



HAL
open science

Cycling of nutrient base cations in a twelve year old Sitka spruce plantation in upland mid-Wales

B. Reynolds, M. J. Wood, A. M. Truscott, S. A. Brittain, D. L. Williams

► **To cite this version:**

B. Reynolds, M. J. Wood, A. M. Truscott, S. A. Brittain, D. L. Williams. Cycling of nutrient base cations in a twelve year old Sitka spruce plantation in upland mid-Wales. *Hydrology and Earth System Sciences Discussions*, 2008, 4 (2), pp.311-321. hal-00304611

HAL Id: hal-00304611

<https://hal.science/hal-00304611>

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Cycling of nutrient base cations in a twelve year old Sitka spruce plantation in upland mid-Wales

B. Reynolds¹, M.J. Wood², A.M. Truscott³, S.A. Brittain¹ and D.L. Williams¹

¹Centre for Ecology and Hydrology Bangor, UWB, Deiniol Road, Bangor, Gwynedd LL57 2UP, UK

²HYSED (Hydrodynamics and Sedimentology Laboratory), Department of Geography, Lancaster University, Lancaster LA1 4YB, UK

³Centre for Ecology and Hydrology Banchory, Hill of Brathens, Glassel, Banchory, Kincardineshire AB31 4BY, UK

e-mail for corresponding author: br@echi.ac.uk

Abstract

The effects of the early growth of plantation forestry on the biogeochemical cycling of potassium, calcium and magnesium have been investigated in a stand of 12 year old Sitka spruce and adjacent moorland growing on acid peaty podzol soils in mid Wales. Element budgets have been calculated for both systems using measurements of soil and vegetation base cation pools and fluxes. In the moorland, the magnesium budget is approximately at steady-state with no net change to the soil store whilst the soil is accumulating potassium. The calcium budget is approximately balanced but contains significant uncertainties due to between plot variability in calcium leaching losses. Afforestation has greatly increased the above-ground living biomass which holds 7 to 15 times more nutrients compared to the living aerial biomass in the moorland. With the exception of magnesium, the base cation stores within the forest soil are being depleted as the increase in atmospheric deposition due to the forest canopy provides only a small offset to the much larger accumulation of base cations within the trees. The current net rate of change in the soil store of calcium is sustainable for only 65 years. However, as the trees mature, their demand for calcium will be reduced and they should be able to 'tap' deeper sources of calcium in the soil profile as well as in the drift and regolith material.

Keywords: Forestry, base cations, element cycling, calcium, magnesium, potassium

Introduction

Plantation conifer afforestation represents one of the major changes in land use affecting the UK uplands. For example, in Wales forest and woodland cover about 11% of the land area (2410 km²) and roughly two thirds of this consists of conifer forest planted in the last 60 years (Forestry Commission, 1985). In Britain, the majority of forest plantations have been planted with Sitka spruce (*Picea sitchensis*) on exposed upland moorland sites with infertile, poorly drained, acid soils. Plantations consist typically of closely spaced (1.5–2 m) trees grown over a 40–60 year rotation. Growth of the forest to canopy closure usually takes 10–15 years during which time the pre-existing vegetation is progressively shaded out. Beyond canopy closure, trees have the dominant environmental role and ground flora are limited to gaps where trees have failed or have not been planted, roadside verges, rides and riparian margins. Afforestation therefore causes large changes in soils and plant cover with major impacts on ecosystem processes such as plant uptake, organic matter mineralisation and atmospheric inputs (Hornung and Newson, 1986).

The upland location of the majority of plantation forests

means that at least part of the headwater catchments of many rivers in Wales, drain afforested land. As these rivers sustain nationally important game fisheries and are ecologically valuable, there has been considerable research over the last 10–15 years into the potential impacts of afforestation on upland water resources (eg, Stoner *et al.*, 1984; Neal *et al.*, 1990; Harriman *et al.*, 1994). The majority of this research has been directed towards understanding acidification processes in upland forests often using mature forest plantations in comparison with semi-natural acid grassland and moorland catchments (eg, Stevens *et al.*, 1994). As a result, relatively little is known about the initial stages of afforestation up to and including canopy closure when some of the major changes in ecosystem structure and function occur (Miller, 1995). Models of the environmental impacts of plantation forests therefore have to extrapolate between pre-existing acid grassland and moorland ecosystems to mature forestry (eg, Emmet *et al.*, 1997) with few data to verify predicted trends during the first ten to twenty years of forest development.

This paper reports new data comparing the biogeochemical cycling of base cations in a 12 year old Sitka spruce plantation with adjacent ungrazed moorland. With the

exception of the Coalburn catchment experiment (Robinson *et al.*, 1998), this early transitional phase of forest development has been little studied in the UK. This paper, therefore, provides important new information concerning the potential effects of young forest plantations on soil nutrient status, acidification and runoff water quality. The work described here is part of a larger study within the Cwm catchment at Llanbrynmair in mid-Wales (Roberts *et al.*, 1986; Roberts *et al.*, 1989; Hudson *et al.*, 1997).

Materials and methods

SITE DESCRIPTION

The Cwm catchment, which is described in detail by Roberts *et al.* (1986), is 300 ha in area and drains southwards off Llanbrynmair Moor into the Afon Dyfi. The catchment ranges in altitude between 285 and 523 m above sea-level and is covered by acid stagnopodzol, gley and blanket peat soils overlying Lower Palaeozoic grits and shales. Eighty-seven percent of the catchment has been afforested mainly with Sitka spruce planted in four phases between 1983 and 1986 following a variety of ground preparations (Hudson *et al.*, 1997). Prior to afforestation the vegetation comprised wet heathland communities on the blanket peats, acid grassland on the steeper podzolic soils and *Molinia* grassland on the valley bottom peats and gleys.

Three 10 m by 10 m plots were established beneath 12 year old Sitka spruce growing on un-ploughed peaty podzol soils (Table 1). The tree growth rates were very different in each of the plots reflecting the variability in the crop within this part of the catchment. Each tree plot was accompanied by a similar plot established in adjacent open ground supporting mixed acid grassland and wet heath vegetation communities. The plots were at an altitude of 450 m above sea level with an annual average rainfall of 1750 mm.

SOIL AND SOIL WATER SAMPLING

Within each plot, suction lysimeters were installed below the rooting zone at approximately 50 cm depth in the Bs horizon; three lysimeters were located beneath the Sitka spruce canopy and three in open ground. Samples were

collected monthly and bulked by plot for chemical analysis. Multiple samples were collected because of the highly heterogeneous nature of the soil solution in both space and time.

Two pits were dug in the peaty podzol soil outside the plots beneath open ground between the trees. The thickness of each horizon (Oh, Eag and Bs) was recorded and samples collected for total chemical, mineralogical and particle size analysis. Two further pits were dug and duplicate cores collected from each horizon for bulk density determination using standard methods (Avery and Bascombe, 1974).

GROUND VEGETATION SAMPLING

Four 0.5 m × 0.5 m quadrats positioned along two eight metre transects were erected both under the spruce canopy and in open terrain in each of the plots. The quadrats were positioned at least 2 m away from soil solution samplers to ensure that no disturbance to soil water sampling occurred. Vegetation was cut at ground level in July and subsequently divided into the following categories: shrub, moss, grass, sedge, herb, dead but standing biomass and needles. The species present in each quadrat were recorded and an indication was given of their abundance.

TREE SAMPLING

The diameter of each tree within the three forest plots was measured at 30 cm above the ground/root collar in accordance with guidelines set out in Hamilton (1975). Nine trees representative of the range of stem diameters were then selected from the plots for destructive sampling. Trees were divided into branches, needles and stem. Each component was weighted and subsampled for chemical analysis.

NUTRIENT FLUXES

Rainfall to the Cwm catchment was recorded fortnightly from three storage raingauges located at 287, 470 and 487 m. Every fortnight, samples of rainfall were collected from a continuously open 'bulk' collector located at 470 m and cloudwater was sampled using a passive 'harp' type collector (Reynolds *et al.*, 1996). Throughfall beneath the trees was sampled monthly using eight 110 mm diameter collectors randomly distributed in each forest plot to overcome the spatial variability in throughfall volumes and chemistry (Reynolds and Neal, 1991). Volumes of water from each collector were recorded separately and samples were bulked by plot for chemical analysis. Forest litterfall was collected monthly using twelve 287 cm² plastic litter collectors distributed randomly in each plot. Samples were bulked

Table 1. Characteristics of the forest study plots.

	Plot 1	Plot 2	Plot 3
Stems ha ⁻¹	2500	2900	2800
Mean diameter, cm	9.6	12.0	14.8
Basal area, m ² ha ⁻¹	19.4	34.5	50.3
Mean height, m	3.1	3.8	6.0

by plot, weighed and dried prior to grinding and chemical analysis.

CHEMICAL ANALYSIS

Total soil chemistry and mineralogy were determined on the fine earth fraction of soil samples dried at 105°C by the Macaulay Land Use Research Institute using X-ray fluorescence techniques and X-ray diffractometry respectively. Soil particle size was analysed using the hydrometer method of Dewis and Freitas (1970).

Plant and tree samples were dried at 80°C, ground and digested using a sulphuric acid-hydrogen peroxide mixture. The digests were analysed for calcium, magnesium and potassium using flame atomic absorption spectrophotometry (AAS).

Water samples were analysed for dissolved calcium, magnesium, potassium, ammonium-N, nitrate-N, sodium, sulphate and chloride by ion chromatography using a Dionex 2000i system following filtration through 0.45 µm membrane filters. Dissolved organic carbon (DOC) was determined by autoanalyser using a UV digestion procedure.

Data processing

BASE CATION POOLS

The total above-ground biomass and base cation content of the trees in each plot was calculated using regressions of biomass on basal area combined with the mean chemistry for each tree component. The amount of base cations held in tree roots was estimated from literature values of the ratio of total to below-ground base cation content (Helmisaari, 1995). There are few data comparing above- and below-ground base cation contents for Sitka spruce and those which exist are for mature trees (Carey and O'Brien, 1979). As the relative distribution of nutrients changes with tree age (Helmisaari, 1995), the data for mature spruce are likely to underestimate the amount of base cations held in the roots of young trees. Thus, the below-ground base cation components were estimated using ratios of below-ground to total base cation content for young Scots pine growing on nutrient poor podzols in Finland (Helmisaari, 1995). Whilst this represents an important assumption, comparison of the ratios of total to below-ground base cations were very similar for mature Sitka spruce in Ireland, growing on peaty gley soils (Carey and O'Brien, 1979) and mature Scots pine at the Finnish site.

The above-ground base cation content of ground flora in each plot was calculated as the product of the biomass of each of the seven vegetation categories and their respective chemical compositions. The total base cation pool in each soil horizon was calculated as the product of horizon depth, horizon bulk density and the total chemical concentration.

BASE CATION FLUXES

Atmospheric deposition to the catchment was modelled in three components. A Geographic Information System (GIS) was used to derive a digital elevation map of the catchment overlaid by the distribution of forest and moorland vegetation. The catchment was segmented into 100 m altitude bands and the area of moorland and forest vegetation within each band calculated from the GIS. Rainfall amount to each band was estimated using a hypsometric curve derived from the storage raingauge data. Base cation deposition in rainfall to each band was calculated as the product of annual rainfall amount and the observed rainfall volume-weighted annual mean solute chemistry adjusted for the effects of seeder-feeder enhancement over high ground according to the method of Dore *et al.* (1992). Occult (cloud water) inputs were estimated for each altitude band using the annual geometric mean cloudwater chemistry, assuming an annual cloud duration of 1500 hours similar to that at Plynlimon approximately 20 km to the south (Reynolds *et al.*, 1997). A simple momentum transfer model (RGAR, 1997) was applied to each altitude band using a different roughness length for forest and moorland vegetation. Rainfall and occult inputs to individual altitude bands were summed to give a total wet deposition for the catchment. Catchment inputs were calculated both for the current mix of forest and moorland vegetation and for one hundred percent cover by moorland vegetation. The inputs to the forest component alone were calculated by difference. The deposition to the forest plots was assumed to be the same as that to the forested parts of the catchment as a whole. Given the topography of the catchment and the location of the plots, this is unlikely to introduce a significant error in the base cation budgets.

Monthly throughfall fluxes were calculated for each forest plot as the product of the chemical concentrations and the mean volume of throughfall from the eight collectors. Monthly totals were then summed to an annual flux. Canopy leaching of base cations was estimated as the difference between the throughfall flux and atmospheric deposition to the forest canopy. Leaching losses below the Bs horizon in each plot under the trees were calculated from the mean soil solution chemistry weighted by the amount of throughfall and then multiplied by the estimated annual water flux. The latter was calculated as 95% of the throughfall water flux, allowing a five percent loss of water through transpiration (Kirby *et al.*, 1990). Leaching losses beneath moorland vegetation were calculated in a similar way except that the annual water flux below the Bs horizon was estimated as 85% of the annual rainfall (Kirby *et al.*, 1990).

Mineral weathering rates were derived for the podzol soil beneath both forest and moorland vegetation using the geochemical model PROFILE (Svedrup and Wafvinge, 1993). This steady-state model uses measurable soil properties such as soil texture, mineralogy, soil moisture

conditions together with measured atmospheric deposition, climate and plant uptake. Within the model, the soil profile is divided into several layers which correspond to the natural soil horizons. Each soil layer is treated as a perfectly mixed tank reactor. Mineral weathering within PROFILE relies on the hypothesis that the surface reactions of minerals follow universal rate laws even though the chemical environment of the mineral may vary. The weathering rate for the soil profile is the sum of the dissolution rates of the individual minerals. Dissolution rates increase in response to increasing concentrations of hydrogen ions, organic acids and higher partial pressures of CO₂. Dissolution rates are inhibited by the accumulation of weathering products such as inorganic aluminium and base cations. Temperature dependence of weathering reactions is expressed using an Arrhenius equation. Soil water saturation is used to estimate the fraction of the exposed mineral surface area in contact with water and thus able to participate in weathering reactions. The weathering of secondary minerals is represented by the dissolution of vermiculite. Maximum uptake rates for plant nutrients are defined as inputs to the model whilst nitrification is modelled using Michaelis-Menten kinetics with user-specified bands of high, medium, low or none. Inorganic aluminium concentrations are modelled assuming that they are controlled by equilibrium with Gibbsite. Soil water concentrations of DOC are input to the model; DOC participates in the formation of weak acids but does not enter into complexation reactions with aluminium.

The input data to PROFILE for each soil layer are shown in Tables 2 and 3. The same default values for pCO₂ and pK_{Gibbsite} (Sverdrup *et al.*, 1990) were used for forest and moorland soils, whilst other values were measured at the site. Concentrations of DOC in the Oh and Eag horizons were taken from data for moorland and forest on similar soils at Plynlimon (Hughes *et al.*, 1990); measured values were used for the Bs horizon. Exposed mineral surface area was estimated using a relationship between soil particle size and surface area published by Sverdrup *et al.* (1990). In the absence of measurements, annual average soil moisture and annual average temperature data were taken from a site at similar altitude in the Plynlimon catchments (Reynolds, 1997).

Base cation uptake by the trees was calculated so as to satisfy the annual requirements for biomass increment, litter production and canopy exchange; where annual biomass increment was estimated from the total tree base cation content divided by tree age (12 years) and canopy exchange as the difference between atmospheric input and throughfall flux. The ground vegetation in the open plots and amongst the trees was assumed to be in steady-state for the period of the study so that the estimated total annual production was assumed to be returned as litter (Schlesinger, 1991; Emmett *et al.*, 1997); i.e. the biomass increment was assumed to be zero. Annual production was estimated using a production to above-ground biomass ratio of 0.7. Ratios between 0.7

Table 2. Soil input parameters for the PROFILE model.

Parameter	Soil horizon		
	Oh	Eag	Bs
Horizon thickness, m	0.15	0.30	0.20
Bulk density, kg m ⁻³	99	783	700
pCO ₂ , times ambient	7.5	10	17.5
DOC, mg l ⁻¹ (forest)	10.6	9.2	3.2
DOC, mg l ⁻¹ (grassland)	10.0	5.0	3.5
pK Gibbsite	6.5	7.5	8.5
Exposed surface area, m ² m ⁻³	5.5e5	1.4e6	8.5e5
Mineral (% of total)	Oh	Eag	Bs
K-feldspar	0.1	0.4	0.6
Muscovite	52.2	43.2	43.8
Chlorite	0.0	6.6	10.5
Albite	8.0	7.5	7.1
Quartz	39.7	42.3	38.0

and 4.0 have been reported with lower values where, as at this site which was fenced to exclude sheep, there is light or no grazing pressure (Heal and Perkins, 1978). In the absence of reliable throughfall data for the ground vegetation, canopy exchange was not determined.

The mass balances of base cations for the moorland and forest were assessed in two ways. Firstly, annual input-output budgets were calculated with respect to the pool of 'available base cations' as: wet deposition + canopy exchange + soil mineral weathering + net mineralisation of organic matter = output in soil leachate + uptake by the vegetation. Net mineralisation of soil organic matter was calculated by difference knowing the other fluxes (Emmett *et al.*, 1997) and is a balancing term in the equation.

Table 3. Climatic and atmospheric input data for the PROFILE model.

Parameter	Forest	Grassland
Throughfall/precipitation, m year ⁻¹	1.151	1.793
Soil percolation, m year ⁻¹	1.093	1.524
Soil moisture, m ³ m ⁻³	0.43	0.43
Soil temperature, deg C	8.4	8.4
Sulphate, keq ha ⁻¹ yr ⁻¹	1.86	1.04
Chloride, keq ha ⁻¹ yr ⁻¹	4.08	2.43
Nitrate, keq ha ⁻¹ yr ⁻¹	0.50	0.44
Ammonium, keq ha ⁻¹ yr ⁻¹	0.56	1.05
Calcium, keq ha ⁻¹ yr ⁻¹	0.65	0.29
Magnesium, keq ha ⁻¹ yr ⁻¹	1.19	0.57
Potassium, keq ha ⁻¹ yr ⁻¹	0.59	0.07
Sodium, keq ha ⁻¹ yr ⁻¹	3.27	2.09

Table 4. Summary of base cation pools within the forest and open moorland plots; mean values from three plots \pm 1 se, except for soil total base cation contents which are means from two soil pits.

	Biomass t ha ⁻¹	Potassium kg ha ⁻¹	Calcium kg ha ⁻¹	Magnesium kg ha ⁻¹
Soil – total	—	90755	1140	15033
Forest plots				
Trees – above ground	123.6 \pm 28.6	329 \pm 74.8	191 \pm 43.3	32 \pm 32.2
Trees – below ground	41.2 \pm 9.5	135 \pm 30.6	39 \pm 8.9	17 \pm 3.8
Live ground flora – above ground	1.3 \pm 0.56	7 \pm 3.3	2.2 \pm 1.2	0.9 \pm 0.4
Standing dead	0.3 \pm 0.14	0.4 \pm 0.2	0.7 \pm 0.5	0.1 \pm 0.1
Needles	0.5 \pm 0.25	0.8 \pm 0.4	1.5 \pm 0.8	0.2 \pm 0.1
Open moorland plots				
Live ground flora – above ground	6.8 \pm 2.05	29 \pm 3.6	13 \pm 4.4	5 \pm 1.4
Standing dead	1.9 \pm 0.48	8 \pm 1.7	1.1 \pm 0.5	0.8 \pm 0.1
Needles	0.1 \pm 0.05	0.1 \pm 0.1	0.2 \pm 0.1	0.02 \pm 0.02

Functionally, it represents release of base cations from the decomposition of returning litter (foliar and roots), any net release from soil ion exchange pools plus any net release from soil organic matter due to decomposition which is not included in the weathering rate calculations. Secondly, the net change to the soil store was estimated using the mass balance method proposed by Johnson (1992), whereby the net change in the soil store of a base cation = (atmospheric inputs + weathering) – (leaching losses + biomass increment).

Results and discussion

BIOMASS AND BASE CATION POOLS

The largest store of base cations is in the soil, although for calcium in the forest plots, about 17% of the total pool (biomass + soil to the base of the Bs horizon) resides in the trees and ground vegetation reflecting the low calcium status of the soil and its parent material (Table 4). In contrast, the largest soil reserve is for potassium (91 t ha⁻¹); less than 1% of the total site capital of potassium and less 0.5% of the total magnesium is held in the trees.

In the open moorland, shrubs accounted for the largest proportion of the alive biomass (Fig. 1) particularly in two of the plots; the third plot, in contrast, was dominated by fine grasses and the herb *Galium saxatile*. The grasses and herbs were relatively enriched in potassium while the herbs were relatively enriched in magnesium compared to the other plant groups. The shrubs held relatively more calcium compared to biomass whereas the opposite was true of the grasses (Fig. 1).

The combined data for the three pairs of plots showed a highly significant difference (*t*-test; *p* < 0.01) between total alive biomass in the open moorland compared to that underneath the tree canopy (Table 5), presumably reflecting

differences in light, water and nutrient availability. Only very small quantities of shrub occurred underneath the Sitka spruce canopy; none was recorded in one of the plots. Although the shrub *Vaccinium myrtillus* was recorded beneath the tree canopy in two plots, only small quantities were present and its growth appeared to be limited by the amount of light coming through the trees. *Empetrum nigrum* appeared to be restricted by light as it only occurred in the open. In all three pairs of plots, the amount of grass was significantly greater (*t*-test; *p* < 0.001) in the open moorland than underneath the forest canopy. Herbs and sedge were not found growing underneath the spruce canopy but were present in the open moorland. The quantity of dead biomass in each plot was very closely related to the quantity of alive biomass (Fig. 2).

A greater diversity of moss species was recorded in the open moorland and, in all three pairs of plots, mosses were more abundant in the open moorland than underneath the forest canopy. However, mosses accounted for a signifi-

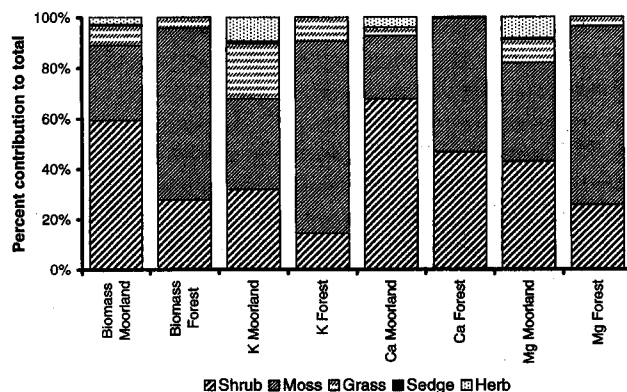


Fig. 1. Distribution of above-ground biomass and nutrients amongst living ground flora in grassland and forest plots in the Cwm catchment, Llanbrynmair.

Table 5. Biomass and base cation content of above-ground plant species in open moorland and beneath the Sitka spruce canopy at Llanbrynmair; mean values from three plots \pm 1 se. Sedges and herbs were absent from below the forest canopy.

Open moorland	Biomass t ha ⁻¹	K kg ha ⁻¹	Ca kg ha ⁻¹	Mg kg ha ⁻¹
Shrub	4.0 \pm 1.7	9.4 \pm 3.2	8.8 \pm 3.5	2.0 \pm 1.0
Moss	2.0 \pm 0.9	10.5 \pm 4.7	3.2 \pm 1.9	1.8 \pm 1.0
Grass	0.5 \pm 0.2	6.4 \pm 4.0	0.4 \pm 0.4	0.4 \pm 0.2
Sedge	<0.1	0.3 \pm 0.1	<0.1	<0.1
Herb	0.2 \pm 0.2	2.8 \pm 2.8	0.5 \pm 0.5	0.4 \pm 0.4
Total	6.7 \pm 2.1	29.4 \pm 3.6	12.9 \pm 4.4	4.6 \pm 1.4
Tree canopy	Biomass t ha ⁻¹	K kg ha ⁻¹	Ca kg ha ⁻¹	Mg kg ha ⁻¹
Shrub	0.4 \pm 0.2	1.0 \pm 0.6	1.0 \pm 0.6	0.2 \pm 0.1
Moss	0.9 \pm 0.4	5.3 \pm 2.5	1.1 \pm 0.6	0.7 \pm 0.3
Grass	0.1 \pm 0.1	0.7 \pm 0.6	<0.1	<0.1
Total	1.4 \pm 0.6	7.0 \pm 3.3	2.1 \pm 1.2	0.9 \pm 0.4

cantly greater proportion of the overall alive biomass and base cations underneath the spruce canopy than they did in the open moorland (t -test; $p < 0.001$; Fig. 1). Shrub, grass and herb growth appeared to be restricted underneath the spruce canopy whereas mosses were capable of growing at lower light levels. Further, mosses may have been less able to compete in the open moorland where conditions were more favourable for higher plants.

Growth of the trees increased greatly above-ground biomass compared to the pre-existing vegetation with the above-ground tree biomass holding between 7 and 15 times more base cations compared to the living aerial vegetation in the open plots (Table 4). Within the trees, approximately 30% of the above-ground biomass was held in the needles which also contained approximately 50% of the base cations

(Table 6). The stem wood which accounted for 32% of the total above-ground biomass held the lowest proportion (c.20%) of the total base cations. Although the absolute quantities of biomass and base cations were larger in this study, their distribution amongst the individual above-ground components was very similar to those for a Sitka spruce stand of the same age in Scotland (Miller *et al.*, 1993).

ATMOSPHERIC DEPOSITION

The presence of an approximately 4 m high forest canopy has increased atmospheric inputs of all base cations compared to those to the moorland (Table 7) reflecting the greater canopy roughness which will have increased substantially cloudwater deposition (Fowler *et al.*, 1989). The capture of cloud droplets is an important mechanism whereby forests enhance deposition of base cation cloud-water concentrations of most solutes are generally a factor of 2 to 5 times greater than those in bulk precipitation (Reynolds *et al.*, 1996). This effect is reflected in the increased base cation deposition to the forest which was about 1.5 times larger than the inputs to the moorland.

WEATHERING

The weathering flux of potassium (6.3 kg ha⁻¹ yr⁻¹) was supplied primarily from the breakdown of dioctahedral mica (Chapman, 1986) and exceeded inputs from atmospheric deposition in both the moorland and forest systems. The total soil reserve of potassium is very large (Table 4) and is sufficient to supply the system for over 10000 years at the current rate of weathering. In contrast, the modelled

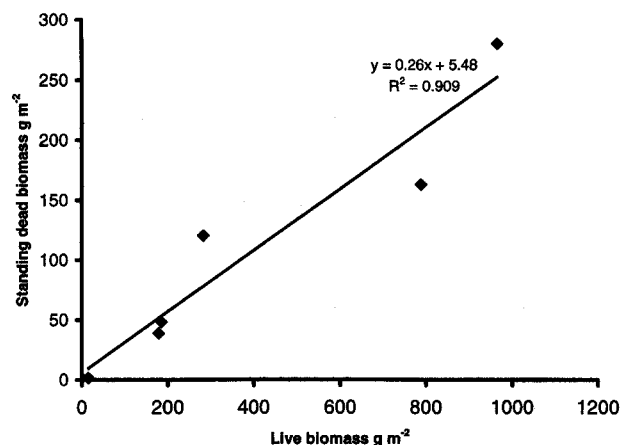


Fig. 2. Relationship between standing dead and live above-ground biomass in grassland and forest plots in the Cwm catchment, Llanbrynmair.

Table 6. Distribution of base cations between above-ground tree components; mean values from three plots ± 1 se.

	Stem	Branches	Needles	Above-ground total	Stem as % of above-ground total	Branches as % of above-ground total	Needles as % of above-ground total
Biomass, t ha ⁻¹	39.8 \pm 9.3	46.3 \pm 11.0	37.5 \pm 8.3	123.6 \pm 28.6	32 \pm 0.1	37 \pm 0.3	31 \pm 0.4
K, kg ha ⁻¹	66.7 \pm 15.5	85.4 \pm 20.3	177.1 \pm 39.0	329.4 \pm 74.8	20 \pm 0.1	26 \pm 0.3	54 \pm 0.4
Ca, kg ha ⁻¹	32.8 \pm 7.6	55.5 \pm 13.2	102.5 \pm 22.5	190.8 \pm 43.3	17 \pm 0.1	29 \pm 0.4	54 \pm 0.5
Mg, kg ha ⁻¹	6.4 \pm 1.5	10.8 \pm 2.6	15.0 \pm 3.3	32.2 \pm 7.4	20 \pm 0.1	33 \pm 0.4	47 \pm 0.5

weathering rate for calcium was extremely small (0.3 kg ha⁻¹ yr⁻¹), reflecting the generally low calcium status of the soil (Table 4) and its parent material (Chapman, 1986). In comparison to weathering, atmospheric deposition contributed 22 and 36 times more calcium to the moorland and forest respectively. At the present rate of weathering, soil calcium reserves would be depleted in about 4500 years. Weathering of chlorite is the main source of magnesium from the soil (Chapman, 1986) and at current weathering rates (4.7 kg ha⁻¹ yr⁻¹), soil magnesium reserves would last about 3200 years. Atmospheric deposition of magnesium exceeded weathering inputs in both the moorland and the forest by about 1.5 and 2.5 times respectively.

The weathering rates predicted by PROFILE are very comparable with values for similar soils formed from Lower Palaeozoic greywackes in Scotland and Wales (Langan *et al.*, 1996). The latter quote an average total weathering rate to

50 cm of 0.67 keq ha⁻¹ yr⁻¹ for the sum of (Na + Ca + Mg + K), which compares with 0.68 keq ha⁻¹ yr⁻¹ for both the forest and moorland in the Cwm catchment. These values are about 1.7 times larger than weathering rates calculated by Langan *et al.* (1996) using element depletion techniques (0.39 keq ha⁻¹ yr⁻¹) but much smaller than values calculated from catchment mass balance studies (average 2.49 keq ha⁻¹ yr⁻¹; Langan *et al.*, 1996). The latter include contributions from deeper weathering sources within the drift and bedrock of the catchment which, in some cases, may be influenced by the presence of rapidly weathering carbonate minerals.

Predicted weathering rates were virtually identical in the forest and moorland which suggests that the differences in deposition inputs and DOC concentrations had only a minor effect on model results. This is consistent with a sensitivity analysis of the PROFILE model published by

Table 7. Base cation fluxes in open moorland and forest plots; fluxes (except deposition and weathering) are means of three plots ± 1 se.

Grassland	K kg ha ⁻¹ yr ⁻¹	Ca kg ha ⁻¹ yr ⁻¹	Mg kg ha ⁻¹ yr ⁻¹
Wet + dry deposition	2.8	5.8	7.0
Weathering	6.3	0.3	4.7
Leaching	3.0 \pm 0.9	8.5 \pm 3.3	11.7 \pm 2.1
Ground flora production	20.5 \pm 2.6	9.1 \pm 3.1	3.2 \pm 1.0
Net mineralisation	14.4 \pm 2.3	11.5 \pm 2.5	3.2 \pm 1.2
Net change to soil store	6.1 \pm 0.7	-2.4 \pm 2.7	0.0 \pm 0.6
Forest	K kg ha ⁻¹ yr ⁻¹	Ca kg ha ⁻¹ yr ⁻¹	Mg kg ha ⁻¹ yr ⁻¹
Wet + dry deposition	4.1	9.4	11.2
Throughfall	23.1 \pm 3.7	13.0 \pm 1.7	14.5 \pm 2.6
Litterfall	4.4 \pm 3.8	9.8 \pm 5.0	0.8 \pm 0.4
Weathering	6.5	0.3	4.7
Leaching	1.5 \pm 0.5	8.1 \pm 2.9	8.8 \pm 1.0
Tree accumulation	38.7 \pm 8.8	19.2 \pm 4.4	4.1 \pm 0.9
Ground flora production	4.9 \pm 2.3	1.5 \pm 0.8	0.7 \pm 0.3
Canopy exchange	19.0 \pm 3.7	3.6 \pm 1.7	3.3 \pm 2.6
Net mineralisation	38.9 \pm 2.6	28.9 \pm 3.8	-1.6 \pm 1.0
Net change to soil store	-29.6 \pm 6.9	-17.6 \pm 3.2	3.0 \pm 1.5

Hodson *et al.* (1996), although these authors have shown that PROFILE is sensitive to variations in soil temperature, moisture content and exposed surface area. In the absence of comparative measurements, these variables were assumed to be the same under both vegetation types. This assumption is reasonable on three grounds. Firstly, unpublished data from Aber in north Wales, has shown that the mean annual soil temperature at 30 cm measured over two years was only 0.2°C cooler beneath closed canopy forest compared to that under open moorland at the same altitude (300 m above sea level). This makes an insignificant difference to the predicted weathering rates. Secondly, a study at Plynlimon showed no significant differences in annual average soil moisture conditions for undrained soils beneath closed canopy conifer forest and semi-natural acid grassland under 'normal' climatic conditions (Hudson, 1988). Soil moisture deficits beneath the forest were larger and more prolonged in years with a summer drought. Thirdly, the twelve year growth of forest is unlikely to have altered the soil particle size distribution used to calculate the exposed surface area term.

LEACHING LOSSES

Leaching losses of potassium approximately balanced atmospheric inputs in the moorland, but accounted for only 36% of inputs under the forest (Table 7). Leaching losses of calcium and magnesium exceeded atmospheric inputs to the moorland, although the additional weathering input of magnesium (4.7 kg ha⁻¹ yr⁻¹) balanced leaching losses (11.7 kg ha⁻¹ yr⁻¹). In the forest, leaching losses were less than atmospheric inputs for all three base cations.

MOORLAND BASE CATION BUDGET

The difference between atmospheric inputs and leaching losses reflects the balance between the internal sources and sinks of base cations within the soil-plant system. For the moorland system, the vegetation is assumed to be in 'steady-state', i.e. there is no net accumulation of base cations into the biomass (Schlesinger, 1991) and all vegetative production is returned as litter.

Budgets differ considerably amongst the base cations, reflecting both the different plant requirements and the contrasting weathering rates (Table 7). The weathering flux of potassium (6.3 kg ha⁻¹ yr⁻¹) is about twice the atmospheric input demonstrating that weathering is an important component of the potassium cycle in these systems. Net mineralisation of potassium provides about two thirds of the 'internal' soil-derived flux which, together with weathering, roughly balances annual vegetation production. Leaching losses (3 kg ha⁻¹ yr⁻¹) are relatively small and balanced by atmospheric inputs as potassium is tightly cycled within the soil-plant system and low soil water concentrations are commonly observed (Hornung *et al.*, 1986).

The modelled weathering rate for calcium is extremely small (0.3 kg ha⁻¹ yr⁻¹), therefore plant demand has to be satisfied by other inputs. To close the budget, the net mineralisation term (11.5 kg ha⁻¹ yr⁻¹) has to become larger than the annual return of above-ground litter (assumed to equal above-ground production) resulting in a net depletion of the soil store by 2.5 kgCa ha⁻¹ yr⁻¹. However, this figure is associated with a large standard error (Table 7) reflecting the influence of an unusually large calcium leaching loss from one of the plots. The mean soil water calcium concentration in this plot was nearly 1 mg l⁻¹, 2–5 times greater than in the other plots. Soil water magnesium concentrations in the same plot were also about 40% greater than in the other plots. Together, this may indicate that the soil in this plot has been derived from a localised pocket of base-rich drift or that the suction lysimeters have intercepted base-rich, shallow ground water. In either case, the effective 'weathering' supply of calcium from the soil will be greater than that predicted by PROFILE thereby reducing the need to supply calcium from other sources. Shallow, base-rich ground water has been observed in the Plynlimon catchments which are about 20 km to the south (Neal *et al.*, 1997; Chapman *et al.*, 1993), and a low flow stream survey of the Cwm catchment has also identified a source of calcium-bearing water close to the centre of the catchment (CEH unpublished data).

The budget for magnesium (Table 7) shows that leaching losses (11.7 kg ha⁻¹ yr⁻¹) are balanced by atmospheric deposition and weathering implying a very tight cycle of magnesium between soil and vegetation. The vegetation production and mineralisation fluxes (c. 3 kg ha⁻¹ yr⁻¹) are the smallest of the three base cations and there is effectively no net change in the soil store. This result is also influenced by the large magnesium leaching flux in one of the plots. The budgets for the other plots show small but similar net increases in soil magnesium storage of 2.4 and 1.8 kg ha⁻¹ yr⁻¹ respectively.

FOREST BASE CATION BUDGET

Afforestation of the site has resulted in significant changes to the balance of base cation supply and demand within the system (Table 7) and there are distinct differences in the way that individual base cations are cycled within the young forest. As reported by other studies on coniferous trees (Stevens, 1987; Ragsdale *et al.*, 1992), there was considerable canopy leaching of potassium resulting in a more than five fold increase in the flux to the forest floor. Calcium and magnesium were also leached from the canopy resulting in a 30% and 40% increase in flux respectively compared to atmospheric deposition; these results are consistent with data from coniferous stands in the United States (Ragsdale *et al.*, 1992) and the UK (Reynolds *et al.*, 1989).

The importance of canopy leaching compared to canopy litterfall for returning nutrients to the forest floor varied

considerably amongst the base cations reflecting their different physiological roles within the tree. The potassium flux from foliar leaching ($19 \text{ kg ha}^{-1} \text{ yr}^{-1}$) was over four times that in canopy litterfall whereas for calcium, canopy litterfall ($9.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$) was about three times the foliar leaching flux (Table 7). Potassium remains in ionic form within plant tissue where it plays a major osmoregulatory role whereas calcium is incorporated as a permanent structural component; hence, they are returned by different pathways from the tree canopy (Likens *et al.*, 1994, 1998). Magnesium is also readily leached from the spruce canopy; canopy leaching ($3.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$) dominated the return of magnesium to the forest floor, accounting for 80% of the total canopy litterfall plus leaching flux.

Of the three base cations, magnesium had the lowest uptake rate into vegetation ($8.2 \text{ kg ha}^{-1} \text{ yr}^{-1}$) of which 50% contributed to biomass accumulation in the trees. The remainder was recycled as litterfall and canopy leaching. In comparison, the uptake of potassium was about $62 \text{ kg ha}^{-1} \text{ yr}^{-1}$ and about two thirds of this was retained as accumulated tree biomass. For both potassium and calcium, the budgets show that the soil store is being depleted with net mineralisation contributing a major proportion of the base cations in circulation. Given the limited soil calcium reserve, this could have important implications for sustainability; the predicted net rate of change to the soil store ($-17.5 \text{ kg Ca ha}^{-1} \text{ yr}^{-1}$) would deplete the total soil store in 65 years. However, the growth rate of the trees will slow as they mature reducing the annual demand for calcium to below that currently observed (Miller *et al.*, 1993). In contrast, atmospheric deposition provides the main supply of magnesium to the forest, and there is net immobilisation of magnesium in the soil reflecting the influence and importance of sea-salt deposition in this part of Wales and the low biomass increment in the trees.

Assessment of the budget approach

The nutrient budget approach inevitably contains large uncertainties because of the number of inherent assumptions and the variability in many of the measurements. Within the constraints of time and resources, the problems of measurement variability have been tackled using replicated plots and bulked, multiple samples within the plots. Ideally, a longer study period is required to account for annual variations in climate and its effect on base cation cycling.

The effects of the assumptions on the base cation budget calculations are more difficult to assess. Those included in the modelling of atmospheric inputs and weathering rates are unlikely to have a major influence on the overall results. Variations in atmospheric deposition across the catchment are likely to be small compared with the effects on deposition rates of the difference in aerodynamic roughness between forest and moorland canopies. Thus, using catch-

ment values for atmospheric inputs is unlikely to have introduced a significant error. However, this study has ignored the input of base cations from dry deposition as very few data are available, there being no systematic measurement of particulate base cations in the UK (CLAG, 1994). Approximate estimates of the dry deposition of non-seasalt aerosol calcium for Wales range between 0.2 and $0.6 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (CLAG, 1994). These values are relatively small compared to most components of the calcium budget, but are of a similar order of magnitude to the calcium weathering rate.

Weathering rates are notoriously difficult to determine. Whilst the PROFILE model itself includes a large number of assumptions, a catchment mass balance approach would have given misleading results at this site because there is evidence from stream chemistry studies of base-rich water at depth below the soil profile. Element depletion methods contain major assumptions concerning the age of the soil profile and they assume that the long-term weathering rate over the period of soil development is representative of current weathering rates. Recent work suggests that this is not the case (Taylor and Blum, 1995). Better predictions would have been obtained from PROFILE if field measurements of soil moisture and soil temperature had been used. However, even a $\pm 20\%$ change in weathering rates has only a small effect on net mineralisation rates and the net change in the soil store, thus having little effect on the overall conclusions.

The assumptions concerning allocation of base cations to above and below ground tree biomass are more fundamental but the considerable effort required to sample below ground biomass reliably was beyond the resources of the project. The scarcity of such data for Sitka spruce suggests that this may often be the case. Overall, the results from this study compare well with data from similar work in the UK and elsewhere. This gives a measure of confidence in the results suggesting that the uncertainties in the approach have not had a major effect on the outcome of the study.

Conclusions

Afforestation of the Cwm catchment has resulted in some major changes in the allocation and cycling of base cations compared to the pre-existing moorland. In the remaining moorland, the magnesium cycle is approximately at steady-state with no net change to the soil store whilst the soil is accumulating potassium. The calcium budget contains significant uncertainties due to between plot variability in calcium leaching losses. There is an indication that for one plot, the weathering supply of calcium may be larger than that predicted from soil mineralogy using the PROFILE model. Using figures averaged across the three plots, the budget suggests that soil calcium reserves are being depleted slowly at a rate of $2.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$. However, a re-calculated budget omitting the exceptional plot, shows that the calcium

cycle is approximately balanced with a small ($0.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$) net accumulation of calcium in the soil. With the exception of magnesium, the net mineralisation term is an important component of the base cation budget as weathering rates and atmospheric inputs are relatively small. For magnesium, weathering and atmospheric deposition ($11.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$) approximately balance leaching losses, and net mineralisation rates are low ($3.2 \text{ kg ha}^{-1} \text{ yr}^{-1}$) reflecting the small uptake of magnesium by the ground flora.

Afforestation has greatly increased the above-ground living biomass compared to the pre-existing vegetation. The base cation pool contained in above ground tree biomass is 7 to 15 times larger than in the living aerial biomass of the acid moorland. In consequence, but with the exception of magnesium, the base cation stores within the soil are being depleted as the increase in atmospheric deposition due to the forest canopy provides only a small offset to the much larger accumulation of base cations within the trees. For magnesium, the small net uptake by the trees ($4 \text{ kg ha}^{-1} \text{ yr}^{-1}$) is more than balanced by weathering ($4.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and only small amounts are cycled through tree litter ($0.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and ground flora production ($0.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$).

Within the forest, the patterns of cycling differ considerably amongst individual base cations. Canopy leaching ($19 \text{ kg ha}^{-1} \text{ yr}^{-1}$) is a major pathway for the return of potassium to the ground and contributes about five times more potassium to throughfall compared with atmospheric deposition ($4 \text{ kg ha}^{-1} \text{ yr}^{-1}$). In contrast, litterfall is more important for calcium reflecting the different physiological behaviour of the two nutrients. Net mineralisation is a major term in the budget for potassium and calcium but not for magnesium. The current net rate of change in the soil store of calcium is sustainable for only 65 years. However, as the trees mature, their demand for calcium will be reduced. Furthermore, as tree roots develop, they should be able to 'tap' deeper sources of calcium in the soil profile as well as in the drift and regolith material.

Acknowledgements

The authors would like to thank Dave Norris and Bronwen Pugh for assistance with the regular field sampling programme. Dave Norris also undertook the GIS analysis of the catchment and Ron Smith of ITE Edinburgh modelled catchment deposition fluxes.

REFERENCES

Avery, B.W. and Bascomb, C.L. (eds.), 1974. *Soil Survey Laboratory Methods*. Soil Survey Technical Monograph No. 6, Soil Survey of England and Wales, Harpenden, UK.
 Carey, M.L. and O'Brien, D., 1979. Biomass, nutrient content and distribution in a stand of Sitka spruce. *Irish Forestry* 36, 25–35.
 Chapman, P., 1986. *Geochemical and Mineralogical Studies of the*

Weathering of Silurian Argillaceous Rocks. PhD Thesis, University College of North Wales, Bangor.
 Chapman, P.J., Reynolds, B. and Wheeler, H.S., 1993. Hydrochemical changes along stormflow pathways in a small moorland headwater catchment in mid-Wales. *J. Hydrol.* 151, 241–265.
 CLAG, 1994. *Critical Loads of Acidity in the United Kingdom. Critical Loads Advisory Group Summary Report*, Institute of Terrestrial Ecology, Edinburgh, 61 pp.
 Dewis, J. and Freitas, F., 1970. *Physical and Chemical Methods of Soil and Water Analysis*. Soils Bulletin No. 10, FAO, Rome.
 Dore, A.J., Choularton, T.W. and Fowler, D., 1992. A new map of wet deposition over the UK. *Atmos. Environ.* 26A, 1375–1381.
 Emmett, B.A., Cosby, B.J., Ferrier, R.C., Jenkins, A., Tietema, A. and Wright, R.F., 1997. Modelling the ecosystem effects of nitrogen deposition: Simulation of nitrogen saturation in a Sitka spruce forest, Aber, Wales, UK. *Biogeochemistry* 38, 129–148.
 Forestry Commission, 1985. *Facts and Figures*. Forestry Commission, Edinburgh, UK.
 Fowler, D., Cape, J.N. and Unsworth, M.H., 1989. Deposition of atmospheric pollutants to forests. *Phil. Trans. Roy. Soc. London* B324, 247–265.
 Hamilton, G.J., 1975. *Forest Mensuration Handbook*, Booklet 39, Forestry Commission, Edinburgh, UK.
 Harriman, R., Likens, G.E., Hultberg, H. and Neal, C., 1994. Influence of management practices in catchments on freshwater acidification: Afforestation in the United Kingdom and North America. *Acidification of freshwater ecosystems: Implications for the future*. (eds. C.E.W. Steinburg and R.F. Wright), 83–101. Wiley, Chichester, UK.
 Heal, O.W. and Perkins, D.F. (eds.), 1978. *Production Ecology of British Moors and Montane Grasslands*. Ecological Studies 27, Springer-Verlag, Berlin.
 Helmissaari, H.-S., 1995. Nutrient cycling in *Pinus sylvestris* stands in eastern Finland. *Plant Soil* 168–169, 327–336.
 Hodson, M.E., Langan, S.J. and Wilson, M.J., 1996. A sensitivity analysis of the PROFILE model in relation to the calculation of soil weathering rates. *Appl. Geochem.* 11, 835–844.
 Hornung, M. and Newson, M.D., 1986. Upland afforestation influences on stream hydrology and chemistry. *Soil Use Manage.* 8, 61–65.
 Hornung, M., Stevens, P.A. and Reynolds, B., 1986. The impact of pasture improvement on the soil solution chemistry of some stagnopodzols in mid-Wales. *Soil Use Manage.* 2, 18–26.
 Hudson, J.A., 1988. The contribution of soil moisture storage to the water balances of upland forested and grassland catchments. *Hydrological Sci. J.* 33, 289–309.
 Hudson, J.A., Crane, S.B. and Robinson, M., 1997. The impact of the growth of new plantation forestry on evaporation and streamflow in the Llanbrynmair catchments. *Hydrol Earth System Sci.* 1, 463–475.
 Hughes, S., Reynolds, B. and Roberts, J.D., 1990. The influence of land management on concentrations of dissolved organic carbon and its effects on the mobilization of aluminium and iron in podzol soils of Mid-Wales. *Soil Use Manage.* 6, 137–144.
 Johnson, D.W., 1992. Base cation distribution and cycling. *Atmospheric Deposition and Forest Nutrient Cycling*. Ecological Studies 91, (eds D.W. Johnson and S.E. Lindberg). 275–333. Springer-Verlag, Berlin.
 Kirby, C., Newson, M.D. and Gilman, K., 1990. *Phylinion research: The first two decades*. Report No. 109, Institute of Hydrology, Wallingford, UK.
 Langan, S.J., Reynolds, B. and Bain, D.C., 1996. The calculation of base cation release from mineral weathering in soils derived from Palaeozoic greywackes and shales in upland UK. *Geoderma* 69, 275–285.
 Likens, G.E., Driscoll, C.T., Buso, D.C., Siccama, T.G., Johnson, C.E., Lovett, G.M., Ryan, D.F., Fahey, T. and Reiners, W.A., 1994. The biogeochemistry of potassium at Hubbard Brook. *Biogeochemistry* 25, 61–125.
 Likens, G.E., Driscoll, C.T., Buso, D.C., Siccama, T.G., Johnson, C.E., Lovett, G.M., Fahey, T., Reiners, W.A., Ryan, D.F., Martin, C.W. and Bailey, S.W., 1998. The biogeochemistry of calcium at Hubbard Brook. *Biogeochemistry* 41, 69–173.
 Miller, H.G., 1995. The influence of stand development on

- nutrient demand, growth and allocation. *Plant Soil* 168–169, 225–232.
- Miller, J.D., Cooper, J.M. and Miller, H.G., 1993. A comparison of above-ground component weights and element amounts in four forest species at Kirkton Glen. *J. Hydrol.* 145, 419–438.
- Neal, C., Smith, C.J., Walls, J., Billingham, P., Hill, S. and Neal, M., 1990. Hydrogeochemical variations in Hafren forest stream waters, mid-Wales. *J. Hydrol.* 116, 185–200.
- Neal, C., Robson, A.J., Shand, P., Edmunds, W.M., Dixon, A.J., Buckley, D.K., Hill, S., Harrow, M., Neal, M., Wilkinson, J. and Reynolds, B., 1997. The occurrence of groundwater in the Lower Palaeozoic rocks of upland Central Wales. *Hydrol. Earth System Sci.* 1, 3–18.
- Ragsdale, H.L., Lindberg, S.E., Lovett, G.M. and Schafer, D.A., 1992. Atmospheric deposition and throughfall fluxes of base cations. *Atmospheric Deposition and Forest Nutrient Cycling*. Ecological Studies 91, (eds D.W. Johnson and S.E. Lindberg). 235–253, Springer-Verlag, Berlin.
- Reynolds, B., 1997. Predicting soil acidification trends at Plynlimon using the SAFE model. *Hydrol. Earth System Sci.* 1, 717–728.
- Reynolds, B. and Neal, C., 1991. Trough versus funnel collectors for measuring throughfall volumes. *J. Environ. Qual.* 20, 518–521.
- Reynolds, B., Cape, J.N. and Paterson, I.S., 1989. A comparison of element fluxes in throughfall beneath larch and Sitka spruce at two contrasting sites in the United Kingdom. *Forestry* 62, 29–39.
- Reynolds, B., Fowler, D. and Thomas, S., 1996. Chemistry of cloud water at an upland site in mid-Wales. *Sci. Total Environ.* 188, 115–125.
- Reynolds, B., Fowler, D., Smith, R.I. and Hall, J.R., 1997. Atmospheric inputs and catchment solute fluxes for major ions in five Welsh upland catchments. *J. Hydrol.* 194, 305–329.
- RGAR, 1997. *Acid Deposition in the United Kingdom 1992–1994*. Fourth Report of the Review Group on Acid Rain, AEA Technology, Harwell, UK.
- Roberts, G., Hudson, J.A. and Blackie, J.R., 1986. *The Llanbrynmair Moor Afforestation Study*. Introductory Report, Institute of Hydrology, Wallingford, UK.
- Roberts, G., Reynolds, B. and Talling, J. (eds.), 1989. *Upland Management and Water Resources*. Report to the Department of the Environment and Welsh Office, Institute of Hydrology, Wallingford, UK.
- Robinson, M., Moore, R.E., Nisbet, T.R. and Blackie, J.R. 1998. *From Moorland to Forest: The Coalburn Catchment Experiment*. Report No. 133, Institute of Hydrology, Wallingford, UK.
- Schlesinger, W.H., 1991. *Biogeochemistry*. Academic Press, New York.
- Stevens, P.A., 1987. Throughfall chemistry beneath Sitka spruce of four ages in Beddgelert Forest, North Wales, UK. *Plant Soil* 101, 291–294.
- Stevens, P.A., Norris, D.A., Sparks, T.H. and Hodgson, A.L., 1994. The impacts of atmospheric inputs on throughfall, soil and stream water interactions for different aged forest and moorland catchments in Wales. *Water Air Soil Pollut.* 73, 297–317.
- Stoner, J.H., Gee, A.S. and Wade, K.R., 1984. The effects of acidification on the ecology of streams in the Upper Twyi catchment in West Wales. *Environ. Pollut. A* 35, 125–157.
- Sverdrup, H. and Warfvinge, P., 1993. Calculating field weathering rates using a mechanistic geochemical model PROFILE. *Appl. Geochem.* 8, 272–282.
- Sverdrup, H., de Vries, W. and Henriksen, A., 1990. *Mapping Critical Loads*. Environmental Report 1990: 14, Nordic Council of Ministers, Copenhagen.
- Taylor, A. and Blum, J.D., 1995. Relation between soil age and silicate weathering rates determined from the chemical evolution of a glacial chronosequence. *Geology* 23, 979–982.