the different methods (Malcolm et al*.,* submitted). Recent work suggests that labile aluminium provides a better predictor of the sensitivity of brown trout to acidification but does not contradict the use of ANC 20 as an appropriate threshold for protecting this species depending on expected levels of fish presence and providing that the considerable uncertainty over the value is recognised (Malcolm et al*.,* submitted). Overall ANC remains the parameter favoured by managers and regulators for applying the critical loads approach at national and international levels and can provide a useful metric for predicting the recovery of freshwaters to declining pollutant emissions, providing the limitations and uncertainties are acknowledged.

The lowest ANC concentrations in 1860 were estimated to occur at Green Burn (5th percentile 65.5 μeql^{-1}, median 74.2 μeql^{-1}, and 95th percentile 83.3 μeql^{-1}) and Dargall Lane (5th percentile 56.1 μeql^{-1}, median 78.1 μeql^{-1}, and 95th percentile 89.2 μeql^{-1}) (Figure 14). Model simulations suggest that significant surface water acidification occurred between 1860 and the 1970s, a time representing peak acid deposition across the UK. A clear reduction in ANC is predicted in response to increasing S deposition, which peaked in 1970, and to a lesser extent, increasing N deposition, which peaked 10 years later. Although a declining ANC is predicted at all sites between 1860 and 1970, the rate of decline is not uniform. At Dargall Lane the ANC decreases by 0.7 $\mu eql^{-1} yr^{-1}$, which contrasts to a gentler decline at Green Burn of 0.24 $\mu eql^{-1} yr^{-1}$ and Cardoon Burn of 0.25 $\mu eql^{-1} yr^{-1}$. Acidification of surface waters during this period is driven primarily by acid deposition as only a small area of forestry had been planted by then (only in the Waterside and Cuttie Shallow catchments). By 1970 modelled ANC remained above ANC 20 μeql^{-1} at all sites except the moorland Dargall Lane, where the simulated ANC declined to 0.5 μeql^{-1}(note the lowest ANC was predicted to occur at this site, reaching a median value of -7.55 μeql^{-1} in 1990).

ANC predictions representing key time periods, when the rate of deposition changed significantly, demonstrate a range of outcomes from the Monte Carlo Markov Chain simulation. The data are presented as probability density frequency plots to show the distribution of simulated ANC (from a 1000 iterations) to give an indication of the degree of uncertainty for selected parameters. Within the uncertainty window it is clear that during the simulation, ANC seldom declines below the threshold of 20 μeql^{-1} (Figure 20); Dargall Lane is the only site where the median ANC threshold is breached. Further investigations into why the range of outcomes for ANC remains similar throughout the simulation period is necessary (Figure 14).

Surface water pH reflects the same historical deposition drivers as ANC with a clear reduction in pH from 1860 to 1970 for all sites except Waterside, where the change in pH throughout the simulated period is minimal. Care should be taken when interpreting the uncertainty ranges of the pH simulations as the width of the confidence window is partially influenced by the log scale (Figure 15). To put this uncertainty into context, when pH is converted to an H ion concentration, for example at a higher pH of >5.5 (lower H^+ ion concentration) the uncertainty in the range between the 5th and 95th percentiles for H^+ is reduced giving greater confidence in the model results (Figure 16). The width of the uncertainty ranges can therefore be misleading when interpreting pH. To demonstrate this issue, the uncertainty ranges for pH and H is described at Green Burn and Dargall Lane, where the highest historical pH was simulated. At Green Burn in 1970 stream pH 5th and 95th percentile values were 5.26 and 5.43 respectively (or H^+ 5.50 $ueql^{-1}$ and 3.72 $ueql^{-1}$ with a difference of 1.78 $ueql^{-1}$) compared to the narrower range in 1860 when we have more confidence in the predictions (5th and 95th percentiles of 5.95 and 6.36 (or H^+ 1.12 $ueql^{-1}$ and 0.44 $ueql^{-1}$ with a difference of 0.75 $ueql^{-1}$) respectively (Figure 16). In contrast at Dargall Lane in 1970 stream pH 5th and 95th percentile values were 4.93 and 6.13 respectively (or H^+ 11.75 $ueql^{-1}$ and 0.74 $ueql^{-1}$ with a difference of 11.01 $ueql^{-1}$) compared to the narrow range in 1860 when we have more confidence in the predictions (5th and 95th percentiles of 6.50 and 7.0 (or H^+ 0.32 $ueql^{-1}$ and 0.1 $ueql^{-1}$ with a difference of 0.22 $ueql^{-1}$) respectively (Figure 16). These results may represent a best case scenario as the contribution of rising DOC concentrations, which could depress the pH, are not currently represented in the uncertainty model structure.

The increase in simulated surface water NO_3 reflects the N deposition trend particularly from 1940–1970 (Figure 17), yet by 1970 NO_3 is a fraction of the total acid anion concentration and SO_4 at this time dominates the acid chemistry at all sites (Figure 18). What is clear from Figure 17 is the window of uncertainty around the median NO_3 concentrations in 1970 is greater compared to earlier in the simulation, but relative to other ions, this window is narrow in terms of the absolute concentration. For example in 1970 the 5th, 50th, and 95th percentile for NO_3 at Green Burn was 8.02 µeql^{-1}, 10.57 µeql^{-1}, and 13.03 µeql^{-1}.

Soils developed from granites and greywackes are sensitive to the effects of acidification. In 1860 the median soil base saturation of all sites was estimated to be greater than 14 % (Figure 19). At this time acid inputs were negligible and base cations derived from atmospheric deposition interacted with exchange sites in the organic soil complex. From 1860 to 1970, model outputs suggest the soils rapidly acidify as base cations are stripped from the soil exchange sites and consequently lower the soil base saturation (to ~10 % in 1970 for all sites). In general terms, the Green Burn and Dargall Lane sites with the highest historic base saturation (21 % and 16% respectively) are predicted to acidify the most by 1970 as a result of higher acid deposition at this time and, with fewer cation exchange sites in these more mineral soils, the exchangeable base cations decreased by 58% and 73% respectively. Another reason for the significant loss of base cations was the higher modelled selectivity coefficients of the mineral soils, indicating that base cations are held more loosely on the soil exchange complex compared to the other sites in this study and as a consequence more likely to be leached in soil drainage. Green Burn and Dargall Lane also had the highest weathering rates of 130 meq m^{-2} and 170 meq m^{-2} respectively, but this process was insufficient to balance the significant loss of base cations from the soil caused by higher acid deposition at these sites (Table 9). The uncertainty surrounding the base saturation in the past is large compared to the calibration period (Figure 19) and care should be taken in interpreting these results. This is particularly the case for Green Burn and Dargall Lane with their much smaller organic pool and lower cation exchange capacity compared to the other sites in this study, which can be expected to make them more responsive to increases in acid deposition during this period.

Figure 14: Median acid neutralising capacity with 5th and 95th percentile ranges

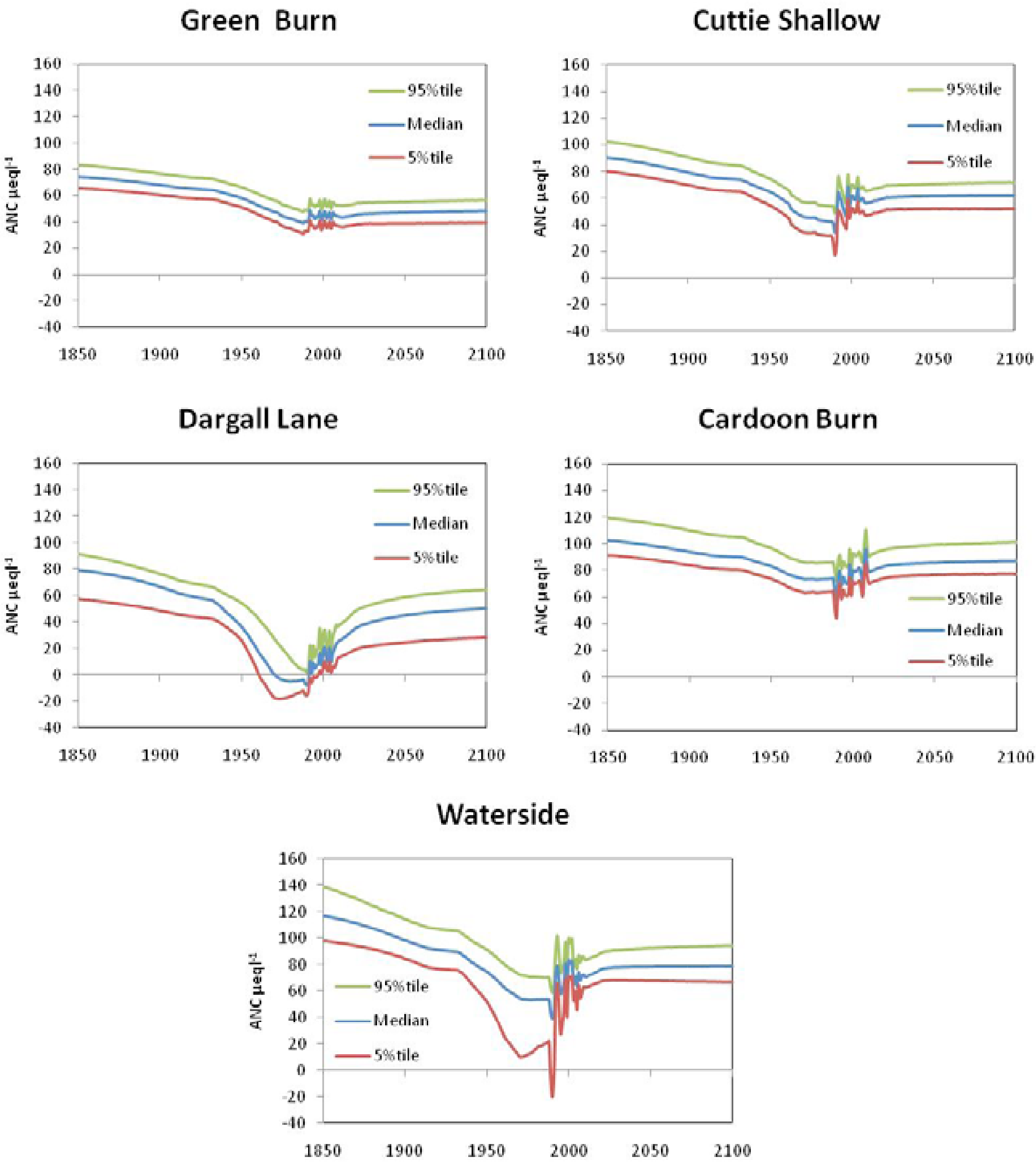


Figure 15: Median pH values with 5th and 95th percentile ranges

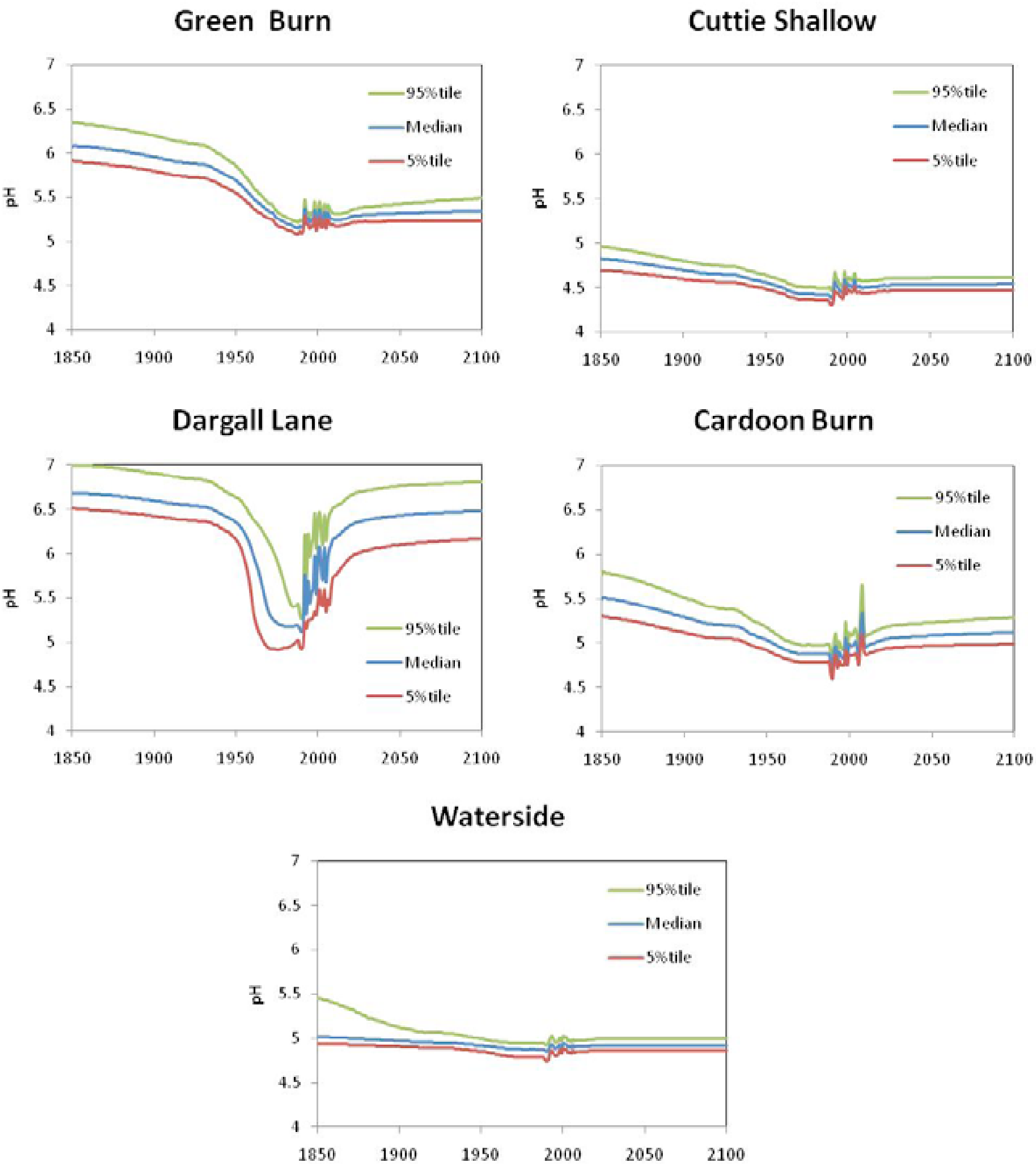


Figure 16: Median H ion concentration with 5th and 95th percentile ranges

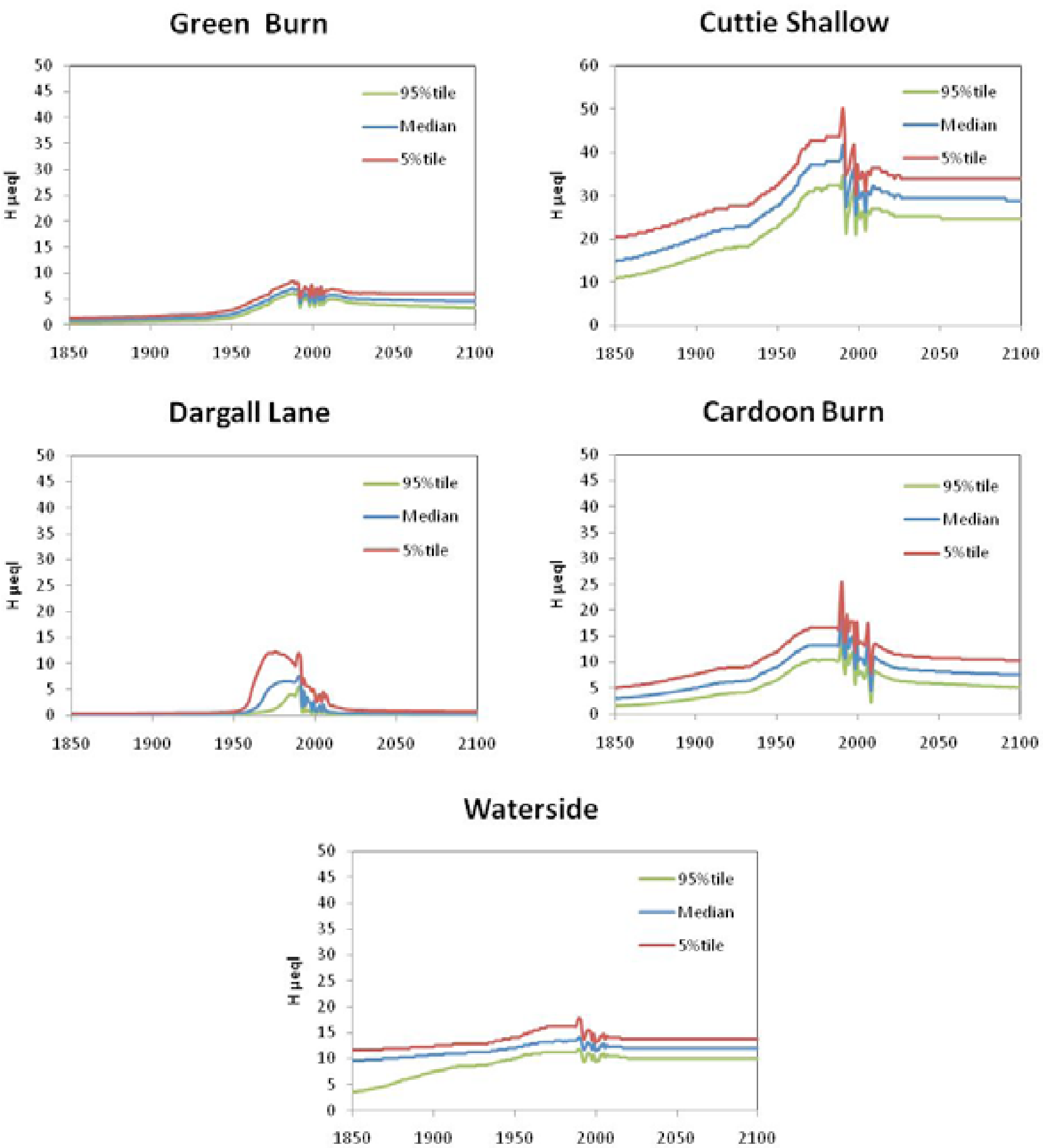


Figure 17: Median NO_3 values with 5th and 95th percentile ranges

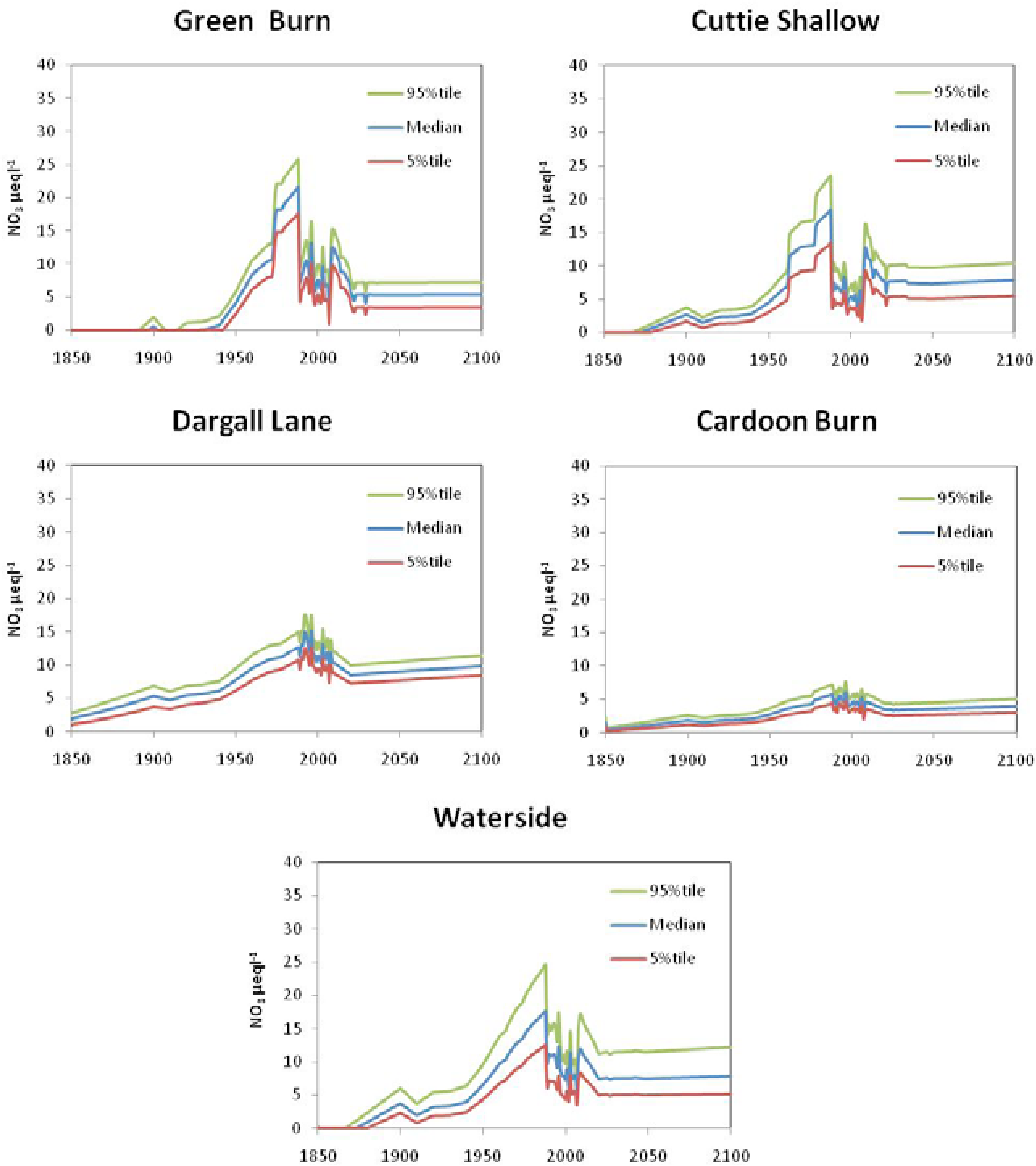


Figure 18: Median non-marine SO_4 concentrations with 5th and 95th percentile ranges

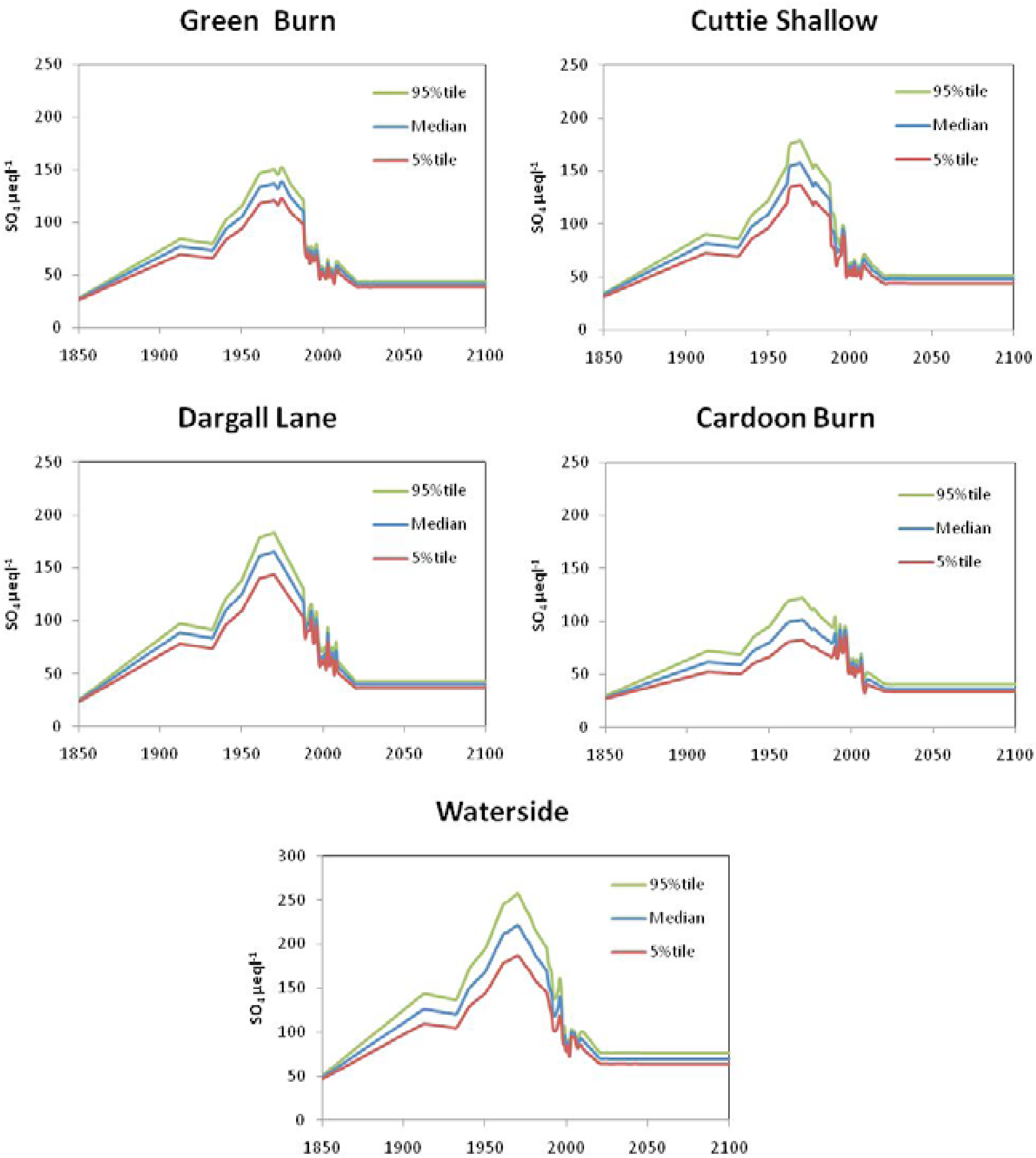


Figure 19: Median soil base saturation with 5th and 95th percentile ranges

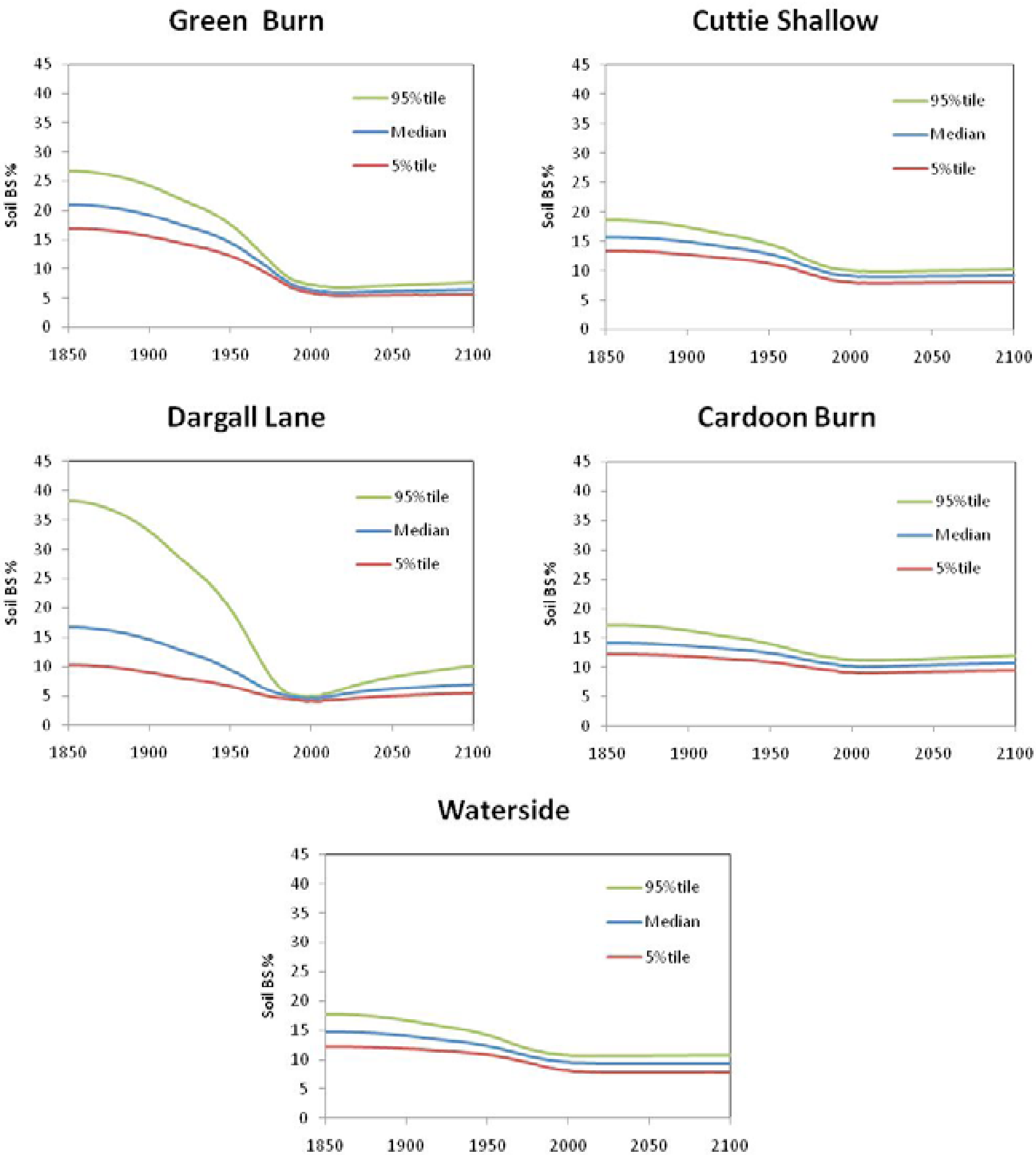


Table 9: Base cation budget for the study sites meq/m^2 *(note: no deposition sequence was applied to this model application due to the absence of an observed trend in the deposition network).*

		PRE-AFFORESTATION			PLANNED FORESTRY			NO FORESTRY			DIFFERENCE meq/m^2		
		1860	1970	1980	2010	2050	2100	2010	2050	2100	2010	2050	2100
GB	DEPOSITION	681	681	681	681	681	681	681	681	681	0	0	0
	SOIL	20313	10471	8467	5922	6018	6266	5974	6855	7784	53	837	1519
	WEATHERING	130	130	130	130	130	130	130	130	130	0	0	0
	UPTAKE	0	0	17	18	14	14	0	0	0	-18	-14	-14
	RIVER	830	1044	1022	838	792	794	816	787	794	-22	-5	0
DL	DEPOSITION	568	568	568	ND	ND	ND	568	568	568	ND	ND	ND
	SOIL	10727	3690	2886	ND	ND	ND	2552	3410	3945	ND	ND	ND
	WEATHERING	170	170	170	ND	ND	ND	170	170	170	ND	ND	ND
	UPTAKE	0	0	0	ND	ND	ND	0	0	0	ND	ND	ND
	RIVER	726	896	812	ND	ND	ND	668	672	687	ND	ND	ND
CS	DEPOSITION	541	541	541	541	541	541	541	541	541	0	0	0
	SOIL	5639	3981	3642	3222	3236	3278	3234	3408	3587	12	172	309
	WEATHERING	112	112	112	112	112	112	112	112	112	0	0	0
	UPTAKE	0	0	14	14	9	9	0	0	0	-14	-9	-9
	RIVER	652	792	762	655	630	631	639	626	630	-17	-4	-1
CB	DEPOSITION	434	434	434	434	434	434	434	434	434	0	0	0
	SOIL	4674	3706	3551	3300	3409	3514	3303	3437	3559	2	28	46
	WEATHERING	119	119	119	119	119	119	119	119	119	0	0	0
	UPTAKE	0	0	4	4	2	2	0	0	0	-4	-2	-2
	RIVER	539	600	583	528	524	527	526	524	527	-2	0	0
BW	DEPOSITION	458	458	458	458	458	458	458	458	458	0	0	0
	SOIL	6548	4884	4585	4174	4149	4147	4182	4306	4440	8	157	294
	WEATHERING	86	86	86	86	86	86	86	86	86	0	0	0
	UPTAKE	0	3	10	12	10	10	0	0	0	-12	-10	-10
	RIVER	537	639	613	535	519	520	530	519	521	-5	0	2

b) **1970-2010**

Since the 1970s, non-marine SO_4 concentrations in surface waters have drastically decreased in response to a c.80% reduction in UK SO_2 emissions and associated decreases in S deposition (Figure 1). Assuming a linear reduction in surface water SO_4 from the peak in 1970 (Waterside 221.2 μeql^{-1}, Dargall Lane 165.3 μeql^{-1}, Cuttie Shallow 157.6 μeql^{-1}, Green Burn 136.68 μeql^{-1}, Cardoon Burn 101.7 μeql^{-1}) the annual reduction to 2010 equates to 3.25 μeql^{-1}yr^{-1}, 2.75 μeql^{-1}yr^{-1}, 2.34 μeql^{-1}yr^{-1}, 1.99 μeql^{-1}yr^{-1} and 1.39 μeql^{-1}yr^{-1} respectively (Figure 18). The inter-year variability in the model simulation between 1988 to 2008 represents the period when the model was being driven by observed deposition data. There was little or no plantation forestry in the study catchments at the time when SO_4 concentrations peaked (1970), and in subsequent years when forest planting began, the forested sites behaved broadly similarly in terms of absolute reductions compared to the moorland control (Dargall Lane). In 2010 surface water SO_4 concentrations ranged from 45.96 μeql^{-1} at Dargall Lane to 91.04 μeql^{-1} at the Waterside, and whilst these concentrations are significantly lower than those modelled in 1970, they are twice as high as pre-acidification values. Differences between current (2010) and pre-acidification concentrations are 12.22 μeql^{-1} (Cardoon Burn), 20.56 μeql^{-1} (Green Burn), 20.72 μeql^{-1} (Dargall Lane), 23.13 μeql^{-1} (Cuttie Shallow), and 29.74 μeql^{-1} (Waterside). The longer-term impact of afforestation on soil and water quality is investigated in more detail in the next section. Interpretation of SO_4 results from Waterside requires extra caution since only two annual data points were used in the calibration. Figure 18 demonstrates the range of uncertainty in simulated SO_4 at all sites. The uncertainty bands were narrowest for 1860 and 2050–2100, whilst the greatest uncertainty in the model prediction occurred between 1970 and 1980 when S deposition fluxes were at their highest with considerable inter-annual variability.

Nitrogen deposition between 1970 and 2010 significantly declined in response to international legislation, and since inputs of oxidised and reduced forms of N are only marginally lower than SO_4 in more recent times there is considerable interest regarding the fate of this N in forested systems. Nitrogen is however notoriously difficult to model due to the complex interactions of biogeochemical processes, particularly in forested systems. Whilst recent input fluxes of total N and S are relatively similar, SO_4 remains the dominant anion in surface waters because a significant fraction of N is either immobilised by soils, or removed through uptake by trees or by tree harvesting.

Post the mid 1980s, significant reductions in surface water NO_3 were simulated at all sites. The forested sites responded quickly to the initial reductions in N deposition in the late 1980's and early 1990s and to the rising demand for nitrogen by soils and trees, with a rapid decline in surface water NO_3. From the early 1990s to 2010 it was difficult to identify any clear trend due to the large inter annual variability in the observed and simulated concentrations. Predictions from the paired catchment study suggest that at the time of greatest N deposition in 1980 the afforested Green Burn catchment leached 19.3 μeql^{-1} of NO_3 compared to the Dargall Lane catchment of 11.6 μeql^{-1}. By 1980 the Green Burn catchment contained a 40% cover of young (6-7 year old) trees with a significant demand on the soil N pool in their early stages of growth (Figure 17). This process alone would have the opposite effect on NO_3 leaching as the N uptake demand of young trees is high. In addition it is unlikely that an immature tree canopy could intercept significant amounts of N from the atmosphere. Disturbance of forest soils by ploughing prior to tree planting is known to activate soil microbes and mineralization processes, but releases of NO_3 from the soil are generally short lived and would not account for the prolonged simulated NO_3 signal in the burn. Pre-planting fertilisation with potassium and phosphorus took place in 1982 at Green Burn but since no nitrogen fertiliser was applied to the soil (Langan and Hirst, 2004) this cannot explain the elevated NO_3 concentrations. These findings indicate that not all N processes are adequately represented in the model. Whilst the majority of NO_3 observations were reproduced well during the calibration period, the peaks simulated during the mid 1980s are a response to a problem with the hindcast N deposition sequence (Figure 17).

It is clear that the dominant driver behind the simulated ANC recovery at all sites from 1970 to 2010 is the significant reduction in deposition. ANC, as a chemical indicator of acidification, represents many complex processes and an attempt is made to disentangle forest effects from deposition effects by comparing the simulations from the Green Burn and Dargall Lane sites. Initial tree planting took place in the Green Burn catchment in 1973 and whilst young trees exert a high demand on the soil N pool, they also tap into the base cation pool for nutrients (Table 9). ANC recovery is influenced by the balance of ions from these processes, although compared to the flux of base cations in deposition, soil, weathering, and surface water, the losses through tree uptake are minuscule (<1% of the total base cation flux in 2010, a time of significant forestry activity in the catchments). At Green Burn the density plots for ANC show continued acidification from 1970 to 1980 with a shift in the distribution of ANC from a median of 47.8 μeql^{-1} to 42.66 μeql^{-1} respectively, which thereafter recovers by 2010 to the mid point of these two values (44.03 μeql^{-1}). Despite forest acidification processes, throughout the simulation, ANC at Green Burn remains significantly above the ANC threshold of 20 μeql^{-1} (the minimum ANC simulated for this site was 39.22 μeql^{-1} in 1989) which accords with the recorded presence of brown trout. In contrast, surface water ANC at Dargall Lane is more responsive to changes in deposition due to the smaller base cation pool in 1980 (2886 meq m^{-2} compared to 8467 meq m^{-2} for Green Burn) (Table 9). The ANC simulation for Dargall Lane (Figure 14) exhibits a much greater degree of uncertainty compared to Green Burn. Surface waters also respond quicker from the extreme acidification in the 1970s and 1980s (median ANC 0.5 μeql^{-1} and -4.71 μeql^{-1} respectively), rising to a simulated ANC of 26.16 μeql^{-1} by 2010. However of the 1000 model iterations presented for 2010 at Dargall Lane, data from 248 were below ANC 20 μeql^{-1}. Despite chemical conditions breaching this ANC threshold, brown trout have been recorded in Dargall Lane in most years since measurements began in 1984, although densities of fry and parr are low (below those in Green Burn) and display high inter-annual variability. There appeared to be poor agreement between salmon status and ANC at the other three sites, where despite the simulated median ANC remaining well above the critical ANC 20 threshold, past survey work shows low salmon and/or trout densities and low egg survival. However, in the absence of fish data under non-impacted conditions, it is difficult to establish exactly how impacted the fish densities are. While egg survival may be an indicator of locally poor acid water quality, it can also reflect a wide range of other controls, for example, egg survival in the Waterside area was reduced (51%), but in the upper Bladnoch catchment survival ranged from 0–98% (SNH, 2007). Indeed 0% survival has been observed in near-pristine, naturally acidic upland streams. Alternatively this result could indicate one or more of the following: that the model calibration was poor due to the limited number of observations at Waterside; the underlying data used to calibrate the model at Waterside is dubious; the ANC threshold is inappropriate for healthy fish populations at higher densities (although the threshold is broadly adequate to permit embryo and juvenile survival); or an inappropriate ANC metric has been used (Cantrell vs. ion balance). Caution therefore needs to be exercised when discussing the biological significance of the simulated ANC data.

c) **2010-2100**

In general the majority of recovery in the future is simulated between 2010 and 2020 in response to the predicted emission reductions under the Gothenburg protocol; thereafter deposition remains constant. During this time, future Forest Design Plans were implemented in the forested sites to simulate reduced restocking and an introduction of more broadleaf species etc. Since the contribution of dry deposition is predicted to be small relative to wet deposition, and base cation uptake is predicted to be a minor loss from the soil pools (Table 9), the impact of future forestry on rates of recovery is estimated to be minor. While no site will achieve full recovery to the background ANC of 1860, such a target is unlikely to be appropriate in view of changes in climate and other factors. In terms of the protection of salmonid fish, the extent of improvement can be best quantified by assessing the percentage recovery towards recognised ANC thresholds. Table 10 presents the degree of recovery using two different ANC thresholds; the value of 20 adopted by the UK critical loads approach and the WFD method of assessing lakes, and a higher limit of 50 applied in some other countries (e.g. Sweden).

Based on the 50th percentile ANC, all sites are predicted to have an ANC above the biological threshold of 20 μeql^{-1} from 2010 to 2100 (Table 10, Appendix 2a) under planned forest practices and emission reductions. These results indicate that all sites would be predicted to achieve good ecological status by 2015 if the ANC 20 standard that is set under the WFD for lakes is applied to rivers. This threshold (20 μeql^{-1} ANC) is only breached at the non forested site, Dargall Lane in 1970 (50th percentile) and for the 5th percentile (representing the more acid extremes of the 1000 iterations) from 1970-2015. Waterside was the only forested site to display a temporary breach in the ANC threshold, with the decline in the 5th percentile ANC to 10.43 μeql^{-1} in 1970 driven mainly by increases in acid deposition since the trees were young (6 years old) at this time with a limited cover (14%).

For the much higher biological threshold applied in some countries (ANC 50 ueql^{-1}), future predictions of median and 5th percentile ANC lie above this for Cuttie Shallow, Cardoon Burn, and Waterside but below it for Green Burn (in 2015 & 2100) and Dargall Lane (in 2015). Table 10 shows that the median ANC for Green Burn is very close to reaching the threshold by 2100 (48.51 μeql^{-1}) while that for the Dargall Lane just rises above it (50.4 μeql^{-1}). The 5th percentile ANC values are predicted to continue to breach the higher threshold for both sites. Removal of the forest in Green Burn is predicted to increase the median ANC by a small margin (5.57 μeql^{-1}) but this is sufficient to take the value above the threshold (54.08 μeql^{-1}); the 5th percentile ANC would remain below the threshold. However, past monitoring shows the presence of brown trout fry and parr in both sites in most years over the period 1988–2008, suggesting that the 50 μeql^{-1} threshold is too stringent and an ANC of 20 μeql^{-1} is more credible for this type of river system (Malcolm et al., submitted).

As already stated, the majority of recovery is forecast to take place by 2020 since deposition sequences were held constant thereafter through to 2100. Any recovery post 2020 is relatively minor except for Dargall Lane where the median ANC increased from 35.65 μeql^{-1} in 2020 to 50.40 μeql^{-1} in 2100 (Figure 14, 20, Appendix 2a). Given that modelled deposition remains constant during this period, the increase in ANC is thought to be due to a small source of Na that is most probably weathered from the catchment soil. Figure 10 shows that toward the end of the calibration period surface water Na concentrations gradually increase and the model projections indicate that Na and to the less extent Mg increase to 2100. This result is unusual and requires further investigation.

Table 10 Predicted ANC (with uncertainty ranges) for the forestry scenarios. Breaches of biological thresholds (ANC 20 and ANC 50 ueql^{-1}) are highlighted in red

(Graphically presented in Appendix 2a)

Biological target	
ANC <20	ANC threshold adopted in UK Critical loads approach and Water Framework Directive
ANC <50	Higher threshold applied in some countries

		With Forestry			No forestry		
Site	Year	5th centile	50th centile	95th centile	5th centile	50th centile	95th centile
GB	1860	64.94	73.99	82.42	64.94	73.99	82.42
GB	1970	40.72	47.8	56.12	40.72	47.8	56.12
GB	2010	37.07	44.03	52.38	38.59	45.58	53.77
GB	2015	37.3	44.27	52.53	39.29	46.29	54.34
GB	2100	39.75	48.51	56.19	45.57	54.08	61.53
DL	1860	ND	ND	ND	56.05	78.04	89.18
DL	1970	ND	ND	ND	-17.13	0.5	27.42
DL	2010	ND	ND	ND	13.13	26.16	37.46
DL	2015	ND	ND	ND	16.14	30.54	42.42
DL	2100	ND	ND	ND	28.3	50.4	64.45
CS	1860	78.91	89.21	100.87	78.91	89.21	100.87
CS	1970	34.55	46.34	56.92	34.55	46.34	56.92
CS	2010	47.22	56.46	65.43	50.14	59.15	67.97
CS	2015	48.89	58.01	66.98	51.78	60.73	69.58
CS	2100	51.98	62.1	71.68	57.96	67.89	77.64
CB	1860	90.51	101.8	117.9	90.51	101.8	117.9
CB	1970	63.36	73.64	85.93	63.36	73.64	85.93
CB	2010	70.15	79.06	90.84	70.56	79.47	91.29
CB	2015	72.63	81.51	94.05	72.99	82.05	94.5
CB	2100	77.37	87.43	101.25	78.13	88.16	102.37
BW	1860	96.42	114.87	134.41	96.42	114.87	134.41
BW	1970	10.43	54.95	72.58	10.43	54.95	72.58
BW	2010	62.53	71.01	83.75	64.23	72.64	85.24
BW	2015	65	73.56	86.04	66.95	75.81	88.01
BW	2100	66.82	79.13	94.52	72.09	85.42	102.65

To allow a comparison of the forestry effects on acid sensitivity of surface waters and the achievement of the biological target (ANC 20 μeql^{-1}) with uncertainty limits, data are shown as density plots in Figures 20-24. As described previously the 'no forest' scenario assumes that all forested areas revert to moorland from 2010 to 2100. Under the scenario of complete forest removal, a shift towards a small improvement in acid status of soil and surface waters is predicted for all sites. As expected, the improvement is least for the site with the lowest level of forest cover (0.7 μeql^{-1} rise in median ANC by 2100 for Cardoon Burn; 20% forest cover) but is similar for the other three forested sites (increase ranging from 5.6 to 6.3 μeql^{-1} for 48% to 89% forest cover). This residual forest effect equates to a difference of 8–12% in ANC (based on the 50 percentile) and while it shows that a forest effect could theoretically still be sufficient to cause a given site to breach an ANC threshold, the risk of damage is likely to be small when considered in terms of Lien et al (1992) fish-ANC response curve (ANC 20 represents a 90% probability of trout being undamaged and the forest effect equates to a <1 μeql^{-1} increase in ANC per 10% forest cover). As already noted, the ANC distribution for the studied forestry sites is above the ANC 20 threshold (including the 5 percentile tails), which suggests that in terms of biological targets, the ANC improvements predicted to result from complete forest removal are unlikely to significantly influence fish recovery. The authors are however mindful of the caveats already discussed regarding the choice of ANC threshold in this type of analysis. It is also important to note that the x-axes of the density plots are variable and due to software limitation can not be standardised so careful interpretation of information is therefore necessary. Nonetheless, the results agree with long-term monitoring data from the UKAWMN, which show evidence of continuing recovery of forest sites and convergence with non-forest sites, in line with reductions in acid deposition (UKAWMN, 2010).

A general shift to slightly less acid conditions is shown by the increase in pH from 2010 to 2100 at all sites. Recovery appears least at the more acid forested sites, although this reflects the log scale of pH. Complete forest removal is predicted to have a minimal effect on the pH response, ranging between an increase of 0.01 to 0.04 pH units for both median and 5th percentile values at three of the four forest sites. (Table 11, Figure 21, Appendix 2b). The greatest difference between forest and no-forest scenarios was predicted at Green Burn, which increased from 0.04 to 0.18 pH units between 2010 and 2100. This difference is broadly associated with forest scavenging processes. Overall, no relationship was found between the extent of forestry in the catchments and surface water pH.

Table 11: Future surface water pH between land use scenarios (Graphically presented in Appendix 2b)

pH		Forest			No Forest			Difference (Forest - no forest)		
		5th	50th	95th	5th	50th	95th	5th	50th	95th
GB	2010	5.18	5.24	5.31	5.21	5.28	5.35	-0.03	-0.04	-0.04
GB	2050	5.23	5.32	5.42	5.33	5.43	5.57	-0.1	-0.11	-0.15
GB	2100	5.23	5.34	5.49	5.39	5.52	5.7	-0.16	-0.18	-0.21
DL	2010	ND	ND	ND	5.74	6.17	6.53	ND	ND	ND
DL	2050	ND	ND	ND	6.1	6.43	6.77	ND	ND	ND
DL	2100	ND	ND	ND	6.16	6.48	6.81	ND	ND	ND
CS	2010	4.44	4.5	4.57	4.45	4.51	4.59	-0.01	-0.01	-0.02
CS	2050	4.47	4.53	4.6	4.5	4.56	4.64	-0.03	-0.03	-0.04
CS	2100	4.47	4.54	4.61	4.51	4.58	4.67	-0.04	-0.04	-0.06
CB	2010	4.87	4.96	5.08	4.87	4.97	5.08	0	-0.01	0
CB	2050	4.97	5.09	5.23	4.98	5.1	5.25	-0.01	-0.01	-0.02
CB	2100	4.99	5.12	5.29	5	5.14	5.32	-0.01	-0.02	-0.03
BW	2010	4.85	4.91	4.98	4.85	4.91	4.98	0	0	0
BW	2050	4.86	4.92	5	4.87	4.93	5.02	-0.01	-0.01	-0.02
BW	2100	4.86	4.92	5	4.88	4.94	5.04	-0.02	-0.02	-0.04

The efficacy of N emission control is demonstrated by the decline in median NO_3 concentrations from 2010 to 2050 under both land use scenarios (Figure 17, 22, Table 12, and Appendix 2c). During this period median NO_3 concentrations are predicted to decrease to a greater extent in the forest sites (12-55%) compared to the Dargall Lane (4%), which is dominated by the planned reductions in N emissions. Forest removal is predicted to reduce the concentrations further, driven by the small amount of interception deposition to the forest canopy, a process that was removed for the 'no forest scenario'. Whilst the forest does act as a sink for N through uptake processes the net effect of this process is considered to be small (Table 12) and as a consequence some N is leached to surface waters under the forested scenario. Concentrations are however very low and NO_3 leaching is variable between sites (Figure 22). The range of NO_3 concentrations presented for the 1000 model iterations is greatest in 2010, with the largest uncertainty predicted for the planned forestry scenario due to the additional process representation in the model simulations for dry deposition mechanisms, N uptake and changes in discharge (Figure 22). A very small increase in the NO_3 concentrations between 2050 and 2100 was predicted at all sites, which was greatest at the non forested site (Dargall Lane) and at Waterside, for both the forest and no-forest scenarios. However, it is important to recognise that the concentrations of NO_3 remain very low for both scenarios for the entire forecast period. A comparison of concentrations and the percentage increase in NO_3 between the two land use scenarios in the future is shown in Table 12. Whilst the greatest change is predicted for Green Burn under the forestry scenario, the concentrations were low and as a consequence NO_3 leaching would have a very minor impact on the overall acid status of the Burn. By comparison, future NO_3 concentrations at Dargall Lane remain the greatest throughout the simulation, which is in line with recent observations.

Table 12: Future nitrate leaching and percent difference between land use scenarios (µeql^{-1}) (Graphically presented in Appendix 2c)

NO_3 ueql^{-1}		Forest			No Forest			Difference (Forest - no forest)		
		5th	50th	95th	5th	50th	95th	5th	50th	95th
GB	2010	9.4	12.16	14.86	3.86	5.83	7.69	5.54	6.33	7.17
GB	2050	3.44	5.37	7.19	0.06	1.45	2.87	3.38	3.92	4.32
GB	2100	3.46	5.42	7.24	0.06	1.45	2.88	3.4	3.97	4.36
DL	2010	ND	ND	ND	8.8	10.33	12.01	ND	ND	ND
DL	2050	ND	ND	ND	7.78	9.1	10.49	ND	ND	ND
DL	2100	ND	ND	ND	8.5	9.88	11.44	ND	ND	ND
CS	2010	8.62	12.01	15.55	4.18	6.05	8.12	4.44	5.96	7.43
CS	2050	5.08	7.31	9.74	2.38	3.74	5.25	2.7	3.57	4.49
CS	2100	5.45	7.82	10.4	2.45	3.89	5.45	3	3.93	4.95
CB	2010	3.39	4.51	5.6	2.97	3.96	4.93	0.42	0.55	0.67
CB	2050	2.68	3.59	4.47	2.52	3.37	4.2	0.16	0.22	0.27
CB	2100	2.97	3.96	5.05	2.77	3.7	4.7	0.2	0.26	0.35
BW	2010	8.11	11.53	16.61	5.76	8.4	12.43	2.35	3.13	4.18
BW	2050	5	7.48	11.44	3.16	5.06	8.18	1.84	2.42	3.26
BW	2100	5.16	7.83	12.16	3.24	5.22	8.56	1.92	2.61	3.6

In contrast to the significant reductions in S deposition from the mid 1980's to 2010, the extent of the reduction in both S deposition inputs and the SO_4 predicted in the surface waters from 2020 and beyond is small (Figure 18 and 23). It is clear that in the future SO_4 is likely to play a minor role in surface water acidification as concentrations approach baseline levels predicted in 1860. This result is indicative of the success of EU protocols in reducing S emissions. In terms of the land use effects on surface water SO_4, Table 13 (Appendix 2d) shows that slightly higher concentrations are predicted under the forest plan scenario compared to the no forest scenario due to removal of the pollutant scavenging effect. Decreases in median SO_4 values resulting from forest removal range between 0.3 to 2.8 µeql^{-1} by 2050 (0.8-5.9% of 2010 levels). These small increases may in themselves be overestimates since no sink for S in the form of tree uptake is modelled in this study.

Table 13: Future sulphate concentration and difference in the concentration between land use scenarios (μeql^{-1}) (Graphically presented in Appendix 2d)

SO_4 ueql^{-1}		Forest			No Forest			Difference (Forest - no forest)		
		5th	50th	95th	5th	50th	95th	5th	50th	95th
GB	2010	51.94	56.7	60.9	48.35	52.54	56.25	3.59	4.16	4.65
GB	2050	39.39	42.23	44.69	37.74	40.32	42.55	1.65	1.91	2.14
GB	2100	39.39	42.23	44.69	37.74	40.32	42.55	1.65	1.91	2.14
DL	2010	ND	ND	ND	49.52	55.27	60.17	ND	ND	ND
DL	2050	ND	ND	ND	36.25	39.75	42.79	ND	ND	ND
DL	2100	ND	ND	ND	36.25	39.75	42.79	ND	ND	ND
CS	2010	58.37	64.06	70.02	52.44	57.09	61.85	5.93	6.97	8.17
CS	2050	44.42	47.85	51.15	42.05	45.02	47.87	2.37	2.83	3.28
CS	2100	44.42	47.85	51.15	42.06	45.02	47.87	2.36	2.83	3.28
CB	2010	40.74	45.96	51.84	39.82	44.77	50.36	0.92	1.19	1.48
CB	2050	33.84	36.89	40.37	33.63	36.6	40	0.21	0.29	0.37
CB	2100	33.84	36.89	40.37	33.63	36.6	39.99	0.21	0.29	0.38
BW	2010	82.02	91.04	101.28	78.94	87.3	96.76	3.08	3.74	4.52
BW	2050	63.98	69.87	76.59	62.22	67.72	74.04	1.76	2.15	2.55
BW	2100	63.97	69.87	76.61	62.25	67.74	74.06	1.72	2.13	2.55

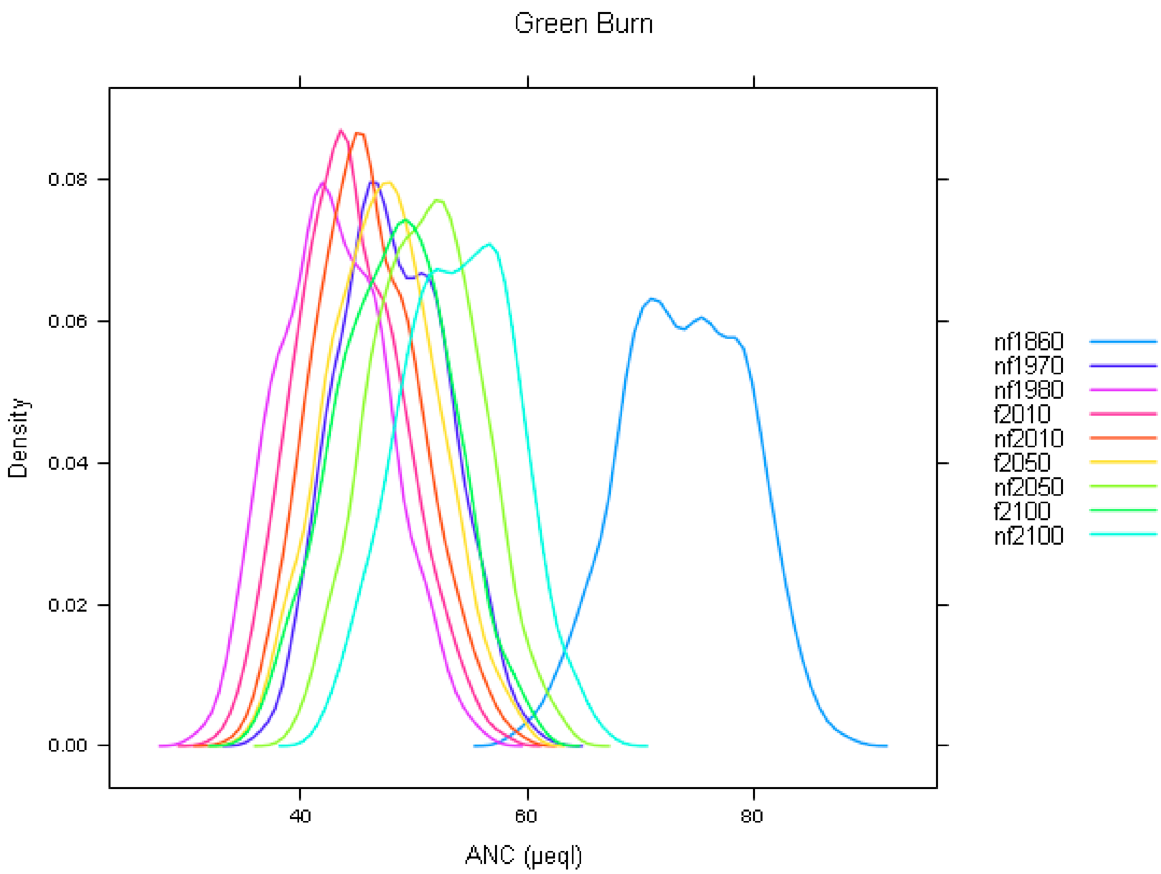
The rate of recovery of the soil base cation pool from 2010 to 2100 is much slower than the rapid decline during the acidification phase (described in the previous section). As already discussed, irrespective of forestry activities, recovery of acidified soil is dependant upon the replenishment of base cations from mineral weathering of the parent material. Recovery of soil base saturation under the forest plan scenario results in a minor improvement in status at all sites except Waterside. The greatest recovery was simulated at Dargall Lane (2.11%) and at Cardoon Burn (0.63 %). Future projections of soil base saturation at Dargall Lane have a wide uncertainty window (Table 14, Figure 24) and although the median values in 2050 and 2100 were 6.16% and 6.92%, the 5th and 95th percentiles were 4.93% and 8.28% for 2050 and 5.42% and 10.13% for 2100 (Figure 24, Appendix 2e). The marginal reduction in soil base saturation at Waterside (declining from 9.52% in 2010 to 9.42% in 2100) was predicted to be reversed by forest removal, although the difference between the two scenarios was relatively small (10.07% for no forest vs 9.42% for forest).

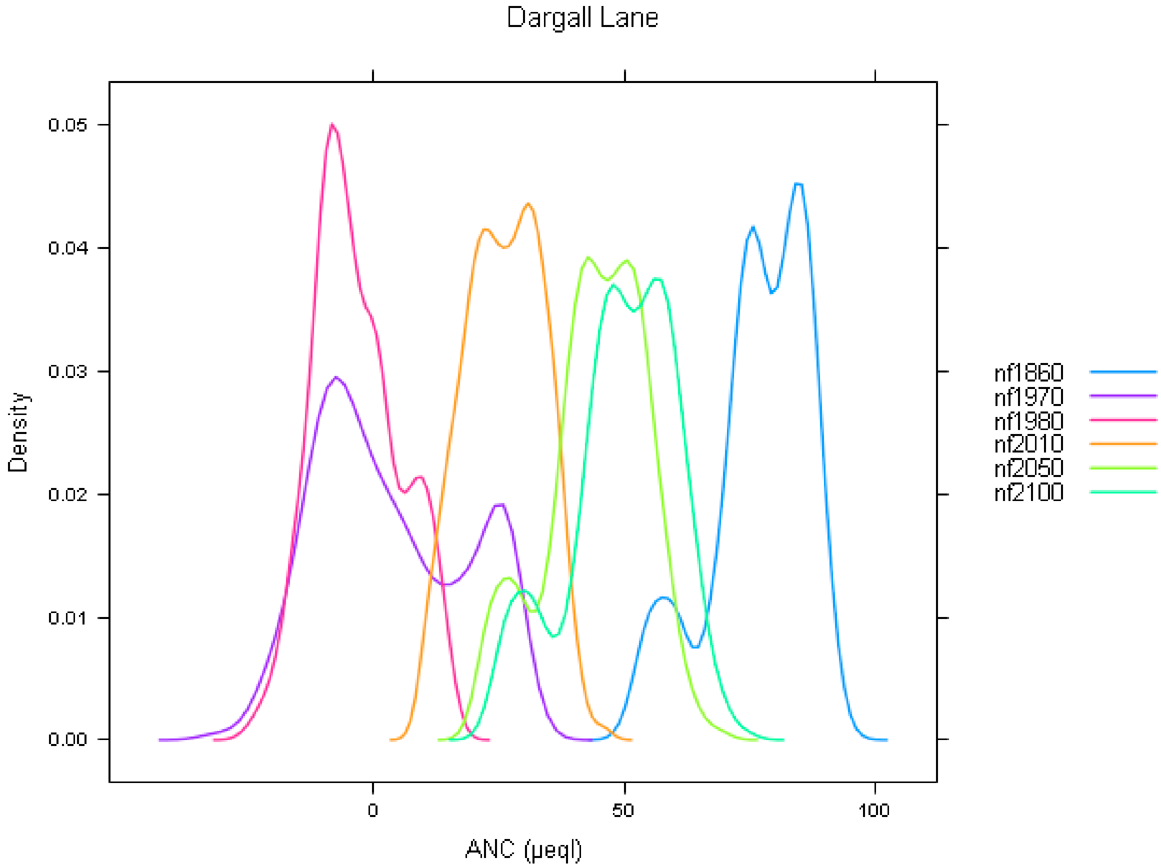
Table 14: Future soil base saturation (%) and percent difference between land use scenarios

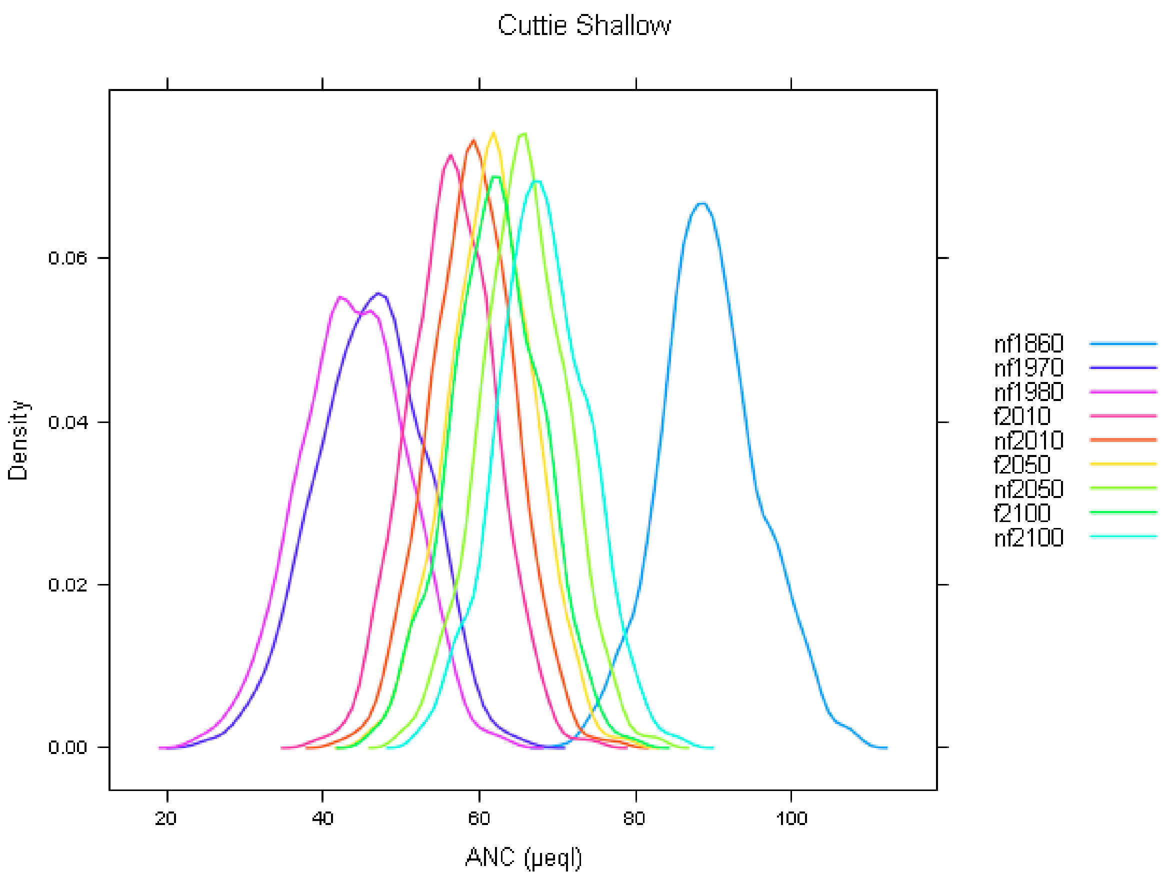
(Graphically presented in Appendix 2e)

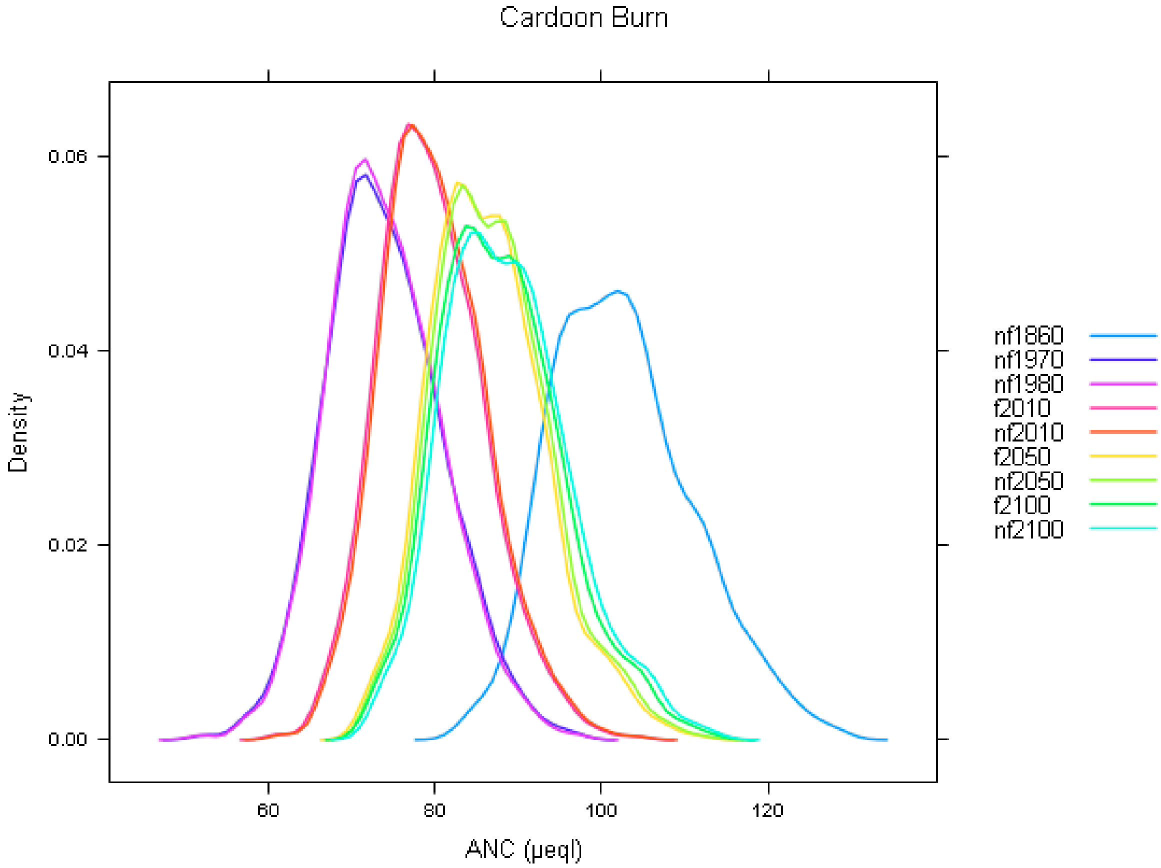
BS %		Forest			No Forest			Difference (Forest - no forest)		
		5th	50th	95th	5th	50th	95th	5th	50th	95th
GB	2010	5.48	6.17	6.92	5.54	6.23	6.97	-0.06	-0.06	-0.05
GB	2050	5.46	6.3	7.1	6.34	7.17	8.07	-0.88	-0.87	-0.97
GB	2100	5.51	6.56	7.64	7.03	8.11	9.39	-1.52	-1.55	-1.75
DL	2010	ND	ND	ND	4.21	4.81	5.46	ND	ND	ND
DL	2050	ND	ND	ND	4.93	6.16	8.28	ND	ND	ND
DL	2100	ND	ND	ND	5.42	6.92	10.13	ND	ND	ND
CS	2010	8.02	9.03	9.95	8.05	9.06	9.98	-0.03	-0.03	-0.03
CS	2050	8.06	9.06	10.02	8.51	9.54	10.54	-0.45	-0.48	-0.52
CS	2100	8.14	9.17	10.19	8.92	10.05	11.16	-0.78	-0.88	-0.97
CB	2010	9.06	10.15	11.17	9.06	10.15	11.17	0	0	0
CB	2050	9.31	10.48	11.49	9.38	10.56	11.59	-0.07	-0.08	-0.1
CB	2100	9.51	10.78	12	9.61	10.91	12.2	-0.1	-0.13	-0.2
BW	2010	8.02	9.52	10.59	8.04	9.53	10.61	-0.02	-0.01	-0.02
BW	2050	7.88	9.44	10.62	8.31	9.77	10.98	-0.43	-0.33	-0.36
BW	2100	7.89	9.42	10.7	8.66	10.07	11.38	-0.77	-0.65	-0.68

Figure 20 Density plots of acid neutralising capacity for land use scenarios (f = future forest plans, nf= no forest) between 1860 and 2100




Dargall Lane
Density
0.05
0.04
0.03
0.02
0.01
0.00
0
50
100
ANC (μeql)
nf1860
nf1970
nf1980
nf2010
nf2050
nf2100


Cuttie Shallow
Density
0.06
0.04
0.02
0.00
20
40
60
80
100
ANC (μeql)
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100


Cardoon Burn
Density
0.00
0.02
0.04
0.06
60
80
100
120
ANC (µeql)
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100

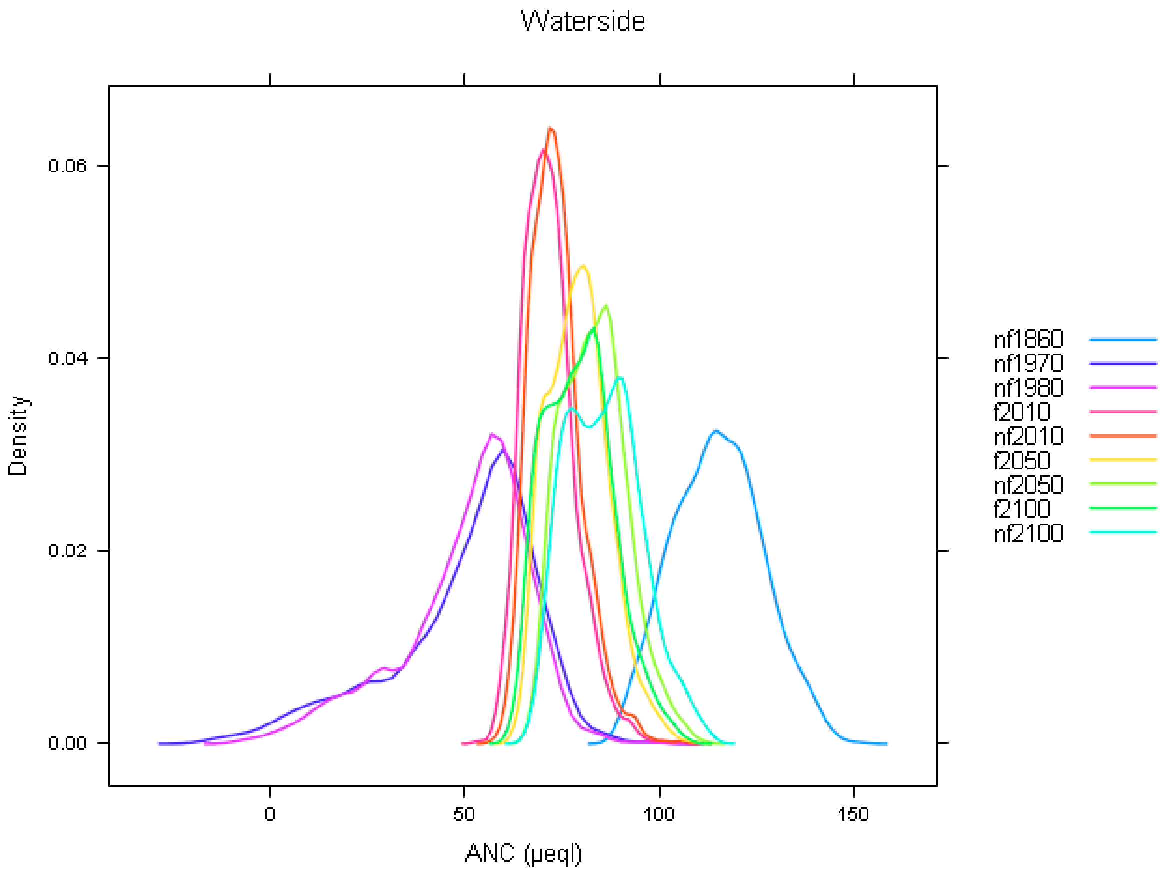
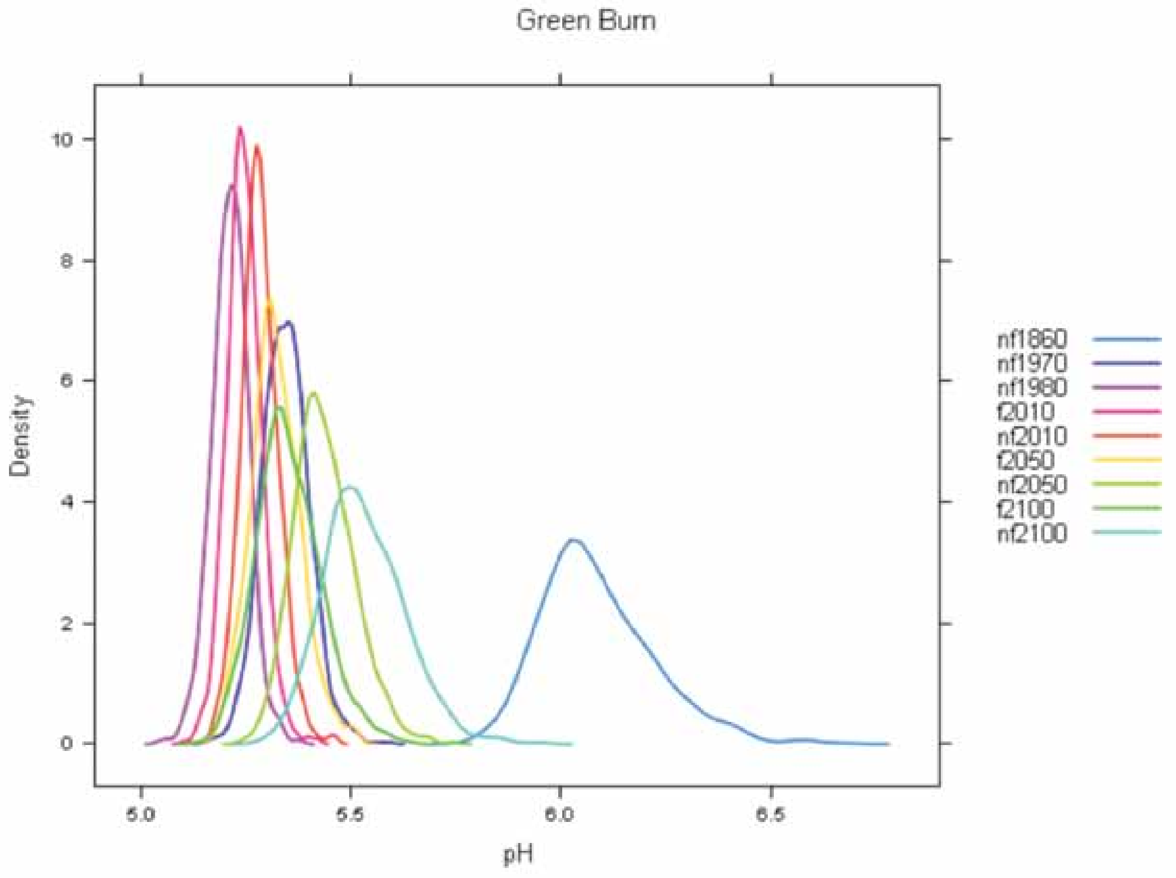
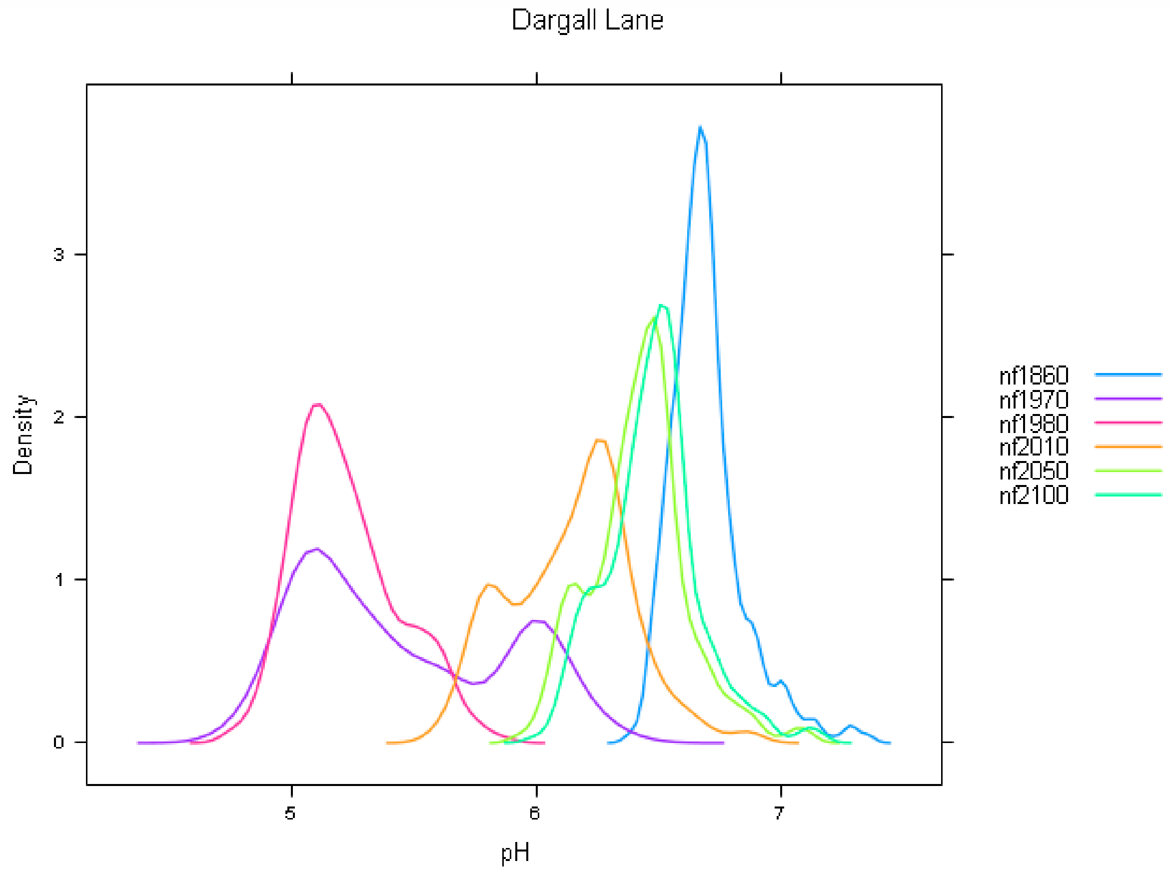
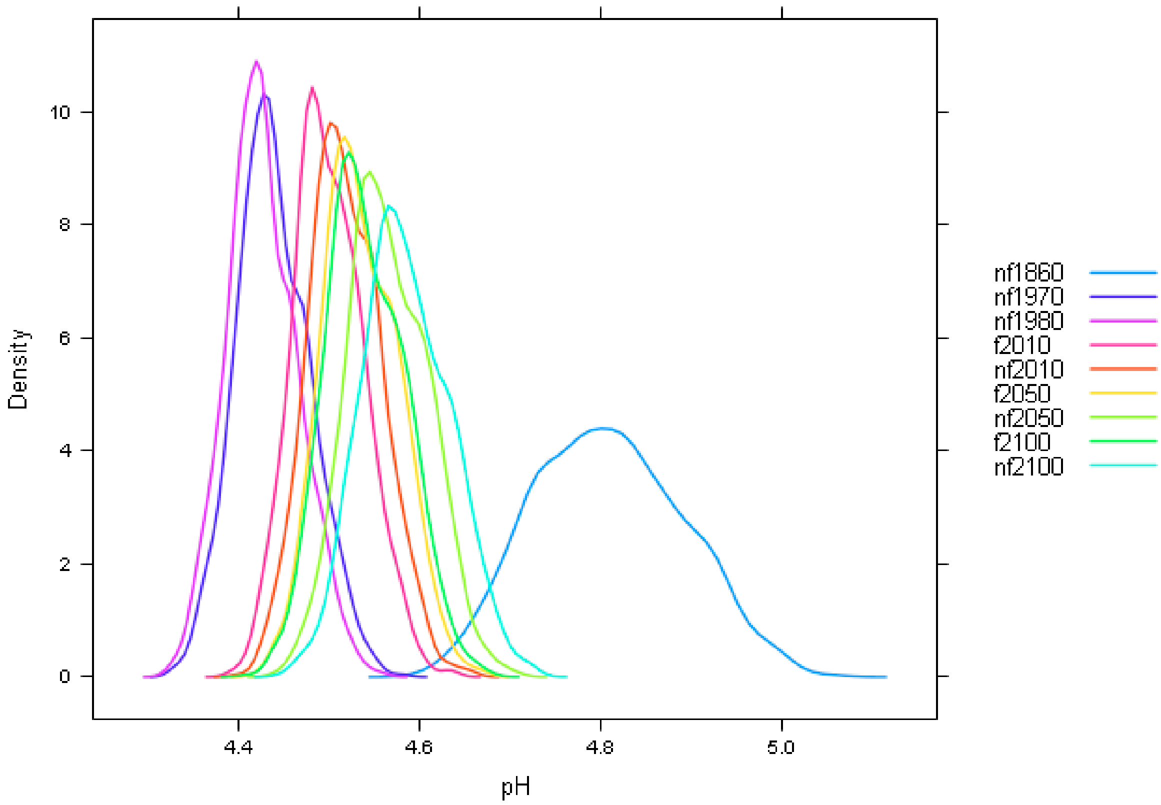

Waterside
Density
0.00
0.02
0.04
0.06
0
50
100
150
ANC (µeql)
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100

Figure 21 Density plots of surface water pH for land use scenarios (f = future forest plans, nf= no forest) between 1860 and 2100.

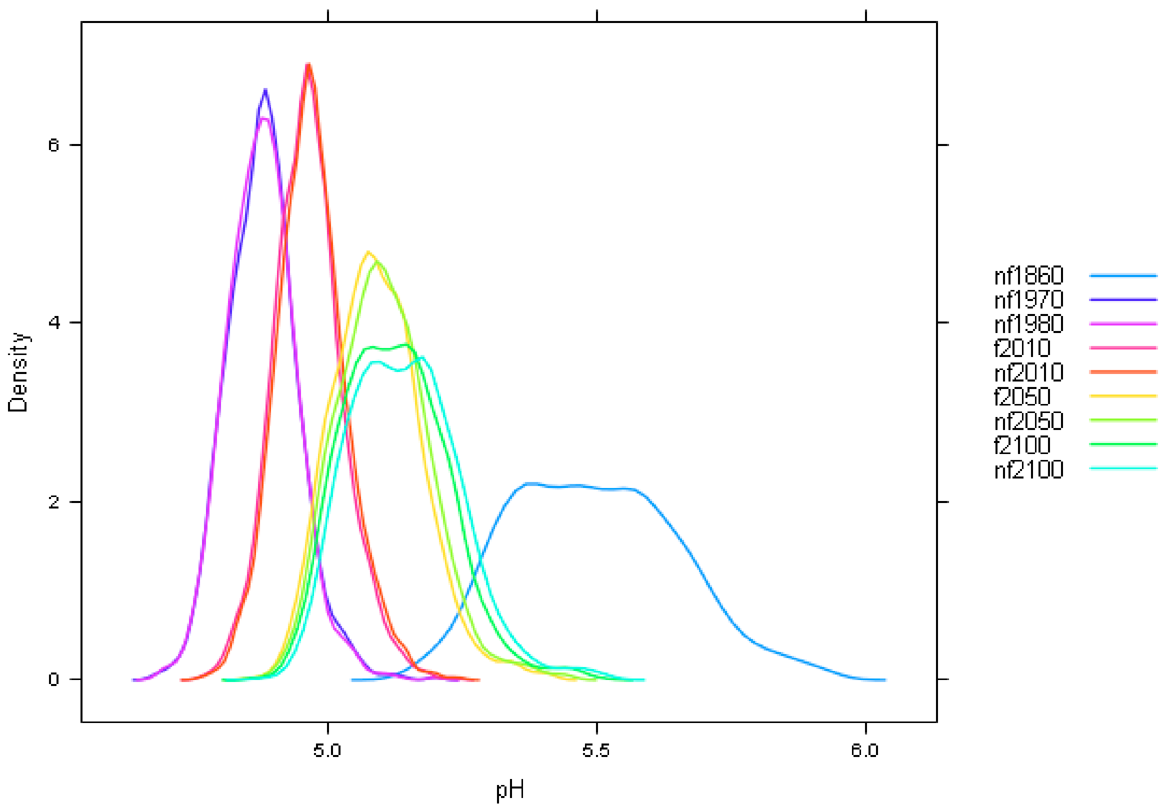




Cuttie Shallow



Cardoon Burn



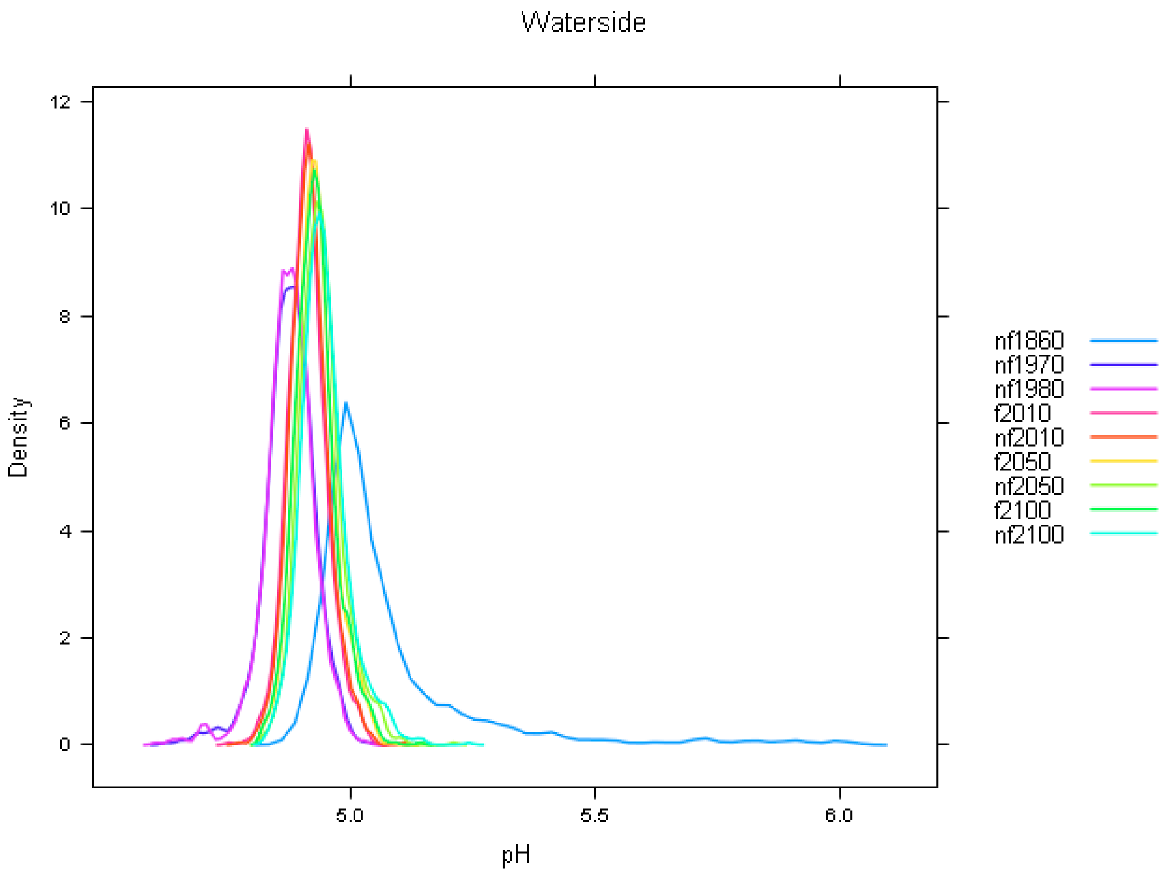
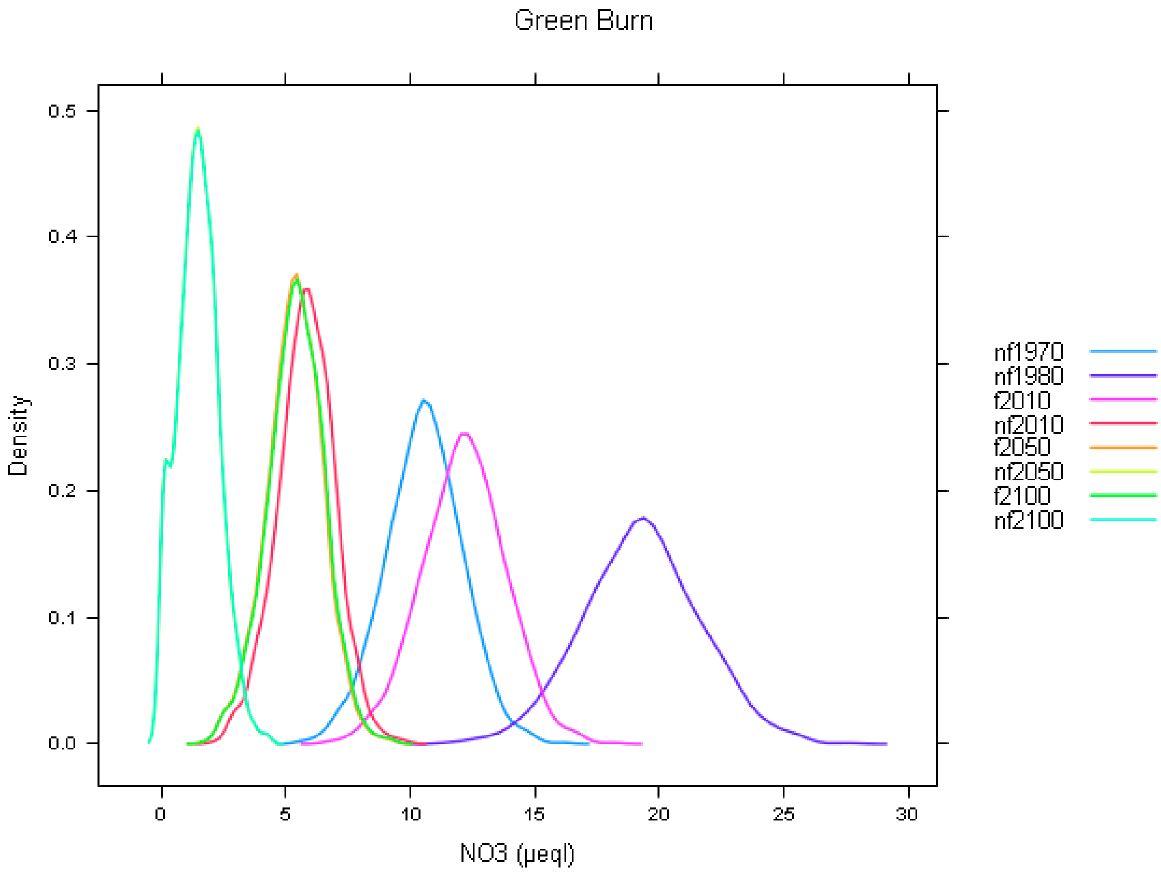
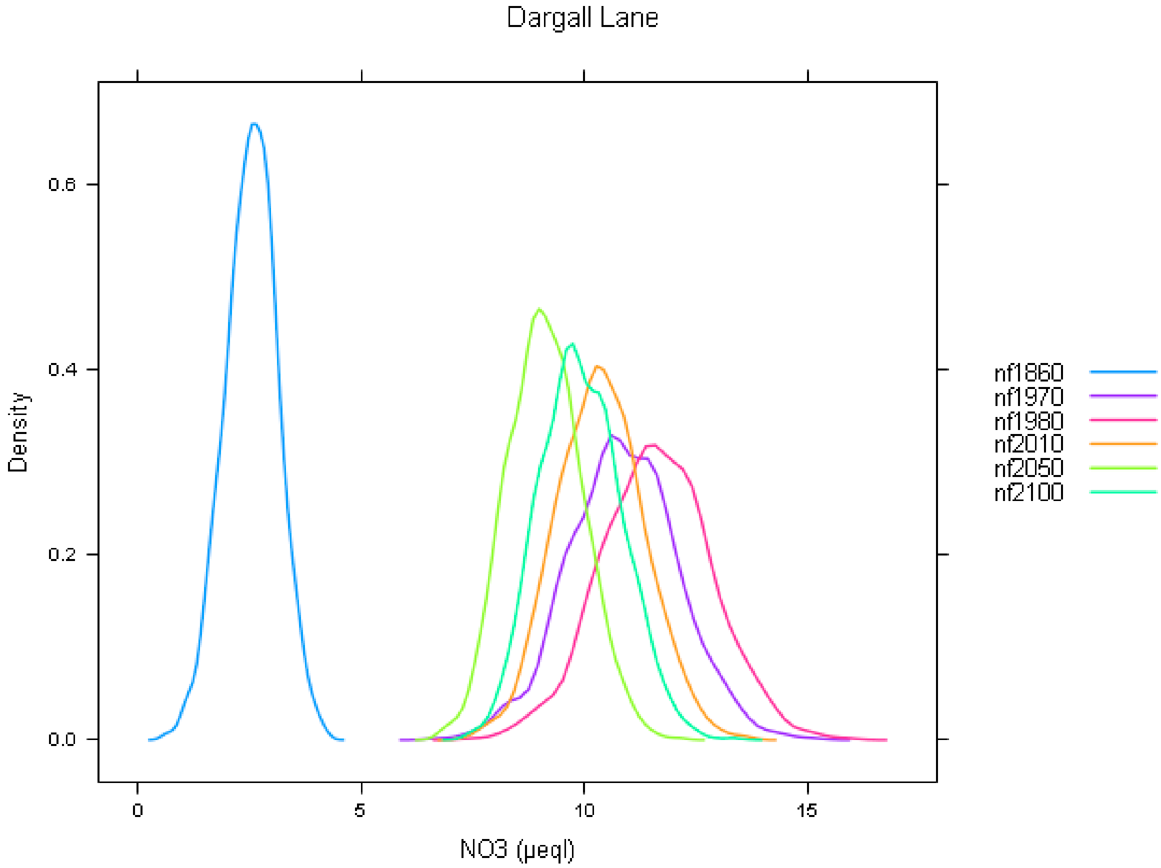
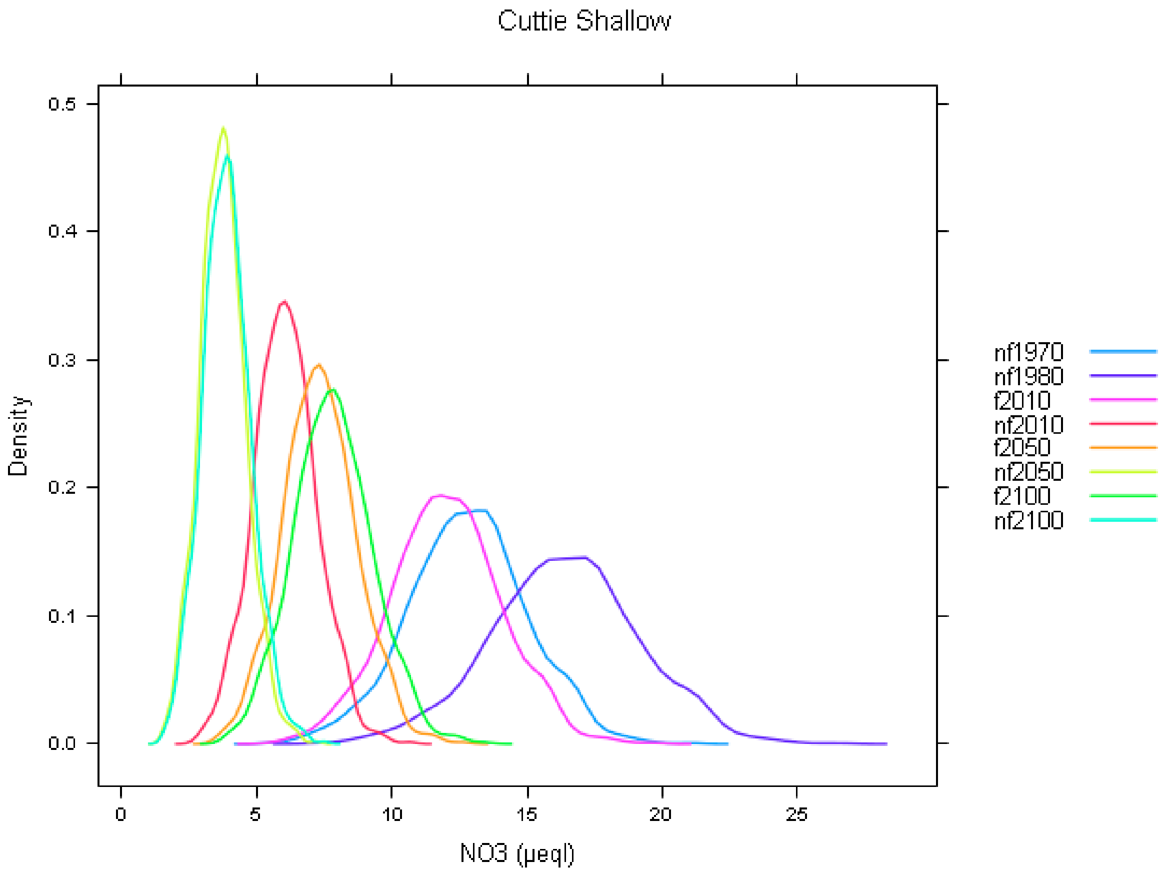
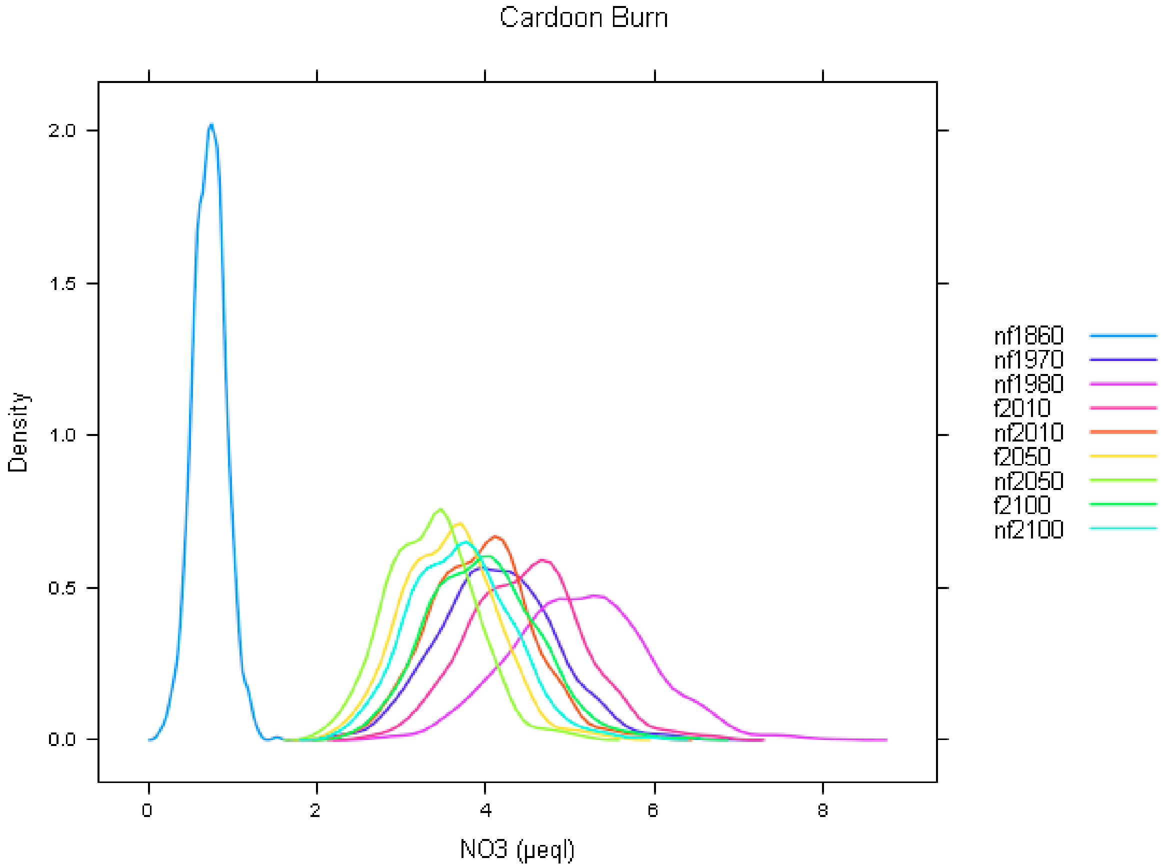

Waterside
Density
pH
12
10
8
6
4
2
0
5.0
5.5
6.0
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100

Figure 22 Density plots of surface water NO_3 for land use scenarios (f = future forest plans, nf= no forest) between 1860 and 2100. (NB. No NO_3 simulated in 1860 for Green Burn, Cuttie Shallow and Waterside)




Dargall Lane
Density
0.0
0.2
0.4
0.6
0
5
10
15
NO3 (μeql)
nf1860
nf1970
nf1980
nf2010
nf2050
nf2100


Cuttie Shallow
Density
0.0
0.1
0.2
0.3
0.4
0.5
0
5
10
15
20
25
NO3 (μeql)
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100


Cardoon Burn
Density
NO3 (μeql)
0.0
0.5
1.0
1.5
2.0
0
2
4
6
8
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100

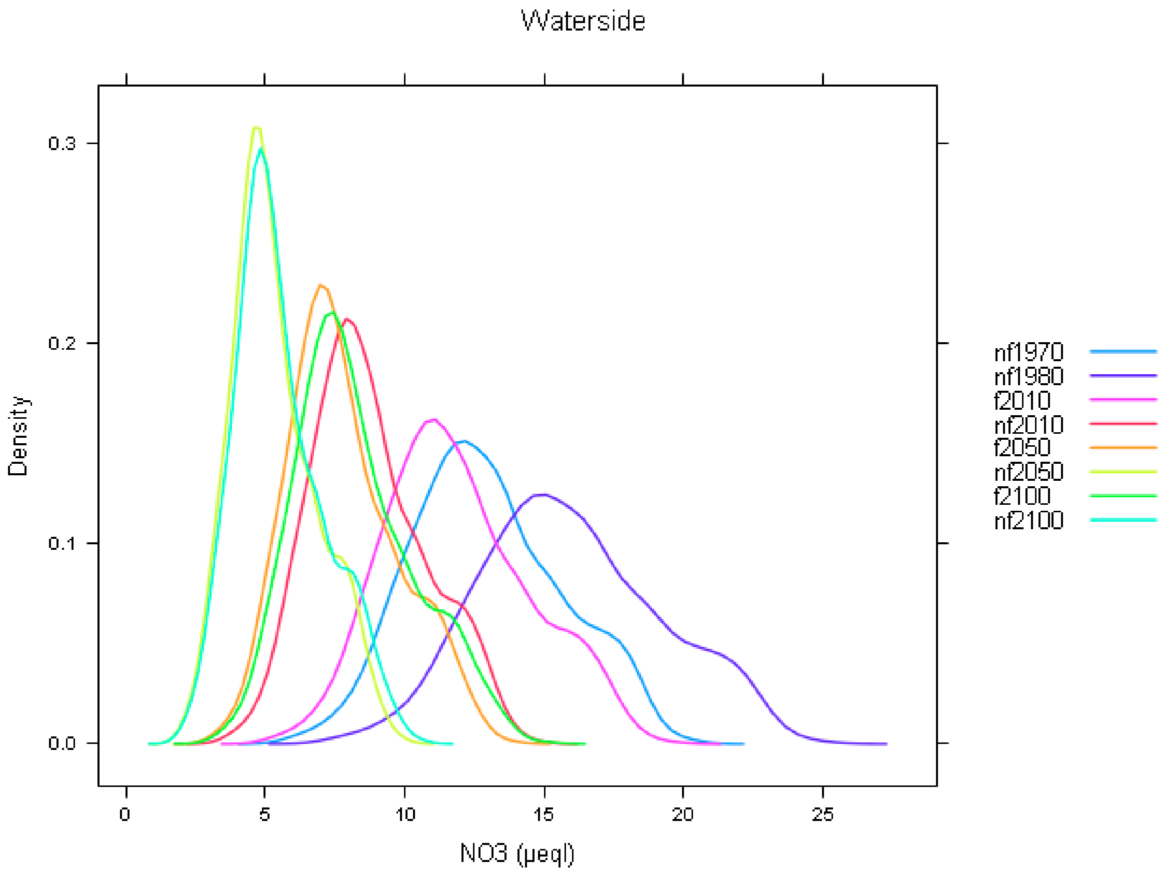
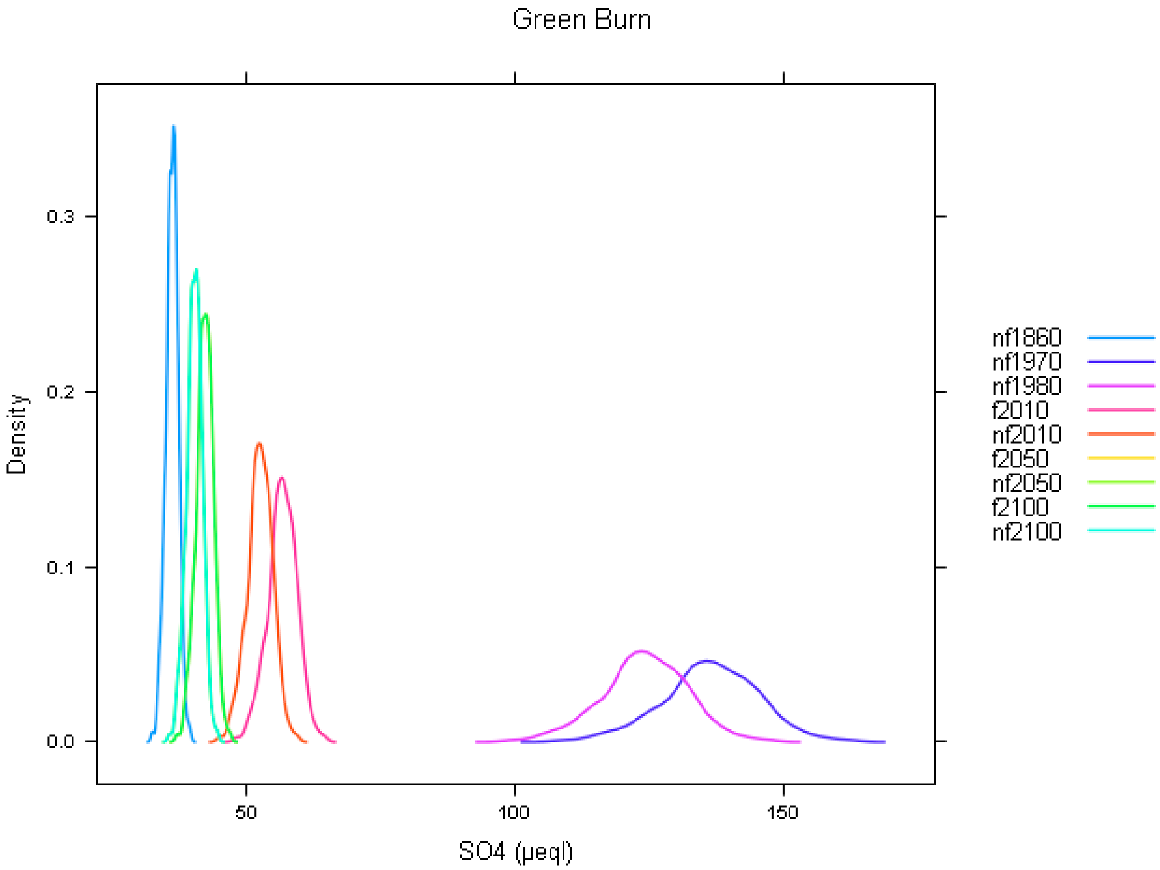
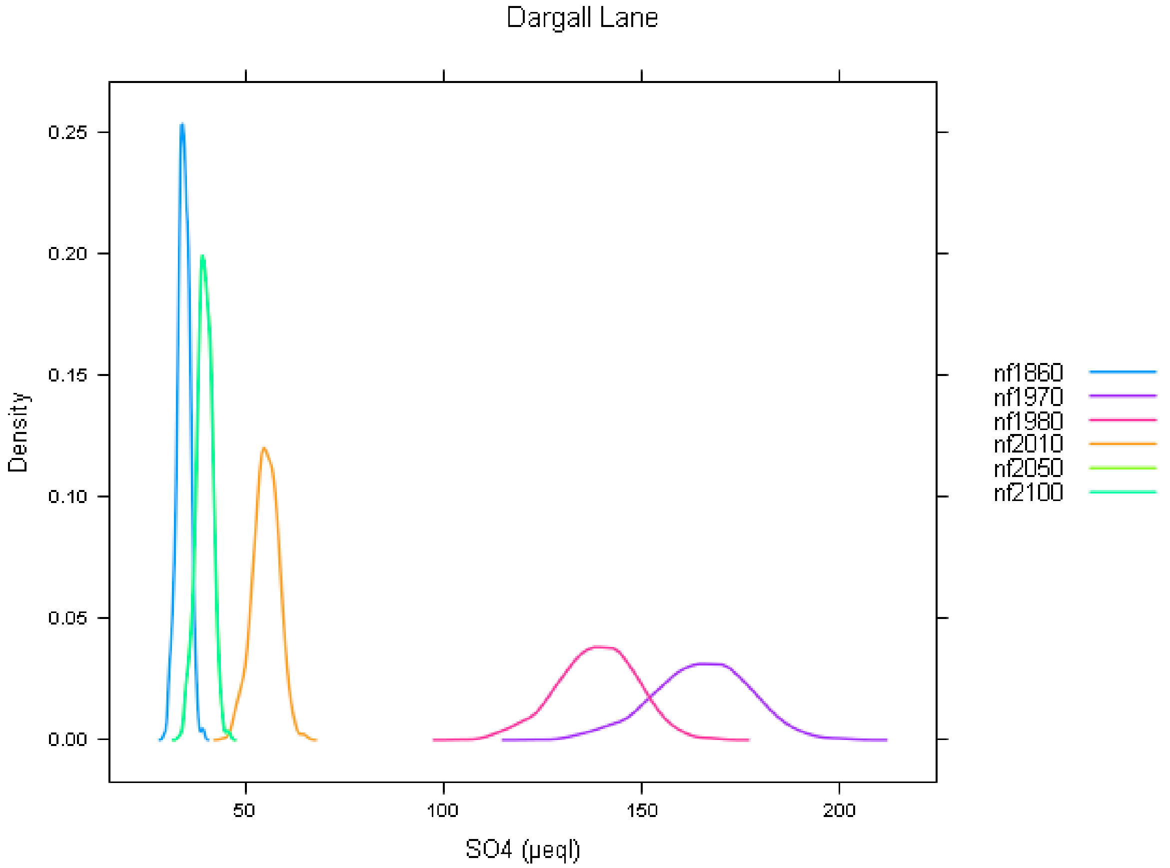
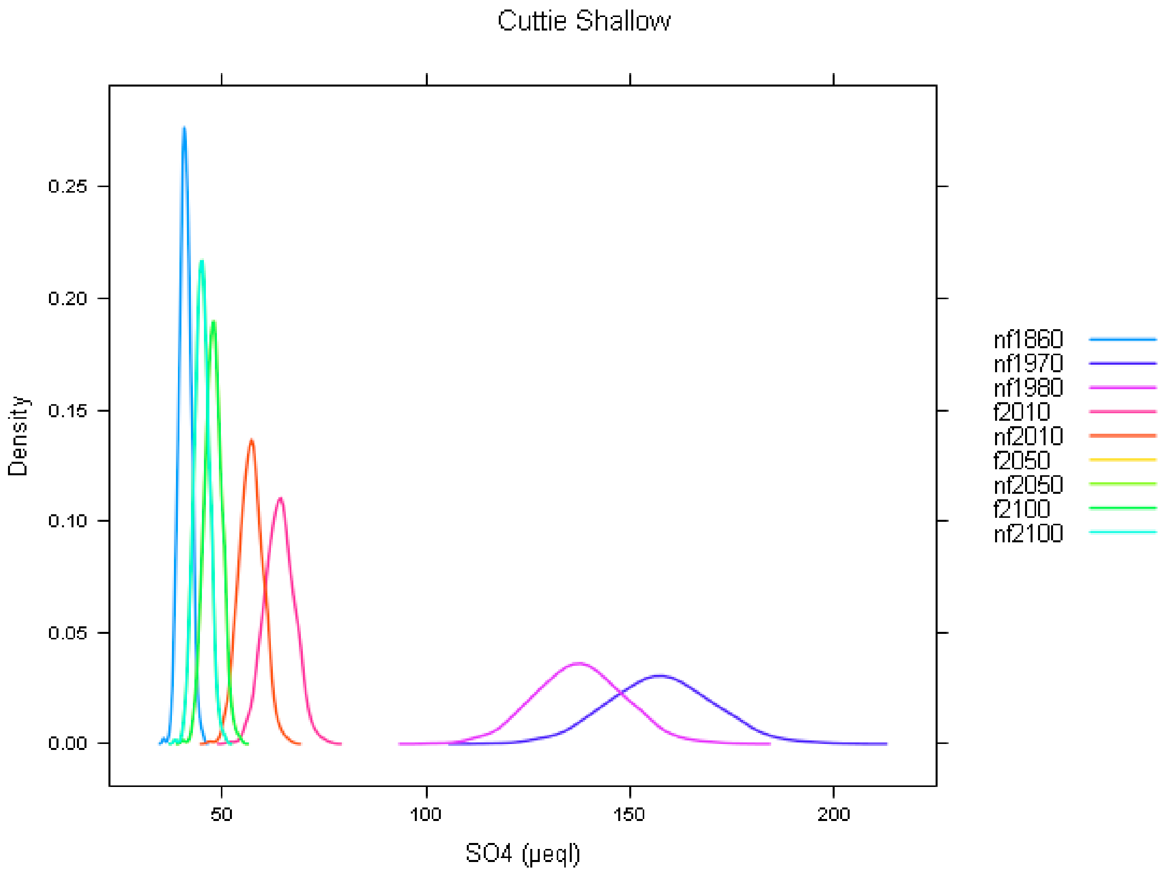
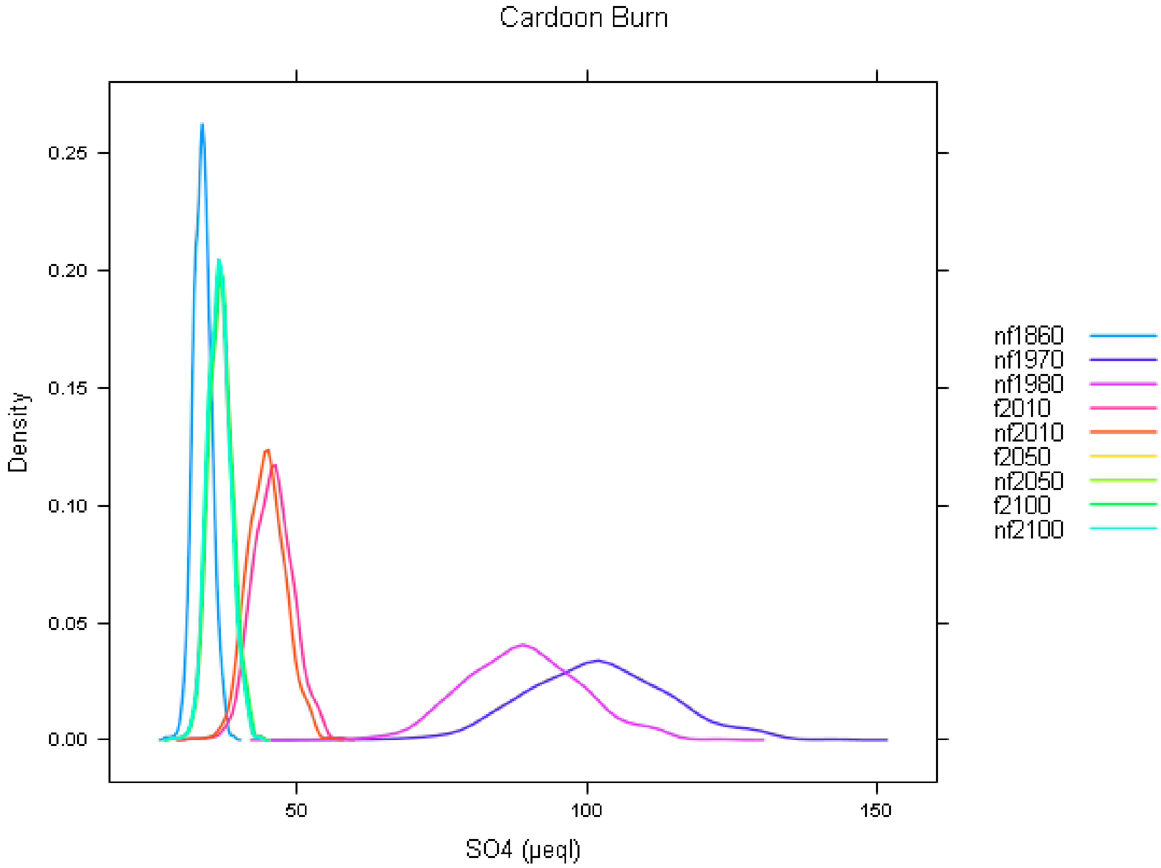

Waterside
Density
NO3 (μeql)
0.0
0.1
0.2
0.3
0
5
10
15
20
25
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100

Figure 23 Density plots of surface water SO_4 for land use scenarios (f = future forest plans, nf= no forest) between 1860 and 2100 (note, S in deposition is constant from 2020 to 2100, therefore no change in surface water SO_4 is evident during this period)




Dargall Lane
Density
0.25
0.20
0.15
0.10
0.05
0.00
50
100
150
200
SO4 (μeql)
nf1860
nf1970
nf1980
nf2010
nf2050
nf2100


Cuttie Shallow
Density
0.25
0.20
0.15
0.10
0.05
0.00
50
100
150
200
SO4 (μeql)
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100


Cardoon Burn
Density
0.00
0.05
0.10
0.15
0.20
0.25
50
100
150
SO4 (μeql)
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100

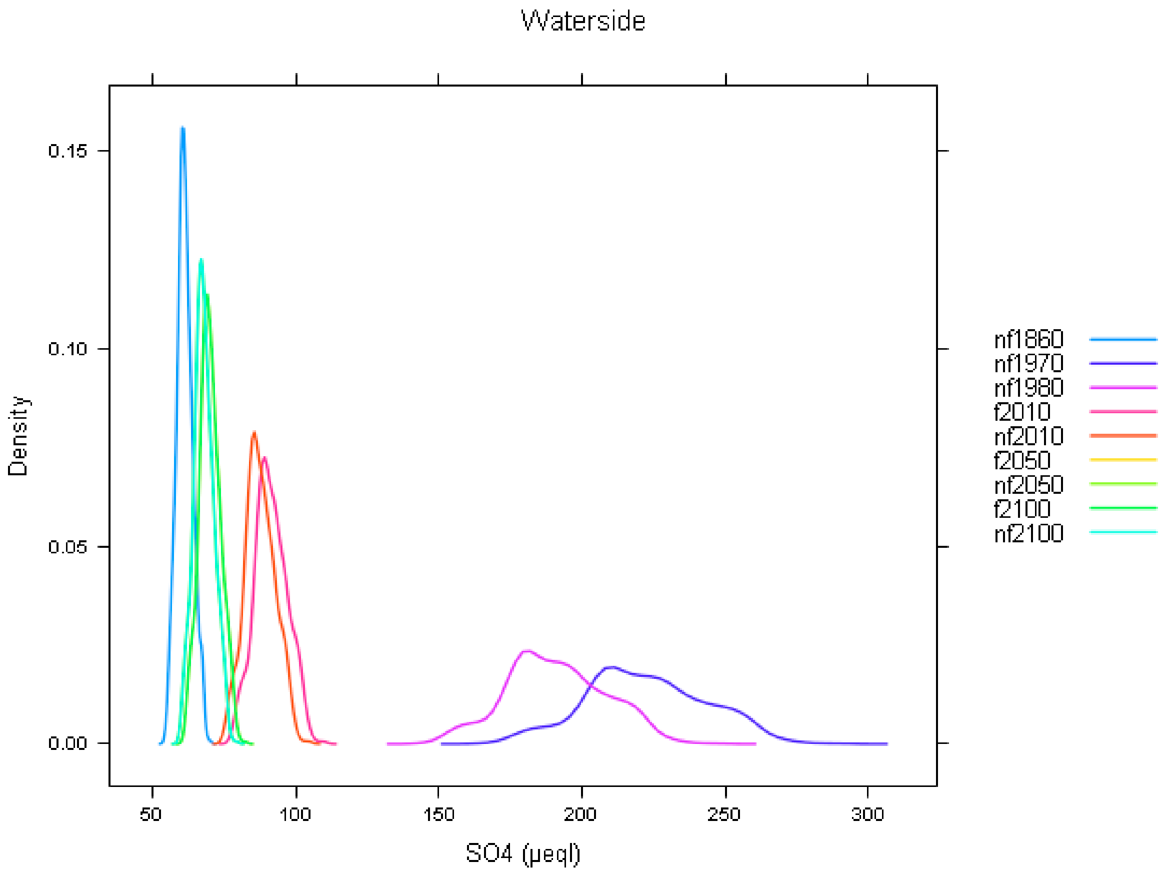
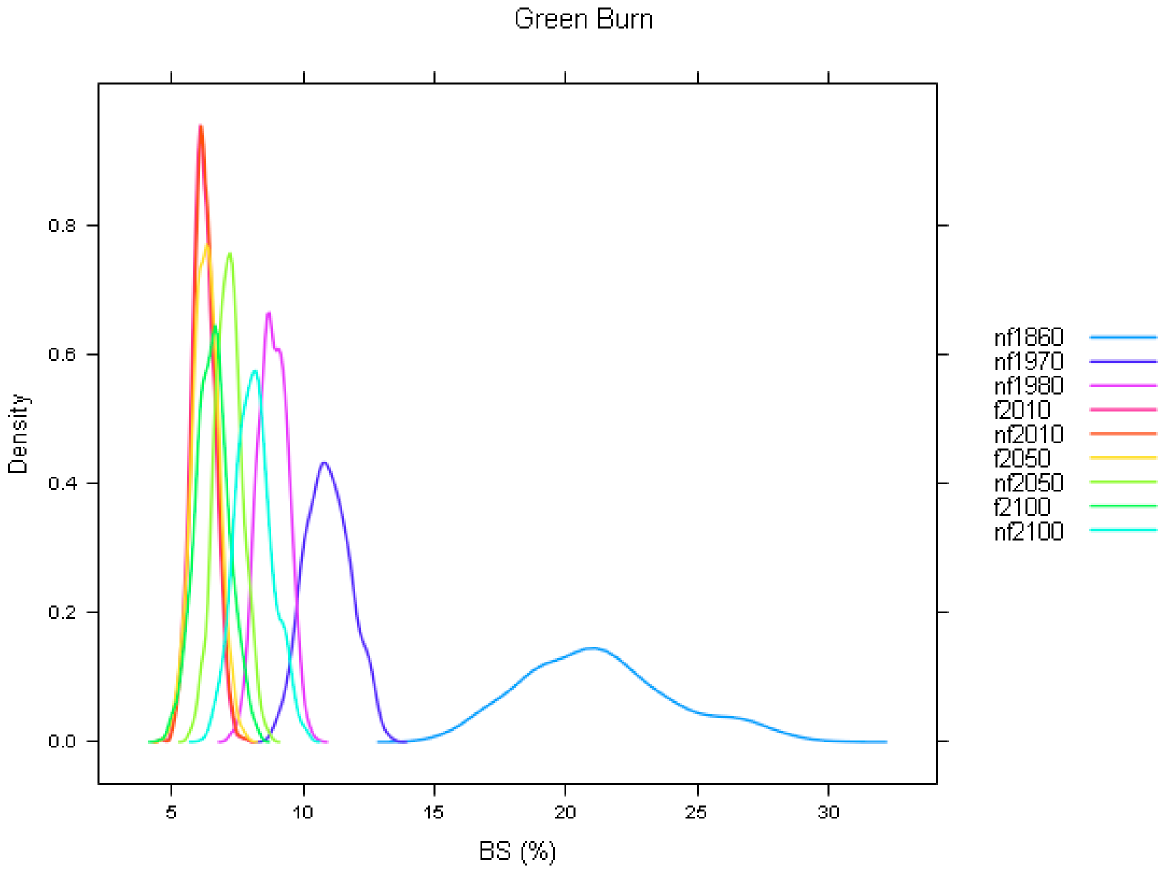
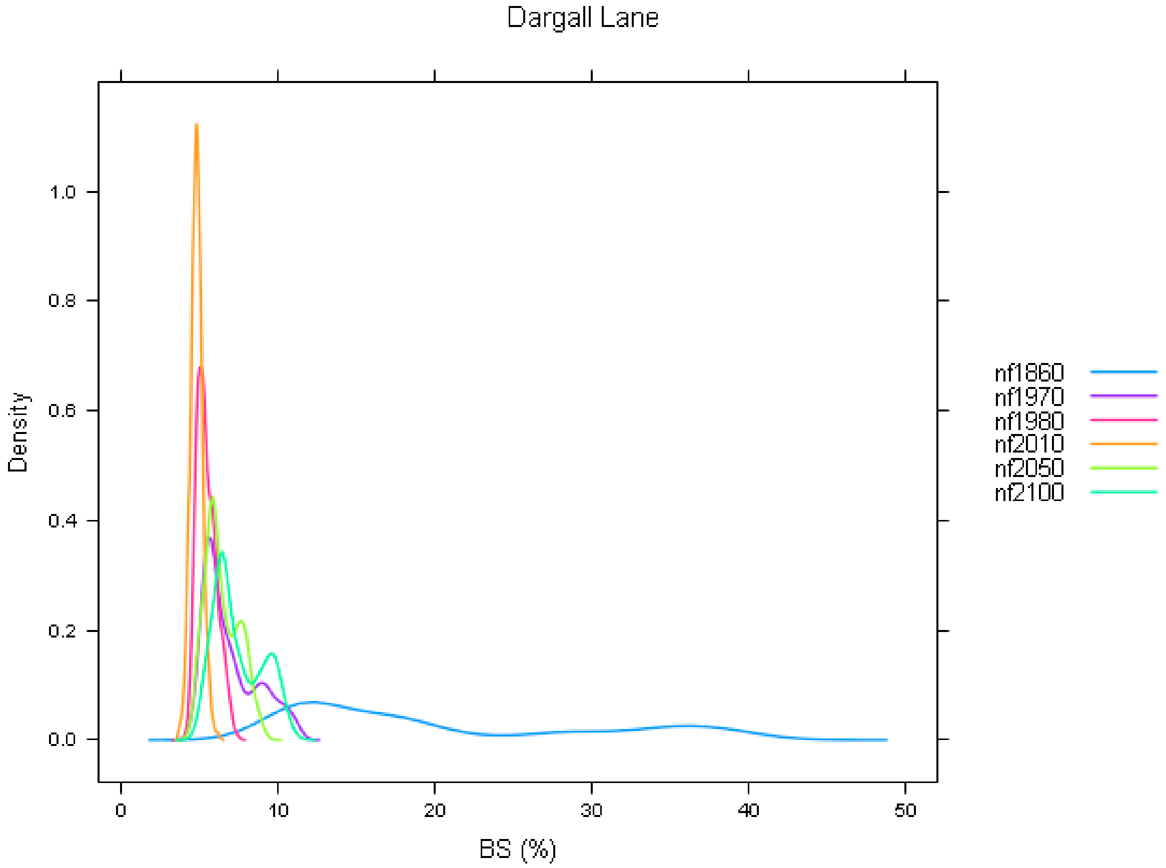
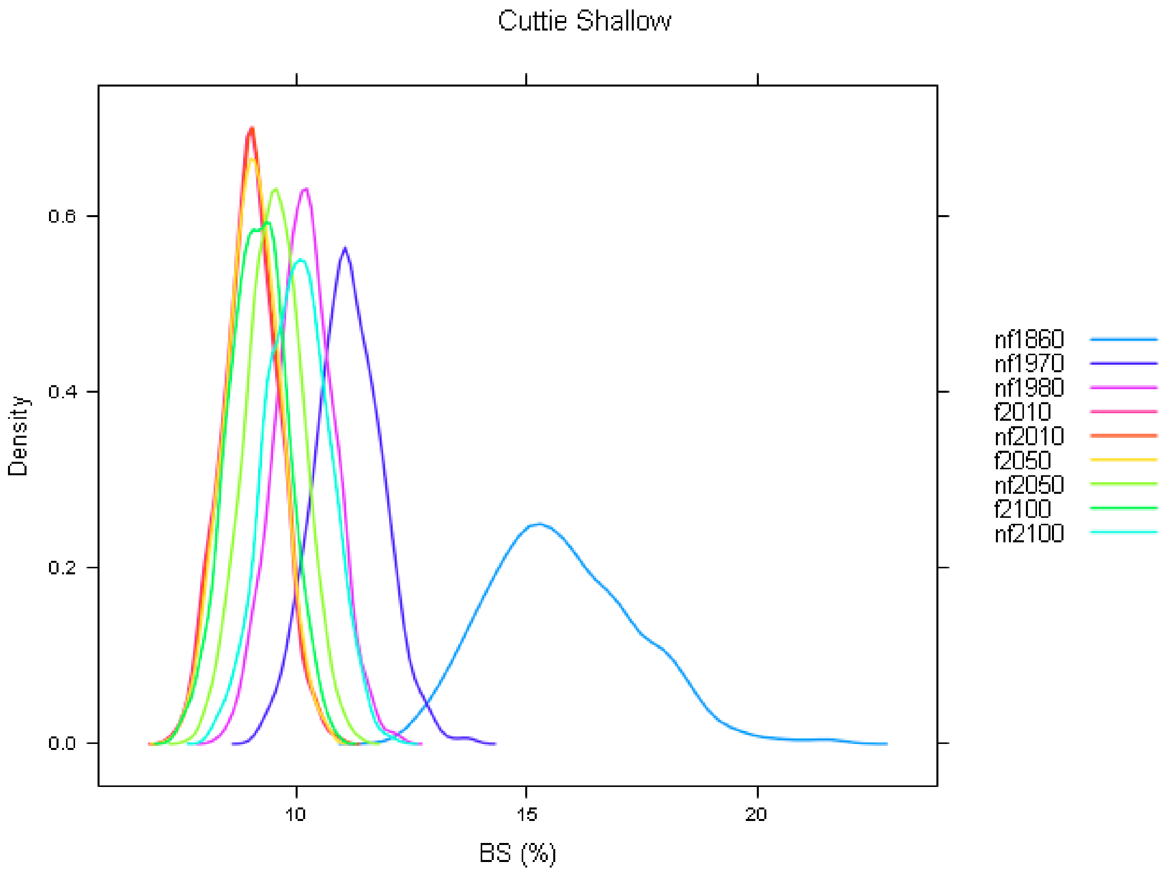
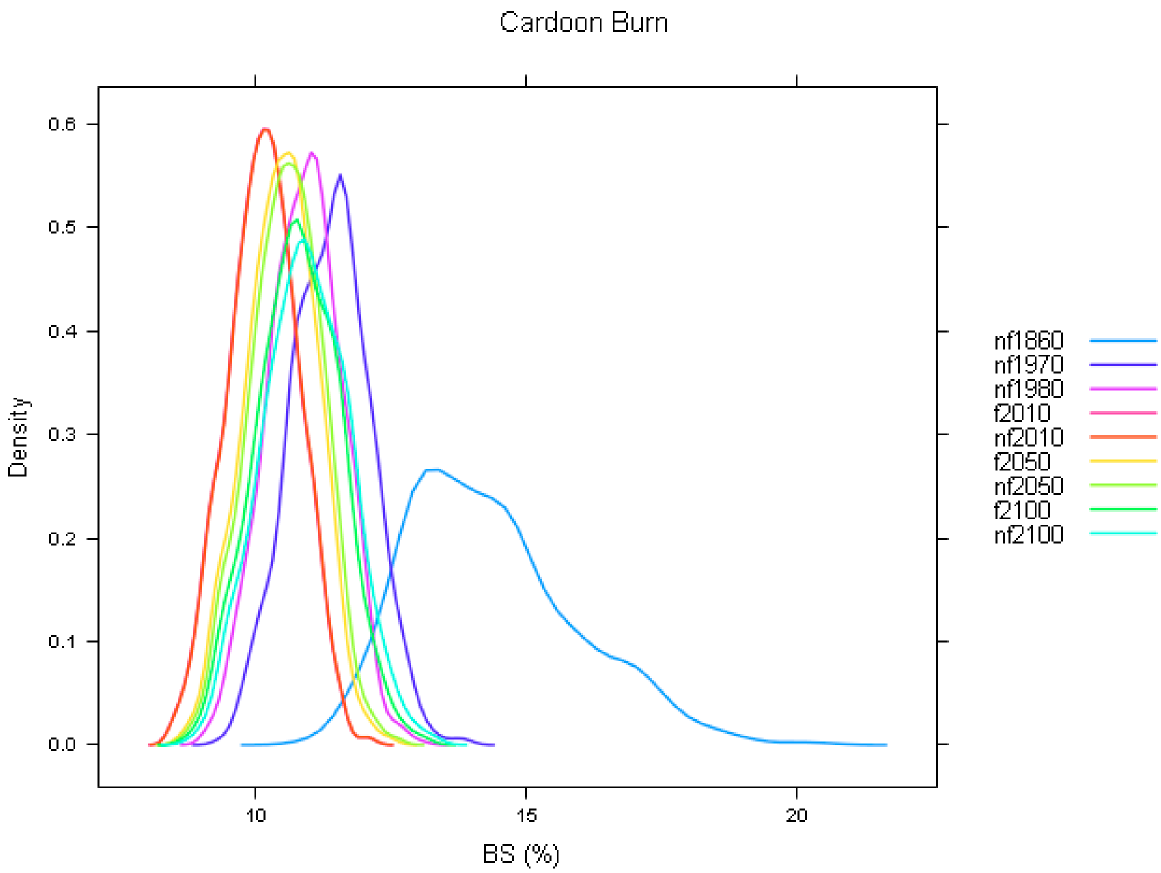

Waterside
Density
0.00
0.05
0.10
0.15
50
100
150
200
250
300
SO4 (μeql)
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100

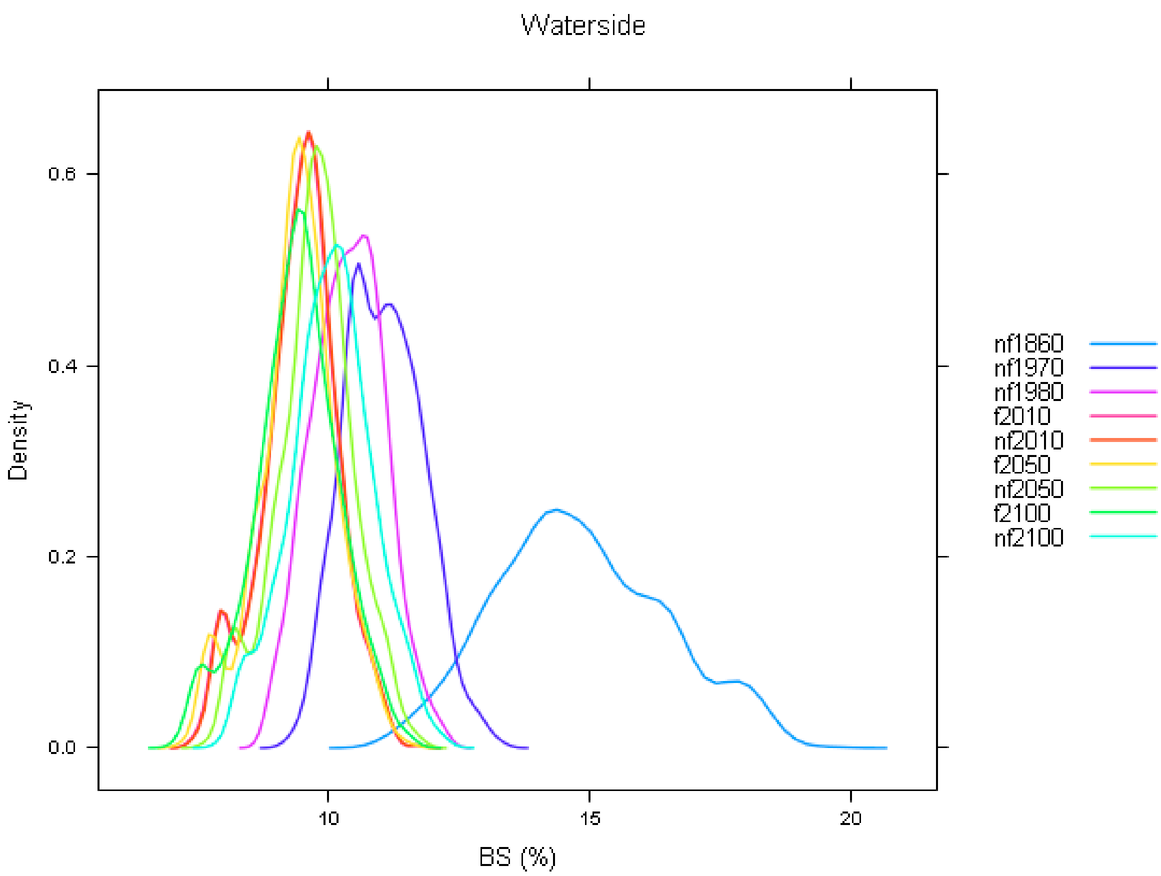
Figure 24 Density plots of soil base saturation for land use scenarios (f = future forest plans, nf= no forest) between 1860 and 2100.




Dargall Lane
Density
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
BS (%)
nf1860
nf1970
nf1980
nf2010
nf2050
nf2100


Cuttie Shallow
Density
0.6
0.4
0.2
0.0
10
15
20
BS (%)
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100


Cardoon Burn
Density
0.0
0.1
0.2
0.3
0.4
0.5
0.6
10
15
20
BS (%)
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100


Waterside
Density
0.0
0.2
0.4
0.6
10
15
20
BS (%)
nf1860
nf1970
nf1980
f2010
nf2010
f2050
nf2050
f2100
nf2100

7.8. Review of the model approach and uncertainty

In forested catchments the mechanisms that promote surface water acidification and recovery operate under constantly varying deposition and the direct effect of any one factor is difficult to identify without the use of dynamic models. The MAGIC model provides a valuable approach for quantifying past and future soil and water quality changes brought about by afforestation provided that the mechanisms of the forest effect can be identified and adequately quantified. In most model applications, in particular those linked to decision support or policy making, uncertainty analyses are commonly ignored. Uncertainty analysis is often considered complicated and may even be seen as undermining the conclusions from the model simulations because it actually reveals that the results are uncertain. In the development of our approach we have been mindful that, although the method itself is technically complex, the final outputs from the analysis should be easy to communicate to a range of interested parties including the forestry industry, fishery groups, Scottish Environment Protection Agency (SEPA) and other interested stakeholders.

Following the inclusion of forestry processes in the uncertainty framework and extensive testing, the model was, in general, successfully applied to all sites. The sum or aggregation of all the slight errors in the ions used to simulate ANC resulted in observations beyond the uncertainty window, however on the whole MAGIC predictions represent the general trend and magnitude of ANC observations. One of the significant challenges faced in this project was the amount (number of years) of observed stream chemistry data available at the study sites. It is well documented that when the number of observation years decrease the uncertainty in the model output values increases (Larssen et al., 2007, MacDougall et al., 2009), therefore the model performance is better at those sites with a longer record of observations, such as at Dargall Lane and Green Burn. A second challenge concerns the availability of catchment relevant deposition data. The framework is dependent on a continuous time series of deposition data (missing values were interpolated). In this study deposition data were used from the only reliable long term deposition collector in the vicinity of the study catchments, which was at Loch Dee. Furthermore, the uncertainty framework only uses a single year of soil physico-chemical data, not a time series, although the spatial and profile variability is accounted for in the catchment weighting procedure. There may be concerns about the limited quantity of soil chemistry data due to the heterogeneity of soils and scarcity of soil pits in catchments, but because the requirements of the framework are modest (see section 5.5 on profile and catchment weighting procedures for soil physico-chemical properties), it has a small impact on the viability of using the framework. An additional uncertainty in the present study concerns the modelling of forest growth and nutrient uptake. There is no feedback between availability of nutrients from the soil and the growth of forests, or consideration of the impact of climate change on biogeochemical cycling and therefore forest growth and productivity. Neither is any allowance made for the impact of soil cultivation on soil weathering rates or the expected enhanced canopy scavenging of base cations. While N dynamics are represented in the current model application as a function of the soil C and N pool, N processes are not driven by changes in temperature or soil moisture. Further improvement in NO_3 predictions is dependant on the future inclusion of this functionality.

8. Conclusions

A model of the combined long-term effects of acidic deposition and forest management practices has been developed and calibrated for selected sites in the Galloway region of SW Scotland. The model was used to assess the relative effects of forestry and acidic deposition on the acidification and recovery of soil and surface water chemistry. The aim of the report was to assess (a) the simulated historical effects of increased acidic deposition and forest planting and growth; and (b) the future effects of reductions in deposition in combination with planned forestry management, and to compare results with a scenario of forest removal from 2010 onwards.

The key findings from this study are:

a) Prior to the industrial revolution the reference ANC of all sites was above the suggested annual mean critical threshold for acid sensitive aquatic organisms (20 μeql^{-1}).

b) Widespread soil and surface water acidification was simulated between 1860 and 1970 as a direct response to the rapid increase in S deposition and to a lesser extent N deposition. There was little or no forest cover in the study sites during this period. The moorland site (Dargall Lane) was the most sensitive to the effects of acidification throughout the simulation and the only site where the median ANC critical threshold was exceeded. It is unclear whether the breaching of this threshold resulted in a loss of brown trout, although fry and parr have been recorded at low densities in most years since 1980.

c) Since the 1970s, SO_4 concentrations in surface waters have drastically decreased mainly in response to a c.80% reduction in UK SO_2 emissions and associated decreases in S deposition. The rate of decline in surface water SO_4 from the peak in 1970 was unrelated to the extent of forest cover in the catchments.

d) Nitrate concentrations show substantial inter-annual variability at all sites but no obvious trends are observed. The efficacy of N emission control is demonstrated by the decline in simulated median NO_3 concentrations from 2010 to 2050 under both land use scenarios. This response is dominated by N emissions reductions, and to a lesser extent, by land use.

e) Despite planned reductions in acid deposition to 2020 and in forest cover to 2050 based on planned felling and restocking, no site is predicted to recover to the chemical reference condition of 1860. The greatest recovery was simulated at Dargall Lane, reflecting its more acidified status. All sites have now recovered to the extent that the median ANC is greater than the 20μeql^{-1} threshold for the protection of fish, and three of the four forested sites exceed the much higher threshold of ANC 50 applied in some countries. Only Green Burn marginally fails to exceed this threshold by 2100 while Dargall Lane just passes.

f) Under the scenario of 'no forestry' post 2010, the ANC increased by a small amount (0.7-6.3 μeql^{-1}) between the four forested sites and was weakly related to the extent of forest cover removed. These increases were unlikely to be biologically significant as median ANC values greatly exceeded the ANC 20 threshold (exceeded ANC 50 in three of the four sites).

g) Whilst the complete removal of forestry was predicted to improve water quality the absolute effects were marginal compared to the extent of recovery solely from reductions in acid deposition (e.g. forest removal increased pH by only 0.02–0.04 pH units by 2100 in three of the four forested sites). The chemical recovery of surface waters in the Galloway region was dominated by the reduction in S deposition, the main driver of acidification. By 2020 surface water SO_4 (average for 5 sites 48.01 μeql^{-1}) is predicted to decline close to levels simulated in 1860 (average for 5 sites 41.29 μeql^{-1}) with obvious potential benefits to fish populations. The average reduction in surface water SO_4 from 1980 to 2020 for the 5 sites was 64.3 % with the greatest simulated reduction at Dargall Lane (71.3 %) and the smallest at Waterside (62.5 %).

h) Stream ecology has been very slow to respond to observed chemical improvements but there are increasing signs of a positive response in some parts of Galloway. For example, there is now evidence of improving fish numbers in the acid sensitive Lochs Valley, Neldricken and Grannoch, which managed to retain small populations of trout. However, while such anecdotal information is encouraging, further scientific monitoring is required to confirm the durability of this apparent recovery. In other parts of Galloway such as the River Cree, salmon numbers remain very low within acid sensitive reaches. Further research is required to determine an appropriate reference condition for peaty upland catchments with a naturally low buffering capacity in order to determine appropriate recovery targets for fish.

i) Discrepancies were noted between simulated ANC and fish status at some of the studied sites, raising questions about the most appropriate ANC threshold for protecting fish. However, while other chemical indicators may show better relationships with fish presence, ANC remains the parameter favoured by managers and regulators for applying the critical loads approach at national and international levels. ANC provides a useful metric for predicting the recovery of freshwaters to declining pollutant emissions providing the limitations and uncertainties are acknowledged.

j) The uncertainty in model predictions has been quantified to aid interpretation of results.

Acknowledgements

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References

Aherne, J., Posch, M., Forsius, M., Vuorenmaa, J., Tamminen, P., Holmberg, M. and Johansson, M (2008). Modelling the hydro-geochemistry of acid-sensitive catchments in Finland under atmospheric deposition and biomass harvesting scenarios. Biogeochemistry 88:233–256. DOI 10.7007/s10533-008-9206–7.

Bettelheim J. and Littler A. (1979). Historical trends of sulphur oxide emissions in Europe since 1865. CEGB report PL-GS/E/1/79. CEGB, London.

Bridcut, E.E., Mcnish, J. and Harriman, R. (2004). Incorporating episodicity into estimates of Critical Loads for juvenile salmonids in Scottish streams. Hydrology and Earth System Sciences 8:366-376.

Burns, J.C., Coy, J.S., Tervet, D.J., Harriman, R., Morrison, B.R.S. and Quine, C.P. (1984). The Loch Dee Project: a study of the ecological effects of acid precipitation and forest management on an upland catchment in south-west Scotland. Fisheries Management 15:145–167.

Department of Environment & Forestry Commission (1991). Forests & Surface Water Acidification Report. Darlington Workshop.

Forestry Commission, (2003). Forests & Water Guidelines (Fourth Edition). Forestry Commission, Edinburgh.

Fowler, D., O'Donoghue, M.O., Muller, J.B.A., Smith, R.I., Dragosits, U., Skiba, U. Sutton, M.A., and Brimblecombe, P. (2004). A chronology of nitrogen deposition in the UK between 1900 and 2000. Water, Air and Soil Pollution 4:9-23.

Gardner, M. (2008). Long-term proficiency testing for the UK Acid Waters Monitoring Network. Accreditation and Quality Assurance 13:255-260.

Griffin, A., Fraser, A., Kent,A., Loader, A., Martinez, C., Stedman, J., Stevenson, K., Vincent, K., Willis, P., Yardley, R. and Bush, T. (2009). Air Pollution in the UK 2009 – Edition B. Published by the Department for Environment, Food and Rural Affairs, December 2010.

Gundersen, P., Callesen, I. and de Vries, W. (1998). Nitrate leaching in forest ecosystems is related to forest floor C/N ratios. Environmental Pollution 102:403-407.

Hamilton, G.J. and Christie, and J.M. (1971). Forest Management Tables (Metric). Forestry Commission Booklet No 34. HMSO.

Harriman, R., Morrison, B.R.S., Caines, L.A., Collen, P. and Watt, A.W. (1987). Long-term changes in fish populations of acid streams and lochs in Galloway South West Scotland. Water, Air and Soil Pollution 32:89–112.

Harriman, R., Watt, A.W., Christie, A.E.G., Collen, P., Moore, D.W., McCartney, A.G., Taylor, E.M. and Watson, J. (2001). Interpretation of trends in acidic deposition and surface water chemistry in Scotland during the past three decades. Hydrology and Earth System Sciences, 5: 407–420.

Harriman, R., Watt, A.M., Christies, A.E.G., Moore, D.M., McCartney, A.G. and Taylor, E.M. (2003). Quantifying the effects of forestry practices on the recovery of upland streams and lochs from acidification. The Science of the Total Environment 310:101–111.

Helliwell, R.C., Ferrier, R.C., Evans, C., and Jenkins, A. (1998). A comparison of methods for estimating soil characteristic in regional acidification models: an application of the MAGIC model to Scotland. Hydrology and Earth System Sciences 2:509–520.

Hrachowitz, H., Soulsby, C., Tetzlaff, D., Malcolm, I.A. and Schoups, G. (2010). Gamma distribution models for transit time estimation in catchments: Physical interpretation of paramaters and implications for time-variant transit time assessment. Water Resources Research 46 doi:10.1029/2010WR009148.

Jenkins, A., Ferrier, R.C. and Helliwell, R.C. (2001). Modelling nitrogen dynamics at Lochnagar, NE Scotland. Hydrology and Earth System Sciences, Special Issue, RECOVER : 2010, 5:519–527.

Kernan, M., Battarbee, R.W., Curtis, C.J., Monteith, D.T. and Shilland, E.M. (eds.) (2010). Recovery of Lakes and Streams in the UK from the Effects of Acid Rain. UK Acid Waters Monitoring Network 20 Year Interpretative Report. Report to Defra. Environmental Change Research Centre, University College London, 465 pp.

Kirchner, J.W and Lydersen, E. (1995). Base Cation Depletion and Potential Long-Term Acidification of Norwegian Catchments. Environmental Science and Technology, 29: 1953–1960.

Langan, S.L. and Hirst, D. (2004). An analysis of the long-term variation in stream water quality for three upland catchments at Loch Dee (Galloway, S.W. Scotland) under contrasting land management. Hydrology and Earth Systems Sciences, 8:422–435.

Larssen, T., Hogasen, T. and Cosby, B. J. (2007). Impact of time series data on calibration and prediction uncertainty for a deterministic hydrogeochemical model. Ecological Modelling 207:22–33.

Larssen, T., Huseby, R., Cosby, B.J., Høst, G., Høgåsen, T., Aldrin, M. (2006). Forecasting Acidification Effects Using a Bayesian Calibration and Uncertainty Propagation Approach. Environ. Sci. Technol. 40:7841-7847.

Lawrence,H., Vincent, K., Smith, M., Colbeck, C., Tang, Y.S., Sutton, M.A., Simmons, I., Love, L., Vogt, E., van Dijk, N., Cape, J.N., and Smith, R.I (2006). UK Acid Deposition Monitoring Network Report: Data summary 2006. AEA Energy & Environment and Centre for Ecology and Hydrology Report AEAT/ENV/R/2534 Issue 2.

Lien, L., Raddum, G.G. and Fjellheim, A. (1992). Critical loads of acidity to freshwater-fish and invertebrates. Norwegian Institute for Water Research (NIVA). Report 0-89185: 36pp.

MacDougall, G., Aherne, J. and Watmough, S. (2009). Impacts of acid deposition at Plastic Lake: forecasting chemical recovery using a Bayesian calibration and uncertainty propagation approach. Hydrology Research 40.2-3, 249-260.

Malcolm, I., Bacon, P., Middlemas, S., Collen, P. and Shilland, E. (2010). Salmonid fish populations. In: Recovery of lakes and streams in the UK from acid rain. The United Kingdom Acid Waters Monitoring Network 20 year interpretative report. ECRC Research Report #141. Report to the Department for Environment, Food and Rural Affairs (Contract EPG 1/3/160). Eds M.Kernan, R.W.Battarbee, C.J.Curtis, D.T.Monteith & E.M.Shilland. pp 125-150.

Malcolm, I.A., Bacon, P.J., Middlemas, S.J., Fryer, R.J., Shilland, E.W. and Collen, P (Submitted). Relationships between hydrochemistry and the presence of brown trout (Salmo trutta) in headwater streams recovering from acidification. Ecological Indicators.

Malcolm, I.A., Gibbins, C., Fryer, R.J., Keay, J., Tetzlaff, D. and Soulsby, C. (Submitted). Long-term hydrochemical and invertebrate data provide evidence of acid recovery in the Loch Ard area of central Scotland. Environmental Indicators.

Malgorzata, M., Dore, A., Hall, J., Dore, C.J, Blas, M, Kryza, M, Smith, R and Fowler, D. (2009). The influence of long term trends in pollutant emissions on deposition of sulphur and nitrogen and exceedance of critical loads in the United Kingdom. Environmental Science and Policy, 12. 882896. 10.1016/j.envsci.2009.08.005.

McCartney, A.G., Harriman, R., Watt, A.W., Moore, D.M., Taylor, E.M. and Keay, E.J. (2003). Long-term trends in pH, aluminium and dissolved organic carbon in Scottish fresh waters; implications for brown trout (*Salmo trutta*) survival. The Science of the Total Environment 310:133–141.

McKay H., Hudson, J.B. and Hudson, R.J. (2003). Woodfuel Resource in Britain: Appendices. FES B/W3/00787/REP/2. DTI/Pub URN 03/1436. Forestry Contracting Association.

Miller, J.D., Anderson, H.A., Cooper, J.M., Ferrier, R.C. and Stewart, M (1991). Evidence for enhanced atmospheric sulphate interception by Sitka spruce from evaluation of some Scottish catchment study data. The Science of the Total Environment 103:37-46.

Monteith, D.T. Hildrew, A.G. Flower, R.J. Raven, P.J. Beaumont, W.R.B. Collen, P. Kreiser, A.M. Shilland, E.M. and Winterbottom, J.H. (2005). Biological responses to the chemical recovery of acidified fresh waters in the UK. Environmental Pollution 137:83-101.

Morrison, B.R.S and Collen, P. (1993). The trout (Salmo trutta L.) and invertebrate populations of Loch Dee and its inflowng streams. Proceedings of the Loch Dee Symposium, Gatehouse of Fleet, Dumfries & Galloway, 8-9 December 1992. Foundation for Water Research, Marlow, 171 pp.

Neal, C., Smith, C.J., Hill, S. (1992). Forestry impact on upland water quality. Institute of Hydrology Report. No. 119. ISBN 0 948540 42 7.

Ormerod, S.J., Brown, A.P., and Brown, S.J. (1989). The influence of plantation forestry on the pH and aluminium concentration of upland welsh streams: A re-examination. Environmental Pollution 62:47-62.

Rendall, D. and Bell, A. (2008). Current acidification status and evidence of recovery in some Dumfries & Galloway watercourses. Ecology Report No. DF08/01, Scottish Environment Protection Agency, 23 pp.

Robson, A., Jenkins, A. and Neal, C. (1991). Towards predicting episodic changes in stream water chemistry. Journal of Hydrology 125:161-174.

Simpson, D., Olendrzynski, K., Semb, A., Storen, E. and Unger, S. (1997). Photochemical oxidant modelling in Europe: multi-annual modelling and source–receptor relationships. EMEP/MSC-W Report 3/97. Norwegian Meteorological Institute, Oslo.

Smith, J., Gottschalk, P., Bellarby, J., Chapman, S., Lilly, A., Towers, W., Bell, J., Coleman, K., Nayak, D., Richards, M., Hillier, J., Flynn, H., Wattenbach, M., Aitkenhead, M., Yeluripurti, J., Farmer, J., Milne, R., Thomson, A., Evans, C., Whitmore, A., Falloon, P. and Smith, P. (2010). Estimating changes in Scottish soil carbon stocks using ECOSSE. II. Application. Climate Research 45: 193–205.

SNH, (2007). River Bladnoch SAC. Atlantic Salmon Catchment Management Plan. Scottish Natural Heritage, 102 pp.

Warren Spring Laboratory (1987). Acid Deposition in the United Kingdom, 1981–85. Warren Spring Laboratory, Stevenage, UK.

Welsh, W.T., Tervet, D.J. and Hutchinson, P. (1986). Acidification investigations in south-west Scotland. Paper presented to North Eastern branch of the Institute of Water Pollution Control, Selby, 12 March 1986.

Appendices

Appendix 1a Electrofishing data from Waterside, River Bladnoch (at GR229150 572100). Records supplied by the Galloway Fisheries Trust

All figures are minimum estimates of fish per 100m² of water. The salmon fry (0+) and parr (1++) have either been directly stocked at Waterside or just upstream, or are believed to have originated from stocked fish. No trout stocking has taken place.

2001	Salmon	0+	0
		1++	0
	Trout	0+	6.39
		1++	0.80

2002	Salmon	0+	1.12
		1++	0.37
	Trout	0+	2.62
		1++	1.87

2003	Salmon	0+	0
		1++	0.74
	Trout	0+	0.99
		1++	1.98

2004	Salmon	0+	0.37
		1++	0
	Trout	0+	3.36
		1++	0.37

2005	Salmon	0+	2.52
		1++	0
	Trout	0+	1.26
		1++	0

2006	Salmon	0+	0
		1++	0
	Trout	0+	2.39
		1++	0.60

2007	Salmon	0+	22.40
		1++	0
	Trout	0+	1.40
		1++	0

2009	Salmon	0+	0
		1++	0
	Trout	0+	0
		1++	2.22

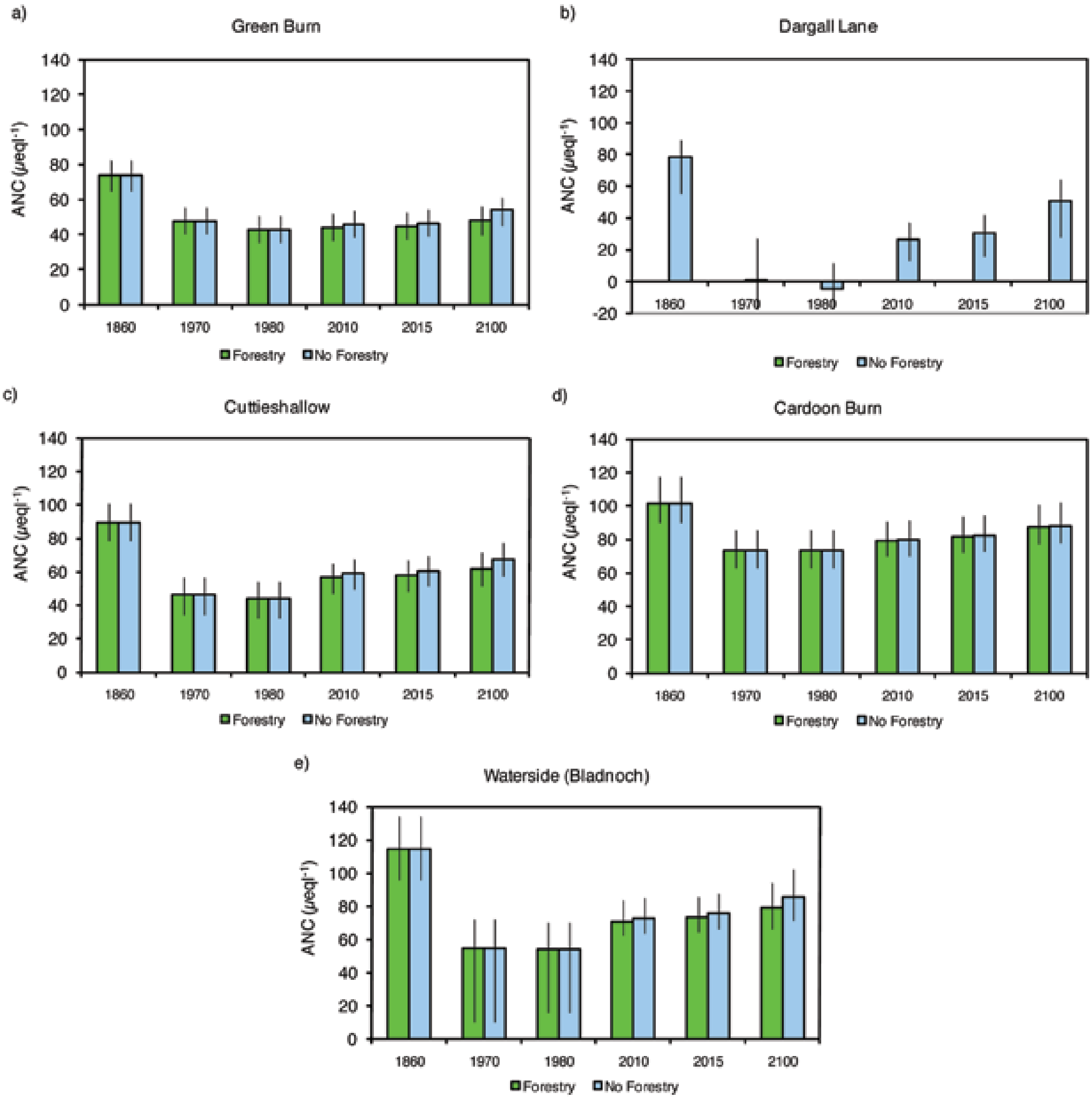
Appendix 1b Electrofishing data from Cardoon Burn (at GR 253400 565200). Records supplied by the Galloway Fisheries Trust

All figures are minimum estimates of fish per 100m² of water. The salmon fry (0+) and parr (1++)

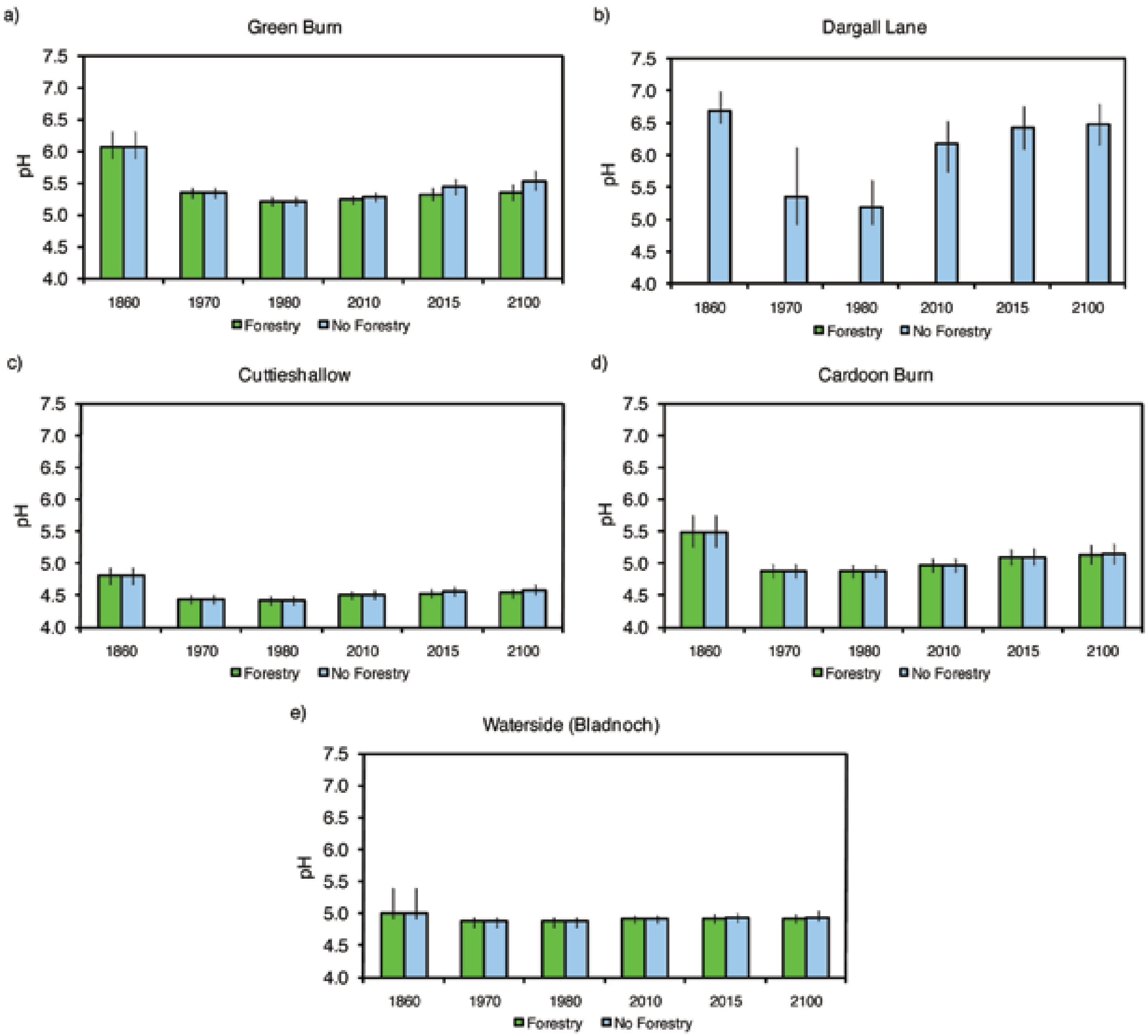
1999	Salmon	0+	0
		1++	0
	Trout	0+	18.61
		1++	11.45

2002	Salmon	0+	0
		1++	0
	Trout	0+	5.39
		1++	9.43

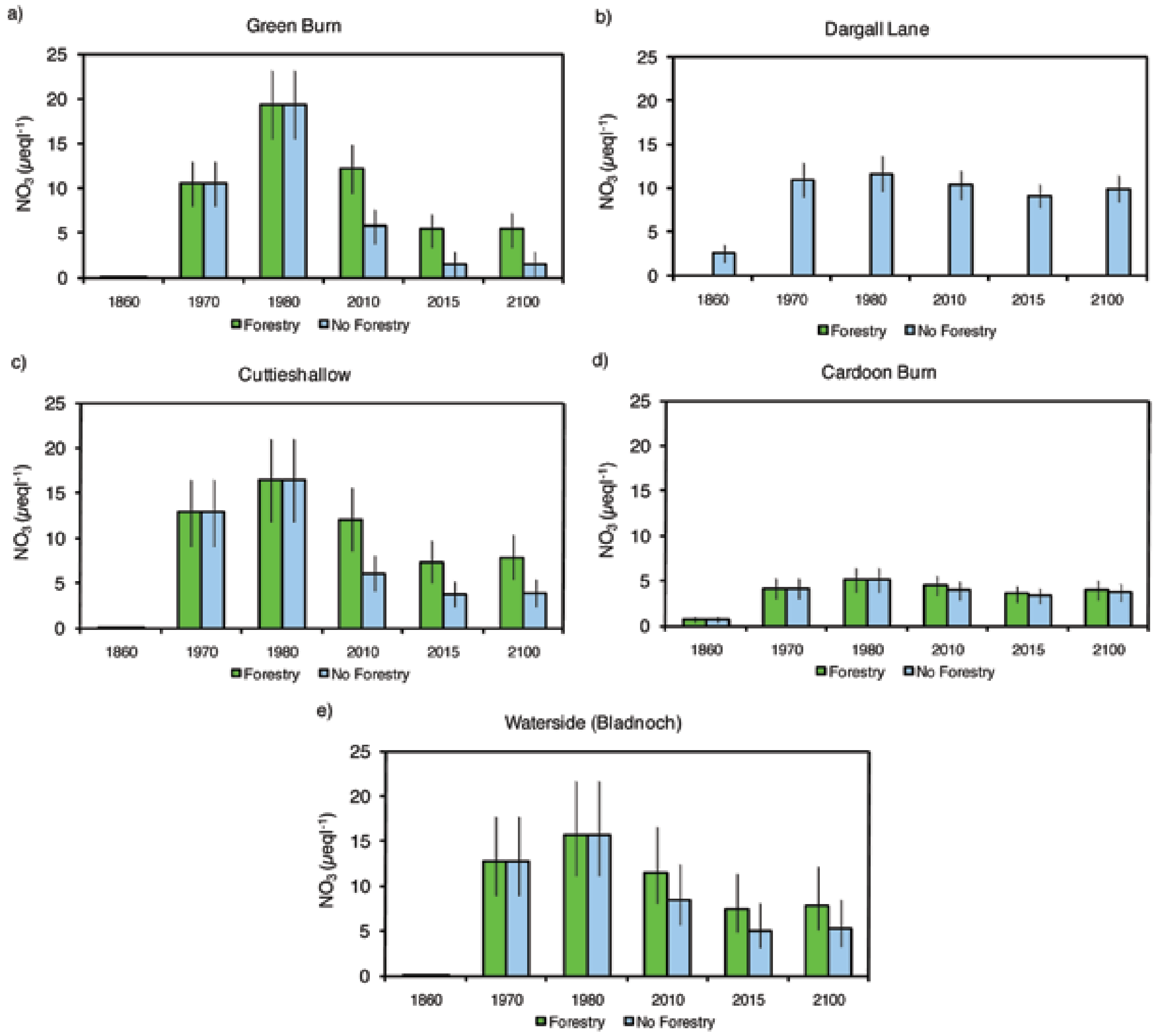
Appendix 2a Median surface water ANC between land use scenarios (the error bars indicate the 5th and 95th percentile)



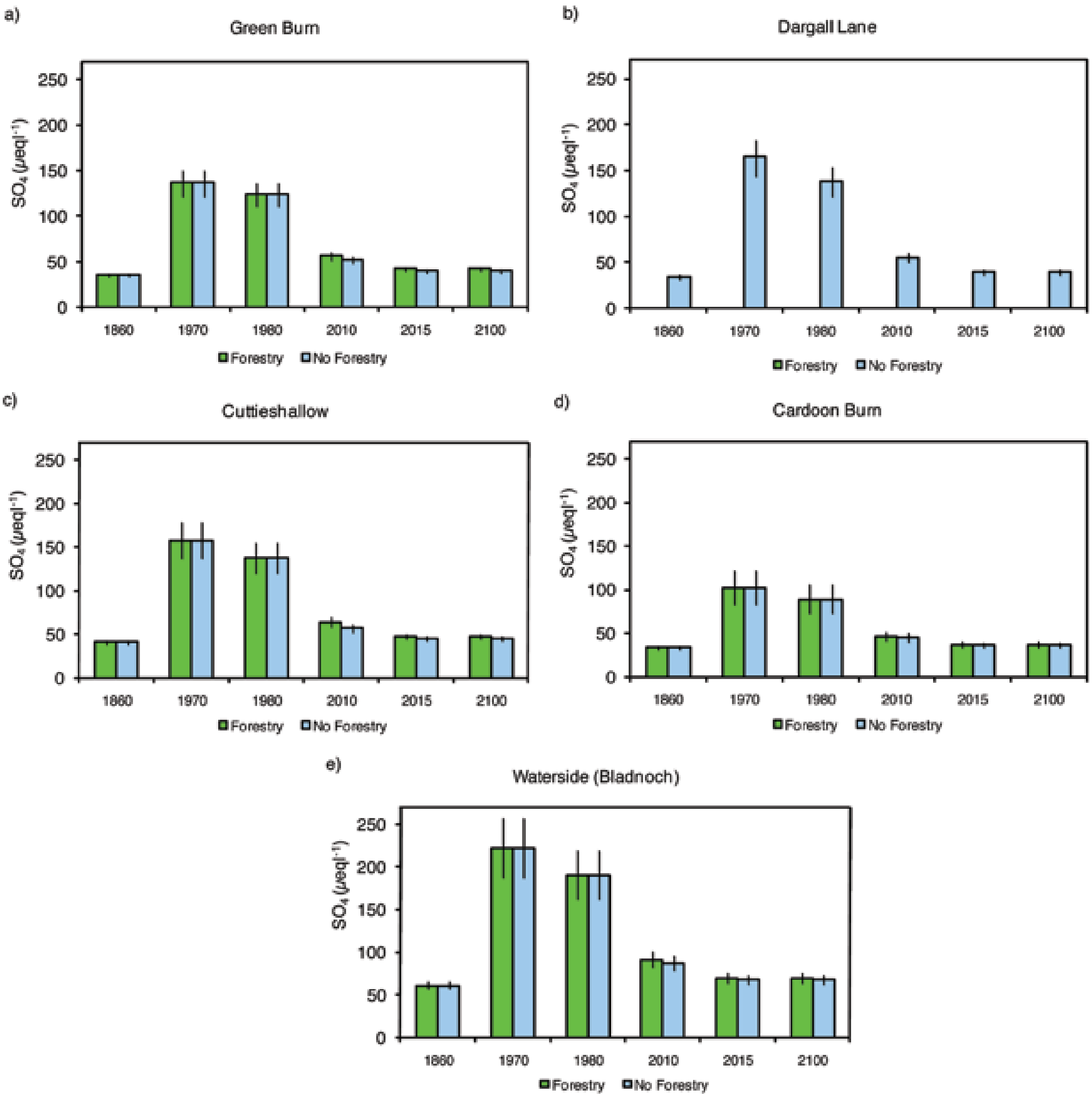
Appendix 2b Median surface water pH between land use scenarios (the error bars indicate the 5th and 95th percentile)



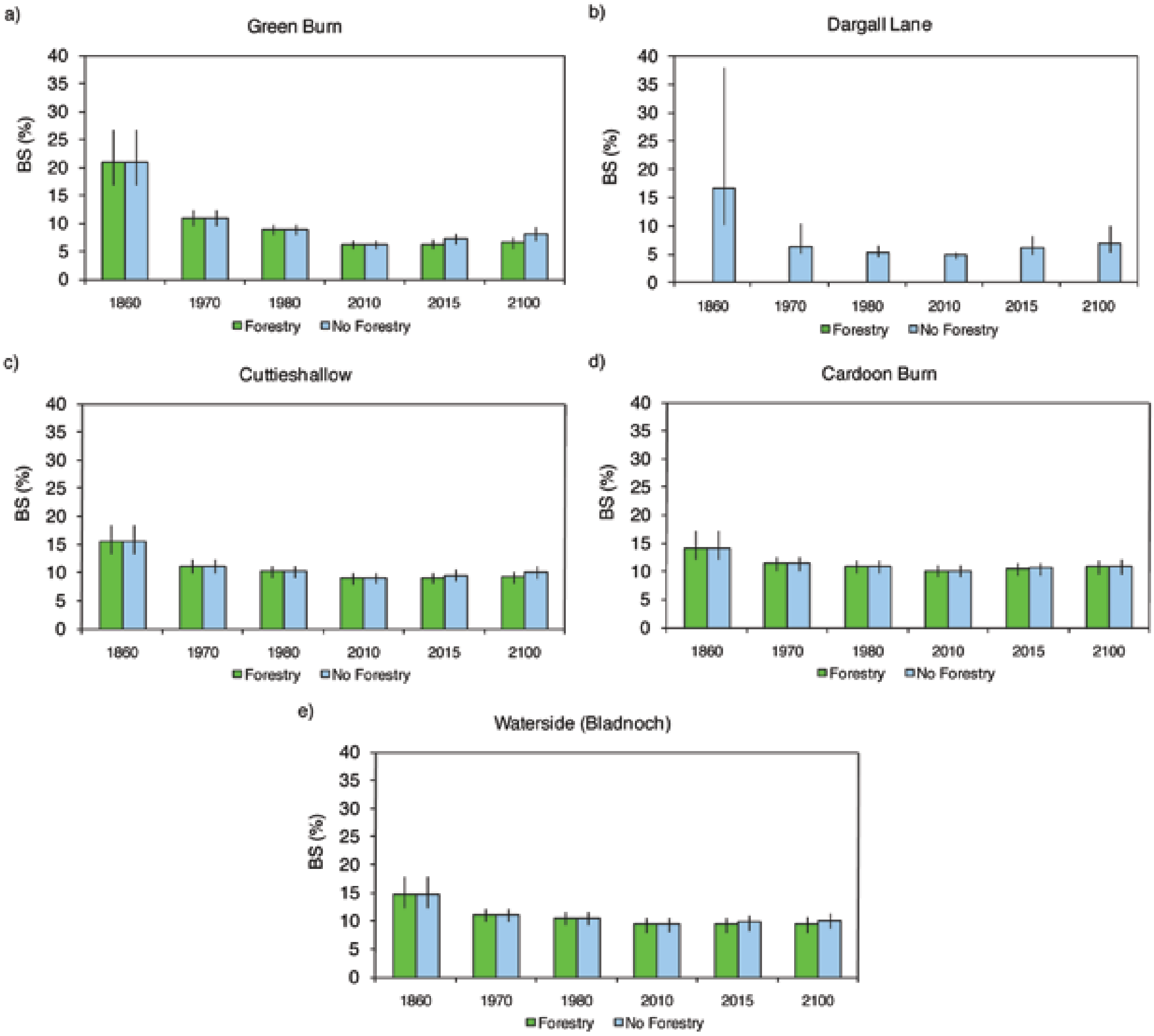
Appendix 2c Median surface water NO_3 between land use scenarios (the error bars indicate the 5th and 95th percentile)



Appendix 2d Median surface water SO_4 between land use scenarios (the error bars indicate the 5th and 95th percentile)



Appendix 2e Median soil base saturation between land use scenarios (the error bars indicate the 5th and 95th percentile)



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