

Biogeochemical controls on river water quality in a forested drainage basin, Warwickshire, UK

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ABSTRACT Spatial variations in river water quality are frequently attributed to differences in vegetation type and density at the mesoscale and microscale, but associations between temporal variations in ecosystem dynamics and river water quality are poorly documented. This paper attempts to identify direct links between monitored hill-slope nutrient fluxes and stream solute behaviour over a 19 month period. It is suggested that temporal variability in throughfall chemistry and nutrient assimilation in vegetation and soils are not clearly reflected in seasonal river water quality behaviour.

*Controles biogéochimiques sur la qualité de l'eau de
rivière en zone forestière, Warwickshire, RU*

RESUME Les variations spatiales de la qualité de l'eau des rivières sont fréquemment attribuées aux différences de types et de densité du couvert végétal à l'échelle meso ou micro. Il existe peu d'informations sur les associations entre les variations temporelles des écosystèmes et la qualité de l'eau des rivières. La présente communication s'efforce d'identifier les liens directs entre l'étude des flux des substances nutritives de versants et les matières solubles des ruisseaux sur une période de 19 mois. Il apparaît que la variabilité temporelle de la chimie des flux et l'assimilation des substances nutritives dans les sols et dans la végétation ne se reflètent pas directement dans le comportement saisonnier de la qualité de l'eau des rivières.

INTRODUCTION

River water quality reflects the chemistry and volume of precipitation entering a drainage basin, the interaction of ecological, pedological and geochemical processes within the drainage basin and the excess of runoff over rainfall capable of transporting material in solution to river channel networks. The link between the atmosphere, biosphere

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and lithosphere is provided by hydrological pathways which control the fluxes of water and dissolved material through the system. Such an explanation of river water chemistry is encompassed in many recent studies of biogeochemical processes in forested ecosystems (cf. Likens *et al.*, 1977; Verstraten, 1977; Reid *et al.*, 1981, Foster & Grieve, 1983). Many authors have identified and quantified temporal variations in throughfall chemistry and nutrient uptake by growing vegetation; in the return of solutes via litterfall and decomposition, and in the nutrient content of soils in isolation (e.g. Carlisle *et al.*, 1966; Gosz *et al.*, 1972; Frankland, 1976; Burt, 1979; Weaver & Forcella, 1979). Direct links between temporal variations in these components and their consequent effect on river water quality have yet to be adequately determined. The apparent complexity of factors governing water chemistry behaviour is not represented in models relating annual or storm-period solute concentrations to instantaneous stream discharge. These simple models often explain a high proportion of variance in the data, although seasonal or nonlinear rating curves may significantly increase levels of explained variance in some cases (Gregory & Walling, 1973; Foster, 1978, 1980). Successful application of such models may imply that direct interactions between hillslope biochemical processes and the streamflow output do not occur over relatively short time periods unless rapid and devastating ecosystem change, such as forest clearance, are identified (e.g. Hornbeck *et al.*, 1970). For these dramatic changes or in cases where spatial variations in background water chemistry may be directly associated with the type and density of vegetation cover (cf. Douglas, 1972; Walling & Webb, 1975), the most important impact may only relate directly to a modification of hydrological pathways and the relative balance of erosion and denudation.

The present study, which is part of a small drainage basin experiment designed to trace sediment and solute pathways in a forested ecosystem, attempts to identify direct links between hillslope biogeochemical processes and the quality of river water. The investigation was prompted by previous work (Foster & Grieve, 1983) which has shown the general inadequacy of solute discharge rating curves for predicting river water solute levels.

EXPERIMENTAL AREA AND METHODOLOGY

The experimental area (Fig.1) comprises a small second order drainage basin in north Warwickshire which has been described in detail elsewhere (Dearing *et al.*, 1982; Foster & Grieve, 1983). Data reported in this paper derive from hillslope investigations conducted at site 2 and from river water quality monitoring adjacent to site 1 (Fig.1). The sub-basin to the south and west of the central coniferous plantation is underlain by a variable thickness of boulder clay which overlies the Keele Beds of Upper Carboniferous age. This series is dominated by sandstone and shales, although thin bands of Spirorbis limestone have also been identified by the Geological Survey. Limited outcrops of these deposits in the local area have precluded a comprehensive mineralogical assessment, but qualitative X-ray fluorescence analyses highlight the most important chemical components of the bedrock (Table 1). Soils of the area have been mapped by Whitfield &

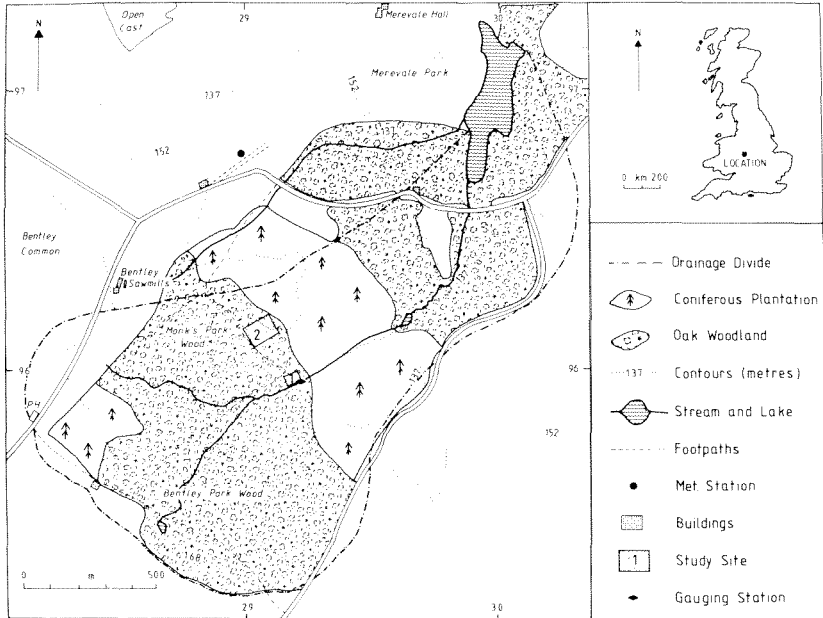


FIG.1 Location of the experimental drainage basin and sampling sites.

TABLE 1 Qualitative X-ray fluorescence analysis of Keele Bed outcrops

	Sandstone	Shale
Major element	K, Si, Ti, Fe	Ca, Ti, K, Fe
Minor element	Al, Ba, Ca	Si, Al
Trace element*	Zr, Rb	Ba, Zr, Rb

*Other trace elements include Mg, P, S, Cl, Cr, Mn, Co, Ni, Cu and Zn.

Beard (1980) and comprise a Melbourne/Bardsey transition series. The major particle size, mineralogical and chemical properties of samples collected from site 2 are presented in Table 2. The deciduous woodland is dominated by Oak (*Quercus petraea*), planted in c. 1840, with an understorey of bracken (*Pteridium aquilinum*). Silver birch (*Betula pendula*), hazel (*Corylus avellana*) and alder (*Alnus glutinosa*) are also found in the basin, the latter usually confined to narrow flood plain sites where the ground flora is also more diverse.

Detailed analysis of solute pathways was undertaken at site 2 by collection of water, soil and vegetation samples for chemical analysis. Background precipitation chemistry data were obtained from analysis of samples collected weekly at a meteorological station to the north of the basin (Fig.1), and throughfall samples below the oak and bracken canopies were collected in randomly located and orientated 1-m long plastic gutters (Fig.2). Bulked soil samples were collected

TABLE 2 Soil characteristics at site 2

Horizon	Ah	B	B/C
Depth (cm)	10-16	16-56	56-140
Organic carbon (%)	5.70	1.00	1.90
pH(H ₂ O) 1:2.5	3.70	4.15	-
pH (CaCl ₂) 1:2.5	3.05	3.25	-
Dry bulk density (g cm ⁻³)	1.25	1.22	-
Moisture (% dry weight)	45.20	21.70	-
Pore volume (%)	54.00	55.10	-
Particle size (%)			
2 mm-600 µm	2.12	1.62	1.36
600-200 µm	14.84	16.19	27.15
200-60 µm	43.63	30.04	28.87
60-2 µm	21.71	32.80	29.79
< 2 µm	17.70	19.35	12.83
Cation exchange			
Capacity (me (100 g) ⁻¹)	27.80	10.40	6.0
Mineralogy (%):			
kaolinite	25-50	> 50	10-25
mica	25-50	25-50	> 50
chlorite	10-25	10-25	5-10
smectite	5-10	5-10	10-25
class	mixed	kaolinitic	mixed
Chemistry (% dry weight):			
N x 10 ⁻³	99.00	45.00	13.00
P x 10 ⁻³	30.00	9.00	0.15

from the southern section of the hillslope plot at fortnightly intervals. Litterfall collectors of 1 m² area were randomly located beneath the oak canopy and sampled monthly. The oak canopy, bracken fronds and rhizomes were harvested at the same sampling frequency for biomass calculations. Detailed hydrological studies in the same area have included construction of throughflow pits, continuous monitoring of soil moisture tension at 22 locations, weekly monitoring of borehole levels and drainage channel flow and periodic infiltration and dye tracing experiments (Fig.2). In addition to hillslope studies, river water samples were collected at 8-h intervals from the main stream adjacent to hillslope site 1.

All water samples following filtration were analysed by flame photometry, autoanalysis, colorimetry and atomic absorption spectrophotometry. Vegetation samples were digested to provide suitable material for total chemical analysis, and soil samples subjected to soluble and exchangeable extractions as described by Hesse (1971). Although analyses of specific conductance, pH and the concentrations of Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺, NO₃⁻, NO₂⁻, Cl⁻ and PO₄³⁻ have been undertaken, this paper concentrates on the biogeochemical processes involved in the cycling of nitrogen, phosphorus, potassium and magnesium only. Input-output budgets for the basin have been reported elsewhere (Foster & Grieve, 1983), and show that approximately one third of incoming precipitation (635 mm) is lost as runoff. Over 90%

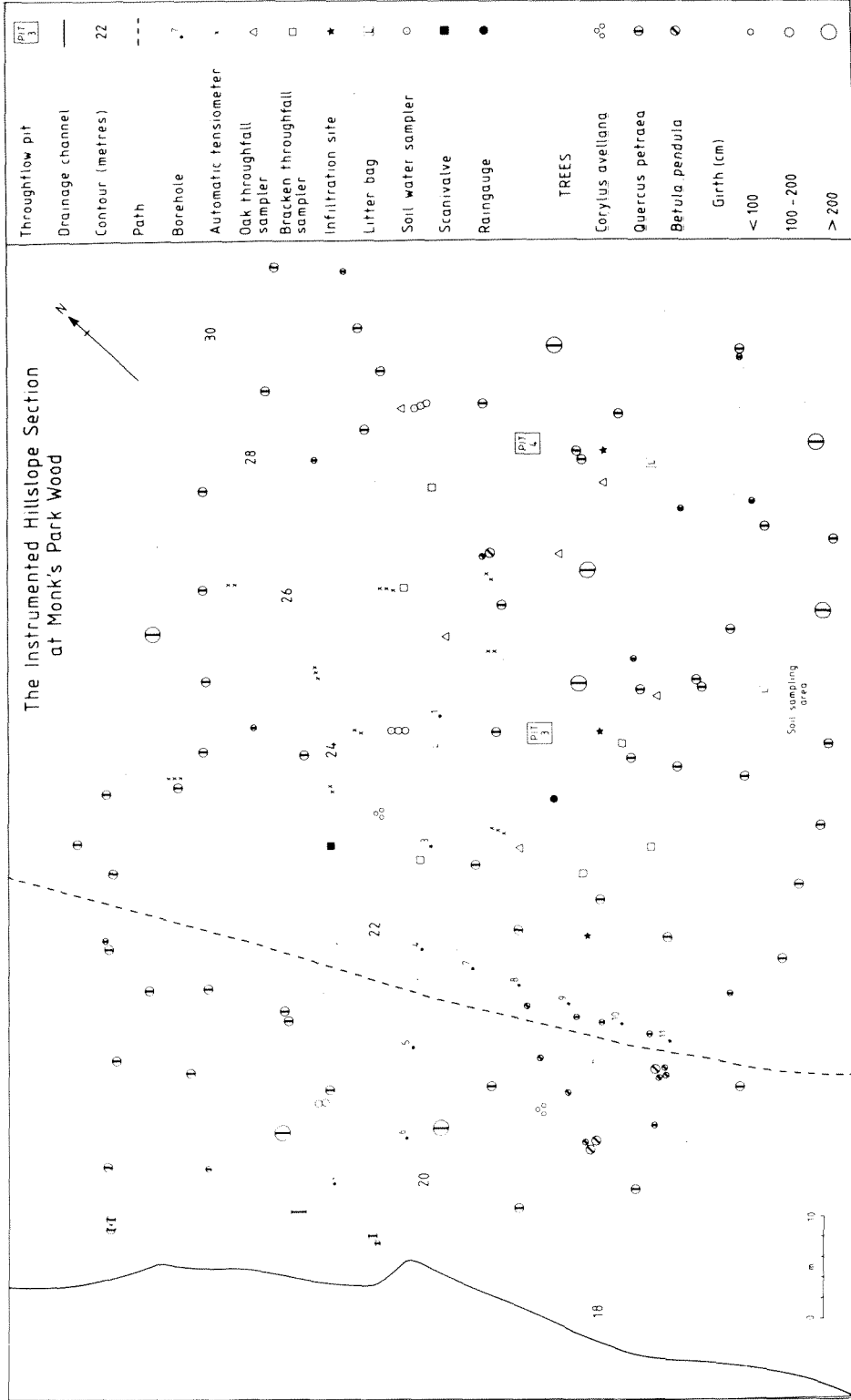


FIG.2 Details of instrumentation and sampling sites on the monitored hillslope.

of total steam output comprises dissolved material, and these losses are dominated by Ca^{2+} and HCO_3^- rich waters. It has also been shown that K^+ , NH_4^+ , NO_3^- and H^+ are a net gain to the basin as a whole and are derived directly from precipitation inputs.

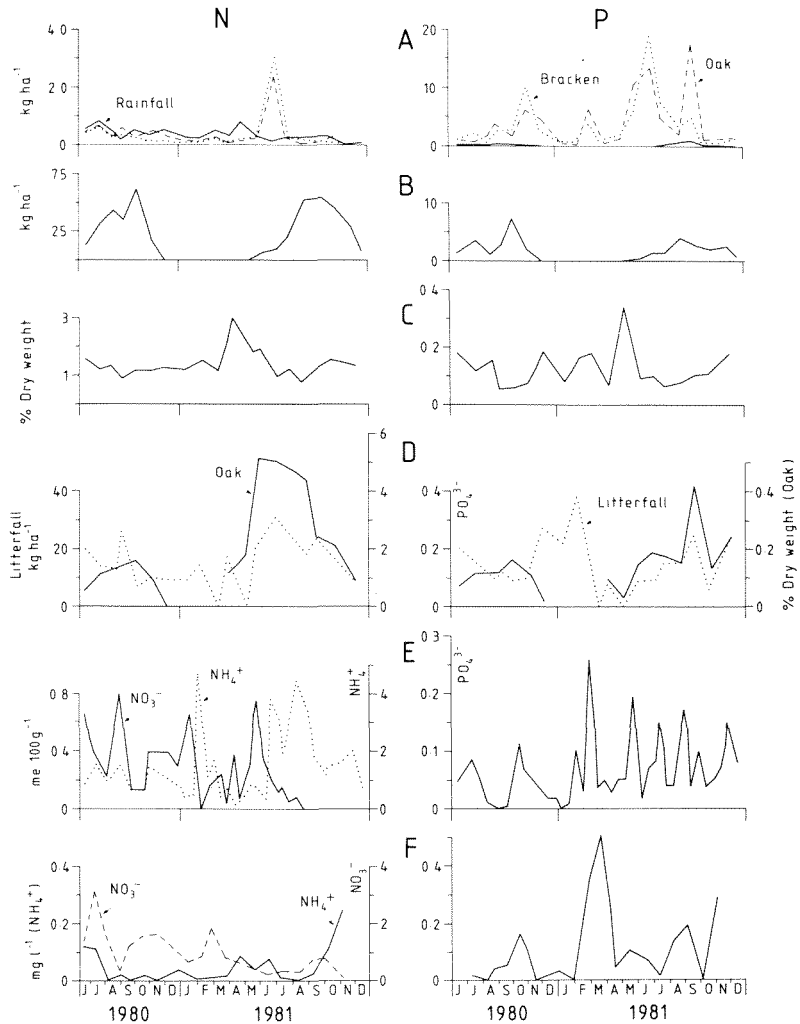


FIG.3 Nitrogen and phosphorous loadings and concentrations (monthly except where stated). (a) loadings in bulk precipitation, oak and bracken throughfall samples (kg ha^{-1}); (b) loadings in the standing crop of bracken fronds (kg ha^{-1}); (c) nutrient concentrations in the soil litter layer (% dry weight); (d) nutrient loadings (kg ha^{-1}) and concentrations (% dry weight) of oak litterfall and harvested oak leaves and twigs respectively; (e) water soluble extracts (NO_3^- and PO_4^{3-}) and exchangeable NH_4^+ in soil Ah horizon (fortnightly samples: $\text{me } (100 \text{ g})^{-1}$); (f) flow weighted nutrient concentrations in streamflow (monthly average from 8-h samples: mg l^{-1}).

TRENDS IN LOADINGS AND CONCENTRATIONS

Figures 3 and 4 illustrate the trends in the concentration and loadings of the major plant nutrients (N, P and K) and Mg^{2+} in hydrological pathways and the major soil and vegetation storage

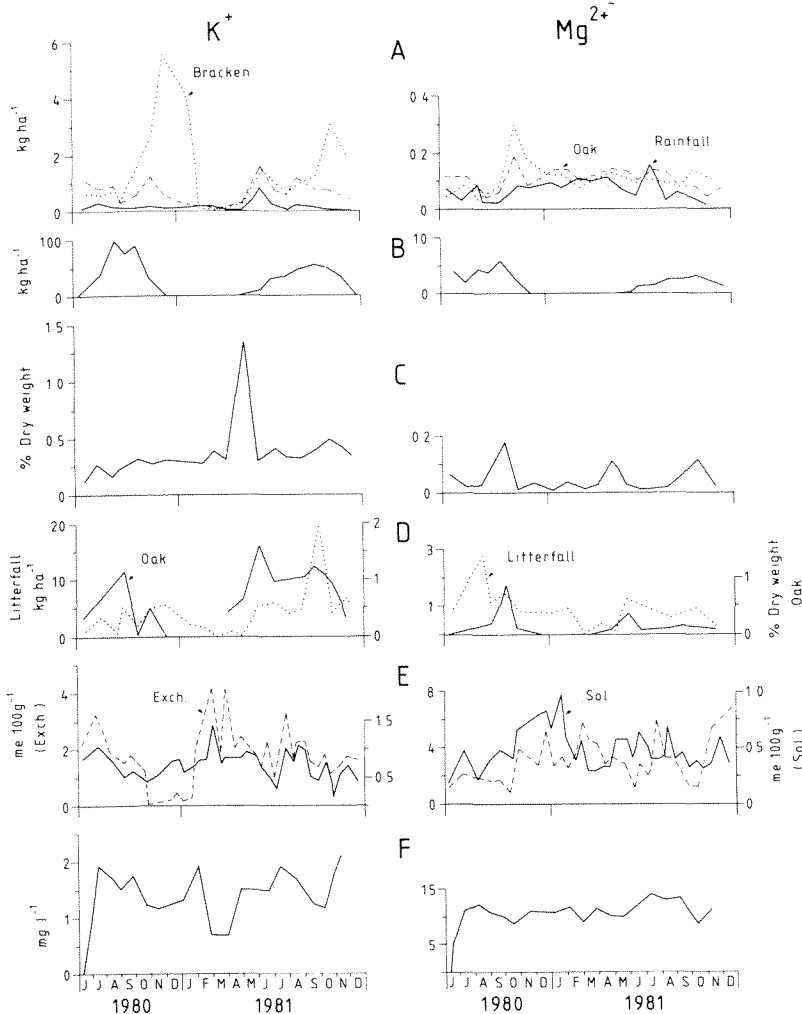


FIG. 4 Potassium and magnesium loadings and concentrations (monthly except where stated). (a) loadings in bulk precipitation, oak and bracken throughfall samples ($kg\ ha^{-1}$); (b) loadings in the standing crop of bracken fronds ($kg\ ha^{-1}$); (c) nutrient concentrations in the soil litter layer (% dry weight); (d) nutrient loadings ($kg\ ha^{-1}$) and concentrations (% dry weight) of oak litterfall and harvested oak leaves and twigs respectively; (e) water soluble and exchangeable extracts in soil Ah horizon (fortnightly samples: $me\ (100\ g)^{-1}$); (f) flow weighted nutrient concentrations in streamflow (monthly average from 8-h samples: $mg\ l^{-1}$).

components during a 19 month period between June 1980 and December 1981. Inputs from bulk precipitation and subsequent modification in throughfall samples are represented in Figs 3(a) and 4(a). Nitrogen occurs mainly as NO_3^- and NH_4^+ in incident precipitation and loadings generally decrease with passage through the vegetation canopy. Peak throughfall levels were detected in June 1981 and were associated with a six-fold increase in NH_4^+ but similar trends in precipitation inputs were not apparent. No obvious seasonal trends in nitrogen loadings were detected in either gross or net precipitation, although NH_4^+ levels in rainfall tended to be higher in the winter period. Phosphate levels in precipitation were frequently below the detection limits of the molybdenum blue method employed, yet throughfall samples contained significant amounts of soluble phosphorous. Major increases in loadings occurred in the autumn and in June 1981, and bracken throughfall levels were generally higher than those of oak. Potassium demonstrated a similar pattern with gross precipitation inputs usually below 0.5 kg ha^{-1} over the four weekly period at which results are reported. Peak loadings in throughfall occurred during the autumn period and in June 1981. Magnesium loadings also exhibited similar patterns to the other nutrients, although background input levels generally increased during the winter months, and the autumn and midsummer peaks in throughfall loadings were less pronounced. A detailed summary of the impact of precipitation chemistry for the sampling period is given in Table 3 and indicates that, with the exception of nitrogen, all loadings increased after passage through the vegetation canopy.

Figures 3(b) and 4(b) show the mean monthly accession rates of each nutrient in the standing crop of bracken fronds. Rhizome biomass and nutrient concentrations were also monitored, but the seasonal trends were less apparent than in the aerial parts of the plant. All four nutrient levels closely followed the pattern of frond growth with rapid uptake in June and an equally rapid decline in November,

TABLE 3 Mean solute loadings of incident precipitation and through-fall (kg ha^{-1}) June 1980-December 1981

Solute	Incident Precipitation	Through-fall below oak	Net change	Through-fall below bracken	Net change of bracken through-fall to: Rain-fall Oak through-fall	
Ca^{2+}	2.8	4.1	+1.3	4.1	+ 1.3	0.0
Mg^{2+}	0.06	0.11	+0.05	0.12	+ 0.06	+0.01
Na^+	2.6	2.8	+0.2	3.2	+ 0.6	+0.4
K^+	1.4	9.7	+8.3	12.6	+11.2	+2.9
$\text{NO}_3^- \text{-N}$	1.6	1.2	-0.4	1.1	- 0.5	-0.1
$\text{NH}_4^- \text{-N}$	1.9	1.5	-0.4	2.3	+ 0.4	+0.8
$\text{NO}_2^- \text{-N}$	0.1	0.3	+0.2	0.1	0.0	-0.2
$\text{PO}_4^- \text{-P}$	0.0	0.4	+0.4	0.4	+ 0.4	0.0
Cl^-	7.8	8.8	+1.0	12.3	+ 4.5	+3.5
H^+	0.026	0.234	+0.208	0.150	+ 0.124	-0.084

although magnesium was the least responsive element to changes in biomass. Nutrient concentrations in the soil litter layer are given in Figs. 3(c) and 4(c), and are expressed as a percentage of dry weight. Biomass calculations were precluded by the high spatial variability of litter depth. Nitrogen levels peaked during May and June 1981, but concentrations were relatively stable in the remaining period. Phosphate concentrations exhibited a similar peak and were generally lowest during the autumn months of both years. Potassium and magnesium levels also exhibit midsummer peaks, and significant increases in magnesium were apparent in autumn months. The nutrient loadings of oak litterfall and the nutrient content of harvested oak leaves and twigs are presented in Figs. 3(d) and 4(d). The major litterfall inputs occurred in the late summer and autumn and the summer peak of 1981 represents inputs produced by severe storms. The relative proportion of nutrients in harvested leaves and twigs show a temporal pattern similar to that of bracken fronds. Concentrations increased after budbreak during May and rose rapidly to a maximum in late summer. Magnesium levels were generally lower than those of the major nutrients, but the pattern of rising concentrations during the growth period was still apparent.

Figures 3(e) and 4(e) present trends in soil chemical extracts for the Ah horizon. Water soluble extracts were obtained for NO_3^- , PO_4^{3-} , K^+ , and Mg^{2+} and exchangeable extracts for K^+ , Mg^{2+} and NH_4^+ . Although temporal patterns in all elements, especially phosphorous, were highly variable, broad trends may be identified. High concentrations of NO_3^- and NH_4^+ occur in autumn and midsummer, although the NO_3^- peak generally precedes that of NH_4^+ . Exchangeable and soluble K^+ extracts demonstrate a similar pattern, with the former exhibiting a greater amplitude of variation and a dramatic decrease during the winter of 1980. Flow-weighted nutrient concentrations in river water samples derived from 8-h sampling and averaged for four-weekly periods are given in Figs. 3(f) and 4(f). NH_4^+ levels peaked during the autumn and summer periods, whereas NO_3^- concentrations generally decreased throughout the 19 months of observation with variable peaks in concentration. PO_4^{3-} concentrations peaked in river water samples during the autumn and spring, whereas K^+ levels were generally at a minimum during these periods. Mg^{2+} concentrations exhibited little seasonal variability.

DISCUSSION AND CONCLUSIONS

Rainfall is the main form of precipitation input to the experimental catchment and supplies many essential plant nutrients directly from atmospheric sources. This contribution represents a net gain of nitrogen and potassium to the basin as a whole and has been shown to be important in many ecosystems (e.g. Allen *et al.*, 1968). Seasonal trends in precipitation and throughfall chemistry have been identified for the majority of solutes under consideration in this investigation and discrete inputs are superimposed upon general trends at different times of the year. Similar trends in the precipitation record, obtained by calculation of a monthly antecedent precipitation index (cf. Gregory & Walling, 1973), have not been observed, since convective summer storms maintain a generally uniform rainfall distribution.

Solutes in precipitation are mainly derived from oceanic, terrestrial and anthropogenic sources. Both NH_4^+ and Mg^{2+} demonstrate increased concentrations and loadings during winter months. This trend for the former ion may reflect increased combustion of fossil fuels at near-by power stations, whereas higher winter levels of Mg^{2+} may be related to a predominantly marine origin and to the more frequent occurrence of frontal rainfall which moves into the study area from the west coast of Britain. K^+ and PO_4^{3-} are generally thought to be derived from terrestrial sources, although levels of both ions are low in bulk precipitation input.

The passage of rainfall through a vegetation canopy considerably modifies solute concentrations (Likens *et al.*, 1977) by the washing of surface deposits from vegetation surfaces or by the leaching of labile ions and compounds from within. The latter effect is particularly noticeable during autumn months when cellular breakdown encourages the release of readily available ions before abscission. This process is especially important in relation to K^+ , Cl^- , H^+ and PO_4^{3-} . Increased mobility derives from the physiological role which the nutrient plays in the plant. K^+ and Cl^- , for example, occur as osmotic regulators in cell sap, are therefore not part of the plant fabric and thus may be easily leached. Most ions in throughfall follow the pattern of incident precipitation chemistry during the dormant period with the exception of H^+ concentrations, which increase in winter months and perhaps emphasize the importance of leaf surface leaching by hydrogen ion exchange in summer. Nitrogen is the only nutrient to exhibit a decline in concentrations during passage through the vegetation canopy, and this phenomenon has also been observed in a similar study undertaken by Carlisle *et al.* (1966). Nitrogen is probably absorbed directly by the plant or by micro-organisms and algae in the canopy. All ions may be subject to this process but the pattern may be obscured by a greater loss than uptake. The most noticeable feature of the throughfall nutrient data is the peak which occurred for several ions during June 1981. This was attributable to the contamination of water samples by insect frass produced by *Tortrix viridana* larvae and by the larvae of various fly species. Excessive defoliation of the oak occurred for approximately three weeks causing an estimated 60% reduction in oak leaf biomass. A secondary flush of leaves appeared in late June and early July. Other documentary evidence exists in the literature for frassfall in woodland areas (Carlisle *et al.*, 1966), and analysis of a frass sample showed it to be rich in NH_4^+ and PO_4^{3-} . Similar trends were not recorded during June 1982 probably due to the severity of the preceding winter which reduced insect larval populations. The frass input of 1981 proved to be an extremely valuable reference point since naturally enriched inputs to the system could be traced during the summer and autumn months and were immediately followed by rapid nutrient uptake in emergent bracken fronds. Such events also emphasise the importance and variability in ecosystem dynamics which relate directly to the release and transfer of solutes.

Bud break of the oak and the emergence of bracken fronds occurred in mid May and was accompanied by rapid nutrient uptake, especially of nitrogen, phosphorous and potassium. Rapid rates of nutrient uptake in bracken also have been reported by Hunter (1944), Frankland (1976) and Watt (1976). Expression of concentrations of nutrients as

a percentage of dry weight permits assessment of the uptake rate. Between 30 and 50% of nitrogen and potassium, and 70% of phosphorous requirements are taken up during the first four weeks of growth. Maximum biomass and nutrient concentrations are achieved for both bracken and oak in September, followed by a rapid decline attributable to leaching and translocation to rhizomes or other storage organs. Magnesium concentrations do not decline in the same manner and remain in the leaf or frond until abscission. The input of nutrients via litterfall exhibits a distinctly seasonal trend with most input occurring in the autumn. Nutrient rich litter may also be provided throughout the year by inputs of bud scales, flowers and pollen and through the impact of destructive storms, such as those recorded during April 1981. The decomposition of litter in this woodland is probably slow due to the acidity of the soil (pH 3.7-4.2) which is capable of supporting only a limited population of soil fauna and flora. Furthermore, complete bracken frond decomposition may take from eight to ten years because of the high lignin content (Frankland, 1976). A considerable store of nutrients is contained in the litter layer but this can only be released slowly as leaching and decomposition occur. Of the nutrients studied, only magnesium exhibits an increase in concentration, as a percentage of dry weight, in the litter layer during the autumn months.

Most workers have been unable to identify seasonal trends in the nutrient content of soils. This largely reflects the problems of sampling the inherently large spatial variability of the soil (e.g. Frankland *et al.*, 1963; Ball & Williams, 1968), although Weaver & Forcella (1979) have recognized seasonal variations in soil chemistry under six vegetation types in the Rocky Mountains. Several water soluble ions in the present study exhibited significant seasonal variations with peaks in concentration occurring in the winter months. Although depletions of soil nutrient levels have been observed under various agricultural crops (Russell, 1973), in woodland ecosystems nutrients are supplied continuously to the soil from litter and throughfall inputs. Seasonal increases in concentration may therefore relate to rapid decomposition followed by winter leaching of accumulated mineralized material. Soils of the area are dominated by kaolinite which together with the low cation exchange capacity of the B and B/C horizons suggest a nutrient-poor and well weathered soil. Furthermore, exchange sites occupied by major cations (Ca^{2+} , Mg^{2+} , NH_4^+ , Na^+ and K^+) represent less than 40% of cation exchange capacity. Soils on the hillslope site exhibit high permeabilities. Tensiometer and throughflow pit studies have shown that lateral water movement within the soil matrix is a rare phenomenon, which only occurs when soil water levels approach saturation throughout the profile. Most water percolates to a clay layer located at 140 cm depth and forms a perched water table. Subsurface flow occurs downslope towards the main stream and a small ephemeral drainage channel where flow is controlled by fluctuations in groundwater levels.

Volume weighted river water concentrations draining the entire deciduous woodland area do not exhibit marked seasonal trends, and the fluctuations in nutrient levels in the hillslope subsystem are not generally apparent in the river. Small increases in K^+ and Mg^{2+} concentrations occur in June following the period associated with frass inputs, whereas peak nitrogen and PO_4^{3-} levels are related to

times of maximum runoff. No single hillslope biogeochemical process may therefore be identified as exerting a controlling influence on river quality behaviour, although isolated events may affect concentrations in the short term. The overall interaction of the ecosystem masks the seasonal influence which vegetation and soils have been shown to exert on hillslope water chemistry. The apparent elimination of such patterns in river water may reflect the buffering effects of the narrow flood plain (Foster & Grieve, 1983) and the impact of groundwater chemistry on the river water quality in this area. Furthermore, since solute concentrations in river water are volume weighted, the high winter PO_4^{3-} outputs may be associated with erosional processes rather than biogeochemical cycling, which is in direct contrast to the behaviour of K^+ and Mg^{2+} .

Detailed chemical analyses have been undertaken in many components of this forested ecosystem and hillslope biogeochemical interactions may be identified. Few of the hillslope variables, however, correlate directly with river water behaviour but individual events can be seen to exert some influence. This finding may have an important bearing on the future modelling of water quality dynamics in this and other similar areas.

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