Hydrological Sciences - Journal - des Sciences Hydrologiques, **34**, 6, 12/1989

Chemistry of streams draining grassland and forest catchments at Plynlimon, mid-Wales

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Abstract The chemistry of streamwater, bulk precipitation, throughfall and soil waters has been studied for three years in two plantation forest and two moorland catchments in mid-Wales. Na and Cl are the major ions in streamwater reflecting the maritime influence on atmospheric inputs. In all streams, baseflow is characterised by high pH waters enriched in Ca, Mg, Si and HCO_3. Differences in baseflow chemistry between streams reflect the varying extent of calcite and base metal sulphide mineralization within the catchments. Except for K, mean stream solute concentrations are higher in the unmineralized and mineralized forest catchments compared with their respective grassland counterparts. In the forest streams, storm flow concentrations of H^+ are approximately 1.5 times and Al four times higher than in the moorland streams. Annual catchment losses of Na, Cl, SO_4, NO_3, Al and Si are greatest in the forest streams. In both grassland and forest systems, variations in stream chemistry be explained by mixing waters from different parts of the catchment, although NO_3 concentrations may additionally be controlled by N transformations occurring between soils and streams. Differences in stream chemistry and solute budgets between forest and moorland catchments are related to greater atmospheric scavenging by the trees and changes in catchment hydrology consequent on afforestation. Mineral veins within the catchment bedrock can significantly modify the stream chemical response to afforestation.

Composition des eaux s'écoulant de bassins versants à végétation de prairies ou de forêts, à Plynlimon, centre du Pays de Galles

Résumé La composition chimique des eaux des ruisseaux, des pluies incidentes, des pluviolessivats et des eaux dans le sol a été

Open for discussion until 1 June 1990

étudiée pendant trois années dans quatre bassins versants situés dans le centre du Pays de Galles. Deux sont couverts de prairies, les deux autres de forêts. Le sodium et le chlore sont les ions dominants dans les eaux des émissaires, reflétant ainsi l'influence maritime des apports atmosphériques. Dans tous les ruisseaux, le débit de base est caractérisé par un pH élevé avec des eaux enrichies en Ca, Mg, Si et HCO_3. Par rapport à ce niveau moyen, les différences de composition observées entre les ruisseaux reflètent l'extension plus ou moins grande dans les bassins de la calcite et de filons de minéraux sulfurés divers. Sauf pour le potassium, la concentration moyenne des produits dissous dans l'eau est plus élevée dans les deux bassins forestiers, qu'il y ait ou non des filons de minéraux, que dans les bassins analogues en zone de prairies. Dans les eaux des ruisseaux issus des zones de forêts, la concentration au cours des événements torrentiels est 1.5 fois plus élevée pour l'ion H^+ et quatre fois pour l'aluminium que dans celles des zones de prairies. Pour les éléments Na, Cl, SO_4, NO_3, Al et Si les pertes annuelles à l'exutoire sont les plus fortes pour les bassins forestiers. Dans les deux systèmes, prairies et forêt, les variations de composition chimique des eaux des ruisseaux peuvent être expliquées par des mélanges d'eau de diverses origines à l'intérieur de chaque bassin, néanmoins l'ion NO_3 reste contrôlé par des transformations de l'azote à l'interface sol-ruisseau. Entre les deux types de bassins, les différences dans la composition des eaux des ruisseaux et dans les bilans des produits solubles quittant ces bassins sont liées à ce que sous forêt l'interception est plus élevée, que l'effet filtre est plus éfficace et que le reboisement a modifié le fonctionnement hydrologique du système. Par rapport à l'effet du reboisement, la présence de filons minéraux dans la roche mère des bassins versants peut influencer significativement la composition chimique de l'eau du ruisseau.

INTRODUCTION

Over the last 40 years, large-scale afforestation in the UK has been concentrated in upland areas. Streams draining such areas in Wales constitute an important resource for public water supply and sports fishing. Consequently, there is much concern over the possible impacts of land use change, particularly afforestation, on the chemistry of upland streams. Recent studies have reported increased acidity and Al concentrations in streams draining forest compared with adjacent moorland catchments (Stoner *et al.*, 1984; Reynolds *et al.*, 1986). Such changes have been implicated in alterations to freshwater invertebrate communities and fisheries in afforested catchments (Stoner & Gee, 1985). The study reported here compares the chemistry of major ions in streams draining adjacent moorland and forest catchments in the relatively unpolluted area of Plynlimon, mid-Wales.

SITE DESCRIPTION

The catchments of the Afon Cyff and Afon Gwy form part of the headwaters of the River Wye, and the Afon Hafren and Afon Hore catchments are situated in the headwaters of the River Severn. Both headwater areas lie to the east of Plynlimon, approximately 24 km from the west coast of Wales.

The geology of the Plynlimon catchments consists of lower Palaeozoic mudstones, shales and grits, containing mineral veins in the Hore and Cyff catchments (see Table 1 and Newson, 1976). Locally derived glacial and post-glacial drift occurs in all the catchments. Soil cover consists of a mosaic of acid upland types including peats, brown earths, stagnogleys and stagnopodzols. The latter predominate and detailed profile descriptions are given in Reynolds *et al.* (1988).

Table 1 *Summary features of the Plynlimon catchments*

	Afon Gwy	*Afon Cyff*	*Afon Hafren*	*Afon Hore*
Catchment area (ha)	*390*	*308*	*347*	*335*
Altitude range (m)	*380-730*	*355-690*	*350-690*	*339-738*
Hill-top peat (%)	*37*	*14*	*52*	*33*
Improved grassland (%)	*7*	*39*	*0*	*0*
Forest cover (%)	*1*	*0*	*48*	*77*
Mean annual rainfall 1983-1985 (mm)	*2385*	*2360*	*2328*	*2458*
Mean annual runoff 1983-1985 (mm)	*2111*	*2007*	*1823*	*1870*
Bedrock mineralization	*None*	$CaCO_3$ *veins*	*None*	*Pb/Zn sulphides* + $CaCO_3$

The vegetation of the Cyff and Gwy catchments consist of an acid grassland dominated by *Nardus*, *Festuca* and *Agrostis* species with *Eriophorum* species on the peats. Parts of these catchments have been agriculturally improved by the periodic addition of lime and compound fertilizers over the last 40 years (Hornung *et al.*, 1986). The Hafren and Hore catchments were planted mainly with Sitka spruce (*Picea sitchensis*) in three phases between 1937 and 1964. More detailed information about the catchments is contained in Newson (1976).

The area has "clean air", with estimated mean annual SO_2 concentrations of 4 to 5 ppbv (Martin & Barber, 1978; Martin, 1982) and measured mean NO_2 and NH_3 concentrations of 6 and 3 ppbv respectively (Atkins, personal communication, 1988). Mean monthly air temperatures for February and August are 1.8°C and 13.1°C respectively.

METHODS

Streamflow from the catchments is monitored using steep stream flumes

(Smart, 1977) while precipitation input data are obtained from a network of ground level and canopy level raingauges (Institute of Hydrology, 1977) together with automatic weather stations. For this study, samples of stream water were collected weekly from a point upstream of the flumes and bulk precipitation was sampled fortnightly using a continuously open collector in the Cyff catchment.

Throughfall was sampled fortnightly from beneath 40 year old Sitka spruce and an unimproved *Nardus-Festuca* grass canopy. Soil water samples were also collected fortnightly from stagnopodzols at the forest and grassland throughfall sites using zero-tension lysimeters in the Oh horizon and suction samplers in the mineral horizons. Details of the methodology are contained in Reynolds *et al.* (1988 & 1989).

On the day following sampling, after return to the laboratory, pH and HCO_3 were determined on unfiltered samples. During 1983 and 1984 HCO_3 concentrations were estimated by acid titration to pH 4.5 on unfiltered sub-samples. This method was later abandoned as unsuitable (Reynolds & Neal, 1987) and for 1985, HCO_3 was determined by Gran titration. The first two years' HCO_3 data have been adjusted (Neal, 1988) so that the values are equivalent to those determined by Gran titration. Concentrations of major cations, anions, Si and Al were determined on filtered samples (0.45 μm membrane) using standard methods described in Reynolds *et al.* (1986 & 1988).

RESULTS

Atmospheric inputs

Bulk precipitation at Plynlimon has a low solute content and is acidic with a volume weighted mean pH of 4.67 (Tables 2 and 3). Marine-derived Na, Cl and Mg are the major constituents, although there are significant amounts of Ca, SO_4 and NO_3 of non-marine origin (Reynolds *et al.*, 1984).

Streamwater chemistry

Stream chemistry data are summarized as discharge weighted mean solute concentrations in Tables 2 and 3. The maritime influence on the precipitation chemistry is reflected in the streams. Thus, Na and Cl are the major ionic components of stream water accounting for approximately 52% and 60% of the cation and anion sums respectively. Ratios of Na and K to Cl are similar to those in precipitation and sea water (Table 4) and Na, Cl and Mg are positively correlated ($p = 0.01$) in all the streams.

Stream water concentrations of all solutes, except NH_4, are enhanced compared with precipitation and ratios of Ca, Mg and SO_4 to Cl are greater than for rainfall or sea water (Tables 2, 3 and 4). Temporal variations in the concentrations of most stream solutes are considerably less than in rainfall (e.g. Fig. 1) and there are no significant correlations between precipitation and

***Table 2** Volume weighted mean and range (in brackets) of pH and cation concentrations in streamwater and bulk precipitation at Plynlimon*

	Na	*K*	*Ca*	*Mg*	*Al*	*NH_4*	*H*	*pH*
Cyff	*147* *(109-204)*	*4* *(<1-9)*	*35* *(23-82)*	*35* *(24-63)*	*<2* *(<2-30)*	*<5*	*4* *(<1-16)*	*5.43* *(4.80-7.20)*
Gwy	*143* *(100-200)*	*3* *(<1-10)*	*18* *(12-34)*	*27* *(20-47)*	*3* *(<2-22)*	*<5*	*13* *(<1-62)*	*4.89* *(4.21-6.56)*
Hafren	*185* *(148-262)*	*3* *(<1-8)*	*22* *(11-42)*	*33* *(27-51)*	*11* *(<2-52)*	*<5*	*20* *(<1-76)*	*4.69* *(4.12-6.83)*
Hore	*202* *(144-248)*	*3* *(<1-11)*	*36* *(20-120)*	*36* *(28-58)*	*11* *(<2-37)*	*<5*	*15* *(<1-17)*	*4.83* *(4.17-7.37)*
Bulk pptn[1]	*85* *(<1-361)*	*2* *(<1-17)*	*4* *(<1-40)*	*10* *(<1-42)*	*<2*	*17* *(<5-200)*	*21* *(<1-299)*	*4.67* *(3.64-6.38)*

Sampling period: 18 January 1983 - 30 December 1985

[1] *Fortnightly samples*

Units: $\mu mol\ l^{-1}$

***Table 3** Volume weighted mean and range (in brackets) of anions and Si concentrations in streamwater and bulk precipitation at Plynlimon*

	NO_3	*SO_4*	*Cl*	*HCO_3*	*Si*
Cyff	*13* *(<1-51)*	*47* *(<9-144)*	*161* *(102-310)*	*14* *(<1-171)*	*36* *(20-61)*
Gwy	*15* *(<1-48)*	*36* *(<9-181)*	*155* *(99-282)*	*4* *(<1-55)*	*35* *(24-64)*
Hafren	*28* *(<1-59)*	*50* *(<9-103)*	*199* *(133-339)*	*3* *(<1-43)*	*58* *(43-89)*
Hore	*23* *(<1-52)*	*57* *(15-140)*	*218* *(144-367)*	*12* *(<1-253)*	*54* *(39-85)*
Bulk pptn[1]	*12* *(<1-129)*	*21* *(<9-100)*	*106* *(<3-451)*	*<1*	*<2*

Sampling period: 18 January 1983 - 30 December 1985

[1] *Fortnightly samples*

Units: $\mu mol\ l^{-1}$

stream water chemistry. These factors reflect the high degree to which physical mixing and vegetation-soil and/or bedrock interactions modify the chemistry of rainfall as it passes through the catchments.

Except for K, mean stream solute concentrations (Tables 2 and 3) are greater in the mineralized and unmineralized forest catchments compared with their respective grassland counterparts (i.e. Hafren > Gwy and Hore > Cyff). Mean Ca, Mg, HCO_3 and Si concentrations are also greater in the Hore and

Table 4 *Mean molar ratios to Cl for stream water and bulk precipitation at Plynlimon*

	Na	*K*	*Ca*	*Mg*	*SO_4*
Cyff	*0.91*	*0.018*	*0.219*	*0.219*	*0.295*
Gwy	*0.93*	*0.019*	*0.114*	*0.170*	*0.236*
Hafren	*0.93*	*0.015*	*0.111*	*0.165*	*0.244*
Hore	*0.91*	*0.013*	*0.158*	*0.162*	*0.258*
Pptn	*0.80*	*0.014*	*0.40*	*0.98*	*0.199*
Sea water	*0.86*	*0.019*	*0.019*	*0.096*	*0.052*

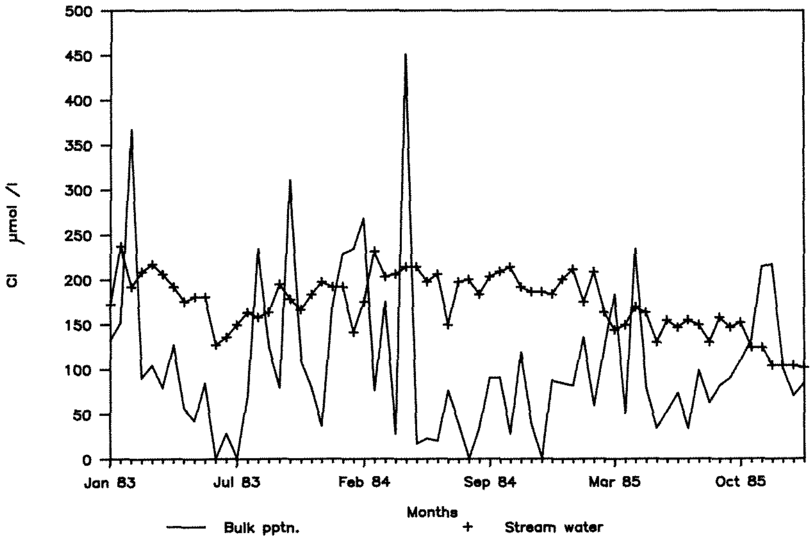

Fig. 1 *Variations in Cl concentration in bulk precipitation and stream water in the Cyff catchment.*

Cyff catchments than in the Hafren and Gwy. These solutes are positively correlated with each other (p = 0.01) and are negatively correlated with flow in all four streams, although the relationships with flow are not linear (Fig. 2), indicative of dilution with increasing discharge (Hem, 1970).

In all streams, baseflow is characterized by waters low in acidity and Al but enriched in Ca, Mg, Si and HCO_3 (Table 5 and Fig. 3). Baseflow concentrations of Ca, Mg and HCO_3 differ between the catchments in the order Hore ≈ Cyff > Gwy ≈ Hafren, reflecting:

(a) the major influence of mineral veins in the bedrock of the Hore and Cyff catchments on stream water chemistry; and

(b) the differing proportions of hill-top peat in the catchments.

Higher baseflow SO_4 concentrations in the Hore and Cyff can be related to known sulphide mineralization within the former catchment and may be indicative of unmapped sulphide veins in the Cyff. Baseflow Si concentrations are greater in the forest streams which suggests higher silicate weathering

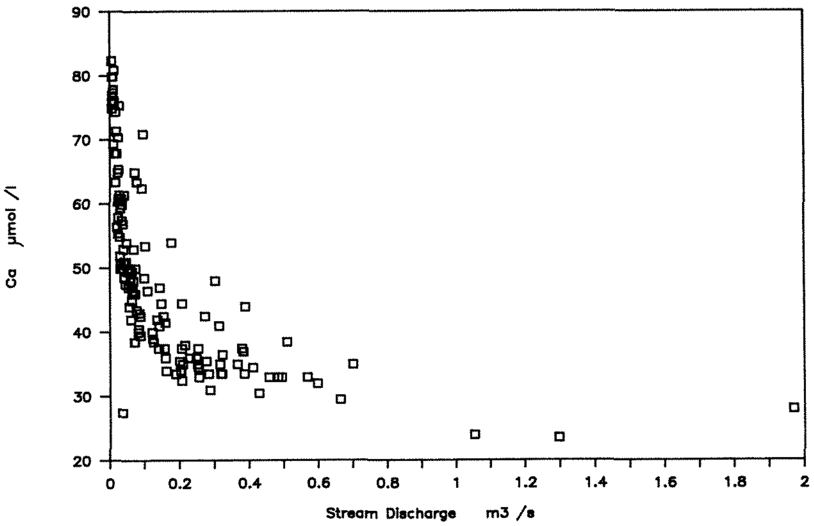

Fig. 2 Plot of stream Ca concentration versus instantaneous stream discharge for the Afon Cyff.

rates in the drift or bedrock of the forest catchments as noted by Williams *et al.* (1987). However, Si concentrations may be buffered by solubility controls involving crystalline or partially crystalline SiO_2. In this case, equilibrium Si concentrations could vary between 36 and 107 μmol l^{-1} depending on temperature and crystallinity (Casey & Neal, 1986). Thus Si concentrations cannot be used as a primary indicator of aluminosilicate weathering rates.

Storm flow chemistry shows more complex variation in that the behaviour of several ions differs between catchments. In the grassland catchments, Na and Cl concentrations decrease at high flows whereas the

***Table 5** Typical baseflow and stormflow stream chemistry for the Plynlimon catchments for the period January 1983 to December 1985*

	Baseflow				*Stormflow*			
	Cyff	*Gwy*	*Hafren*	*Hore*	*Cyff*	*Gwy*	*Hafren*	*Hore*
pH	*6.82*	*6.32*	*6.39*	*7.10*	*5.15*	*4.76*	*4.44*	*4.53*
H	*1*	*1*	*1*	*1*	*7*	*18*	*37*	*30*
Na	*179*	*166*	*177*	*196*	*148*	*126*	*190*	*213*
K	*2*	*1*	*2*	*3*	*4*	*3*	*4*	*3*
Ca	*73*	*29*	*29*	*101*	*29*	*14*	*19*	*24*
Mg	*55*	*35*	*34*	*53*	*32*	*23*	*32*	*34*
Al	*2*	*2*	*2*	*2*	*1*	*4*	*18*	*16*
Si	*51*	*54*	*76*	*78*	*34*	*28*	*50*	*57*
NO_3	*2*	*4*	*11*	*12*	*16*	*13*	*32*	*26*
SO_4	*46*	*37*	*30*	*48*	*46*	*25*	*56*	*60*
Cl	*183*	*170*	*181*	*203*	*169*	*136*	*220*	*242*
HCO_3	*117*	*27*	*29*	*178*	*3*	*2*	*3*	*2*
Na/Cl	*0.99*	*0.99*	*0.99*	*0.97*	*0.89*	*0.83*	*0.88*	*0.91*

Units: $\mu mol\ l^{-1}$

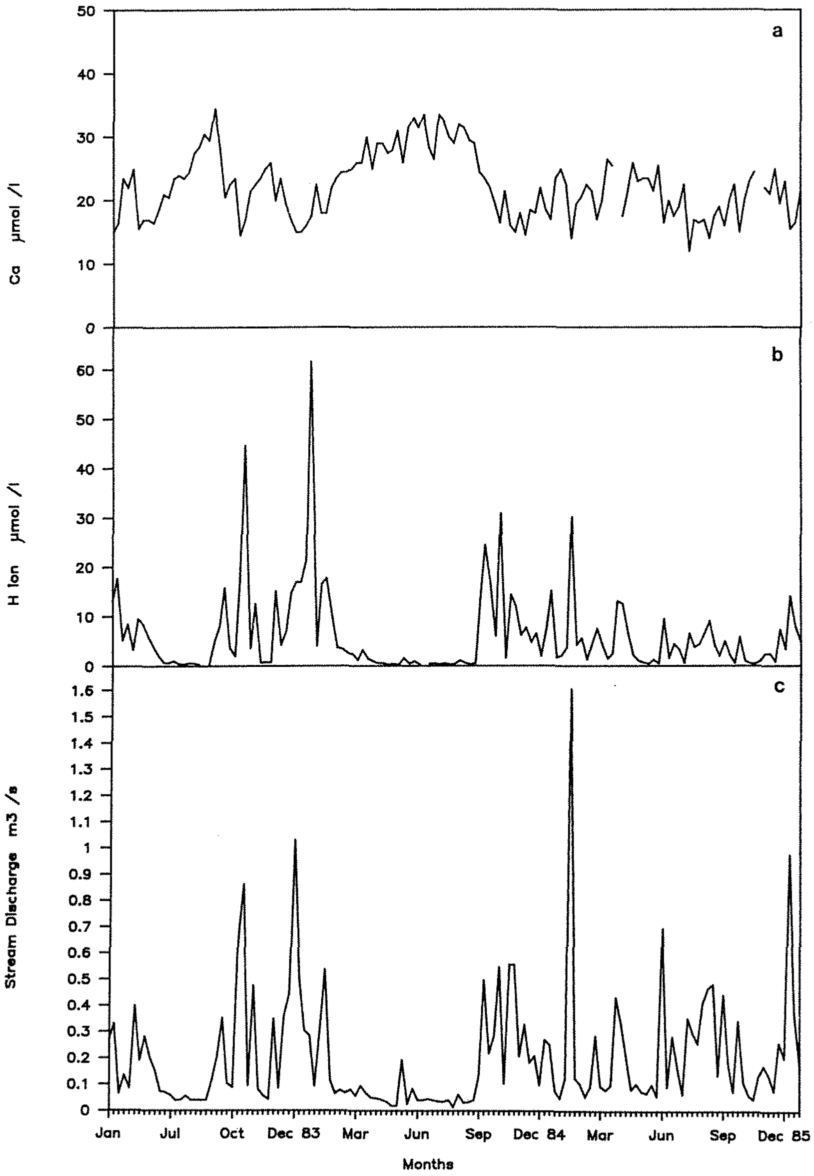

Fig. 3 Variations in stream water concentrations of (a) Ca, (b) H ion and (c) stream discharge in the Afon Gwy.

reverse is observed in the forest streams (Table 5). The variation of Cl in the streams is not matched by that of Na (Fig. 4). In all streams, the mean baseflow Na/Cl ratio is higher than in precipitation (0.99 compared with 0.80). As Cl is of atmospheric origin and behaves "conservatively", this suggests a weatherable source of Na within the drift or bedrock of the catchments. Under storm flow conditions, the ratio declines to and occasionally falls below that of incoming rainfall (Fig. 4), suggesting retention of Na relative to Cl in the soils of the

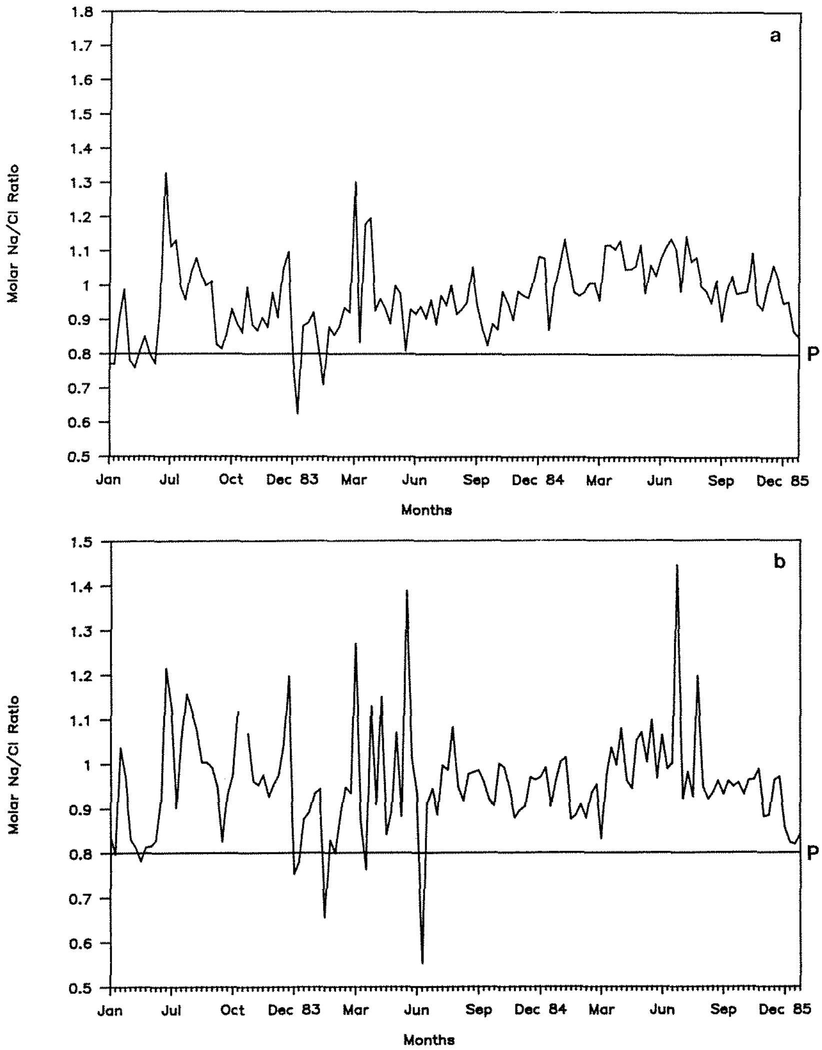

Fig. 4 Variations in stream water Na/Cl ratios for (a) the Afon Gwy and (b) the Afon Hafren. Mean ratio in precipitation denoted by line 'P'.

catchment (Neal *et al.*, 1986). Exchange of Na for H^+ in peats and peaty top soils has been proposed to explain episodic acidification of streams following large inputs of sea-salts to catchments (Skartveit, 1981; Langan, 1987). Long term acidification by this means seems improbable as soil retention of the exchanged Na is apparently short lived (Langan, 1987; Sullivan *et al.*, 1988).

In all streams, H^+ and Al concentrations increase with flow whilst Ca, Mg, Si and HCO_3 decrease. Storm flow acidity and Al concentrations are at least 1.5 and four times higher, respectively, in the forest streams. Storm flow SO_4, NO_3 and Cl concentrations are also greater in the forest streams. Indeed, in the grassland catchments, storm flow and baseflow SO_4

concentrations are very similar. In the Cyff and the Hore the total concentration of inorganic anions is lower under storm flow conditions than at baseflow due to depletion of HCO_3.

Storm flow pH and Ca concentrations are highest in the Cyff and storm flow K and NO_3 concentrations are also higher in this stream than in the Gwy. This suggests that runoff from the areas of improved land within the Cyff catchment contributes to stream chemistry particularly by buffering stream acidity.

DISCUSSION

Stream solute concentrations differ between forest and grassland catchments as a result of interactions in the vegetation canopy and soils and differences in catchment hydrology.

Vegetation canopy

Solute concentrations in throughfall beneath Sitka spruce and *Nardus-Festuca* grasses are greater than in bulk precipitation with the exception of NO_3 which is taken up by both vegetation canopies (Table 6). Sodium, Cl, SO_4, NO_3 and H^+ throughfall concentrations are higher under Sitka than *Nardus-Festuca* reflecting greater scavenging of fog and cloud water by the forest canopy and increased capture of aerosol particles by the trees (Lovett *et al.*, 1982; Unsworth, 1984). Dry deposition of gases onto and into leaves will also occur. For nitrogen gases, dry deposition will be greater to the forest canopy, whereas SO_2 dry deposition will be similar for both vegetation canopies (Fowler & Cape, 1989). Evaporative moisture loss (interception loss) from the vegetation canopies will further enhance solute concentrations in throughfall relative to rainfall and this effect will be more pronounced in the forest (Reynolds *et al.*, 1988). Canopy leaching will also increase throughfall concentrations of ions such as Ca and K, although its significance for other ions, particularly SO_4, is still debated (Cape *et al.*, 1987; Lindberg *et al.*, 1988).

Soil waters

Grassland and forest soil water chemistry at Plynlimon has been discussed in detail elsewhere (Reynolds *et al.*, 1988; Neal *et al.*, 1989), so that only a summary is presented here. Soil water concentrations of SO_4, Cl, Al, Na, Ca and Si are greater in the forest compared with the grassland soils (Table 7). The largest difference in H^+ is observed in the Oh horizons whereas the difference in Al concentrations between the two sites increases with depth.

Higher SO_4 and Cl concentrations in the forest soil waters reflect the increased concentration of these solutes in throughfall. Increased mineralization of organic S compounds, leading to higher soil water SO_4 concentrations, may also occur in the drier forest soils. The lower NO_3 levels in the forest

Table 6 *Volume weighted means and ranges (in brackets) of solute concentrations in bulk precipitation and throughfall at Plynlimon*

	pH	*H*	*Na*	*K*	*Ca*
Bulk precipitation	*4.63* *(3.64 - 6.38)*	*21* *(1 - 229)*	*85* *(1 - 361)*	*2* *(<1 - 17)*	*4* *(<1 - 40)*
Throughfall (Nardus-Festuca)	*4.62* *(4.30 - 5.32)*	*24* *(5 - 50)*	*94* *(13 - 305)*	*38* *(5 - 274)*	*15* *(5 - 51)*
Throughfall (Sitka spruce)	*4.52* *(3.74 - 5.90)*	*30* *(1 - 182)*	*128* *(39 - 831)*	*43* *(15 - 427)*	*17* *(6 - 100)*

	Mg	NH_4	NO_3	SO_4	*Cl*
Bulk precipitation	*10* *(<1 - 42)*	*17* *(<5 - 200)*	*12* *(<1 - 129)*	*21* *(<9 - 100)*	*106* *(3 - 451)*
Throughfall (Nardus-Festuca)	*18* *(7 - 75)*	*10* *(<5 - 43)*	*4* *(<1 - 25)*	*27* *(<9 - 88)*	*124* *(40 - 423)*
Throughfall (Sitka spruce)	*20* *(7 - 181)*	*16* *(<5 - 599)*	*10* *(<1 - 264)*	*54* *(15 - 406)*	*152* *(40 - 846)*

Units: All solutes in $\mu mol\ l^{-1}$
Sampling period: 31 January 1984 - 30 December 1985 except Nardus-Festuca throughfall: 9 October 1984 - 17 December 1987

Al: below detection limit (<2 $\mu mol\ l^{-1}$*) in precipitation and throughfall*

Table 7 *Arithmetic mean solute concentrations (± standard error) in soil waters under grassland and forest at Plynlimon*

	Grassland			*Forest*		
	Oh	*Eag*	*Bs*	*Oh*	*Eag*	*Bs*
H	*77 ± 4*	*55 ± 4*	*15 ± 1*	*139 ± 5*	*79 ± 3*	*48 ± 4*
Al	*10 ± 1*	*18 ± 1*	*44 ± 4*	*46 ± 4*	*132 ± 4*	*162 ± 5*
Na	*100 ± 8*	*187 ± 15*	*173 ± 11*	*112 ± 7*	*213 ± 11*	*270 ± 10*
K	*8 ± 2.0*	*4 ± 0.4*	*4 ± 0.4*	*2 ± 0.6*	*3 ± 0.4*	*5 ± 0.5*
Ca	*7 ± 0.5*	*10 ± 0.4*	*7 ± 0.3*	*15 ± 1*	*56 ± 3*	*46 ± 3*
Mg	*20 ± 2*	*22 ± 1*	*20 ± 1*	*30 ± 3*	*53 ± 2*	*57 ± 2*
NH_4	*<5*	*<5*	*<5*	*8 ± 3*	*<5*	*<5*
Si	*18 ± 1*	*42 ± 2*	*36 ± 2*	*30 ± 3*	*54 ± 3*	*55 ± 2*
SO_4	*68 ± 10*	*87 ± 5*	*71 ± 5*	*108 ± 12*	*159 ± 10*	*206 ± 7*
Cl	*124 ± 12*	*209 ± 18*	*184 ± 15*	*135 ± 10*	*233 ± 16*	*327 ± 22*
NO_3	*29 ± 6*	*39 ± 5*	*28 ± 4*	*13 ± 2*	*11 ± 3*	*1 ± 1*
pH	*4.11*	*4.26*	*4.36*	*3.86*	*4.10*	*4.32*
Org^-	*50*	*30*	*35*	*88*	*139*	*56*

Sampling period: Oh horizon 9 October 1984 - 30 December 1985, mineral soil 3 January 1984 - 30 December 1985
Units: $\mu mol\ l^{-1}$
Organic anions (Org^-*): estimated as difference between mean of cation sums and mean of inorganic anion sums*
Units: $\mu eq\ l^{-1}$

are probably due to greater utilization of N by the trees, compared with grasses, and different nitrification rates.

Differences in base cation and H^+ concentrations between grassland and forest soils are partly due to different inputs from throughfall. For K and Ca, biological uptake and cycling are also significant. The Oh horizon is also a major source of H ions. Organic anion concentrations (Table 7) indicate that organic acid production occurs in both systems being greatest in the forest soils. Ammonium is generally below the detection limit (5 μmol l^{-1} NH_4) in the soils and may be lost from solution by nitrification, direct plant uptake and adsorption onto soils.

Differences in soil water concentrations of Al and Si are ultimately related to different rates of release from primary aluminosilicates via weathering. Soil water Si concentrations may, however, be buffered by SiO_2 solubility controls. None of the soil waters is in equilibrium with any single form of $Al(OH)_3$ or $Al(OH)SO_4$ (Neal *et al.*, 1989). Cubic relationships between Al^{3+} and H^+ are not observed and the slope of the Al^{3+}/H^+ plot varies between soil horizons (Neal *et al.*, 1989). This may be due to exchange reactions which occur at surfaces selective to H^+ and Al^{3+} with the other cations in solution but where no H^+/Al^{3+} exchange occurs. Weathering reactions may be involved so that ion exchange explains episodic fluctuations with depleted exchange sites being replenished by mineral weathering during more stable periods.

Soil - stream water relationships

The soil hydrology of the Upper Wye catchments, described in some detail by Knapp (1970) and Bell (1972), is complex and will only be outlined here. Hill-top and interfluve peats are an important source of water to the grassland streams, either directly in source areas, or indirectly via first order streams and perennial soil pipes. These peats are one of the main contributors of water to the baseflow component of the main channel hydrograph (Bell, 1972). Drainage water from hill-top peat is acid (pH 3.85) but contains less Ca, Si, SO_4 and NO_3 than baseflow in the unmineralized, semi-natural grassland Gwy catchment (Tables 5 and 8). Thus baseflow comprises a mixture of peat water and high pH "groundwater", enriched in Ca, Si and HCO_3, not sampled in this study. Variations in the composition of "groundwater" will reflect the different degree of bedrock mineralization in the catchments.

Baseflow NO_3 concentrations cannot be explained in terms of simple mixing. Peat water has a lower NO_3 content than baseflow and it is unlikely that groundwater in this area contains significant amounts of NO_3. Rather, it is probable that dissolved organic N (DON), not determined in this study, in peat water is converted to NO_3 either *en route* to or in the stream channel. Data from preliminary studies indicate that DON concentrations in water from organic rich soil horizons are *c.* 70 μmol l^{-1} N. Stream water concentrations for the Upper Wye catchment as a whole are between 9 and 11 μmol l^{-1} N (Roberts *et al.*, 1983). Stream NO_3 concentrations also vary cyclically through the year with winter maxima and summer minima (Fig. 5) and are negatively correlated with soil temperature (p = 0.01). Taking soil temperature as an index of soil biological activity, it is probable that available NO_3 in the soil is utilized by plant growth in the summer, but is available for

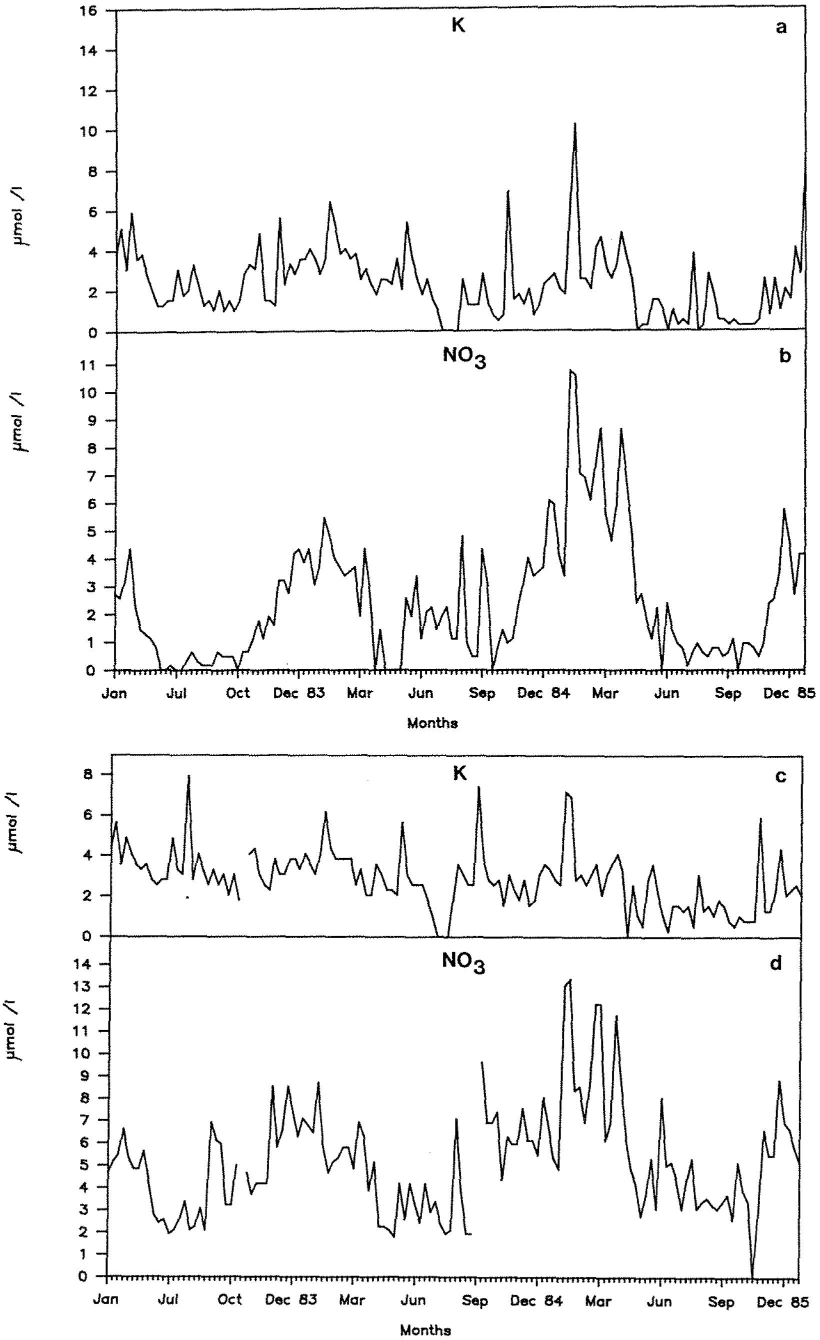

Fig. 5 *Variations in stream water concentrations of K and* NO_3 *in the Afon Gwy (a & b) and the Afon Hafren (c & d).*

leaching to the stream in the absence of plant uptake in the winter. Potassium follows a similar pattern of variation in the grassland streams (Fig. 5) with significant negative correlations ($p = 0.01$) with soil temperature. In the forest streams, the pattern is more damped (Fig. 5), and there are no significant correlations between K and soil temperature.

During storms, a variety of flow pathways operate in the soils, of which throughflow at the base of the podzol Oh horizon and drainage from naturally occurring soil pipes (perennial and ephemeral) are probably the most important (Knapp, 1970; Bell, 1972; Gilman & Newson, 1980). Although some of this water will pass through valley bottom peats before entering the stream, storm flow chemistry can be thought of in terms of mixing "groundwater" with peat drainage, throughflow and pipe flow.

The spatial variability in the composition of throughflow and ephemeral pipe flow has not been generally established. Data for one ephemeral pipe, draining the area of semi-natural grassland for which soil water data are available, are shown in Table 8. Assuming that throughflow chemistry is similar to Oh/Eag horizon soil waters from the grassland stagnopodzols (Table 7), then pipe flow and throughflow can contribute to the increase in stream water H^+, Al, K and NO_3 concentrations observed during storms. In contrast, concentrations of Si, Ca, Mg, Na, Cl and SO_4 are generally lower in pipe flow and throughflow than in either baseflow or storm flow.

The soil hydrology of the forested parts of the Hafren and Hore catchments has been altered from the semi-natural state by site preparation and tree growth. Prior to planting, much of the area was ploughed and drainage ditches were dug. The main impact of this is to allow direct and rapid transport of soil-derived water to the main stream channel during storms. This process is assisted by the development of drying cracks and root

***Table 8** Arithmetic mean and range of pH and solute concentrations in soil pipe and peat drainage water*

	Soil pipe		*Peat drainage*	
	mean	*range*	*mean*	*range*
pH	*3.95*	*3.67 - 4.39*	*3.85*	*3.52 - 4.14*
H	*12*	*41 - 214*	*141*	*72 - 302*
Na	*128*	*44 - 235*	*165*	*83 - 470*
K	*7*	*<1 - 26*	*4*	*1 - 26*
Ca	*5*	*2 - 14*	*11*	*4 - 45*
Mg	*16*	*3 - 44*	*29*	*12 - 145*
Al	*4*	*<2 - 15*	*<2*	*<2*
Si	*14*	*5 - 31*	*9*	*<2*
NO_3	*9*	*1 - 71*	*1*	*<1 - 17*
SO_4	*30*	*9 - 78*	*21*	*<9 - 104*
Cl	*144*	*45 - 339*	*197*	*68 - 451*
HCO_3	*<1*	*<1*	*<1*	*<1*

Units: $\mu mol\ l^{-1}$
Sampling period: Soil pipe 9 September 1980 - 26 February 1985
Peat drainage 8 January 1980 - 31 December 1984

channels within the soil as a direct result of increased interception losses and root development with tree growth. These changes in soil hydrology facilitate the input to the streams of acid water derived from the near surface soil horizons, increasing stream acidity at high flows. The precise chemistry of the soil derived waters will vary with soil type and the detailed hydrological pathway from soil to stream. For the stagnopodzols, water with high Al, SO_4 and Cl concentrations (Table 7) is drawn from both the near surface organic and mineral horizons (Oh and Eag) and moves down furrows and ditches floored and walled by mineral material from which further Al may be acquired (Reynolds & Hughes, 1989). Storm flow concentrations of these solutes in the forest are higher than in the grassland catchments, reflecting differences in soil water chemistry.

The increase in stream NO_3 concentrations in the forest during storms is not adequately explained by mixing stagnopodzol soil waters with baseflow, as soil water NO_3 concentrations are lower than those in stream water. This suggests that there is either a source of NO_3-rich water not sampled within the catchment or that DON is converted to NO_3 in the stream or along plough furrows and drainage ditches. This has yet to be confirmed directly. Preliminary data for DON in Oh horizon forest soil waters indicated concentrations of *c.* 90 μmol l^{-1} N. Mean annual streamwater concentrations of DON for the Severn catchment as a whole were 7–9 μmol l^{-1}N (Roberts *et al.*, 1983). As in the grassland streams, NO_3 varies over an annual cycle (Fig. 5) and is negatively correlated with soil temperature ($p = 0.01$).

Catchment solute fluxes

Net stream solute losses (bulk precipitation input – stream output) were calculated for individual years and the mean and range over the three-year period are presented in Table 9. Inputs were calculated as the product of the annual rainfall weighted mean bulk precipitation chemistry and annual rainfall. Stream solute loads for H^+, Ca, Mg, HCO_3 and Si were determined using simple rating curves of the form $\log_{10} C = a + b \log_{10} Q$ (where C = solute concentration, Q = stream discharge and a and b are constants) in conjunction with 15-min interval stream discharge data. For each catchment, a single curve was constructed for each ion for the entire three-year period. Although errors may be introduced by assuming that concentration/flow relationships are consistent between years, a larger number of data points will increase the representativeness of the rating equation and reduce the uncertainty in the coefficients. The rating equations were all significant at $p = 0.01$ and were adjusted for statistical bias (Ferguson, 1986).

In the absence of simple concentration/discharge relationships, solute loads for NO_3, SO_4, Cl, Na, K and Al were determined using the following expression: $L = C' \bar{Q} T$ where L = solute load, C' = discharge weighted mean concentration, $\bar{Q}$ = mean discharge calculated from the 15-min flow data and T = time period over which the load is estimated.

Several sources of error can be identified in solute load estimates but these are not easily quantified without detailed studies (e.g. Walling, 1978). A

Table 9 *Arithmetic means (and range in brackets) of net solute fluxes from the Plynlimon catchments from 1983–1985 inclusive*

	Cyff	*Gwy*	*Hafren*	*Hore*
Na	-23.6 (-22.1 to -24.3)	-25.0 (-22.0 to -26.6)	-33.1 (-25.1 to -42.8)	-39.6 (-33.5 to -46.5)
K	-1.1 (-0.3 to -2.0)	-1.1 (-0.2 to -2.2)	-0.8 (-0.7 to -1.0)	-0.5 (-0.5 to -0.6)
Ca	-23.6 (-20.7 to -25.5)	-10.2 (-8.8 to -11.2)	-11.8 (-10.5 to -13.3)	-18.0 (-15.5 to -20.3)
Mg	-11.1 (-9.0 to -12.6)	-7.5 (-5.7 to -8.9)	-8.7 (-7.3 to -11.1)	-9.2 (-6.8 to -11.7)
Al	-0.5 (-0.4 to -0.5)	-1.1 (-0.6 to -1.7)	-5.4 (-4.3 to -6.7)	-5.5 (-3.6 to -6.8)
Si	-20.3 (-17.8 to -22.4)	-19.3 (-17.2 to -21.2)	-28.7 (-26.1 to -31.5)	-26.6 (-22.2 to -28.4)
NH_4	+7.0 +5.1 to +9.3)	+7.1 (+5.2 to +9.4)	+6.9 (+5.1 to +8.9)	+7.3 (+5.3 to +9.6)
NO_3	+1.4 (-1.4 to +4.2)	-1.0 (-6.1 to +2.4)	-14.1 (-12.8 to -15.1)	-8.3 (-7.6 to -9.8)
SO_4	-41.1 (-30.2 to -51.0)	-21.3 (-15.7 to -31.5)	-36.1 (-27.4 to -49.2)	-48.8 (-42.5 to -53.0)
Cl	-29.6 (-13.7 to -43.8)	-31.5 (-20.2 to -43.8)	-43.6 (-38.6 to -51.0)	-54.2 (-47.5 to -66.4)
HCO_3	-19.4 (-18.2 to -20.3)	-8.8 (-8.3 to -9.1)	-5.0 (-4.9 to -5.3)	-13.6 (-12.1 to -16.2)
H	+0.43 (+0.38 to +0.47)	-0.34 (-0.04 to -0.83)	-1.25 (-0.94 to -1.82)	-2.01 (-0.92 to -3.75)

Units: $kg\ ha^{-1} year^{-1}$

wide range of stream flows was encountered during the three-year weekly sampling programme; however, the number of samples at high flow is limited. Thus, the rating curve estimates assume that concentration/discharge relationships established for the sample data hold for higher unsampled flows. Any deviations in these relationships will introduce errors leading to under- or over-estimates of the solute load. The inverse correlations between concentration and discharge for Ca, Mg, Si and HCO_3 mean, however, that transport is relatively uniform over time making unrepresentative rating curves unlikely. For H^+, which is positively correlated with discharge, transport at high flows will be more important. Estimates from average instantaneous loads ($\bar{C}'\ \bar{Q}$) are more subject to sampling variability than rating curves but give an unbiassed estimate of solute load (Ferguson, 1987).

The net solute fluxes cannot be regarded as nutrient "budgets" as factors such as fertilizer inputs and biomass storage and turnover have not been estimated. They are useful for comparison and point to processes operating within the catchments, supporting the earlier consideration of solute concentrations. Differences in the net stream fluxes between the catchments do not simply reflect variations in bulk precipitation inputs as these are broadly similar across the sites. The range in annual fluxes is large for several solutes (Table 9), reflecting the desirability of long term experiments. For example, the recent analysis of 25 years of data from Hubbard Brook (Driscoll *et al.*, 1989) would suggest that studies of at least five years, and preferably more than ten years duration, are necessary to accommodate the effects on catchment solute fluxes of such factors as climatic variation and changes in industrial emissions.

The export of Cl exceeds precipitation input for all the catchments. Assuming conservative behaviour, the Cl imbalance represents additional atmospheric inputs (occult and aerosol deposition) not collected in precipitation samples. The larger net flux from the forest indicates more efficient atmospheric scavenging by the trees compared with the grass canopy. The aerosol component in the net fluxes of the other sea-salt ions (Na, Mg, K) has been estimated from the product of the net Cl flux and the ionic ratios to Cl in precipitation (Wright & Johannessen, 1980). The revised fluxes are shown in Table 10.

For Na, the revised fluxes (Table 10) are greatest for the forest catchments. This may result from more intense mineral weathering in the forest, Na being found in feldspars and micas within the bedrock (Evans, 1973). This is supported by larger net losses of Si and Al in the forest streams. However, the revised Mg fluxes are very similar for the Gwy and the two forest sites. The main weathering reaction during pedogenesis in this area is chlorite breakdown accompanied by the release of Mg (Adams *et al.*, 1971). Thus a larger Mg flux would be anticipated where weathering was more intense. It is possible that biomass immobilization of Mg is greater in the forest or that chlorite has largely disappeared from the main zones of water movement within the catchments. The greater net loss of Mg from the Cyff can be attributed to release from Mg-rich limestone applied during agricultural improvement (Hornung *et al.*, 1986). The effects of the lime and calcite mineralization within the Cyff are also reflected in the large Ca, HCO_3 and SO_4 fluxes, and the net accumulation of protons. The SO_4 flux will also be influenced by fertilizer inputs. The large fluxes of Ca, HCO_3 and SO_4 from the Hore are also attributable to bedrock mineralization. Atmospheric scavenging will supplement the SO_4 flux in the Hore and is also reflected in the greater loss of SO_4 from the Hafren compared with the Gwy catchment.

The revised budgets for K (Table 10) suggest adequate K supply to the grassland system from both internal and external sources as net losses occur. There is accumulation or very slight leakage from the forest, possibly reflecting a greater biomass demand.

The nitrogen net solute fluxes are incomplete as there are no estimates of DON fluxes. The net accumulation of NH_4 is determined solely by bulk precipitation inputs and represents a minimum figure. Estimates for Kielder

Table 10 *Net stream solute fluxes of Na, Mg and K adjusted for aerosol inputs*

	Na	*Mg*	*K*
Cyff	*-8.2*	*-9.1*	*-0.6*
Gwy	*-8.6*	*-5.4*	*-0.6*
Hafren	*-10.4*	*-5.8*	*-0.1*
Hore	*-11.4*	*-5.6*	*+0.4*

Units: kg $ha^{-1} year^{-1}$

forest in northern England suggest that dry deposition of NH_3 can contribute up to two thirds of the NH_x-N flux to forest canopies and about 30% of the flux to grassland (Fowler & Cape, 1989). Similarly dry deposition of HNO_3 and NO_2 can more than double the NO_3-N flux measured as wet (bulk) deposition and increases the input to grass by *c.* 40% (Fowler & Cape, 1989). These figures cannot be applied directly to Plynlimon due to the 1000 mm difference in rainfall between the two sites, although atmospheric concentrations of NH_3 and NO_2 and concentrations of dissolved NO_3 and NH_4 in bulk precipitation are very similar. The increased N deposition to the forest is probably reflected in the larger net NO_3 fluxes, although rates of N immobilization, nitrification/denitrification will differ between the grassland and forest systems.

Conversion of NH_4 to NO_3 will generate H^+ ions contributing to the larger net fluxes of H^+ in the forest compared with the grassland streams. This will be supplemented by increased atmospheric scavenging and organic acid production within the forest soils. The external and internal H^+ sources appear to more than compensate for any increase in weathering intensity within the forest catchments.

CONCLUSIONS

There is a pronounced maritime influence on stream water chemistry at Plynlimon with Na and Cl as the major ions in solution. Baseflow is characterized by waters of high pH enriched in HCO_3, Ca, Mg and Si. Differences in baseflow chemistry between the streams reflect the varying extent of bedrock mineralization within the catchments.

Storm flow is acid and Al bearing. In the forest streams storm flow H^+ concentrations are approximately 1.5 and Al four times higher respectively, than in the grassland streams. Changes in catchment hydrology resulting from site preparation and tree growth facilitate the transfer of acid, Al-rich soil water to streams during storms.

Evaporative concentration of solutes on needle surfaces and increased atmospheric scavenging by the tree canopies result in higher throughfall, soil water and stream water concentrations and catchment losses of Na, Cl and SO_4 at the forest sites. Mineral veins within the catchments can, however, modify the stream chemical response to afforestation by buffering stream acidity and increasing SO_4 concentrations.

In both grassland and forest systems the observed stream chemistry can be explained by mixing waters derived from different parts of the catchments depending on the prevailing hydrological conditions. However, the chemistry of NO_3 is not adequately explained by water mixing processes. Conversion of DON to NO_3 may be significant within the stream channel or as water is transferred from soils to the stream.

Net stream fluxes for Al, Si and Na suggest that mineral weathering is more intense within the forest catchments. Larger net fluxes of H^+ indicate that consumption of H^+ by weathering in the forest is more than balanced by H^+ from internal and external sources. Higher net fluxes of NO_3 reflect the higher N deposition to the forest compared with the grassland catchments although relative differences in DON fluxes and rates of N immobilization, nitrification and denitrification must also be considered.

Acknowledgements The authors would like to thank J D Roberts and colleagues of the ITE Chemical Service, Merlewood, for performing anion and Si analyses. Mrs S Hill of the Institute of Hydrology, Plynlimon, and Mrs E Peters of ITE, Bangor, are also thanked for assistance with routine water sampling and analysis respectively. Mrs A Roberts (Institute of Hydrology) is thanked for help in obtaining the catchment hydrometric data. The study was part funded by the Department of the Environment and the Welsh Office.

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Received 28 June 1988; accepted 28 March 1989