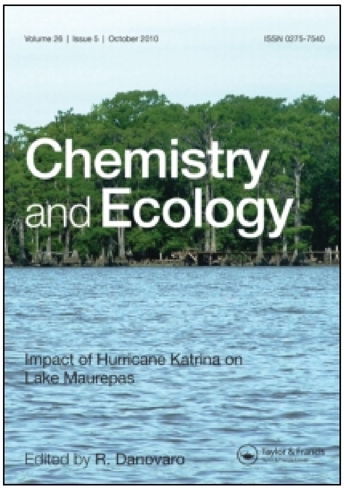

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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To cite this Article Soulsby, C. and Reynolds, B.(1994) 'The Chemistry of Throughfall, Stemflow and Soil Water Beneath Oak Woodland and Moorland Vegetation in Upland Wales', Chemistry and Ecology, 9: 2, 115 — 134

To link to this Article: DOI: 10.1080/02757549408038569

URL: http://dx.doi.org/10.1080/02757549408038569

Chemistry and Ecology, 1994, Vol. 9, pp. 115–134
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Printed in Malaysia

THE CHEMISTRY OF THROUGHFALL, STEMFLOW AND SOIL WATER BENEATH OAK WOODLAND AND MOORLAND VEGETATION IN UPLAND WALES

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(Received 13 June 1994)

The chemistry of bulk precipitation, throughfall, stemflow and soil waters beneath an oak wood (*Quercus petraea*) canopy and soil waters under moorland vegetation were measured at two sites on acid brown podzolic soils near Llyn Brianne in rural mid-Wales, UK. Between March 1986 and November 1988, precipitation was 4354 mm and annual interception losses from the oak canopy averaged 13% of incident precipitation. Throughfall and stemflow were more acid and concentrations of most solutes were increased 2- to 4-fold compared with bulk precipitation. Nitrate was the only solute retained within the tree canopy. Throughfall collected beneath patches of bracken on the forest floor was less acidic but contained substantially higher concentrations of major ions than bulk precipitation and oak throughfall. The moorland soil was more acidic, contained more exchangeable calcium but less exchangeable aluminium and potassium than the woodland soil. Soil waters beneath both vegetation types were acidic (mean pH range 4.5- 4.9) and dominated by sodium and chloride. With the exception of calcium, soil water solute concentrations were greater beneath oak. These differences are ascribed to larger atmospheric inputs beneath the oak canopy compared with the shorter grasses, combined with the effect of differences in nutrient dynamics and water fluxes. Variations in soil water aluminium chemistry are explained in terms of ion exchange and podzolisation processes. The water quality implications of increased upland afforestation of moorland by broadleaved trees are discussed.

KEY WORDS: Oak wooland, moorland, major ions, throughfall, soil water.

INTRODUCTION

Mixed broadleaved woodland was the natural vegetation cover of much of the British uplands below 600 m following the last glaciation (Peterken, 1981). However, subsequent forest clearance and continuing land management favouring grazing and burning have resulted in moorland grass and heath communities becoming the dominant upland vegetation type (Dimbleby, 1961).

Since the creation of the Forestry Commission in 1919, reafforestation of the uplands has been dominated by plantations of fast-growing exotic conifers; usually monocultures of sitka spruce (*Picea sitchensis*) (Zehetmayr, 1987). Further expansion (of this type of forestry) was curtailed abruptly in 1988 following a reduction in government subsidies (Newson, 1990). Recent diversification of forestry policy has also resulted in increased grants to encourage planting with broadleaves (Forestry Commission, 1985). These factors, together with increased economic pressures on hill farming and the more general need to reduce agricultural production, have recently led to increased afforestation with broadleaved tree species in the uplands (Atherden, 1993). The expansion of broadleaved forestry has largely been welcomed by both foresters and conservationists as enhancing the conservation and amenity value of upland habitats (Blyth *et al.*, 1987). Nevertheless, the replacement of moorland vegetation with a broadleaved tree canopy may, in acid sensitive areas, still exacerbate the acidification of soils and surface waters. In upland catchments dominated by acidic soils and base-poor rocks, conifer plantations have been associated with problems of freshwater acidification (Ormerod *et al.*, 1989; Hornung *et al.*, 1990a). One important mechanism by which conifers contribute to acidification is through the "scavenging" by the tree canopies of anions such as sulphate, chloride and nitrate in occult and dry deposition (Fowler *et al.*, 1989). The increased flux of these anions to acidic soils may result in the mobilization of inorganic aluminium species into acid soil waters (Reynolds *et al.*, 1988) which are then transported to streams during storm events (Soulsby and Reynolds, 1992). Some broadleaved tree species have been shown to have a similar effect in other acid-sensitive areas such as Central Europe (Ulrich *et al.*, 1980; van Breemen *et al.*, 1987), Scandinavia (Hultberg, 1985); and northern and eastern USA (Cronan, 1985; Lawrence *et al.*, 1986; Johnson and Van Hook, 1989). A recent study in a beech (*Fagus sylvatica*) woodland in southern England also demonstrated that the broadleaved canopy increased the concentration and flux of most solutes in throughfall by 50–100% compared to bulk deposition outside the woodland (Neal *et al.*, 1991a).

Whilst a number of studies have compared the influence of conifers and moorland vegetation on soil and stream water chemistry in the British uplands (Reynolds *et al.*, 1986; 1988), similar studies involving broadleaved woodland are rare in the UK. This paper presents data on the chemistry of bulk precipitation, throughfall, stemflow and soil water in a semi-natural oak (*Quercus petraea*) woodland on brown podzolic soils near Llyn Brianne in upland Mid-Wales and compares these with data for the same soil type under a grazed, *Molinia*-dominated moorland vegetation community.

STUDY AREA AND METHODOLOGY

Experimental setting

The study area was located close to the Llyn Brianne reservoir in the headwaters of the Afon Tywi in Mid Wales (Figure 1). The area has a mean annual rainfall of 2031 mm (at 360 m altitude) with frontal systems bringing most rain in the winter months. The underlying geology consists of base-poor Lower Palaeozoic shales and mudstones. A complex coverage of acidic soil associations has developed from the bedrock, including brown podzolics, stagnopodzols, stagnohumic gleys and peats.

The land use is characterized by large areas of grazed moorland supporting *Molinia*-dominated grassland containing *Nardus*, *Festuca*, and *Agrostis* species on

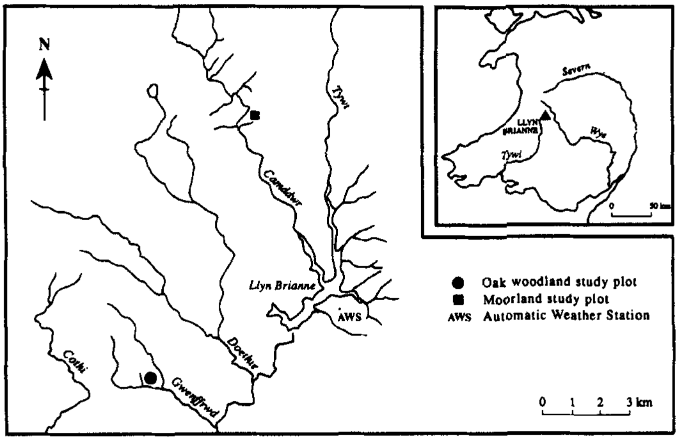


Figure 1 Location of study area.

steeper slopes and *Molinia* bog in flatter peat-dominated areas (Ecological Surveys 1991). Large areas of moorland have been planted with commercial *Sitka* spruce forest since the 1960's, but some of the steeper valley slopes still retain a cover of semi-natural broadleaved woodland dominated by sessile oak (*Quercus petraea*). These sites are thought to have had a continuous woodland cover since the last glacial period (Countryside Council for Wales, pers. comm.) but are currently subject to sheep grazing. They have been managed intensively in the past as a source of timber and fuel wood.

Study sites

An experimental plot (with an area of $400\,m^2$) was established within a stand of broadleaved woodland and another located on an area of open moorland (Figure 1). The woodland vegetation is dominated by sessile oak (*Quercus petraea*) although some birch (*Betula* spp.) and hazel (*Corylus avellana*) are present. Understorey vegetation is dominated by grasses and mosses, though some extensive stands of bracken (*Pteridium aquillinum*) cover parts of the forest floor. The woodland was unfenced, grazed by sheep and unmanaged, but the presence of many multiple stemmed trees indicated that the stand was an abandoned coppice system (Peterken, 1981). The vegetation of the moorland site was classified under the National Vegetation Classification (NVC); (Rodwell 1986; 1989) as NVC type M15d/U5d (Ecological Surveys, 1991). This is *Molinia*-dominated grazed moorland containing *Festuca ovina*, *Agrostis capillaris* and *Deschampsia flexuosa* with a sub-community of *Nardus stricta-Galium saxatile* grassland.

Both sites were located on brown podzolic soils of the Manod series. This is the commonest soil type associated with the steeply sloping sites supporting semi-natural broadleaves in the Welsh uplands (Rudeforth *et al.*, 1984). They are freely draining (being dominated by vertical hydrological pathways in the upper profile), generally with slopes of about 15° and are likely to be sites favoured for future planting of broadleaves (Pyatt, 1977).

The brown podzolic soil beneath the oak has an Ah horizon of variable depth (1–5 cm), being deepest where bracken dominates the understorey and traps large quantites of leaf litter. The dark brown A horizon (up to 5 cm deep) beneath is sharply differentiated from the underlying B horizon which is usually about 50 cm deep, but can vary between 30–90 cm. The fine root network is most dense in the A horizon, although coarse roots are common in the B and C horizons. The B horizon merges with the little altered C horizon at depth and the shale bedrock is usually within 1 m of the soil surface. The plot altitude was c. 310 m and it had a southerly aspect.

The moorland soil has similar profile characteristics, though significant differences are that the well-humified Ah horizon is overlain by a thin O horizon and the B horizon tends to be shallower. In addition, root penetration from the grasses is shallower, being mainly restricted to the O, Ah and upper B horizons. Deforestation in the post-glacial period will have accelerated leaching, though the influx of material delivered from upslope and the absence of waterlogging appear to have limited the process of podzolization (Adams and Raza, 1980). The moorland plot was at an altitude of c. 420 m with a south westerly aspect.

Methodology

Precipitation was monitored continuously outside the oak woodland plot and bulk precipitation samples were collected weekly from an Automatic Weather Station (AWS) close to the Llyn Brianne dam (Figure 1). Twelve throughfall collectors, each consisting of a 15 cm diameter funnel inserted into a 5 litre bottle, were deployed randomly across the forest floor of the oak woodland experimental plot. Total amounts of water were measured and proportional volumes from each collector were bulked for fortnightly chemical analysis. Eight trees in the plot were fitted with stemflow collectors of the type described by Reynolds and Stevens (1987). Stemflow volumes were measured with a tipping bucket device and bulked proportional samples were collected at 2 week intervals. Simple plastic collecting trays were installed beneath the canopy of bracken to collect throughfall for chemical analysis.

Lysimeters were used to sample soil waters at 2-weekly intervals. Triplicate samples were taken from each horizon and bulked prior to analysis. Plastic tensionless tray lysimeters were installed beneath the A horizon of the woodland soil and the O horizon of the moorland soil. In the deeper horizons (B and C in the woodland, A, B, and C in the moorland) porous ceramic cup suction samplers were used. The samplers used were 4.8 cm diameter, 2 bar air entry value ceramic cups (Stevens, 1981). The cups were leached in the laboratory prior to installation and allowed to equilibrate *in situ* for three months. Samples were collected during this period but they are not included in the data presented here. These procedures have been shown to minimise chemical interactions between the samples and the ceramic cups (Hughes and Reynolds, 1990). Bulk precipitation, throughfall and stemflow samples were collected between March 1986 and November 1988. Operational problems with the samplers restricted of soil water sample collection to the period January 1987 to November 1988. The soil water samplers were protected from sheep interference by plastic fencing.

Analytical Techniques

All solutions were collected in clean polyethylene bottles and were filtered (0.45 μm membrane) on return to the laboratory; analysis began the day after collection and was usually complete within 3 working days. Inductively Coupled Plasma Emission Spectroscopy was used to determine total filterable aluminium (Al (tot)), calcium, magnesium, sodium, potassium and iron. Dissolved organic carbon (DOC), sulphate, chloride, nitrate, ammonium and silica were determined colorimetrically using autoanalyzer techniques.

A small number of soil water samples were operationally fractionated to determine non-labile aluminium (mainly organically complexed); Al (org)) and labile aluminium (mainly inorganic, Al (inorg)) using the exchange column procedure described by Driscoll (1984). Unfiltered sub-samples were used for electrometric pH measurements.

Soil samples were collected from three pits dug at each plot and bulked by horizon prior to chemical analysis using standard methods (Allen, 1989). Briefly, soil pH was determined on field moist soil in 1:2.5 w/w water suspension. Exchangeable base cations were determined by atomic absorption spectrophotometry (AAS) following extraction from air-dried soil with 1M ammonium acetate at pH 7. Exchangeable aluminium was also determined by AAS following extraction with 1M potassium chloride. The same potassium chloride extracts were used to determine exchangeable hydrogen by Gran titration. Cation Exchange Capacity (CEC) was estimated from the sum of exchangeable base cations, aluminium and hydrogen.

RESULTS

Precipitation Chemistry

A total of 4354 mm of precipitation was measured during the study period near the oak plot (Table I). Rainfall chemistry was typical (of that described) for this area of Wales (Donald *et al.*, 1990) being dilute and acidic with a weighted mean pH of 4.8 (Table II). Marine-derived sodium, chloride and magnesium were the dominant ions, though there were significant amounts of sulphate, nitrate and calcium of non-sea salt origin.

Throughfall and stemflow in the oak woodland

Throughfall accounted for approximately 79% of incoming precipitation. Persistent malfunction of some stemflow recorders prevented an accurate assessment of this component of the canopy water balance. The data available suggest that it accounted for about 8% of incoming precipitation. Although this is similar to stemflow totals measured in other oak stands (Newson, 1991), it must be regarded as only tentative.

Table I Canopy water balance of oak woodland stand at Llyn Brianne March 1986–November 1988.

	mm	*% of total*
Precipitation	4354	100
Throughfall	3433	78.8
Stemflow	348	8.0
Interception	573	13.2

Table II Volume weighted and range (μeq l^{-1}) of major solutes in bulk precipitation, oak throughfall, oak stemflow and bracken throughfall at Llyn Brianne 1986-1988.

		Bulk Precipitation	*Oak Throughfall*	*Oak Stemflow*	*Bracken Throughfall*
pH	mean	4.8	4.73	4.11	5.13
	range	3.4-8.2	4.0-6.1	3.7-6.6	4.1-7.0
H^+	mean	16	19	77	7
	range	0.001-40	1-100	3-200	0.1-79
[1]Al	mean	1	1	1	2
	range	< 1-8	< 1-3	< 1-17	< 1-18
Na	mean	97	201	432	225
	range	4-561	57-900	122-1492	48-787
K	mean	6	38	98	112
	range	3-212	5-366	< 1-386	20-1207
Ca	mean	26	33	107	107
	range	5-1457	10-140	25-549	35-374
Mg	mean	26	53	116	93
	range	2-413	12-213	33-579	30-369
NH_4	mean	23	34	48	250
	range	< 1-164	1-670	4-378	1-2210
NO_3	mean	25	13	19	49
	range	7-328	< 1-121	< 1-200	0-285
SO_4	mean	51	78	218	129
	range	2-398	40-446	79-1268	50-1100
Cl	mean	116	262	592	386
	range	28-762	56-1157	197-2088	85-2680
DOC*	mean	0.9	5.15	16.94	35.51
	range	0-7.8	1.1-43	5.2-65	6.1-127.5
[1]SiO2	mean	3	1	3	19
	range	< 2-17	< 2-11	< 2-25	< 2-89

* mg l^{-1} [1] μmol l^{-1}

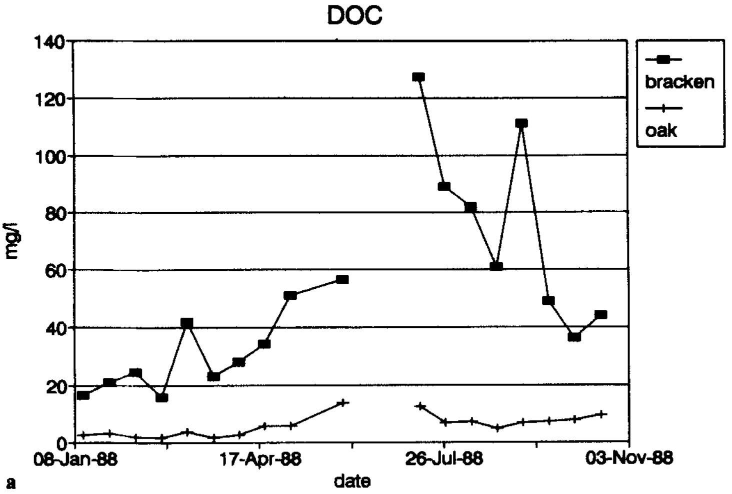
The resulting interception loss of 13% must therefore also be treated with caution, although this is similar to interception losses recently reported from broadleaved stands in lowland England (Harding *et al.*, 1992).

On average, throughfall and stemflow beneath the oak canopy were respectively 0.07 and 0.69 pH units more acidic than precipitation. Mean concentrations of chloride and sulphate were increased by factors of 1.5 and 2 respectively in throughfall and by factors of 4 and 5 in stemflow. Nitrate was the only solute retained in the tree canopy.

Throughfall collected beneath the patches of bracken on the forest floor was less acidic but contained substantially higher concentrations of most components (chloride, sodium, sulphate, nitrate, ammonium, potassium, calcium and silica) than rainfall and oak throughfall. In particular, nutrient leaching (as indicated by DOC and nitrate) from the bracken was highest in the late summer and early autumn when the fronds begin to age and subsequently to decompose (Figure 2).

Soil and soil water chemistry under oak and moorland vegetation

The soils beneath both vegetation types were acidic throughout the profile (pH range 4.05–4.87) and aluminium was the dominant exchangeable cation (Table III). The



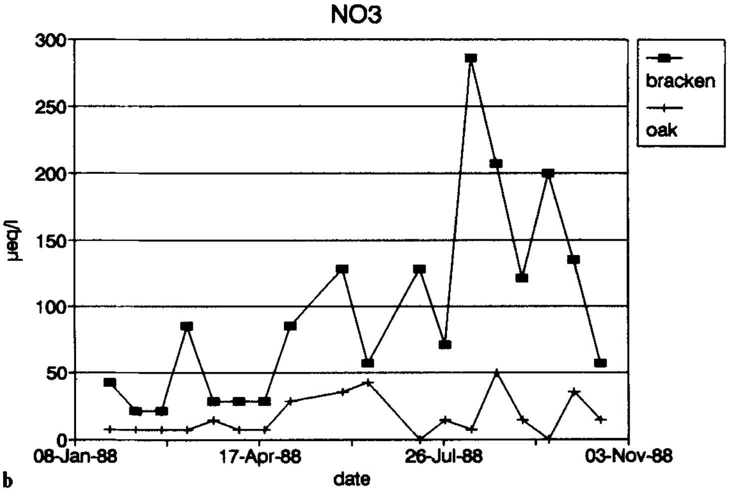


Figure 2 Concentrations of (a) Dissolved Organic Carbon and (b) nitrate in throughfall beneath the oak and bracken canopies.

Table III Soil pH, exchangeable cations (meq. 100 g^{-1}), Cation Exchange Capacity (CEC) and base saturation (% BS) in the brown podzolic soil profiles at each site.

	pH	*Na*	*K*	*Ca*	*Mg*	*H*	*Al*	*CEC*	*%BS*
Oak									
Ah	4.35	0.43	0.75	0.64	0.89	1.76	6.68	11.2	24.9
A	4.36	0.31	0.33	0.27	0.33	0.52	5.41	7.26	18.3
B	4.49	0.27	0.23	0.13	0.14	0.32	4.06	5.16	15.1
C	4.87	0.25	0.13	0.08	0.13	0.17	1.56	2.33	25.8
Moorland									
A	4.05	0.33	0.42	0.47	0.42	0.57	3.07	5.39	32.5
B	4.25	0.25	0.17	0.27	0.13	0.39	2.76	4.01	21.4
C	4.43	0.23	0.09	0.24	0.07	0.25	1.81	2.70	23.7

moorland soil was more acidic but contained less exchangeable aluminium than the woodland soil; however, the latter had smaller quantities of exchangeable calcium. The soil waters beneath both vegetation types were acidic (mean pH range 4.5–4.9) and dominated by sodium and chloride (Tables IV and V). With the exception of calcium, solute concentrations were greater beneath the oak compared with the moorland soils. In common with podzolic soils elsewhere in Wales, acidity and concentrations of iron and DOC decreased with depth down the profile. Total filterable aluminium concentrations also varied with depth, but the pattern was not consistent. However, chemical speciation of aluminium in a sub-set of 10 soil water samples from the woodland indicated that while 86% of aluminium was present in organic complexes in the A horizon this was dramatically reduced to 44% and 7% in the B and C horizons, respectively (Figure 3). In contrast, the proportion and concentrations of inorganic aluminium species increased with depth down the profile. Unfortunately, similar data were not available for the moorland site.

In both soils, inorganic-N concentrations were greatest in the surface horizons, and approached limits of detection deeper in the profile. The concentrations of the other

Table IV Arithmetic mean and range (μeq l^{-1}) of major solutes in soil water of brown podzolic soil beneath oak woodland at Llyn Brianne 1987-1988. (A, B, C, are soil horizons.)

Horizon		*A*	*B*	*C*
pH	mean	4.53	4.65	4.86
	range	4.2-4.7	4.4-4.9	4.7-5.0
H^+	mean	30	22	14
	range	20-63	13-40	10-40
[1]Al	mean	22	26	21
	range	1-34	3-93	7-47
Na	mean	215	236	160
	range	78-914	139-666	87-226
K	mean	29	20	12
	range	< 1-92	5-43	< 1-20
Ca	mean	74	22	21
	range	30-220	10-55	10-35
Mg	mean	101	75	53
	range	20-330	34-255	30-81
NH_4	mean	26	< 1	0.1
	range	< 1-250	< 1	< 1-3
Fe	mean	16	1	< 1
	range	< 1-32	< 1-6	< 1
NO_3	mean	15	< 1	1
	range	< 1-143	< 1	< 1-7
SO_4	mean	122	116	111
	range	62-369	60-200	65-156
Cl	mean	291	272	195
	range	85-1580	113-959	85-367
DOC*	mean	18.7	5.81	1.42
	range	7.4-42	3-11	0.8-2.6
[1]SiO_2	mean	10	40	38
	range	< 2-32	14-60	25-50

* mg l^{-1}

[1] μmol l^{-1}

Table V Arithmetic mean and range (μeq l^{-1}) of major solutes in soil water of brown podzolic soil beneath grass moorland at Llyn Brianne 1987-1988. (O,Ah, B, C, are soil horizons.)

Horizon		*O*	*Ah*	*B*	*C*
pH	mean	4.67	4.84	4.89	4.98
	range	4.2-5.3	4.0-6.0	4.5-5.7	4.7-5.2
H^+	mean	21	27	13	10
	range	5-63	1-100	2-32	6-20
^{1}Al	mean	9	19	11	16
	range	4-38	4-125	2-60	7-41
Na	mean	154	271	208	154
	range	48-761	84-1153	104-505	96-283
K	mean	24	4	2	2
	range	< 1-100	< 1-12	< 1-8	< 1-8
Ca	mean	32	74	38	32
	range	10-180	15-419	10-125	10-105
Mg	mean	44	67	49	34
	range	11-176	16-271	16-148	16-92
NH_4	mean	14	0.5	0.1	0.1
	range	< 1-86	< 1-7	< 1-2	< 1-0.2
Fe	mean	9	< 1	1	< 1
	range	< 1-21	< 1	< 1-5	< 1
NO_3	mean	3	< 1	< 1	0.002
	range	0-21	< 1	< 1	< 1-7
SO_4	mean	85	90	74	67
	range	29-228	12-221	41-133	23-91
Cl	mean	193	355	246	189
	range	28-1015	56-2257	56-987	56-621
DOC*	mean	8.75	3.06	1.65	2.03
	range	2.5-20.7	1.4-7.0	< 0.1-3.2	0.6-22
$^1SiO_2$	mean	14	39	28	27
	range	< 2-46	18-110	11-71	< 2-57

* mg l^{-1}
^{1} μmol l^{-1}

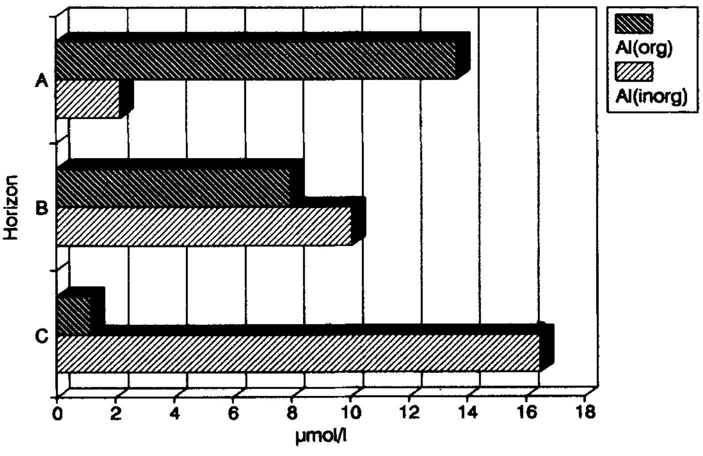


Figure 3 Aluminium speciation in soil waters in a brown podzolic soil beneath oak woodland.

remaining solutes were generally greatest in the surface horizon and lower at depth. An exception was silica in the oak wood, where mean concentrations were lowest in the A horizon and higher at depth.

The dynamic nature of soil water composition was reflected in the large ranges observed for most solutes. Temporal variations in soil water chemistry did not reflect throughfall and stemflow chemistry generally due to the damping effect of water stored within the profile (Reynolds and Pomeroy, 1988). However, early in 1988 the soil waters beneath both vegetation types responded rapidly to a pulse of precipitation containing high concentrations of sea-salts (Figures 4 and 5). Although the two-weekly sampling regime was not ideally suited to monitoring the subsequent movement of sea-salts

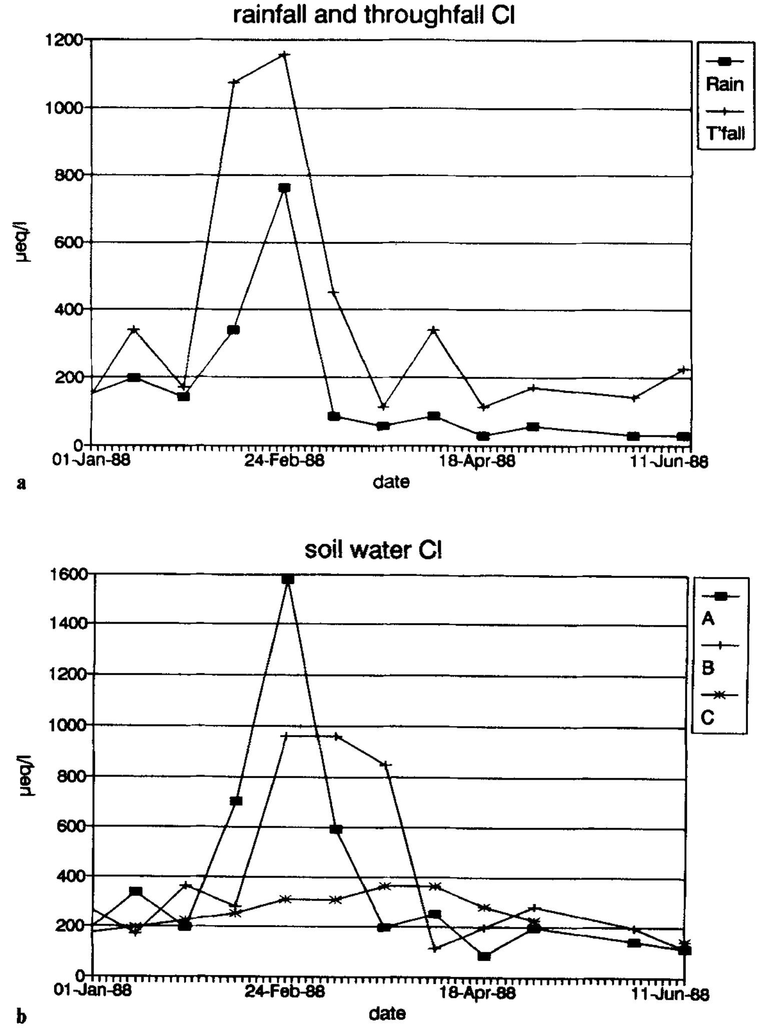


Figure 4 Concentrations of (a) chloride in precipitation and throughfall, and concentrations of (b) chloride, (c) hydrogen ion and (d) aluminium (tot) in oak woodland soil water (A, B and C horizons) in response to a period of high sea-salt deposition in early 1988.

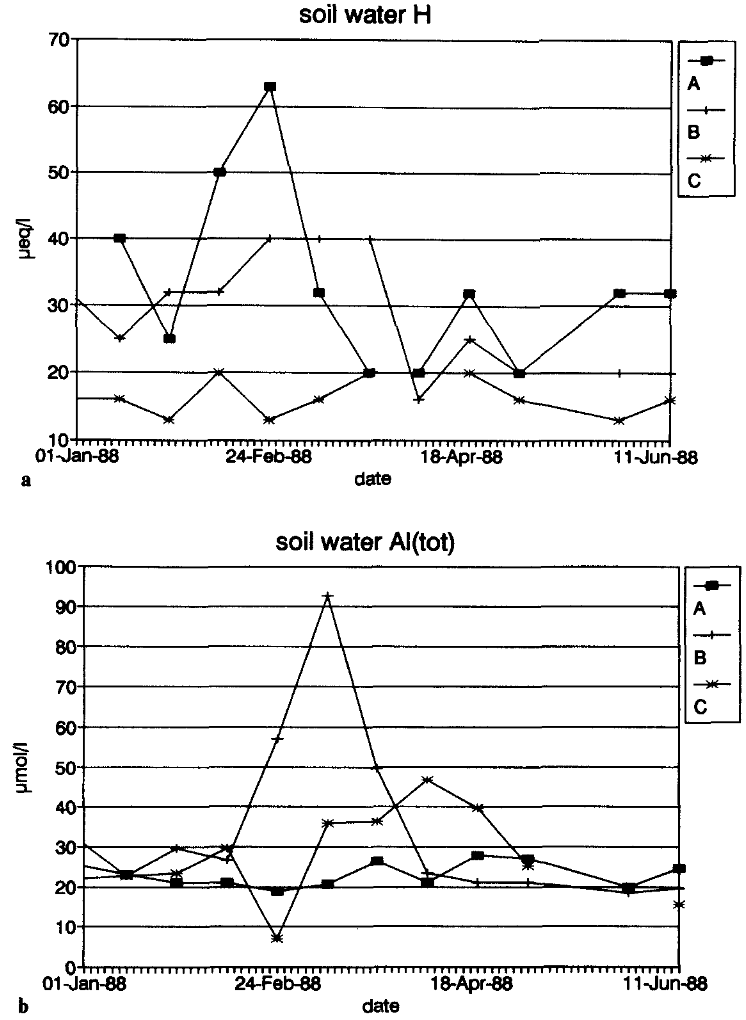


Figure 4 (*Continued*).

through the soil profile, the data provided an interesting insight into the some of the key processes controlling soil water chemistry.

High sea-salt concentrations were detected in precipitation and throughfall during February (Figure 4a). Peak chloride concentrations of 1580 μeq l^{-1} were observed in the woodland soil A horizon in late February with increases in the B and C horizon being damped and slightly lagged as the salt-rich water moved through the profile and mixed with resident soil water (Figure 4b). The high concentrations of marine cations that accompanied the chloride appear to have displaced hydrogen and aluminium ions from the soil exchange complex and increased concentrations in the upper profile (Figure 4c and d). In the woodland soil solutions, increases in total dissolved alumin-

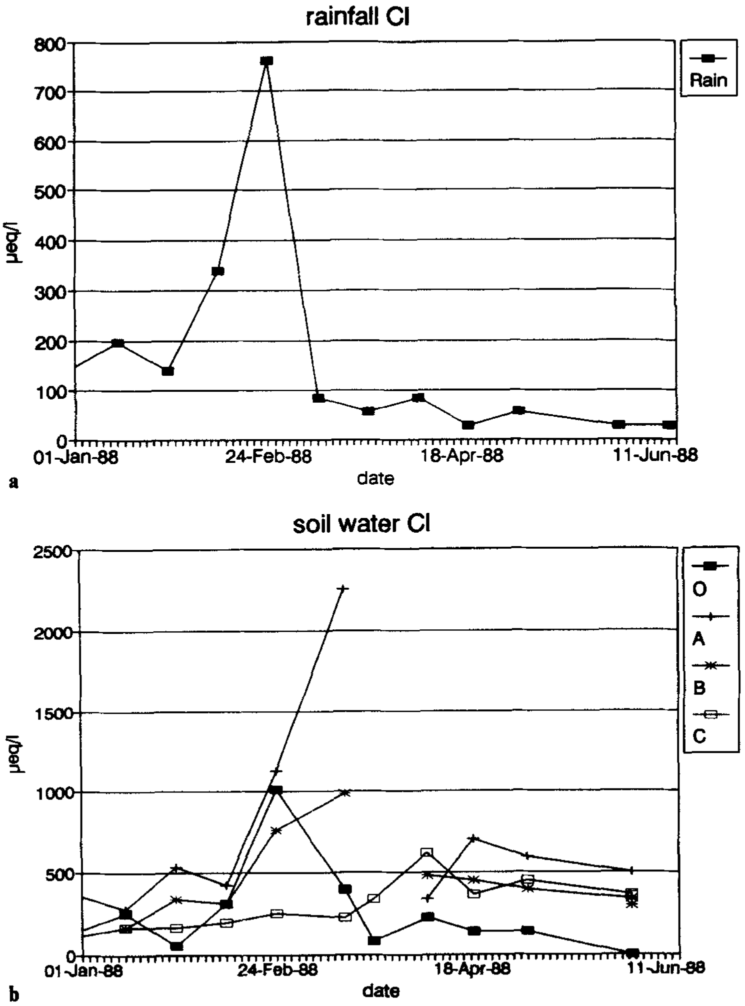


Figure 5 Concentrations of (a) chloride in precipitation, and concentrations of (b) chloride, (c) hydrogen ion and (d) aluminium (tot) in moorland soil water (O, A, B and C horizons) in response to a period of high sea-salt deposition in early 1988.

ium were most dramatic in the B and C horizons, whilst the largest increase in H^+ was observed in the A horizon. This indicates that aluminium dominates the exchange response in the mineral subsoil but hydrogen dominates in the organic-rich upper profile horizon.

Much higher chloride concentrations were observed in moorland soil waters in response to the event, particularly in the A horizon (Figure 5b). This was reflected by the increases in H^+ and dissolved aluminium in the A horizon which was more pronounced than at the oak site (Figures 5c and d). The difference in A horizon aluminium response was unexpected, as the exchange complex of both soils are dominated by aluminium (Table III). Clearly the exact nature of cation exchange

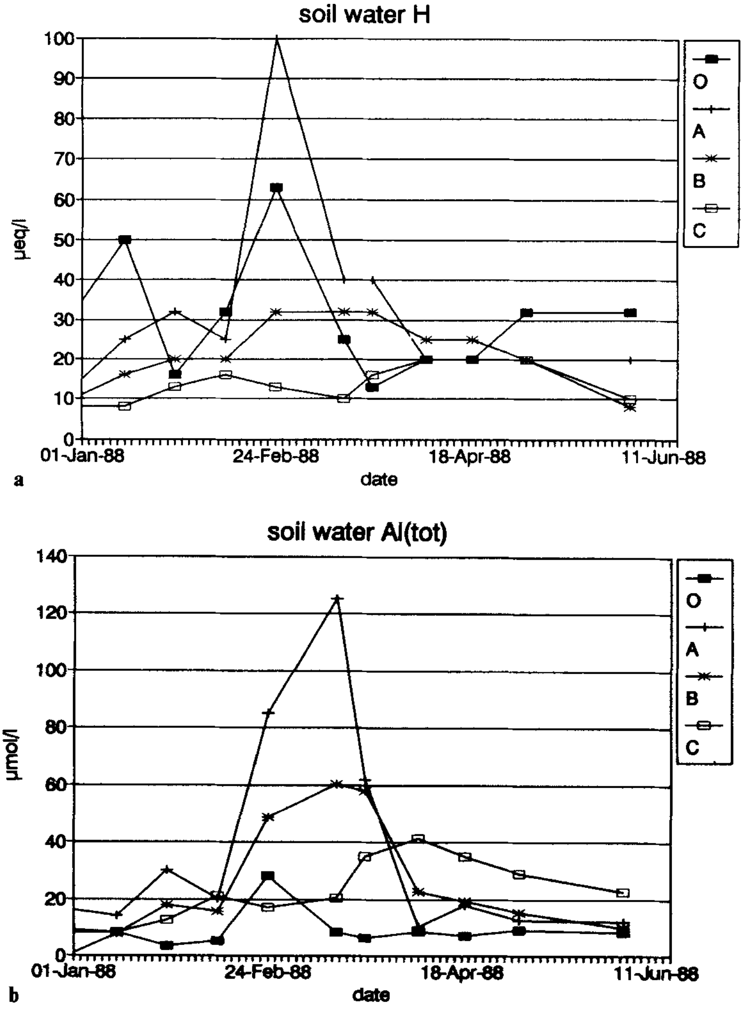


Figure 5 (*Continued*).

processes operating in the soils remain obscure and warrant detailed process studies (Neal *et al.*, 1990). The reasons for the difference in chloride concentrations between the sites are difficult to explain in the absence of detailed input data. It seems likely, however, that chloride concentrations in rainfall must have been greater at the higher altitude moorland site than at either the oak site, or the AWS where the bulk precipitation sample was collected.

DISCUSSION

As water passes through the tree canopy the concentrations of most solutes are modified by comparison with bulk precipitation by a series of complex interactive processes (Parker, 1983). In consequence, temporal variations in throughfall and stemflow chemistry are complex and generally do not reflect rainfall chemistry in a simple manner. The largest changes in concentration tend to occur in stemflow due to its longer contact time with the tree canopy and trunk (and their associated epiphyte communities) compared with throughfall. Cloud and mist droplets, usually with very high solute concentrations, are captured by the forest canopy as occult deposition, whilst gases, aerosols and dust particles are captured as dry deposition. These processes are particularly effective at increasing the deposition rates of marine (chloride, marine-derived sulphate, sodium and magnesium) and pollutant ions (non-marine sulphate, nitrate and ammonium) compared to open funnel collectors and short grass vegetation canopies (Fowler *et al.*, 1989; Hornung *et al.*, 1990b). In addition, some elements (particularly calcium and potassium) can be leached from the canopy as part of the nutrient cycle (Stevens *et al.*, 1989). Potassium is rapidly cycled in forest systems (Parker, 1983) and the leaching of organic acids from the canopy will contribute to observed increases in DOC and acidity. Interception losses will also contribute to a concentration effect. In this study, nitrate concentrations were reduced in oak throughfall compared to bulk precipitation probably via direct absorption through the foliage and uptake by the rich epiphyte (moss and lichen) communities growing on the trunk and branches. This efficient cycling is a common feature of oak woodlands where nitrogen is limiting (Brown, 1974; Melillo, 1981).

The leaching of base cations and ammonium from the bracken canopy is consistent with the higher pH of bracken throughfall relative to oak throughfall and precipitation. The large solute concentrations suggest that throughfall is an important component of the bracken's nutrient cycle, particularly during leaf senescence. The higher concentrations of sea-salts and non-marine sulphate can be explained by both dry and occult deposition to the bracken canopy during the growing season and the concentration effect of further interception losses. However, their individual contribution cannot be assessed by this study. Bracken interception losses were not measured, but the microclimate of the woodland will probably produce lower losses than the 20% recorded from an open bracken stand on a moorland slope on Dartmoor (Williams *et al.*, 1987).

The larger concentrations of atmospherically derived solutes (chloride, sulphate, sodium and magnesium) observed throughout the woodland soil profile are consistent the higher rates of dry and occult deposition to the tree canopy compared with the short grass sward and the concentration effects of higher interception losses from the woodland. The lower chloride and sulphate concentrations in the lower soil profile will reflect higher transpiration losses from the upper horizons where concentrations of tree roots are highest, though some sulphate may be lost from solution by adsorption on to iron and aluminium oxide surfaces in the B horizon (Neal *et al.*, 1991b).

As expected, plant nutrient concentrations (potassium, ammonium, and nitrate) are greatest in the waters extracted from the surface A and O horizons of the woodland and grassland soils respectively. This reflects their high rates of decomposition and nutrient turnover and is linked with relatively large DOC concentrations (Reynolds *et al.*, 1992). Root uptake in the upper profile will partly account for reduced leaching losses of nutrients to the B and C horizons, though immobilization in the soil microbial biomass is probably important, especially for nitrogen (Emmett *et al.*, 1993). More detailed biogeochemical process studies are required to explain the differences in nutrient concentrations between the two systems. These will be related to different nutrient dynamics, litter accumulation rates, water fluxes and atmospheric inputs. However, the larger soil water and soil exchangeable concentrations of potassium throughout the woodland soil profile suggests that potassium may be cycled less tightly in woodland compared to the grassland. In contrast, lower concentrations of calcium on the exchange complex of the mineral B and C horizons and in solutions may indicate a greater demand for calcium by the woodland.

The dynamics of aluminium and hydrogen in the soil waters are controlled by a number of interacting processes. The vertical distribution of inorganic aluminium, organic aluminium, iron and DOC in the woodland soil is similar to variations observed in other podzolic soils in Wales (Hughes *et al.*, 1990). The pattern is consistent with podzolization where aluminium and iron mobilized by organic chelates in the upper profile are redeposited in the B horizon. Both soils are well-structured and freely draining and the dominant vertical hydrological paths facilitate podzolization. The long-term neutralization of acidity in the mineral subsoil, parallelled by an increase in inorganic aluminium concentrations, can be attributed to the weathering of alumino-silicate minerals such as chlorite (Neal *et al.*, 1989). The increased silica concentrations in the subsoil solutions are consistent with this weathering mechanisim. However,

Table VI Selected correlation coefficients of soil water components in different horizons at the two study sites (TIA; total inorganic anions = Cl + SO_4 + NO_3).

Oak woodland		*Horizon*		
		A	*B*	*C*
x	y			
H^+	Al	0.009	0.606***	0.522***
Cl	Al	0.029	0.723***	0.518***
SO_4	Al	0.001	0.205	0.393*
NO_3	Al	0.237		
TIA	Al	0.027	0.746***	0.459**
DOC	Al	0.409*	0.049	0.222
Cl	H^+	0.405*	0.519***	0.340*
SO_4	H^+	0.040	0.130	0.144
TIA	H^+	0.403*	0.524***	0.367*

Moorland		*O*	*Ah*	*B*	*C*
x	y				
H^+	Al	0.231	0.551***	0.714***	0.670***
Cl	Al	0.578***	0.923***	0.935***	0.820***
SO_4	Al	0.137	0.005	0.164	0.309*
TIA	Al	0.571***	0.888***	0.904***	0.816***
DOC	Al	0.045	0.115	0.211	0.048
Cl	H^+	0.311*	0.401*	0.728***	0.626***
SO_4	H^+	0.030	0.021	0.089	0.369*
TIA	H^+	0.280	0.406*	0.713***	0.598***

* $p \leq 0.05$, ** $p \leq 0.01$, ***$p \leq 0.001$

studies on a range of soils in upland Wales have shown that mineral solubility, particularly with secondary minerals such as Gibbsite, does not adequately explain short-term aluminium variations (Neal *et al.*, 1989). Cation exchange appears to be an important controlling mechanism (Reynolds *et al.*, 1988). A regression analysis of the soil water components (Table VI) shows that dissolved aluminium is strongly correlated with chloride and the concentration of total inorganic anions (TIA) in the B and C horizons, indicating a cation exchange control in the woodland soil (Adams *et al.*, 1990; Soulsby and Reynolds, 1992). Correlations between aluminium and anion concentrations were poor in the A horizon where a high correlation with DOC in the woodland soil reflects the importance of chelation in controlling aluminium mobilization in the upper profile. This is reflected by the dominance of organic aluminium species in A horizon soil water (Figure 3). There was a much weaker relationship between aluminium and DOC in the surface horizons of the grassland soil but strong correlations between aluminium and anion concentrations in all horizons.

Hydrogen ion concentrations were also strongly correlated with anion concentrations in the B and C horizons of both soils, again indicating ion exchange control (Table VI). In the surface horizons, de-protonation of organic acids will also contribute to soil water acidity, hence the weaker correlations observed in the upper profile. The complexity of the soil cation exchange response was demonstrated by the major marine-salt perturbation early in 1988. The occurrence of this well known phenomenon (e.g. Wiklander, 1975) is interesting in that it shows how such changes are relatively short-lived as concentrations of most solutes soon returned to pre-event levels in response to subsequent rainfall inputs.

IMPLICATIONS

One of the significant changes in soil water chemistry resulting from broadleaved afforestation will be the increased concentrations of mobile anions (mainly chloride and sulphate) resulting from enhanced dry and occult deposition. This study demonstrates that in upland areas like Mid-Wales where soils are acidic and underlain by base-poor rocks, elevated amounts of aluminium in acid soil waters may result.

It is unlikely, however, that stream acidification experienced with conifer afforestation will occur to the same extent with broadleaves. Lower anion concentrations are observed in throughfall and stemflow beneath oak compared with conifers both at Llyn Brianne (Soulsby , 1991) and other sites (Brown and Iles, 1991). This reflects the less effective scavenging of aerosols and cloudwater by a seasonal broadleaved vegetation canopy relative to conifers (Miller *et al.*, 1993). Aluminium concetrations in soil waters beneath oak are also lower than those observed beneath spruce (Soulby and Reynolds, 1992) so that lower aluminium leaching rates may be expected. Furthermore, only relatively small areas of catchments are likely to be affected by broadleaved afforestation if planting rates continue in their present form (new broadleaved plantations average < 7 ha in area (Harding *et al.*, 1992)). This situation could, however, change if future forest policy further encourages planting of broadleaved trees.

There are two important implications arising from the development of small woodland plantations. The first relates to forest edge effects. In southern England, Neal *et al.*, (1991a) noted enhanced anion deposition and interception on the windward edge of broadleaved woodlands compared with sites located further within the woodland. This resulted in higher anion concentrations and a two-fold increase in the anion flux reaching the forest soil. These effects can extend for distances up to 50 m from the forest edge, therefore the results from our study, where the experimental plots were located well away from edges, may underestimate the effects of atmospheric deposition to small isolated stands of broadleaves. Furthermore, if planting densities in new, managed plantations are higher than in the unmanaged seminatural stand studied here, dry and occult deposition rates could be further enhanced.

The location of broadleaved planting will also be significant with regard to its potential impact on the aquatic environment. Recent trials of riparian management in afforested catchments suggest that broadleaved buffer strips may help to mitigate some of the negative impacts of coniferous forestry (Forestry Commission, 1993). Whilst this may be true for problems associated with sediment movement, riparian habitats and stream temperatures, care should be taken in areas of acid sensitive soils to plant broadleaves at low densities to ensure that aluminium leaching into stream waters is not exacerbated. In this respect, the choice of species is also important. Alder (*Alnus glutinosa*) is a common tree for stream-side planting in the UK but this species is unsuitable for acid sensitive environments as it can provide an additional source of acidity through symbiotic nitrogen fixation and subsequent nitrification (Brown and Iles, 1991). On the most sensitive sites, it may be better to leave buffer strips without any tree cover.

As with impacts on water quality, the wider use of broadleaved stands is unlikely to cause a major reduction in water yields from upland catchments if planting areas remain small. The 13% interception loss measured in this study is a tentative figure and needs to be confirmed by further investigations. Interestingly, despite obvious environmental differences, it is close to values calculated by Harding *et al.*, (1992) in lowland broadleaved stands dominated by ash (*Fraxinus excelsior*) and beech (*Fagus sylvatica*) (11% and 16%, respectively). This loss is substantially lower than interception losses reported for conifer stands in upland Wales which are usually about 30% (Calder, 1990). Nevertheless, the measured interception loss is higher than that which would be expected from moorland vegetation (Kirby *et al.*, 1991). Moreover, the loss will be highest during the summer when additional losses from the bracken understory may be substantial.

Research into the hydrological impacts of broadleaved forestry in the UK is very much in its infancy (Newson, 1991). The Forest and Water Guidelines (Forestry Commission, 1993) are targeted at managers of commercial conifer forests and attempt to encourage forest practice that will have minimal effects on the aquatic environment. In the future, these guidelines will need to consider the role of broadleaves in more detail and further research will be needed at a range of sites in order to predict impacts of broadleaved forest management on the freshwater environment.

Acknowledgements

This work was part of the Llyn Brianne Acid Waters Project, funded by the National Rivers Authority, Department of Environment, the Welsh Office and NERC. The work of NRA (Welsh Region) staff in the collection and analysis of samples and is appreciated and Catherine Shaw is thanked for data retrievals from the Llyn Brianne archive. Helpful comments on an earlier draft by Dr. M. Hornung and Mr. P. Stevens are gratefully acknowledged. Financial support for the preparation of this paper was provided by the Carnegie Trust for the Universities of Scotland.

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